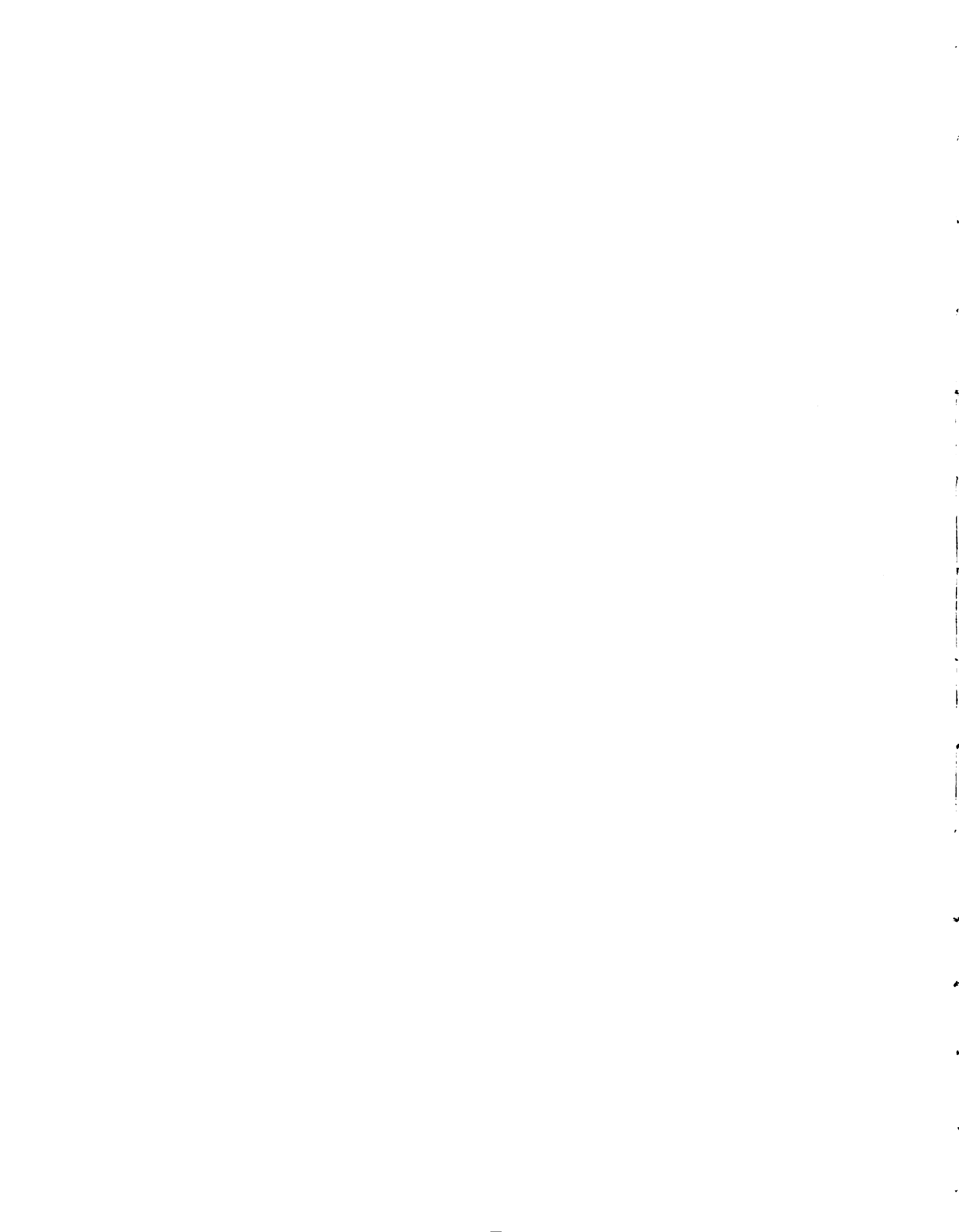# ABSTRACT

PREPARATION OF SILYL- AND SILOXANYL CHROMATES

by Paul M. Dupree

The purpose of this investigation was the preparation of organosilicon-chromium compounds with thermal stabilities greater than known compounds of this type. The heterogeneous reactions, in inert organic solvents, of either silver chromate or dichromate with the appropriate organochlorosilane yielded bis(triphenylsilyl)chromate(VI), bis(diphenylfluorosilyl)chromate(VI), cyclo-bis and tris[diphenylsiloxanylchromate(VI)] and cyclo-bis and tris[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)]. Cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)] was prepared by the reaction of chromyl chloride with 3,3,3-trifluoropropylmethylsilanediol in methylene chloride. With the exception of the light orange crystalline cyclo-tris[diphenylsiloxanylchromate(VI)], the compounds were deep orange viscous liquids at room temperature and only cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)] could be made to crystallize at lower temperatures.

The assignment of cyclic structures to the siloxanylchromates resulted from consideration of their infrared, visible, ultraviolet, and proton magnetic resonance spectra as well as differential thermal analyses. The assignments should

only be considered tentative for although each measurement indicated the existence of a cyclic structure, no completely conclusive data were obtained.

The compounds prepared during this investigation were photolytically unstable. The phenylsiloxychromates were rapidly decomposed in water while the siloxanylchromates containing trifluoropropyl linkages appeared to be very hydrolytically stable.

The thermal stabilities of the silyl and siloxanylchromates were studied by means of differential thermal analysis. Highly electronegative substituents such as fluorine or polyfluoroorganic groups on silicon gave substantial increases in the thermal stabilities of the silyl and siloxanylchromates.

Cyclo-bis and tris[diphenylsiloxanylchromate(VI)] and cyclo-bis and tris[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)] are believed to be the first cyclic compounds with alternating oxygen-metal-oxygen-silicon linkages. Bis(diphenylfluoro)chromate(VI) is the only known transition metal-silicon compound containing a silicon-fluorine linkage and the siloxanylchromates with 3,3,3-trifluoropropyl groups are also the first known siloxychromates containing fluorocarbon substituents.

The infrared absorptions of the siloxychromates at 11-12 μ and 20.6-21.4 μ were tentatively assigned to the asymmetric

Paul M. Dupree

and symmetric stretching vibrations of the chromium-oxygen-
silicon linkage. Crystallographic interatomic spacings for
cyclo-tris[diphenylsiloxanylchromate(VI)] were calculated
from x-ray diffraction data.
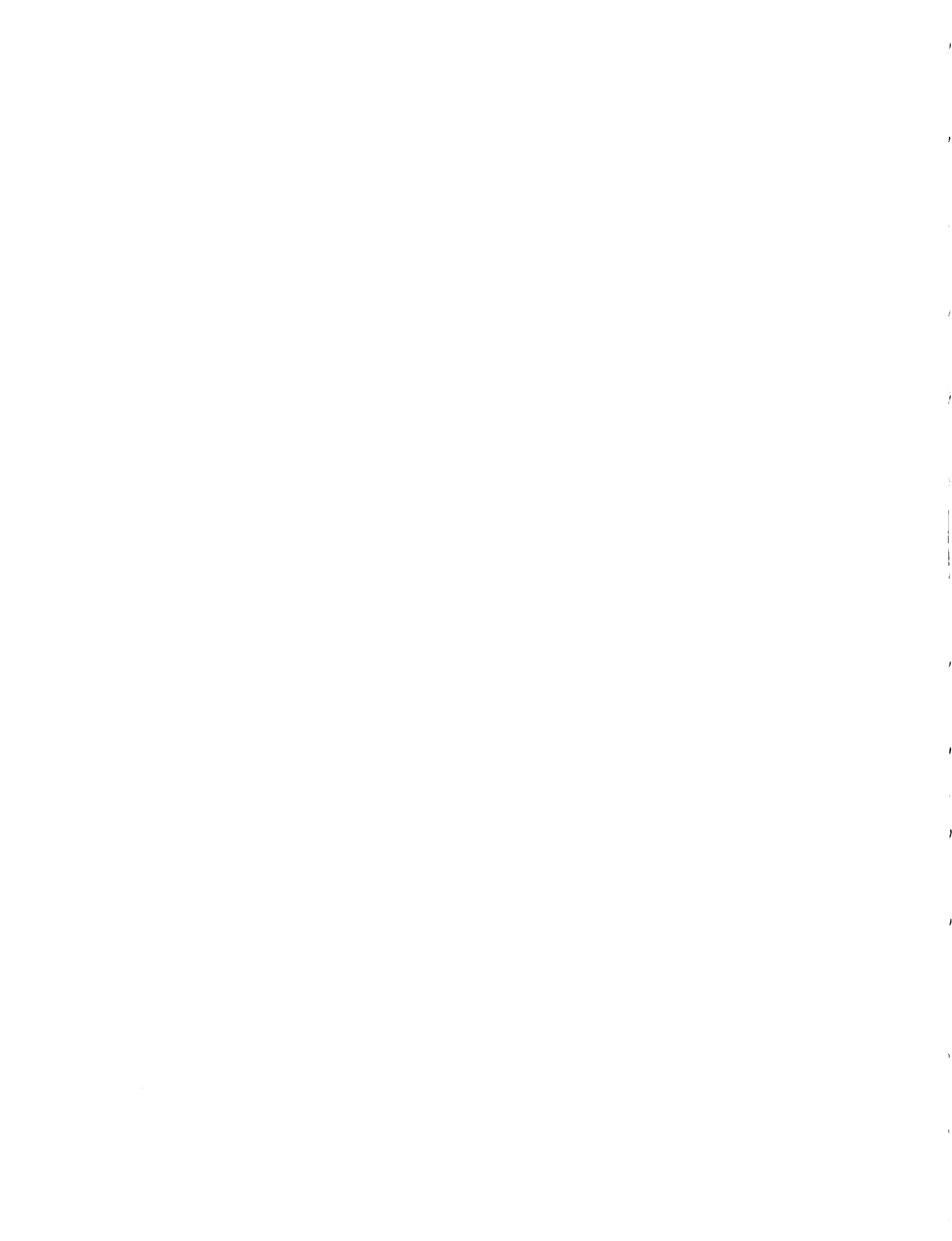
PREPARATION OF SILYL- AND SILOXANYL CHROMATES

by

Paul M. Dupree

A THESIS

Submitted to
Michigan State University
In partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1965

ACKNOWLEDGEMENTS

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INTRODUCTION

During the past fifteen years, there has been a considerable intensification in the study of polymerization chemistry involving inorganic atoms. This has been brought about by the need for synthetic materials which can withstand elevated temperatures for long periods of time; this property is not generally found in organic polymers. Limited success has been obtained with polysiloxanes which usually have better stabilities than organic polymers. However, these materials are unable to withstand temperatures of 500° C. or better.

It has been postulated that the incorporation of metal atoms into the polysiloxane linkages would increase their resistivity toward thermal decomposition. This concept is strengthened by the apparent inertness of metal silicates found in nature. When this research group was initiated in 1958, chromium was chosen as one of the metals to be studied for the following reasons:

(a) It is a strong oxidizing agent and, therefore, is resistant to oxidation.

(b) Compounds of chromium(VI) have a tendency to polymerize as in chromium(VI) oxide, polyacids, polychromates and chromyl chloride (1, 2, 3, 4).

(c) The chromyl group is difunctional.

1

(d) Chromium(VI) displays tetrahedral coordination and has
     very nearly the same radius as silicon in silicates.
     The geometry should therefore be favorable for substi-
     tution.

Initial studies of the chromium-oxygen-silicon system
were performed in this laboratory by Hare (5) who prepared
several organosilylchromates and observed their relative
thermal stabilities. Electron-releasing groups attached to
silicon atoms in silylchromates appear to lower stabilities.
Thus bis(trimethylsilyl)chromate(VI) explodes when heated,
and bis(diphenylmethylsilyl)chromate(VI) as well as
bis(diphenyl-p-tolylsilyl)chromate(VI) decompose when warmed.
Bis(triphenylsilyl)chromate(VI), however, shows considerably
more thermal stability. Similar observations have been made
with silylvanadates and siloxy-titanium compounds.

One of the goals of this investigation was to prepare
and study some silylchromates containing highly electron with-
drawing substituents. Fluorine was chosen as a silicon sub-
stituent because of its high electronegativity and the apparent
thermal stability of silicon-fluorine bonds, as indicated both
by the energy of homolytic cleavage (143 kcal./mole.) (141) and
ionic bond energies (6, 7). Specifically, the preparation of
some silylchromates containing a single Si-F bond was under-
taken.

Hare reported the preparation of a silylchromate telomer of the alternating A-B-C variety (5). An initial study indicated that this alternating form is not as stable thermally as substances containing a higher silicon to chromium ratio. A second purpose of this investigation was to prepare other A-B-C telomers for further study of this hypothesis.

HISTORY

Chemistry of Chromium(VI).

The over-all purpose of this investigation was to prepare inorganic polymers which might be thermally stable at temperatures above 500° C. The high thermal stability of naturally occurring metal silicates suggested that linear metal-oxygen-silicon chains might be similarly stable yet not show the rigidity of a network structure. Hexavalent chromium was a natural choice for the metal component. Compounds of chromium(VI) are strong oxidizing agents; consequently, they are resistant towards oxidation and, like most transition metals, chromium shows a definite tendency towards auto-polymerization. The bifunctionality of the tetrahedral chromyl group would assure formation of linear molecules.

Siloxychromates

Schmidt and Schmidbaur (8), in 1958, were first to report the preparation of an organosilylchromate. Bis(trimethysilyl)-chromate(VI) was synthesized by refluxing hexamethyldisiloxane containing suspended chromium(VI) oxide. Repetition of the experiment by Hare (5) and Abel (9) resulted in explosions. The problem of instability was resolved for Abel by combining the reactants at -40° C. Hare isolated the red oil from heterogenous reactions of chromium(VI) oxide with both hexamethyl-disiloxane and trimethylsilanol in methylene chloride.

Bis(p-tolyldiphenylsilyl)chromate(VI), bis(cyclohexyl-diphenylsilyl)chromate(VI), bis(tricyclohexylsilyl)chromate-(VI) and bis(diphenylmethylsilyl)chromate(VI) were prepared and isolated by Hare. Each of the above compounds was synthesized from the respective silanol and chromium(VI) oxide in refluxing methylene chloride. Bis(p-tolyldiphenylsilyl)chromate(VI) was a yellow crystalline solid which melted at 98.5-99° C., bis(cyclohexyldiphenylsilyl)chromate(VI) and bis(tricyclohexylsilyl)chromate(VI) were red-orange solids with respective melting points of 84-85° C. and 125-126° C. Bis(methyldiphenylsilyl)chromate(VI) was an unstable red liquid. Bis(triphenylsilyl)chromate(VI) (m. 153-4° C.) was prepared from the above reaction by Granchelli and Walker (10) and by Hare. Hare also prepared this substance from chromyl chloride and triphenylsilanol. Hampton (11) studied the kinetics of the reaction between chromyl chloride and triphenylsilanol by following the disappearance of the silicon-hydroxyl stretching frequency at 2.7 μ. The reactants formed an equilibrium after three minutes and the equilibrium could be shifted toward the silylchromate product by addition of calcium oxide. The kinetic data indicated that the reaction was one-half order with respect to the concentration of both triphenylsilanol and chromyl chloride. The fractional order was attributed to the possible dimerization of each reactant before intercombination occurred. Hampton

predicted and isolated the intermediate, triphenylsiloxo-
chlorochromate(VI), by treating chromyl chloride with an ex-
cess of triphenylsilanol. This violet crystalline solid
melted at 100° C.

When Hare treated diphenylsilanediol with either
chromyl chloride or chromium(VI) oxide he obtained mixtures
of two products, a light orange crystalline solid and a dark
orange amorphous gum. His primary characterization indicated
that the respective products were cyclo-bis[tetraphenyldisilox-
anylchromate(VI)] and bis(hexaphenyl-6-hydroxotrisiloxanyl)-
chromate(VI). The reaction of tetraphenyldisiloxane-1,3-diol
and chromium(VI) oxide yielded only the crystalline dimer.
Hampton, subsequently, confirmed the structure of the cyclic
dimer with proton magnetic resonance spectroscopy. Hare
isolated a bright red viscous oil from the methylene chloride
reaction of dicyclohexylsilanediol and chromium(VI) oxide.
Characterization suggested that the product was hydroxo-
$\left\{ \text{penta [dicyclohexylsiloxanylchromate(VI)]} \right\}$ dicyclohexyl-
silanol.

Hare tentatively assigned the strong vibrational frequency
occurring between 11.5 and 12.1 μ to the Si-O-Cr stretch by
qualitative evaluation of the infrared spectra of several
siloxy chromates and by comparing the frequencies and appear-
ances of absorption bands shown by other transition metal-
oxygen-silicon compounds (12, 13).

Ovrutskii (14) obtained a complex containing the silicon-oxygen-chromium linkage from the reaction of silicic acid and hexaaquochromium (III) nitrate. Several organosilicon-chromium coordination compounds having the following basic structure

$$
\begin{array}{c}
\text{O} \;\text{—}\; \text{Cr} \nearrow^{\text{Cl}} \\
\nwarrow \text{Cl} \\
\text{R}_3\text{SiR'C} \qquad\qquad \text{OH} \\
\\
\text{O} \;\text{—}\; \text{Cr} \\
\searrow_{\text{Cl}}
\end{array}
$$
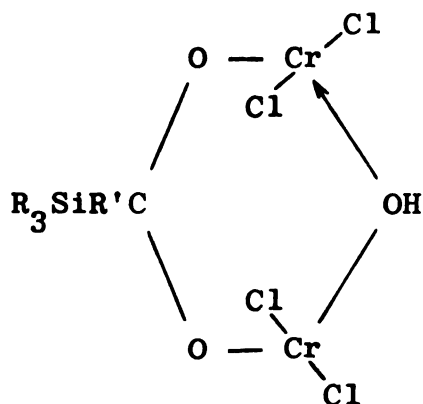
have been prepared by Gilkey (15) from reactions of organic acids, $R_3SiR'COOH$, with dichlorohydroxochromium(III).

Inorganic Chromium(VI) Chemistry.

The inorganic compounds of chromium(VI) includes chromium(VI) oxide, metal chromates, polychromates, peroxo-chromates, and chromyl compounds. Coordination compounds containing chromium(VI) are rare.

Chromium(VI) oxide is obtained as a precipitate by the action of sulfuric acid on concentrated solutions of either sodium or potassium dichromate. The bright red hygroscopic crystals melt at 197° C. (16). The crystalline structure of chromium(VI) oxide was generally considered to consist of six

oxygen atoms surrounding each lattice chromium in a distorted octahedron (17), however, in 1950 Bystrom and Wilhelmi (18) determined that the structure was a distorted tetrahedron with chromium-oxygen distance of 1.79-1.81 $\overset{o}{A}$. The tetrahedra are formed by the sharing of oxygen atoms.

The oxide is an extremely vigorous oxidizing agent, reacting explosively with many substances, particularly organic materials. The oxidative characteristic is employed quite extensively in quantitative analytical chemistry. The oxide is reduced to the more stable chromium(III) oxide. When heated, chromium(VI) oxide loses oxygen progressively and decomposition occurs by the following steps (19):

$$CrO_3 \longrightarrow Cr_3O_8 \longrightarrow Cr_2O_5 \longrightarrow CrO_2 \longrightarrow Cr_2O_3$$
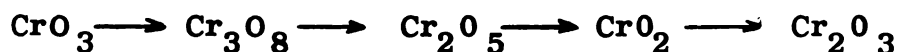
The paramagnetism of chromium(VI) oxide was attributed to incomplete pairing of the ground state electrons (20). Crystalline chromium(VI) oxide is piezoelectric (21), suggesting that a permanent dipole results from the distorted tetrahedra.

Dissolution of the highly soluble oxide occurs with the establishment of a chromate-dichromate equilibrium. The relative concentration influences the polymerization of the solution species. In very dilute solutions the chromate $[CrO_4]^{--}$, species predominates. As the concentration of chromium(VI) increases the predominate solution species becomes first the dichromate, $[Cr_2O_7]^{--}$, then the trichromate, $[Cr_3O_{10}]^{--}$, and finally the tetrachromate, $[Cr_4O_{13}]^{--}$. The formation of polychromate ions also occurs by

increasing the hydrogen ion concentration. In a basic medium
the chromate is quite possibly the only species present.

