THE CHEMISTRY AND KINETICS OF SILYLCHROMATE FORMATION

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This is to certify that the

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ABSTRACT

THE CHEMISTRY AND KINETICS OF SILYLCHROMATE FORMATION

By

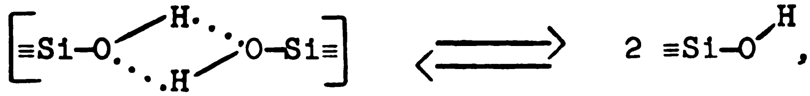
James Franklin Hampton

The main objective of this investigation consisted in undertaking a physico-chemical study of siloxy-chromium chemistry. The preparation of stable polymers containing chromium-oxygen-silicon linkages was attempted. Characterization of the silylchromate isolated from the reactions of diphenylsilanediol with chromyl chloride or chromium(VI) oxide in chlorinated hydrocarbons was the initial objective.

Triphenylsilanol and chromyl chloride react in carbon tetrachloride solution to form bis(triphenylsilyl)chromate and hydrogen chloride. Occurring in consecutive order are several reversible equilibria. A kinetic study of these equilibrium reactions was undertaken. The pseduo-order of reaction with respect to all species was determined experimentally by the method of initial rates. The rate of appearance and dissappearance of triphenylsilanol was followed spectrophotometrically since the silanol has a characteristic and analytically useful absorption band at 2720 $m\mu$. The known association of both the silanols and chromyl chloride in carbon tetrachloride was used in accounting

for results. The mechanism involves associated dimer species of both triphenylsilanol and chromyl chloride in solution which dissociate before intercombination. Furthermore, the kinetic studies were interpreted in terms of a mechanism involving four-centered cyclic transition states which decompose to give reactants or products.

During the course of this investigation, quantitative measurements of triphenylsilanol association in carbon tetrachloride were determined by four independent methods. These included two classical thermal methods (ebulliometry and cryoscopy), a vapor pressure osmometry approach, and by infrared absorption measurements. The results of these molecularity studies clearly indicate that the nature of the self-associated triphenylsilanol aggregate is of the type



, and the extent of such hydrogen bonding is strongly dependent upon conditions of temperature and concentration. The dimeric equilibrium constant was determined at temperatures of -23, 24, 37, and 77°C.

A comparative rate study of the cleavage of M-O-Si linkages (M = Ti, Cr, Sn, and Si) by HCl in carbon tetrachloride is reported. In all metallosiloxane samples tested, this cleavage occurred between the metal and the siloxy

linkage and the rate of cleavage varies in the order:

$$\text{Ti-O-Si} > \text{Cr-O-Si} > \text{Sn-O-Si} > \text{Si-O-Si}.$$

Infrared absorption assignments for the M-O-Si linkages were made from an infrared study of these cleavage reactions.

The reactions of diphenylsilanediol with chromyl chloride or chromium(VI) oxide in chlorinated hydrocarbons were investigated. The previously reported cyclic silylchromate $[(Ph_2SiO)_2CrO_3]_2$ was the principal product isolated. Its preparation and properties were carefully reinvestigated. The compound was named cyclobis[tetraphenyldisiloxanylchromate(VI)].

Attempts to prepare high molecular weight silylchromates from acid and base catalytic action on cyclobis[tetraphenyldisiloxanylchromate(VI)] proved unsuccessful.

The intermediate compound triphenylsiloxychromyl chloride, $Ph_3SiOCrO_2Cl$, was isolated from the reaction of triphenylsilanol and chromyl chloride in carbon tetrachloride. This compound represents the first organosilylchlorochromate isolated and characterized. Triphenylsiloxychromyl chloride is a red-orange, crystalline solid that melts sharply at 97°C.

Elemental analysis, x-ray diffraction, infrared spectra, proton resonance spectra, ultraviolet and visible spectra, molecularity measurements, and chemical reactions were used to characterize the silylchromates which were prepared during this investigation.

James Franklin Hampton

A very extensive equilibrium is involved in silylchromate formation when chlorinated hydrocarbons are used as solvents. Success in isolation of silylchromates depends primarily on one's ability to shift and control this equilibrium. This may involve not only temperature and concentration effects but also the experimental method of mixing reactants.

THE CHEMISTRY AND KINETICS OF SILYLCHROMATE FORMATION

By

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TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF TABLES - Continued

LIST OF TABLES - Continued

LIST OF FIGURES

LIST OF FIGURES - Continued

I. INTRODUCTION

Inorganic chemistry is presently marked by extensive research dealing with polymeric materials. Early investigations stemmed from the growing need of industry and the military services for materials stable above 500°C. Because organic polymers based on a framework of linear carbon-carbon bonds do not possess this required thermal stability, inorganic polymer chemistry is an active research field.

Of all the inorganic polymeric materials investigated to date, the polyorganosiloxanes or silicones have been most successful. The name "silicone" was introduced by Wöhler in 1863 to describe a composition of silicon, hydrogen, and oxygen he had obtained from hydrolysis of calcium silicide, and was used by Kipping in 1901 to describe the compounds of empirical formula $(C_6H_5)_2SiO$ by analogy with ketones, R_2CO. It was soon realized that the silicon compounds were in fact polymers containing Si-O-Si links, but the term "silicone" continued to be used for the polymers. When organic groups are attached to the Si-O-Si framework, polymeric materials with many desirable properties are obtained. At high temperatures, however, these polymers are restricted in their uses because of their tendency to rearrange into cyclic structures of low molecular weight. Thermal stability might be improved by modifying the electronic character of the siloxane bond since it is generally recognized that as covalent bonds become more polar, greater thermal stability results. Polymetallosiloxane chemistry resulted from these considerations. It is a study of compounds in which some Si-O units are replaced with M-O units, where M represents a metal. If the metal is more electropositive than silicon, a more polar and perhaps stronger bond might result.

Hexavalent chromium lends itself to incorporation into the siloxane linkage. Chromium(VI) oxide and chromyl chloride are difunctional reactants and both possess nearly tetrahedral coordination. The ability of hexavalent chromium compounds to form aggregates could make them desirable in polymeric chemistry. Thus, chromyl chloride undergoes self-polymerization (1) and chromium(VI) oxide is composed of long chains of CrO_4 tetrahedra (2). These considerations made a study of the hexavalent chromium-oxygen-silicon linkage seem attractive.

When this investigation was undertaken, siloxy-chromium chemistry was in the early stages of synthetic exploration. There was an immediate need for structural interpretation of some siloxy-chromium compounds. Secondly, research that was concerned with polycondensation and degradation, as well as with an understanding of their mechanism, was lacking. Finally, some quantitative information about properties was needed to better understand the silicon-oxygen-chromium linkage. The preparation and characterization of organo-

silylchromates and also the kinetics of the silyl-chromate formation and degradation are the subject of this investigation. This was realized in the pseudo-order rate study of the chromyl chloride--triphenylsilanol reaction with the postulation of a reaction mechanism. The availability of chromyl chloride, chromium(VI) oxide, and the large variety of silicon intermediates, provides an opportunity for undertaking such an investigation.

II. HISTORY

A. Chemistry of Silanols

Of the organosilicon compounds dealt with in this investigation, the most extensively used were the organosilanols and diols. A brief description of their chemistry will then be presented.

Oxygen-containing organosilicon compounds present a broad and most interesting field of chemistry. Silanol derivatives in which hydroxyl groups are attached to a silicon atom are perhaps the most interesting class of oxygen-containing organosilicon compounds. Investigations of these compounds have been of theoretical and practical significance. Since the mid-1940's both industrial and fundamental aspects have received intensive and increasing attention.

Silanols have found application in industry for preparation of various resins, thermostable coatings, bactericidal substances, adhesives, water repellent media, and for lubricating oils. Detailed information is compiled in Eaborn's Organosilicon Compounds (3) and in Shostakovski's review on silanols (4).

In 1860, Lavrov (5) discussed a series of hydrolysis reactions of silicon tetrachloride and for the first time pointed out the possibility of the existence of trichlorosilanol, which has been obtained only recently (6). In 1871, Ladenburg (7) obtained the first silanol, triethylsilanol.

Stable organosilanols of the types R_3SiOH, $R_2Si(OH)_2$, and $RSi(OH)_3$ are known. This is in contrast to the analogous carbinols. A molecule may contain more than one silicon atom bearing a hydroxyl group. For example, diols of the types $(HOSiR_2)_2O$ and $(HOSiR_2)_2CH_2$ are known.

Only two triols have been isolated. Phenylsilanetriol, $PhSi(OH)_3$, has been made by hydrolysis of phenyltrimethoxysilane (8) or of phenyltrichlorosilane (9) while dichlorophenylsilanetriol, $Cl_2C_6H_3Si(OH)_3$, has been made by hydrolysis of dichlorophenyltriacetoxysilane (10).

The most general method of silanol preparation involves hydrolysis of various organosilicon derivatives. Silanols are formed by the hydrolysis of organosilicon halides, pseudo-halides, sulfides, amines, hydrides, alkoxides, phenoxides, and esters. In recent years a method of preparing silanols from silanolates based on disiloxane cleavage has become popular. Tatlock and Rochow (11) carried out the cleavage of siloxanes by sodium or potassium hydroxides. Sodium salts of methyldiphenyl-, dimethylphenyl-, and triphenyl-silanols are best prepared by treatment of the corresponding disiloxanes with alcoholic sodium hydroxide (12).

Under hydrolysis conditions the silanols frequently condense to siloxanes. It is impossible to list general conditions necessary to produce silanols rather than siloxanes. Siloxane formation is, however, minimized by using inert diluents which decrease the chances of intermolecular interactions, and by keeping the hydrolysis reaction temperature as low as possible. Since alkali and acid hydrolyses favor condensation of the silanols, hydrolysis reactions should be kept as nearly neutral as possible.

For the preparation of silanols that easily condense to siloxanes, organosilicon amines, alkoxides, or acetates are convenient when hydrolyzed by water under neutral or near-neutral conditions. Thus one of the first preparations of trimethylsilanol involved conversion of trimethylchlorosilane into hexamethyldisilazane and hydrolysis of the latter (13).

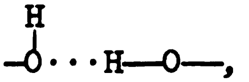
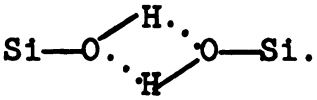
The organosilicon triols and most all the diorganosilanediols are solids. The triorganosilanols vary from volatile liquids to high melting solids, depending largely on the size of the organic group present. Intermolecular hydrogen bonding between hydroxyl groups raises melting and boiling points above the values which would be expected from the molecular weight alone. Table I lists the melting and boiling points of some organosilanols. Triorganosilanols dissolve poorly in water but very well in organic solvents. Solubilities of the silanediols and silanetriols increase in water and decrease in organic solvents.

X-ray diffraction methods (28,29) have been used to prove the existence of strong intermolecular hydrogen bonding in simple diorganosilanediols. The hydrogen bonding seems

Table I. Some Organosilanols

Compound	Boiling Point (°C)	Melting Point (°C)	Reference
$PhSi(OH)_3$		128-130	8
$Cl_2C_6H_3Si(OH)_3$		188	10
$Me_2Si(OH)_2$		100-101 100.5	14 78
$MeEtSi(OH)_2$		79-80	15
$Et_2Si(OH)_2$		95-96	16
$\underline{n}$-$Pr_2Si(OH)_2$		99-100	16
$\underline{i}$-$Pr_2Si(OH)_2$		114	17
$Ch_2Si(OH)_2$		164-165	17
$(PhCH_2)_2Si(OH)_2$		101	18
$MePhSi(OH)_2$		74-75	19
$EtPhSi(OH)_2$		68.5	19
$Ph_2Si(OH)_2$		148 dec. 128-132 dec. 155 165	20 21 22 78
Me_3SiOH	98.6		13
Et_3SiOH	153.5-154.5		23
Ch_3SiOH		177-178	17
$(PhCH_2)_3SiOH$		104	24
$MePh_2SiOH$	184-187		25
Ph_3SiOH		150.5-151.5	26
$(Me_2SiOH)_2O$		67-68 68.5	27 78
$(Ph_2SiOH)_2O$		113-114 115	20,21 78
$HO(Pr_2SiO)_3H$		111	20,21 78

Ph = phenyl; Me = methyl; Et = ethyl; Pr = propyl; Ch = cyclohexyl.

not to be of the usual linear type,  $-\overset{\overset{H}{|}}{O}\cdots H-O-$, but involves association of the type . Vibrational spectrum studies have shown that triorganosilanols and diorganosilanediols are highly associated in the liquid state (30,31,78,91). Trialkylsilanols have been shown to be highly associated in solution by both cryoscopic measurements (30,32,102) and infrared studies (30,31,33,102). Cryoscopic measurements in cyclohexane solution indicate that trimethylsilanol tends toward a limiting molecularity value between 3 and 4 as the concentration is increased (30).

Several items of evidence indicate that triorganosilanols are much more acidic than the corresponding carbinols. Since silicon is more electropositive than carbon, the opposite results would be expected from inductive effects alone, but engagement of the oxygen lone-pairs in $\underline{d}\pi$-$\underline{p}\pi$ bonding with silicon counteracts these effects. Triorganosilanols react with aqueous sodium hydroxide to give sodium triorganosilanolates. Nuclear magnetic resonance spectra (34) also indicate that trimethylsilanol is more protonic than trimethylcarbinol. Triphenylsilanol is a far stronger acid than the trialkylsilanols and can be titrated with tetrabutylammonium hydroxide in pyridine solution (35). This greater acidity of triphenylsilanol compared with trialkylsilanols is explained by the inductive electron withdrawal of phenyl groups.

The stability of organosilanols toward siloxane condensation falls steeply in the order:

$$R_3SiOH > R_2Si(OH)_2 > RSi(OH)_3.$$

The stability of dialkylsilanediols and trialkylsilanols appears to be closely related to the size of the organic group. Sterically hindered groups on organosilanols have something to do with the chemical reactivity of the hydroxyl groups but more important are the electron attracting and releasing tendencies associated with the neighboring groups.

Triorganosilanols are similar in their structure to tertiary alcohols, but silanediols and triols have no analogues among organic compounds. Organosilanols react with alkali metals with formation of silanolates, exchange hydroxyl for halogen by the action of halides of phosphorus, and form ethers and esters. Unlike the organic alcohols, they easily dehydrate to form siloxanes when heated with acids and alkalis. Thus diphenylsilanediol gives the trisiloxane $(Ph_2SiO)_3$ when its ether solution is boiled in contact with concentrated hydrochloric acid, and gives the tetrasiloxane $(Ph_2SiO)_4$ when heated with dilute alcoholic alkali (36).

Hydroxyl groups attached to silicon may be accurately determined by the standard Zerewitinoff procedure, involving measurement of methane gas evolved on treatment with methylmagnesium halide (13). Silanol hydroxyl groups may also be determined by measuring the hydrogen evolved in interaction

with lithium aluminum hydride in di-*n*-butyl ether (14). Titration with Karl-Fischer reagent gives excellent results, one SiOH group being equivalent to one molecule of water (37). The quantitative determination of silanols is complicated by the fact that water interferes in the analysis by reacting with the reagents in a way similar to the silanols. Analysis of mixtures of water and silanols cannot be done accurately at the time of this writing.

B. Chemistry of Hexavalent Chromium

Important chemistry concerning chromium(VI) will be reviewed in as much as it affects the nature of the silicon-oxygen-chromium linkage more than any other. Two of the most common compounds of hexavalent chromium are chromium(VI) oxide and chromyl chloride, and special attention will be given them.

Except for trivalent chromium, the hexavalent oxidation state is the most stable oxidation state of chromium. Chromium(VI) has lost the five *3d* and one *4s* electrons which chromium(0) possesses and has vacant *3d* and *4s* orbitals. All compounds of hexavalent chromium are strong oxidizing agents, and trivalent chromium is the usual reduction product. Chromyl compounds, CrO_2, are extensively used to oxidize organic materials. These Étard reactions involve the addition of a chromyl compound to an organic molecule to form an addition product, followed by hydrolysis or alcoholysis to yield the oxidation product. Violent oxidations are avoided if an inert solvent is used as the reaction medium.

Hexavalent chromium compounds exhibit approximately tetrahedral coordination in both the solid state and in solution (2,30). There is a strong tendency among hexavalent chromium compounds to form aggregates. Molecularity studies (1,39) indicate self-association of chromyl chloride in non-aqueous solvents. Polychromate formation in strongly acidic chromate solution also indicates these self-association tendencies.

Chromium(VI) Oxide

Bystrom and Wilhelmi (2) have determined that the oxygen atoms form a distorted tetrahedron around each chromium atom in chromium(VI) oxide. These tetrahedra form chains with the corners of each group being shared so that a polymeric aggregate results. Preparation of the compound is accomplished by precipitation from alkali chromate or dichromate solutions by addition of a large excess of sulfuric acid. Its action is violent as an oxidizing agent, especially for organic substances, being reduced to green Cr_2O_3. Chromium(VI) oxide is very soluble in water but can be recrystallized from a small quantity of the solvent to give bright red needles which melt sharply at 197°C.

Chromyl Chloride

Berzelius (40) first prepared chromyl chloride when he obtained the pure species by distillation of a mixture of sodium chromate, sodium chloride, and sulfuric acid. The compound is most conveniently prepared by the reaction of chromium(VI) oxide with concentrated hydrochloric acid in the presence of sulfuric acid (41). Chromyl chloride has a sharp melting point at -96.5°C and its boiling point is 115.7°C at one atmosphere pressure. The appearance and odor of the compound are similar to those of bromine; it is deep red as the solid, liquid, and vapor. Electron diffraction measurements by Palmer (38) indicate that chromyl chloride has approximately a tetrahedral configuration.

Chromyl chloride is miscible without reaction with chlorinated hydrocarbons, SO_2Cl_2 and $SnCl_4$. Homogeneous solutions of chromyl chloride in glacial acetic acid, n-hexane, benzene, nitrobenzene, and carbon disulfide slowly decompose because of the inherent reduction of chromium(VI). Violent oxidation reactions involving chromyl chloride are controllable when carried out in carbon tetrachloride, chloroform, or carbon disulfide.

Table II lists the results of molecularity studies of chromyl chloride in various solvents. These molecularity measurements reflect the high degree of self-association of chromyl chloride in solution. It is greatest in the most non-polar solvents such as carbon tetrachloride.

Chromate esters make up an interesting class of compounds containing hexavalent chromium. They are important to this work in that similarities might be expected for the silicon

Table II. Molecular Weight Determinations of Chromyl Chloride

Solvent	Method	Molecular Weight	Molecularity	Reference
carbon tetrachloride	cryoscopy	225-243 222-273	1.4 - 1.6 1.4 - 1.8	39 1
carbon tetrachloride	ebulliometry	145-172	0.94- 1.1	42
carbon disulfide	ebulliometry	165-171	1.1	42
ethylene dibromide	cryoscopy	178-299	1.1 - 1.9	1
benzene	cryoscopy	165-175	1.1	39
acetic acid	cryoscopy	208-218	1.3 - 1.4	43
nitrobenzene	cryoscopy	173-229	1.1 - 1.5	1
phosphorus oxytrichloride	cryoscopy	159	1.0	1

analogues since silicon is directly under carbon in the periodic table. A chromate ester was first prepared by Gomberg (45) when he obtained bis(triphenylcarbinyl)chromate from the reaction of silver chromate and triphenylmethyl chloride in benzene. Several other methods have been described for the preparation of chromate esters. The most common is to add chromium(VI) oxide to a solution of the alcohol in an inert solvent. The reaction of the alcohol with chromyl chloride in chlorinated hydrocarbons can also be used.

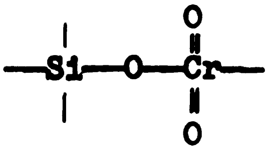
Chromium(VI) compounds are dangerously toxic. Chromate salts and presumably all chromium(VI) compounds are strongly suspected of being carcenogenic and are associated with other physiological disturbances. Skin contact or the inhalation of vapors or dust should be scrupulously avoided, and laboratory workers should be acquainted with the literature on toxicity (46).

In addition, dangerous fire and explosion hazards can arise when chromium(VI) compounds come in contact with organic matter or reducing agents. Certain methylsilyl chromates are known to detonate under certain conditions (47). The unstable nature of silylchromates will be described further in the section to follow.

C. Siloxy-Chromium Chemistry

When this investigation was undertaken in 1961, very little information about silicon-oxygen-chromium chemistry could be found in the literature. Increased interest in this area has developed in recent years. Certain water-soluble chromium coordination compounds had been reported (48) as reagents which interact with various surfaces through bonding which was thought to involve Si-O-Cr linkages. Surfaces of silica and glass which are thought to contain hydroxyl groups are particularly susceptible to such bond formation. The bonding between "Volan" (methacrylatochromic chloride) and the surface of glass is through Si-O-Cr linkages (48) and has become industrially useful. Similarly, "Quilon" (stearatochromic chloride) interacts with glass and is believed to cover the surface completely with stearate groups as a result of this Si-O-Cr bonding (48).

Nearly all of the siloxychromium compounds that have been described so far have involved chromium in the hexavalent state. This linkage is best described as a metallosiloxane with a chromyl group directly attached to a siloxy group:



$$-\overset{|}{\underset{|}{Si}}-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr}}}}- \;.$$

Schmidt and Schmidbaur (49) in 1958 first reported the preparation of bis(trimethylsilyl)chromate from the reaction of hexamethyldisiloxane and chromium(VI) oxide,

$$(CH_3)_3SiOSi(CH_3)_3 \quad + \quad CrO_3 \quad \longrightarrow \quad [(CH_3)_3SiO]_2CrO_2,$$

but complete characterization of the compound was not reported.

E. W. Abel (50), using the method of Schmidt and Schmidbaur (49), later prepared bis(trimethylsilyl)chromate in good yields. The brilliant red-orange liquid was purified by careful vacuum distillation (b.p. 60°C/0.2 mm. Hg). Such distillation procedures involving silyl chromates have resulted in dangerously violent explosions (47, 50, 51, 52). Such explosions are known to occur with the analogous bis(trimethyllead)chromates (53). E. G. Rochow has reported similar unexplained explosions in experiments involving certain methylstannyl chromates (54).

F. E. Granchelli and G. B. Walker (55) in working with organosilyl esters containing chromium, vanadium, molybdenum, and tungsten, claimed to have prepared bis(triphenylsilyl)-chromate on the basis of analytical data. They treated triphenylsilanol with chromium(VI) oxide in glacial acetic acid or xylene:

$$2(C_6H_5)_3SiOH + CrO_3 \longrightarrow [(C_6H_5)_3SiO]_2CrO_2 + H_2O.$$

Their patent indicated the suitability of these compounds as corrosion inhibitors. These organosilyl esters were shown to be superior to the comparable carbon-containing esters in ability to inhibit corrosion. This increased stability as partially explainable on the basis of bond strengths (Si-O 89.3 kcal./mole, C-O 70 kcal./mole).

Hare (47) in 1958 undertook a synthetic study of siloxy compounds containing hexavalent chromium. To study the effects of silicon substituents on the stability of the silicon-oxygen-chromium linkage, Hare prepared bis(tricyclohexylsilyl)-chromate, bis(p-tolyldiphenylsilyl)chromate, bis(triphenylsilyl)chromate, and bis(cyclohexyldiphenylsilyl)chromate. An explosion resulted when an attempt was made to follow Schmidt and Schmidbaur's procedure (49) for the preparation of bis(trimethylsilyl)chromate. Bis(methyldiphenylsilyl)-chromate and bis[tri(1-naphthyl)silyl]chromate could not be obtained, perhaps because of steric hindrance in the latter case. The instability of a red liquid, possibly bis(phenyldimethylsilyl)chromate, prevented the isolation of this compound. Three types of reactions were used under varying conditions to prepare these silylchromates: the reaction of a triorganosilanol with chromium(VI) oxide, the reaction of a triorganosilanol with chromyl chloride in the presence of a base (calcium oxide), and cohydrolysis of a triorganochlorosilane and chromyl chloride. Refluxing carbon tetrachloride and methylene chloride were used as solvents. The first reaction was used most extensively. Only small amounts of the silylchromates were formed in the third reaction.

All of the silylchromates investigated by Hare decompose into black amorphous solids on prolonged exposure to light. The triorganosilylchromates are soluble in methylene chloride, carbon tetrachloride, chloroform, acetone, and ethanol. All are decomposed by homogeneous hydrolysis in an acetone and water mixture. The presence of electron donor groups in the silylchromates seems to lower the thermal stability. Of the compounds prepared, stability is greatest for bis(triphenylsilyl)chromate which decomposes above its melting point, whereas bis(trimethylsilyl)chromate is explosive when heated.

Certain organosilyl chromates have also been obtained by other routes. Thus, sodium triphenylsilanolate reacts with chromyl chloride in benzene to form bis(triphenylsilyl)chromate and sodium chloride (56).

$$2(C_6H_5)_3SiONa + CrO_2Cl_2 \longrightarrow [(C_6H_5)_3SiO]_2CrO_2 + 2\ NaCl$$

Quantitative yields of bis(triorganosilyl)chromates can also be obtained from the metathetical reaction between silver chromate or silver dichromate and a triorganochlorosilane (57).

$$Ag_2CrO_4 + 2\ R_3SiCl \longrightarrow (R_3SiO)_2CrO_2 + 2\ AgCl$$

Attempts to prepare silyl-chlorochromates (chlorochromic acid derivatives of silanols), $R_3SiO\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr}}}}Cl$, have been unsuccessful. Schmidbaur (52) could not detect any reaction between trimethylchlorosilane and chromium(VI) oxide below 50°C. A redox reaction with the evolution of chlorine gas occurred at higher temperatures.

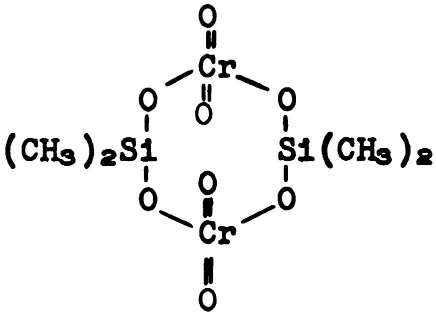
All of the silylchromate explosions reported in the literature have involved methyl substituted derivatives (47, 50,51,52). Such hazardous working conditions account for the extremely limited amount of characterization data available for these methylsilylchromates and related compounds. Recently, several investigators (58-61) claimed to have prepared certain organosilylchromates but no attempt to isolate and characterize the reaction products was made. Thus, the dangerous silylchromates need not be isolated and characterized to be effectively used as catalysts for the polymerization of olefins (58-61). Schmidbaur (52) has employed solutions of silylchromates in an excess of hexamethyldisiloxane as a homogeneous oxidizing agent for organic compounds.

Basi and Bradley (63) have reported the only siloxychromium compound not containig hexavalent chromium. They prepared tetrakis(triethylsiloxy)chromium(IV) from the reaction of triethylsilanol and tetravalent chromium alkoxides.

$$4\ (C_2H_5)_3SiOH + Cr(OC_4H_9)_4 \longrightarrow [(C_2H_5)_3SiO]_4Cr + 4\ C_4H_9OH$$

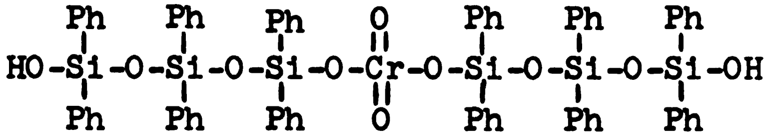
Polymeric chromosiloxanes have been reported in the literature but characterization data for the polymers described are even more limited than for the bis(triorganosilyl)chromates. Schmidbaur (52) reported that chromium(VI) oxide and octamethylcyclotetrasiloxane react to give deep yellow products in which some of the siloxane bonds have been converted into silylchromate bridges. Owing to the danger of explosion, no attempt was made to isolate and characterize the reaction products. Schmidbaur described the product obtained by the general formula,

$[O\text{-}Si(CH_3)_2]\text{-}[CrO_4\text{-}Si(CH_3)_2]_a\text{-}[O\text{-}Si(CH_3)_2\text{-}]_b$ $(a,b = 1,2,3\ldots)$, but conjectured that a distillation would afford a dimeric dimethylsilylchromate with an eight-membered ring structure:



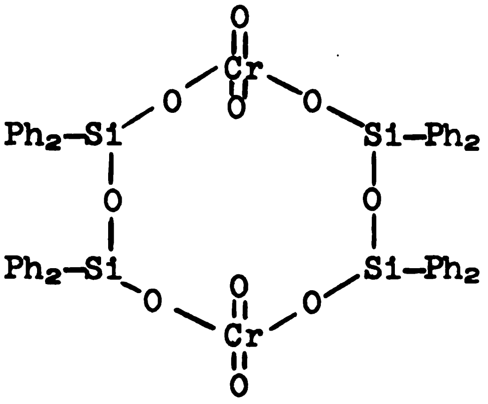
Saunders (51) reported that a violent explosion resulted when a mixture of chromic acid and a methylpolysiloxane was heated to 140°C.

From diphenylsilanediol and chromium(VI) oxide or chromyl chloride in chlorinated hydrocarbons, Hare was unable to prepare poly(diphenylsilylchromates) with repeating Cr-O-Si linkages, but two interesting silylchromates were obtained. Compound I, a dark orange amorphous substance containing six atoms for every chromium atom, was tentatively assigned the structure (Ph = phenyl):



$$HO-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{O}{\overset{O}{Cr}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-OH \quad (I).$$

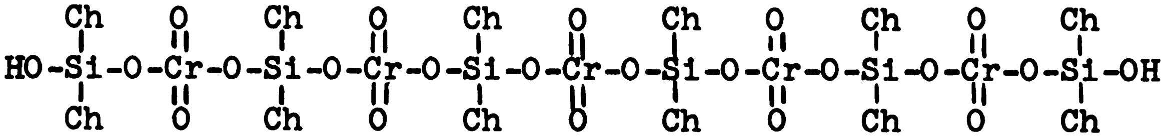
It decomposes at about 275°C. Compound II, a yellow-orange crystalline solid having a silicon-to-chromium ratio of two-to-one, showed properties consistent with the cyclic structure:



(II).

It decomposes sharply at 169°C.

Hare proposed the following structure for the dark red, amorphous solid obtained from dicyclohexylsilanediol and chromium(VI) oxide (Ch = cyclohexyl):



$$\mathrm{HO{-}\overset{Ch}{\underset{Ch}{Si}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}O{-}\overset{Ch}{\underset{Ch}{Si}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}O{-}\overset{Ch}{\underset{Ch}{Si}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}O{-}\overset{Ch}{\underset{Ch}{Si}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}O{-}\overset{Ch}{\underset{Ch}{Si}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}O{-}\overset{Ch}{\underset{Ch}{Si}}{-}OH}$$

(III).

Recent patents (59-61) have indicated the suitability of certain "poly(diorganosilylchromates)" as catalysts for the polymerization of olefins. Reaction products were not isolated and polymer characterization was not reported. In many instances the method of preparation was not described.

Table III lists all the siloxychromium(VI) compounds known or believed to have been prepared, together with their physical properties and method of preparation when available. The condensation reactions used for their syntheses involve the following reactant combinations:

1. Chromium(VI) oxide and hexaorganodisiloxane
2. Chromium(VI) oxide and triorganosilanol
3. Chromium(VI) oxide and diorganosilanediol
4. Chromium(VI) oxide and diorganocyclopolysiloxane
5. Chromyl chloride and triorganosilanol
6. Chromyl chloride and triorganosilanolate
7. Chromyl chloride and diorganosilanediol
8. Chromyl chloride, triorganochlorosilane, and water
9. Silver chromate or silver dichromate and organochlorosilane.

Table III. Siloxy-Chromium(VI) Compounds

Compound	M.P. (°C)	B.P. (°C/mm.)	Index of Refraction n_D (°C)	Preparation	Reference
$(Me_3Si)_2CrO_4$	—	~75/1.0	—	1	49
	—	62/1.0	—	1	52
	-20	60/0.2	1.4937^{20}	1	50
	—	—	—	1	47
	—	—	—	– (not isolated)	59,60,61
$(Ph_3Si)_2CrO_4$	—	—	—	2 (isolated)	55
	138-140	—	—	6	56
	153-154	—	—	2,5,8	47
	—	—	—	2 (not isolated)	58
	—	—	—	– (not isolated)	59,60,61
	—	—	—	9	57
$[\underline{p}\text{-tolylSi}(Ph)_2]_2CrO_4$	98-99	—	—	2	47
$(Ch_3Si)_2CrO_4$	125-126	—	—	2	47
$(ChSiPh_2)_2CrO_4$	84-85	—	—	2	47
$(Et_3Si)_2CrO_4$	—	—	—	2 (not isolated)	58
	—	—	—	– (not isolated)	60,61
$(Bu_3Si)_2CrO_4$	—	—	—	2 (not isolated)	58
	—	—	—	– (not isolated)	60,61
$(Pr_3Si)_2CrO_4$	—	—	—	2 (not isolated)	58
$(hexyl_3Si)_2CrO_4$	—	—	—	2 (not isolated)	58

continued

Table III - continued

Compound	M.P. (°C)	B.P. (°C/mm.)	Index of Refraction n_D (°C)	Preparation	Reference
$(\underline{\text{iso}}\text{-Pe}_3\text{Si})_2\text{CrO}_4$	—	—	—	– (not isolated)	60,61
$(\text{decyl}_3\text{Si})_2\text{CrO}_4$	—	—	—	– (not isolated)	60,61
$(\text{2-ethylhexyl}_3\text{Si})_2\text{CrO}_4$	—	—	—	– (not isolated)	60,61
$(\text{tetradecyl}_3\text{Si})_2\text{CrO}_4$	—	—	—	– (not isolated)	60,61
$(\text{benzyl}_3\text{Si})_2\text{CrO}_4$	—	—	—	– (not isolated)	60,61
$(\text{xylyl}_3\text{Si})_2\text{CrO}_4$	—	—	—	– (not isolated)	60,61
$(\text{naphthyl}_3\text{Si})_2\text{CrO}_4$	—	—	—	– (not isolated)	60,61
"$\text{poly}(\text{Me}_3\text{SiOCrO}_3)$"	—	—	—	4 (not isolated)	52
"$\text{poly}(\text{Et}_2\text{SiOCrO}_3)$"	—	—	—	– (not isolated)	60,61
"$\text{poly}(\text{Ph}_2\text{SiOCrO}_3)$"	—	—	—	3 (not isolated)	60,61
$[(\text{Ph}_2\text{SiO})_2\text{CrO}_3]_2$	dec. 169	—	—	3,7	47
$[\text{HO}(\text{Ph}_2\text{SiO})_3]_2\text{CrO}_4$	dec. 275	—	—	3,7	47
$\text{HO}(\text{Ch}_2\text{SiOCrO}_3)_5\text{Si}(\text{Ch}_2)\text{OH}$	—	—	—	3	47

Ph = phenyl, Me = methyl, Et = ethyl, Ch = cyclohexyl, Bu = butyl, Pr - propyl, Pe = pentyl.

D. Inorganic Polymers

The outstanding ability of carbon to form polymeric chains of its own atoms distinguishes it from all other elements. Such polymers are vitally important, but organic carbon compounds have inherent limitations associated with the ease with which they undergo pyrolysis and oxidation. Few saturated, totally organic compounds are stable in air at temperatures in excess of 300°C. These limitations have been the driving force behind the search for inorganic polymeric compounds of greater thermal and oxidative stability. Inorganic polymer chemistry is concerned with the study of high molecular weight compounds containing regular repeating units other than carbon.

The field of inorganic polymers is in the very early stages of development and, except for the silicones, progress in the production of useful technological materials has been very limited. Before considering the type of polymers which are encountered in inorganic compounds it should be noted that many common inorganic materials are highly associated and polymeric in nature. The silicates, for example, all contain a skeleton of linked silicon and oxygen atoms, with varying degree of cross-linking. There is similar oxygen cross-linking in neutral molecules as in the case of orthorhombic P_4O_{10} and cubic antimony trioxide. Sulfur is a familiar example of many elements which possess polymeric character. An elastic material is obtained when rhombic sulfur (S_8) is heated and slowly cooled. These two examples illustrate the general classifications of inorganic polymers, homoatomic and heteroatomic. The silicates are heteroatomic since the skeleton consists of atoms of different sorts, while sulfur is homoatomic with a skeleton of atoms of the same kind. Amorphous phases of selenium, tellurium, phosphorus, arsenic, antimony, and bismuth are examples of homoatomic polymeric states (64).

In contrast to homoatomic chain compounds, the possibilities of developing a heteroatomic polymeric material are diverse and extensive. The most important inorganic heteropolymers are the silicones in which the skeleton is based on strongly bonded alternating oxygen and silicon atoms. Since carbon-containing groups are present on silicon in these siloxanes, the name organopolysiloxanes is sometimes used to described these materials. Silicone formation may be illustrated by the hydrolysis of diorganodichlorosilanes to the unstable diol compound, $R_2Si(OH)_2$, which loses water intermolecularly to give a mixture of linear and cyclic polymers. Terminal groups may be provided in the form of a triorganochlorosilane. Silicon tetrachloride or an organotrichlorosilane may provide crosslinking. By varying the organic groups attached to silicon, silicones with a variety of properties can be prepared.