Metal chromates and polychromates are generally prepared
utilizing the above equilibrium. In 1931 Mellor (27) listed
two hundred and fifty-seven dichromates, thirteen trichromates
and five tetrachromates; many more have been prepared during
the interim.

Silver chromate was originally prepared by Vauquelin (21)
in 1809 by precipitating the silver salt from silver nitrate
and potassium chromate solutions. Silver chromate precipitates
as monoclinic crystals (46) which vary in color from bright red
to deep green. The color variations were reported by Bush (22)
to be dependent upon the rate of precipitation. Nisikida (44)
found that the red and green products were identical by x-ray
powder patterns and he attributed the colors to differences
in crystal grain sizes. The shape of the precipitated particle
ranged from powders to large acicular or tabular (micaceous)
crystals. The density of silver chromate is 5.52 g/cc and the
molar volume 60.1 cc (23). The solubility of silver chromate
in water is quite low; Kohlrousch (24) reported 2.56×10^{-4} g./l.
from conductivity measurements while G. S. Whitby (25), using
colormetric observations, found a solubility of 2.52×10^{-4} g./l.

Vauquelin (21) was also the first to prepare silver dichro-
mate. He obtained the dichromate from an acidified solution of
silver chromate. The usual preparation consists of precipitating

silver dichromate from a silver nitrate solution by the addition of an acidified potassium dichromate solution. Color and crystal shape variations are obtained from different preparative techniques, however silver chromate generally occurs as violet acicular crystals with a density of 4.77 g/cc (26). Schabus (45) reported that silver dichromate was a member of the triclinic crystal system and has the axial ratios: a : b : c: = 1.5320 : 1 : 1.0546.

Metal dichromates are generally quite water soluble and silver dichromate (8.2 x 10^{-2}g/l) (28) has been found to be the least soluble of any known dichromate.

The reactions of silver salts with organohalometallic compounds have been discussed in the literature. Schmidt and Schmidbaur (29) prepared tris(trimethylsilyl)arsenate(V) when they preformed the heterogenous reaction of silver orthoarsenate with trimethylchlorosilane in an organic solvent, while an analogous reaction using triphenylchlorosilane yielded tris-(triphenylsilyl)orthoarsenate(V) for Chamberland and MacDiarmid (30). The reaction of silver orthoarsenate with dimethyl-dichlorotin (31) in water yielded a white polymer with the following structure:

$$
\begin{array}{c}
\left[O \underset{\displaystyle \begin{array}{c} O \\ | \end{array}}{\overset{\displaystyle \begin{array}{c} CH_3 \\ | \\ O-Sn-O \\ | \\ CH_3 \end{array}}{}} As \underset{\displaystyle \begin{array}{c} CH_3 \\ | \\ O-Sn-O \\ | \\ CH_3 \end{array}}{\overset{}{}} As - O - \underset{CH_3}{\overset{CH_3}{|}} Sn \right]_x
\end{array}
$$
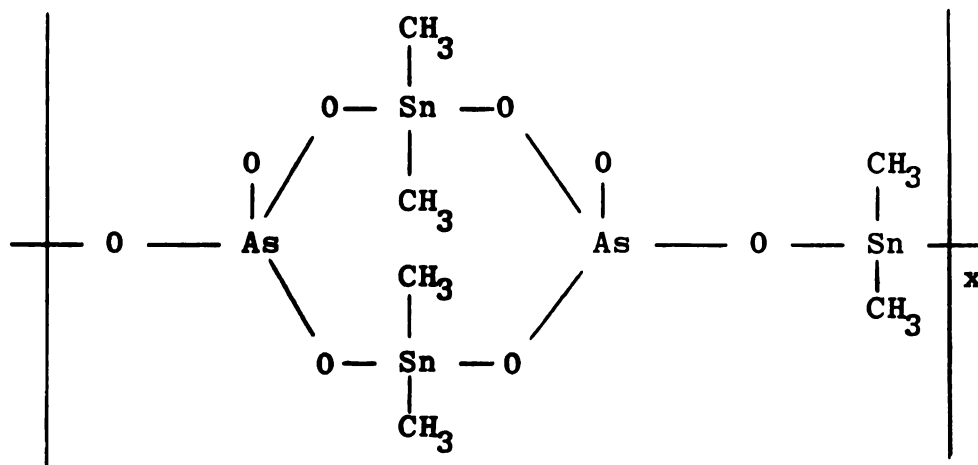
Tris(trimethylsilyl)orthophosphate(V) was prepared from the
reaction of trimethylchlorosilane and silver orthophosphate
(29). The reactions of silver perchlorate with triorgano-
chlorosilanes (32) gave trimethylsilylperchlorate, triethyl-
silylperchlorate, tripropylsilylperchlorate, triphenylsilyl-
perchlorate and tri-p-tolylsilylperchlorate. Harder, et al.,
(33) prepared chromyl borate, $CrO_2(BO_2)_2$, from the reaction
of chromyl chloride with silver borate.

Numerous chromyl compounds have been reported. A few
of these are chromyl fluoride, chloride, acetate, nitrate,
perchlorate, borate, bromide, sulfate, pyrosulfate, azide,
thiocyanate, and cyanate. The chloride is the only chromyl
compound whose chemistry has been studied to any extent. The
bright red transparent liquid (m. -96.5^o C., b. 115.7^o C.) was
first prepared by Berzelius (34) from the distillation of a
chromate, sodium chloride-sulfuric acid mixture. Chromyl
chloride is generally prepared by the reaction of chromium(VI)

oxide with hydrogen chloride containing small amounts of sulfuric acid as a dehydrating agent (35). The structure of chromyl chloride was shown to be a slightly distorted tetrahedron by electron diffraction measurements (36). The nearly symmetric structure was also indicated by its low dipole moment (37) and low dielectric constant (38); these and other measurements substantiate the non-polar nature of chromyl chloride.

Chromyl chloride is soluble in most common organic solvents, however it will often react violently with some of them. It is highly soluble in halogenated organic compounds and inorganic covalent halides. It is immiscible with water and hydrolyzes very slowly at the liquid interface.

Molecular weight studies of chromyl chloride (1, 2, 3, 4) indicate a degree of polymerization of one to three molecular units. The vapor density suggests the presence of the chromyl chloride monomer in the gas phase. When exposed to light the red liquid decomposes to chlorine and a black solid. The mechanism for photolytic decomposition of chromyl chloride has been reported by Schwab and Prakash (39). It is thermally stable to 180° C. Decomposition begins above this temperature and at approximately 400° C. A magnetic oxide is formed having the composition of Cr_5O_9. Chromium(III) oxide occurs at temperatures above 400° C. (35).

Chromyl compounds are generally very reactive. The lability of the two substituents is used fairly extensively in preparative chemistry involving chromium(VI).

Chromium (VI) Organic Compounds.

The first organochromium compound prepared was bis(triphenylcarbinyl)chromate. Gomberg (40) isolated this material from the reaction of silver chromate with triphenylmethyl-chloride in benzene. The usual method for the preparation of chromate esters is the addition of chromium(VI) oxide to a solution of an alcohol in an inert solvent. The esters have also been prepared from reactions of the alcohol with chromyl chloride in alkylhalide solvents or with alkali metal dichromates in glacial acetic acid.

Most chromate esters are derivatives of tertiary alcohols. The reaction of primary and secondary alcohols with chromium(VI) oxides in an inert solvent yields yellow to yellow-orange solutions. The color, however, remains only for a short time and as yet none of these unstable chromates have been isolated.

Zeiss and Matthews (41) obtained very pure chromate esters by using a freeze-drying technique for purification.

The alcoholysis of chromate esters yields the parent alcohol and a reduced chromium species, possibly H_2CrO_3. The hydrolysis of bis(tert-butyl)chromate (42) occurs through cleavage of the chromium-oxygen bond while the hydrolysis of bis(triphenylmethyl)-

chromate proceeds by breaking the carbon-oxygen linkages.

Other organochromium compounds include numerous carbonyl derivatives of chromium(VI) and arylchromium chemistry (43). Although these two topics are extremely interesting, they are not closely related to this investigation and are much too extensive to be included.

Chemistry of Fluorine.

Physical Properties.

Hare (5) noted that the thermal stabilities of organo-siloxychromates were enhanced when the organosilicon substituents exhibited strong electron-withdrawing tendencies (p. 140 and 141). It was postulated, therefore, that siloxy-chromates with either silicon-fluorine or silicon-fluoroorganic linkages might show even greater resistance to thermal decomposition than that seen with previously prepared compounds of this type.

The term "electronegativity" has been defined by Pauling (48) as the "power of an atom or molecule to attract electrons to itself." Although this concept is not susceptible to direct experimental measurement, the three principal methods for electronegativity assessments (Pauling, Mulliken, and Malone) suggest that fluorine is the most electronegative element (47). It is also quite possible that atomic fluorine exhibits this electron-withdrawing tendency to a greater degree than any known molecular

species. The physical property of di- and poly-atomic mole-
cules containing the halogen homologues generally follow
predictable trends through iodine, bromine, and chlorine only
to go completely off course upon reaching the fluorine species.
A classic example of this anomalous behavior is shown by the
melting points, boiling points, and heats of fusion and vapori-
zation of the hydrogen halides (49). The property values
decrease progressively from hydrogen iodide to hydrogen chloride,
however hydrogen fluoride property values are considerably higher
and with the exception of the melting point, all hydrogen fluor-
ide values were greater than that of hydrogen iodide. This
deviation from progressive trends is attributed to intramole-
cular association of hydrogen fluoride resulting from hydrogen
bonding which in turn is caused by the abnormally high electro-
negativity of fluorine. Not all anomalies shown by fluorine-
containing molecules can be explained by electronegativity
alone. For example, fluorine, unlike the remaining members of
the series, does not have d orbitals available for bonding
which results in a somewhat different chemistry.

The silicon-fluorine bond has one of the highest known
energies for a single bond (143 kcal./mole.), being only slightly
weaker than the boron-fluorine linkage (150 kcal./mole.)
(Table I). It should be noted, however, that high bond energy
is not the only criterion for stability. Many other factors,
such as kinetic considerations, influence molecular thermal
resistance (p. 142).

TABLE I

ENERGIES OF RELATED CHEMICAL BONDS

BOND	ENERGY (kcal./mole.)	REF.	BOND	ENERGY (kcal./mole.)	REF.
Si-F	143	48	Si-Cl	95	50
F-F	37	49	Si-Br	69	48
H-F	135	49	Si-H	76	49
C-F	111	52	C-C	83	49
B-F	150	50	C=C	146	49
Si-O	110	50	C≡C	200	49
Si-C	64	51	C≡N	213	50

The high strength of the silicon-fluorine bond has been attributed to partial double bond character. Kriegsmann (53) calculated the force constants for ideal Si-X single bonds where X - F, Cl, Br, I, O, S, N, C, and H. When X is a highly electronegative element, he found a strengthening of the linkage that corresponded to appreciable double bond character. Pauling (48) also reached this conclusion for silicon-fluorine and silicon-chlorine linkages by means of theoretical interpertations of the interatomic distances in various silanes. Rochow (54) attributed the magnetic shielding of the fluorine exhibited in the F^{19} nuclear magnetic resonance spectra of methyl- and ethyl-fluorosilanes to both the inductive effect and a π bonding effect. Interpertations of electric moment measurements

of halosilanes (55) and alkylhalosilanes (56) also indicated
appreciable double bond character for the silicon-chlorine
and silicon-fluorine linkages.

Recently the Dow Corning Corporation has been marketing
silicon polymers with considerably higher thermal stability
than has been seen previously. This greater resistance to
elevated temperature resulted from the replacement of the
normal organic groups with fluoroorganic substituents.

The bond energy term for the carbon-fluorine linkage
varies from 107-116 kcal./mole. The strength of the carbon-
fluorine bond increases as fluorine atoms successively dis-
place hydrogen atoms attached to the same carbon. The energy
term for carbon tetrafluoride is one-quarter of the heat of
atomization of this compound or 116 kcal./mole. and the CF_3,
$-CF_2$, and monofluorinated structures have respective carbon-
fluorine energy terms of 114, 109, and 107 kcal. A change in
bond strength does not accompany the successive increase in the
number of chloro or bromo substituents on a particular carbon
atom. This hypothesis is clearly illustrated by a comparison
of the bond energy term for the carbon-halogen linkages in the
fluoro, chloro, and bromo halomethane families (Table II).

TABLE II

BOND LENGTHS AND BOND ENERGY TERMS IN HALOMETHANES (57)

Compound	X = F		X = Cl		X = Br	
	B(C-F) (kcal.)	r(C-F) ($\overset{o}{A}$)	B(C-Cl) (kcal.)	r(C-Cl) ($\overset{o}{A}$)	B(C-Br) (kcal.)	r(C-Br) ($\overset{o}{A}$)
CX_4	116	1.317	78.2	1.766	66.6	1.942
CX_3H	114.6	1.332	78.3	1.767	66.1	1.930
CX_2H_2	109.6	1.358	77.9	1.772	65.5	
CXH_3	107	1.385	78.0	1.78	66.6	1.939

B = bond energy, r = bond lengths

The strengthening of the carbon-fluorine bond is accompanied by a corresponding decrease in bond length. The energy terms and bond lengths for the chloro and bromo methanes remain relatively constant. Pauling (48) explained that the increased strength and contraction in length of the carbon-fluorine linkage can be accounted for by the contribution of resonance structures of the type:

$$F^- \quad F-C=X^+ \quad F$$

$$F^- \quad F-C^+-X \quad F$$

$$F^+ \quad F-CX^- \quad F$$
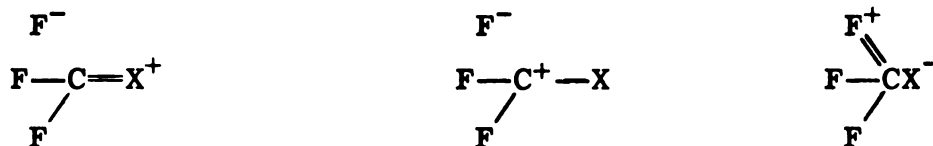
The degree of influence that each of the above resonance contributors has upon an individual molecule depends upon the identity of X. The number of fluorines in each molecule determines the number and importance of each resonance structure. Meyers and

Gutowsky (58) found that the F^{19} chemical shift in nuclear magnetic resonance spectra of the fluoromethane family decreased progressively with decreasing carbon-fluorine bond lengths. They postulated that if this bond shortening resulted from an increased ionic character of the bond, the trend of the chemical shift values would be in the opposite direction. However, if the contraction in bond length was related to a greater degree of double-bond character the observed chemical shift trend would be expected.

Lagowski (59) has shown the electronegativity of the trifluoromethyl group to be approximately 3.3 on the Pauling scale. The value was obtained from a number of calculations involving the use of bond dissociation energies and infrared absorption frequencies. According to Lagowski the electronegativity of the trifluoromethyl group is equal to or greater than chlorine and considerably larger than the alkyl groups which are of the order of 2.0. Cullen, et al., (60) substantiated Lagowski's electronegativity value from ultraviolet measurements of trifluoromethyl arsines; however, at a later date (61), he determined the ionization potential of a series of perfluoroalkylarsines by electron impact mass spectrometry and suggested that the electronegativity of the CF_3 group was slightly less than that of the chloro group. The approximate covalent diameter of the perfluoromethyl group is 3.3 angstrom units, which is slightly larger than the methyl

group at 2.8 Å. It has been suggested (62) that the larger
size of the fluorine atom compared with that of hydrogen,
provides much greater protection of the carbon skeleton in.
a fluorocarbon in contrast to a hydrocarbon. The greatest
physical significance of the highly electronegative fluorine
atoms in organic fluorine molecules is their electron-with-
drawing or "inductive" effect which leads to a decrease in
electron density at adjacent reaction centers. Direct evi-
dence of this effect is the repeatedly encountered shifts to
shorter wavelengths by other infrared absorbing linkages with-
in a fluorine-containing molecule. Another clear example of
the inductive effect exerted by organic fluorine groups is
illustrated by trifluoroacetic acid which has a considerably
greater acidic nature than acetic acid (63).

Thermal Stability.

The increased thermal stability obtained by the inclusion
of fluorine in molecules has been effectively demonstrated by
the Dow Corning Corporation with their high heat resistant
fluororganic-silicones (64). Haszeldine, et al., (65) and
Pierce (64) found that the thermal and hydrolytic stability of
polyfluoroalkyl silicones and polysiloxanes depends markedly
on the position of fluorine relative to silicon. Both groups
concluded that molecules in which fluorine is attached to the
gamma carbon atom exhibit the greatest thermal and hydrolytic
stabilities. Thermal stability increases, resulting from the

replacement of fluorine for lower electronegative substituents,
have been observed with many varied molecular types. Emeléus,
Haszeldine, and Brandt (66) found that perfluoroalkyl sulfides
exhibited much greater resistances to heat and chemical attack
than did their corresponding alkyl analogues. The boron-
phosphorus linkages in certain compounds have shown considerable
increases in bond strength from the replacement of fluorine for
alkyl or hydrogen substituents attached to the phosphorus atom
of the molecule (67). Tetrakis(trifluoromethyl)diphosphine,
diarsine, and distibine (68, 69, 70, 71, 72) compounds of the
type $(CF_3)_2M-M(CF_3)_2$ have been found to be more resistant to
thermal cleavage of the metal-metal bond than their correspond-
ing methyl analogues. Burg suggested that this greater stability
resulted from the electronegative trifluoromethyl groups stabil-
izing the metal-metal bonds by strengthening the π bonds which
involve the metal lone-pair electrons of the 3d orbitals of the
neighboring metal atom. Inorganic polymers with phosphorus-
phosphorus and phosphorus-boron back-bone linkages with thermal
stabilities approaching 500° C. have been prepared (73).
Perfluoroalkyl-transition metal derivatives such as
$R_fFe(CO)_4I$ $(R_f = CF_3, C_2F_5, C_3F_7)$ and $C_3F_7Re(CO)_5$
are much more stable to thermal decomposition than their
alkyl analogues (74, 76). The thermal decomposition of
$R_fFe(CO)_4I$ involves cleavage of the Fe-I and apparently not
the R_f-Fe bonds. McClellan (75) prepared and studied eleven

manganese and three cobalt carbonyls containing fluorocarbon
linkages and found them all to show greater thermal stabili-
ties than their hydrocarbon analogues. It is interesting to
note that the authors listed in the preceeding section invari-
ably explained that the thermal stability increases shown by
fluorine-containing molecules resulted from the highly electron-
withdrawing property of the fluorine atom.

Hydrolytic Stability.

The relative hydrolytic stability, like thermal stability,
of fluorine-containing compounds as compared to their hydrogen
or halo analogues can generally be explained in terms of electro-
negativities.

Alkyl-, trialkyl-, and triaryl-silyl fluorides have been
found to be considerably more resistant to hydrolysis than the
corresponding chlorides and bromides (77, 78, 79). The hydroly-
sis of triphenylsilyl fluorides in aqueous acetone was retarded
by p-methyl substituents and the reactions of these fluorides
were more than a million times faster in alkaline solutions
than in water. A nucleophilic bimolecular substitution has
been proposed as the mechanism for hydrolysis (77). The silicon
bond in alkyl fluorosilicates (80) is considerably less reactive
than the silicon-chlorine bond in analogous compounds; however,
the hydrogen fluoride that is formed acts as a powerful catalyst
for the further hydrolysis or alcololysis of the compounds.

A study of the nuclear magnetic resonance spectra of the tetrafluoroborate and trifluoromethylfluoroborate ions in aqueous solutions (81) indicated that the degree of hydrolysis of these substances was quite small. The hydrolytic stability of fluoroalkylsilanes and polysiloxanes has been discussed on p. 22. Trifluoromethyl-trihalogermanes, CF_3GeX_3, were found to be fairly stable in cold water but evolved trifluoromethane in hot water or alkaline solutions (82). The reduction in donor character (decreased bascity) of perfluoroalkyl amines results in a much more hydrolytically stable species than the corresponding alkyl tertiary amines (83). The perfluoroalkyl derivatives of phosphorus, arsenic, and antimony are fairly resistive to aqueous hydrolysis. However, in the presence of alkali these materials decompose quickly. Haszeldine and West (84) found that the ease of attack by hydroxyl ions was facilitated by the replacement of trifluoromethyl for methyl substituents in trimethyl compounds of group V elements. They established the following order of increasing ease of hydrolysis:

$$M(CH_3)_3 \quad < \quad CF_3M(CH_3)_2 \quad < \quad (CF_3)_2MCH_3 \quad < \quad (CF_3)_3M$$

The ease of hydrolysis also increased as the atomic radius of the group V atoms increased, i.e., P As Sb. Kolditz and Haage (85) prepared a linear arsenate having an unknown molecular weight based upon the following structure:

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$$\left[\begin{array}{c} F \quad F \\ \diagdown \diagup \\ As \quad - \quad 0 \\ \diagup \diagdown \\ F \quad F \end{array} \right]_x$$
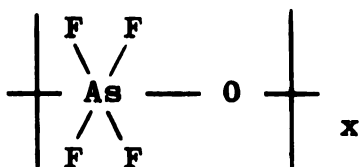
They found that complete hydrolysis could only be obtained by refluxing the polymer in an alkaline solution for several hours. They attributed the stability to a fluorine screening effect which limited the availability of the arsenic-oxygen-arsenic linkage to hydroxyl attack.

The perfluoroalkyl derivatives of sulfur such as CF_3SF_5, $CF_2(SF_5)_2$, $CF_2(SF_3)_2$, $(CF_3)_2SF_4$, and $(CF_3)_2SO_2$ have been found to be completely unreactive in alkaline solutions at 100° C. (86). The limited number of perfluoro derivatives of iron, manganese, cobalt, and rhenium that have been prepared have shown a much greater resistance towards alkaline hydrolysis than either their hydrogen analogues or the perfluoroalkyl derivatives of the main group metals (74, 75, 76).

Inorganic Polymer Chemistry.

It is generally assumed that inorganic polymer chemistry is a relatively new field, i.e., that no more than two decades have seen investigations concerning macromolecules composed essentially of skeletons other than carbon. In a sense, this assumption is both true and false. The investigation of inorganic macromolecules is in actuality far from being a new field.

The structures of silicates and borates as well as those of
the polymeric forms of phosphorus and transition metal oxy-
acids have been known for some time. The structures of
rhombic sulfur and metallic selenium are considered polymeric
by some authors. In fact, under a strict definition of the
term, inorganic polymers would necessarily include all crystal-
line lattices in which the bonding is primarily covalent.
Transition metal compounds are often polymeric in the solid
state; for example, vanadium pentoxide tetrahedra form large
sheets through shared oxygen atoms. The rather complex poly-
phosphomolybdates and tungstates have confused and delighted
structural chemists for decades. Polymeric forms of phospho-
nitrilic chloride were discovered in 1834 by Liebig and Wahler.
In 1897 Stokes reported the preparation of a so-called "inor-
ganic rubber" from thermal treatment of phosphonitrilic chloride.

During the past two decades, the space development program
has prompted the chemist to initiate investigation of inorganic
polymeric systems. This came about primarily because polymers
with carbon-carbon or carbon-oxygen skeletal systems had been
unable to withstand the temperature gradient required for
practical application in space. The inorganic polymeric
forms which have been isolated and investigated in the past
also were unsuited for these applications primarily because of
their somewhat rigid mechanical properties. The new inorganic
polymer investigations have consisted primarily of searching

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for polymeric materials which combine the temperature resist-
ant properties of inorganic material with the flexibility and
toughness of plastics or the viscosity of oils.

Many different combinations of elements have been used
in an attempt to prepare these utopian materials; however,
complete success has continued to elude the inorganic polymer
chemist. The synthesis of materials which decompose at fairly
high temperatures (300-400° C.) has often been negated by
their inability to withstand the attack of chemical reagents.
A perusal of the many review articles concerning inorganic
polymers would lead one to believe that the most difficult
problem facing the inorganic polymer chemist is that of classi-
fication of the many polymeric systems developed during the past
few years. These systems include materials such as phosphoni-
trilic halides and related phosphorus-nitrogen macromolecules;
the phosphorus-phosphorus, boron-boron, phosphorus-boron sys-
tems studied extensively by Burg; silicon-oxygen-metal polymers
which include the vast number of silicones developed by numerous
private and commercial laboratories, coordination polymers, and
many other systems. The listing or discussion of these numerous
inorganic polymer systems is completely out of the scope of this
dissertation; therefore, an attempt will be made to limit the
coverage to polymerization reactions which are directly related
to this investigation.

As was stated previously, chromium(VI) was chosen as a constituent in the silicon-oxygen-metal system because of its polymeric tendencies and the difunctionality of the tetrahedral chromyl group. The polymeric tendencies of chromium(VI) are evident in the polyanionic aggregates which exist in either acid solution of chromium(VI) or highly con-centrated aqueous solutions (87). Large linear molecules such as the metal tetrachromates can be precipitated from these solutions. The crystalline form of chromium(VI) oxide consists of CrO_6 octahedra which make up a continuous network stretching throughout the entire crystal.

Cryoscopic and ebullioscopic measurements of the molecular weight of chromyl chloride in the liquid state have suggested a degree of polymerization equal to 1.5-3 molecular units (1, 2, 3, 4). During the thermal decomposition of chromyl chloride an elimination of chlorine occurs at approximately 200° C. Analysis of the residue indicates the existence of the trimer and tetramer of $(CrO)_n CL_2$ (88).

Numerous coordination polymers of chromium have been pre-pared. Block, et al., have reported the preparation of a mono-meric chromium(II) compound (89) with polymeric properties, dimers of chromium(III) coordination compounds (90), and chro-mium(III) coordination polymers with molecular weights from 400 to 1400 (91). Schmitz-DuMont (92) has prepared a variety of chromium(III) amide and alkoxo chromium(III) amide polymeric

coordination compounds. A chromium(III) coordination polymer marketed under the trade name of "Valan" has been used primarily as an adhesive between organic resins and glass (87). The only known chromium(VI) coordination polymer was prepared by Podall and Iapalucci (93) from photochemical oxidative decarbonylation of chromium hexacarbonyl by diphenylhypophosphorus acid, (Ph_2PO_2H). The resulting solid was stable up to 360° C., insoluble in water or hydrochloric acid, and had the following structure:

$$\left[\begin{array}{c} CO \\ | \\ \underset{\underset{|}{\overset{|}{CO}\ CO}}{Cr} \end{array} \begin{array}{c} OP(Ph)_2 : O \\ \\ O : P(Ph)_2O \end{array} \right]_8$$
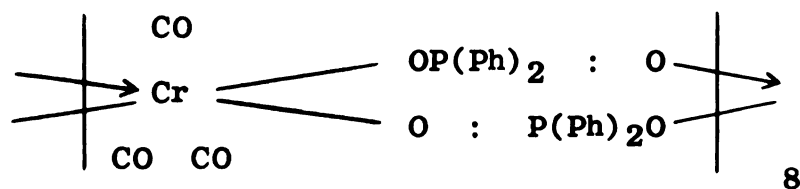
Silicon polymers containing silicon-fluorine linkages have been prepared in several laboratories. J. Goubeau and H. Grosse-Ruyken (94) reported the preparation of the hydrolytically unstable hexafluorodisiloxane, octafluorotrisiloxane, and a difluoropolysiloxane having an unknown molecular weight. Schmeisser (95) and Pease (96) simultaneously reported the preparation of Polydifluorosilanes, $(SiF_2)_x$, with as many as ten molecular units. In 1949 a British patent was granted to the Dow Chemical Company for phenylfluoropolysiloxanes of unknown molecular weights (97). Numerous polysiloxanes with fluoroorganic silicon linkages have been prepared in the

laboratories of McBee, Haszeldine, and the Dow Corning Corporation.

Silicon-oxygen-X polymers and telomers have been prepared using many different elements. Silicon, titanium, vanadium, aluminum, tin, lead, germanium, arsenic, antimony, boron, and phosphorus as the X atom have accounted for most but not all of the work accomplished in this field. A complete discussion of the silicon-oxygen-X systems is outside the scope of this thesis, primarily because of the vast number of publications relating to compounds of this type.

EXPERIMENTAL

Preparation of Reactants.

Preparation of Silver Chromate.

Silver chromate was prepared by the method of Vauquelin (21). A 1.2 molar solution of potassium chromate (2.4 moles) containing a catalytic amount of aqueous ammonia was added to a 1.2 molar silver nitrate solution (2.4 moles). The silver nitrate solution was stirred vigorously throughout the addition and the resultant dark reddish-brown precipitate was extensively washed with warm water. When this preparation was carried out with more concentrated solutions of silver nitrate and dilute potassium chromate solution or when both solutions were concentrated, the resulting silver chromate was found to be badly contaminated with the potassium salt. The product was dried at 110° C. for twenty-four hours.

When the pure silver chromate was heated on an aluminum melting block it showed a gradual color change between 300 and 400° C., indicating the possibility of decomposition at this point. A differential thermal analysis of this material, however, showed that little or no physical change took place over this temperature range. The thermogram of silver chromate gave a pronounced exothermic peak extending from 480 to 580° C. with a maximum at 535° C. It is believed that this is the actual temperature range for the thermal decomposition of silver chromate.

30

The molecular spectrum (Figure 5, p. 104) from 200 to 500 millimicrons gave absorption peaks at 503 and 274 mμ with respective molar extinction coefficients of 4.27 x 10^3 and 3.14 x 10^3. The x-ray powder pattern of silver chromate is tabulated on p. 137 . The chromium analysis of the compound was 15.62 percent. (Theory: 15.68% Cr).

Preparation of Silver Dichromate. Silver dichromate (80% yield) was precipitated from an acidic one molar potassium dichromate solution by the addition of a one molar solution of silver nitrate (98). The resulting deep violet precipitate was purified by recrystallization. A concentrated solution of silver dichromate was prepared by adding an excess (approx. 100 g.) of the product to 400 ml. of water and 50 ml. of concentrated nitric acid. The mixture was stirred at its boiling point for thirty minutes, filtered hot to remove the excess reaction product and stored in a refrigerator for six hours. Approximately twenty grams of silver dichromate crystallized as long violet needles. After filtration, the pure material was dried at 110° C.

The melting range of the silver dichromate was found to be from 358 to 362° C. when observed visually. The thermogram also showed this melting point as a very intense and sharp endothermic peak at 380° C. A broad exothermic peak between 480 and 580° C. and a maximum at 540° C. corresponded to the decomposition of silver dichromate.

The visible and ultraviolet spectra (Figure 5, p. 104)
showed strong absorption at 258, 344, and 470 mμ, with molar
extinction coefficients of 1.75 x 10^3, 1.98 x 10^3, and
3.36 x 10^3 respectively. The infrared spectrum of silver
dichromate in a potassium bromide matrix gave a strong ab-
sorption at 11.3 μ which corresponded closely to the M-O-Cr
absorptions found in several dichromates by Miller and
Wilkins (99). The x-ray powder pattern is tabulated on
p. 138. The chromium analyses were 24.09 and 24.01 percent
(theory: 24.11% Cr).

Characterization of Triphenylchlorosilane. Commercial
grade triphenylchlorosilane was obtained from K and K labora-
tories and purified by recrystallizing the white solid from
methylene chloride. The melting point of 96 to 97° C. agreed
well with the literature value of 97° C. (6). Silicon analyses
of this material gave experimental values of 9.61 and 9.58 per-
cent (theory: 9.54% Si). The infrared spectrum of triphenyl-
chlorosilane in the sodium chloride and cesium iodide regions
are shown in Figures 10 and 11 (p. 109 and 110).

Triphenylchlorosilane hydrolyzed very easily and was,
therefore, purified prior to each reaction.

Preparation of Diphenyldifluorosilane. Diphenyldifluoro-
silane was prepared by the method of Sommer et al. (133).
Aqueous hydrogen fluoride (49%) (40 g., 1.0 mole) was treated

with twenty grams (0.074 mole) of diphenyldiethoxysilane in a polyethylene beaker. This immiscible mixture was stirred magnetically for four hours during which the mixture was cooled in an ice bath. Diphenyldiethoxysilane had been purified previously by vacuum distillation. The two resulting layers were separated with a separatory funnel. The organic layer (diphenyldifluorosilane) was then added to an equal volume of methylene chloride containing five grams of anhydrous magnesium sulfate which removed the water trapped in the organic layer. After standing for at least one day, the magnesium sulfate was removed by filtration and the methylene chloride by evaporation at reduced pressure (water aspirator). The dry diphenyldifluorosilane was distilled at several reduced pressures with boiling points of 151° C. at 43 mm. Hg, 75° at 0.4 mm. Hg, and 68° at 0.05 mm. Hg. Emeléus and Wilkins (100) cited a boiling point of 156 to 160° C. at 50 mm. of Hg. Yields of 65 to 75 percent were obtained. Diphenyldifluorosilane has a density of 1.15129 g./cc. at 250° C. and a refractive index of 1.5269 at 20° C. The infrared spectrum in the sodium chloride and cesium iodide regions are shown on Figures 14 and 15 (p. 113 and 114).

The elemental analysis of diphenyldifluorosilane is listed on the next page.

TABLE III

ELEMENTAL ANALYSIS OF DIPHENYLDIFLUOROSILANE

Element	Theory (%)	Experimental (%)
C	65.42	64.35, 65.61
H	4.58	4.55, 4.74
Si	12.75	12.37
F	17.25	17.45

Characterization of Diphenyldichlorosilane. Crude diphenyldichlorosilane was obtained from General Electric Company and purified by vacuum distillation. The boiling point was 110° C. at 1.5 mm. of Hg and 304° C. at 1 atm. The melting point was -22° C. and the refractive index 1.5792 at 20° C.

The infrared spectrum of diphenyldichlorosilane is shown in Figures 12 and 13 (p. 111 and 112). The chlorine analysis was 28.00 percent (theory: 27.93% Cl).

Preparation of Diphenylchlorofluorosilane. Pletcher and Nutting (101) prepared diphenylchlorofluorosilane by the fluorination of diphenyldichlorosilane with lead tetrafluoride. Booth et al. (102-107) using the Swarts reaction (antimony trifluoride) prepared dimethylfluorochlorosilane and several trihaloalkylsilanes with various degrees of fluorination.

Antimony trifluoride (5.95 g., 0.033 mole) was added
quickly to a three necked flask containing 25 g. (0.10 mole)
of liquid diphenyldichlorosilane. The reaction was cooled in
an ice bath while being stirred magnetically. After three
hours the mixture was distilled at reduced pressure (1.0 mm.).
The first fraction to be removed was antimony trifluoride which
collected as white crystals on the cold finger. Several frac-
tions of the remaining liquid were obtained; however, analysis
of these fractions by vapor phase chromatography showed only
two of the expected three peaks. The retention time of these
components corresponded exactly with diphenyldifluorosilane
and diphenyldichlorosilane. Distillation of a second reaction
mixture was performed at 1 atm., after which the vapor phase
chromatograph gave an entirely new peak equidistant between
the two previously shown. It was therefore assumed that
diphenylchlorofluorosilane was produced by elemental exchange
between diphenyldifluorosilane and diphenyldichlorosilane at
the high temperatures (245-305° C.) required for distillation.
Equal molar quantities of diphenyldichlorosilane and diphenyl-
difluorosilane were refluxed at temperatures between 275 and
285° C. for ten hours. The vapor phase chromatograph showed
three distinct equidistant peaks. The above reaction was
continued and samples were analyzed (V. P. C.) at approximately
ten-hour intervals. An equilibrium was apparently established
after one hundred and fifty hours. The reaction rate did not

appear to increase when catalytic amounts of silicon tetra-chloride were used. The resulting diphenyldihalosilanes were separated by fractional distillation using a vacuum jacketed column containing glass helices. This method was somewhat cumbersome because several distillations were necessary before pure diphenylchlorofluorosilane could be obtained. When molecular distillation was attempted at pressures of 10^{-3} mm., the separation was even poorer than with the less refined vacuum distillation. Yields of twenty to twenty-five percent were obtained.

Diphenylchlorofluorosilane has a boiling point of 274° C. at 1 atm. and 72° C. at 1.0 mm. of Hg. The three homologues in this series (Ph_2SiCl_2, b. 304° C.; PhSiClF, b. 274° C. and Ph_2SiF_2, b. 247° C.) follow the Swarts rule (108) which states that the boiling point lowering is constant as successive fluorine atoms replace other halogen atoms in a given poly-halogen.

The clear liquid, diphenylchlorofluorosilane, was viscous at -78° C. and froze to a clear glass-like substance when it was immersed in liquid nitrogen (-196° C.); however, upon warming, no definite melting point could be distinguished. The density at 25.0° C. was 1.1860 g./cc. which is in good agreement with Pletcher (101) who obtained a value of 1.181 g./cc. at 25.5° C. The refractive index was 1.5539 at 20.0° C.

The infrared spectrum of diphenylchlorofluorosilane (Figures 16 and 17, p. 115 and 116) exhibits the normal absorptions characteristic of silicon-phenyl linkages. The strong carbon-silicon stretch at 8.89 μ was resolved into two peaks similar to diphenyldichlorosilane. This splitting is not observed in triphenylmonohalosilanes or phenyltrihalosilanes (115). The two out-of-plane hydrogen deformation peaks which normally occur between 13.5 and 14 μ were masked by solvent (CCl₄) absorption. The silicon-fluorine asymmetric stretching mode (123) at 11.42 μ was extremely strong and sharp. The silicon-chlorine asymmetric stretching mode (113) was similar in appearance and absorbed in the cesium iodide region at 17.6 μ. This absorption masked the silicon-fluorine asymmetric deformation mode which appears at 17.6 μ in the spectrum of diphenyldifluorosilane. The elemental analysis is tabulated below.

TABLE IV

ELEMENTAL ANALYSIS OF DIPHENYLCHLOROFLUOROSILANE

Element	Theory (%)	Experimental (%)
C	60.78	60.77
H	4.26	4.38
Si	11.86	11.70
F	8.03	7.85
Cl	14.98	14.79

<u>Characterization of 3,3,3-trifluoropropylmethyldichloro-
silane</u>. The 3,3,3-trifluoropropylmethyldichlorosilane was
received from the Dow Corning Corporation. The elemental
analyses gave 33.40 percent Cl and 27.18 percent F (theory:
33.40% Cl and 26.87% F), and the clear liquid was used as a
reactant without further purification. The infrared spectra
are shown in Figures 28 and 29 (p. 127 and 128) and are tabu-
lated on p. 81-4. There was no absorption in the ultraviolet
region. The nuclear magnetic resonance spectrum is shown in
Figure 2 (p. 91) Table XII (p. 90) and discussed on p. 87.

This material was first prepared by McBee et al. (109)
from the reaction of 3,3,3-trifluoropropene with methyldi-
chlorosilane using <u>tert</u>-butyl peroxide as a catalyst. A
sealed tube was charged with the reactants and the catalyst
under a nitrogen atmosphere and then heated at 125 to 130° C.
for sixty hours. The major product, 3,3,3-trifluoropropyl-
methyldichlorosilane, was purified by distillation. Its boil-
ing point at 751 mm. of Hg was 112.8 to 113.7° C.

<u>Preparation of 3,3,3-trifluoropropylmethylsilanediol</u>.
The method of Holbrook and Brown (110) for the hydrolysis of
3,3,3-trifluoropropylmethyldichlorosilane was used to prepare
3,3,3-trifluoropropylmethylsilanediol. Over a period of
three hours 0.1 mole (21.1 g.) of 3,3,3-trifluoropropylmethyl-
dichlorosilane in 340 ml. of anhydrous ether was added to 250
ml. of water containing twenty-four grams of twenty-eight

percent ammonium hydroxide. This mixture was stirred magnet-
ically and cooled with an ice bath. When the addition was
complete the water layer was removed by means of a separatory
funnel. The ether layer was washed with equal volumes of
water until the wash water was no longer alkaline; normally
three washings were sufficient.