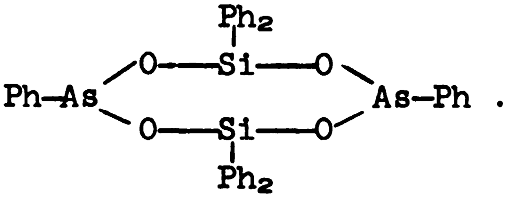
The phosphonitrilic chlorides and their derivatives are some of the best known synthetic inorganic polymers containing nitrogen. When phosphorus pentachloride is heated with ammonium chloride several products are formed, depending upon temperature, reaction time, and ratio of reactants (65,66). Linear polymers $(PNCl_2)_x$, as well as the cyclic tetramer and trimer are products of the reaction.

Closely related to the phosphonitrilics are the polymers containing P-O-N linkages, which have phosphorus atoms linked through nitrogen, with oxygen atoms attached directly to phosphorus.

Borazine, $B_3N_3H_6$, and its derivatives illustrate a group of polymers in which strong bonds are formed by nitrogen with other nonmetallic elements.

Another active field of inorganic polymer research is that of the polymetallosiloxanes. Only a few generalizations will be made on the chemistry of metallosiloxanes since detailed information is compiled in Lapperts and Leigh's Developments in Inorganic Polymer Chemistry (48). More recently, Schindler and Schmidbaur (62) have reviewed the siloxane compounds of the transition metals.

Success in the silicone area has led to considerable research on related backbone structures. It is felt by many active in this field that greater thermal stability should result from alteration of the siloxane linkage by a metal atom. Table IV lists some of the polymetallosiloxanes which have been investigated. A cyclic, dimeric species of composition $PhAs(OSiPh_2O)_2AsPh$ was prepared by condensation of diphenylsilanediol with diiodophenylarsine in the presence of ammonia (76). The crystalline cyclic product melts, possibly with some change in composition, at 145°C and has the structure



A second resinous polymeric species of the type $(O\text{-}SiPh_2OAsPh)_x$ was also believed formed in the reaction. It has an identical empirical composition and infrared spectrum to that of the dimer, but it could not be isolated in the pure state.

Dimeric dimethylsilyl sulfate, a polyfunctional silanol ester of sulfuric acid, is obtained in high yield by the reaction of dimethyldichlorosilane and sulfuric acid (74). It can also be obtained from the reaction of polymethylsiloxane and sulfur trioxide (74). This crystalline material reacts vigorously with water and methanol giving polymethylsiloxane, and with hydrogen chloride to give dimethyldichlorosilane. The following structure has been assigned to this compound:

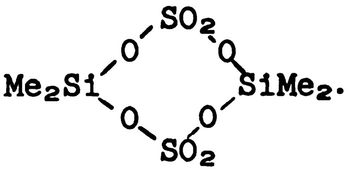


Table IV. Some Siloxy-Containing Structural Units

Linkage	Reference*
-Si-O-Al-	67,77
-Si-O-B-	67,70
-Si-O-Ti	62,67,69
-Si-O-Sn-, -Si-O-Sn-	67,68
-Si-O-As-, -Si-O-As-	71,72,76
-Si-O-V-	62
-Si-O-Cr-	47,62
-Si-O-S-	73,74
-Si-O-Zr-	62,75
-Si-O-Pb-	67,68
-Si-O-P-	67

* The references given are to key papers or reviews.

III. SYNTHESIS

A. Preparation of Reactants

Organosilicon starting compounds were purchased from the Dow Corning Corporation (Midland, Michigan) and Anderson Chemical Company, now a division of Stauffer Chemical Company (Weston, Michigan). They were used without further purification for syntheses but were purified before use in rate studies as described in the section dealing with kinetics. The infrared spectra of diphenylsilanediol and triphenylsilanol were recorded and are shown in Figures III, IV, and IX.

1. Preparation of Chromyl Chloride

The method of Sisler (41) was used to prepare chromyl chloride (chromium(VI) dioxychloride). A mixture of chromium(VI) oxide and concentrated hydrochloric acid was dehydrated with concentrated sulfuric acid at 0°C in an ice-salt mixture to give chromyl chloride. The chromyl chloride layer was separated and after distillation (116°C), was stored in a brown glass bottle closed with a Teflon cap and covered with aluminum foil. The compound was further identified as CrO_2Cl_2 on the basis of its infrared spectrum. Figures V and XI are infrared spectra of a carbon tetrachloride solution of the distilled product.

2. Preparation of Hexaphenyldisiloxane

The method of Daudt and Hyde (25) was used to prepare hexaphenyldisiloxane. An ethanol solution of triphenylsilanol was treated with a small pellet of sodium hydroxide, and the mixture was refluxed for several hours in a single-necked flask fitted with a condenser. Crude product was obtained by removing solvent with a rotary evaporator. The product was easily recrystallized from cyclohexane. The white needles obtained had a melting point of 225-226°C (reported, 225-226°C). The compound was further identified as hexaphenyldisiloxane on the basis of its infrared spectrum.

3. Preparation of Hexaphenylcyclotrisiloxane

The method of Burkhard (20) was used for the preparation of hexaphenylcyclotrisiloxane. Ten grams of diphenylsilanediol was dissolved in 200 ml. of ethyl ether and 5 ml. of concentrated hydrochloric acid added. After the mixture was refluxed for three hours on a steam bath, ether was removed with a rotary evaporator and the crude product was recrystallized from acetone to give white crystals which melted at 188-189°C (reported, 190°C). On the basis of its infrared spectrum the compound was further identified as $[(C_6H_5)_2SiO]_3$. The molecular weight of the recrystallized product in benzene was found by cryoscopic measurements to be 599 ± 10, compared with a formula weight of 594 for $[(C_6H_5)_2SiO]_3$ (see Table X).

4. Preparation of Octaphenylcyclotetrasiloxane

The method described by Burkhard (20) was used to prepare octaphenylcyclotetrasiloxane. A few drops of aqueous potassium hydroxide were added to a boiling solution of

diphenylsilanediol in 95 per cent ethanol, and white crystals soon separated. The mixture was cooled and the crystals were removed by filtration and recrystallized from benzene-ethanol. The white needles obtained melted at 201-202°C (reported, 201-202°C). On the basis of its infrared spectrum the compound was further identified as $[(C_6H_5)_2SiO]_4$. The molecular weight of the recrystallized product in benzene was found by cryoscopic measurements to be 798 ± 20, compared with a formula weight of 793 for $[(C_6H_5)_2SiO]_4$ (see Table X).

B. Reactions Involving Siloxy-Chromium Compounds

At the beginning of this study of siloxy-chromium compounds, the work of Hare (47) was reviewed and partially repeated. Some observations differed from those of Hare. For example, since refluxing conditions seemed only to lower the yield, all reactions were carried out at room temperature. Because of the very reactive nature of chromium(VI) compounds, chlorinated hydrocarbons were always used as solvents; carbon tetrachloride and methylene chloride served equally well. Dow Corning diphenylsilanediol (containing 3 to 5 per cent $[(C_6H_5)_2SiO]_3$ by infrared) and Anderson Chemical triphenylsilanol were used. These compounds were stored in polyethylene ware to prevent reaction with glassware and to keep self-condensation to a minimum.

1. Preparation of Cyclobis[tetraphenyldisiloxanylchromate(VI)]

Cyclobis[tetraphenyldisiloxanylchromate(VI)] can be prepared by the reaction of diphenylsilanediol with either chromium(VI) oxide or chromyl chloride. Cyclobis[tetraphenyldisiloxanylchromate(VI)], the yellow-orange, crystalline solid which Hare (47) labeled compound II, was the principal product and was the only one ever isolated. The viscous residue left after complete separation of cyclobis[tetraphenyldisiloxanylchromate(VI)] did contain a Si-O-Cr linkage as shown by the infrared spectrum, but all attempts to isolate other silylchromates by distillation and chromatographic methods failed.

The linear silylchromate (compound I) proposed by Hare (47) could not be isolated. Infrared and proton resonance spectra, as well as inconsistent elemental analysis, were used as arguments against this structure. The absence of a SiOH linkage was shown by both the infrared and proton resonance spectra.

a. Reaction of Diphenylsilanediol with Chromium(VI) Oxide

Diphenylsilanediol and chromium(VI) oxide react in both methylene chloride and carbon tetrachloride to form principally cyclobis[tetraphenyldisiloxanylchromate(VI)]. Neither a variation in reaction time nor method of mixing affected the yield of cyclobis[tetraphenyldisiloxanylchromate(VI)], but reflux conditions gave a lower yield than was obtained at room temperature. Addition of freshly ground chromium(VI) oxide increased the yield. In a typical reaction, a slurry of 43 g. of diphenylsilanediol in 200 ml. of methylene chloride was added in small portions with rapid stirring to about 20 g. of freshly ground chromium(VI) oxide covered with 200 ml. of methylene chloride. Forty-five minutes after the addition of the diphenylsilanediol, the mixture was filtered through a fluted filter paper to remove excess chromium(VI) oxide. The volume of the filtrate was then reduced to 50 ml. by evaporation of solvent with a rotary evaporator, and the resulting solution was stored in the dark at 0°C for about 12 hours. Crystals of cyclobis[tetraphenyldisiloxanylchromate(VI)] formed and were removed by filtration through a Hirsch funnel with a coarse fritted disc. The filtrate was further concentrated and filtered until no more product could be obtained. This crude material was washed with pre-cooled methylene chloride to give 9.8 g. (20% based on diol) of yellow-orange crystals of cyclobis[tetraphenyldisiloxanylchromate(VI)]. It is easily recrystallized from either methylene chloride or carbon tetrachloride. Characterization and physical properties of cyclobis[tetraphenyldisiloxanylchromate(VI)] are discussed in a separate section of this thesis.

b. Reaction of Diphenylsilanediol and Chromyl Chloride

Investigation has shown that cyclobis[tetraphenyldisiloxanylchromate(VI)] is best prepared from the reaction of diphenylsilanediol and chromyl chloride in methylene chloride. In a typical synthesis, 12 ml. of freshly distilled chromyl chloride was pipetted into 200 ml. of recently distilled methylene chloride in a 500 ml. round bottom flask. A slurry of 30 g. of diphenylsilanediol in 200 ml. of methylene chloride was added portion-wise over a 30 minute period while the reaction was stirred with a Teflon-covered magnetic stirring bar. Thirty minutes after the addition of diphenylsilanediol, excess chromyl chloride was destroyed with solid sodium bicarbonate, the mixture was filtered through a fluted filter paper, and solvent was evaporated from the filtrate until the solution volume was reduced to about 50 ml. The liquid was stored in the dark at 0°C for about 12 hours Crude product then was easily obtained as yellow-orange crystals upon further removal of solvent from the solution. No other siloxy-chromium compounds could be isolated from the remaining viscous residue by distillation or chromatographic procedures. However, the infrared spectrum of this material showed that substances containing Si-O-Cr bonds probably were still present.

The temperature at which the reaction of chromyl chloride and diphenylsilanediol is carried out has a pronounced effect on the yield of cyclobis[tetraphenyldisiloxanylchromate(VI)]. The results of a study of yield as a function of reaction temperature are summarized in Table V. Methylene chloride was used as the solvent.

Table V. Temperature Effect on the Chromyl Chloride--Diphenylsilanediol Reaction

Temperature (°C)	Yield[1] of Compound II
40	16%
24	18%
0	25%
-78	55%

[1] Yield calculated from diphenylsilanediol consumption.

2. Characterization of Cyclobis[tetraphenyldisiloxanylchromate(VI)]

Because of the importance attached to cyclobis[tetraphenyldisiloxanylchromate(VI)], the experimental evidence relating to its structure has been thoroughly investigated. The elemental analysis, proton nuclear magnetic resonance spectrum, infrared spectrum, molecularity measurements, and chemical reactivity were given particular attention.

a. Physical Properties

Cyclobis[tetraphenyldisiloxanylchromate(VI)] has a sharp decomposition point at 169°C which is unchanged by recrystallization. An x-ray powder diffraction pattern was obtained on a finely ground sample of what was believed to be cyclobis[tetraphenyldisiloxanylchromate(VI)]. The sample was loaded in a glass capillary in a dry box, sealed, and placed into a North American Philips powder diffraction unit using chromium K_α radiation ($\lambda = 2.2909$ Å) and a vanadium filter. Crystallographic *d*-spacings were calculated from the resulting film pattern using standard techniques. Table VI lists these data; analytical data are reported in Table VII. The elemental analysis indicates a ratio of two silicon atoms for each chromium atom and is consistent with the empirical formula $[(C_6H_5)_2SiO]_2CrO_3$.

Considerable effort was made to find a satisfactory solvent for cyclobis[tetraphenyldisiloxanylchromate(VI)]. The following substances do not dissolve it sufficiently or are otherwise unsatisfactory: CH_2Cl_2, CCl_4, CBr_4, CS_2, CH_2Br_2, $HCON(CH_3)_2$, $(CH_3)_2CO$, CS_2--CBr_4, CH_2Cl_2--CBr_4, ethers, aliphatic hydrocarbons, F_3CCOOH, and $(CH_3)_2SO$. The $(CH_3)_2SO$ at first appeared to be a good solvent but it was found that a chemical reaction occurs.

Table VI. Interatomic Spacings for Cyclobis[tetraphenyldisiloxanylchromate(VI)]

Line	θ (degrees)	d_{hkl}(Å)	Relative Intensity
1	5.673	11.59	8
2	6.827	9.61	7
3	7.455	8.83	10
4	8.911	7.39	3
5	9.764	6.75	1
6	10.657	6.25	1
7	11.421	5.78	1
8	13.855	4.78	10
9	15.160	4.38	9
10	15.788	4.21	8
11	16.114	4.13	3
12	17.269	3.86	3
13	18.323	3.64	3
14	19.854	3.37	1
15	20.858	3.22	2
16	22.138	3.04	2
17	23.293	2.90	1
18	31.877	2.17	1

Table VII. Elemental Analysis of Cyclobis[tetraphenyldisiloxanylchromate(VI)]

Element	% Calculated For $[(C_6H_5)_2SiO]_2CrO_3$	% Found
Silicon	11.30	11.27, 11.46, 11.30
Chromium	10.48	10.41, 10.32, 10.38
Carbon	58.05	58.29, 58.16
Hydrogen	4.06	4.39, 4.15

b. Chemical Properties

As with most siloxy-chromium compounds, cyclobis[tetraphenyldisiloxanylchromate(VI)] is light sensitive. After a few minutes of exposure to sunlight, the yellow-orange crystals turn brown-green in color. The apparent decomposition of methylene chloride solutions of cyclobis[tetraphenyldisiloxanylchromate(VI)] in darkness and light at various temperatures is summarized in Table VIII. No attempt was made to isolated any decomposition products, but a lower oxidation state of chromium was always formed as apparent by the characteristic color. The increasing tendency of cyclobis[tetraphenyldisiloxanylchromate(VI)] to decompose at higher temperatures is consistent with the decreased yield of the compound when its synthesis is conducted with heating.

Table VIII. Decomposition of Methylene Chloride Solutions of Cyclobis[tetraphenyldisiloxanylchromate(VI)] in Storage

Conditions	Decomposition After 1 Hour	 5 Hours	 24 Hours
25°C, room light	slight	complete	complete
25°C, darkness	none	slight	considerable
0°C, room light	none	none	slight
0°C, darkness	none	none	slight
-78°C, room light	none	none	very slight
-78°C, darkness	none	none	none

Water hydrolyzes cyclobis[tetraphenyldisiloxanylchromate(VI)] in acetone solution, and tetraphenyldisiloxane-1,3-diol has been isolated as one of the products:

$$\left\{[(C_6H_5)_2SiO]_2CrO_3\right\}_2 + 4\ H_2O \longrightarrow 2\ [HOSi(C_6H_5)_2]_2O + 2\ H_2CrO_4.$$

This reaction was used in the quantitative determination of chromic acid and for the analysis of the cyclic silylchromate.

Tetraphenyldisiloxane-1,3-diol is also produced when cyclobis[tetraphenyldisiloxanylchromate(VI)] is cleaved with anhydrous hydrogen chloride in carbon tetrachloride:

$$\left\{[(C_6H_5)_2SiO]_2CrO_3\right\}_2 + 4\ HCl \longrightarrow 2\ [HOSi(C_6H_5)_2]_2O + 2\ CrO_2Cl_2.$$

Formation of the tetraphenyldisiloxane-1,3-diol in these reactions was indicated by infrared spectroscopy. After the solution of cyclobis[tetraphenyldisiloxanylchromate(VI)] had reacted with water and HCl gas, the Si-O-Si absorptions at 9.3 μ remained and the SiOH absorptions (2.7, 3.0, 11.3, and 11.8 μ) appeared. In each case the siloxy compound isolated gave an infrared spectrum consistent with tetraphenyldisiloxane-1,3-diol (47,78,91).

If cyclobis[tetraphenyldisiloxanylchromate(VI)] is not a cyclic structure, it must contain a siloxy chain-terminating group. Two likely chain terminators in chlorinated hydrocarbon solutions are chlorine and the hydroxyl group. A negative chloride test was obtained from a sodium fusion of the compound.

The most common terminator in siloxy chemistry is the hydroxyl group (3,20,21) and it is easily detectable in both the infrared and proton resonance spectra. These were therefore examined.

Two extremely clean sodium chloride and potassium bromide solution cells were used to record the infrared spectrum over the ranges 2-15 μ (Figure VI) and 15-25 μ (Figure XI) using the Perkin Elmer Model 21 and Beckman

Model 7 infrared spectrophotometers. Carbon disulfide and carbon tetrachloride were used as solvents. Compounds containing the SiOH group exhibit the usual OH stretching bands between 2.7 μ and 3.0 μ as found in organic alcohols (78,81,91) as well as the asymmetric SiO stretching absorptions at about 11 μ and 12 μ present in the spectra of silanols (80). Complete absence of the SiOH group was noted in spectra of concentrated solutions of cyclobis[tetraphenyldisiloxanylchromate(VI)]. From examination of the near infrared (1000 mμ-3300 mμ) spectrum of cyclobis[tetraphenyldisiloxanylchromate(VI)] recorded on the Beckman DK-2 Spectrophotometer, complete absence of SiOH was further verified.

The presence of Si-O-Si, Si-O-Cr, and Cr=O absorptions in the infrared region are in agreement with proposed structures. The very strong and broad absorption at 11.1 μ can be tentatively assigned to the Si-O-Cr linkage (47,58).

The absence of SiOH in cyclobis[tetraphenyldisiloxanylchromate(VI)] was demonstrated by proton nuclear magnetic resonance spectroscopy (Figure I). Samples were dissolved in CH_2Cl_2--CBr_4 or CCl_4--CBr_4 mixtures and proton resonance spectra were recorded at 60 Mc. on a Varian A-60 Spectrometer. Tetramethylsilane was used as an internal reference. For comparison, spectra of diphenylsilanediol, triphenylsilanol, diphenyldichlorosilane, and hexaphenylcyclotrisiloxane

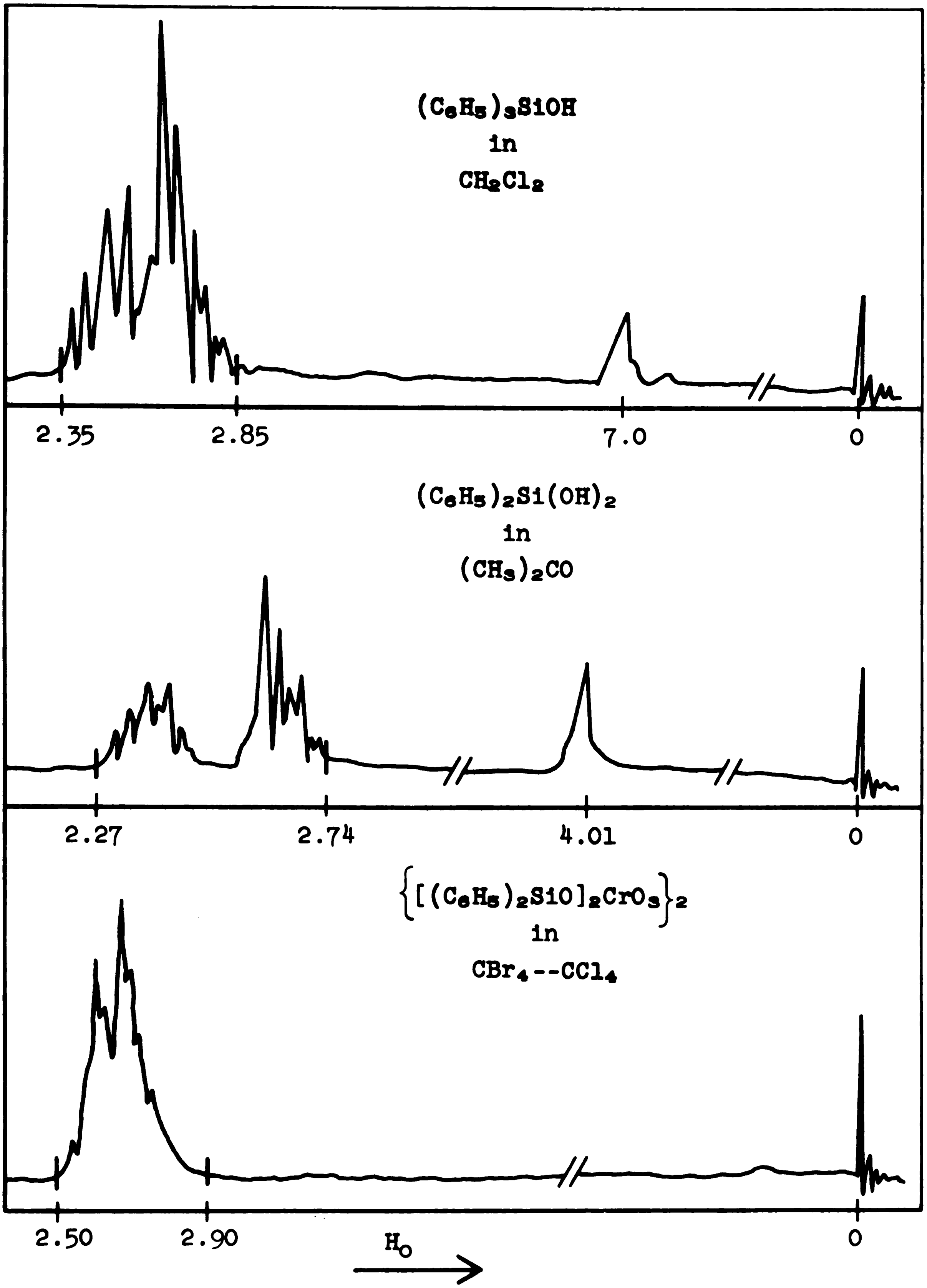


Figure I. Proton resonance spectra of triphenylsilanol, diphenylsilanediol, and cyclobis[tetraphenyldisiloxanylchromate(VI)].

also were recorded (Figure I). Results are reported in Table IX. Because the OH proton chemical shift is highly dependent on the concentration of the sample (87,88), a general inspection of the cyclobis[tetraphenyldisiloxanylchromate(VI)] spectrum was made for SiOH. However, proton resonance attributable to SiOH was completely absent.

Table IX. τ-Values[1] for Proton Chemical Shifts in Some Siloxy Compounds

Compound	Phenyl	OH	Solvent[2]
$(C_6H_5)_3SiOH$	2.62 m	7.10 s	CH_2Cl_2
$(C_6H_5)_2Si(OH)_2$	2.60 m	4.83 s	$(CH_3)_2CO$
$(C_6H_5)_2SiCl_2$	2.60 m	none	$(CH_3)_2CO$
$[(C_6H_5)_2SiO]_3$	2.62 m	none	$(CH_3)_2CO$
$\{[(C_6H_5)_2SiO]_2CrO_3\}_2$	2.66 m	none	CCl_4--CBr_4
$\{[(C_6H_5)_2SiO]_2CrO_3\}_2$	2.64 m	none	CH_2Br_2--CBr_4

[1] τ (in p.p.m.) = chemical shift = $[10.00 - 10^{8}(H_{Si(CH_3)_4} - H_{obs})]$-$H_{Si(CH_3)_4}$.

[2] 5-10 weight per cent solutions; m = multiplet, s = singlet.

In all cases the signal strengths were large enough that the SiOH proton resonance could easily be seen if present. Anticipated (88) and experimentally recorded spectra agree well for the five aromatic protons of cyclobis[tetraphenyldisiloxanylchromate(VI)]. The two ortho hydrogens of the phenyl groups are equivalent, as are the other three.

In order to distinguish between cyclic $[(C_6H_5)_2SiO]_2CrO_3$ and its dimer, $\{[(C_6H_5)_2SiO]_2CrO_3\}_2$, an accurate value of the molecular weight of the compound is necessary. Cryoscopy, however is difficult because of the limited solubility of cyclobis[tetraphenyldisiloxanylchromate(VI)] in almost all solvents. A Rast determination cannot be used because decomposition occurs when the sample is heated. Although solubility in carbon tetrabromide is reasonably good, this substance in unsuitable in the liquid state because it sublimes and decomposes slightly when heated.

Cryoscopic molecular weight measurements were made on benzene solutions. Benzene was selected as the solvent to be used in the cryoscopic measurement since the solutions were stable for sufficient time to allow measurement. Considerable time and effort was spent in increasing the sensitivity of the cryoscopic apparatus used so that the molecularity of the compound could be determined experimentally. Results are summarized in Table X. A detailed description of the cryoscopic apparatus used, along with the operating procedures, is presented in the Analytical Section of this thesis. The molecular weight was independent of concentration in the range from 15 to 100 mg. per 40 ml.

Table X. Cryoscopic Molecular Weight Determinations of Siloxy Compounds

Sample		Theoretical	Found
standard			
C_6Cl_6		285	281,284,285,286
$[(C_6H_5)_2SiO]_3$		594	599
$[(C_6H_5)_2SiO]_4$		793	798
cyclo[tetraphenyldisiloxanyl-chromate(VI)]	-monomer	497	
	-dimer	993	998,997,1004,995

of benzene and the values obtained clearly indicate that the species in solution has a molecular weight double that of the analytical formula.

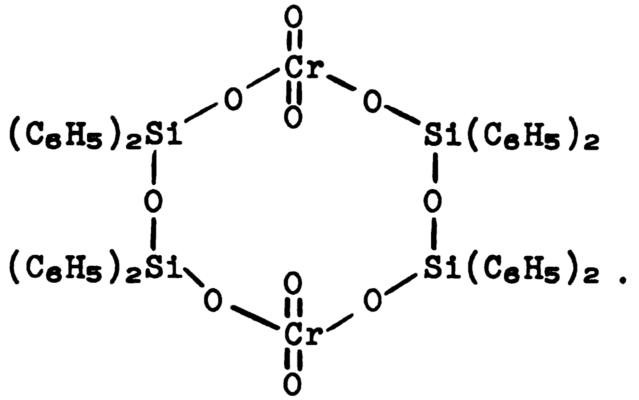
In addition, vapor pressure osmometry was used to obtain number average molecular weight data on a highly purified sample of what was believed to be cyclo[tetraphenyldisiloxanyl-chromate(VI)]. The molecular weight of this compound in benzene was found to be 930 ± 3%, compared with a formula weight of 497 for $[(C_6H_5)_2SiO]_2CrO_3$ and 993 for $\{[(C_6H_5)_2SiO]_2CrO_3\}_2$. The molecular weight data were independent of the concentration ranges examined (20 to 500 mg. per 100 g. of benzene).

An attempt was made to record the mass spectrum of cyclobis[tetraphenyldisiloxanylchromate(VI)] so that the molecular formula might be deduced. However, the sample did not have enough vapor pressure to permit a mass spectrum to be obtained. No decomposition was noted below 300°C and the sample was not heated above that temperature. This attempt was made by the Dow Corning Corporation Analytical Laboratories, Midland, Michigan.

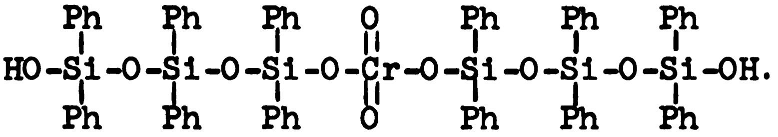
The conversion of cyclic siloxanes into linear polymers by acid or base catalysts is well known (89,90). Because of the many similarities between cyclobis[tetraphenyldisiloxanylchromate(VI)] and cyclosiloxanes, an attempt was made to polymerize the cyclic silylchromate with catalytic amounts of strong acids, bases, and other substances effective in opening a siloxane ring. Viscosity was selected as a polymerization indicator, and measurements were made in a Cannon-Fenske tube viscometer at constant temperature (0°C). Precautions were taken to keep the system anhydrous. Very small amounts of reagents were added to solutions of cyclobis[tetraphenyldisiloxanylchromate(VI)] and their viscosities were recorded with time. No change in viscosity was observed with any of the catalysts tested. These included pyridine, anhydrous HCl, potassium hydroxide, and triethylamine in methylene chloride solutions of cyclobis[tetraphenyldisiloxanylchromate(VI)], as well as phenylmagnesium bromide in tetrahydrofuran or benzene solutions of cyclobis[tetraphenyldisiloxanylchromate(VI)]. No further polymerization attempts were made.

C. Discussion

The previous two sections consisted of a rather extensive review and continuation of some work reported by Hare (47) which dealt with diphenylsilanediol--chromium(VI) reactions. Owing to the importance of the yellow-orange, crystalline silylchromate isolated from these reactions, considerable time and effort was given to characterizing it more completely. On the basis of this more recent and detailed characterization data, the compound can unequivocally be identified as cyclobis[tetraphenyldisiloxanylchromate(VI)], $\left\{[(C_6H_5)_2SiO]_2CrO_3\right\}_2$. This interesting substance possesses the following structure which is consistent with Hare's previous study (47):

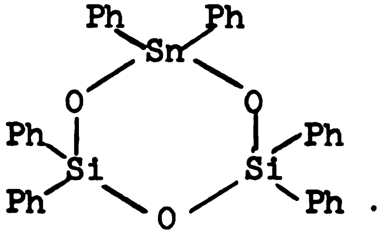


Results of the present study were not all in accord with those of reported by Hare. This investigation shows that cyclobis[tetraphenyldisiloxanylchromate(VI)] is best prepared by the diphenylsilanediol--chromyl chloride reaction and is the only siloxy-chromium compound that could be isolated from such reactions. At no time could the linear silylchromate proposed by Hare be isolated: (Ph = phenyl)

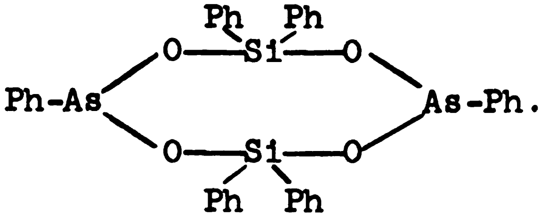


$$\mathrm{HO{-}\overset{Ph}{\underset{Ph}{Si}}{-}O{-}\overset{Ph}{\underset{Ph}{Si}}{-}O{-}\overset{Ph}{\underset{Ph}{Si}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}O{-}\overset{Ph}{\underset{Ph}{Si}}{-}O{-}\overset{Ph}{\underset{Ph}{Si}}{-}O{-}\overset{Ph}{\underset{Ph}{Si}}{-}OH.}$$

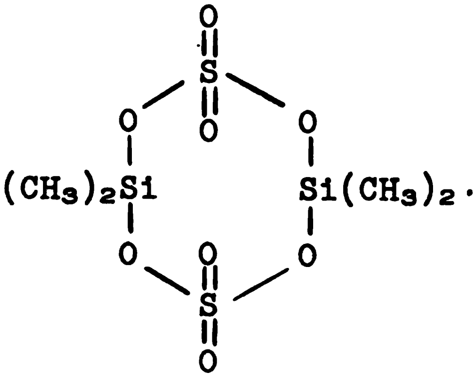
The cyclic nature of this polyfunctional silanol ester of chromic acid is interesting. It is the first such cyclic silylchromate reported, although Schmidbaur (52) conjectured that a dimeric dimethylsilylchromate could be distilled from a reaction mixture of chromium(VI) oxide and octamethylcyclotetrasiloxane. There are, however, similar cyclic species reported in the literature for other metallosiloxane compounds. Cyclic siloxanes containing metals have been reported by Koenig (125), Chamberland and MacDiarmid (76) and by Schmidt and Schmidbaur (74). Koenig (125) obtained the following compound from the reaction of dibutyltin oxide and diphenylsilanediol in dioxane:



It is interesting to note that this cyclic compound also contains a disiloxanyl linkage. Chamberlain and MacDiarmid (76) have reported the preparation of the following substance by condensation of diphenylsilanediol with diiodophenylarsine in the presence of ammonia:



Finally, Schmidt and Schmidbaur (74) were able to isolate dimeric dimethylsulfate by the reaction of dimethyldichlorosilane and sulfuric acid. The following structure was assigned:



After the cyclic nature of cyclobis[tetraphenyldisiloxanylchromate(VI)] was established, it was anticipated that this intermediate could be converted into a high molecular weight linear silylchromate polymer. All attempts to polymerize this cyclic substance failed to produce linear poly(diphenylsilylchromate) even though these same polymerization conditions are known to convert cyclic siloxanes into linear polysiloxanes. This suggests that cyclobis[tetraphenyldisiloxanylchromate(VI)] has little or no ring strain so that the Si-O-Cr and Si-O-Si bonds are not highly susceptible to redistribution and ring opening reactions. However, by further analogy to the cyclic siloxane polymerizations where it is well known (126) that the cyclotrisiloxanes, $(R_2SiO)_3$, are much more reactive than higher homologues, a smaller silylchromate ring system might easily be converted to polymer.

3. Preparation of Bis(triphenylsilyl)chromate

Bis(triphenylsilyl)chromate was prepared by the methods of Hare (47) with certain modifications. Two reactions were used:

$$2\ (C_6H_5)_3SiOH + CrO_3 \longrightarrow [(C_6H_5)_3Si]_2CrO_4 + H_2O$$

$$2\ (C_6H_5)_3SiOH + CrO_2Cl_2 \longrightarrow [(C_6H_5)_3Si]_2CrO_4 + 2\ HCl.$$

In both methods, the chromium compound was in moderate excess, and both are capable of giving quantitative yields of bis(triphenylsilyl)chromate.

a. Reaction of Triphenylsilanol with Chromium(VI) Oxide

The preparation of bis(triphenylsilyl)chromate from triphenylsilanol and chromic oxide is convenient because excess chromium(VI) oxide can be removed easily by filtration, and no base (hydrogen chloride acceptor) is needed to insure complete reaction. In a typical synthesis, a slurry of 5.5 g. of triphenylsilanol and 200 ml. of methylene chloride was added portion-wise to a mixture of 3.0 g. of chromium(VI) oxide in 100 ml. of methylene chloride contained in a single-necked 500 ml. round-bottom flask. A magnetic stirrer was used. The reaction was quite rapid, and after an hour the mixture was filtered through a fluted filter paper to remove excess chromium(VI) oxide. Crude product was obtained when the solvent was removed with a rotary evaporator.

b. Reaction of Triphenylsilanol with Chromyl Chloride

The preparation of bis(triphenylsilyl)chromate from triphenylsilanol and chromyl chloride was carried out in methylene chloride with calcium oxide present to remove hydrogen chloride. In a typical synthesis, a slurry of 5.5 g. of triphenylsilanol and 200 ml. of methylene chloride was added portion-wise to 6.0 ml. of chromyl chloride in 100 ml. of methylene chloride contained in a single-necked 500 ml. flask. Two grams of calcium oxide was added, and the slurry was stirred for 30 minutes after which it was filtered through

through a fluted paper. Crude product was obtained by evaporation of solvent with a rotary evaporator. Crude bis(triphenylsilyl)chromate was recrystallized from cold methylene chloride; yellow-orange crystals (m.p. 153°C) were obtained. The infrared spectrum for the 2 μ to 15 μ region was recorded (Figure VII) in carbon tetrachloride solution and found to be consistent with that reported by Hare (47). The infrared spectrum of the 15 μ to 25 μ region was also recorded (Figure X) and found to be consistent with the proposed structure. Investigation of both the crude and recrystallized products described above by infrared spectroscopy indicated that no hexaphenyldisiloxane was formed. This conclusion was based on the fact that the complete absence of the strong Si-O-Si absorption at 9.3 μ (80) was noted.

An x-ray powder diffraction pattern was obtained on a finely ground sample of what was believed to be bis(triphenylsilyl)chromate. The sample was loaded in a glass capillary in a dry box, sealed, and placed into a North American Philips powder diffraction unit using chromium K_α radiation (λ = 2.2909 Å) and a vanadium filter. Crystallographic d-spacings were calculated from the resulting film pattern using standard techniques. Table XI lists these data.

Table XI. Interatomic Spacings for Bis(triphenylsilyl)chromate

Line	θ (degrees)	d_{hkl} (Å)	Relative Intensity
	Chromium K_α Radiation (λ = 2.2909 Å)		
1	5.673	11.47	6
2	7.580	8.68	8
3	9.187	7.17	5
4	9.739	6.77	1
5	11.295	5.85	1
6	12.224	5.42	1
7	13.880	4.77	3
8	15.135	4.39	10
9	16.240	4.10	2
10	17.043	3.90	1
11	19.754	3.39	1
12	20.632	3.25	1

c. Equilibrium in the Triphenylsilanol-Chromyl Chloride Reaction

The chemical properties of bis(triphenylsilyl)-chromate were not specifically investigated since Hare (47) previously examined these. However, in this investigation the reaction of chromyl chloride and triphenylsilanol has been found to be a reversible process with all components present in significant concentrations under normal conditions:

$$2\ (C_6H_5)_3SiOH + CrO_2Cl_2 \rightleftharpoons [(C_6H_5)_3Si]_2CrO_4 + 2\ HCl.$$

This was demonstrated by the following evidence. The Si-OH absorption band, under the measurement conditions, does not disappear but falls to a constant value after about three minutes. The Si-OH absorption at 2720 mμ (81,91) was examined on a Beckman DK-2 Spectrophotometer using a lead sulfide detector. Addition of CaO to the system immediately removes the 2720 mμ absorption, presumably by shifting the position of equilibrium through removal of HCl, whereas the addition of anhydrous gaseous HCl to the system increases the intensity of the SiOH absorption by reversal of the reaction.

$$2\ CaO(\underline{s}) + 2\ HCl(\underline{g}) \longrightarrow CaCl_2(\underline{s}) + Ca(OH)_2(\underline{s})$$

Traces of water would be immediately consumed by the excess calcium oxide reagent:

$$H_2O + CaO \longrightarrow Ca(OH)_2.$$

Furthermore, calcium oxide was shown not to cause condensation of the triphenylsilanol in carbon tetrachloride at 25°C. This was demonstrated by infrared spectroscopy and based on the fact that no Si-O-Si absorption at 9.3 μ was observed and the Si-OH absorption at 2.7 μ remained.

In the early stages of this study it was anticipated that the intermediate triphenylsiloxychromyl chloride did not exist in any significant amount in the equilibrated mixture. The overall equilibrium constant for the reaction was determined spectrophotometrically in the following approach:

$$(C_6H_5)_3SiOH + CrO_2Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (C_6H_5)_3SiOCrO_2Cl + HCl$$

$$(C_6H_5)_3SiOCrO_2Cl + (C_6H_5)_3SiOH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [(C_6H_5)_3Si]_2CrO_4 + HCl$$

and

$$2\ (C_6H_5)_3SiOH + CrO_2Cl_2 \overset{K_{eq}}{\rightleftharpoons} [(C_6H_5)_3Si]_2CrO_4 + 2\ HCl$$

and

$$K_{eq} = \frac{k_1k_3}{k_2k_4} = \frac{[\{(C_6H_5)_3Si\}_2CrO_4][HCl]^2}{[(C_6H_5)_3SiOH]^2[CrO_2Cl_2]}$$

The following procedure was used to calculate equilibrium concentrations. If the subscript zero designates the initial concentration of a species and $\underline{x}$ the number of moles per liter consumed in the reaction, then

$$[(C_6H_5)_3SiOH] = [(C_6H_5)_3SiOH]_0 - \underline{x}$$

$$[CrO_2Cl_2] = [CrO_2Cl_2]_0 - \frac{\underline{x}}{2}$$

$$[\{(C_6H_5)_3Si\}_2CrO_4] = [\{(C_6H_5)_3Si\}_2CrO_4]_0 + \frac{\underline{x}}{2}$$

$$[HCl] = [HCl]_0 + \underline{x}\ .$$

When initial concentrations of all species and the amount of triphenylsilanol consumed ($\underline{x}$) are known, the equilibrium constant can be obtained from absorbancy readings of the silanol absorption band at 2720 mμ when equilibrium is attained. Absorbancies were conveniently converted to molar concentrations using the following equation:

$$\underline{y} = 0.32711 + 7.803714\underline{x} + 15.725541\underline{x}^2,$$

where $\underline{y}$ is the concentration in millimoles of triphenylsilanol per liter of carbon tetrachloride and $\underline{x}$ is the absorbancy at 2720 mμ. This equation was derived from regression analysis ("curve fitting") of the Beer's law data described later in this thesis. Table XII shows the results of such an experiment and it may be seen that the equilibrium constants are all essentially constant over the range of concentrations examined. The scattering is ascribed to limitations of experimental measurements since there is no definite trend to concentration. There is no indication from this work that HCl gas escapes during the reaction of triphenylsilanol and chromyl chloride in carbon tetrachloride. On the contrary, this possibility was ruled out using a standard method of quantitative chloride ion balance. Identical chloride ion determinations were obtained on samples of a 1.00 ml. aliquot of a stock solution of chromyl chloride in carbon tetrachloride and a 1.00 ml. aliquot of this same sample that was allowed to

Table XII. Equilibrium Constant Data for the $(C_6H_5)_3SiOH$--CrO_2Cl_2 Reaction

$$2\ (C_6H_5)_3SiOH + CrO_2Cl_2 \underset{}{\overset{k_{eq}}{\rightleftharpoons}} [(C_6H_5)_3Si]_2CrO_4 + 2\ HCl$$

Absorbancy Si-OH at 2720 mμ	$[(C_6H_5)_3SiOH]$ x 10^2 <u>M</u>	Initial $[(C_6H_5)_3SiOH]$ x 10^2 <u>M</u>	Initial $[CrO_2Cl_2]$ x 10^2 <u>M</u>	$[CrO_2Cl_2]$ x 10^2 <u>M</u>	[HCl] x 10^2 <u>M</u>	$[\{(C_6H_5)_3Si\}_2CrO_4]$	K_{eq}
0.277	0.370	1.194	2.14	1.73	0.826	0.413	1.2
0.274	0.365	1.194	2.14	1.72	0.829	0.415	1.2
0.271	0.360	1.194	2.14	1.72	0.834	0.417	1.3
0.310	0.426	1.400	2.21	1.72	0.974	0.487	1.5
0.266	0.351	1.15	1.77	1.37	0.80	0.40	1.5
0.533	0.895	2.19	1.77	1.12	1.30	0.65	1.2
0.340	0.480	1.39	1.42	0.97	0.91	0.45	1.7
0.567	0.981	2.22	1.42	0.80	1.24	0.62	1.2
0.421	0.640	1.54	1.18	0.73	0.90	0.45	1.2
0.596	1.056	2.24	1.18	0.59	1.18	0.59	1.2
						K_{eq} (Ave.) = 1.3	

attain equilibrium with triphenylsilanol in the one centimeter spectrophotometer cell used in the equilibrium constant experiments.

4. Preparation of Triphenylsiloxychromyl Chloride

The existence of a new compound, triphenylsiloxychromyl chloride, $(C_6H_5)_3SiOCrO_2Cl$, was first suspected when infrared spectra of triphenylsilanol and chromyl chloride solutions mixed in various proportions were compared. Bis(triphenylsilyl)chromate is formed in such solutions, but it was noted that the Si-O-Cr absorption at 11.4 μ of bis(triphenylsilyl)chromate is shifted to 11.1 μ in mixtures containing excess chromyl chloride. Because this observation suggested the existence of triphenylsiloxychromyl chloride, an effort was made to synthesize the compound.

a. Reaction of Triphenylsilanol with Chromyl Chloride

A slurry of 2.7 g. of triphenylsilanol in 100 ml. of methylene chloride was added in small portions to 2 ml. of recently distilled chromyl chloride in 100 ml. of methylene chloride. The mixture in a 300 ml. round-bottom flask at room temperature was allowed to stand for 30 minutes after the last addition of triphenylsilanol. The reaction mixture was then filtered through a fluted paper, and solvent was evaporated until the solution volume was reduced to about 10 ml. Dark red-orange crystals were obtained, and additional crop was formed from solutions by addition of *n*-hexane.

The crude product was easily recrystallized from methylene chloride or carbon tetrachloride. After drying in vacuo, the purified triphenylsiloxychromyl chloride had a sharp melting point at 97°C. Characterization data, including physical and chemical properties, of the purified triphenylsiloxychromyl chloride are discussed in a separate portion of this thesis.

b. Reaction of Hexaphenyldisiloxane with Chromyl Chloride

A slurry of 2.7 g. of hexaphenyldisiloxane in 100 ml. of carbon tetrachloride was mixed with 4 ml. of chromyl chloride in 100 ml. of carbon tetrachloride contained in a single-necked 300 ml. round-bottom flask. The reaction mixture was stirred with a Teflon covered magnetic stirring bar at room temperature. Aliquots were taken for infrared analysis after 1, 8, and 24 hours after the addition of the hexaphenyldisiloxane carbon tetrachloride slurry. The infrared spectra of the 2 μ to 15 μ and 15 μ to 25 μ regions of these solutions revealed that no reaction between the hexaphenyldisiloxane and chromyl chloride had occurred. Only absorptions characteristic of these starting materials were observed. The absence of the Si-Cl infrared absorption at 18.2 μ and the Si-O-Cr bands at 11.1 and 11.4 μ indicated that triphenylchlorosilane, triphenylsiloxchromyl chloride, and bis(triphenylsilyl)chromate had not formed under the reaction conditions used.

5. Characteristics of Triphenylsiloxychromyl Chloride

a. Physical Properties

Analytical data for triphenylsiloxychromyl chloride reported in Table XIII indicates a ratio of one silicon atom for each chromium and chlorine atom and is consistent with the basic formula $(C_6H_5)_3SiOCrO_2Cl$.

Table XIII. Elemental Analysis of Triphenylsiloxychromyl Chloride

Element	Per Cent Calculated For $(C_6H_5)_3SiOCrO_2Cl$	Per Cent Found
Carbon	54.75	54.59, 54.67
Hydrogen	3.83	4.02, 4.04
Chromium	13.17	13.40, 13.30
Silicon	7.11	6.85, 6.95, 7.03
Chlorine	8.98	8.82, 8.90

The molecular weight of triphenylsiloxychromyl chloride in carbon tetrachloride was found by ebullioscopic measurements to be 378 ± 10, compared with a formula weight of 394 for $(C_6H_5)_3SiOCrO_2Cl$. This measurement was made by Huffman Microanalytical Laboratories, Wheatridge, Colorado. Cryosopic measurements in carbon tetrachloride made in this laboratory gave a value of 416 ± 10.

An x-ray powder diffraction pattern was obtained on a finely ground sample of what was believed to be triphenylsiloxychromyl chloride. The sample was loaded in a glass capillary in a dry box, sealed, and placed in a North American Philips powder diffraction unit using chromium K_α radiation (λ = 2.2909 Å) and a vanadium filter. Crystallographic d-spacings were calculated from the resulting film using standard techniques. These data are listed in Table XIV. They clearly differ from d-spacings of chromium(VI) oxide (92) and triphenylsilanol (92) as well as from those of bis(triphenylsilyl)chromate (p. 53, Table XI).

The infrared spectra of the 2 μ to 15 μ and 15 μ to 25 μ regions of triphenylsiloxychromyl chloride in carbon tetrachloride in solutions are shown in Figures VIII and X and are summarized in Table XV. The infrared spectrum shows strong Cr-Cl, strong Si-O-Cr shifted from the usual Si-O-Cr position, no Si-OH, and strong Cr=O absorptions.

The ultraviolet and visible spectrum of triphenylsiloxychromyl chloride in methylene chloride was recorded and is compared with the spectra of chromyl chloride, bis(triphenylsilyl)chromate, and cyclobis[tetraphenylsiloxanylchromate(VI)] in Figure II. Absorptions at approximately 350 mμ and in the 260-280 mμ region are observed and are characteristic of all phenylsilylchromates (47).

Table XIV. Interatomic Spacings for Triphenylsiloxychromyl Chloride

Line	θ (degrees)	d_{hkl} (Å)	Relative Intensity
1	6.913	9.52	4
2	7.367	8.93	1
3	7.693	8.56	1
4	8.183	8.05	2
5	8.936	7.37	4
6	9.676	6.81	2
7	9.977	6.61	2
8	10.555	6.25	3
9	11.797	5.60	2
10	12.349	5.36	2
11	13.328	4.97	1
12	13.969	4.75	8
13	14.433	4.60	3
14	14.859	4.47	3
15	15.160	4.38	1
16	15.851	4.19	10
17	16.353	4.07	1
18	18.047	3.70	3
19	19.026	3.51	1
20	19.804	3.38	2
21	20.293	3.30	2

Table XV. Infrared Absorptions of Triphenylsiloxchromyl Chloride in CCl_4

Position (μ)	Intensity	Assignment
3.5	medium	C-H
6.9	strong	Si-phenyl
8.9	strong	Si-phenyl
10.1	strong	Cr=O
10.3	strong	Cr=O
11.1	strong (broad)	Si-O-Cr
14.1	medium	Si-phenyl
14.3	strong	Si-phenyl
19.2	strong	Si-phenyl
20.0	strong	Cr-Cl

b. Chemical Properties

The red-orange crystals of triphenylsiloxychromyl chloride are only slowly decomposed by sunlight. Methylene chloride solutions show extensive decomposition after a few hours in light.

Triphenylsiloxychromyl chloride reacts reversibly with triphenylsilanol in carbon tetrachloride to give bis(triphenylsilyl)chromate:

$$(C_6H_5)_3SiOCrO_2Cl + (C_6H_5)_3SiOH \rightleftharpoons [(C_6H_5)_3Si]_2CrO_4 + HCl.$$

However, the equilibrium position is far to the left unless it is shifted by addition of a large excess of triphenylsiloxychromyl chloride or by the addition of a base such as calcium oxide. On the other hand, addition of anhydrous hydrogen chloride forces the position of equilibrium to the left and will convert triphenylsiloxychromyl chloride into triphenylsilanol and chromyl chloride through the reaction:

$$(C_6H_5)_3SiOCrO_2Cl + HCl \rightleftharpoons (C_6H_5)_3SiOH + CrO_2Cl_2.$$

Triphenylsiloxychromyl chloride is thus an intermediate that participates in the two equilibria. Changes in the equilibrium can be followed by observing relative increases and decrease in the Si-O-Cr and SiOH infrared absorptions.

Triphenylsiloxychromyl chloride is attacked slowly by cold water. It can be completely hydrolyzed by sodium hydroxide solutions. This reaction was used in the quantitative determination of chromic acid and for the analysis

$$(C_6H_5)_3SiOCrO_2Cl + 2\ H_2O \longrightarrow (C_6H_5)_3SiOH + H_2CrO_4 + HCl$$

of the triphenylsiloxychromyl chloride. The white crystalline siloxane isolated from this reaction was shown to be principally triphenylsilanol by infrared analysis.

c. Discussion

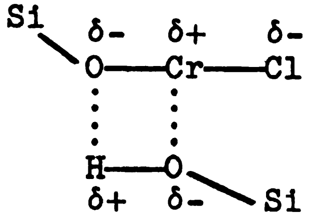
The purpose of this present account is to outline the important features of the intermediate compound that was isolated from the reaction mixture of triphenylsilanol and chromyl chloride in carbon tetrachloride. On the basis of the characterization data presented in the two preceeding sections, the compound can unequivocally be identified as triphenylsiloxychromyl chloride, $(C_6H_5)_3SiOCrO_2Cl$. This compound represents the first silyl chlorochromate (a chlorochromic acid derivative of an organosilanol) isolated and characterized. Previous attempts to isolate such species were reported by Schmidbaur (52) but in every case, proved unsuccessful. It should be noted, however, that Schmidbaur's study dealt only with trialkylsiloxy intermediates and illustrates the importance of the nature of the organosubstituent groups attached to silicon.

There are, however, certain analogies that can be drawn by comparing such chemical stability of $(C_6H_5)_3SiOCrO_2Cl$ to other transition metal compounds. Thus, several workers have reported (117) that in general, transition metal chlorides undergo solvation and/or solvolysis with aliphatic alcohols, but in no case is replacement of the chloride complete. Wardlaw and co-workers (118) report that preparation of $ClTi(OC_2H_5)_3$. Bradley and co-workers (119) were unable to prepare a pure stannic alkoxide directly from the reaction of stannic chloride and an alcohol. Moreover, attempts to prepare thorium and zirconium alkoxides by a similar method were also unsuccessful because the replacement of the chloride was incomplete (120). Skelcey (93) reports the preparation of three triorganosiloxybis(cyclopentadienyl)titanium chlorides which he obtained from the condensation reactions of bis(cyclopentadienyl)titanium chloride and sodium triorganosilanolates. He isolated and characterized the triphenyl, trimethyl, and dimethylphenylsiloxy derivatives.

Sisler (116) has reported a somewhat similar but completely inorganic monochlorochromate. The methods for the preparation of potassium monochlorochromate included the action of hydrochloric acid on potassium dichromate, the reaction of potassium chloride with chromium(VI) oxide in aqueous solution, and the action of chromyl chloride on potassium chromate dissolved in water or glacial acetic acid.

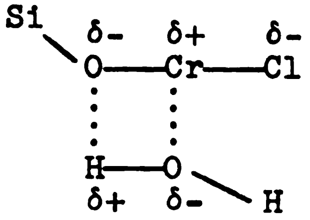
Although the data for the triorganosiloxychromyl chloride derivatives are limited to those with $(C_6H_5)_3Si$ and $(CH_3)_3Si$ moieties, one is tempted to compare the relative stability of these compounds in terms of the nature of these substituent groups. The phenyl group is much larger than the methyl group and $(C_6H_5)_3Si$ is considerably more electron-withdrawing in nature than is the $(CH_3)_3Si$ moiety. In view of the extreme difference between the two derivatives, a reasonable conclusion to reach would be that both steric and electronic-inductive effects are important.

Even more surprising than the fact that triphenylsiloxychromyl chloride can be conveniently synthesized is the fact that once isolated, the molecule reacts only very slowly with triphenylsilanol unless a base such as calcium oxide is present. Likewise, triphenylsiloxychromyl chloride is attacked only slowly by cold water unless promoted by some suitable base such as sodium hydroxide. The reason for the stability of this compound and the apparent low reactivity towards hydrolysis and silanolysis is perhaps due to several considerations. The steric hindrance of the chloride in the triphenylsiloxychromyl chloride molecule by the large and bulky triphenylsiloxy group is no doubt involved. Also important is the state of bonding in this silyl chlorochromate which results from an electron-release from silicon by the phenyl substituents and the $\underline{d}\pi$-$\underline{p}\pi$ bonding between silicon and oxygen permitted by the availability of $\underline{d}$ orbitals on silicon. A more reasonable explanation of this phenomenon concerns the formation of stable covalent complexes between the silyl chlorochromate and molecules of solvent. Two such coordination complexes for water and an organosilanol are represented on the following page:



Silanol complex of silyl chlorochromate

and



Water complex of silyl chlorochromate

Such complexes would be expected to form in view of the strong proton donor nature of the solvating molecules and the equally strong proton accepting nature of the silylchromate linkage. Similar interactions are of course involved in the self-associated (hydrogen-bonded) aggregates of several hydroxy-containing compounds discussed throughout this thesis. It should be mentioned here that similar complexes between alkali metal triorganosilanolates and molecules of alcohol or water have been reported (12).

C. Spectroscopic Data

1. Ultraviolet and Visible Spectra

These spectra were recorded with a Cary Model 11 recording spectrophotometer and a Beckman DK-2 recording spectrophotometer. Conventional 1 cm. silica cells closed with ground glass stoppers were used. The ultraviolet and visible absorption spectra of chromyl chloride, bis(triphenylsilyl)chromate, and cyclobis[tetraphenyldisiloxanylchromate(VI)] were remeasured (47) in methylene chloride. In addition, similar measurements were obtained for the new compound, triphenylsiloxychromyl chloride. While the results and interpretations are in full agreement with Hare's (47), the additional measurements of triphenylsiloxychromyl chloride serve to strengthen some of the absorption assignments. Figure II compares the ultraviolet and visible absorption spectra of these compounds. The absorbancies are arbitrary. The phenyl-containing siloxychromium compounds all show an absorption in the 330-370 mμ region and the characteristic phenyl absorptions in the 240-280 mμ region. There are no predominate absorption bands in this region characteristic of the Si-O-Si linkage. In general, the ultraviolet and visible absorption spectra are not as suitable for characterization of siloxy-chromium compounds as are infrared spectra.

2. Infrared Spectra

The infrared spectra of compounds involved in this investigation (Figures III through XI) were recorded in carbon disulfide or carbon tetrachloride solutions, or in potassium bromide pellets where appropriate. Spectra in the near infrared region (1000-3300 mμ) were recorded on a Beckman Model DK-2 Spectrophotometer. Spectra in the 2-15 μ region were recorded on a Perkin-Elmer Model 21

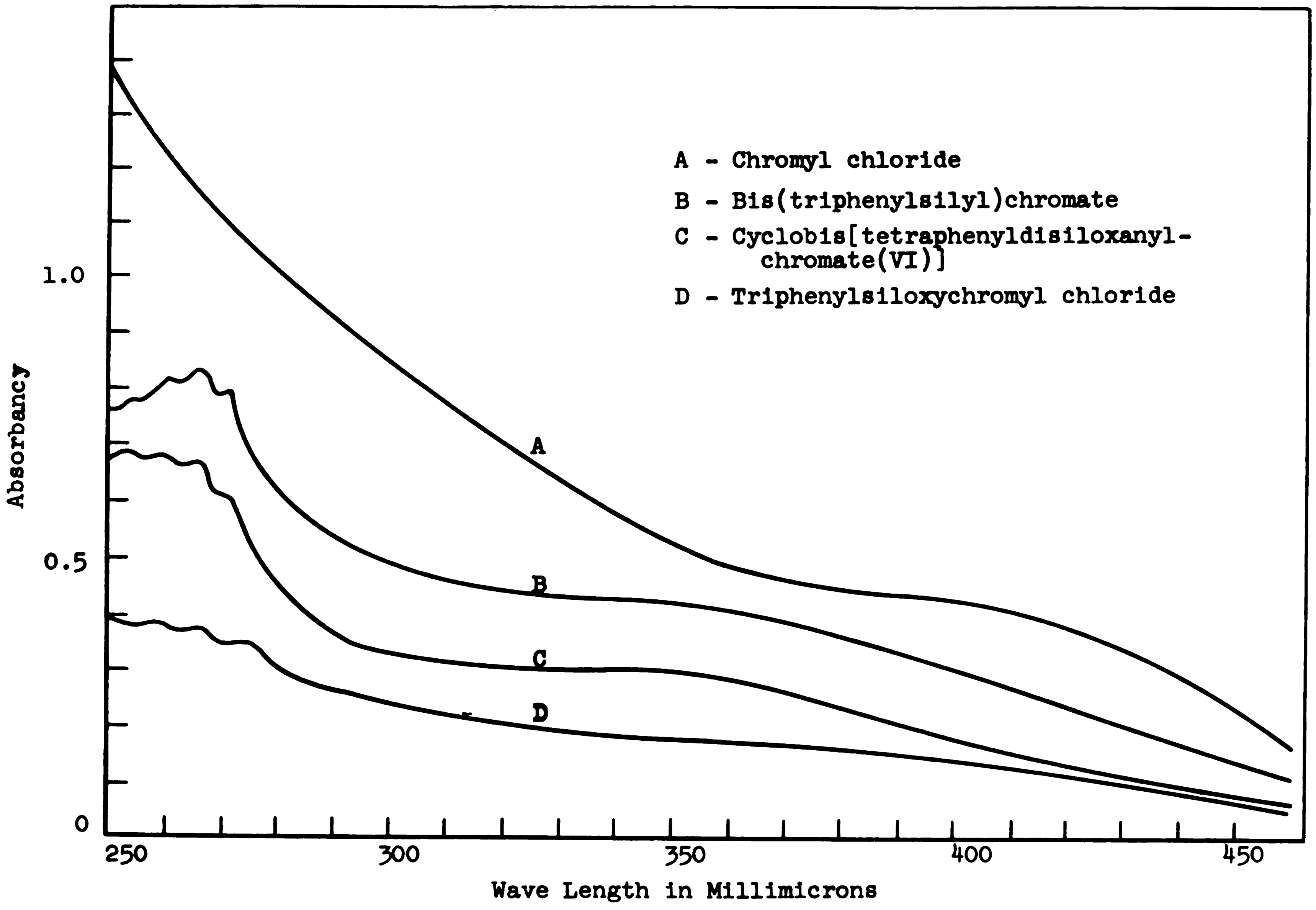


Figure II. Ultraviolet and visible spectra of chromyl chloride, bis(triphenylsilyl)-chromate, cyclobis[tetraphenyldisiloxanylchromate(VI)], and triphenylsiloxychromyl chloride.

Recording Spectrophotometer, and those in the 15-25 μ region on a Beckman Model 7 Recording Spectrophotometer with cesium iodide optics. Hare (47) has reported results for several siloxy-chromium compounds. While the results and interpretations of this study are in full agreement with Hare's (47), a wider spectral range was examined, and the additional measurements with triphenylsiloxychromyl chloride serve to strengthen some of the vibrational assignments.

Some of the infrared spectra recorded in this investigation were described in separate portions of this thesis when product identification (via infrared) was essential to the discussion.

There is evidence that the Si-O-M (M = metal) linkage absorbs in the 10-11.5 μ region (80-83,93). Compounds containing silicon-oxygen-chromium bonds likewise all have strong broad absorptions in the 11.0-12.0 μ region which Hare (47) tentatively assigned to the silicon-oxygen-chromium stretching frequency. When siloxy-chromium compounds are allowed to react completely with water or anhydrous HCl, the infrared spectra of the reaction products no longer show these characteristic Si-O-Cr absorption bands (see Appendix I for a related study involving Si-O-M compounds and reactions with anhydrous HCl).

There is evidence that the position of the band center maximum of the Si-O-Cr infrared absorptions is uneffected by changes in concentrations. Thus, the position of the Si-O-Cr absorption at 11.4 μ was independent of concentration in the range from 10 to 300 mg. of bis(triphenylsilyl)chromate per 10 ml. of carbon tetrachloride.

The Si-O-Cr absorption bands are affected by electron donating properties of the substituent groups on silicon (47). Thus, the Si-O-Cr absorption in the infrared spectrum of triphenylsiloxychromyl chloride is located at 11.1 μ and at 11.4 μ in bis(triphenylsilyl)chromate. Skelcey (93) has reported analogous infrared results from some siloxy derivatives of bis(cyclopentadienyl)titanium(IV). The Si-O-Ti absorption band for $(C_5H_5)_2Ti[OSi(C_6H_5)_3]_2$ is located at 11.0 μ compared to 10.5 μ for $(C_5H_5)_2TiCl[OSi(C_6H_5)_3]$.

All phenylsilylchromates exhibit strong absorptions characteristics of the silicon-phenyl groups (80,93) at 6.9, 8.9, 13.5, 13.9, 14.3, and 19.2 microns, as well as medium absorptions at 3.3 and 10.0 microns, and a weak band at 9.7 microns. Spialter, Priest, and Harris (86) attribute the 13.5 and 14.3 μ bands to the out-of-plane hydrogen deformation modes. Absorption bands at 10.1 and 10.3 μ which correspond to the asymmetric and symmetric stretching frequencies of Cr=O reported for chromyl chloride (84,85) are observed in the infrared spectra of all silylchromates.

Important to this investigation was the detection of the presence or absence of the Si-O-Si linkage by infrared spectroscopy. A strong absorption band at about 9.3 μ was exhibited by hexaphenyldisiloxane, tetraphenyldisiloxane-1,3-diol, and cyclobis[tetraphenyldisiloxanylchromate(VI)] and is attributed to the disiloxane linkage in all three compounds (47,80,91). This same Si-O-Si absorption was particularly useful in determining the extent to which triphenylsilanol condenses to hexaphenyldisiloxane under various reaction conditions.

Detection of the presence or absence of the Si-OH linkage by spectroscopic methods has been important to this investigation. Organosilanols in the solid state or in concentrated solutions show a broad band centered around 3.0-3.1 μ which is characteristic of strong hydrogen-bridge formation. Richards and Thompson (91) have reported that the broad band centered around 3250 cm.$^{-1}$ (3.08 μ) for triphenylsilanol and several poly(diphenylsiloxane)-α,ω-diols gives way in dilute solution in carbon tetrachloride to a sharp band near 3690 cm.$^{-1}$. They attribute this absorption to the stretching vibration of the free Si-OH group and note that it is equal to the absorption found in organic alcohols. Compounds containing the Si-OH group also exhibit useful asymmetric stretching absorptions at about 11 μ and 12 μ (80). More recently Harris (78) measured the infrared

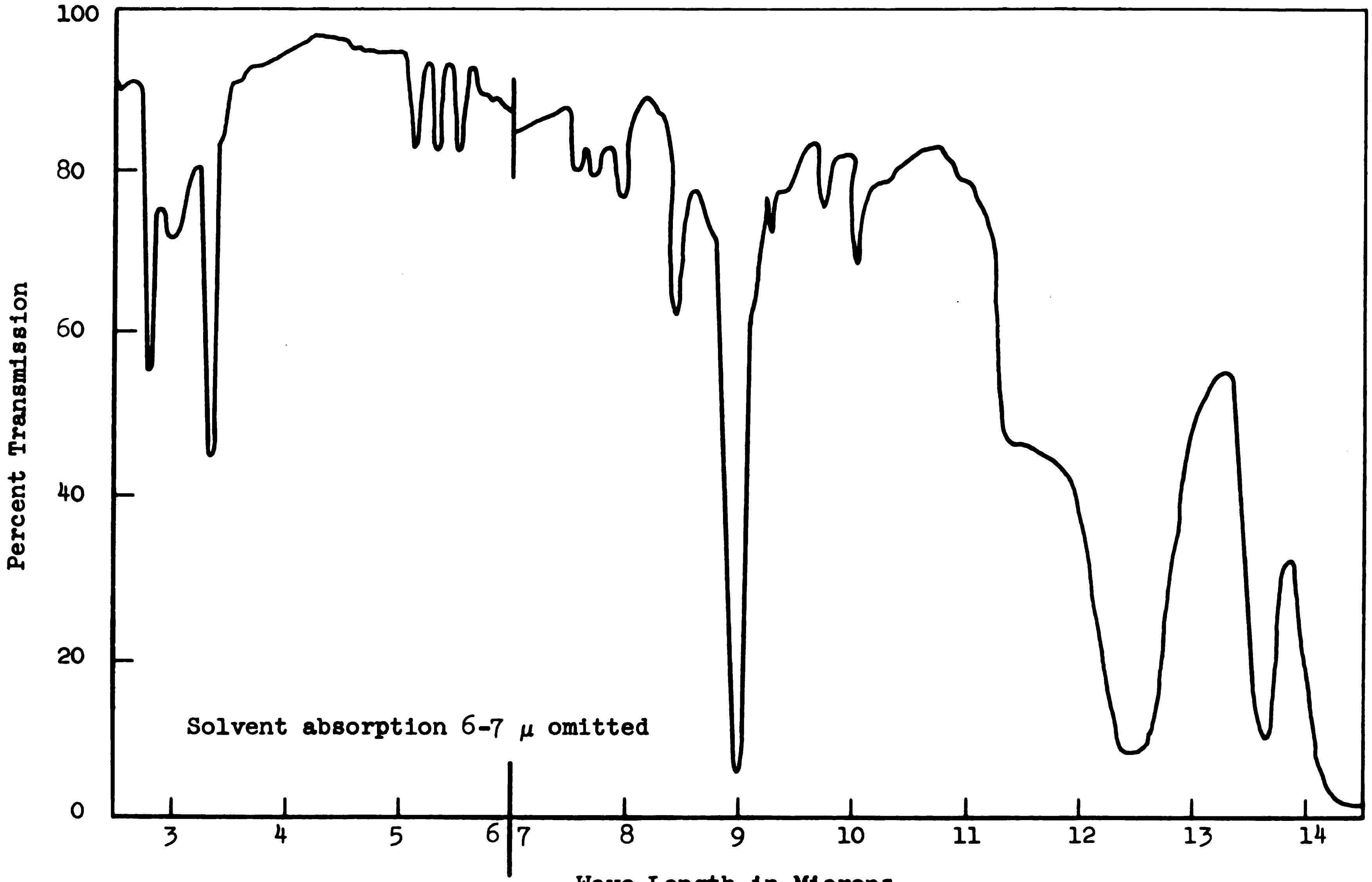
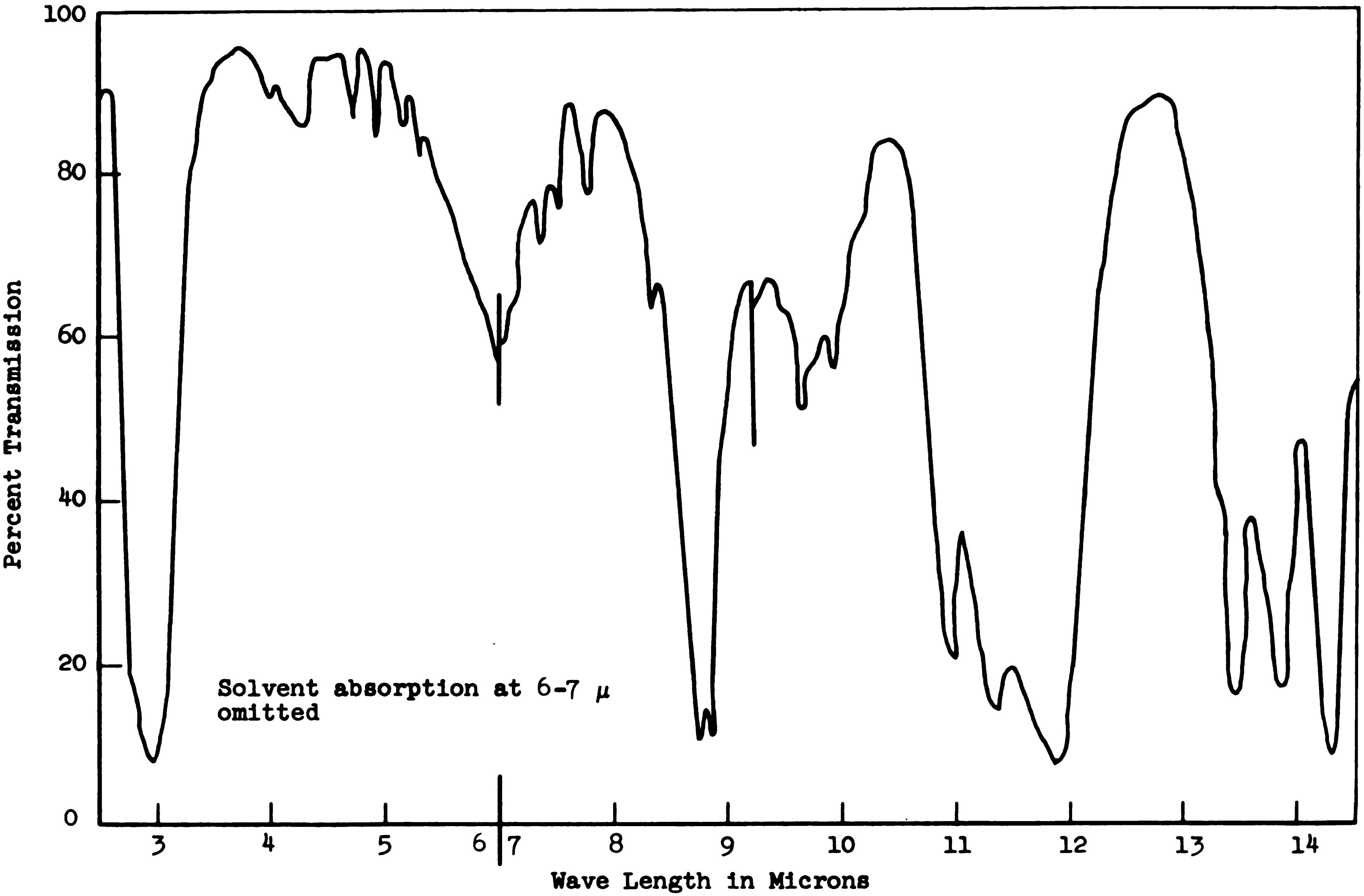


Figure III. Infrared spectrum of triphenylsilanol in carbon disulfide (2-15 μ region).



Solvent absorption at 6-7 μ omitted

Figure IV. Infrared spectrum of diphenylsilanediol in carbon disulfide (2-15 μ region).