Purification by recrystallization from the reaction
solvent (ether) as proposed by Holbrook and Brown (110) was
found to be unsatisfactory. The reaction mixture was cooled
in a Dry Ice bath. After a short time, crystals of water
appeared, which were removed by filtration. Repeated crystal-
lization removed most of the water trapped in the ether layer
by the vigorous stirring. The ether was evaporated under a
stream of air, leaving a white solid. This solid was easily
sublimed at room temperature with pressures of approximately
1.0 mm. Hg. Yields of the pure material ranged from eighty-
five to ninety-five percent. The melting range was 82-83° C.
which agreed with the 82-85° C. range found by Holbrook and
Brown (110).

The silicon analyses gave 16.35 and 16.22 percent
(theory: 16.12% Si). The infrared spectrum is shown in
Figures 30 and 31 (p. 129 and 130), and the proton magnetic
resonance spectrum is recorded in Figure 3 (p. 92).

Preparation of Silylchromates .

Generally silyl- and siloxanylchromates have been prepared by the reactions of organosilanols or disiloxanes with chromyl chloride or chromium(VI) oxide. The preparation of organosilicon compounds having both a fluoride and a hydroxyl group attached to silicon is quite improbable; therefore it was necessary to investigate other synthetic routes for the preparation of silylchromates containing a silicon-fluoride bond. Numerous organosilicon compounds having both chloride and fluoride groups bonded to silicon have been prepared. Investigations of these substances have shown that the reactivity of the chloride substituent is far greater than that of the fluoride. Consequently, the initial experiments in this study were performed to determine whether organochlorosilanes react with metal chromates to yield silylchromates and if this were the case whether only the chloride substituent on an organochlorofluorosilane would be replaced.

I. Reactions of Triphenylchlorosilane.

A. With Silver Chromate. Yields of up to ninety percent of pure bis(triphenylsilyl)chromate(VI) were obtained by the reaction of silver chromate with triphenylchlorosilane. A heterogenous mixture of 3.0×10^{-2} mole (10 g.) of silver chromate in 150 ml. of freshly distilled methylene chloride was magnetically stirred in a 300 ml. reaction flask. As a

means of eliminating hydrolysis of both the reactant and the
product, the vessel was flushed with a continuous stream of dry
nitrogen. The reaction flask was also covered with aluminum
foil to reduce photolytic decomposition of the product. The
triphenylchlorosilane (1.70 x 10^{-2} mole or 5.00 g.) in fifty
milliliters of methylene chloride was added dropwise to the
silver chromate slurry over a period of thirty minutes. The
reaction continued for twelve hours at room temperature. The
excess silver chromate was removed by filtration in a dry box
after which the solution was condensed to approximately thirty
milliliters by means of a rotary evaporator (Rinco). Bright
orange crystals of bis(triphenylsilyl)chromate(VI) precipitated
from the concentrated reaction mixture at Dry Ice temperatures.
The material was recrystallized from fresh methylene chloride
and gave a melting point of 155-156° C. which corresponds well
with the value of 153.5-4° C. found by Hare (5).

The unreacted chromate was subsequently dissolved in six
hundred milliliters of boiling 0.6 $\underline{M}$ nitric acid leaving a
light tan solid residue which was identified as silver chloride
by comparing its x-ray powder pattern with a known pattern.
The calculated yield for silver chloride from this reaction was
1.70 x 10^{-2} mole (2.43 g.); however, because of the crudeness
in the separation technique the 1.47 x 10^{-2} mole (2.11 g.) ob-
tained was believed to be a satisfactory indication of the
completeness of the reaction.

B. **With Silver Dichromate**. A ten-fold excess of silver dichromate (3.4×10^{-2} mole or 14.7 g.) was treated with 6.8×10^{-3} mole (2.0 g.) of triphenylchlorosilane using a procedure similar to the above silver chromate reaction in all but one respect i.e., several preparations were carried out at the reflux temperature of methylene chloride (34° C.) and several at room temperature. The reaction times were varied from twelve to eighty hours and the best yields ($>90\%$) were obtained at reflux temperatures and with shorter times. The large orange twinning crystals which were precipitated from the concentrated reaction solution had a melting point of $153-6^\circ$ C. The calculated amount of silver chloride for the reaction was 6.8×10^{-3} mole (0.97 g.) and 5.9×10^{-3} mole (0.85 g.) was found. This product was shown to be bis(triphenylsilyl)chromate(VI) by its x-ray powder pattern (a), infrared spectrum, and elemental analysis. It was surprising, as well as disappointing, when the product of this reaction proved to be bis(triphenylsilyl)chromate(VI) instead of the dichromate. A mechanism for this reaction has been proposed and is discussed on p. 161 .

(a) The x-ray powder pattern for this material did not correspond to either the pattern or the table of interatomic spacings shown by Hare (5). After careful inspection it was found that Hare had interchanged the pattern and tabulated values of bis(triphenylsilyl)chromate(VI) with those of bis(p-tolyldiphenylsilyl)chromate(VI).

C. <u>With Potassium Chromate</u>. A four-fold excess
(3.1 x 10^{-2} mole or 6.0 g.) of potassium chromate was
treated with 1.67 x 10^{-2} mole (5 g.) of triphenylchloro-
silane in a manner similar to that of silver dichromate.
The mixture was refluxed for two days and at unevenly spaced
intervals 10 ml. samples of the reaction mixture were re-
moved and checked for a color change. The solution remained
clear and colorless for the forty-eight hour reaction period.
The mixture was filtered and condensed, and the infrared
spectrum of the white solid residue corresponded to that of
the starting material, triphenylchlorosilane.

D. <u>With Potassium Dichromate</u>. Similar amounts (grams)
of potassium dichromate and triphenylchlorosilane were re-
fluxed and stirred in methylene chloride. A reaction between
these two substances was not evident after twenty-one hours.

E. <u>With Sodium Dichromate</u>. A gram of triphenylchloro-
silane in five milliliters of methylene chloride was mixed
with approximately five grams of sodium dichromate in a six-
inch test tube. The mixture was shaken for ten minutes,
allowed to stand overnight, and then filtered. The colorless
filtrate indicated that a reaction had not occurred.

II. <u>Reactions of Diphenylchlorofluorosilane</u>.

A. <u>With Silver Chromate</u>. The procedure described below
for the reaction of silver chromate with diphenylchlorofluoro-
silane was the general method used for most of the syntheses

in this study and will apply to most of the succeeding reactions.

A three-fold excess of silver chromate (3.0×10^{-2} mole or 10 g.) which had been stored at 110° C., was added to 250 ml. of methylene chloride in a 500 ml. three-necked round bottom flask. All solvents used during this study were freshly distilled from drying agents, generally phosphorus pentoxide, and then stored over molecular sieves for no longer than three days. A reflux condenser and a dropping funnel were connected to the reaction vessel which was covered with aluminum foil. A continuous stream of oil-pumped nitrogen was passed through a sulfuric acid drying tower and then through the reaction system. The reacting compound was stirred by means of an internal magnet and heated by a mantle to maintain reflux conditions. A solution of 9.7×10^{-3} mole (2.3 g.) of diphenyl-chlorofluorosilane in fifty milliliters of methylene chloride was added to the silver chromate slurry dropwise over a period of thirty minutes. The reaction continued for a total of six and one-half hours.

When the reaction was complete, a filtering tube was connected to both the reaction vessel and a 500 ml. one-necked round bottom flask. The one inch (O. D.) tube was curved so that the standard taper male ends were separated by ninety degrees. A glass frit at the center of the bend allowed the separation of excess silver chromate from the solution in a

:1
30
Ta
13
va
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vit
ci
no
-78
ce
no
co
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i a
'Vp
Fig

relatively inert atmosphere. A decanting action was used in order to maintain a constant pressure throughout the system. The 500 ml. flask containing the product and solvent was transferred quickly to a rotary evaporator where the solvent was removed at pressures of approximately 1 mm. of Hg. One preparation was attempted using diethyl ether as the solvent; after fifteen hours no color change was observed.

Bis(diphenylfluorosilyl)chromate(VI) (80 to 90% yields) was a dark orange viscous liquid which failed to crystallize with numerous crystallizing techniques. The amount of silver chloride separated from the reaction residue was 1.01×10^{-2} mole (1.45 g.) (theory: 0.97×10^{-2} mole or 1.40 g.). At -78° C. the liquid froze to a red-orange glass which melted between -45 and -25° C. Attempts to purify the product by molecular distillation at 10^{-3} mm. of Hg and 80° C. and by column chromatography were unsuccessful. The product was purified to some extent by dissolving the viscous liquid in fresh methylene chloride, filtering, and evaporating the solvent. Trace amounts of solvent were removed at room temperature and a pressure of 10^{-3} mm. of Hg. Because of this crude purification technique, fresh product was prepared before each physical measurement to insure that decomposition would be at a minimum. Analytical data of bis(diphenylfluorosilyl)chromate-(VI) are given in Table V (p. 57) and the spectrum is shown in Figures 20 and 21 (p. 120 and 121).

B. **With Silver Dichromate.** A solution of 4.85×10^{-3} mole (1.15 g.) of diphenylchlorofluorosilane in methylene chloride was added to a three-fold excess of silver dichromate (1.15×10^{-2} mole or 5.00 g.). A reaction time of four hours for this synthesis was established by following the growth of the chromyl absorption in the visible spectrum. The reaction did not take place when pentane was used as the solvent. Characterization of the product revealed that diphenylchloro-fluorosilane and silver dichromate also yielded bis(diphenyl-fluorosilyl)chromate(VI). Crude yields of greater than ninety percent were obtained. Analytical data are shown in Table V (p. 57).

III. Reactions of Diphenyldifluorosilane.

A. **With Silver Chromate.** Pure diphenyldifluorosilane (0.105 mole or 23.0 g.) was added dropwise to twenty-five grams of silver chromate in a one hundred milliliter flask. The heterogenous mixture was stirred at room temperature for fifteen hours after which time no color change was observed. The mixture was then heated to 100° C. for another two hours and an infrared spectrum of the liquid phase was identical to that of diphenyldifluorosilane.

Three hundred milliliters of methylene chloride were added to this mixture. The components were refluxed for fifteen hours and again the lack of color and the infrared spectrum revealed that a reaction had not occurred.

B. **With Silver Dichromate**. Similar preparations were attempted using silver dichromate. In both instances, with and without a solvent, the reaction failed to take place. The product resulting from the reaction of diphenylchlorofluoro- silane and the unreactivity of diphenyldifluorosilane shows clearly that the silicon-fluorine bond in organochlorofluoro- silanes is quite stable under the conditions employed during this study.

IV. **Reactions of Diphenyldichlorosilane**.

A. **With Silver Chromate**. The preparation was performed using the general method described on p. 43 . A solution of 3.96×10^{-3} mole (1.00 g.) of diphenyldichlorosilane in methy- lene chloride was added to a slurry of a ten-fold excess of silver chromate (3.98×10^{-2} mole or 13.2 g.). The mixture was stirred at room temperature for two hours followed by isolation of the product in the manner described previously.

The product was a deep orange gum which was soluble in most organic solvents. The silver chloride obtained from the reaction was one hundred three percent of the calculated amount (7.92×10^{-3} mole) which indicated that both chloride groups of the diphenyldichlorosilane had been removed during the reaction.

Attempts to crystallize this oil were unsuccessful. The oil would not distil at 10^{-3} mm. of Hg and 50° C. and column chromatography proved unsatisfactory. The methods for preparing

this material for physical measurements varied with the
measurement being made. For qualitative elemental analysis
trace quantities of solvent were removed from the gum at
pressures of 10^{-3} mm. of Hg and 50° C. and then the material
was stored for at least two days in a vacuum oven at 60° C.
This treatment resulted in a brittle black glass which was
shown to be amorphous by an x-ray powder pattern. The spectra
were analyzed immediately after the reaction had been completed
and the product separated. This procedure was carried out in
order to minimize the amount of decomposed product present.
Specific syntheses were made before each molecular weight
determination and cryoscopic measurements immediately followed
each synthesis. After the reaction solvent had been removed
by evaporation, the product was washed with approximately fifty
milliliters of the very pure cryoscopic solvent (benzene) and
filtered. The bulk of this benzene was removed by rotary
evaporation and trace amounts at 50° C. and 10^{-3} mm. of Hg.
Analytical data are given in Table V (p. 57). This characteri-
zation indicated that this compound was the cyclic dimer of

$$\left[\begin{array}{ccccc} & O & & Ph & \\ & \| & & | & \\ Cr & - O - & Si & - O \\ & \| & & | & \\ & O & & Ph & \end{array}\right]_x \quad . \text{ The compound will therefore}$$
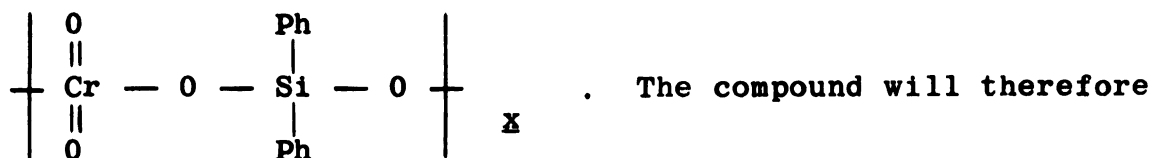
be designated as cyclo-bis[diphenylsiloxanylchromate(VI)].

Other synthetic techniques were employed in an attempt to prepare species larger than the dimer. Silver chromate (13.2 g.) was stirred vigorously in one liter of methylene chloride under anhydrous conditions. Diphenyldichlorosilane (1.00 g.) in two hundred milliliters of solvent was added to the chromate slurry by means of a Hershberg dropping funnel (111). The reaction was stopped at the end of this addition period (forty hours).

A mixture of twenty-five grams of silver chromate, 1.2 grams of diphenyldichlorosilane and ten milliliters of methylene chloride were sealed in a thick walled glass tube and heated to 100° C. for seventy hours.

In both cases the isolated product was the red-orange viscous liquid observed previously.

B. With Silver Dichromate. Two products resulted from the reaction of a large excess (4.9 x 10^{-2} mole or 21.0 g.) of silver dichromate with 3.96 x 10^{-3} mole (1.00 g.) of diphenyldichlorosilane. The reactants, in methylene chloride, were stirred at room temperature for twenty hours and separation followed the general procedure. Bright orange crystals formed as the solvent was removed. After the solution had been reduced to a minimal amount (10 ml.) the crystals were removed by filtration, washed with very dry, cold carbon tetrachloride and dried in an Abderhalden apparatus (112).

A deep red-orange viscous liquid was obtained by removal of the solvent from the filtrate fraction. Attempts to purify the crystalline fraction by recrystallization were unsuccessful for regardless of the purity of the solvent or the concentration of the solution, recrystallization did not occur and the crystals were not reformed with evaporation of the solvent. In all attempts the residue was a red-orange oil. For molecular weight determinations the crystals were washed with cold benzene instead of carbon tetrachloride. Yields of from ten to twenty percent of the crystalline organosiloxanylchromate were obtained while separation of silver chloride gave 8.16×10^{-3} mole (1.17 g.) (theory: 7.92×10^{-3} mole or 1.14 g.). Melting point determinations of the orange crystals showed a color change between 93 and 97° C., indicating decomposition. The thermal properties of this material are discussed in greater detail in relation to the analysis of its thermogram (p. 147). Purification treatments of the viscous oil were similar to those used for cyclo-bis[diphenylsiloxanyl-chromate(VI)]. The liquid product freezes to a glass at -78° C. and melts over a wide range between -50 and 0° C.

Elemental analyses established the basic structure of both
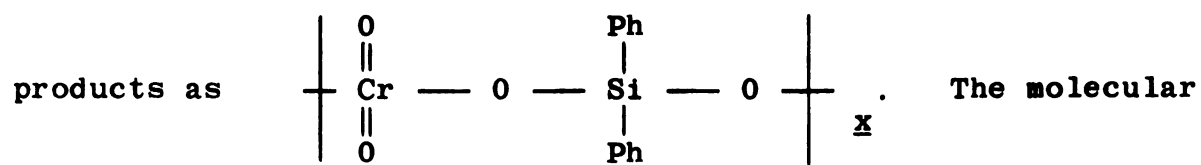
products as $\left[\begin{array}{c} O \\ \| \\ Cr \\ \| \\ O \end{array} - O - \begin{array}{c} Ph \\ | \\ Si \\ | \\ Ph \end{array} - O \right]_{\underline{x}}$. The molecular

weight and the nuclear magnetic spectrum of the crystalline material indicated that it was the cyclic trimer or cyclo-tris[diphenylsiloxanylchromate(VI)]. The analytical data of both reaction products are listed in Table V.

V.   Reaction of 3,3,3-trifluoropropylmethyldichlorosilane.

A. **With Silver Chromate.** The reaction of 1.19×10^{-2} mole (2.51 g.) of 3,3,3-trifluoropropylmethyldichlorosilane and a two-fold excess of silver chromate (2.4×10^{-3} mole or 8.0 g.) in methylene chloride occurred over a period of fifteen hours. The reaction mixture was transferred to a dry box for filtration, followed by removal of the solvent by means of rotary evaporation. Yields of from ninety to ninety-two percent of a very dark orange gum were obtained. The silver chloride recovered from the reaction (2.39×10^{-2} mole or 3.43 g.) agreed quite well with the theoretical value of 2.38×10^{-2} mole (3.42 g.). Purification of the crude product was accomplished by molecular distillation at 10^{-3} mm. of Hg at 50° C. Because of the photolytic instability of the viscous material, separate distillations were performed before each measurement. The complete distillation apparatus was sealed off and transferred to a dry box for the preparation of solutions for spectrophotometric examination. For molecular weight determinations and elemental analyses the distillation apparatus was dismantled in the vicinity of an analytical balance and

a swab of the viscous material was removed from the collection
tube with a nickel spatula. The spatula and liquid were
weighed and immersed in the appropriate solvent as quickly as
possible. Pure microanalytical samples were prepared by dis-
tilling into a narrow collection tube which then was sealed
at the reduced pressure. The orange oil, like other viscous
materials prepared during this study, froze at Dry Ice tempera-
ture and softened over a very wide temperature range. The
analytical and molecular weight data (Table X) suggests a

$$\text{cyclic dimer of the basic}\quad \left[\begin{array}{c} CH_2CH_2CF_3 \\ | \\ Si \\ | \\ CH_3 \end{array} - 0 - \begin{array}{c} 0 \\ \| \\ Cr \\ \| \\ 0 \end{array} - 0 \right]_x$$
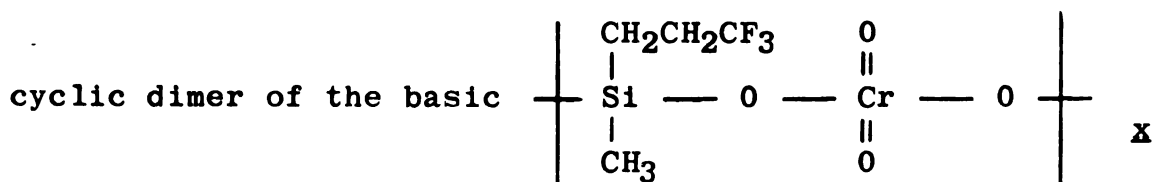
· unit or cyclo-bis[3,3,3-trifluoropropylmethylsiloxanyl-
chromate(VI)].