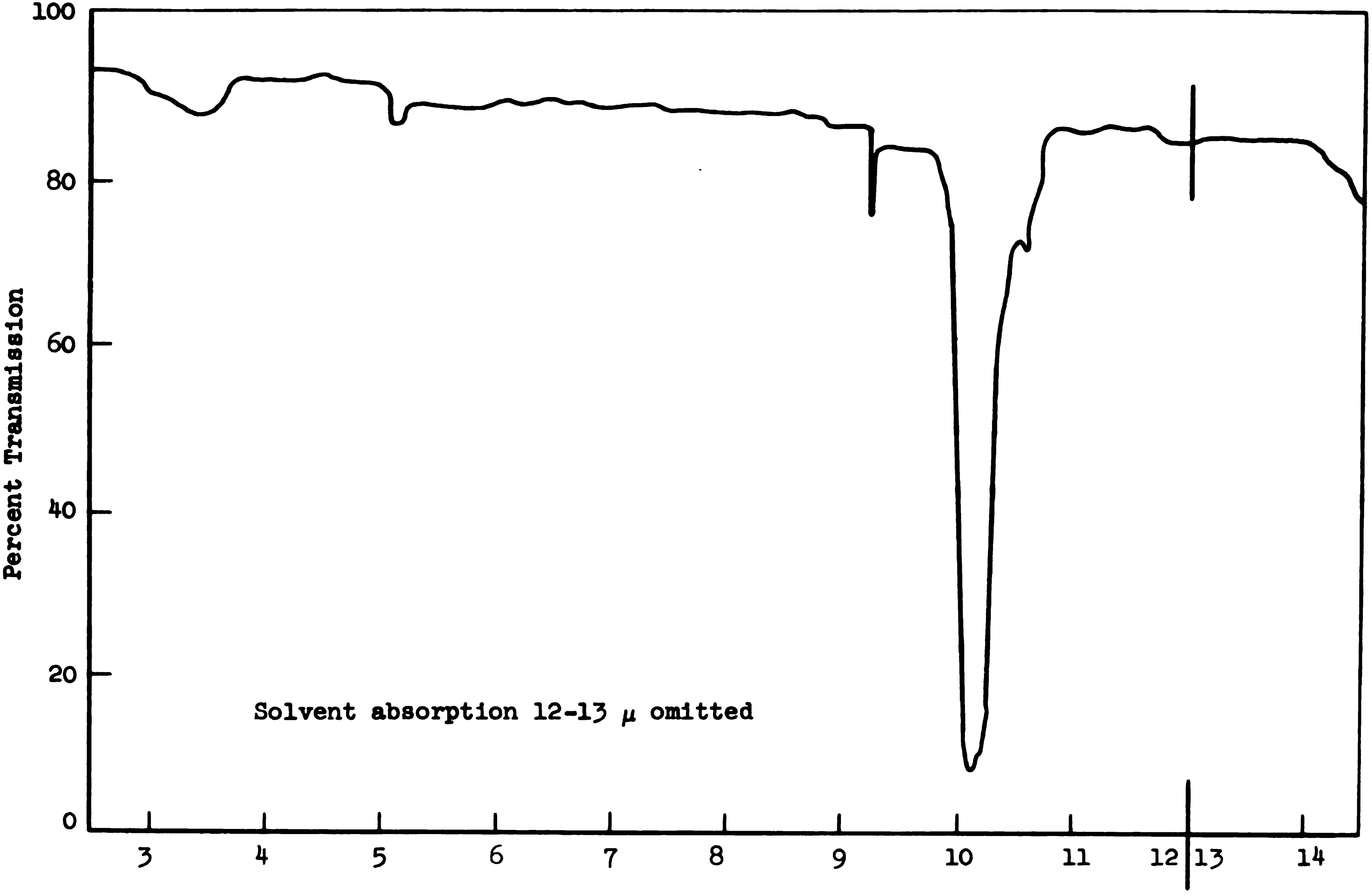


Figure V. Infrared spectrum of chromyl chloride in carbon tetrachloride (2-15 μ region).

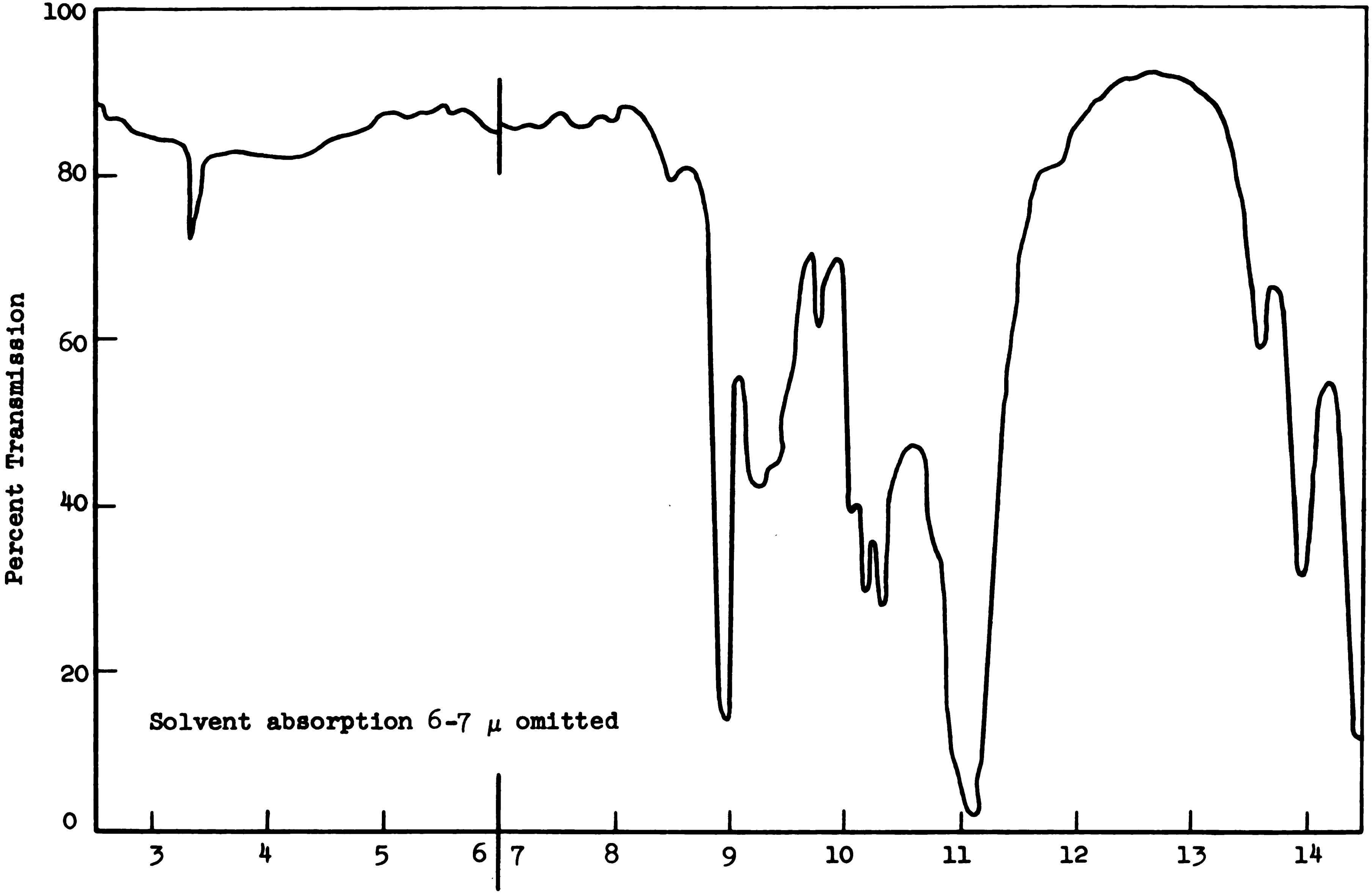


Figure VI. Infrared spectrum of cyclobis[tetraphenyldisiloxanylchromate(VI)] in carbon tetrachloride (2-15 μ region).

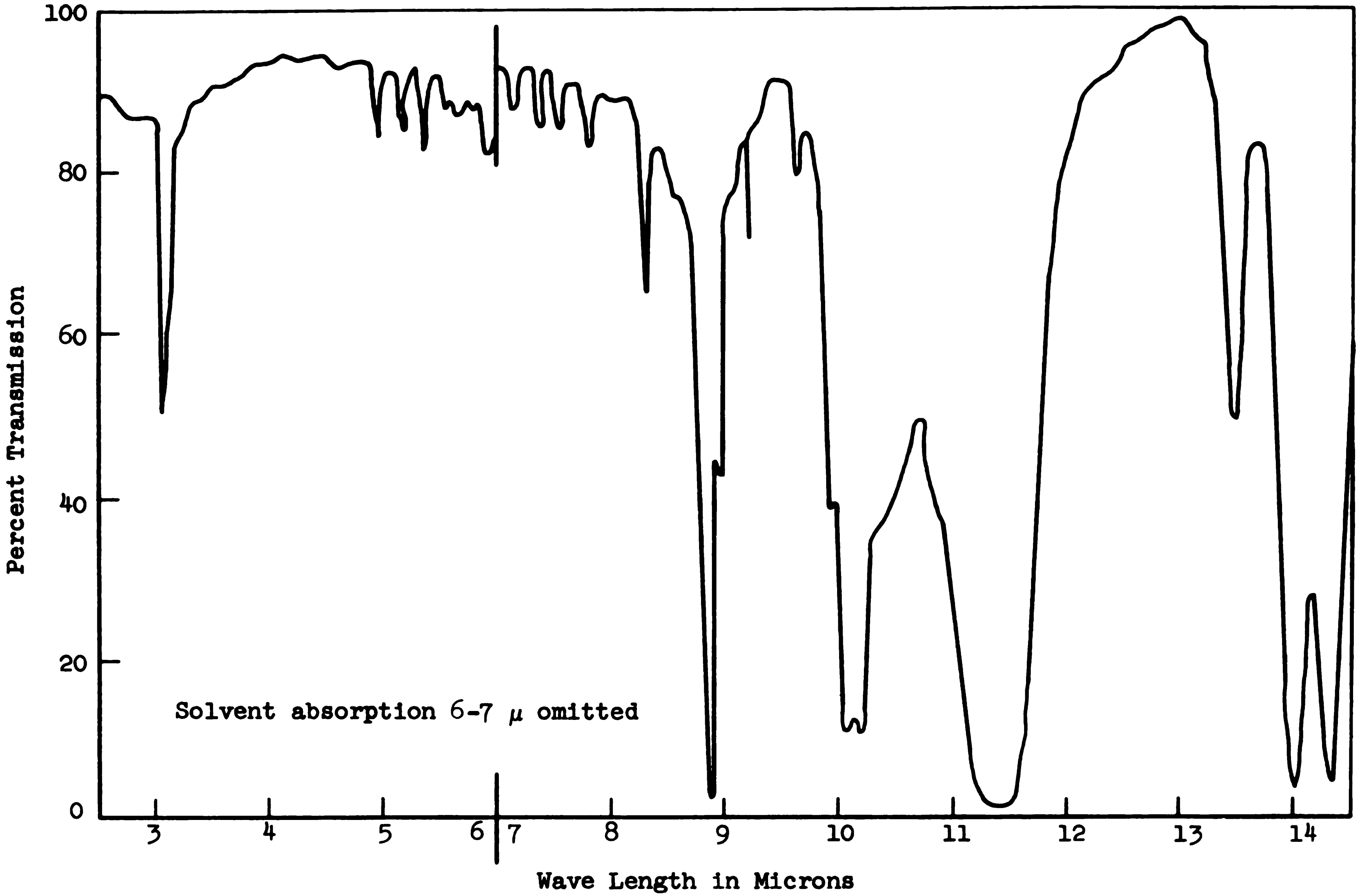


Figure VII. Infrared spectrum of bis(triphenylsilyl)chromate in carbon tetrachloride (2-15 μ region).

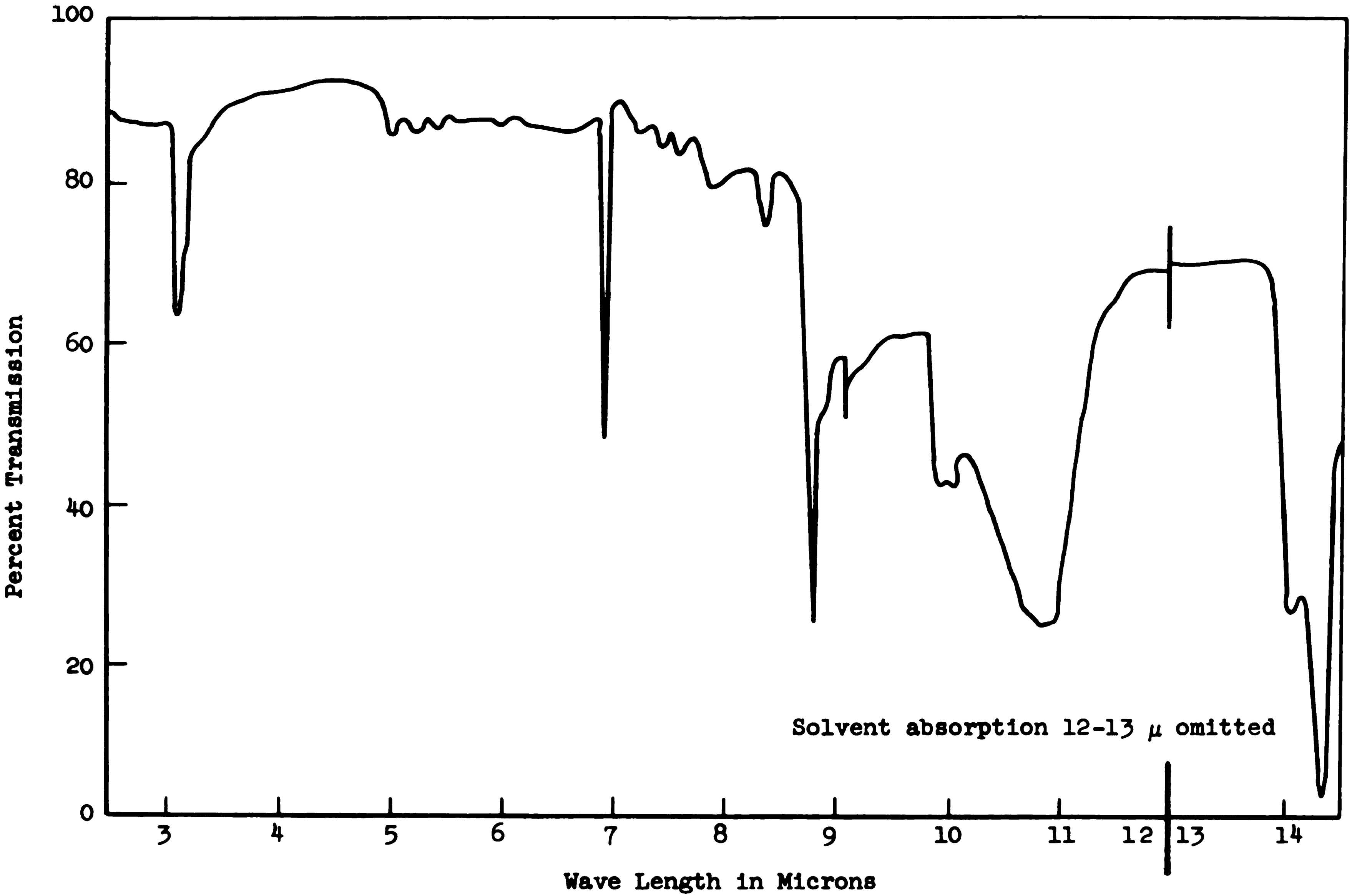


Figure VIII. Infrared spectrum of triphenylsiloxychromyl chloride in carbon tetrachloride (2-15 μ region).

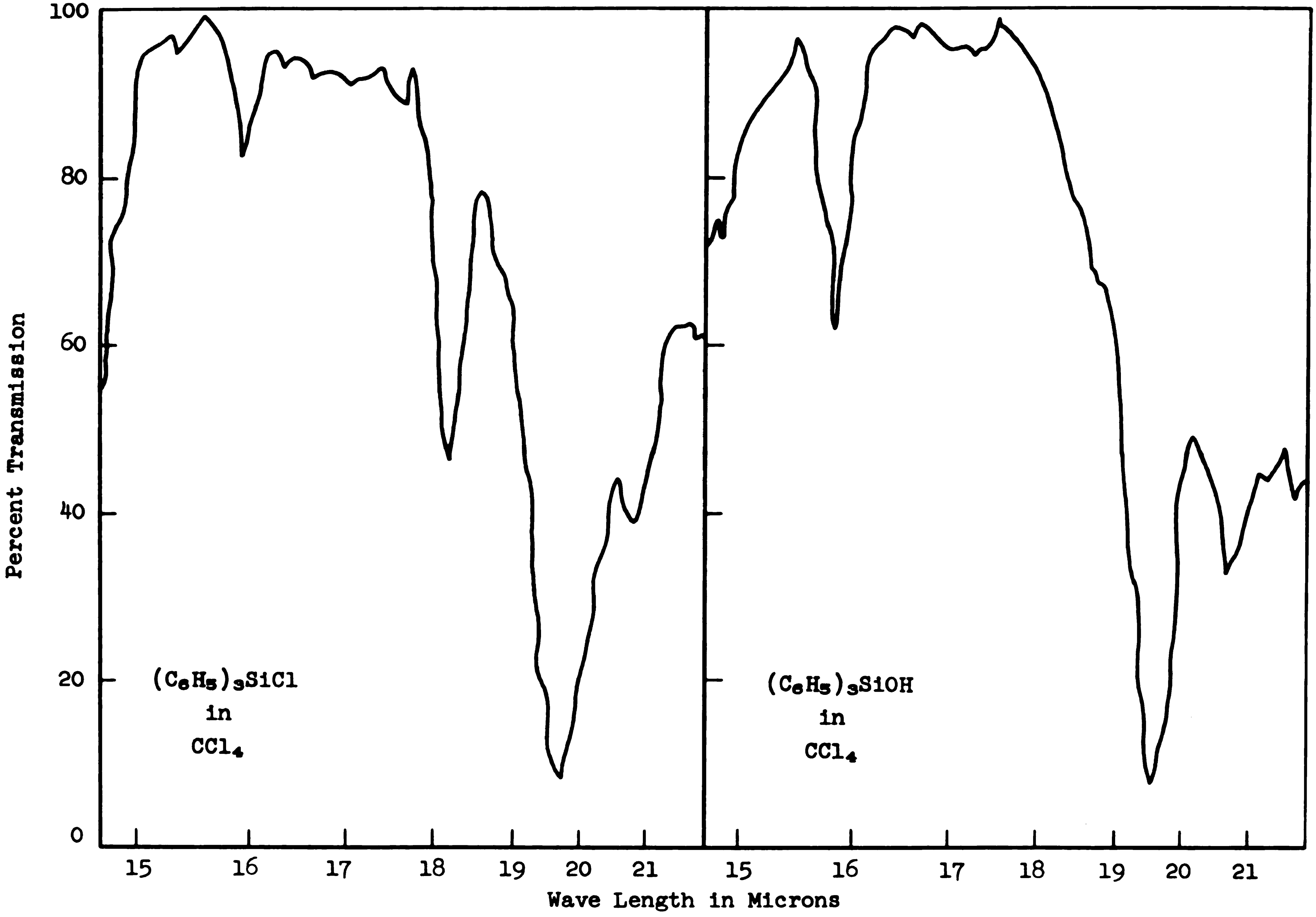


Figure IX. Infrared spectra of triphenylchlorosilane and triphenylsilanol in carbon tetrachloride (15-25 μ region).

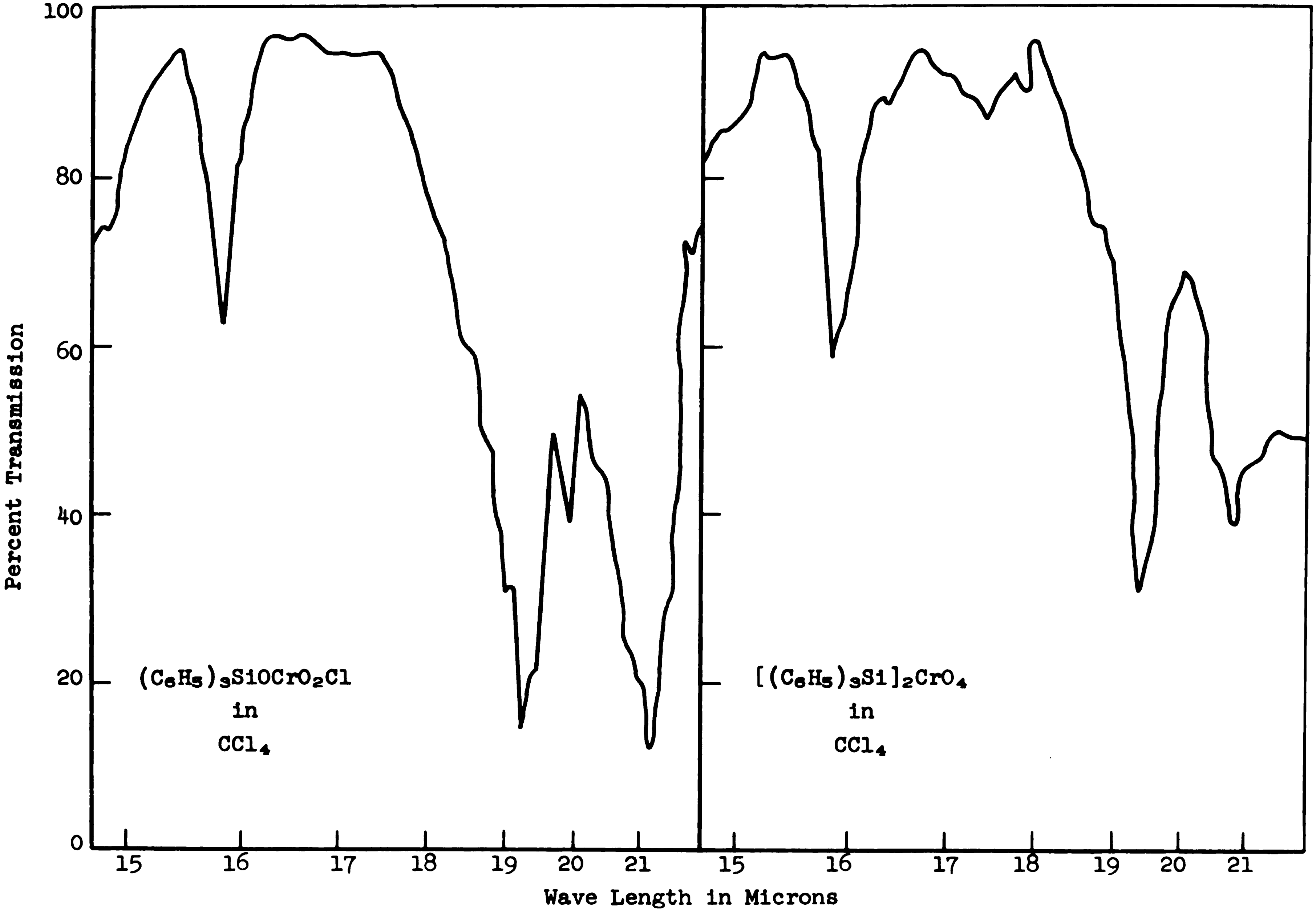


Figure X. Infrared spectra of triphenylsiloxychromyl chloride and bis(triphenylsilyl)-chromate in carbon tetrachloride (15-25 μ region).

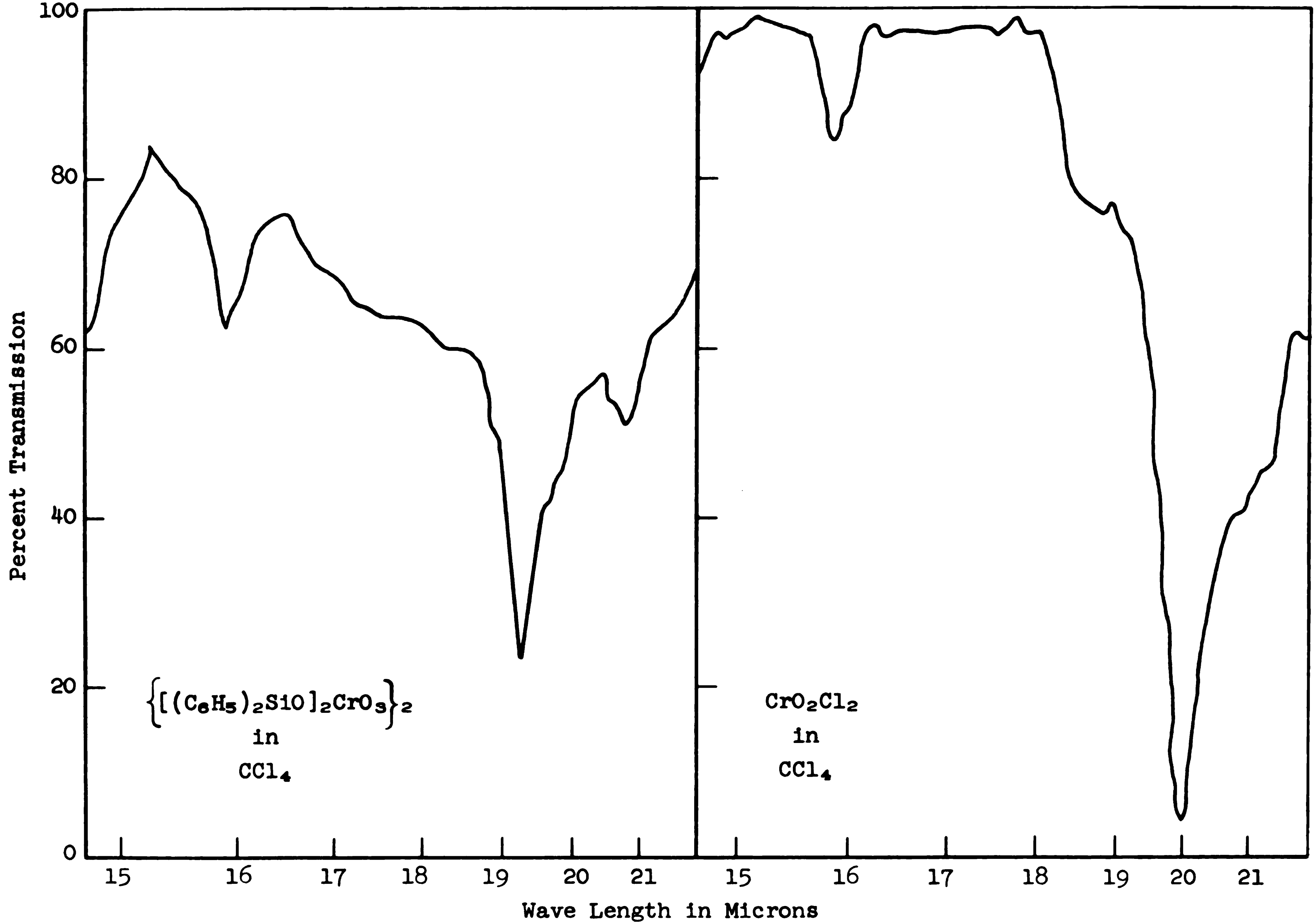


Figure XI. Infrared spectra of cyclobis[tetraphenyldisiloxanylchromate(VI)] and chromyl chloride in carbon tetrachloride (15-25 μ region).

spectra of diphenylsilanediol, tetraphenyldisiloxane-1,3-diol, and hexaphenyltrisiloxane-1,5-diol in carbon tetrachloride solutions and as films. He reported that all three diols exhibit a free Si-OH band at 3674 cm.$^{-1}$. These assignments and others (80,33,81,102) made for the free and associated Si-OH are in complete agreement with the measurements made in this investigation. Thus, this investigation indicated a value of 2.7 μ for the free Si-OH in triphenylsilanol when measured from the infrared spectrum recorded on a Perkin-Elmer Model 21 Spectrophotometer. A value of 2720 mμ was obtained from spectra recorded in the near infrared region on a Beckman Model DK-2 Spectrophotometer. Unlike the silanol band at about 3 μ which is characteristic of the associated hydrogen-bonded species (dimer), the free Si-OH absorption at exactly 2720 mμ is analytically useful. It was demonstrated in this investigation that the free Si-OH absorption of triphenylsilanol at 2720 mμ was useful for making kinetic measurements as indicated in a special portion of this thesis. However, a plot of absorbance *versus* concentration of $(C_6H_5)_3SiOH$ in carbon tetrachloride is not linear for triphenylsilanol concentrations greater than about 3 x 10^{-3} molar. At higher concentrations, negative deviation from Beer's law occurs as a result of self-association of triphenylsilanol through hydrogen bonding described above.

E. Analytical Methods

Carbon and hydrogen analyses in this investigation were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan, and by Alfred Bernhardt Microanalytical Laboratory, Mulheim (Ruhr), Germany. The following methods were found satisfactory for the determination of silicon, chromium, and chlorine in silylchromates.

1. Silicon Analysis

Silicon analysis based on the procedure of Skelcey (93) was used in this study. A sample of the siloxychromium compound was weighed into a 250 ml. beaker and treated with 25 ml. of concentrated sulfuric acid and 0.1 g. of ammonium peroxydisulfate. After decomposition had started, the mixture was slowly heated on a hot plate until fumes of sulfur trioxide appeared. Ammonium peroxydisulfate was cautiously added in approximately 0.1 g. portions until decomposition of the sample was complete. In this manner decomposition was accomplished in approximately one-half hours. When all black color had disappeared, the mixture was cooled and diluted to 200 ml. The silicon dioxide was filtered off and ignited in a platinum crucible. Sulfur trioxide was driven off and the crucible was gradually brought to red heat. The weight of the residue was taken as a mixture of chromium oxides and silicon dioxide. The residue was then treated with five drops of water, 1 ml.

of concentrated sulfuric acid, and 5 ml. of 49 per cent hydrofluoric acid. After all the volatile silicon tetrafluoride had evaporated from the sample by gently warming, the crucible was brought to constant weight. The weight loss was taken as silicon dioxide and per cent silicon was calculated.

2. Chromium Analysis

In the determination of chromium, the rapid hydrolytic reaction that siloxy-chromium compounds undergo with strong base was used to convert the substance to a soluble chromate. The quantitative determination of the chromic acid may be used for the analysis of the compound, i.e., $[(C_6H_5)_3SiO]_2CrO_2$.

$$[(C_6H_5)_3SiO]_2CrO_2 + 2\ H_2O \longrightarrow 2\ (C_6H_5)_3SiOH + H_2CrO_4.$$

A sample of a siloxy-chromium compound was weighed into a 100 ml. beaker and treated with 20 ml. of 12 N sodium hydroxide until hydrolysis was complete. The solution was cooled, and diluted to 80 ml., acidified with sulfuric acid, and the dichromate titrated with recently standardized ferrous ammonium sulfate solution. The end point was determined amperometrically using a rotating platinum anode and a saturated calomel reference electrode at a potential difference of one volt (95,96). The current was measured with the recording system of a Sargent Model XXI Polarograph operating at a sensitivity of 0.300 microamphere per millimeter.

3. Chlorine Analysis

Chlorine analysis based on the procedure of Kolthoff and Laithinen (97) was used in this investigation. A weighed sample in a 100 ml. beaker was warmed with 50 ml. of 1 N sodium hydroxide to hydrolyze it to the soluble chloride and chromate. After cooling, the solution was acidified with nitric acid, 5 ml. of 0.05 per cent gelation was added, and the chloride ion was titrated with recently standardized silver nitrate solution. The end point was determined amperometrically using a rotating platinum electrode and a saturated calomel reference at a potential difference of 0.05 volt. The current was measured with the recording system of a Sargent Model XXI Polarograph operating at a sensitivity of 1.000 microampere per millimeter. A potentiometric titration of chloride ion in the presence of a chromate was found to be unsatisfactory.

4. Molecular Weights

Molecularity measurements have been important throughout this investigation and have been determined experimentally by the methods of cryoscopy, ebulliometry, and with vapor pressure osmometry.

a. Cryoscopy

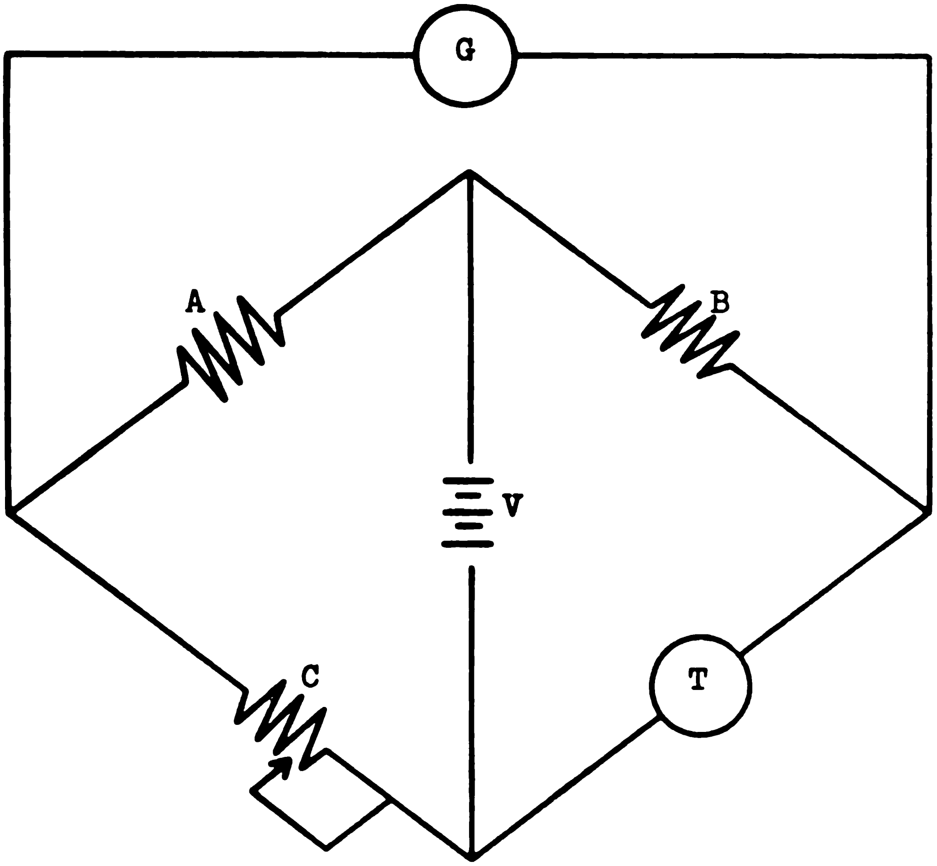
Molecular weights were determined cryoscopically in benzene or carbon tetrachloride solutions. The apparatus used for molecular weight determinations consisted of a

Wheatstone bridge in which a thermistor was used as the temperature sensing element. The bridge output was connected to a current-time recorder which automatically plotted the cooling curves of the solutions.

The Wheatstone bridge was constructed using a temperature dependent resistor (100,000 ohm thermistor), a 1000 ohm resistor, a 10,000 ohm resistor and a 100,000 ohm ten-turn Helipot (Beckman Instruments, Inc., Fullerton, California) variable resistor (Figure XII). Current for the bridge was supplied by a 12 volt dry cell battery. The current flowing through the bridge was recorded on a Sargent Model XXI Polarograph recording system operating at a sensitivity of 0.003 microamphere per millimeter.

The thermistor was cemented to the end of a glass tube which was held by a 10/30 standard taper joint in the glass cryoscopic cell (Figure XIII). A motor operating at a constant 600 r.p.m. drove the ground glass stirring assembly, and the cell was immersed in a Dewar flask containing a coolant. An ice-water bath was used for benzene and a liquid nitrogen-bromobenzene slush (-30.6°C) for carbon tetrachloride (freezing point -22.9°C).

The apparatus was carefully calibrated with a sample of high purity recrystallized hexachlorobenzene supplied by Dr. J. S. Skelcey. The freezing point of purified solvent was established by pipetting 40 ml. into the cell and



A = 1,000 ohms
B = 10,000 ohms
C = 100,000 ohm Variable Resistor
T = 100,000 ohm Thermister (VECO 51A1)
G = Sargent Model XXI Polarography Recording System
V = Dry Cell Battery (12.0 volts)

Figure XII. Wheatstone bridge for cryoscopic molecular weight apparatus.