B. **With Silver Dichromate.** A ten-fold excess of silver
dichromate (4.73 x 10^{-2} mole or 20.4 g.) and 4.74 x 10^{-3} mole
(1.0 g.) of 3,3,3-trifluoropropylmethyldichlorosilane were
stirred for twelve hours in methylene chloride. A distillable
red-orange gum was produced in yields of ninety percent.
Separation and purification techniques were similar to those
used in the previous reaction. Ninety-eight percent of the
calculated amount of silver chloride was obtained from the
excess silver dichromate. The analytical date (Table X)

indicated a basic unit similar to the previous product, <u>i.e.</u>

$$\left[\begin{array}{c} CH_2CH_2CF_3 \\ | \\ Si \\ | \\ CH_3 \end{array} - O - \begin{array}{c} O \\ || \\ Cr \\ || \\ O \end{array} - O \right]_{\underline{x}}, \text{ and the molecular}$$
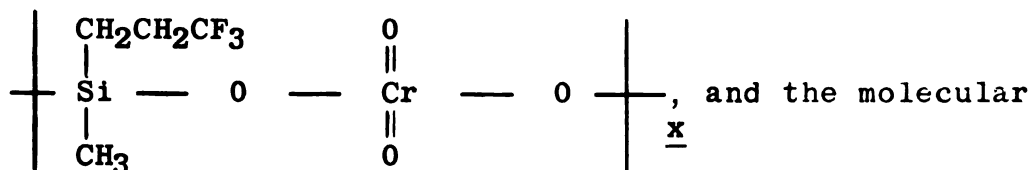
structure is believed to be the cyclic trimer or cyclo-tris[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)].

An unusual phenomenon was observed during the purification of this material. On several occasions the black tar-like residue left in the distillation apparatus ignited explosively when it was scraped with a nickel spatula. The residue from this violent reaction was a light green powder indicating the presence of a chromium(III) compound. Similar explosions were not observed with residues from the silver chromate 3,3,3-trifluoropropylmethyldichlorosilane reaction. The organic substituents in the residue are possibly oxidized by chromium(VI) in a manner similar to the explosive decomposition of bis(trimethylsilyl)chromate(VI); however, neither the reaction nor its products were investigated further.

VI. <u>Reaction of 3,3,3-trifluoropropylmethylsilanediol with Chromyl Chloride</u>. A solution of 5.08 x 10^{-3} mole (0.79 g.) of chromyl chloride in five hundred milliliters of methylene chloride was stirred magnetically in a three-necked one liter round bottom flask while a stream of dry nitrogen was passed over the solution and through a reflux condenser connected to

the reaction flask. A slurry of 9.34 x 10^{-3} mole (1.74 g.) of 3,3,3-trifluoropropylmethylsilanediol in one hundred milliliters of methylene chloride was added to this solution over a period of thirty minutes. The reaction was shown to be complete in one hour by following the disappearance of the "free" hydroxyl stretching frequency at 2.75 μ. Excess chromyl chloride was destroyed by addition of sodium bicarbonate to the reaction mixture until there was no longer any effervescence. The reaction mixture was filtered and the filtrate condensed with a vacuum rotary evaporator. The residue from the condensation was a bright orange liquid which yielded orange crystals from a concentrated methylene chloride solution at -78° C. The solvent was removed by decantation and the crystals melted slightly above Dry Ice temperatures. The extremely low melting point made the possibility of filtration difficult; therefore, purification was accomplished by crystallization at -78° C.; decantation of the excess solvent followed by removal of trace amounts of the solvents at 50° C. and 10^{-3} mm. of Hg. The analytical data, molecular weight, and nuclear magnetic resonance spectrum indicated that this substance was cyclo-bis [di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)].

Characterization of Reaction Products.

I. Reactions of Triphenylchlorosilane.

A. With Silver Chromate. The reaction of silver
chromate with triphenylchlorosilane gave high yields of
bis(triphenylsilyl)chromate(VI). This compound has been
prepared previously by other synthetic means (5, 10). The
chromium analyses (Table V) agreed well with the theoretical
values. Both the x-ray powder photograph and the vibrational
spectrum in the sodium chloride region were identical to the
results reported by Hare (5). The spectrum between 15-29 μ
(Table VII, p. 63) showed absorptions at 16.5, 19.5, and
22.4 μ which Smith (113) has assigned to in-the-plane ring
bending, out-of-plane ring bending, and the phenyl-silicon
antisymmetric stretching mode. The remaining peak at 21.2 μ
will be tentatively assigned to the Cr-O-Si symmetric stretch-
ing mode, and the absorption found between 11 and 12 μ to the
Cr-O-Si asymmetric stretching mode (a). The absorption between
20.6 and 21.2 μ was seen only with compounds containing the
Cr-O-Si linkage. The ratio of the intensities of the out-of-
plane ring bending to the Si-O-Cr absorption for bis(tri-
phenylsilyl)chromate(VI) and cyclo-bis [tetraphenyldisiloxanyl-
chromate(VI)] were 17 and 5 respectively, which compares

(a). These Cr-O-Si vibration assignments were tentatively
made with particular reference to their relative intensities,
order of occurence, and their similarity to Si-O-Si absorp-
tion frequencies (113).

favorably to calculated values of 3 and 1. The cesium
iodide spectrum of cyclo-bis[tetraphenyldisiloxanyl-
chromate(VI)] is shown in Figure 19 (p. 118).

B. **With Silver Dichromate.** It was predicted that the
reaction of silver dichromate and triphenylchlorosilane
would yield bis(triphenylsilyl)dichromate(VI). However,
extensive evaluations established conclusively that the
orange crystalline product was bis(triphenylsilyl)chromate(VI).
The analytical data shown in Table V agree well with the
chromate structure. The sodium chloride infrared spectrum
and the x-ray powder photograph are identical to the results
found by Hare (5) for bis(triphenylsilyl)chromate(VI). Exami-
nation of the spectrum of silver dichromate between 200 and
560 mμ (Figure 5, p. 104) shows a peak with its maximum at
343 mμ which has no counterpart in the spectrum of silver
chromate. This absorption results from the Cr-O-Cr linkage
(134) and was not observed with the silver dichromate tri-
phenylchlorosilane reaction product. It has also been shown
by Stammreich (114) that the Cr-O-Cr linkage has a weak sym-
metric vibration at 17.7 μ and a strong asymmetric vibration
at 13.1 μ. These absorptions were not observed in the spectrum
of the reaction product.

Although attempts to prepare silyldichromates failed
during this study, it is felt from the results of this investi-
gation that their preparation is possible. This topic is dis-
cussed in more detail in the section concerning recommendations
for future work.

TABLE V

ELEMENTAL ANALYSES OF PHENYL-SILOXYCHROMATES

Compound	bis(triphenyl-silyl)chromate-(VI)		bis(diphenyl-fluorosilyl)-chromate(VI)		cyclo-bis di-phenylsiloxanyl-chromate(VI)		cyclo-tris-[diphenyl-siloxanyl-chromate(VI)]
	from Ag_2CrO_4	from $Ag_2Cr_2O_7$	from Ag_2CrO_4	from $Ag_2Cr_2O_7$	from Ag_2CrO_4	from $Ag_2Cr_2O_7$	
r calc. (%)	8.19		10.03	10.03	17.45	17.45	17.45
found (%)	8.24		9.92	10.09	17.77	17.23	17.32
	8.23		10.00	9.84	17.46	17.27	17.34
			10.13	9.87	17.55		17.30
					17.39		
i calc. (%)		8.85	10.83		9.38		9.38
found (%)		9.08	11.01		9.54		9.47
		8.89	10.91		9.40		9.26
							9.23
calc. (%)		68.11	55.58		48.30	48.30	48.30
found (%)		67.10	51.96		46.91	47.93	47.54
		67.02	52.13		48.1		47.31
			52.85				
			53.46				
H calc. (%)		4.76	3.89		3.38	3.38	3.38
found (%)		5.60	4.22		3.37	3.93	3.58
		5.36	4.38		4.33		3.29
			4.28				
			4.40				
F calc. (%)			7.33				
found (%)			6.54				
			8.28				
O calc. (%)			12.34				
found (%)			14.34				
Molecular Weight calc.					597	597	895
found					541	463	902
					570	453	858
					574	470	835
							865

II. Reactions of Diphenylchlorofluorosilane with Silver Chromate and Silver Dichromate.

The deep orange liquid resulting from the reactions of diphenylchlorofluorosilane with silver chromate and silver dichromate had a silicon-chromium ratio of 2.02. The elemental analyses (Table V) of the remaining structural elements agreed fairly well with the calculated values for bis(diphenylfluorosilyl)chromate(VI).

The infrared spectrum (Figures 20 and 21, p.119 and 120) (Tables VI and VII) showed the normal silicon-phenyl absorptions. The presence of chromium in the molecule is confirmed by the unresolved Cr=O stretching absorption at 10.15 µ and the two Si-O-Cr vibrations at 11.17 µ (5) and 20.6 µ. The shoulder at 11.40 µ corresponds to the silicon-fluorine asymmetric stretching frequency (115). The weaker silicon-fluorine asymmetric deformation mode (115) appears at 17.4 µ in the cesium iodide region. The spectrum of bis(diphenyl-fluorosilyl)chromate(VI) from 240 to 600 mµ (Figure 6, p. 105) shows one chromyl absorption at 475 mµ with a molar extinction coefficient of 1.93 x 10^3. The intense phenyl absorption at 260 mµ masked the second chromyl absorption. This second chromyl absorption which occurred between 240 and 300 mµ did not appear in any of the siloxychromates containing phenyl groups. The presence of the ultraviolet chromyl absorption could possibly account for poor resolution of phenyl peaks. The deep orange viscous liquid was quite sensitive to light and

decomposed in direct sunlight. The material was soluble in aliphatic and aromatic hydrocarbons, alkylhalides, ether, acetone, dioxane, tetrahydrofuran, carbon disulfide, and pyridine; it was insoluble in water, formic acid, and mineral acids. The oil was soluble but decomposed in simple alcohols and acetic acid. When placed in water the liquid formed small droplets at the bottom of the container. These droplets changed to a light orange solid in approximately twelve hours after the solution had been made slightly acidic. This solid was identified as cyclo-bis [tetraphenyl-disiloxanylchromate(VI)] by means of its infrared spectrum, x-ray pattern, melting point, and chromium analysis. It is believed that hydrolysis of the fluorine-containing silyl-chromate occurred in the following manner:

Ph
|
Ph — Si...F...H⁺
| O H H
O = Cr = O $\xrightarrow[-2HF]{H_3O^+}$
|
O
|
Ph — Si...F...H⁺
| O
Ph H H

Ph
|
Ph — Si — O⁺(H)(H)
|
O
|
O = Cr = O $\xrightarrow{-2H^+}$
|
O
|
Ph — Si — O⁺(H)(H)
|
Ph

Ph
|
Ph — Si — OH
|
O
|
O = Cr = O
|
O
|
Ph — Si — OH
|
Ph

$\xrightarrow{-H_2O}$

O
||
Ph₂–Si–O–Cr–O–Si–Ph₂
              ||
              O
       | |
       O   O
       | |
Ph₂–Si–O–Cr–O–Si–Ph₂
              ||
              O
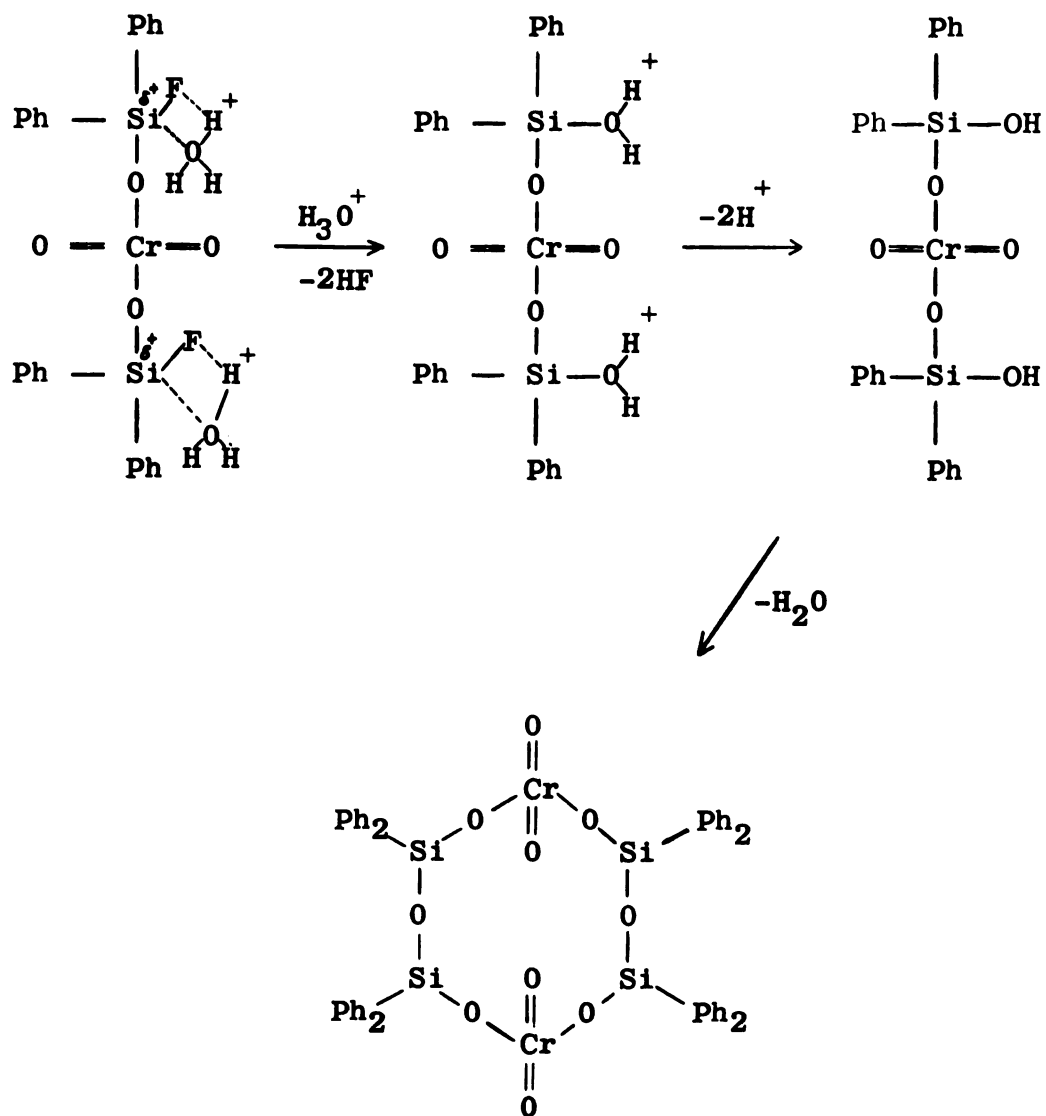
This reaction scheme resembles the mechanism proposed for the formation of cyclo-bis [tetraphenyldisiloxanylchromate(VI)] from chromyl chloride and diphenylsilanediol (5).

TABLE VI

INFRARED SPECTRA OF PHENYL-SILOXYCHROMATES (2-15 μ)

Peak	Reference Absorption (μ)	Assignment	Ref.	bis(diphenyl-fluorosilyl-chromate(VI))		cyclo-bis[diphenylsiloxanyl-chromate(VI)] from Ag2CrO4		from Ag2Cr2O7		cyclo-tris[di-phenylsiloxanyl-chromate(VI)]	
			Solvent→	CCl$_4$ (μ)	I	CCl$_4$ (μ)	I	CCl$_4$ (μ)	I	CCl$_4$ and CS$_2$ (μ)	I
1	2.7	"Free" Si-OH stretch	116								
2	3.25	C-H aromatic stretching mode	121			3.29	w(a)	3.32	b(a)	3.30	w, b
3	3.30	C-H symmetric stretching mode	115	3.35	m(a)	3.36	sh				
4	6.25	C=C ring stretching mode	121							6.28	w
5	6.99	Ph-Si stretch	121	7.05	m	7.00	m	7.01	m	7.02	m
6	7.97	Ph-Si ring deformation	121			7.94	s(a)	7.97	w	7.90	vw(a)
7	8.9	Si-C stretch (Ph-Si)	122	8.92	s(a)	8.91	s	8.90	s	8.91	s
8	(b)	Si-C stretch (Ph$_2$Si)	115	8.99	sh(a)	9.00	sh	8.98	sh	8.98	sh
9	9.3-9.8	Si-O-Si asymmetric stretch	117 118 119								
10	9.68	Si-Ph characteristic mode	121	9.82	sh	9.75	sh				

TABLE VI (cont.)

Peak	Reference Absorption (μ)	Assignment	Ref.	bis(diphenylfluorosilyl)chromate(VI) CCl$_4$ (μ)	I	cyclo-bis[diphenylsiloxanyl]chromate(VI) from Ag$_2$CrO$_4$ CCl$_4$ (μ)	I	from Ag$_2$Cr$_2$O$_7$ CCl$_4$ (μ)	I	cyclo-tris[diphenylsiloxanyl]chromate(VI) CCl$_4$ and CS$_2$ (μ)	I
11	10.1	Cr=O asymmetric stretch	12	10.15	m	10.12	s	10.14	s	10.11	vs
12	10.3	Cr=O asymmetric stretch	12			10.26	sh	10.28	sh	10.27	sh
13	11-12	Cr-O-Si asymmetric stretch	5(c)	11.17	vs(a)	11.08	vs	11.05	vs	11.13	vs
14	11.5	Si-F asymmetric stretch	123	11.40	sh						
15	13.5	Phenyl, out-of-plane ring deformation	121							13.60	m
16	13.6	Phenyl, out-of-plane ring deformation	121							13.97	m
17	14.3	Phenyl, out-of-plane ring deformation	121	14.40	s	14.42	s	14.40	s	14.43	s

(a) w-weak; vs-very strong; s-strong; m-medium; b-broad; sp-sharp; sh-shoulder.
(b) The 8.9 μ silicon-phenyl absorption often resolves into two peaks when two phenyl groups are present on the same silicon, but reverts to a single band with Ph$_3$Si groups.
(c) (cf. p. 6 and 97)

TABLE VII

INFRARED SPECTRA OF PHENYL-SILOXYCHROMATES (15-29 μ)

Peak	Reference Absorption (μ)	Assignment	Ref.	bis(triphenylsilyl)chromate(VI)	cyclo-bis[tetraphenyl-disiloxanylchromate(VI)]	bis(diphenylfluorosilyl)chromate(VI)	cyclo-bis[diphenylsiloxanylchromate(VI)] from Ag_2CrO_4	cyclo-bis[diphenylsiloxanylchromate(VI)] from $Ag_2Cr_2O_7$	cyclo-tris[diphenyl-siloxanylchromate(VI)]
		Solvent		CS_2	CS_2	CCl_4	CCl_4	CS_2	CS_2
	(μ)			(μ) I	(μ) I	(μ) I	(μ) I	(μ) I	(μ) I
18	16.2	Si-Ph in-the-plane ring bending	113	16.5 w(a)	16.1 w	16.1 m(a)	15.6 w	15.6 w	15.5 m
19		Si-F asymmetric deformation				17.4 m			
20	17.0-17.5	Si-O-Si symmetric stretch	113		16.9 m,b(a)				
21	20.7	Si-Ph out-of-plane ring bending	113	19.5 s(a)	19.3 s	19.5 vs(a)	19.6 s	19.6 s	19.6 vs
22		Cr-O-Si symmetric stretching mode	113 (b)	21.2 m(a)	20.8 m	20.6 w	20.9 m	20.7 m	20.9 s
23	22.4	Si-Ph antisymmetric stretching mode	113	22.4 w	22.1 w	21.2 sh(a)	21.7 w	21.9 w	21.9 w

(a) w-weak; vs-very strong; s-strong; m-medium; b-broad; sh-shoulder.
(b) (cf. p. 97)

III. **Reactions of Diphenyldichlorosilane.**

A. With Silver Chromate. The reaction of silver chromate
with diphenyldichlorosilane yielded a deep orange viscous
liquid. The chemical analyses (Table V) gave a silicon-
chromium ratio of 1.00 and the carbon hydrogen analyses were
in good agreement with the calculated percentages for

$$
\left[\begin{array}{c} Ph \\ | \\ Si \\ | \\ Ph \end{array} - O - \begin{array}{c} O \\ \| \\ Cr \\ \| \\ O \end{array} - O \right]_{\underline{x}} .
$$
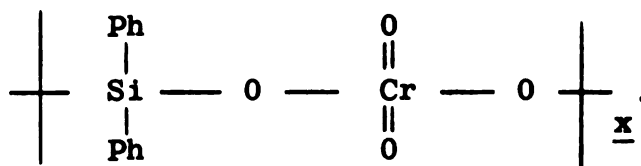
Cryoscopic molecular weight determination of 574, 541,
and 570 corresponded fairly well to the calculated value
for the dimer, 597. The infrared spectrum (Figures 22 and
23, p. 121 and 122) (Tables VI and VII) exhibited the normal
silicon-phenyl absorption frequencies in both the sodium
chloride and the cesium iodide regions. The chromyl absorp-
tions were present at 10.12 and 10.26 μ. A broad and strong
Cr-O-Si asymmetric stretching vibration appeared at 11.08 μ
and the weaker symmetric mode at 20.9 μ. The absence of a
Si-O-Si absorption at either 9.2-9.8 μ (116) or 17.0-17.5 μ
(113) tends to substantiate the A-B-C structure type.

Termination of the dimeric unit could be accomplished by
cyclization or end-blocking. In characterizing a linear
siloxyanylchromate as being end-blocked with hydroxyl groups,
Hare (5) rested the full burden of proof for the existence

of these two terminating ligands upon the free hydroxyl stretching frequency at 2.7 μ. Examination of the spectrum of bis(hexaphenyl-6-hydroxotrisiloxyanyl)chromate(VI) reveals a minute shoulder at approximately 2.7 μ. This absorption could be traced to background noise, the presence of small amounts of starting material (diphenylsilanediol) or to a solvent containing water.

The fact that the diphenyldichlorosilane-silver chromate reaction product was a liquid at room temperature and becomes a glass-like material at -78° C. is highly indicative that the structure is not cyclic. A cyclic (therefore symmetrical) molecule having such a high molecular weight would be expected to be a solid under normal conditions. This conjecture, however, is strictly intuitive and is far from being conclusive. The spectrum of the dimer gave an extremely weak shoulder at 2.95 μ which in all honesty cannot be assigned to the Si-OH stretching mode for the reasons stated previously. The viscous liquid hydrolyzed to cyclo-bis[tetraphenyldisiloxanylchromate(VI)] in a slightly acidic solution. Both proposed structures could lead to this product. The hydrolytic cleavage of the cyclic compound would yield the hydroxyl-terminated form. Hydrolysis of this linear structure would give chromic acid and bis(diphenylhydroxosilyl)chromate(VI) which in turn dehydrates to cyclo-bis-[tetraphenyldisiloxanylchromate(VI)]. Examination of the bond angles and lengths show that the cyclic structure is

feasible (5) and that little or no intramolecular stress would be developed.

Hare (5) produced several trialkylsilylchromates and assigned the Cr-O-Si stretching vibration to the region between 11 and 12 μ. It can readily be seen from the tabulation below that all but one of these linear silylchromates absorb above 11.4 μ.

TABLE VIII

THE CHROMIUM-OXYGEN-SILICON INFRARED ABSORPTION FREQUENCIES
OF SEVERAL ORGANOSILOXY CHROMATES

Compound	Ref.	Si-O-Cr μ	Stretch
1 $(Me_3Si)_2CrO_4$	5	12.1	vs
2 $(Ph_3Si)_2CrO_4$	5	11.4	vs
3 (p-tol*$Ph_2Si)_2CrO_4$	5	11.5	vs
4 $(Ph_2ch*Si)_2CrO_4$	5	11.4	vs
5 $(Ch_3Si)_2CrO_4$	5	11.6	vs
6 $(Ph_6Si_3O_2OH)_2CrO_4$	5	11.5	s broad
7 $(Ph_2FSi)_2CrO_4$		11.2	vs
8 $[(Ph_4Si_2O)CrO_4]_2$	5	11.0	vs
9 $(Ph_2SiCrO_4)_3$		11.1	vs
10 $(Ph_2SiCrO_4)_2$		11.1	vs

*p-tol = p-tolyl;   ch = cyclohexyl

The Cr-0-Si absorption of bis(diphenylfluorosilyl)-chromate(VI) at wavelengths lower than the other linear siloxychromates is easily understood for it is well known that fluorine increases the stretching frequencies for adjacent groups (113). The Cr-0-Si stretching vibration of the known cyclic siloxanylchromates (Nos. 8 and 9) appear at lower wavelengths (11.0 to 11.1 μ). Several extensive and conclusive infrared studies dealing with the Si-0-Si asymmetric stretching frequencies of linear and cyclic siloxanes(117, 118, 119) have shown that the cyclic siloxanes absorb at lower wavelengths than linear siloxanes. It is therefore possible to draw a parallel between these results and the Cr-0-Si vibrations shown above. This would suggest that the dimer in question could well be cyclic for the Cr-0-Si asymmetric stretching vibration occurs at 11.1 μ. It should also be noted at this point that the above argument would favor Hare's characterization of bis(hexaphenyl-6-hydroxotrisiloxanyl)chromate(VI) as being end-blocked for this substance shows an asymmetric Cr-0-Si absorption at 11.5 μ. The Si-0-Si asymmetric stretching mode of open-chain siloxanes containing more than one Si-0-Si group resolved into separate peaks for each Si-0-Si linkage present in the molecule while cyclic siloxanes yield only one absorption maximum regardless of the number of siloxy-linkages present. This phenomenon has been observed with linear organosiloxanes with as many as five

3

linkages (117, 119). The Si-O-Si symmetric vibration at

higher wavelengths also shows this characteristic (113).

Hare (5) obtained a bright red viscous oil when he treated

dicyclohexylsilanediol with chromium(VI) oxide which he

characterized as hydroxo {penta[dicyclohexylsiloxanyl-

chromate(VI)]} dicyclohexylsilanol, or

```
      Ch    O    Ch    O    Ch    O    Ch    O    Ch    O    Ch
      |     ‖    |     ‖    |     ‖    |     ‖    |     ‖    |
HO-Si-O-Cr-O-Si-O-Cr-O-Si-O-Cr-O-Si-O-Cr-O-Si-O-Cr-O-Si-OH.
      |     ‖    |     ‖    |     ‖    |     ‖    |     ‖    |
      Ch    O    Ch    O    Ch    O    Ch    O    Ch    O    Ch
```
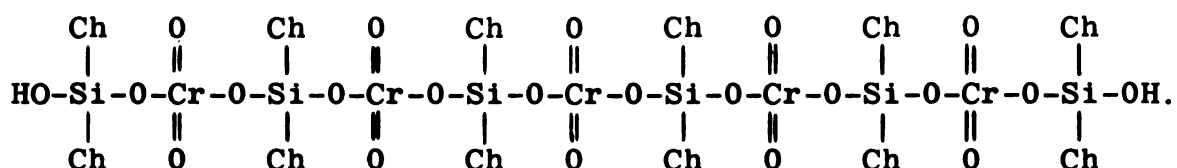
The infrared spectrum between 11 and 12 μ gave two strong

absorption maxima, two definite shoulders, and with a great

deal of imagination the fifth Cr-O-Si asymmetric stretching

mode can be discerned. This evidence although far from being

conclusive indicates very strongly that the Cr-O-Si stretching

frequencies exhibits the same resolution phenomenon shown by

linear siloxanes. Both Cr-O-Si stretching frequencies of the

diphenylsiloxanylchromate(VI) dimer were unresolved, lending

further evidence to the possibility of a cyclic structure.

The proton magnetic resonance spectrum of this oil was

determined in carbon tetrachloride using a Varian A-60 proton

magnetic resonance spectrometer. With a linear hydroxyl end-

blocked material three absorption peaks would be expected, one

rather intense phenyl hydrogen peak and two weaker hydroxyl

hydrogen absorptions. The hydroxyl absorptions would be split,

$$\text{for in} \quad HO \left| \begin{array}{c} Ph \\ | \\ Si \\ | \\ Ph \end{array} \right. — O — \left. \begin{array}{c} O \\ \| \\ Cr \\ \| \\ O \end{array} \right|_2 OH \quad \text{one hydrogen}$$
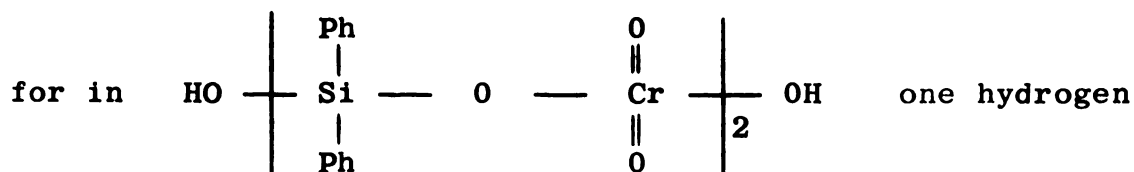
would be influenced by silicon and the other by chromium. The Si-OH hydrogen generally absorbs in the vicinity of 80 c.p.s. (11). The liquid dimer showed only one intense peak at 460 c.p.s. which corresponds well with the spectrum of cyclo-tris-[diphenylsiloxanylchromate(VI)] (Figure 1, p. 73) and the phenyl hydrogen absorption at 460 c.p.s. shown by cyclo-bis-[tetraphenyldisiloxanylchromate(VI)] (11).

The possibility of a linear structure with a terminating linkage other than hydroxyl groups was not investigated. It is fairly obvious from the bias emanating from the above discussion that the author favors the cyclic structure; however, the assignment of a cyclic structure to the diphenylsiloxanyl-chromate(VI) dimer is made with considerable reservation.

This deep orange liquid becomes exceedingly more viscous and eventually turned to a black brittle solid on standing in a vacuum oven at 60° C. The x-ray powder pattern of the brittle glass-like material had two wide bands at 6.7 and 19.3 Å indicating a very low order of crystallinity. The liquid was soluble in numerous aliphatic and aromatic hydrocarbons, alkyl halides, and carbon disulfide; it decomposed in simple

alcohols. The material, like most siloxychromates, decomposed in the presence of light. It also decomposed slowly in water, and as mentioned previously, it changed fairly rapidly to cyclo-bis [tetraphenyldisiloxanylchromate(VI)] in the presence of a weak acid.

The spectrum between 240 and 600 mµ of bis[diphenylsilox-anylchromate(VI)] (Figure 7, p. 106) exhibited two absorption maxima, the chromyl peaks at 475 mµ and the unresolved phenyl absorption at 246 mµ. The molar extinction coefficient for the chromyl absorption was 8.1 x 10^3.

B. **With Silver Dichromate**. The bright orange crystal-line solid resulting from the reaction of diphenyldichloro-silane with silver dichromate had a silicon-chromium ratio of 1.00, and the carbon-hydrogen analyses (Table V) also agreed with the calculated values for a basic diphenylsiloxanyl-chromate(VI) structure. The infrared spectrum from 2-29 µ (Figures 24 and 25, p. 123 and 124) (Tables VI and VII) showed the normal vibrations associated with silicon-phenyl linkages. The chromyl absorptions were resolved at 10.11 and 10.27 µ, and the Cr-O-Si asymmetric stretching mode appeared at 11.13 µ. The Cr-O-Si symmetric stretching mode at 20.9 µ was considerably stronger than similar absorptions seen with other siloxanyl and silylchromates. The two Si-O-Si stretch-ing vibrations which normally appear at 9.3-9.8 µ and 17.0-17.5 µ were not present. The analytical and infrared data

therefore suggest that the compound is constructed from the

basic $-\!\!\!\!\left|\begin{array}{c} Ph \\ | \\ Si \\ | \\ Ph \end{array}\right.\!\!\!\!- O -\!\!\!\!\begin{array}{c} O \\ \| \\ Cr \\ \| \\ O \end{array}\!\!\!\!- O \left.-\!\!\!\!\right|_{\underline{x}}$ unit. Molecular
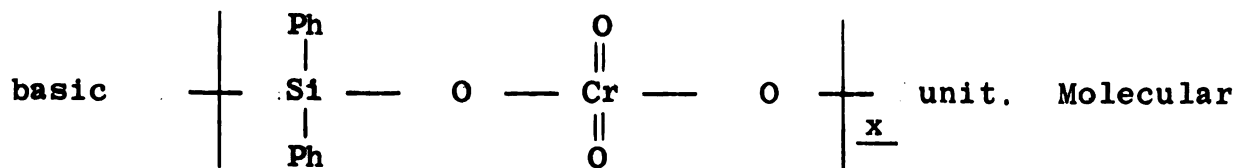
weight determination (Table V) indicates that the crystals are a trimer of this unit.

The proton magnetic resonance spectrum of these crystals (Figure 1, p. 73) was obtained in a mixed carbon tetrachloride-carbon tetrabromide solvent, a rather. intense absorption maximum at 463 c.p.s. was the only peak observed. This absorption was quite similar in appearance to the 460 c.p.s. phenyl-hydrogen peak of cyclo-bis[tetra-phenyldisiloxanylchromate(VI)] (11).

The infrared spectrum also indicated that the compound was cyclic. An Si-OH absorption at 2.7 μ was very definitely not present. The Cr-O-Si asymmetric stretching frequency appears at wavelengths lower than those normally shown by linear siloxychromates and both the asymmetric and symmetric Cr-O-Si absorptions were obviously singular in nature.

The x-ray powder diffraction pattern of cyclo-tris-[diphenylsiloxanylchromate(VI)] (Table XI) gave rather large values, indicating a large unit cell. An attempt at indexing these interatomic spacings was unsuccessful; however, it was

shown that the crystal was not cubic and a comparison of the spacings with the Hull-Davey charts (120) indicated that it might possibly be hexagonal.

The visible and ultraviolet spectrum between 240 and 600 mμ (Figure 7, p. 106) showed a chromyl absorption at 490 mμ with a molar extinction coefficient of 2.4 x 10^3. The phenyl absorption occurred at 268 mμ.

The crystals were soluble in most organic solvents; however, like cyclo-bis [tetraphenyldisiloxanylchromate(VI)] the degree of solubility was much less than that of liquid siloxychromates. Once dissolved, cyclo-bis [diphenylsilox- anylchromate(VI)] could not be made to recrystallize. Re- evaporation of the solvent left a red-orange oil. Hydrolysis in an acidic medium resulted first in an orange gum and then cyclo-bis [tetraphenyldisiloxanylchromate(VI)]. It is believed that the crystals were initially changed to cyclo-bis[diphenyl- siloxanylchromate(VI)] and then by hydrolysis and subsequent dehydration to the light orange crystals of cyclo-bis[tetra- phenyldisiloxanylchromate(VI)].

The material was light sensitive but to a much less degree than any siloxychromates prepared to date. The thermal proper- ties of cyclo-tris[diphenylsiloxanylchromate(VI)] are covered in the Discussion section.

The elemental analyses of the liquid product resulting from the reaction of diphenyldichlorosilane with silver
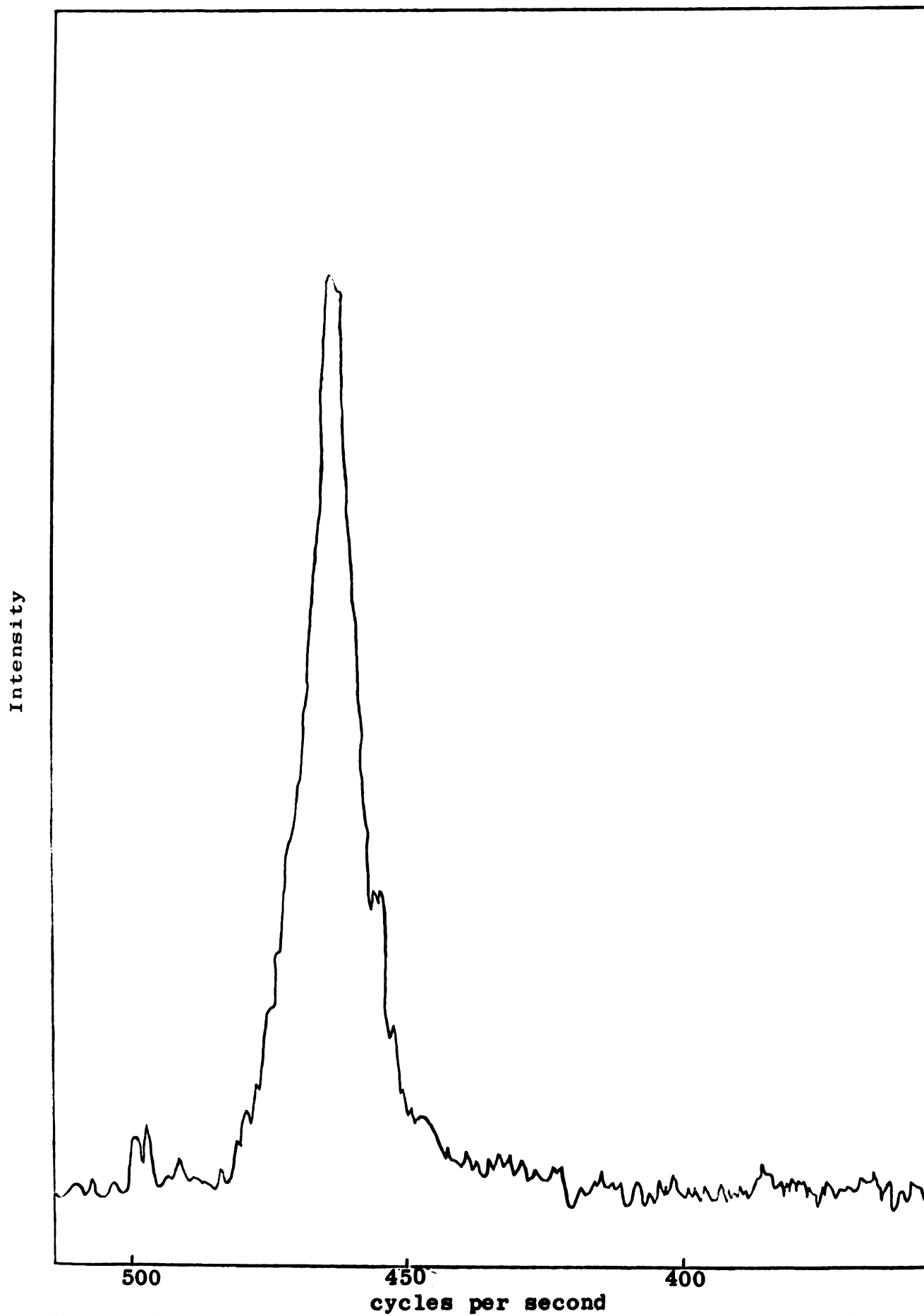
Figure 1.   Proton magnetic resonance spectrum of cyclo-tris-
[diphenylsiloxanylchromate(VI)].

TABLE IX

INTERATOMIC SPACINGS FOR CYCLO-BIS [DIPHENYLSILOXANYLCHROMATE(VI)]

(Cr K_α radiation, $\lambda = 2.2909$ Å)

Line	θ (Degrees)	d_{hkl} (Å)	Relative Intensity
1	6.97	9.42	10
2	7.35	8.95	2
3	7.95	8.28	2
4	8.85	7.45	5
5	9.53	6.92	5
6	10.55	6.25	4
7	10.78	6.13	4
8	12.35	5.35	1
9	13.63	4.86	2
10	14.23	4.66	8
11	14.90	4.45	10
12	16.45	4.05	6
13	17.05	3.91	1
14			<1
15			<1
16	19.28	3.47	4
17	20.00	3.35	1
18	20.80	3.23	4
19	23.10	2.92	1
20	23.73	2.85	1
21	24.43	2.77	1

dichromate were in fair agreement with calculated values for

the $\quad$ structure (Table V).

$$\left[\begin{array}{c} \text{O} \\ \| \\ \text{Cr} \longrightarrow \text{O} \longrightarrow \begin{array}{c} \text{Ph} \\ | \\ \text{Si} \\ | \\ \text{Ph} \end{array} \longrightarrow \text{O} \end{array}\right]_x$$
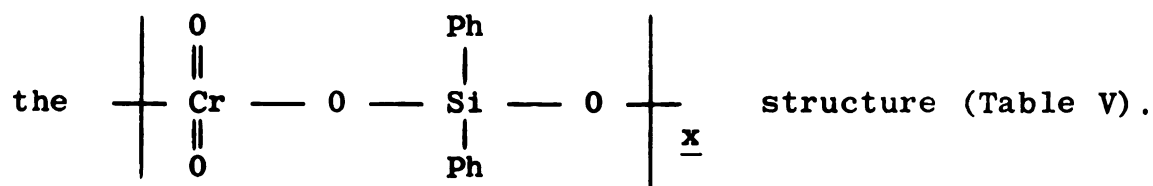
The infrared spectrum between 2 and 29 μ (Figures 26 and 27,

p. 125 and 126) (Tables VI and VII) was identical to that of

cyclo-bis[diphenylsiloxanylchromate(VI)] . There was no

visible evidence of an Si-OH absorption in the range of 2.7 μ,

and the Cr-O-Si (11.05 μ) absorption appeared at a lower

wavelength than linear siloxychromates.