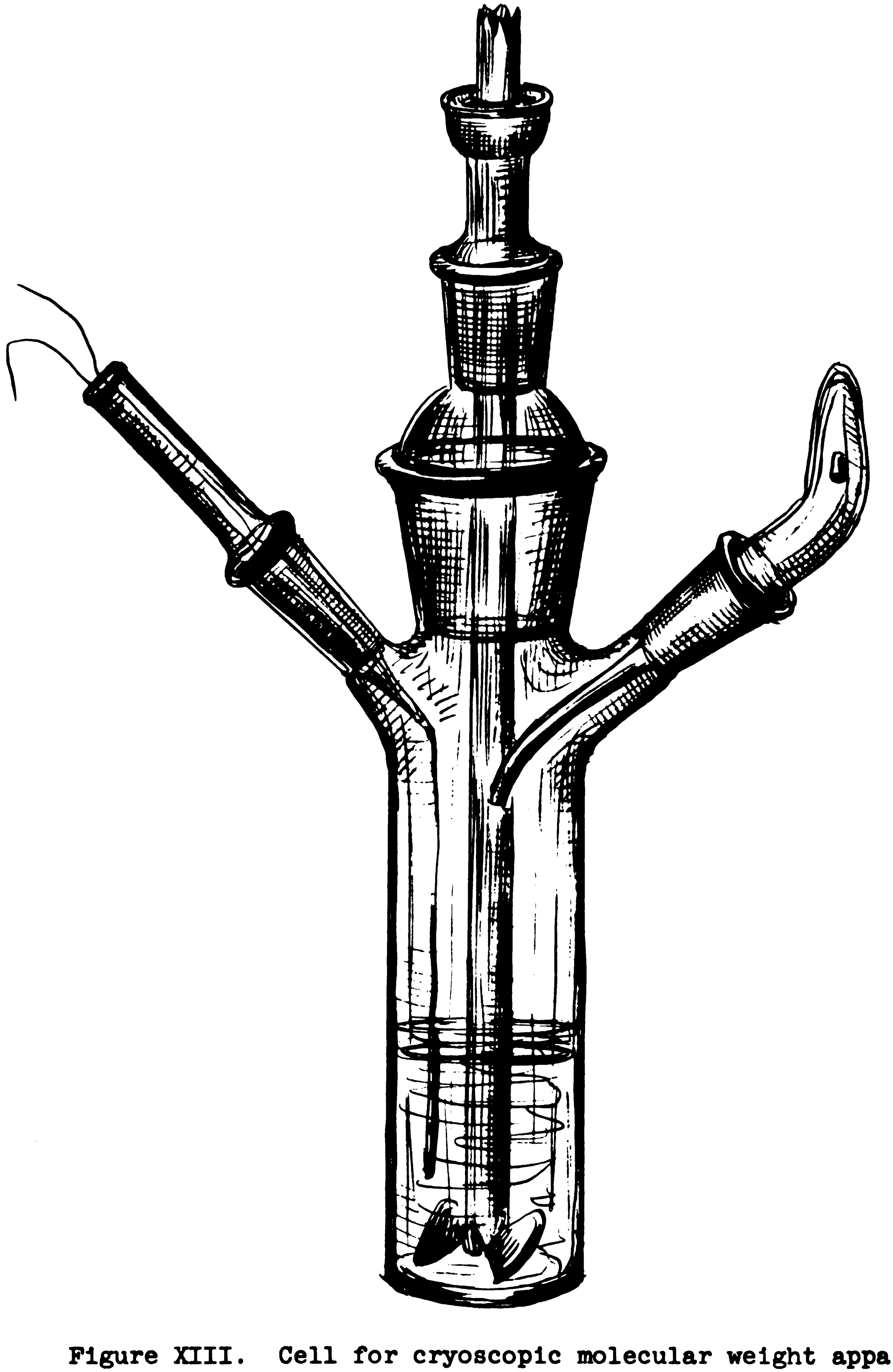


Figure XIII. Cell for cryoscopic molecular weight apparatus.

recording its cooling curve. Just before freezing began, the regular cooling bath was momentarily replaced with a Dry Ice--acetone bath to initiate freezing. Extrapolation of the freezing portion of the curve back to the cooling portion gave the freezing point. An average of five determinations was used in the calculations.

Next, pellets of a known weight of the cryoscopic standard, hexachlorobenzene, were added to the solvent, and five freezing curves were recorded. The cell was cleaned and dried. The above procedure was then repeated for the compound whose molecular weight was to be determined.

The freezing point depressions of the standard and the unknown solutions were expressed in chart divisions (mm) which are proportional to ΔT. The freezing point constant of the solvent was assumed to be the same for both solutions, so that the molecular weight of the unknown could be calculated from the following equation:

$$M_1 = M_2 \frac{\Delta T_2}{\Delta T_1} \frac{W_1}{W_2}$$

where: M_1 = molecular weight of unknown

M_2 = molecular weight of standard

W_1 = weight of unknown

W_2 = weight of standard

ΔT_1 = freezing point depression of unknown solution

ΔT_2 = freezing point depression of standard solution.

This apparatus can be adapted for various solvents by simply setting the resistance box of the Wheatstone bridge to the approximate resistance of the thermistor at the freezing point of the solvent.

b. Vapor Pressure Osmometry

Some molecular weight data were experimentally determined using vapor pressure osmometry methods. The apparatus used was a Mechrolab Model 302 high temperature vapor pressure osmometer made available by Dow Corning Corporation, Physical Chemistry Laboratories, Midland, Michigan. All measurements were obtained at a constant operating temperature of 37°C.

Measurements were made at various concentrations in benzene or carbon tetrachloride. Molecular weights were calculated using standard osmometry techniques according to the following equation:

$$\text{M.W.} = KC/\Delta R$$

where: M.W. = molecular weight of unknown
ΔR = resistance reading
C = concentration
K = solvent calibration constant.

The value of $\Delta R/C$ used in the above equation is the intercept (at zero concentration) of the plot of resistance, ΔR, versus concentration, C, for the unknown. The solvent calibration curve obtained by plotting $\Delta R/C$ versus ΔR for a known osmometry standard. In this investigation, K had values of 931 and 308 for carbon tetrachloride and benzene, respectively. Recrystallized samples of benzil for carbon tetrachloride and 2,5-diphenyloxazole for benzene (supplied by Dow Corning Corporation, Physical Chemistry Laboratories) were used in the instrument calibrations.

IV. KINETICS OF TRIPHENYLSILANOL--CHROMYL CHLORIDE REACTION IN CARBON TETRACHLORIDE

A. Introduction

Perhaps the most frequent cause of failure in attempts to obtain high molecular weight inorganic polymers is the great tendency for formation of small ring compounds rather than linear aggregates. The silylchromates indeed show results consistent with this limitation; thus cyclic cyclobis-[tetraphenyldisiloxanylchromate(VI)] was the major product isolated from the reactions of chromium(VI) oxide or chromyl chloride with diphenylsilanediol.

Better insight into the formation of silylchromates was not arrived at through any of the synthetic approaches taken on this problem. The reaction conditions could not be altered to favor linear silylchromate formation because the mechanisms of the reactions were not well enough understood. Since the literature contains no rate data on reactions which lead to the formation of compounds containing silicon-oxygen-chromium bonds, a kinetic study was undertaken of the reaction of triphenylsilanol with chromyl chloride in carbon tetrachloride:

$$2\ (C_6H_5)_3SiOH + CrO_2Cl_2 \longrightarrow [(C_6H_5)_3Si]_2CrO_4 + 2\ HCl.$$

This reaction was selected because it appeared to be free from side reactions and could be made to give an apparently quantitative yield of bis(triphenylsilyl)chromate. It seemed to represent a useful prototype of the more complex reactions of silanediols and triols which are of interest in polymerization schemes. Spectrophotometry was chosen as a satisfactory method for following the reaction rate because diagnostic absorptions appeared to be available for the silanol in the near infrared region at 2.7 μ (Si-OH) or for chromyl chloride in the infrared at 20 μ (Cr-Cl) or in the visible at 412 mμ. The Cr-Cl absorption was unsatisfactory because of an overlapping silicon-phenyl band, and the disappearance of the chromyl chloride absorption at 412 mμ was ruled out because a similar absorption at 412 mμ was found in the reaction product, bis(triphenylsilyl)chromate. The Si-OH absorption of triphenylsilanol at 2.7 μ (2720 mμ) was found to be useful for kinetic measurements as indicated below.

B. Experimental Method

The rate of disappearance of triphenylsilanol when it reacts with chromyl chloride in carbon tetrachloride can be followed spectrophotometrically at 2720 mμ. The position of this Si-OH absorption was found to be independent of concentration throughout the solubility range of triphenylsilanol in carbon tetrachloride, and all other species in the system are essentially free of absorption at this wavelength.

Rate data were obtained as follows. After carbon tetrachloride solutions of reactants were mixed, absorbancy at 2720 mμ was recorded as a function of time until the value became constant. The reaction was begun at the moment of mixing ($\underline{t_o}$), and the first absorbancy was recorded ten seconds later. Calibrated syringes were used to introduce the reactants. Rapid and complete mixing was obtained by stirring with a Teflon rod. This was demonstrated by recording absorbancy data at 2720 mμ as a function of time for a triphenylsilanol-carbon tetrachloride solution prepared using the methods of mixing described above. The initial absorbancy reading was recorded ten seconds after mixing and did not change with time.

1. Materials

Commercial grade triphenylsilanol was repeatedly recrystallized from benzene until the melting point was 150.0-151.5°C; a literature value (26) for the melting point is 150.5-151.5°C. Owing to the fact that melting point data for organosilanols are highly dependent upon the melting point procedure and are very sensitive to traces of acids and bases (98), the rather broad melting point obtained was not unexpected. The infrared spectrum of the recrystallized product was recorded in carbon tetrachloride and carbon disulfide and showed bands attributable to Si-O, Si-C_6H_5, C-H, and Si-OH but no Si-O-Si bands. The substance was further identified as triphenylsilanol on the basis of its proton nuclear magnetic resonance spectrum recorded in dimethyl sulfoxide (105). (Dow Corning Corporation Analytical Laboratories, Midland, Michigan.) The spectrum showed a multiplet at 2.3 to 2.8 p.p.m. and a sharp singlet at 2.90 p.p.m. (15.00:1.06 ratio) due to the $Si-C_6H_5$ and Si-OH protons, respectively. Active hydrogen determinations were made by Dow Corning Corporation Analytical Laboratories, Midland, Michigan (interaction with $LiAlH_4$ gave 6.04, 6.37, average 6.13% OH and titration with $LiAl(NBu_2)_4$ gave 6.32, 6.25, average 6.28% OH compared to theory for $C_{18}H_{16}SiO$ of 6.16% OH).

Freshly distilled chromyl chloride prepared and characterized by the methods described previously was used. Before each series of measurements, chromyl chloride solutions were standardized by amperometric titration of the chromate obtained from hydrolysis of an aliquot portion.

Bis(triphenylsilyl)chromate prepared in the synthetic part of this work was repeatedly recrystallized from methylene chloride until the melting point was constant at 154°C.

Anhydrous hydrogen chloride was obtained by bubbling commercial grade hydrogen chloride (Matheson Co.) through concentrated sulfuric acid. Solutions were prepared by bubbling anhydrous hydrogen chloride through carbon tetrachloride. The saturated solutions were then diluted with more solvent and allowed to equilibrate. Titration of samples on successive days indicated that no hydrogen chloride escaped from solutions prepared in this manner. Solutions of hydrogen chloride in carbon tetrachloride were standardized by aqueous titration to the phenolphthalein end point with standard sodium hydroxide.

Carbon tetrachloride used as the solvent was a spectroscopically pure grade from the Matheson, Coleman, and Bell Co.

2. Apparatus

Absorbancy as a function of time was recorded at constant wavelength (2720 mμ) on a Beckman DK-2 Spectrophotometer using the lead sulfide detector. Conventional one centimeter silica cells closed with ground glass stoppers were used. Time was recorded with a stop watch. The temperature of the air at the spectrophotometer was 24°C ± 0.5°C at all times, and the temperature of the samples during measurement probably did not differ greatly from this.

3. Beer's Law Data for Triphenylsilanol in Carbon Tetrachloride

Important to this investigation were the absorbancy measurements of the Si-OH absorption in the near infrared at 2720 mμ for triphenylsilanol in carbon tetrachloride. Such measurements were necessary for the determination of the equilibrium constant for the triphenylsilanol--

chromyl chloride reaction described previously. In addition, the kinetic portion of this investigation involved the monitoring of the appearance as well as the disappearance of the absorbancy at 2720 mμ for triphenylsilanol. Therefore, the absorbancy--concentration relationship was established in the following way.

Stock solutions of known concentration were prepared by dilution of a weighed amount of triphenylsilanol to a specified volume with freshly opened carbon tetrachloride. These solutions were then adjusted to various concentrations by further dilution with additional solvent. The absorbancy of each solution was recorded at constant wavelength (2720 mμ) on a Beckman DK-2 Spectrophotometer fitted with a lead sulfide detector. The measurements were made on the day the solutions were prepared to avoid evaporation of solvent. Changes of concentrations were further minimized by the use of the one centimeter silica cells closed with glass stoppers. Table XVI summarizes the experimental results obtained. Figure XIV shows the absorbancies plotted against the analytical concentration (Beer's law plot). This working curve does not obey Beer's law except in the very dilute solutions. This negative deviation is a result of self-association of triphenylsilanol molecules in solution.

Table XVI. Beer's Law Data for Triphenylsilanol in Carbon Tetrachloride

Millimoles/Liter	Absorbancy at 2720 mμ
23.2	0.981
20.9	0.928
15.4	0.761
13.9	0.699
12.0	0.653
11.5	0.633
10.5	0.590
9.00	0.543
7.68	0.490
7.50	0.467
6.97	0.438
6.00	0.412
5.76	0.385
4.50	0.325
3.84	0.279
3.00	0.238
2.32	0.188
2.25	0.182
1.75	0.139
1.54	0.122
1.50	0.125
1.15	0.089
1.12	0.079
0.870	0.062
0.750	0.053

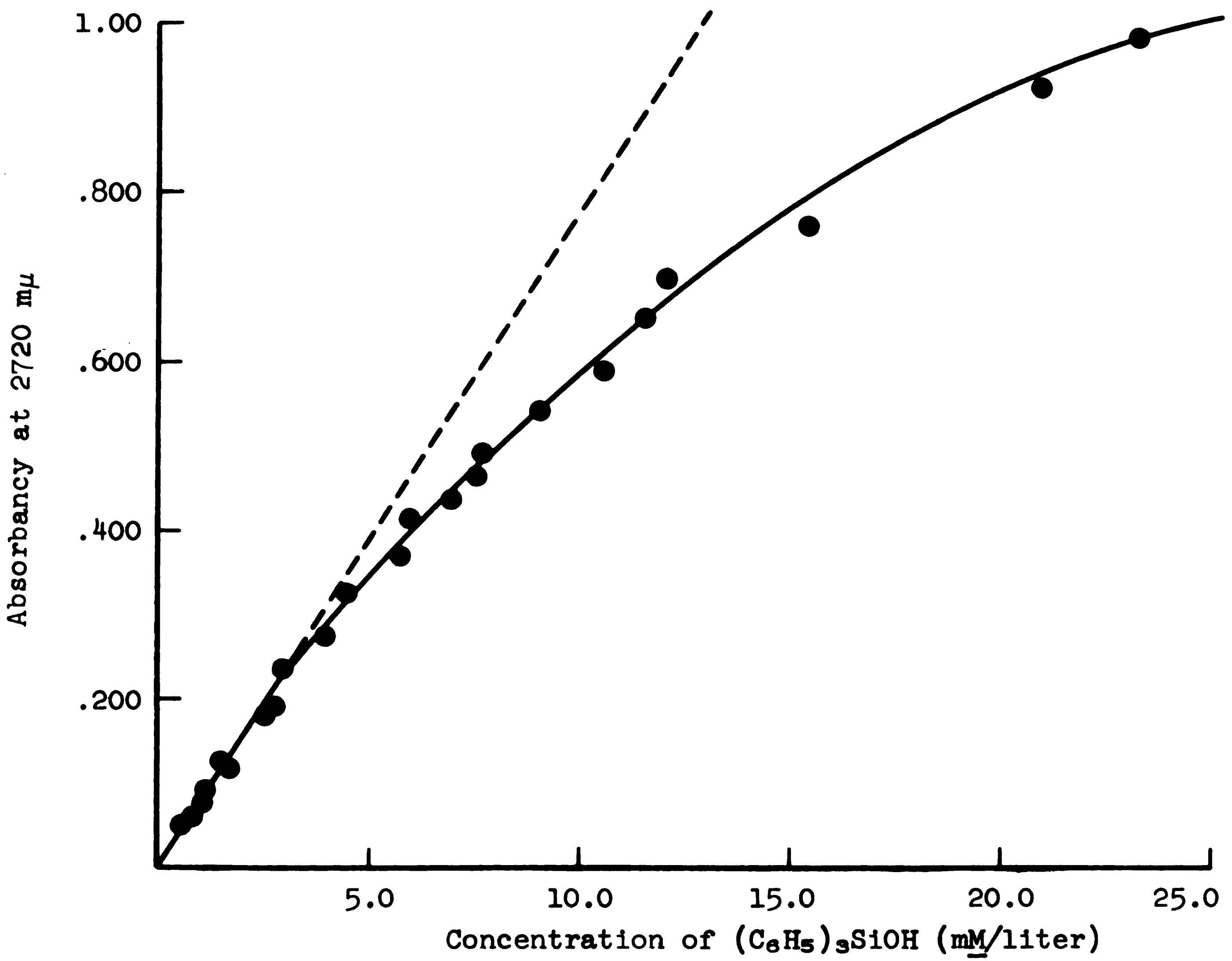


Figure XIV. Absorbancy of triphenylsilanol at 2720 mμ in carbon tetrachloride *versus* concentration.

Rather than estimate concentrations from absorbancy data using the working curve (Figure XIV), a correlation analysis was used in "curve fitting" this set of data so that more consistent data could be obtained. The method of least squares (103) was used to obtain a regression equation for both the linear portion of the curve and the whole curve. The resulting regression equations which best describe the whole curve are:

$$\underline{y} = 0.32711 + 7.803714\underline{x} + 15.725541\underline{x}^2 \qquad (1)$$

and

$$\underline{y} = 0.36975 + 7.30933\underline{x} + 16.95146\underline{x}^2 - 0.860862\underline{x}^3 \qquad (2)$$

where $\underline{x}$ is the absorbancy and $\underline{y}$ is the concentration in millimoles of triphenylsilanol per liter of carbon tetrachloride solution. Twenty-five observations (Table XVI) were used in the regression analysis for both the two and three independent variable cases. The values predicted by equations (1) and (2) have a probable standard deviation of 0.1525 and 0.1554, respectively. Both equations have a correlation coefficient of 0.9997 for the set of data used in the analysis. The linear portion of the curve (up to absorbancies of about 0.250) can be denoted by the following equation for a straight line:

$$\underline{y} = -0.004393 + 12.94236\underline{x} \qquad (3)$$

The values predicted by equation 3 have a probable standard deviation of 0.1148 and a correlation coefficient of 0.9934 for the eleven observations used in the analysis. The molar absorptivity at infinite dilution (ϵ_{∞}) for this free Si-OH absorption was calculated from the slope of the linear region of the Beer's law plot and has a value of 77.4 liter $\text{mole}^{-1}\text{cm.}^{-1}$. It is interesting to compare this value with molar absorptivities calculated at higher concentrations ($\epsilon_{\underline{y}}$). The fraction α of monomeric triphenylsilanol molecules in solution is given by the quotient of the molar absorptivities (104), $\alpha = \frac{\epsilon_{\underline{y}}}{\epsilon_{\infty}}$, if one assumes that only the free OH group of the non-associated molecules contributes to the free Si-OH band at 2720 mμ. Table XVII summarizes measurements of α for triphenylsilanol in carbon tetrachloride at various concentrations. Equation 1 was used to relate absorbancies to concentrations so that $\epsilon_{\underline{y}}$ values could be calculated from Beer's absorption law: $\underline{x} = \epsilon_{\underline{y}}\underline{dy}$, where

$\underline{x}$ = absorbancy

$\underline{y}$ = concentration in molarity

$\underline{d}$ = cell length (1.0 cm.)

$\epsilon_{\underline{y}}$ = molar absorptivity at concentration $\underline{y}$.

Table XVII. Fraction α of Monomeric $(C_6H_5)_3SiOH$ in CCl_4

Concentration in Millimoles/Liter	Absorbancy at 2720 mμ	Molar Absorptivity $\epsilon_{\underline{y}}$ in l mole^{-1}cm^{-1}	$\alpha = \frac{\epsilon_{\underline{y}}}{\epsilon_\infty}$
3.08	0.238	77.3	1.000
4.00	0.295	73.8	0.953
5.00	0.351	70.2	0.906
10.01	0.575	57.4	0.742
14.99	0.749	50.0	0.647
20.02	0.898	44.3	0.573
30.10	1.150	38.2	0.494
40.03	1.360	34.0	0.434
50.20	1.550	30.9	0.400

$\epsilon_\infty = 77.4$ liter mole^{-1}cm.$^{-1}$

If the equilibrium existing in solution involves only dimeric association in the form of a closed hydrogen bonded dimer, then $1-\alpha$ would denote the fraction of dimeric triphenylsilanol molecules in solution.

C. Determination of Reaction Order of the Forward Reaction

There is no general method for determining the order of a chemical reaction. Rate data, however, must first be obtained giving concentrations at various times. Such data were obtained for the reaction of triphenylsilanol with chromyl chloride by the experimental methods described in the preceding section (Experimental Method). Table XVIII summarizes typical rate data obtained for the forward reaction and these same data are plotted in Figure XV. In this study the first approach taken to determine the reaction order involved assumption of a mode of reaction based on the stoichiometry. These assumed expressions were then tested by graphical methods (110). Both first order (logarithm of the concentration *versus* time) and second order (reciprocal of concentration *versus* time) expressions were assumed and treated in this manner. Figures XVI and XVII are graphical tests of the first and second order relationships, respectively. The assumed rate expressions did not consistently reproduce the experimental data obtained. The deviation in the graphical tests for the first order assumptions were very apparent while in the case of the assumed second order expressions, these deviations were more

Table XVIII. $(C_6H_5)_3SiOH + CrO_2Cl_2$ Absorbancy (2720 mμ) and Concentration *versus* Time Data* (Plotted in Figure XV)

Elapsed Time (sec.)	Reaction 1 Absorbancy (2720 mμ)	Reaction 1 $[(C_6H_5)_3SiOH]$ m*M*	Reaction 2 Absorbancy (2720 mμ)	Reaction 2 $[(C_6H_5)_3SiOH]$ m*M*	Reaction 3 Absorbancy (2720 mμ)	Reaction 3 $[(C_6H_5)_3SiOH]$ m*M*	Reaction 4 Absorbancy (2720 mμ)	Reaction 4 $[(C_6H_5)_3SiOH]$ m*M*	Reaction 5 Absorbancy (2720 mμ)	Reaction 5 $[(C_6H_5)_3SiOH]$ m*M*
0	—	28.7	—	19.1	—	9.6	—	4.8	—	2.4
10	0.860	18.67	0.686	13.08	0.418	6.34	0.237	3.06	0.083	1.08
15	0.777	15.88	0.611	10.97	0.358	5.14	0.190	2.38	0.055	0.804
20	0.719	14.07	0.550	9.38	0.312	4.29	0.154	1.90	0.045	0.710
25	0.675	12.76	0.505	8.28	0.275	3.66	0.129	1.60	0.042	0.683
30	0.641	11.79	0.468	7.42	0.243	3.15	0.108	1.35	0.040	0.664
40	0.587	10.33	0.416	6.29	0.198	2.49	0.081	1.06	0.038	0.646
50	0.552	9.43	0.377	5.50	0.163	2.02	0.062	0.871		
60	0.525	8.76	0.346	4.91	0.137	1.69	0.051	0.766		
80	0.486	7.83	0.311	4.28	0.108	1.35	0.035	0.620		
100	0.464	7.33	0.278	3.71	0.084	1.09	0.030	0.575		

* Initial concentration of $(C_6H_5)_3SiOH$ varied and CrO_2Cl_2 held constant at 0.0803 *M*.

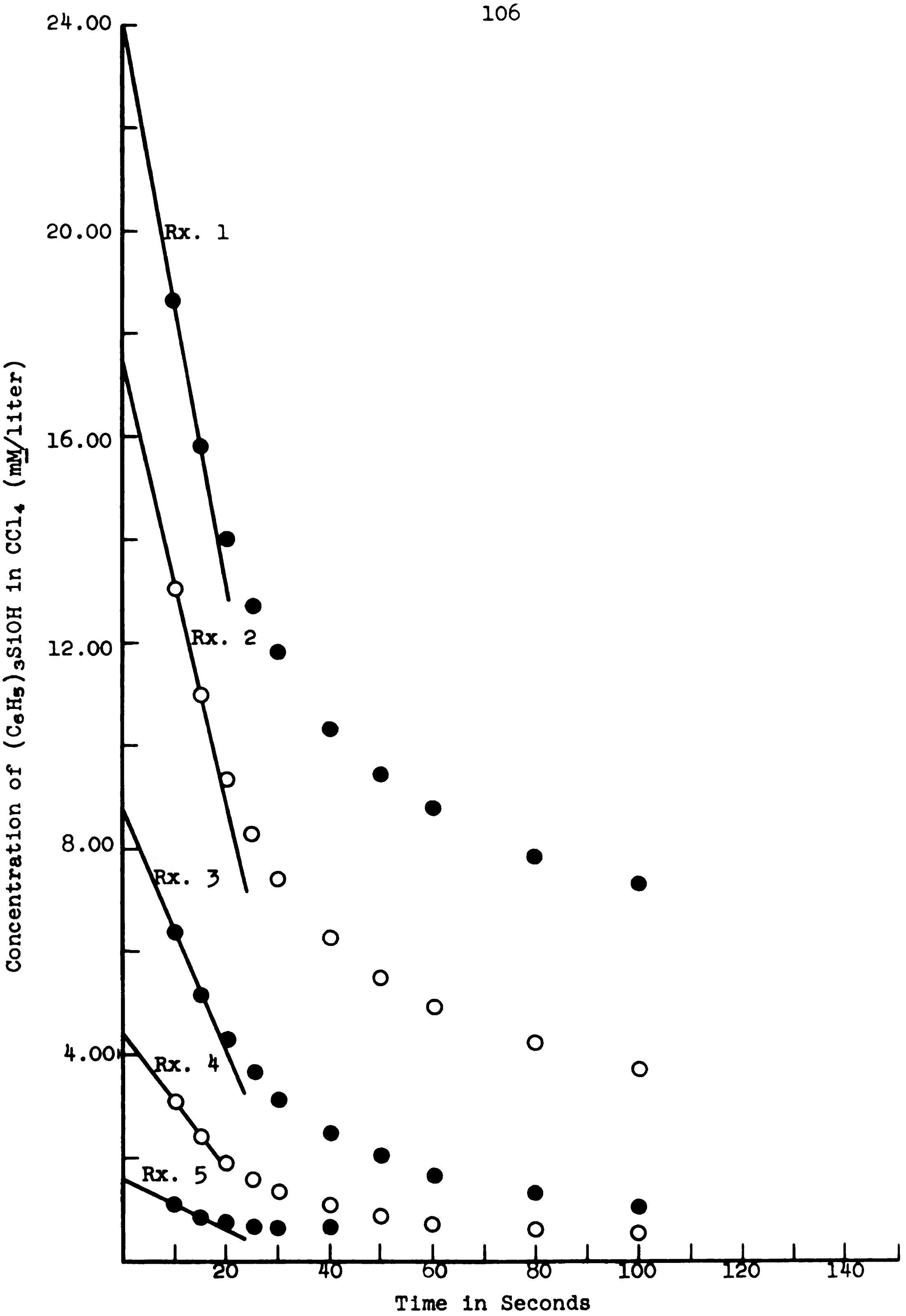


Figure XV. Typical concentration versus time plot for the $(C_6H_5)_3SiOH$--CrO_2Cl_2 reaction.

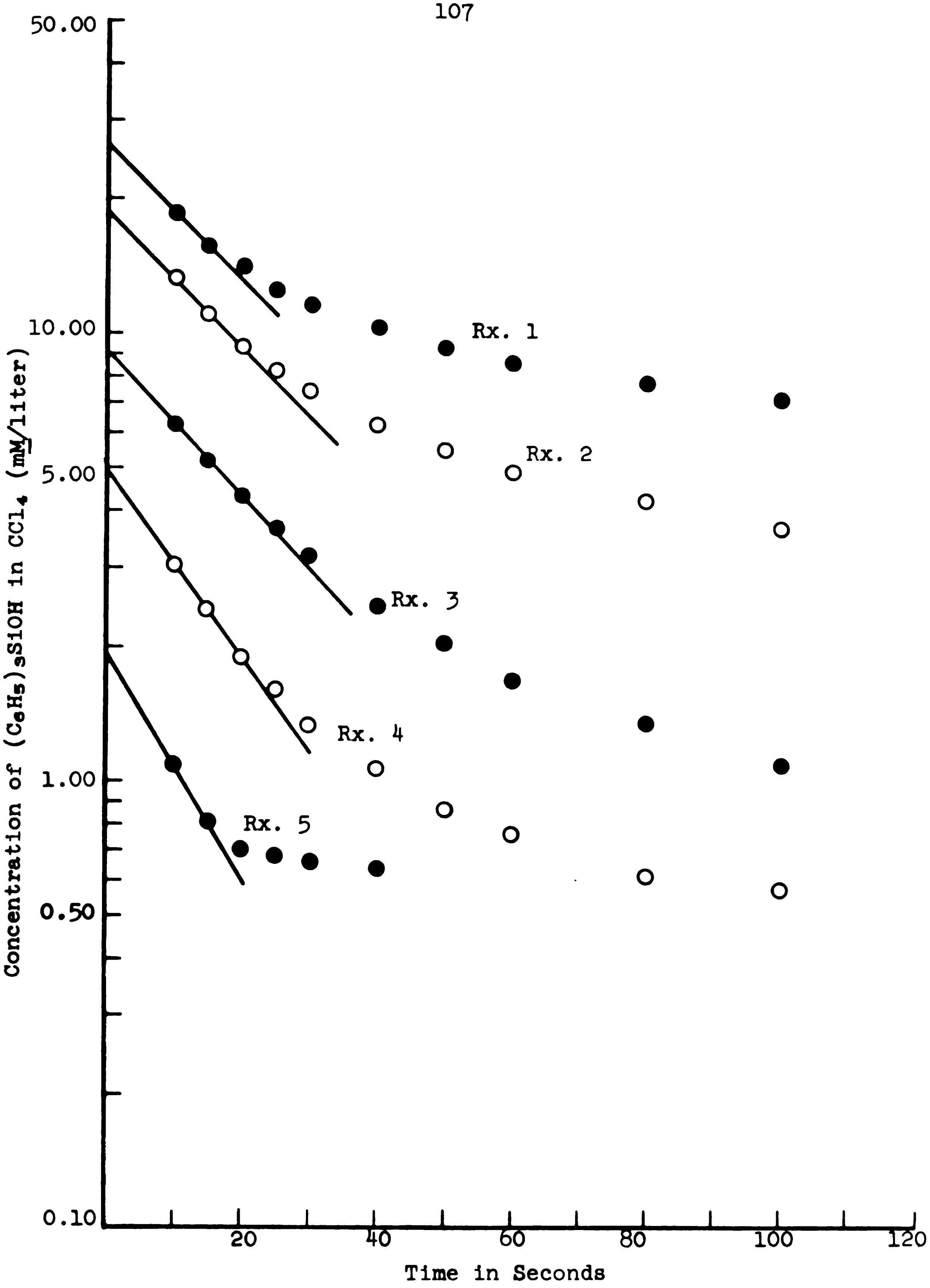


Figure XVI. Reactions of triphenylsilanol and chromyl chloride plotted as first order reactions.

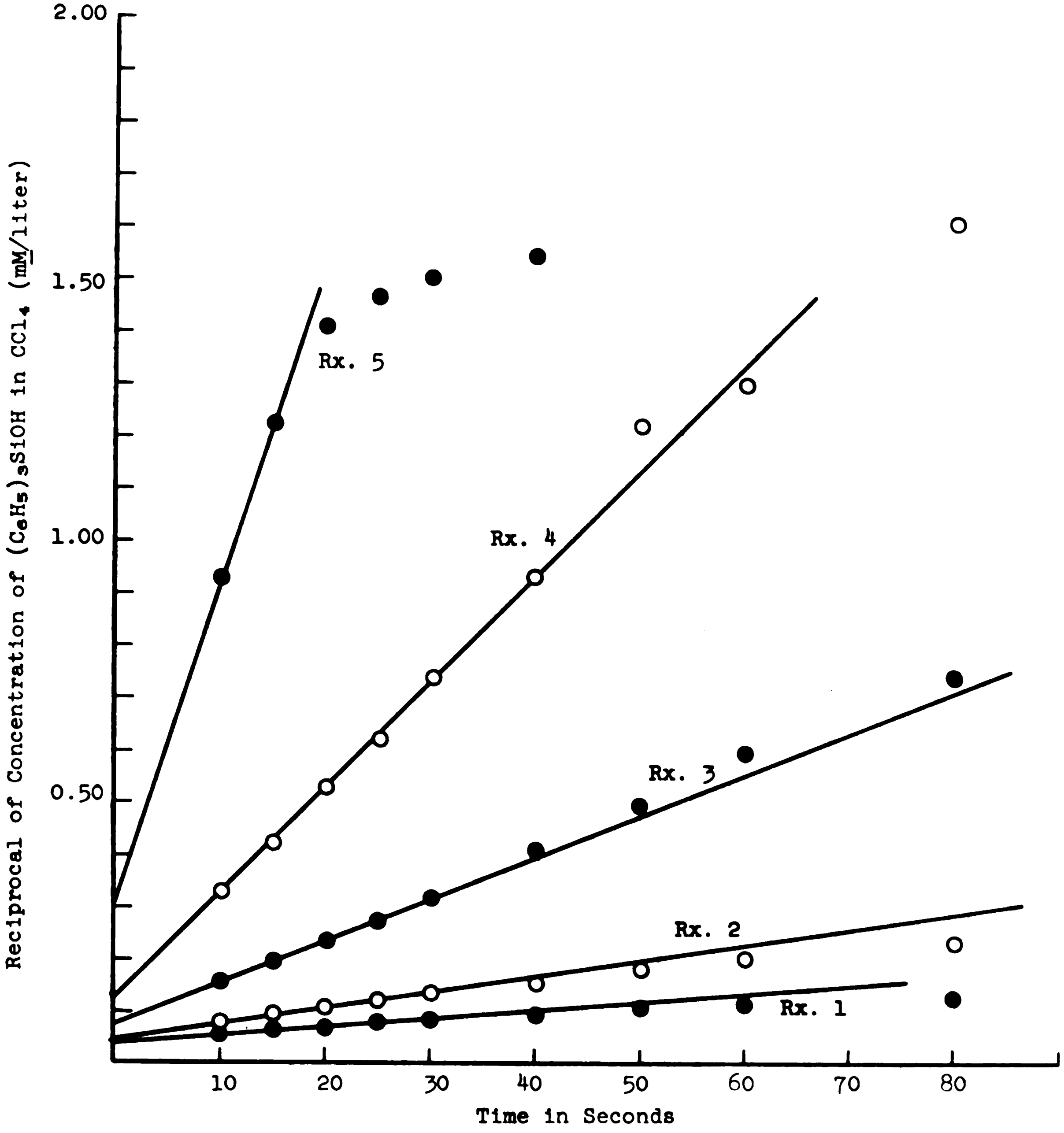
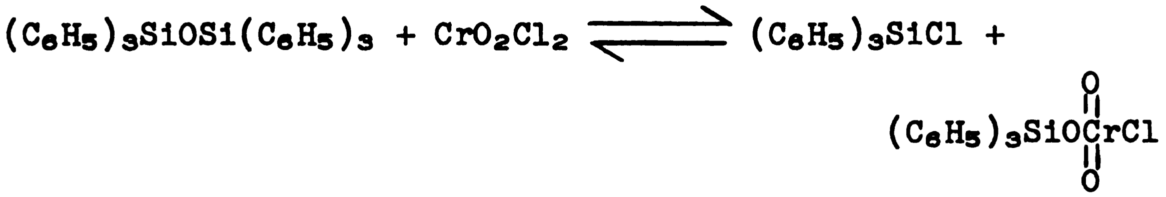


Figure XVII. Reactions of triphenylsilanol and chromyl chloride plotted as second order reactions.

subtle. In particular for the experimental data shown in Table XVIII, straight lines resulted in the graph of reciprocal of concentration <u>versus</u> time for reactions 2, 3, and 4 while reactions 1 and 5 did not. Although this approach did not yield a definite value of two for the order of reaction, it was of interest to consider and test the following reaction scheme involving second order kinetics for triphenylsilanol based on reactions 2, 3, and 4 above.

$$(C_6H_5)_3SiOH + HOSi(C_6H_5)_3 \rightleftharpoons (C_6H_5)_3SiOSi(C_6H_5)_3 + H_2O$$



$$(C_6H_5)_3SiOSi(C_6H_5)_3 + CrO_2Cl_2 \rightleftharpoons (C_6H_5)_3SiCl + (C_6H_5)_3SiO\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr}}}}Cl$$

$$(C_6H_5)_3SiOCrCl + (C_6H_5)_3SiOSi(C_6H_5)_3 \rightleftharpoons [(C_6H_5)_3Si]_2CrO_4 + (C_6H_5)_3SiCl$$

The initial reaction might be expected based on the well known tendencies for organosilanols to undergo self-condensation and to form siloxane structures. The probable presence of HCl, resulting from partial hydrolysis of CrO_2Cl_2, would be expected to promote such condensation reactions. The proposed reaction mechanism would be supported if the intermediate compounds, $(C_6H_5)_3SiCl$ and $(C_6H_5)_3SiOSi(C_6H_5)_3$, had been identified. However, these proposed intermediates were not identified by careful examination of the infrared spectra recorded on mixtures of triphenylsilanol and chromyl chloride. The characteristic infrared absorptions for Si-O-Si (9.3 μ) and SiCl (18.2 μ) were not observed. Furthermore, the product bis(triphenylsilyl)chromate could not be isolated from the reaction mixture of hexaphenylsiloxane and chromyl chloride nor could an SiCl infrared absorption be identified (see Synthesis Section, p. 80). With this in mind, the reaction mechanism proposed above was believed not to be valid.

Rather than continue with the trial-and-error procedure of assuming the reaction order of the forward reaction, the method of initial rates (110) was used to determine the apparent order with respect to each reactant. The initial rate of the reaction of triphenylsilanol with chromyl chloride was studied as a function of initial concentrations. As a first assumption, the rate expression for the reaction was taken to be:

$$\frac{d\underline{x}}{d\underline{t}} = \underline{k}[(C_6H_5)_3SiOH]^{\alpha}[CrO_2Cl_2]^{\beta},\ \text{where}\ \frac{d\underline{x}}{d\underline{t}}\ \text{is a}$$

convenient expression for the rate, and $[(C_6H_5)_3SiOH]$ and $[CrO_2Cl_2]$ are the concentrations of the reactants.