The red-orange liquid was soluble in most organics but

decomposed to cyclo-bis [tetraphenyldisiloxanylchromate(VI)]

in water.

The spectrum between 240 and 600 mμ of the liquid sub-

stance showed absorptions at 475 and 265 mμ with molar ex-

tinction coefficients quite similar to cyclo-bis[diphenyl-

siloxanylchromate(VI)].

So far all the evidence given has been identical to that

shown by cyclo-bis[diphenylsiloxanylchromate(VI)]; however,

the values obtained during molecular weight determinations

this material (Table V) were all somewhat lower than the cal-

culated molecular weight for the dimer, 597.

It is the belief of this investigator that the liquid

was cyclo-bis [diphenylsiloxanylchromate(VI)] and that the low

molecular weight values resulted from small amounts of an impurity not removed by the somewhat crude purification techniques. This impurity was quite possibly a by-product which formed during the silver dichromate diphenyldichlorosilane reaction but did not appear during the silver chromate synthesis. The mechanisms proposed for these reactions (cf. p. 161 and 162) indicate that the situation could exist.

IV. **Reactions of 3,3,3-trifluoropropylmethyldichlorosilane.**

A. **With Silver Chromate.** The reaction of 3,3,3-trifluoropropylmethyldichlorosilane with silver chromate resulted in a distillable deep orange viscous liquid. Elemental analyses (Table X) showed a silicon-chromium ratio of 1.00. The carbon-hydrogen determinations were in fair agreement with the calculated values for 3,3,3-trifluoropropylmethylsiloxanylchromate(VI).

The infrared spectrum (Figures 32 and 33, p. 131 and 132) (Table XI) gave the normal vibrational modes associated with the 3,3,3-trifluoropropyl and methyl-silicon linkages. The chromyl stretching absorptions were very well resolved and occurred at their predicted frequency. The Cr-O-Si asymmetric stretching mode appeared at a slightly lower wavelength (10.9 μ) than those shown by phenylsiloxychromates. This shift could be attributed to the fluorines; however, their influence on the Si-O-Cr stretch should be very slight

TABLE X

ELEMENTAL ANALYSES OF 3,3,3-TRIFLUOROPROPYLMETHYLSILOXANYLCHROMATES

Compound	Cr		Si		C		H		F		Mol. Wt.	
	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc.	Found
Cyclo-bis[3,3,3-tri-fluoropropylmethyl-siloxanylchromate(VI)]	20.30	20.22 20.11 20.07 20.48	10.96	10.95 11.04 10.96 10.99	18.75	19.29	2.76	2.90	22.50	30.76	512	340 659 596 565
Cyclo-tris[3,3,3-trifluoropropyl-methylsiloxanyl-chromate(VI)]	20.30	20.31 20.13	10.96	10.67 10.70	18.75	18.49 18.45	2.76	2.67 3.40	22.50	25.92	769	834 921 848
Cyclo-bis[di-3,3,3-trifluoropropyl-dimethyldisiloxanyl-chromate(VI)]	12.61	12.44 12.53 12.56 12.52	13.62	13.48 13.41 13.55 13.49	23.30	23.03 23.28	3.42	3.35 3.41			825	826 807 790 751

for they are in a gamma position to the silicon. The
Cr-O-Si symmetric vibration for the orange liquid occurred
at 21.0 µ and was singular in nature. Both Si-O-Si stretch-
ing modes were absent from the spectrum.

Cryoscopic molecular weight measurements (Table X) indi-
cated that the compound was a dimer of 3,3,3-trifluoropropyl-
methylsiloxanylchromate(VI).

The termination of the molecule would be expected to be
similar to that of the phenylsiloxychromates -- i.e., either
cyclic or terminated with hydroxyl groups. A definite absorp-
tion occurred at 2.92 µ which was high for the "free" silicon-
hydroxyl vibration. The infrared examination of silanols in
the solid state have shown wavelength absorptions as high as
3.1 µ while solutions of these same compounds had Si-OH
stretching modes at 2.7 µ. This solid state vibrational shift
was attributed to hydrogen bonding between adjacent silanol
molecules (119). It could be postulated that the 2.92 µ ab-
sorption in bis[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)]
resulted from a Si-OH shift caused by intramolecular hydrogen
bonding between the hydroxyl proton and the fluorine substitu-
ents of the molecule. The spectrum of 3,3,3-trifluoropropyl-
methylsilanediol (Figure 30, p. 129) shows the Si-OH absorption
at 2.7 µ. If the postulate were correct, this stretching mode
would be similarly displaced. Therefore, assignment of the
2.92 µ peak to hydroxyl stretching was not possible.

In characterizing the termination of phenylsiloxanylchromate molecules, a great deal of emphasis was placed upon the shift exhibited by the Cr-O-Si asymmetric stretching vibration. A similar approach with the 3,3,3-trifluoropropylmethylsiloxanylchromates is somewhat limited in that linear siloxychromates containing the 3,3,3-trifluoropropyl group have not been prepared. The Cr-O-Si asymmetric stretching mode for bis(trimethylsilyl)chromate(VI) (Table VIII) appears at 12.1 μ (5), which is the longest wavelength reported for organosiloxy chromates. It could be assumed that any linear siloxychromate with a methyl-silicon linkage would have a Cr-O-Si absorption appearing somewhere between 11.5 and 12 μ. Later in this discussion the cyclic nature of cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)] will be established. The asymmetric Cr-O-Si stretching mode for this compound occurs at 10.90 μ. The same vibration for bis[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)] appears at 10.90 μ, indicating the possibility that the structure is cyclic. The Cr-O-Si stretching vibrations are both singular in nature, lending further evidence to a cyclic structural assignment.

The orange liquid product from the reaction of 3,3,3-trifluoropropylmethyldichlorosilane with silver chromate was very sensitive to light and decomposed quickly in direct sunlight to a black gum. The material was soluble in pyridine, ethyl cellosolve, dimethylformamide, dioxane, and chloro-

benzene but only slightly soluble in ether, carbon disulfide,
and aromatic or aliphatic hydrocarbons. The solubility of
this liquid in simple alkylhalides decreased as the number of
attached chloride groups increased; it was only very slightly
soluble in carbon tetrachloride. The most surprising proper-
ties of these fluoroorganosiloxychromates was their solubility
and apparent stability in water. The liquid did not appear to
be affected by cold mineral acids or alkali but decomposed to
green solutions upon heating. It is fairly obvious that the
substitution of a fluoroalkyl group on the silicon greatly
increased the hydrolytic stability of the siloxychromates.

The spectrum of cyclo-bis[3,3,3-trifluoropropylmethyl-
siloxanylchromate(VI)] in the visible and ultraviolet region
(Figure 8, p. 107) exhibited two distinct absorptions. The
chromyl peak occurring at 498 mμ with an extinction coefficient
of 6.50 x 10^3 was observed with all phenylsiloxychromates. The
spectrum showed a second absorption at 250 mμ which also re-
sulted from chromyl absorption (Figure 5, spectra of Ag_2CrO_4
and $Ag_2Cr_2O_7$). The ultraviolet spectrum of 3,3,3-trifluoro-
propylmethyldichlorosilane was void of absorptions, therefore
eliminating the possibility that the ultraviolet peak of
cyclo-bis[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)]
resulted from either organic group in the molecule. The molar
extinction coefficient for this peak was 9.55 x 10^3.

INFRARED SPECTRA OF 3,3,3-TRIFLUOROPROPYLMETHYLSILOXANYLCHROMATES AND RELATED COMPOUNDS

Peak	Reference Absorption (μ)	Assignment	Ref.	3,3,3-trifluoropropylmethyldichlorosilane (CCl$_4$ & CS$_2$) (μ)	I	3,3,3-trifluoropropylmethylsilanediol (CCl$_4$ & CS$_2$) (μ)	I	cyclo-bis-[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)] (CCl$_4$ & CS$_2$) (μ)	I	cyclo-tris-[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)] (CCl$_4$ & CS$_2$) (μ)	I	cyclo-bis-[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate-(VI)] CCl$_4$ (μ)	I
				Solvent→									
1	2.72	"free" Si-OH stretch	116			2.75	m, sp(a)						
2	2.92	(b)				3.02	m, b (a)	2.92	w(a)				
3	3.35	C-H antisymmetric stretching mode	115							3.25	w,b	3.27	w,b
4	3.41	CH_2 antisymmetric stretching mode	115	3.42	w	3.42	w	3.42	w				
5	3.45	CH_2 symmetric stretching mode	115					3.46	vw(a)	3.45	vw	3.47	m
6	6.90	Silicon-(n-propyl)	115	6.92	m	6.93	m	6.94	m	6.92	vw	6.97	m
7	7.10	Si-CH_3 anti-symmetric deformation	115	7.07	w	7.07	w	7.07	w	7.11	vw	7.08	w
8	7.35	Silicon-(n-propyl)	115	7.30	m	7.32	m	7.31	s	7.30	w	7.35	m

(a) (p. 63),   (b)   (p. 78)

TABLE XI (cont.)

INFRARED SPECTRA OF 3,3,3-TRIFLUOROPROPYLMETHYLSILOXANYLCHROMATES AND RELATED COMPOUNDS

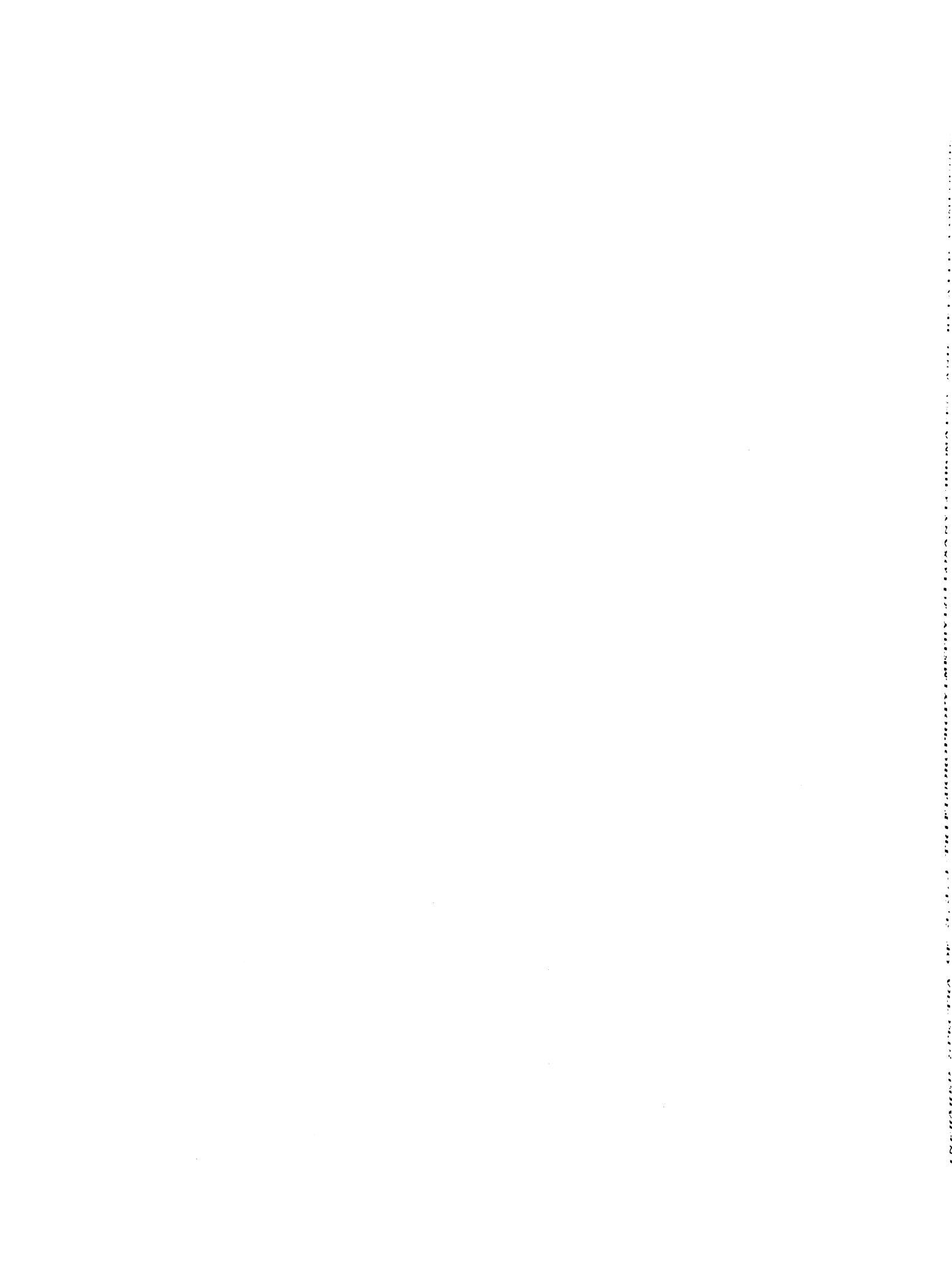| Peak	Reference Absorption (μ)	Assignment	Ref.	3,3,3-trifluoropropylmethyl-dichlorosilane		3,3,3-trifluoropropylmethylsilanediol		cyclo-bis-[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)]		cyclo-tris-[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)]		cyclo-bis-[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate-(VI)]	
			Solvent→	CCl$_4$ & CS$_2$		CCl$_4$ & CS$_2$		CCl$_4$ & CS$_2$		CCl$_4$ & CS$_2$		CCl$_4$	
	(μ)			(μ)	I	(μ)	I	(μ)	I	(μ)	I	(μ)	I
9	7.56	CF$_3$ symmetric stretch	124 125	7.60	m	7.64	m	7.62	s	7.65	m	7.65	m
10	7.90	Si-CH$_3$ symmetric deformation	115	7.96	s	7.95	s	7.96	vs(a)	7.97	vs	7.96	vs
11	8.51	CF$_3$ antisymmetric stretch	125 126 135	8.32	vs	8.30	s	8.32	vs	8.32	vs	8.29	vs
12	8.73	CF$_3$ antisymmetric stretch	125 126 135	8.83	vs	8.88	s	8.85	vs	8.87	vs	8.85	vs
13	9.30	Silicon-(n-propyl)	115	9.26	sh(a)	9.25	sh	9.22	sh	9.22	sh		
14	9.3-9.8	Si-O-Si asymmetric stretch	117 118 119									9.15-9.35	b, sh
15	9.38	CF$_3$ symmetric stretch	135	9.37	vs	9.38	s	9.39	vs	9.38	vs	9.41	vs
16	9.90	Silicon-(n-propyl)	115	9.74	m	9.86	s	9.78	m	9.78	m	9.79	s

TABLE XI (cont.)

INFRARED SPECTRA OF 3,3,3-TRIFLUOROPROPYLMETHYLSILOXANYLCHROMATES AND RELATED COMPOUNDS

Peak	Reference Absorption (μ)	Assignment	Ref.	3,3,3-trifluoropropylmethyldichlorosilane CCl₄ & CS₂		3,3,3-trifluoropropylmethylsilanediol CCl₄ & CS₂		cyclo-bis-[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)] CCl₄ & CS₂		cyclo-tris-[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)] CCl₄ & CS₂		cyclo-bis-[di-3,3,3-trifluoropropyldimethyldisiloxanyldimethyldisiloxanylchromate-(VI)] CS₂	
	(μ)		Solvent→	(μ)	I	(μ)	I	(μ)	I	(μ)	I	(μ)	I
17	10.1	Cr=O asymmetric stretch	12					10.14	s	10.12	vs	10.06	m
18	10.3	Cr=O symmetric stretch	12					10.30	s	10.30	sh	10.25	m
19	11.0–12.1	Cr-O-Si asymmetric stretch	5(c)					10.90	vs	10.90	sh	10.90	s
20	11.2	Silicon-(n-propyl)	115	11.17	vs	11.17	m, b	11.18	sh	11.20	s	11.16	vs
21	11.7	Si-CH₃ deformation	115	11.95	m	11.90	m, b	11.88	m	11.96	m	11.85	m
22	12.25	Si-C stretch	115	12.42	m	12.45	sh	12.45	w				
23	11.3–12.0	Si-O	116			12.77	vs						
24	13.05	unassigned						13.05	w				
25	13.50	CF₃ deformation	124	13.30	vs, b	13.13	s	13.50	m				

(b) (p. 97)

TABLE A1 (cont.)

INFRARED SPECTRA OF 3,3,3-TRIFLUOROPROPYLMETHYLSILOXANYLCHROMATES AND RELATED COMPOUNDS

CESIUM IODIDE REGION

Peak	Reference Absorption (μ)	Assignment	Ref.	3,3,3-trifluoropropyl-dichlorosilane CS₂ (μ)	I	3,3,3-trifluoropropylmethylsilanediol CH₃CN (μ)	I	cyclo-bis-[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)] CCl₄ (μ)	I	cyclo-tris-[3,3,3-trifluoropropylmethylsiloxanylchromate-(VI)] CCl₄ (μ)	I	cyclo-bis-[di-3,3,3-trifluoropropyldimethyldisiloxanylmethyldisiloxanylchromate-(VI)] CCl₄ (μ)	I
1	15.8	CF₃ deformation	135	15.7	m	15.9	m	15.6	m	15.6	m	15.6	m
2	17.0–17.5	Si–O–Si symmetric stretch	113									16.6	m
3	near 17.5	CF₃ asymmetric deformation	126	17.9	s								
4	18.2	CF₃ deformation	135			18.1	s	18.1	s	18.1	s	18.1	s
5	16.8–18.7	Si–Cl asymmetric stretch	113	18.5	s								
6	19.6	CF₃ deformation	135	20.1	w	20.3	w	20.1	w	20.1	w	20.0	w
7	18.6–21.7	Si–Cl symmetric stretch	113	21.0	s			21.0	s	21.2	s	21.4	m
8		Cr–O–Si symmetric stretch	(c)										
9	22–28	CF₃ deformation	135	23.3	w	23.3	m						
10	25.0–	SiCH₃ rock. ν.113		28.6	w	29.2	w					28.7	m

B. **With Silver Dichromate.** The reaction of silver dichromate with 3,3,3-trifluoropropylmethyldichlorosilane yielded a deep orange liquid which was distillable at very low pressures. The chemical analysis of this material (Table X) showed a silicon-chromium ratio of 1.00 and the carbon-hydrogen values agreed with the calculated amounts for 3,3,3-trifluoropropylmethylsiloxanylchromate(VI).

The infrared spectrum (Table XI) (Figures 34 and 35, p. 133 and 134) was very similar to that of cyclo-bis[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)], showing the normal organo-silicon vibrations. There were no absorptions corresponding to the Si-O-Si stretching modes and even the dubious peak at 2.9 μ was absent.

Cryoscopic molecular weight determination (Table X) indicates that the molecule was the trimer of 3,3,3-trifluoropropylmethylsiloxanylchromate(VI).

A cyclic structure was assigned to this compound for reasons similar to those given during the characterization of the cyclic dimer -- i.e. the Cr-O-Si asymmetric stretching mode appeared at a shorter wavelength (10.90 μ), both Cr-O-Si stretching absorptions were singular in nature, and there was no evidence of a Si-OH stretching vibration.