The apparent order with respect to each reactant was determined in a series of reactions starting with varying initial concentrations of one component but a large and constant concentration of the other. For constant initial chromyl chloride concentration,

$\frac{dx}{d\underline{t}} = \underline{k}'[(C_6H_5)_3SiOH]^{\alpha}$, where $\frac{dx}{d\underline{t}}$ is the rate of reaction, k' the effective rate constant under the experimental conditions, and α is the apparent order with respect to triphenylsilanol at constant chromyl chloride concentration. Similarly, for constant initial triphenylsilanol concentration,

$\frac{dx}{d\underline{t}} = \underline{k}''[CrO_2Cl_2]^{\beta}$, where β is the apparent order with respect to chromyl chloride. Then,

$$\log \frac{dx}{d\underline{t}} = \log \underline{k}' + \alpha \log[(C_6H_5)_3SiOH] \text{ and}$$

$$\log \frac{dx}{d\underline{t}} = \log \underline{k}'' + \beta \log[CrO_2Cl_2] \text{ for the two kinds}$$

of runs. The method of initial rates (110) is a special case in which initial concentrations and initial reaction rates are used in the above expressions. Initial rate data as a function of initial concentrations for both of the above situations are summarized in Tables XIX-XXIII (triphenylsilanol concentration varied) and XXIV and XXV (chromyl chloride concentration varied). Initial reaction rates for this forward reaction

Table XIX. $(C_6H_5)_3SiOH$ + CrO_2Cl_2 Initial Rate Data*
(Plotted in Figure XVIII)

Reaction	Time (sec.)	Absorbancy at 2720 mμ	$[(C_6H_5)_3SiOH]$ <u>mM</u>	$[CrO_2Cl_2]$ <u>M</u>	Initial Rate <u>mM</u>/min.
1	0	—	28.7	0.0803	
	10	0.860	18.67		33.48
	15	0.777	15.88		
2	0	—	19.1	0.0803	
	10	0.686	13.08		25.32
	15	0.611	10.97		
3	0	—	9.60	0.0803	
	10	0.418	6.34		14.40
	15	0.358	5.14		
4	0	—	4.80	0.0803	
	10	0.237	3.06		8.16
	15	0.190	2.38		
5	0	—	2.40	0.0803	
	10	0.083	1.08		3.36
	15	0.055	0.80		

(α = 0.78) From log initial rate <u>versus</u> log $[(C_6H_5)_3SiOH]$ after 10 seconds.

*Initial concentration of CrO_2Cl_2 constant and $(C_6H_5)_3SiOH$ varied.

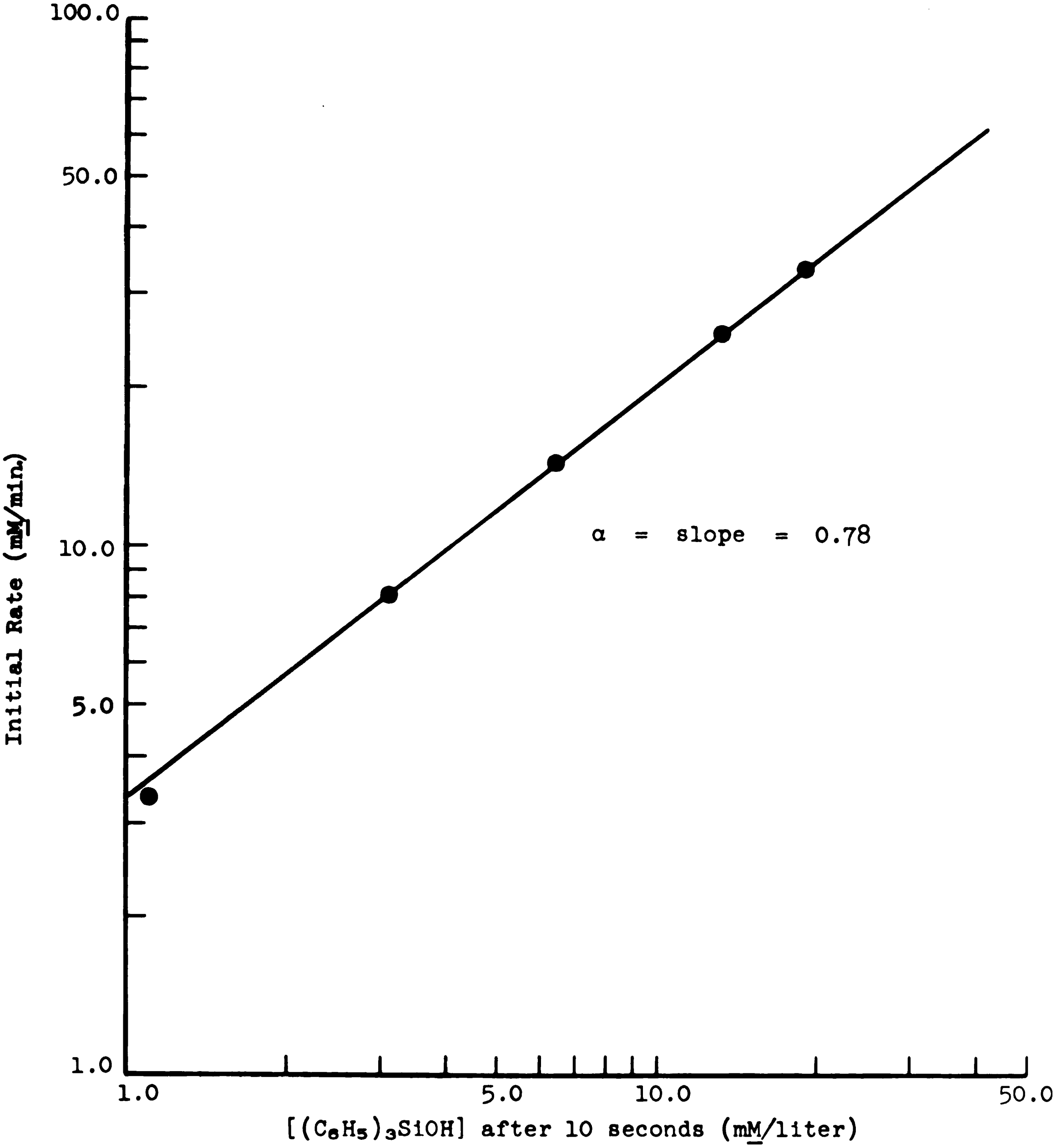


Figure XVIII. Triphenylsilanol--chromyl chloride reaction plotted by initial rates method.

Table XX. $(C_6H_5)_3SiOH$ + CrO_2Cl_2 Initial Rate Data*

Reaction	Time (sec.)	Absorbancy at 2720 mμ	$[(C_6H_5)_3SiOH]$ m<u>M</u>	$[CrO_2Cl_2]$ <u>M</u>	Initial Rate m<u>M</u>/min.
1	0	—	20.6	0.0785	18.12
	10	0.499	8.14		
	15	0.432	6.63		
2	0	—	10.3	0.0785	10.08
	10	0.274	3.65		
	15	0.220	2.81		
3	0	—	5.15	0.0785	4.80
	10	0.120	1.49		
	15	0.084	1.09		
4	0	—	2.52	0.0785	2.92
	10	0.059	0.84		
	15	0.042	0.68		

(α = 0.78) From slope log initial rate <u>versus</u> log $[(C_6H_5)_3SiOH]$ after 10 second.

*Initial concentration of CrO_2Cl_2 constant and $(C_6H_5)_3SiOH$ varied.

Table XXI. $(C_6H_5)_3SiOH$ + CrO_2Cl_2 Initial Rate Data*

Reaction	Time (sec.)	Absorbancy at 2720 mμ	$[(C_6H_5)_3SiOH]$ mM	$[CrO_2Cl_2]$ M	Initial Rate mM/min.
1	0	—	39.3	0.0349	
	10	0.795	16.47		16.56
	15	0.752	15.09		
2	0	—	19.6	0.0349	
	10	0.528	8.83		10.32
	15	0.492	7.97		
3	0	—	9.80	0.0349	6.72
	10	0.370	5.37		
	15	0.341	4.81		
4	0	—	4.90	0.0349	3.84
	10	0.198	2.49		
	15	0.175	2.17		
5	0	—	2.45	0.0349	3.00
	10	0.152	1.88		
	15	0.132	1.63		

(α = 0.79) From slope log initial rate _versus_ log $[(C_6H_5)_3SiOH]$ after 10 seconds.

*Initial concentration of CrO_2Cl_2 constant and $(C_6H_5)_3SiOH$ varied.

Table XXII. $(C_6H_5)_3SiOH$ + CrO_2Cl_2 Initial Rate Data*

Reaction	Time (sec.)	Absorbancy at 2720 mμ	$[(C_6H_5)_3SiOH]$ mM	$[CrO_2Cl_2]$ M	Initial Rate mM/min.
1	0	—	15.7	0.0350	
	10	0.446	6.93		10.44
	15	0.406	6.06		
2	0	—	12.6	0.0350	
	10	0.348	4.94		7.92
	15	0.311	4.28		
3	0	—	7.87	0.0350	
	10	0.267	3.53		5.88
	15	0.236	3.04		
4	0	—	3.93	0.0350	
	10	0.138	1.70		3.12
	15	0.116	1.44		

(α = 0.82) From slope of log initial rate *versus* log $[(C_6H_5)_3SiOH]$ after 10 seconds.

*Initial concentration of CrO_2Cl_2 constant and $(C_6H_5)_3SiOH$ varied.

Table XXIII. $(C_6H_5)_3SiOH$ + CrO_2Cl_2 Initial Rate Data*

Reaction	Time (sec.)	Absorbancy at 2720 mμ	$[(C_6H_5)_3SiOH]$ <u>mM</u>	$[CrO_2Cl_2]$ <u>M</u>	Initial Rate <u>mM</u>/min.
1	0	—	25.7	0.0392	
	10	0.702	13.55		18.72
	15	0.648	11.99		
2	0	—	10.3	0.0392	
	10	0.351	5.00		8.88
	15	0.310	4.26		
3	0	—	5.14	0.0392	
	10	0.200	2.52		5.16
	15	0.169	2.09		
4	0	—	2.57	0.0392	
	10	0.104	1.31		2.88
	15	0.082	1.07		

(α = 0.76) From slope of log initial rate <u>versus</u> log $[(C_6H_5)_3SiOH]$ after 10 seconds.

*Initial concentration of CrO_2Cl_2 constant and $(C_6H_5)_3SiOH$ varied.

were determined from the concentration-time data. This was done graphically by measuring the slope of the concentration versus time curves (Figure XV, page 106). The slope may be found by simply laying a straightedge along the initial points and finding its slope in units of $[(C_6H_5)_3SiOH]$ and time or by using an optical method as described by Pearlson and Simons (111). This involves using a mirror which, when oriented normal to the curve, shows a reflection that is a smooth continuation of the curve. The slope is then drawn perpendicular to the normal. For the situation where the initial concentration of chromyl chloride was held constant and the triphenylsilanol concentration varied, a plot of the logarithm of the initial rate versus logarithm of initial concentration of $(C_6H_5)_3SiOH$ will give a straight line with a slope of α. In this study, values of α, the pseudo-order with respect to triphenylsilanol at constant chromyl chloride concentration, were 0.78, 0.78, 0.79, 0.82, and 0.76 (average 0.79). Figure XVIII is a representative plot of one determination of α. The above α values correspond to data summarized in Tables XIX, XX, XXI, XXII, and XXIII, respectively.

When a similar initial rates approach was taken for the situation of constant initial concentrations $(C_6H_5)_3SiOH$ and varying concentration of CrO_2Cl_2 (Tables XXIV and XXV), troubles were encountered. Initial rates were determined as before, but when the logarithm of the initial rate

Table XXIV. ($(C_6H_5)_3SiOH + CrO_2Cl_2$ Initial Rate Data*
(Plotted in Figure XIX)

Rx.	Time (sec.)	Absorbancy at 2720 $m\mu$	$[(C_6H_5)_3SiOH]$ $\underline{mM}$	$[CrO_2Cl_2]$ $\underline{M}$	Initial Rate $\underline{mM}$/min.
1	0	—	9.50	0.111	
	10	0.236	3.04		8.76
	15	0.185	2.31		
2	0	—	9.50	0.0885	
	10	0.269	3.56		8.76
	15	0.222	2.83		
3	0	—	9.50	0.0665	
	10	0.318	4.41		9.00
	15	0.275	3.65		
4	0	—	9.50	0.0442	
	10	0.368	5.33		8.64
	15	0.330	4.61		
5	0	—	9.50	0.0221	
	10	0.430	6.59		7.56
	15	0.400	5.96		
6	0	—	9.50	0.0111	
	10	0.453	7.09		5.52
	15	0.432	6.63		
7	0	—	9.50	0.00554	
	10	0.490	7.93		3.84
	15	0.476	7.61		
8	0	—	9.50	0.00332	
	10	0.492	7.97		2.76
	15	0.482	7.74		
9	0	—	9.50	0.00111	
	10	0.507	8.33		0.60
	15	0.505	8.28		

*Initial concentration of $(C_6H_5)_3SiOH$ constant and CrO_2Cl_2 varied.

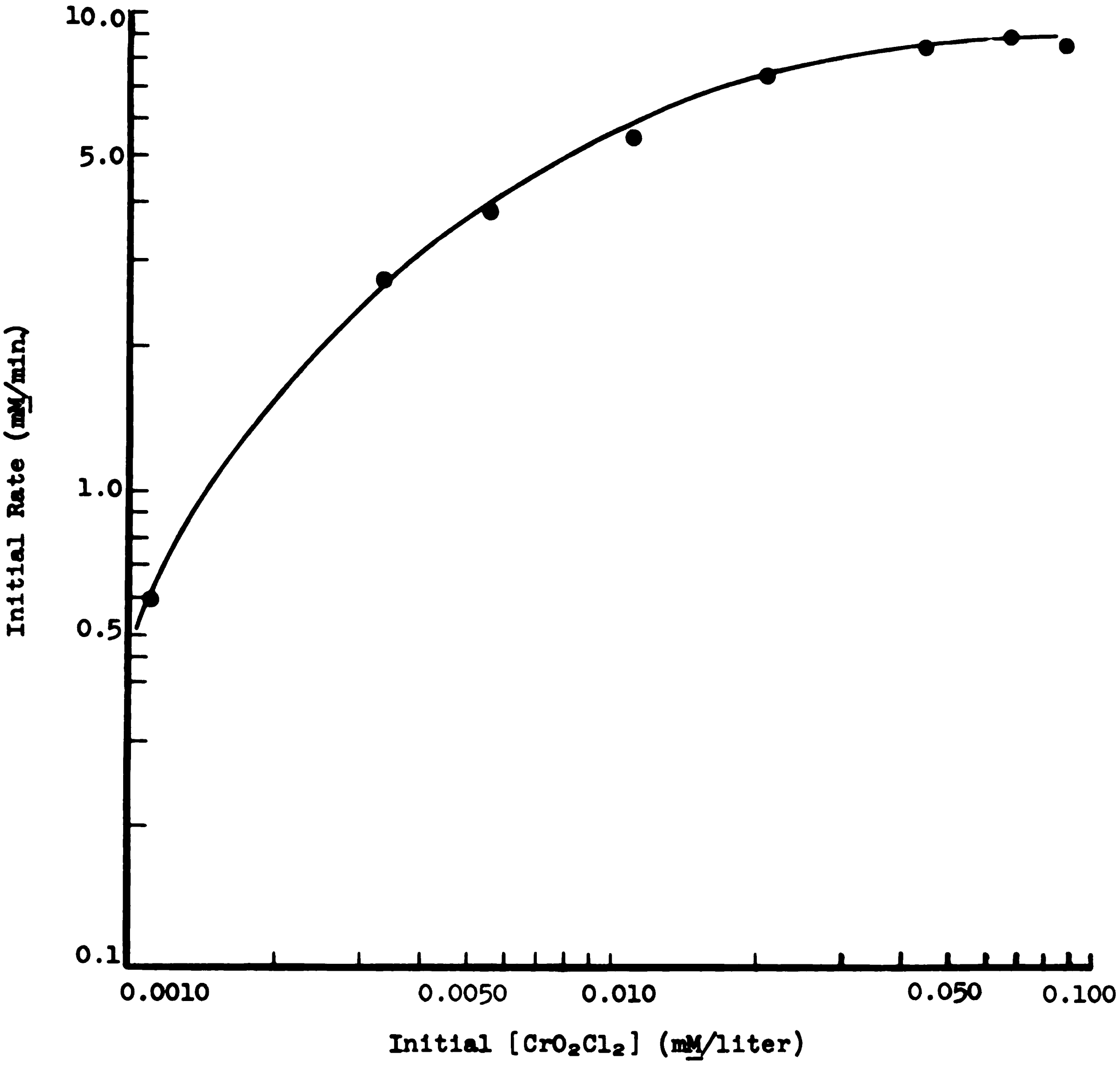


Figure XIX. Triphenylsilanol--chromyl chloride reaction plotted by initial rates method.

Table XXV. $(C_6H_5)_3SiOH$ + CrO_2Cl_2 Initial Rate Data*

Reaction	Time (sec.)	Absorbancy at 2720 mμ	$[(C_6H_5)_3SiOH]$ m<u>M</u>	$[CrO_2Cl_2]$ <u>M</u>	Initial Rate m<u>M</u>/min.
1	0	—	8.91	0.111	
	10	0.282	3.78		10.08
	15	0.229	2.94		
2	0	—	8.91	0.0553	
	10	0.345	4.89		9.24
	15	0.302	4.12		
3	0	—	8.91	0.0275	
	10	0.402	6.01		7.44
	15	0.371	5.39		
4	0	—	8.91	0.0055	
	10	0.486	7.83		5.16
	15	0.467	7.40		
5	0	—	8.91	0.0027	
	10	0.509	8.37		3.12
	15	0.498	8.11		

*Initial concentration of $(C_6H_5)_3SiOH$ constant and CrO_2Cl_2 varied.

versus logarithm of initial concentration of CrO_2Cl_2 was plotted, a straight line did not result. Consequently β, the pseudo-order with respect to chromyl chloride at constant triphenylsilanol, could not be determined in this manner. Figure XIX is a representative curve taken from Table XXIV. This approach failed to determine β because of a solubility limitation that $(C_6H_5)_3SiOH$ has in CCl_4 which prevents having a large enough excess of this reactant present in the rate runs. In fact reactions 1 in Tables XXIV and XXV show initial concentrations of chromyl chloride greater than triphenylsilanol.

Because of these failures to obtain a value of β by the above approach, another method of simplifying the general rate expression was undertaken so that this value of β could be arrived at. This method (112) is to choose the initial concentration of each reactant so that all concentrations throughout the run remain in constant proportion to each other. For the conditions of chromyl chloride and triphenylsilanol initial concentrations in constant proportion,

$$[(C_6H_5)_3SiOH] = \underline{p}[CrO_2Cl_2]$$

and

$$\frac{d\underline{x}}{d\underline{t}} = \underline{k}[(C_6H_5)_3SiOH]^{\alpha}[CrO_2Cl_2]^{\beta}$$

$$\frac{d\underline{x}}{d\underline{t}} = \underline{kp}[CrO_2Cl_2]^{\alpha}[CrO_2Cl_2]^{\beta}$$

$$\frac{d\underline{x}}{d\underline{t}} = \underline{kp}[CrO_2Cl_2]^{\alpha+\beta} .$$

Then,

$$\log \frac{d\underline{x}}{d\underline{t}} = \log(\underline{kp}) + (\alpha + \beta) \log[CrO_2Cl_2].$$

In a similar manner as described above, initial rate data were determined (from Tables XXVI and XXVII) and plotted as the logarithm of intial rate *versus* logarithm of initial $[CrO_2Cl_2]$. Values obtained from the slopes for $(\alpha + \beta)$, the overall order of the forward reaction, were 1.35 and 1.30 (average 1.32). Figure XX is a representative plot for one determination of $(a + \beta)$. The above determinations for $(\alpha + \beta)$ correspond to data summarized in Tables XXVI and XXVII, respectively. Using simple subtraction, the value of β was deduced from the average values determined for $(\alpha + \beta)$ and α. The value of β obtained by this indirect method was 0.53 (1.32 minus 0.79).

D. Determination of the Reaction Order of the Reverse Reaction

A similar rate study was made of the reaction of bis-(triphenylsilyl)chromate with hydrogen chloride (reverse reaction). The initial rate of appearance of triphenylsilanol was studied as a function of initial concentrations. Rate data (absorbancies *versus* time) were obtained by recording absorbancy at 2720 mμ as a function of time until

Table XXVI. $(C_6H_5)_3SiOH$ + CrO_2Cl_2 Initial Rate Data*
(Plotted in Figure XX)

Reaction	Time (sec.)	Absorbancy at 2720 mμ	$[(C_6H_5)_3SiOH]$ <u>mM</u>	$[CrO_2Cl_2]$ <u>M</u>	Initial Rate <u>mM</u>/min.
1	0	—	19.2	0.109	23.88
	10	0.642	11.82		
	15	0.568	9.83		
2	0	—	14.4	0.0815	16.44
	10	0.556	9.53		
	15	0.500	8.16		
3	0	—	8.9	0.0505	8.52
	10	0.483	7.76		
	15	0.451	7.05		
4	0	—	4.8	0.0273	3.60
	10	0.293	3.96		
	15	0.275	3.65		
5	0	—	2.4	0.0136	1.44
	10	0.162	2.00		
	15	0.152	1.84		

($\alpha + \beta = 1.35$) From log initial rate <u>versus</u> log initial $[CrO_2Cl_2]$.

*Initial concentrations of CrO_2Cl_2 and $(C_6H_5)_3SiOH$ varied in constant ratio of 5.67 to 1.00.

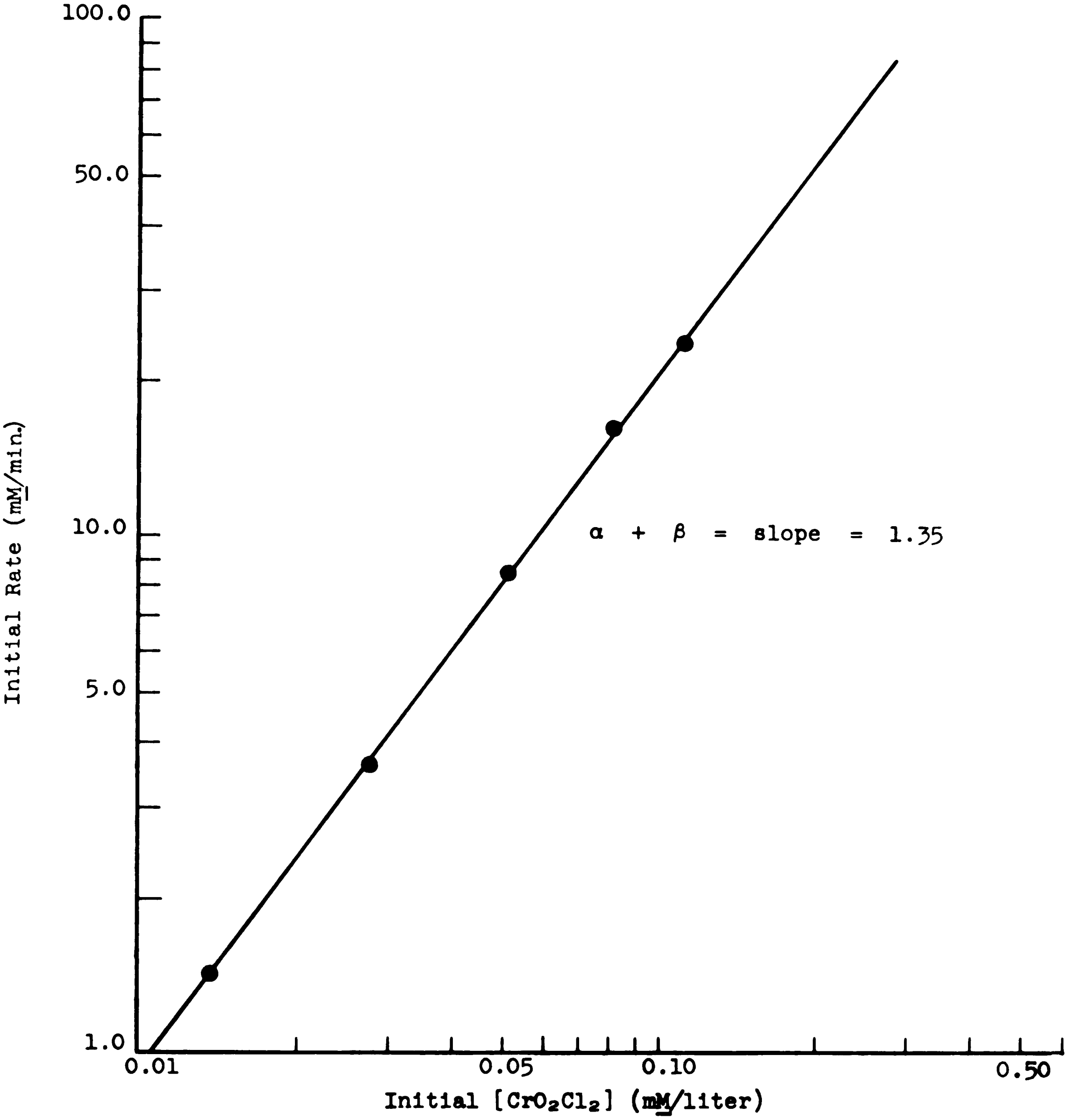


Figure XX. Triphenylsilanol--chromyl chloride reaction plotted by initial rates method.

Table XXVII. $(C_6H_5)_3SiOH$ + CrO_2Cl_2 Initial Rate Data*

Reaction	Time (sec.)	Absorbancy at 2720 mμ	$[(C_6H_5)_3SiOH]$ mM	$[CrO_2Cl_2]$ M	Initial Rate mM/min.
1	0	—	26.0	0.130	
	10	0.705	13.64		28.80
	15	0.621	11.24		
2	0	—	19.5	0.0975	
	10	0.639	11.73		20.88
	15	0.574	9.93		
3	0	—	13.0	0.0650	
	10	0.554	9.48		12.24
	15	0.512	8.46		
4	0	—	6.5	0.0325	
	10	0.391	5.78		4.68
	15	0.371	5.39		
5	0	—	3.3	0.0163	
	10	0.249	3.25		2.04
	15	0.238	3.08		

$(\alpha + \beta)$ From log initial rate *versus* log initial $[CrO_2Cl_2]$.

*Initial concentrations of CrO_2Cl_2 and $(C_6H_5)_3SiOH$ varied in constant ratio of 5.00 to 1.00.

the value became constant. As in the previous section, the absorbancies were converted to molar concentrations by use of the equation which resulted from regression analysis of absorbancy *versus* concentration data and which was described in Section B, 3, p. 101. The reaction was begun at the moment of mixing and the first absorbancy was recorded then seconds later. Table XXVII summarizes in graphical form a typical set of rate data.

As a first assumption, the rate expression for the reaction was taken to be:

$\frac{dx}{dt} = k[\{(C_6H_5)_3Si\}_2CrO_4]^{\alpha'}[HCl]^{\beta'}$, where $\frac{dx}{dt}$ is a convenient expression for the rate, and $[\{(C_6H_5)_3Si\}_2CrO_4]$ and [HCl] are the molar concentrations of reactants. The apparent order with respect to each reactant was then determined in a series of reactions starting with varying concentrations of one component but a constant concentration of the other. Stock solutions of bis(triphenylsilyl)chromate in carbon tetrachloride were prepared by weighing well-characterized bis(triphenylsilyl)chromate into a known volume of freshly opened carbon tetrachloride. These solutions were then diluted as needed. Preparation of hydrogen chloride solutions in carbon tetrachloride have been described previously. These

Table XXVIII. $[(C_6H_5)_3Si]_2CrO_4$ + HCl Absorbancy (2720 mμ) and Concentration _versus_ Time Data* (Plotted in Figure XXI)

Elapsed Time (sec.)	Reaction 1; Initial [HCl] = 0.0155 M		Reaction 2; Initial [HCl] = 0.00775 M		Reaction 3; Initial [HCl] = 0.00385 M		Reaction 4; Initial [HCl] = 0.00155 M	
	Absorbancy	$[(C_6H_5)_3$-SiOH] (2720 mμ) mM	Absorbancy	$[(C_6H_5)_3$-SiOH] (2720 mμ) mM	Absorbancy	$[(C_6H_5)_3$-SiOH] (2720 mμ) mM	Absorbancy	$[(C_6H_5)_3$-SiOH] (2720 mμ) mM
15	0.115	1.43	0.098	1.24	0.085	1.10	0.079	1.04
30	0.149	1.84	0.114	1.42	0.092	1.18	0.085	1.10
45	0.180	2.24	0.129	1.60	0.100	1.26	0.090	1.16
60	0.202	2.55	0.143	1.76	0.111	1.39	0.093	1.19
75	0.225	2.88	0.155	1.91	—	—	—	—
90	0.247	3.21	0.167	2.07	0.121	1.50	0.088	1.24
105	0.264	3.48	0.180	2.24	—	—	—	—
120	0.282	3.78	0.192	2.41	0.134	1.66	0.104	1.31
135	0.294	3.98	—	—	—	—	—	—
150	0.310	4.26	0.212	2.69	—	—	—	—
180	0.332	4.65	0.227	2.91	1.53	1.89	0.115	1.43
210	0.350	4.98	0.243	3.15	—	—	—	—
240	0.364	5.25	0.255	3.34	1.72	2.13	0.124	1.54
270	0.380	5.56	0.266	3.52	—	—	—	—
300	0.392	5.80	0.280	3.75	0.185	2.31	—	—
360	0.412	6.21	0.295	4.00	0.197	2.47	—	—

*Initial concentration of HCl Varied and $[(C_6H_5)_3Si]_2CrO_4$ held constant at 0.00613 M

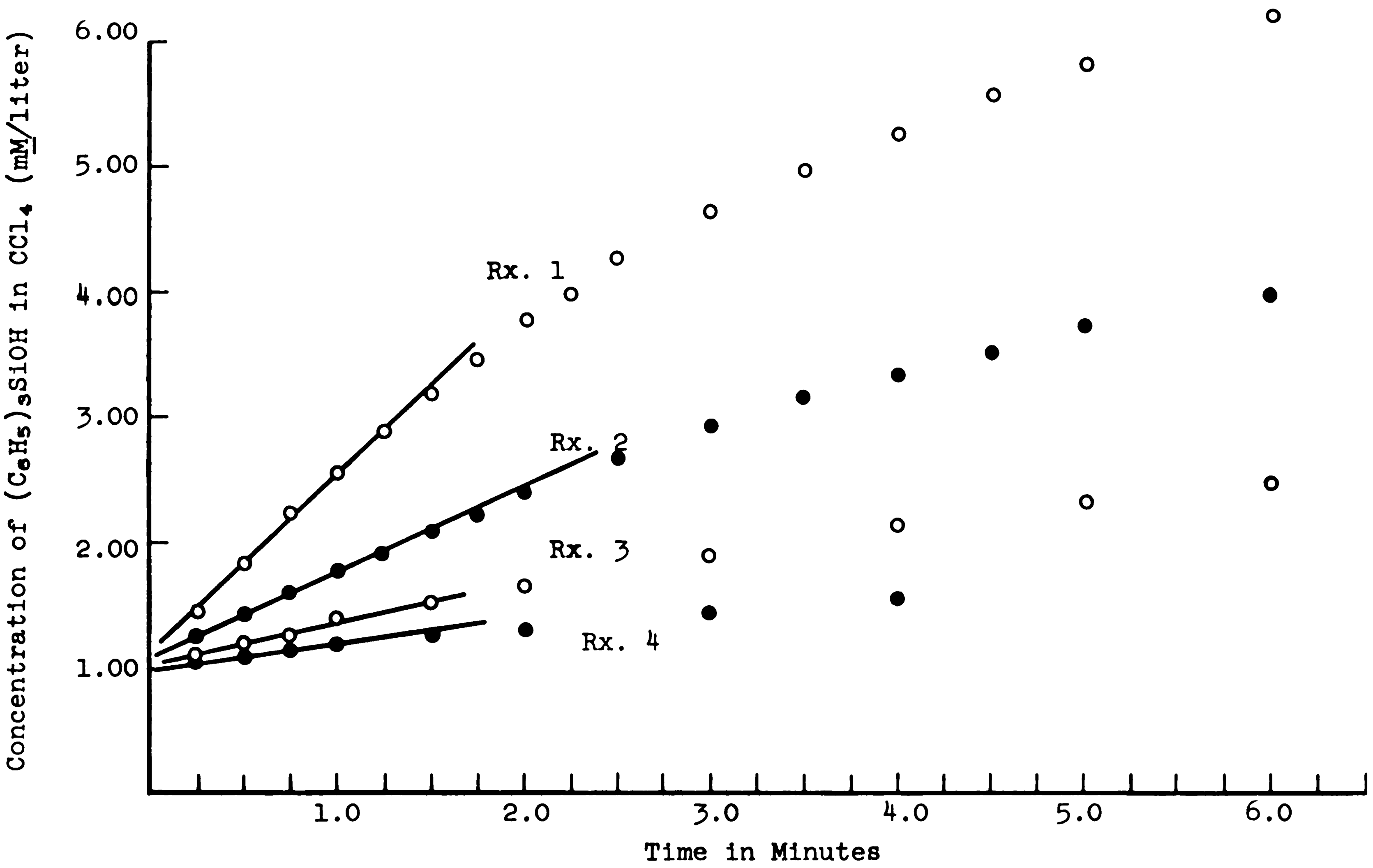


Figure XXI. Typical concentration versus time plot for the $[(C_6H_5)_3Si]_2CrO_4$--HCl reaction.

solutions were then adjusted to various concentrations by further dilution with additional solvent. For constant initial hydrogen chloride concentration,

$$\frac{dx}{dt} = k'\left\{[(C_6H_5)_3Si]_2CrO_4\right\}^{\alpha'},$$ where k' is the effective rate constant under the experimental conditions and α' is the apparent order with respect to bis(triphenylsilyl)chromate. Similarly, for constant initial bis(triphenylsilyl)chromate concentration,

$$\frac{dx}{dt} = k''[HCl]^{\beta'},$$ where β' is the apparent order with respect to hydrogen chloride. It follows then that for the two kinds of experiments

$$\log \frac{dx}{dt} = \log k' + \alpha' \; [(C_6H_5)_3Si]_2CrO_4$$

and

$$\log \frac{dx}{dt} = \log k'' + \beta' \; [HCl]$$

used in the present study constituted a special case of the above expressions in which initial rate data and initial concentrations of reactants were employed. Initial rate data as a function of initial concentrations for both the above situations are summarized in Tables XXVIII-XXXI (hydrogen chloride concentration varied) and Tables XXXII-XXXIV [bis(triphenylsilyl)chromate concentration

Table XXIX. $[(C_6H_5)_3Si]_2CrO_4$ + HCl Initial Rate Data*
(Plotted in Figure XXII)

Reaction	Time (sec.)	Absorbancy (2720 mμ)	$[(C_6H_5)_3SiOH]$ mM	[HCl] mM	$[\{(C_6H_5)_3Si\}_2CrO_4]$ mM	Initial Rate mM/min.
1	0	—	—	82.3	9.45	3.24
	10	0.072	0.97			
	20	0.122	1.51			
2	0	—	—	41.1	9.45	1.50
	10	0.041	0.67			
	20	0.067	0.92			
3	0	—	—	20.5	9.45	0.72
	10	0.020	0.48			
	20	0.033	0.60			
4	0	—	—	8.23	9.45	0.28
	15	0.016	0.45			

(β' = 1.05) From log initial rate _versus_ log initial [HCl].

*Initial concentration of $[(C_6H_5)_3Si]_2CrO_4$ constant [HCl] varied.

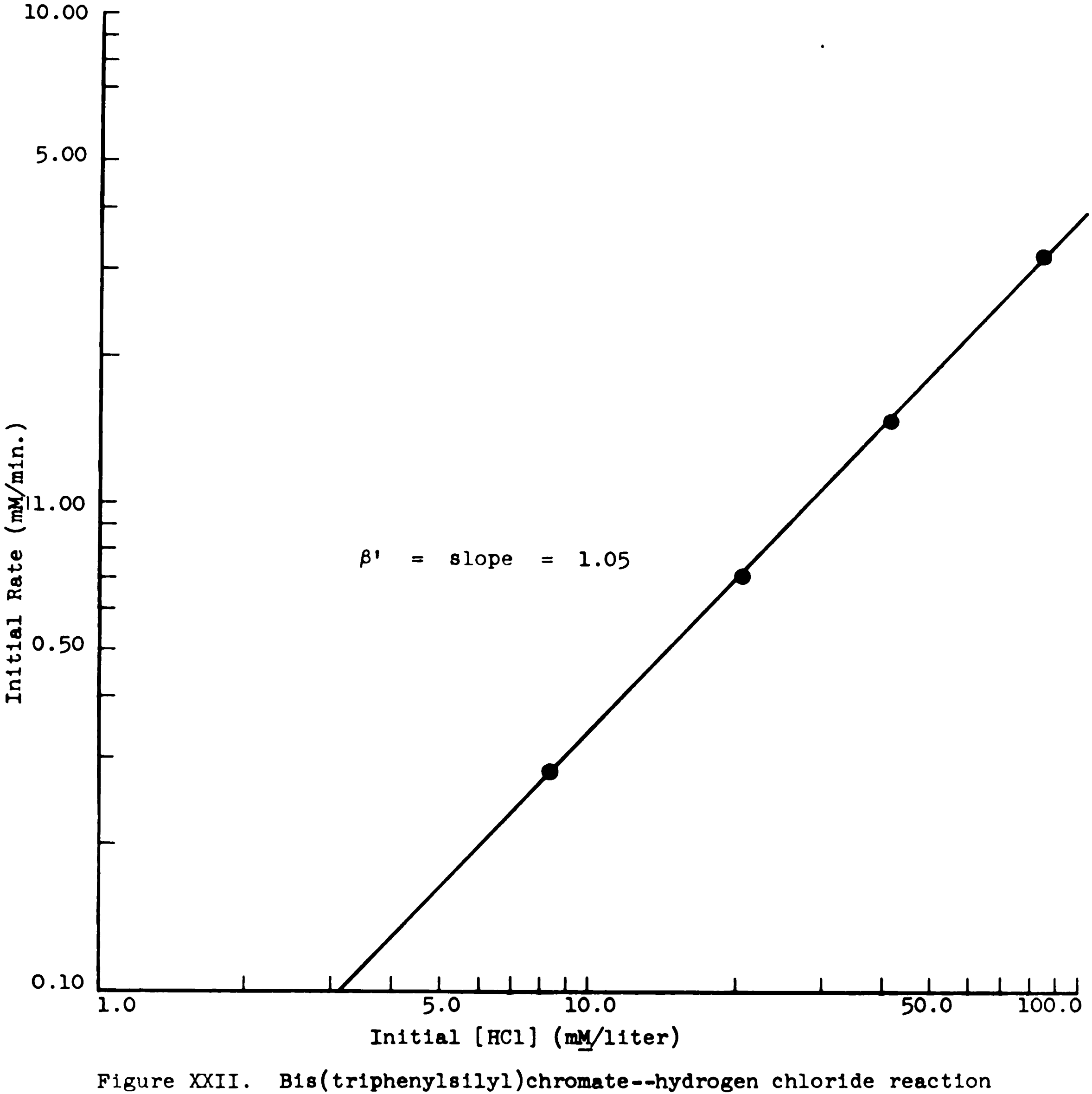


Figure XXII. Bis(triphenylsilyl)chromate--hydrogen chloride reaction plotted by initial rates method.

Table XXX. $[(C_6H_5)_3Si]_2CrO_4$ + HCl Initial Rate Data*

Rx.	Time (sec.)	Absorbancy (2720 mμ)	$[(C_6H_5)_3SiOH]$ m$\underline{M}$	[HCl] m$\underline{M}$	$[\{(C_6H_5)_3Si\}_2CrO_4]$ m$\underline{M}$	Initial Rate m$\underline{M}$/min.
1	0	—	—	0.108	8.97	
	10	0.098	1.24			3.06
	20	0.142	1.75			
2	0	—	—	0.054	8.97	
	10	0.072	0.97			1.44
	20	0.095	1.21			
3	0	—	—	0.027	8.97	
	10	0.053	0.78			0.66
	20	0.064	0.89			
4	0	—	—	0.0108	8.97	
	10	0.045	0.71			0.30
	20	0.050	0.76			

(β' = 1.04) From log initial rate *versus* log initial [HCl].

*Initial concentration of $[(C_6H_5)_3Si]_2CrO_4$ constant and HCl varied.

Table XXXI. $[(C_6H_5)_3Si]_2CrO_4$ + HCl Initial Rate Data*

Rx.	Time (sec.)	Absorbancy (2720 mµ)	$[(C_6H_5)_3SiOH]$ m*M*	[HCl] m*M*	$[\{(C_6H_5)_3Si\}_2CrO_4]$ m*M*	Initial Rate m*M*/min.
1	0	—	—	61.8	6.13	
	30	0.149	1.84			1.37
	90	0.247	3.21			
2	0	—	—	30.9	6.13	
	30	0.114	1.42			0.65
	90	0.167	2.07			
3	0	—	—	15.4	6.13	
	30	0.092	1.18			0.32
	90	0.121	1.50			
4	0	—	—	7.74	6.13	
	30	0.085	1.10			0.14
	90	0.098	1.24			

(β' = 1.02) From log initial rate *versus* log initial [HCl].

*Initial concentration of $[(C_6H_5)_3Si]_2CrO_4$ constant and HCl varied.

Table XXXII. $[(C_6H_5)_3Si]_2CrO_4$ + HCl Initial Rate Data*
(Plotted in Figure XXIII)

Rx.	Time (sec.)	Absorbancy (2720 mμ)	$[(C_6H_5)_3SiOH]$ m*M*	[HCl] m*M*	$[\{(C_6H_5)_3Si\}_2CrO_4]$ m*M*	Initial Rate m*M*/min.
1	0	—	—	61.8	6.13	
	30	0.163	2.02			1.31
	90	0.255	3.33			
2	0	—	—	61.8	3.06	
	30	0.091	1.17			0.62
	90	0.145	1.79			
3	0	—	—	61.8	1.53	
	30	0.053	0.79			0.32
	90	0.086	1.11			
4	0	—	—	61.8	0.77	
	30	0.047	0.72			0.15
	90	0.062	0.87			

(α' = 1.01) From log initial rate *versus* log initial $[\{(C_6H_5)_3Si\}_2CrO_4]$.

*Initial concentration of HCl constant and $[(C_6H_5)_3Si]_2CrO_4$ varied.

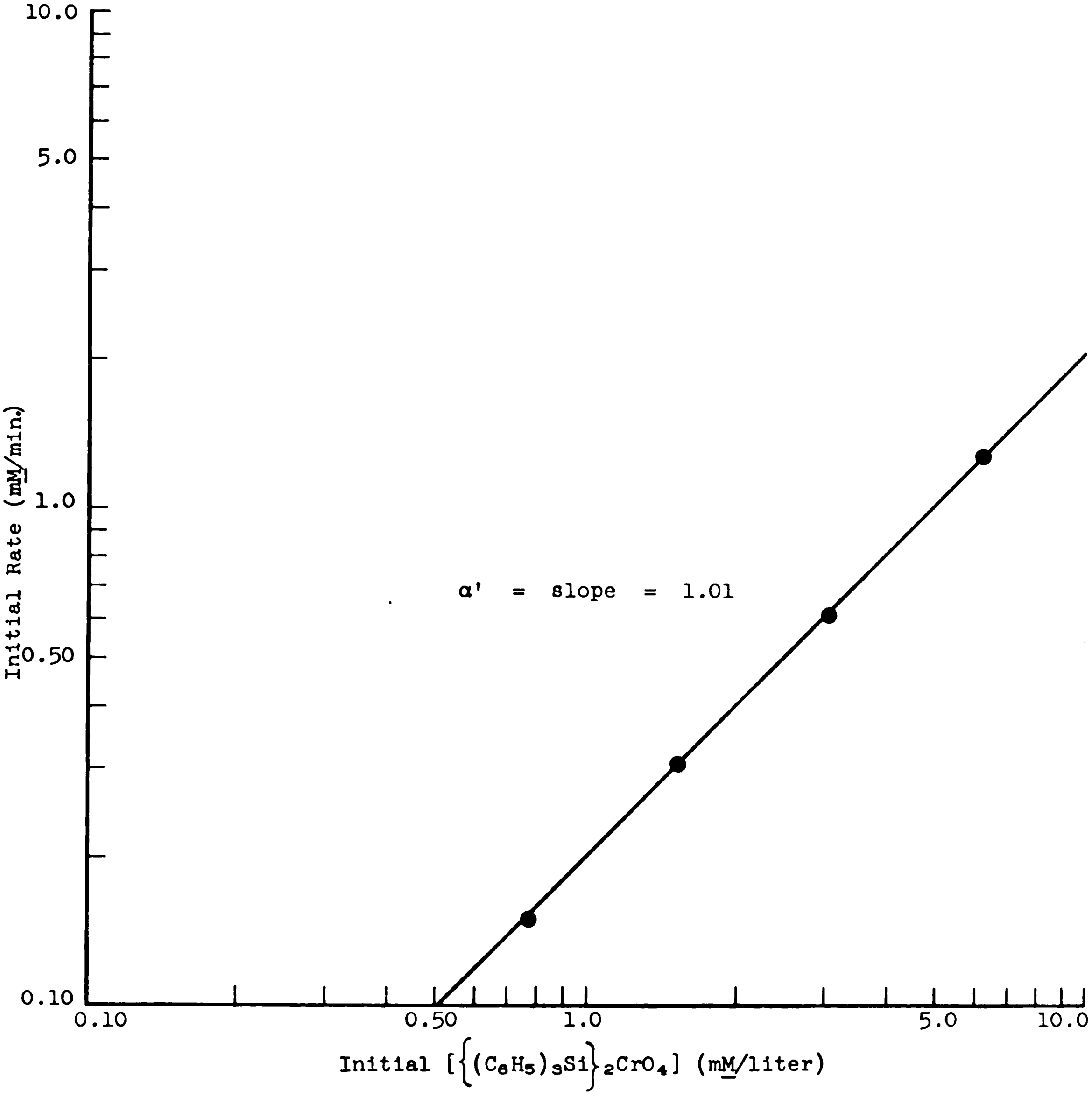


Figure XXIII. Bis(triphenylsilylchromate--hydrogen chloride reaction plotted by initial rates method.

Table XXXIII. $[(C_6H_5)_3Si]_2CrO_4$ + HCl Initial Rate Data*

Rx.	Time (sec.)	Absorbancy (2720 mμ)	$[(C_6H_5)_3SiOH]$ m<u>M</u>	[HCl] <u>M</u>	$[\{(C_6H_5)_3Si\}_2CrO_4]$ <u>M</u>	Initial Rate m<u>M</u>/min.
1	0	—	—	0.109	8.97	2.58
	10	0.088	1.14			
	20	0.127	1.57			
2	0	—	—	0.109	4.49	1.28
	10	0.037	0.64			
	20	0.057	0.82			
3	0	—	—	0.109	2.25	0.60
	10	0.004	0.35			
	20	0.015	0.45			

(α' = 1.05) From log initial rate <u>versus</u> log initial $[\{(C_6H_5)_3Si\}_2CrO_4]$.

*Initial concentration of HCl constant and $[(C_6H_5)_3Si]_2CrO_4$ varied.

Table XXXIV. $[(C_6H_5)_3Si]_2CrO_4$ + HCl Initial Rate Data*

Reaction	Time (sec.)	Absorbancy (2720 mμ)	$[(C_6H_5)_3SiOH]$ mM	[HCl] mM	$[\{(C_6H_5)_3Si\}_2CrO_4]$ mM	Initial Rate mM/min.
1	0	—	—	82.3	9.45	2.94
	10	0.075	1.00			
	20	0.120	1.49			
2	0	—	—	82.3	4.72	1.32
	10	0.044	0.69			
	15	0.055	0.80			
3	0	—	—	82.3	2.36	0.64
	15	0.052	0.77			
	30	0.068	0.93			

(α' = 1.06) From log initial rate <u>versus</u> log initial $[\{(C_6H_5)_3Si\}_2CrO_4]$.

*Initial concentration of HCl constant and $[(C_6H_5)_3Si]_2CrO_4$ varied.

varied]. Initial reaction rates for this reverse reaction were determined by measuring the slope of the concentration <u>versus</u> time curves (Figure XXI). The slope was found by simply laying a straightedge along the initial points (linear region) and finding the slope in units of concentration and time. For the situation where the initial concentration of hydrogen chloride was varied and the bis(triphenylsilyl)-chromate concentration held constant, a plot of the logarithm of the initial rate versus logarithm of initial concentration of HCl will give a straight line with a slope of β'. In this study, values of β', the pseudo-order with respect to hydrogen chloride at constant bis(triphenylsilyl)chromate concentration, were 1.05, 1.04, and 1.02 (average 1.04). Figure XXII is a representative plot of one determination of β'. The above β' values correspond to data summarized in Tables XXIX, XXX, and XXXI, respectively.

Likewise for the situation where the initial concentration of hydrogen chloride was held constant and the bis(triphenylsilyl)chromate was varied (Tables XXIX-XXXI), a plot of the logarithm of the initial rate versus logarithm of initial concentration of $[(C_6H_5)_3Si]_2CrO_4$ will give a straight line with a slope of α'. In this study, values of α' determined in this manner were 1.01, 1.05, and 1.06 (average 1.04).

Table XXXV. $[(C_6H_5)_3Si]_2CrO_2$ + HCl Initial Rate Data*

Rx.	Time (sec.)	Absorbancy (2720 mμ)	$[(C_6H_5)_3SiOH]$ m$\underline{M}$	$[\{(C_6H_5)_3Si\}_2CrO_4]$ m$\underline{M}$	[HCl]	$[CrO_2Cl_2]$	Initial Rate m$\underline{M}$/min.
1	0	—	—	5.68	11.6	None	
	10	0.136	1.68				0.75
	30	0.157	1.93				
	45	0.174	2.16				
	60	0.189	2.37				
	90	0.213	2.70				
2	0	—	—	5.68	11.6	1.10	
	10	0.095	1.21				0.60
	30	0.113	1.41				
	45	0.126	1.56				
	60	0.134	1.65				
	90	0.150	1.85				
3	0	—	—	5.68	11.6	0.55	
	10	0.100	1.26				0.63
	30	0.118	1.47				
	45	0.133	1.64				
	60	0.143	1.76				
	90	0.164	2.03				

*Initial concentration of HCl and $[(C_6H_5)_3Si]_2CrO_4$ held constant and CrO_2Cl_2 varied.

Figure XXIII is a representative curve taken from Table XXIX. The α' values 1.05 and 1.06 were determined in the same way from the data presented in Tables XXX and XXXI.

It was of interest to know whether chromyl chloride acts autocatalytically on the hydrogen chloride--bis(triphenylsilyl)chromate reaction. Consequently, the initial rate of this reaction was compared in the absence and presence of additional chromyl chloride. This was done in a series of three reactions starting with constant initial concentrations of bis(triphenylsilyl)chromate and hydrogen chloride but varying concentrations of chromyl chloride. As shown by experimental data of Table XXXV, chromyl chloride does not catalyze this reaction. Initial rate values of 0.75, 0.63, and 0.60 m<u>M</u>/min. were determined for reactions which had initial chromyl chloride concentrations of zero, 1.10 m<u>M</u>, and 0.55 m<u>M</u>, respectively.

E. <u>Evaluation of Rate Constants</u>

After the order of reaction with respect to each reactant had been determined for the forward and reverse reactions, rate expressions could then be formulated and the rate constants calculated. Since in the case of the forward reaction, $(C_6H_5)_3SiOH + CrO_2Cl_2$, the orders with respect to triphenylsilanol and chromyl chloride were found to be 0.79 and 0.53 respectively, the following initial rate expression can be written:

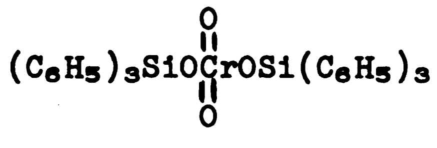
$$\frac{dx}{dt} = k_1[(C_6H_5)_3SiOH]^{0.79}[CrO_2Cl_2]^{0.53}, \quad \text{where } \frac{dx}{dt}$$

is the initial reaction rate and k_1 the forward rate constant. The forward rate constant can then be found from the equation,

$$k_1 = \frac{\frac{dx}{dt}}{[(C_6H_5)_3SiOH]^{0.79}[CrO_2Cl_2]^{0.53}} .$$

In this study, the forward rate constant, k_1, was calculated from each set of experimental rate data involving the triphenylsilanol--chromyl chloride reaction (Tables XIX-XXVII, Part C of this Section). Table XXXVI shows values for the rate constant, k_1, calculated using the above equation. The accepted rate constant should never be based upon a single kinetic run (113). In this case, nine sets of kinetic measurements (46 reaction runs) were used with different initial concentrations. The forward rate constant, k_1, has a value of 0.18 liters $mM^{-1}min.^{-1}$ based on a consideration of the separate constants found for each individual run shown in Table XXXVI.

The rate constant, k_4, for the reaction of bis(triphenylsilyl)chromate and hydrogen chloride,



$$(C_6H_5)_3SiO\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{Cr}}OSi(C_6H_5)_3 \quad + \quad HCl,$$

Table XXXVI. Triphenylsilanol-Chromyl Chloride Reaction Rate Constant ($\underline{k}_1$) Determinations

Table No.	Rx. No.	k_1 (liters $\underline{n}M^{-1}$ min.$^{-1}$)	Table No.	Rx. No.	k_1 (liters $\underline{m}M^{-1}$ min.$^{-1}$)	Table No.	Rx. No.	k_1 (liters $\underline{m}M^{-1}$ min.$^{-1}$)
XIX	1	0.23	XXII	1	0.18	XXV	1	0.15
XIX	2	0.24	XXII	2	0.16	XXV	2	0.19
XIX	3	0.24	XXII	3	0.18	XXV	3	0.22
XIX	4	0.23	XXII	4	0.16	XXV	4	0.37
XIX	5	0.17				XXV	5	0.33
		(ave.) 0.22			(ave.) 0.17			(ave.) 0.25
XX	1	0.16	XXIII	1	0.21	XXVI	1	0.19
XX	2	0.16	XXIII	2	0.20	XXVI	2	0.19
XX	3	0.13	XXIII	3	0.20	XXVI	3	0.19
XX	4	0.14	XXIII	4	0.19	XXVI	4	0.18
							5	0.18
		(ave.) 0.15			(ave.) 0.20			(ave.) 0.19
XXI	1	0.14	XXIV	1	0.12	XXVII	1	0.17
XXI	2	0.15	XXIV	2	0.14	XXVII	2	0.17
XXI	3	0.17	XXIV	3	0.16	XXVII	3	0.18
XXI	4	0.17	XXIV	4	0.20	XXVII	4	0.17
XXI	5	0.22	XXIV	5	0.24	XXVII	5	0.18
			XXIV	6	0.26			
			XXIV	7	0.26			
			XXIV	8	0.25			
			XXIV	9	0.10			
		(ave.) 0.17			(ave.) 0.19			(ave.) 0.17

can be determined using an approach similar to that described for $\underline{k}_1$. The initial rate expression, based on the values of reaction order α' and β' (both 1.04 averages), has the form,

$$\frac{d\underline{x}}{d\underline{t}} = \underline{k}_4[\left\{(C_6H_5)_3Si\right\}_2CrO_4]^{1.04}[HCl]^{1.04} .$$

Similarly, if these reaction order values are considered as unity, then the first order dependence of both $[(C_6H_5)_3Si]_2CrO_4$ and HCl in the initial stages of the reverse reaction can be expressed as

$$\frac{d\underline{x}}{d\underline{t}} = \underline{k}_4[\left\{(C_6H_5)_3Si\right\}_2CrO_4][HCl].$$

Solving these rate expressions for $\underline{k}_4$ yields

$$\underline{k}_4 = \frac{\frac{d\underline{x}}{d\underline{t}}}{[\left\{(C_6H_5)_3Si\right\}_2CrO_4]^{1.04}[HCl]^{1.04}} \tag{1}$$

and

$$\underline{k}_4 = \frac{\frac{d\underline{x}}{d\underline{t}}}{[\left\{(C_6H_5)_3Si\right\}_2CrO_4][HCl]} . \tag{2}$$

With these equations, the observed rate constant, $\underline{k}_4$, was calculated directly from the rate data presented in Tables XXIX-XXXIV (Part D, Section IV). Values obtained by the above equations are summarized in Table XXXVII. The average value of $\underline{k}_4$ using equation 1 is 2.5×10^{-3} liters $m\underline{M}^{-1}$ $min.^{-1}$ while the average value of $\underline{k}_4$ calculated from equation 2 is 3.2×10^{-3} liters $m\underline{M}^{-1}$ $min.^{-1}$.

Table XXXVII. Bis(triphenylsilyl)chromate--Hydrogen Chloride Reaction Rate Constant ($\underline{k}_4$) Determinations

Table No.	Rx. No.	$\underline{k}_4 \times 10^3$ (liters mM^{-1} min.$^{-1}$) Eq. (1)	Eq. (2)	Table No.	Rx. No.	$\underline{k}_4 \times 10^3$ (liters mM^{-1} min.$^{-1}$ Eq. (1)	Eq. (2)
XXIX	1	3.2	4.2	XXXII	1	2.7	3.5
XXIX	2	3.0	3.9	XXXII	2	2.7	3.3
XXIX	3	3.0	3.7	XXXII	3	2.8	3.4
XXIX	4	3.0	3.6	XXXII	4	2.7	3.2
		(ave.) 3.1	(ave.) 3.8			(ave.) 2.7	(ave.) 3.3
XXX	1	2.4	3.2	XXXIII	1	2.0	2.6
XXX	2	2.3	3.0	XXXIII	2	2.1	2.6
XXX	3	2.2	2.7	XXXIII	3	2.0	2.5
XXX	4	2.6	3.1				
		(ave.) 2.4	(ave.) 3.0			(ave.) 2.0	(ave.) 2.6
XXXI	1	2.9	3.6	XXXIV	1	2.3	3.8
XXXI	2	2.7	3.4	XXXIV	2	2.1	3.4
XXXI	3	2.8	3.4	XXXIV	3	2.2	3.3
XXXI	4	2.5	2.9				
		(ave.) 2.8	(ave.) 3.4			(ave.) 2.2	(ave.) 3.5

Comparison between the values determined for $\underline{k}_1$ and $\underline{k}_4$ affords an excellent method by which the initial rates of the forward and reverse reactions can be compared. The ratio of $\underline{k}_1$ to $\underline{k}_4$ is 72 and shows that in the early stage of reaction the forward reaction proceeds at a rate 72 times that of the reverse reaction. It further points out that under the experimental conditions employed in this study, the rate of silylchromate formation is 72 times that of the comparable silylchromate cleavage reaction. This is to say that the condensation reaction of triphenylsilanol with chromyl chloride is much more rapid than the hydrogen chloride cleavage of bis(triphenylsilyl)chromate.

F. Discussion

Triphenylsilanol and chromyl chloride react in carbon tetrachloride to form bis(triphenylsilyl)chromate, triphenylsiloxychromyl chloride, and hydrogen chloride. Under normal conditions this reaction is reversible with all compounds present in significant equilibrium concentrations:

$$(C_6H_5)_3SiOH + CrO_2Cl_2 \underset{\underline{k}_2}{\overset{\underline{k}_1}{\rightleftharpoons}} (C_6H_5)_3SiOCrO_2Cl + HCl$$

$$(C_6H_5)_3SiOCrO_2Cl + (C_6H_5)_3SiOH \underset{\underline{k}_4}{\overset{\underline{k}_3}{\rightleftharpoons}} [(C_6H_5)_3Si]_2CrO_4 + HCl.$$

The overall equilibrium constant, $K_{eq.}$, was determined spectroscopically (Section III, pp. 53-58) and has a value of 1.3. It was further demonstrated that triphenylsiloxychromyl chloride is an intermediate that participates in the reaction (Section III, pp. 53-58) as shown by the following equilibria:

$$(C_6H_5)_3SiOCrO_2Cl + (C_6H_5)_3SiOH \rightleftharpoons [(C_6H_5)_3Si]_2CrO_4 + HCl$$

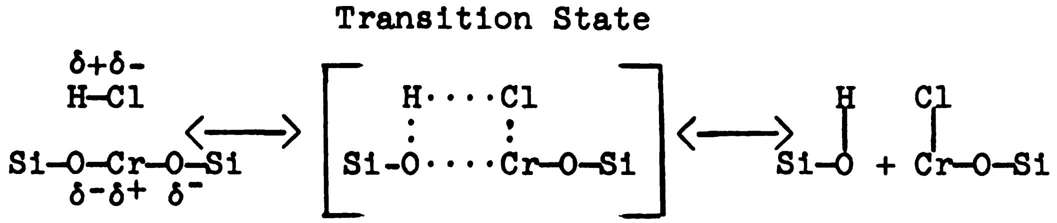
and

$$(C_6H_5)_3SiOCrO_2Cl + HCl \rightleftharpoons (C_6H_5)_3SiOH + CrO_2Cl_2.$$

The kinetics of the above set of equilibrium reactions was undertaken with a pseudo-order rate study of both the triphenylsilanol--chromyl chloride and bis(triphenylsilyl)chromate--hydrogen chloride reactions by the method of initial rates. The first order dependence of both hydrogen chloride and bis(triphenylsilyl)chromate in the early stages of the reverse reaction can be expressed in the following manner:

$$\frac{d[(C_6H_5)_3SiOH]}{d\underline{t}} = \underline{k}_4[HCl][\left\{(C_6H_5)_3Si\right\}_2CrO_4].$$

While other mechanisms cannot be conclusively excluded, this bimolecular interaction of hydrogen chloride and bis(triphenylsilyl)chromate can best be interpreted in terms of an initial coordination by the HCl to the Si-O-Cr linkage. The cleavage step could involve a four-centered concerted cyclic transition state which could decompose (react further) to give either the products or reactants.



$$\underset{\delta^-\delta^+\ \delta^-}{\overset{\overset{\delta+\delta-}{\mathrm{H{-}Cl}}}{\mathrm{Si{-}O{-}Cr{-}O{-}Si}}} \longleftrightarrow \left[\begin{array}{c} \mathrm{H\cdots\cdot Cl} \\ \vdots \qquad \vdots \\ \mathrm{Si{-}O\cdots\cdot Cr{-}O{-}Si}\end{array}\right] \longleftrightarrow \mathrm{Si{-}\overset{\overset{H}{|}}{O}} + \mathrm{\overset{\overset{Cl}{|}}{Cr}{-}O{-}Si}$$

The initial coordination of HCl to the silylchromate is reasonable in view of the polarity of both the hydrogen halide and metallosiloxane linkages. It should be pointed out that metallosiloxanes other than silylchromates undergo similar cleavage reactions with HCl and always so that an organosilanol and metal chloride products result (see Appendix I). Furthermore, the presence of the phenyl substituents (electron withdrawal groups) on silicon would facilitate the reaction shown above by further promoting the tendency of HCl and the silylchromate substrate to polarize each other.

In the case of the forward reaction, the fractional order with repect to each reactant for the combination of triphenylsilanol and chromyl chloride suggests the need for a more complex rate expression than first assumed. The known association of both the organosilanols and chromyl chloride introduces the possibility of accounting for the results by the existence in solution of reactant dimers which dissociate before reaction occurs:

$$[(C_6H_5)_3SiOH]_2 \overset{K'_{eq.}}{\rightleftharpoons} 2\ (C_6H_5)_3SiOH$$

and

$$[CrO_2Cl_2]_2 \xrightleftharpoons{K''_{eq.}} 2\ CrO_2Cl_2.$$

In considering reaction mechanisms involving covalent reactants, it is not uncommon to have incomplete reversible reactions preceding the rate-determining steps (114). Thus, in the case of the reaction between nitric oxide and oxygen, the rate was found (115) to follow a third-order expression:

$$\frac{-d[NO]}{d\underline{t}} = k[NO]^2[O_2].$$

Rather than interpreting this reaction as being a complicated termolecular reaction, consideration was given to a more likely mechanism involving the equilibrium

$$2\ NO \rightleftharpoons N_2O_2$$

preceding the bimolecular rate-determining step so as to agree with the third order expression.

In the present kinetic study, from the equilibrium expressions of these dimer--monomer equilibria, the following relationships are valid:

$$[(C_6H_5)_3SiOH] = (K'_{eq.})^{\frac{1}{2}}[\{(C_6H_5)_3SiOH\}_2]^{\frac{1}{2}}$$

and

$$[CrO_2Cl_2] = (K''_{eq.})^{\frac{1}{2}}[(CrO_2Cl_2)_2]^{\frac{1}{2}}.$$

If $K'_{eq.}$ and $K''_{eq.}$ are small, then the active species in solution would be mostly dimer and the rate expression could be written as:

$$\frac{-d[(C_6H_5)_3SiOH]}{d\underline{t}} = \underline{k}_1(K'_{eq.})^{\frac{1}{2}}(K''_{eq.})^{\frac{1}{2}}[\{(C_6H_5)_3SiOH\}_2]^{\frac{1}{2}}[(CrO_2Cl_2)_2]^{\frac{1}{2}}.$$

Since

$$[\{(C_6H_5)_3SiOH\}_2] = \frac{[(C_6H_5)_3SiOH]}{2} \text{ and } [(CrO_2Cl_2)_2] = \frac{[CrO_2Cl_2]}{2}$$

then

$$\frac{-d[(C_6H_5)_3SiOH]}{d\underline{t}} = \underline{k}'[(C_6H_5)_3SiOH]^{\frac{1}{2}}[CrO_2Cl_2]^{\frac{1}{2}}$$

where

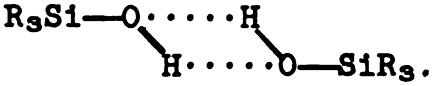
$$\underline{k}' = \frac{\underline{k}_1(K'_{eq.})^{\frac{1}{2}}(K''_{eq.})^{\frac{1}{2}}}{2}$$

If $K'_{eq.}$ and $K''_{eq.}$ are large, then the active species in solution would be mostly monomer and the initial rate could be expressed as follows:

$$\frac{-d[(C_6H_5)_3SiOH]}{d\underline{t}} = \underline{k}'[(C_6H_5)_3SiOH][CrO_2Cl_2].$$

First-order dependence would reflect no self-association and half-order values would indicate complete dimerization. The values obtained for α and β, the orders with respect to triphenylsilanol and chromyl chloride (0.79 and 0.53, respectively), should then be indicative of the extent to which these reactants.

are self-associated in the equilibria preceding the rate-determining reaction. Values obtained clearly indicate that both triphenylsilanol and chromyl chloride are associated as dimers in carbon tetrachloride, but to different degrees. Chromyl chloride appears to be completely dimerized in carbon tetrachloride at 25°C while triphenylsilanol exists as a mixture of significant concentrations of both the monomer and dimer species. Molecular weight determinations of both reactants in carbon tetrachloride are interpreted as being strong supporting evidence of the previous discussion. Thus, Moles and Gomez (1) and Oddo and Serra (39) have postulated extensive dimerization of chromyl chloride from cryoscopic molecularity measurements on carbon tetrachloride and ethylene dibromide solutions. Likewise, in this present investigation, detailed studies of the self-association of triphenylsilanol in carbon tetrachloride are consistent with the postulated equilibria. An extensive discussion of several quantitative measurements of the degree of self-association of triphenylsilanol in carbon tetrachloride is presented in Section V (pp. 157-72) of this thesis. The most important observations noted for the $[\left\{(C_6H_5)_3SiOH\right\}_2]--2(C_6H_5)_3SiOH$ equilibrium pertinent to the present discussion are as follows: (1) The temperature greatly affects the equilibrium; e.g., at identical reagent concentrations of 0.030 M in carbon tetrachloride, the fraction α of monomeric triphenylsilanol was determined to be 1.00, 0.81, 0.49, and 0 at 77°C, 37°C, 24°C, and -23°C temperatures, respectively. (2) In carbon tetrachloride, at the temperatures of 24°C and 37°C, the reagent concentration greatly affects the extent of association; e.g., at 24°C, the fraction α of monomeric triphenylsilanol at 0.010 M, 0.020 M, 0.030 M, and 0.040 M were shown to be 0.74, 0.57, 0.49, and 0.43, respectively. (3) The type of hydrogen bonding in the triphenylsilanol dimerized aggregates appears to be



Baney (33) reported that triphenylsilanol is 19% associated at 0.08 M in carbon tetrachloride*. Even though the literature has several reported studies (1,39,42,43) listing molecular weight data for chromyl chloride in various solvents, no specific structures have been assigned to the associated aggregates involved. One can write reasonable structures for a chromyl chloride dimer involving chlorine or oxygen bridges:

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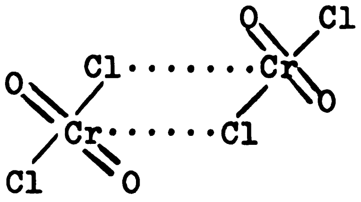
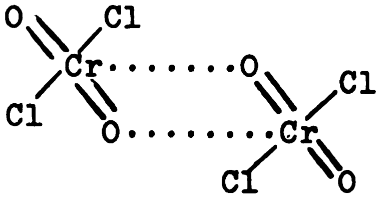
* This value appears to be low. Another point of disagreement is that in the present study, solutions of triphenylsilanol in carbon tetrachloride with concentrations of 0.08 M could not be obtained at 25°C even after vigorous mixing for several days.



or



By analogy to dichromate species and the polymeric chromium(VI) oxide aggregates, the oxygen-bridged structure is more reasonable.

The following postulated equilibria then describe the formation of bis(triphenylsilyl)chromate from triphenylsilanol and chromyl chloride:

$$[(C_6H_5)_3SiOH]_2 \overset{K'_{eq.}}{\rightleftharpoons} 2\ (C_6H_5)_3SiOH$$

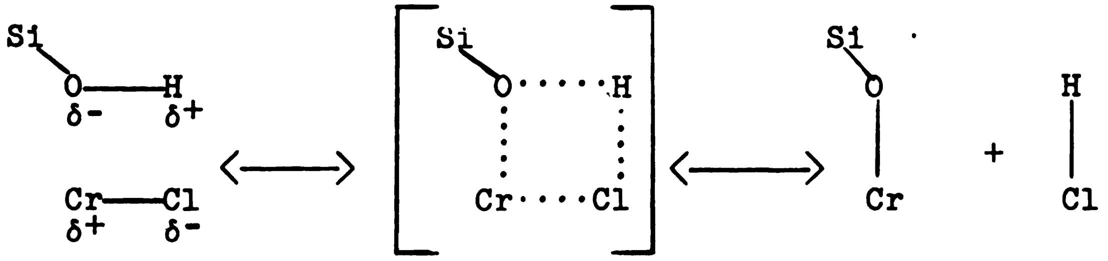
$$[CrO_2Cl_2]_2 \overset{K''_{eq.}}{\rightleftharpoons} 2\ \ CrO_2Cl_2$$

$$(C_6H_5)_3SiOH + CrO_2Cl_2 \underset{\underline{k}_2}{\overset{\underline{k}_1}{\rightleftharpoons}} (C_6H_5)_3SiOCrO_2Cl + HCl$$

$$(C_6H_5)_3SiOCrO_2Cl + (C_6H_5)_3SiOH \underset{\underline{k}_4}{\overset{\underline{k}_3}{\rightleftharpoons}}$$

$$[(C_6H_5)_3Si]_2CrO_4 + HCl.$$

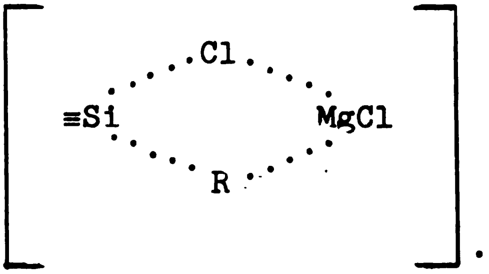
As part of this investigation, values of $K'_{eq.}$, $\underline{k}_1$, $\underline{k}_4$ and the overall equilibrium constant $K_{eq.}$ were determined and are discussed elsewhere in this thesis. The following interactions describe the rate-determining step in the silylchromate formation for the combination of triphenylsilanol and chromyl chloride in carbon tetrachloride:



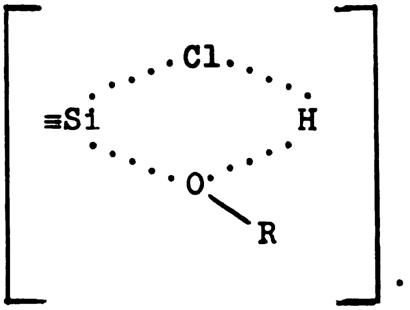
Transition State

This mechanism would involve a transition state with a four-centered cyclic intermediate capable of decomposing to give either organosilanol and chromyl chloride or the silylchromate and hydrogen chloride. The same kind of reaction intermediate was postulated for the hydrogen chloride cleavage of a silylchromate linkage. Again, the initial tendency for the Si-O-H and Cr-Cl linkages to interact with each other is reasonable in view of the polarities of these molecules. Since triphenylsilanol is a far stronger acid than the related carbinols, it is understandable that initial rate of silylchromate formation is fast ($\underline{k}_1 = 0.18$ liters $\underline{mM}^{-1}$ min.$^{-1}$). In considering the several equilibria involved in the present study of silylchromate formation, it is interesting to note how the strong proton donor nature of triphenylsilanol affects these reactions. Since hydrogen bonding is an important factor to consider, it becomes apparent that the rate-determining step and the triphenylsilanol monomer--dimer equilibrium reaction are both influenced. In this respect the kinetics of this reaction between triphenylsilanol and chromyl chloride are complicated. Similar association between triphenylsilanol and silylchromate intermediates would further complicate the kinetics, but this interaction is only conjecture.

In conclusion, it should be mentioned that the four-center cyclic transition states postulated in the reaction mechanism of both silylchromate formation and cleavage are not unique. Results of kinetic studies (121) of Grignard reagents (RMgCl) with organosilicon halides are best interpreted in terms of a cyclic transition state:



Likewise, it has been suggested (122) that the alcoholysis of chlorosilanes involves a four-center cyclic transition state:



V. ASSOCIATION STUDIES OF TRIPHENYLSILANOL

A. Introduction

Molecular weight measurements were made on triphenylsilanol in carbon tetrachloride at various concentrations by the independent methods of:

1. Cryoscopy (~ -23°C)
2. Vapor Pressure Osmometry (~ 37°C)
3. Ebulliometry (~ 77°C).

Measurements were made on highly purified samples of the triphenylsilanol described above and were important to this investigation because of the well-known tendencies for organosilanols to self-associate through hydrogen bonding of SiOH groups (33,78,81,91), thereby affecting the degree of association.

It was of interest to obtain and compare molecularity data at various temperatures and concentrations of triphenylsilanol in carbon tetrachloride because of the lack of understanding of the nature of the associated species present in these solutions. Such information is essential in describing more completely the formation of silylchromates derived from organosilanols. Furthermore, direct comparison of this information could then be made to the results in a previous section where a negative deviation arose in a Beer's law plot.

B. Molecularity Measurements for Triphenylsilanol

1. Cryoscopy

Cryoscopic molecular weight measurements were made on carbon tetrachloride solutions to determine the molecularity of the compound at -23°C. The apparatus used is described in a separate portion of this thesis. Carbon tetrachloride was selected as the solvent to be used since all kinetic measurements were made in it. Results are summarized in Table XXXVIII.

Table XXXVIII. Cryoscopic Molecular Weight Determinations of Triphenylsilanol

Sample	Theoretical	Found
$(C_6H_5)_3SiOH$		
Monomer	276	
Dimer	552	524,576,596,544 (average 560)

The molecular weight was independent of concentration in the range of 5 mg. to 100 mg. of solute per 40 ml. of carbon tetrachloride, and the molecularity values obtained (average 2.03) clearly indicate that triphenylsilanol is predominately dimerized at the temperature of the cryoscopic measurements (~ -23°C).

2. Ebulliometry

Molecular weights were determined ebulliometrically in carbon tetrachloride solutions following the procedures of Baney and Krager (99). The apparatus used was made available by Dow Corning Corporation, Physical Chemistry Laboratories, Midland, Michigan, and consisted of a differential ebulliometer (100) modified in such a way as to effect the rigorous exclusion of mositure (101). The differential thermometer was a multiunit thermopile calibrated (98) by measuring e.m.f. as a function of temperature differential and also as a function of concentration based on the molality ($\underline{m}$) of an ebullioscopic standard, trans-stilbene. The differential e.m.f. was measured on a Rubicon Type B high precision potentiometer with a Kiethley d.c. vacuum tube voltmeter, Model 200B, as the null point detector. Temperatures were read to ± 0.002°C.

Differential e.m.f. measurements were made on the pure solvent and on triphenylsilanol--carbon tetrachloride solutions of various concentrations. Molecular weights were calculated using standard ebulliometric techniques (99,101) from the following equation:

$$\text{M.W.} = \frac{\dfrac{\text{weight of solute}}{\text{weight of solvent}}}{\left(\dfrac{\text{e.m.f.}}{\text{K}}\right)} \times 100,$$

where: M.W. = apparent molecular weight,

e.m.f. = measured differential (millivolts)

K = solvent calibration ebulliometric constant.

The calibration ebulliometric constant (8.59) for carbon tetrachloride was obtained through the kindness of Mr. R. J. Krager (Dow Corning Corporation, Physical Chemistry Laboratories). The value was believed to be highly reliable and was determined experimentally just prior to the boiling point measurements made on triphenylsilanol. The molecularity (degree of association) was calculated from the ratio of the experimentally measured molecular weight to the theoretical molecular weight for the monomer or from the ratio of the measured molality to the analyzed molality as monomer. The boiling point measurements were made on solutions prepared by weighing triphenylsilanol into a known amount of freshly opened carbon tetrachloride. Results are summarized in Table XXXIX and show that the average degree of association of triphenylsilanol in carbon tetrachloride is very nearly one over the range of concentrations examined. No silanol condensation or sample decomposition was observed in any of the measurements after 15-30 minutes of refluxing. The substance recovered after solvent *in vacuo* was identified as triphenylsilanol by comparison of its infrared spectrum with that of an authentic sample and by a mixed melting point determination.

Table XXXIX. Ebulliometric Molecular Weight Determinations of Triphenylsilanol in Carbon Tetrachloride (b.p. 77°C)

Molality (as monomer)	Molality (measured)	Apparent Molecular Weight	Apparent Molecularity
0.192	0.179	296	1.07
0.158	0.157	277	1.00
0.153	0.145	290	1.05
0.116	0.118	271	0.98
0.113	0.115	272	0.99
0.089	0.094	261	0.95
0.082	0.090	253	0.92
		(average 274)	(average 0.99)

Theoretical $(C_6H_5)_3SiOH$ = 276

$[(C_6H_5)_3SiOH]_2$ = 553

3. Vapor Pressure Osmometry

Vapor pressure osmometry measurements were made on triphenylsilanol in carbon tetrachloride so that the molecularity of the compound could be compared to similar data obtained at other temperatures. Carbon tetrachloride was selected as the solvent since all kinetic measurements were made in it and since the solutions were stable for sufficient time to allow measurement. A description of the apparatus used (Mechrolab vapor pressure osmometer), along with the methods of calculation, is presented in the Analytical Section of this thesis. All measurements were obtained at a constant operating temperature of 37°C. Results are summarized in Table XXXX and show that the molecularity of triphenylsilanol in carbon tetrachloride is strongly dependent on concentration.

C. Discussion

During the course of this investigation, quantitative measurements of triphenylsilanol association in carbon tetrachloride were determined by four independent methods. These included two classical thermal methods (ebulliometry and cryoscopy), a vapor pressure osmometry approach, and infrared absorption measurements. These measurements of association have been expressed in various forms, including the apparent molecular weight, the molecularity based on the monomer $(C_6H_5)_3SiOH$, and the fraction α of monomeric $(C_6H_5)_3SiOH$. It is interesting to summarize and compare these measurements in

Table XXXX. **Vapor Pressure Osmometry Molecular Weight Determinations of Triphenylsilanol in Carbon Tetrachloride at 37°C**

Molality (as monomer)	Molarity (as monomer)	Apparent Molecular Weight	Apparent Moleculrity
0.00237	0.00378	282	1.02
0.00448	0.00717	295	1.07
0.00679	0.01082	301	1.09
0.00945	0.01508	314	1.13
0.01125	0.01795	314	1.13
0.01596	0.0255	334	1.21
0.02701	0.0432	354	1.28

Theoretical $(C_6H_5)_3SiOH$ = 276

$[(C_6H_5)_3SiOH]_2$ = 553

terms of α since degree of association data expressed in this form do not presuppose knowledge of the nature of the associated species in solution. Table XXXXI lists the fraction α of monomeric $(C_6H_5)_3SiOH$ at various molar concentrations in carbon tetrachloride and Figure XXIV graphically compares these same data.

The fraction α obtained by cryoscopy methods remains constant at 0 since the experimental molecular weight was independent of concentration over the range examined and indicated that triphenylsilanol is predominately dimerized at -23°C. Similarly, the fraction α obtained by ebulliometry methods remains constant at 1.00 since all experimental molecular weights determined from boiling point measurements indicated a degree of association of nearly unity for triphenylsilanol. Fraction α data obtained by infrared and vapor pressure osmometry measurements are highly dependent on triphenylsilanol concentrations. Values of α were determined from the standard infrared absorption measurements described in a separate portion of this thesis at the particular concentrations shown in Table XXXXI. In the case of the vapor pressure osmometry measurements, values of α were determined using the "best curve" drawn through the previously described apparent molecular weight-concentration data (Table XXXX). Interpolated apparent molecular weights were estimated from this "best curve" at particular triphenylsilanol concentrations and α values determined by comparing these values to the theoretical molecular weight of the $(C_6H_5)_3SiOH$ monomer.

Table XXXXI. Summary of Quantitative Measurements of Fraction α of Monomeric $(C_6H_5)_3SiOH$ in CCl_4

Method	Temperature	Apparent Fraction α of Monomeric $(C_6H_5)_3SiOH$ at Various Molar Concen.							
		0.0050 M	0.0100 M	0.0150 M	0.0200 M	0.0300 M	0.0350 M	0.0400 M	0.0450 M
Cryoscopy	~ -23°C	0	0	0	0	0	0	0	0
Infrared Spectroscopy	~ 24°C	0.91	0.74	0.65	0.57	0.49	0.46	0.43	0.42
Vapor Pressure Osmometry	37°C	0.97	0.92	0.89	0.86	0.81	0.79	0.77	0.75
Ebulliometry	~ 77°C	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

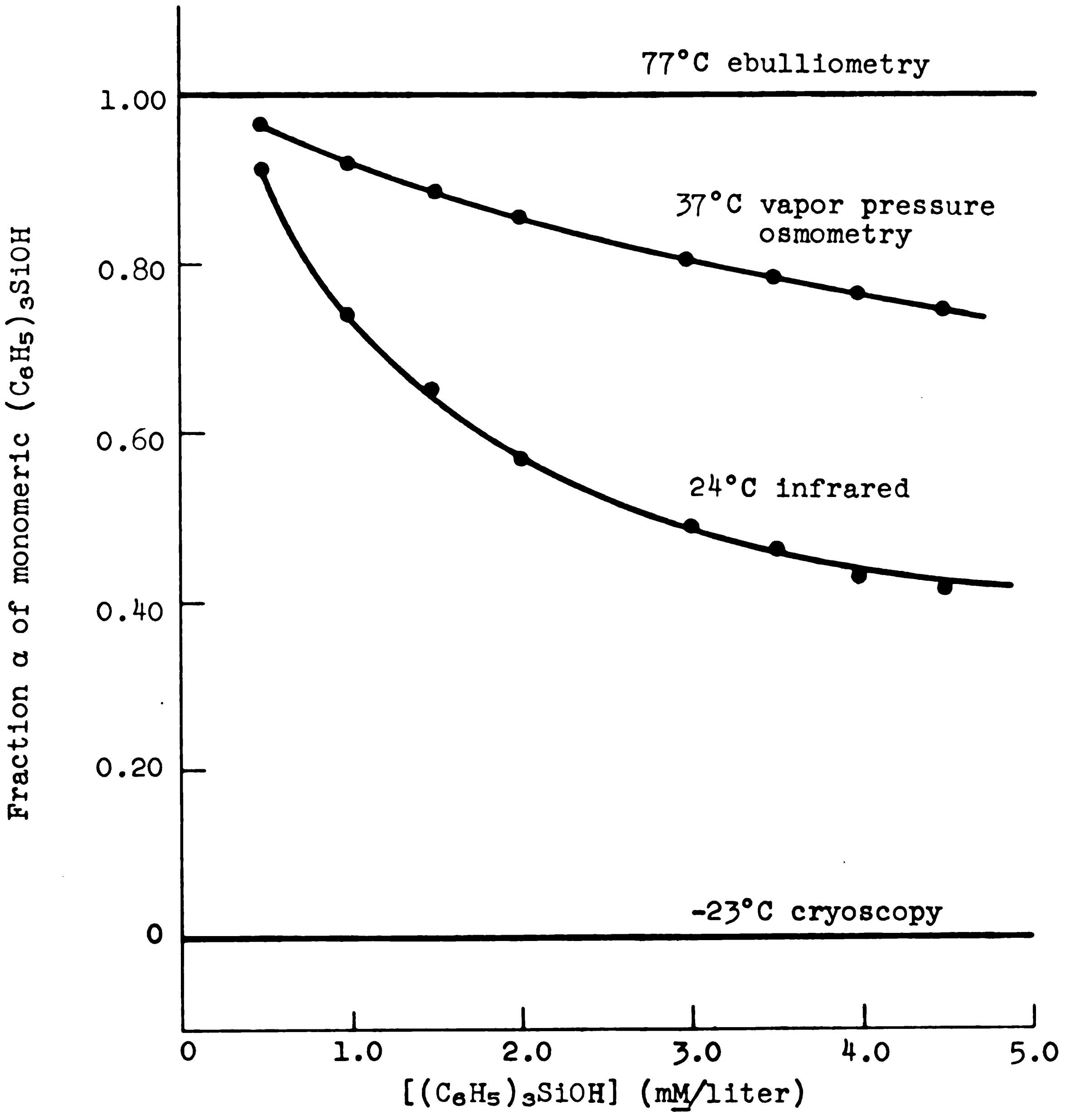
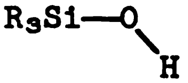


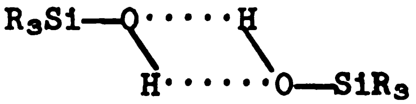
Figure XXIV. Fraction α of monomeric $(C_6H_5)_3SiOH$ in carbon tetrachloride obtained from quantitative measurements.

As noted above, degree of association measurements expressed in terms of α do not require a presupposed knowledge of the nature of the associated species. Nevertheless, such data can be used in better characterizing the nature of the self-associated triphenylsilanol aggregates which actually exist in solution. Various types of hydrogen-bonded triphenylsilanol aggregates are possible, such as the following:

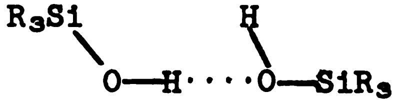
R = phenyl



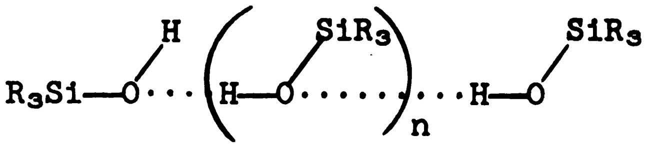
I. Unassociated Monomer



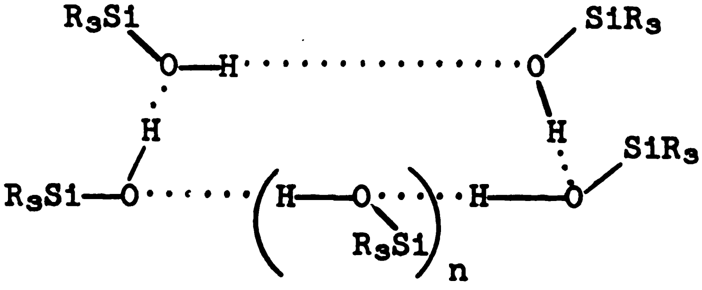
II. Closed Dimer



III. Linear Dimer



IV. Linear Polymer



V. Closed Polymer

The unassociated monomer is the only structure with completely non-hydrogen bonded Si-OH groups. Structures III and IV would have both hydrogen bonded and non-hydrogen bonded silanol linkages while the closed dimer (structure II) and closed polymers (structure V) would have all associated Si-OH bonds. It seems apparent from the above α measurements that structure IV and V probably are not involved in the self-association of triphenylsilanol. This statement is based on the experimental fact that no molecularity determination for triphenylsilanol exceeds a value of 2.00. An associated dimer appears to be the limiting polymeric aggregate formed with triphenylsilanol in carbon tetrachloride. Inasmuch as large organic substituents sterically hinder hydrogen bonding (102, 106,107) it would be expected that triphenylsilanol should associate in dimer forms but should not form higher aggregates. A test of this dimeric equilibrium is possible and may be determined by examination of the equilibrium constant over a range of concentrations. Various authors have derived expressions for the determination of equilibrium constants between monomer and associated species (104, 107, 108, 109). If one considers a dimer equilibrium of the type

$$2\ (C_6H_5)_3SiOH \xrightleftharpoons{K} [(C_6H_5)_3SiOH]_2,$$

the following equilibrium equation can be derived from the law of mass action:

$$K = 2\,\alpha^2 C/(1 - \alpha)$$

where K is the dimeric equilibrium constant, α is the fraction of triphenylsilanol molecules which are unassociated, and C is the concentration in moles per liter of triphenylsilanol material. A necessary and sufficient condition for the above dimeric equilibrium is that the term $2\,\alpha^2\,C/(1 - \alpha)$ remain essentially constant over a range of concentrations. In Table XXXXII may be seen the values of $2\,\alpha^2 C/(1 - \alpha)$ for various concentrations. Equilibrium constant values were calculated from fraction α values obtained by the four independent methods described previously.

The K values at lower concentrations are not reliable because of the $(1 - \alpha)$ term which is quite small and which appears in the denominator. In view of this, the value K calculated for the 0.005 $\underline{M}$ concentration was not used in the averages. With this in mind it may be concluded that the association of triphenylsilanol is dimeric in nature. It is interesting to compare this work with an earlier study of self-association reported by Coggeshall and Saier (107). They determined the equilibrium and concluded that the partially hindered phenols will associate entirely as dimers in carbon tetrachloride.

Table XXXXII. Values of $K = 2\alpha^2C/(1 - \alpha)$ for Triphenylsilanol in Carbon Tetrachloride at Various Temperatures and Concentrations

$$2\ (C_6H_5)_3SiOH \underset{}{\overset{K}{\rightleftharpoons}} [(C_6H_5)_3SiOH]_2$$

Molar Concentration	K (-23°C) Cryoscopy	K (24°C) Infrared	K (37°C) Osmometry	K (77°C) Ebulliometry
0.0050	0	0.092	0.313	∞
0.0100	0	0.042	0.218	∞
0.0150	0	0.036	0.216	∞
0.0200	0	0.030	0.211	∞
0.0300	0	0.028	0.207	∞
0.0400	0	0.026	0.206	∞
	K(ave.) = 0	K(ave.) = 0.032	K(ave.) = 0.21	K(ave.) = ∞

Further identification and characterization of the associated triphenylsilanol dimer is apparent from the present study. Thus, the cryoscopic evidence presented favors the closed dimer form over the linear structure in that molecular weights apparently are not dependent on concentration. One would expect that the non-bonded Si-OH groups shown in structure III (linear dimer) would further associate at higher concentrations and increase the molecular weights. The large phenyl substituents appear to sterically hinder hydrogen-bonding necessary for the formation of all associated structures proposed, except for the closed dimer aggregate. The closed dimer form is also predicted on the basis of a close examination of the various possible hydrogen-bonded structures with the aid of Fisher-Herschfelder-Taylor molecular models. These conclusions are consistent with earlier studies (33,102,107,109) that demonstrated the importance of steric factors in hydrogen bonding and self-association of organic alcohols and organosilanols.

Licht and Kriegsmann (102), in connection with a study of triorganosilanols by infrared and cryoscopic measurements, concluded that silanol association decreases with increasing length of the alkyl groups and the number of the phenyl groups, respectively, in the molecule. Their cryoscopic measurements in benzene showed that $(C_6H_5)_3SiOH$, $(C_6H_5)_2CH_3SiOH$, and

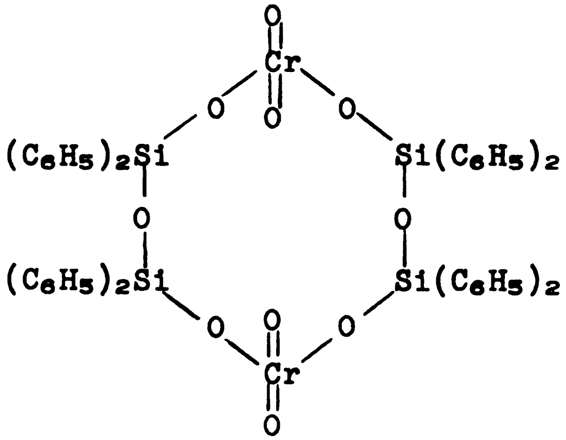
$(CH_3)_2C_6H_5SiOH$ had molecularities less than two while $(CH_3)_3SiOH$, $(C_2H_5)_3SiOH$, $(C_3H_7)_3SiOH$, and $(C_4H_9)_3SiOH$ all had limiting molecularities between two and three. Solvent effects must be important in that $(C_6H_5)_3SiOH$ was not completely dimerized in benzene and in contrast to the present study with carbon tetrachloride, the molecular weight was dependent on concentration. The factor of temperature (5.5°C m.p. of benzene) is certainly responsible for at least part of the association differences.

VI. SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

Of the many things that this research dealt with, the most important seem to be:

1. Confirmation and characterization of cyclobis[tetraphenyldisiloxanylchromate(VI)], $\left\{[(C_6H_5)_2SiO]_2CrO_3\right\}_2$.
2. Examination of the kinetics of a prototype reaction involving silylchromate formation--namely, the interaction of triphenylsilanol and chromyl chloride in carbon tetrachloride.
3. Studies of the equilibrium found to exist in the reaction listed in 2.
4. Isolation and characterization of triphenylsiloxychromyl chloride.
5. Molecularity studies of triphenylsilanol in carbon tetrachloride solutions related to the above mentioned kinetic study.

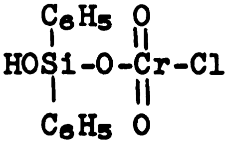
This investigation was begun by considering two initial objectives: (a) To confirm the structure of the previously reported cyclic silylchromate isolated by Hare (47) from the reactions of diphenylsilanediol with chromyl chloride or chromium(VI) oxide, and (b) to explore reasons for the formation of such an unusual molecule. To accomplish these objectives, the preparation and properties of this compound were carefully reinvestigated. On the basis of this more recent and detailed characterization data, the compound can unequivocally be identified as cyclobis[tetraphenyldisiloxanylchromate(VI)]. The substance possesses the following structure which is consistent with Hare's previous study (47):



While the first of the initial objectives was met through the synthetic approaches taken on this problem, better insight into the reason for the formation of the cyclic silylchromate was not arrived at. Consequently, this led to a kinetic study of the reaction of triphenylsilanol with chromyl chloride in carbon tetrachloride which seemed to represent a useful prototype of the more complex reactions of silanediols and triols that are of interest in polymerization schemes.

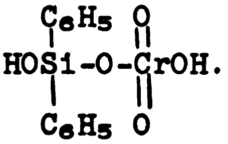
Shortly after the kinetic study was initiated it was found that an equilibrium was involved in the formation and rupture of the organosilylchromate linkage. The system was examined closely and the overall equilibrium constant for the triphenylsilanol--chromyl chloride reaction was determined. In the course of this study, the existence of triphenylsiloxychromyl chloride, $(C_6H_5)_3SiOCrO_2Cl$, was first suspected. Furthermore, it became apparent that this chlorochromate was important in understanding silylchromate formation and might indeed be isolated if the equilibrium could be shifted.

By mass action effects on the equilibrium, triphenylsiloxychromyl chloride was prepared and identified on the basis of data presented in Section III. This preparation was significant to this investigation because it showed that the two chlorine atoms of chromyl chloride do not have the same reactivities; the second chlorine is more difficult to replace than the first. This property of difunctional chromyl compounds would account for some of the difficulties encountered in preparing linear polydiorganosilylchromates. Furthermore, it offers a reasonable explanation of how the disiloxane linkage might be incorporated into cyclobis[tetraphenyldisiloxanylchromate(VI)]. Suggested intermediates in forming this compound are



$$HO\overset{\overset{C_6H_5}{|}}{\underset{\underset{C_6H_5}{|}}{Si}}-O-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Cr}}-Cl$$

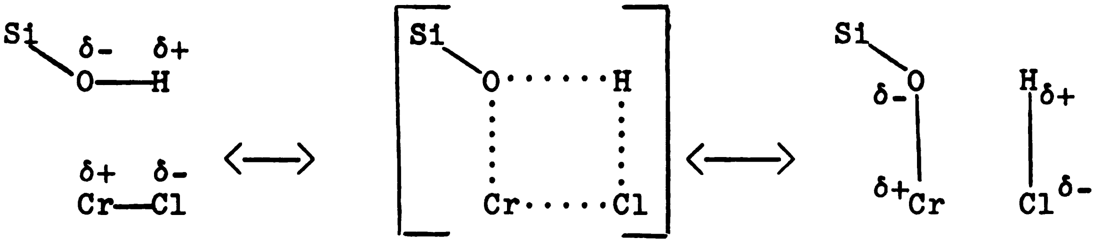
or



$$HO\overset{\overset{C_6H_5}{|}}{\underset{\underset{C_6H_5}{|}}{Si}}-O-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Cr}}OH.$$

The latter intermediate could arise when chromium(VI) oxide is used as a reagent. In either case the remaining chromium(VI) functionality in these intermediates would be rendered less reactive and the net result would be a reduced reaction rate with additional organosilanol molecules. This in turn would encourage the competitive organosilanol condensation reactions to occur and would account for the formation of the Si-O-Si bond.

At this stage of the investigation the continuation of the kinetic study of the triphenylsilanol--chromyl chloride reaction was undertaken. In the system there seem to be several reversible reactions involved in formation of bis-(triphenylsilyl)chromate, triphenylsiloxychromyl chloride, and hydrogen chloride. The pseudo-order of reaction with respect to all species was determined experimentally by the methods of initial rates and suggest a mechanism of silylchromate formation involving a four-centered cyclic transition state capable of decomposing to give either reactants or products:



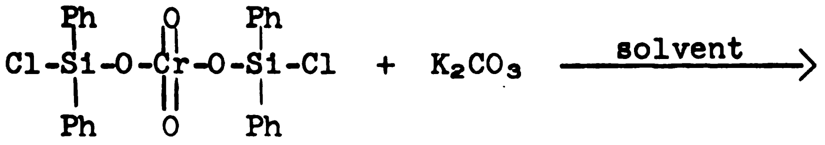
Transition State

The non-integral orders found for $(C_6H_5)_3SiOH$ and CrO_2Cl_2 were accounted for in the proposed mechanism by the existence in solution of reactant dimers which dissociate before reaction occurs. The later conclusions were based on molecularity studies of triphenylsilanol in carbon tetrachloride which clearly indicate that triphenylsilanol associates as a dimer aggregate. Triphenylsilanol is completely dimerized at -23°C in carbon tetrachloride and exists as the monomer at 77°C. These molecularity measurements represented the final experimental effort in this investigation.

In summarizing the present account, several recommendations for future studies involving organosilylchromate chemistry will be presented.

1. Of all the organosilylchromates investigated to date, only the crystalline solid compositions have been purified and identified as individual species. Viscous oils are often produced. Methods need to be devised for isolating these non-crystalline silylchromates so that compound characterization can be accomplished. Such purity might be obtained by the application of gas liquid chromatographic methods. Also, molecular distillation techniques should be considered. Neither of these purification methods have been tried in the silylchromates studied to date.

2. Failure to convert cyclobis[tetraphenyldisiloxanylchromate(VI)] to poly(diphenylsilylchromate) compositions suggests the need for a more thorough investigation of such polymerization techniques. A more highly strained cyclic diorganosilylchromate would undoubtedly serve as a better precursory monomer for obtaining poly(diorganosilylchromate). The synthesis of cyclotetraphenyldisiloxanylchromate(VI), the lower six-membered ring homologue of cyclobis[tetraphenyldisiloxanylchromate(VI)], would be a severe challenge to any chemical researcher. A possible synthetic route to this compound would be a ring closing reaction of the appropriate chlorine end-blocked diorganosilylchromate with anhydrous sodium or potassium carbonate:



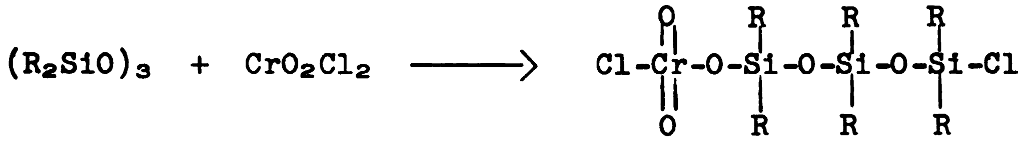
$$\mathrm{Cl{-}SiPh_2{-}O{-}CrO_2{-}O{-}SiPh_2{-}Cl} + K_2CO_3 \xrightarrow{\text{solvent}}$$

$$[(Ph_2SiO)_2CrO_3] + CO_2 + 2\ KCl.$$

Another possible approach would be to employ a "cracking" procedure similar to the methods well known for preparing strained cyclosiloxanes (i.e., $[(CH_3)_2SiO]_3$).

3. An attractive area of study involving organosilylchromate chemistry would be to examine reactions of chromium(VI) intermediates with strained cyclic siloxane compositions under a variety of conditions. Such reactions would utilize

catalytic or stoichiometric amounts of chromium(VI) reagents. One of many possible reactant combinations is illustrated below:



$$(R_2SiO)_3 + CrO_2Cl_2 \longrightarrow Cl-\overset{O}{\underset{O}{Cr}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-Cl$$

$$(R_2SiO)_3 + \text{trace } CrO_2Cl_2 \longrightarrow \text{polydiorganosiloxanes.}$$

In reference to the first equation, it would be interesting to determine which of the functional moieties, Cr-Cl or Si-Cl, would be most reactive and interact with a second molecule of the cyclotrisiloxane.

4. The literature to date contains no mass spectrometry data for organosilylchromates and the one attempt to secure a mass spectrum of cyclobis[tetraphenyldisiloxanylchromate(VI)] in this present study failed. The more volatile but less stable alkylsilylchromates should be examined. Furthermore, from the fragmentation patterns of these unstable compounds, one might gain insight into the reason for their highly unusual and explosive nature, i.e., bis(trimethylsilyl)-chromate(VI).

5. The isolation of the first organosilyl chlorochromate, triphenylsiloxychromyl chloride, an unusually stable yet not anticipated intermediate, suggests the need for further

investigation of these derivatives. Further confirmation of such derivatives might be obtained by more direct synthesis. At the same time, new and unique synthetic approaches would be developed in the field of organosilylchromate chemistry. Possible approaches would include:

1. $CrO_3 + R_3SiCl \longrightarrow R_3SiOCrO_2Cl$

2. $CrO_2Cl_2 + R_3SiOSiR_3 \xrightarrow[\text{sealed tube reaction}]{\text{high temperature}} R_3SiOCrO_2Cl + R_3SiCl$

3. $CrO_2Cl_2 + (R_3Si)_2CrO_4 \longrightarrow 2\ R_3SiOCrO_2Cl$

4. $CrO_2Cl_2 + R_3SiONa \longrightarrow R_3SiOCrO_2Cl + NaCl.$

The availability of $R_3SiOCrO_2Cl$ intermediates would make unsymmetrical bis(triorganosilyl)chromates easily accessible from reactions with other triorganosilanols. Unsymmetrical bis(triorganosilyl)chromates have not yet been reported. Finally, it might be advantageous to see if triphenylsiloxychromyl chloride would interact with a Grignard reagent. The product (i.e., $(C_6H_5)_3SiO\overset{O}{\underset{O}{Cr}}-R$), if formed by such a reaction, would possess unusual chemical bonding worthy of additional study.

6. Qualitative observations from this investigation have indicated that under anhydrous reaction conditions, triphenylsiloxychromyl chloride reacts only slowly with triphenylsilanol at 25°C. It would be of interest to know if hydrogen chloride acts autocatalytically on such reactions. This could be done by measuring the rates of reaction for a series of reactions starting with constant initial concentrations of triphenylsiloxychromyl chloride and triphenylsilanol but varying concentrations of hydrogen chloride.

VIII. APPENDIX I--DETERMINATION OF INFRARED ABSORPTION ASSIGNMENTS FOR SOME SILICON-OXYGEN-METAL LINKAGES

The field of inorganic polymer research has been an active one and for the many reasons mentioned in the historical portion of this thesis. Within this field and receiving a great deal of attention have been the metallosiloxanes. These compositions have structural backbones of silicon-oxygen-metal linkages. In the past, considerable interest has been given to the infrared spectra of these materials and such spectra are often times used to facilitate compound identification. In most cases, however, only tentative infrared assignments could be given the silicon-oxygen-metal absorptions. Hare (47) has tentatively assigned the 11.1-11.5 μ region to the silylchromate linkage. Compounds containing titanium-oxygen-silicon bonds have strong absorptions in the 10.25-11.25 μ region which Zietler and Brown (83) have tentatively assigned to the silicon-oxygen-titanium stretching frequency. Skelcey (93) has made tentative assignments for some siloxy derivatives of bis(cyclopentadienyl)titanium(IV). Thies (123) has also assigned some tentative infrared absorptions to various silicon-oxygen-tin compounds.

The purpose of this present account is to describe some work that shows how some silicon-oxygen-metal infrared absorption assignments were determined for several metallosiloxanes. To accomplish this, infrared spectroscopy was used as a convenient analytical tool in studying the hydrogen chloride cleavage reactions of several well characterized metallosiloxane compounds. It was reasoned that if a solution of a metallosiloxane compound were allowed to react with anhydrous hydrogen chloride, one of two reactions involving the silicon-oxygen-metal linkage could take place*:

$$\text{M-O-Si} + \text{HCl} \longrightarrow \text{M-Cl} + \text{Si-OH}$$

or

$$\text{M-O-Si} + \text{HCl} \longrightarrow \text{M-OH} + \text{Si-Cl}.$$

In either case, the disappearance of the absorption characteristic of the silicon-oxygen-metal bond would occur. The experimental method involved consisted of recording the infrared spectra of a carbon tetrachloride solution of a compound before and after reaction with anhydrous hydrogen chloride. The products formed were further identified by looking for the characteristic absorptions of Si-OH and Si-Cl. Spectra in the 2-15 μ region were recorded on a Perkin-Elmer Model 21 Recording Spectrophotometer, and those in the 15-25 μ region on a Beckman Model

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*Phenyl groups are known to be cleaved by acids (124). However, since the M-O-Si bonds are cleaved much more readily than are Si-phenyl bonds these cleavages were not specifically tested for in the present study.

7 Recording Spectrophotometer using cesium iodide optics. It should be mentioned here that the experimental methods used were nearly the same as those described for the silylchromate intermediates in the main body of this thesis. This present study, however, did not include the isolation and independent characterization of the reaction products obtained from these cleavage reactions. Results of such a study for several metallosiloxane compositions are summarized in Table XXXXIII. In every case the disappearance of the silicon-oxygen-metal absorption was noted. Furthermore, the presence of Si-OH (2.5-3.0 μ) and the absence of Si-Cl (18.2 μ) was observed in all the samples tested. Consequently, anhydrous hydrogen chloride reacted selectively with every metallosiloxane sample tested such that the silicon-oxygen-metal linkage was cleaved between the metal and oxygen, forming the M-Cl and Si-OH bonds. The same reaction mechanism as postulated for the bis(triphenylsilyl)chromate--hydrogen chloride reaction (see Section IV) can be used in accounting for the similar reaction products observed for all metallosiloxane--hydrogen chloride cleavage reactions. This would involve an initial coordination of the hydrogen chloride to the metallosiloxane linkage such that a four-centered concerted cyclic transition state would result:

Table XXXXIII. Infrared Absorption Study of the Metallosiloxane Cleavage by Hydrogen Chloride

Compound	Si-O-M Assignment (μ)	Reaction Products
$[(Ph_3Si)_2CrO_4]$	11.4	Ph_3SiOH; $Ph_3SiOCrO_2Cl$; CrO_2Cl_2
$[Ph_3SiOCrO_2Cl]$	11.1	Ph_3SiOH; CrO_2Cl_2
$[(Ph_2SiO)_2CrO_3]_2$	11.0	$[HOSiPh_2]_2O$; CrO_2Cl_2
$[Cp_2TiCl(OSiPh_3)]$*	10.5	Ph_3SiOH; Cp_2TiCl_2
$[Cp_2TiCl(OSiPh_2Me)]$*	10.6	$Ph_2MeSiOH$; Cp_2TiCl_2
$[Ph_3SnOSiPh_3]$**	10.4	Ph_3SiOH; Ph_3SnCl
$[Ph_3SnOSi(Ph)_2OSnPh_3]$**	10.4	No $\equiv SiCl$

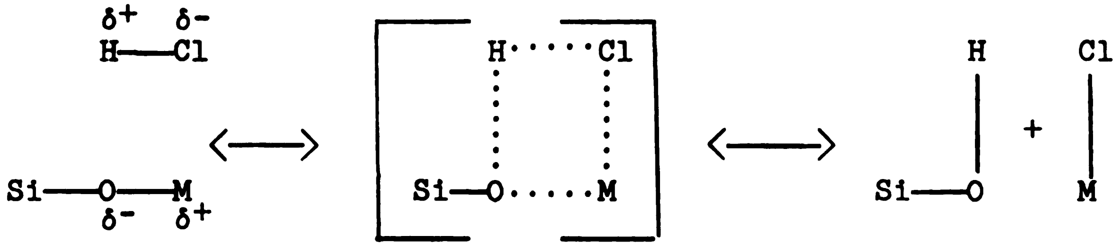
* Samples supplied by Dr. J. S. Skelcey.

** Samples supplied by Dr. J. B. Kinsinger.

Ph = phenyl

Cp = cyclopentadienyl

Me = methyl



Transition State

This transition state could further react to give either products or reactants and is reasonable in view of the polar nature of both the hydrogen chloride and metallosiloxane molecules. Furthermore, the rates of these reactions are strongly dependent on the metal atoms involved which govern the extent to which the metallosiloxane bond is polarized. It should be mentioned here that although the rates of cleavage by HCl of the metallosiloxanes studied were not quantitatively determined, qualitatively the rate of cleavage varied as follows:

Ti-O-Si > Cr-O-Si > Sn-O-Si > Si-O-Si.

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