The fact that the cyclic dimer and timer are liquids at room temperature does not place as much doubt upon a possible cyclic structure as it did with the phenylsiloxanylchromates.

The molecules do not have the same degree of symmetry because of non-identical organic groups. Fluorine-containing compounds are very often liquids regardless of their high molecular weights, a good example of this being the difference between bis(triphenylsilyl)chromate(VI) (m. 155° C.) and bis(diphenylfluorosilyl)chromate(VI) (m. -35 $\pm$ 10° C.).

The physical properties of the cyclic-trimer were quite similar to those listed for the dimer, i.e. light sensitive, hydrolytically stable, and similar solubilities.

The spectrum between 240 and 600 mμ (Figure 8, p. 107) showed chromyl absorption maxima at 246 and 485 mμ. The molar extinction coefficients for these peaks were 9.18 x 10^3 and 5.18 x 10^3.

V. Reaction of 3,3,3-trifluoropropylmethylsilanediol with Chromyl Chloride.

The reaction of 3,3,3-trifluoropropylmethylsilanediol with a slight excess of chromyl chloride yielded a light orange oil which crystallizes at low temperatures. The silicon-chromium ratio was 1.99 and the carbon-hydrogen analyses (Table X) were in good agreement with the calculated values for [di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI).]

The infrared spectra (Figures 36 and 37, p.135 and 136; Table XI) exhibited the normal bands assigned to the two organo groups and their linkage to silicon. The chromyl absorptions were well defined and shifted slightly to shorter wave-

lengths. The two Cr-O-Si absorptions were present. However, they were less intense than the corresponding peaks in the spectra of cyclo-bis and cyclo-tris[3,3,3-trifluoropropyl-methylsiloxanylchromate(VI)].

The Si-O-Si asymmetric stretching mode at 9.15 to 9.35 μ was slightly difficult to distinguish for it appeared as a wide shoulder adjacent to the CF_3 stretching mode. This absorption also masked another shoulder characteristic of Si-($\underline{n}$-propyl) group; however comparisons of spectra from 3,3,3-trifluoropropylmethyldichlorosilane and 3,3,3-trifluoropropylmethylsilanediol with that of the light orange liquid shows that the peaks in this area are obviously different in appearance. The Si-O-Si symmetric stretching vibration absorbed at 16.6 μ.

The values obtained from molecular weight determinations (Table X) agreed with the calculated weights for a dimeric structure.

The proton magnetic resonance spectra of 3,3,3-trifluoropropylmethyldichlorosilane, 3,3,3-trifluoropropyl-methylsilanediol, and bis [di-3,3,3-trifluoropropyldimethyl-disiloxanylchromate(VI)] were examined as a means of determining the termination of this dimer.

The liquid halosilane contained seven hydrogens which were influenced by three separate and distinct regions around the molecules. This in turn led to a spectrum consisting of

three areas of chemical shifts, which were further resolved
into several individual peaks (Figure 2, p. 91) (Table XII).
The high resolution of the higher frequency shifts resulted
from the adjacent highly electronegative fluorine. The peaks
between 17 and 25 c.p.s. resulted from the methyl group while
those lying between 97 and 124 c.p.s. and 43 and 61 c.p.s.
correspond to the methylene hydrogens α and β to the silicon
(127).

The spectrum of the solid silanol (Figure 3, p. 92) was
determined in diethyl ether solution. The shifts were re-
solved in a manner quite similar to that of the dichloro-
silane, however the general chemical shift areas of the
dichlorosilane occurred at somewhat lower frequencies. Clark
et al. (132) found similar shift displacements with a series
of methyl-tin chlorides. They observed equal displacement
increments for each methyl group replaced by chlorine and
explained that the chemical shift change to lower fields
resulted from increases shielding. The silanol with its
hydroxyl hydrogen exhibited a fourth chemical shift between
165 and 190 c.p.s. The area under the four shifts showed
ratios of 3.0 : 2.0 : 2.2 : 1.7.

The spectrum of bis[di-3,3,3-trifluoropropyldimethyl-
disiloxanylchromate(VI)] (Figure 4, p. 93) (Table XII)
obtained in methylene chloride showed very poor resolution.
The chemical shift from a hydroxyl hydrogen was not apparent,

however it could have been masked by the α methylene shift.
The area under these three shifts showed ratios of 6.0 :
4.2 : 4.0 and the calculated ratio for a combined hydroxyl
proton-methylene shift should be 6 : 4 : 5. The proton
magnetic resonance spectra therefore indicated that the com-
pound was cyclo-bis[di-3,3,3-trifluoropropyldimethyldisilox-
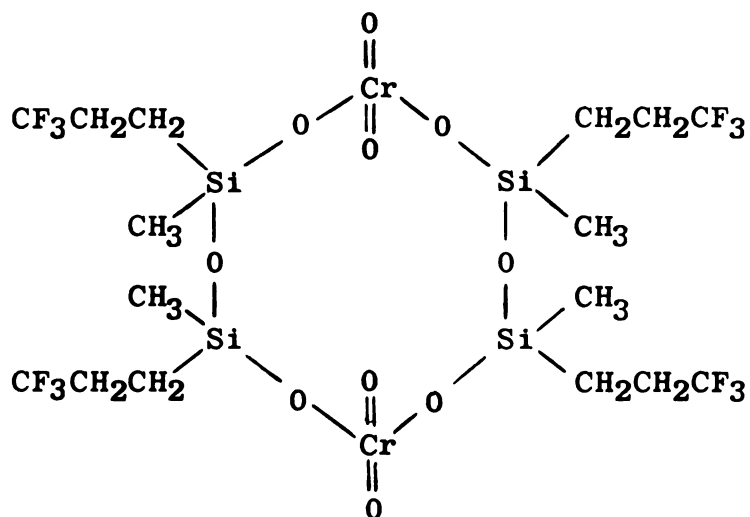anylchromate(VI)] or

TABLE XII

PROTON RESONANCE SPECTRA

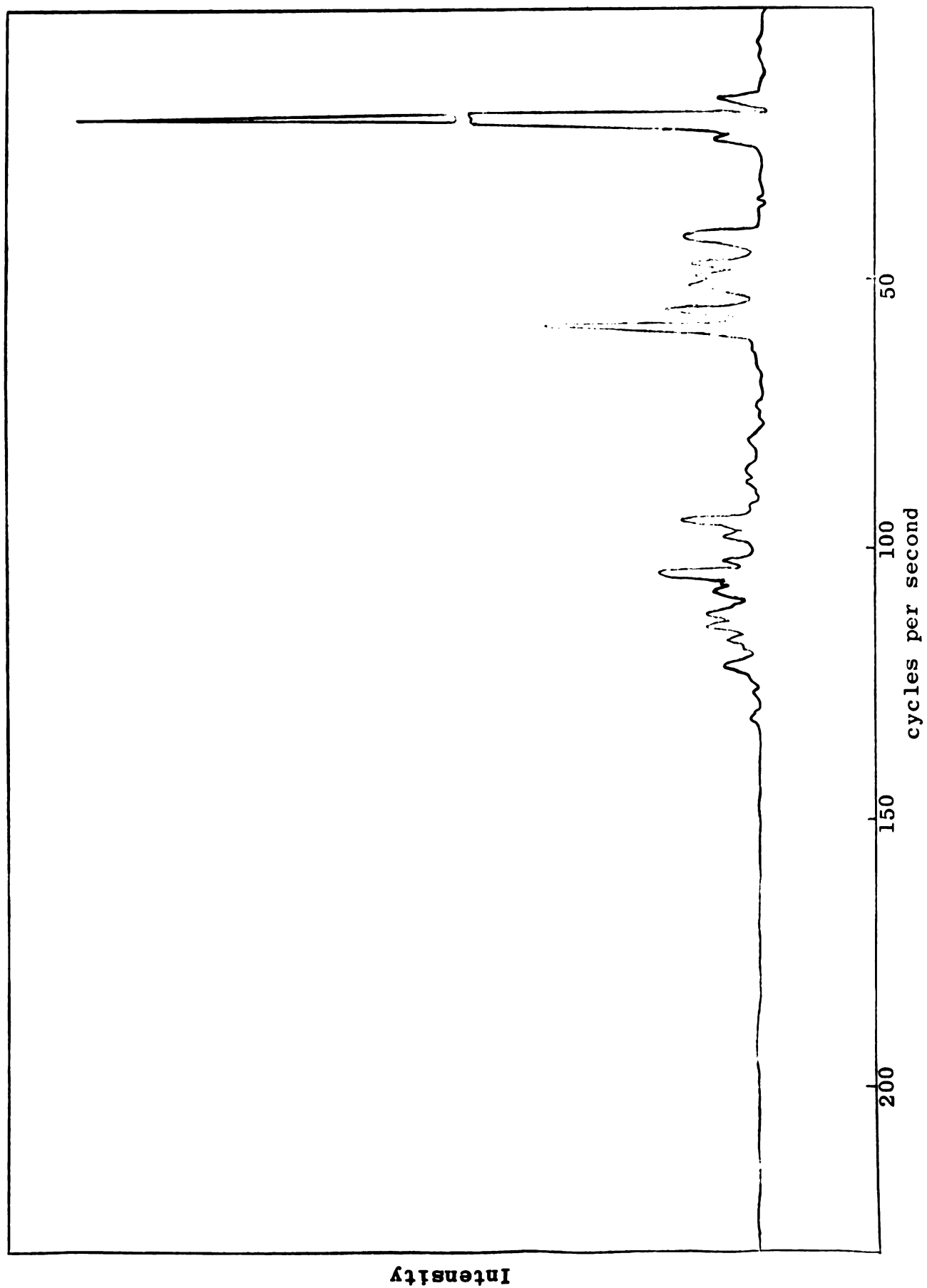|	3,3,3-trifluoropropyl-methyldichlorosilane		3,3,3-trifluoropropylmethylsilanediol		cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)]	
	Chemical Shift		Chemical Shift		Chemical Shift	
	(c.p.s.)	I	(c.p.s.)	I	(c.p.s.)	I
CH_3	17	w	24	vw	21	sh
	22	vs	27	vs	25	vs
	25	w			14-32 at one-half height	
βCH_2	43	m	56	m		
	48	m	61	m		
	50	m	64	m	61 (max.)	b
	52	m				
	57	m	72	m	47-74 at one-half height	
	61	s				
αCH_2			130	w		
	97	m	133	w		
	100	w				
	104	w	137	vw		
	107	m	139	vw		
	109	w	141	w	134	b
	110	w	143	w		
	113	w	145	vw	118-148 at one-half height	
	114	w	147	w		
	116	w	151	vw		
	119	w	154	vw		
	124	w	159	w		
			162	w		
			175	vw		
			176	vw		
			177			
			179	w		
			181	w		

Figure 2. Proton magnetic resonance spectrum of 3,3,3-trifluoropropylmethyldichlorosilane.
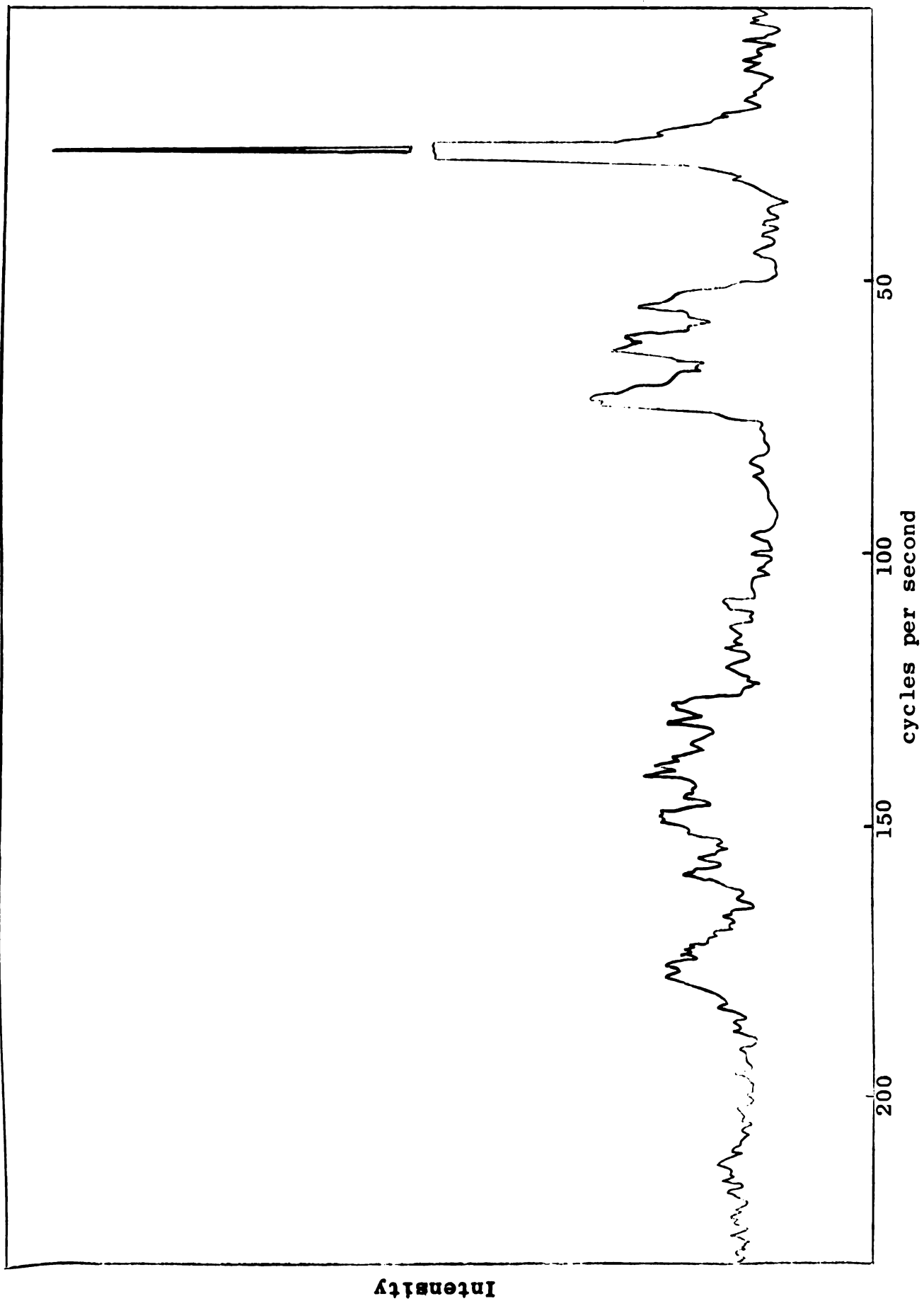
Figure 3. Proton magnetic resonance spectrum of 3,3,3-trifluoropropylmethylsilanediol.
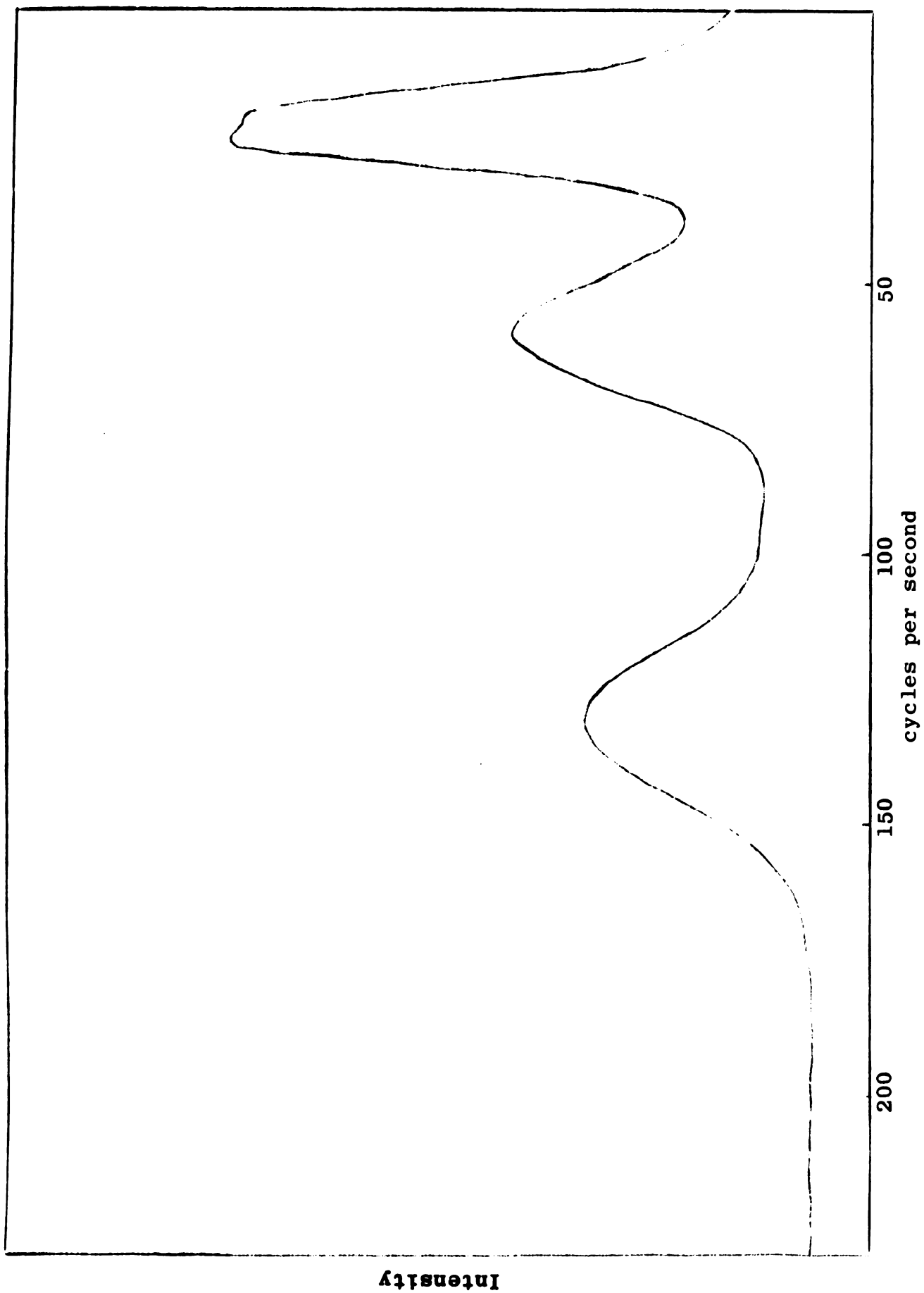
Figure 4. Proton magnetic resonance spectrum of cyclo-bis[di-3,3,3-trifluoropropyldi-methyldisiloxanylchromate(VI)].

The infrared spectrum of this compound also favored a cyclic structure. The Cr-O-Si asymmetric stretching frequency absorbed at low wavelengths and was unresolved. The symmetric stretching vibration mode was also unresolved. Both Si-O-Si stretching modes were found at wavelengths considerably shorter than those exhibited by linear siloxanes. The symmetric peak was definitely singular in nature, but the area around the asymmetric band was much too congested for any determination of peak multiplicity.

Consideration of a cyclic molecule in terms of the bond angles and lengths did not indicate any apparent intramolecular strain.

The spectrum of cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)] between 220 and 600 mμ (Figure 9, p. 108) showed chromyl absorptions at 470 and 240 mμ. The respective molar extinction coefficients were 7.0 x 10^2 and 2.9 x 10^3.

This light orange liquid was slightly soluble in water and was apparently stable for short periods of time. It also was photochemically sensitive and would decompose to a brown powder in diffuse light. The solubilities of this substance in organic solutions were similar to that of the cyclo-bis and cyclo-tris[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)].

Instrumental Measurements.

A. <u>Ultraviolet and Visible Spectra</u>. The ultraviolet and visible spectra of the siloxanylchromates prepared during this investigation were measured in methylene chloride with a Beckman DK-2 recording spectrophotometer. The spectrum of silver chromate, determined in aqueous ammonia, showed peaks occurring at 274 and 503 mμ while water solutions of silver dichromate absorbed at 258, 344, and 470 mμ. The absorptions between 250-280 mμ and 470-500 mμ corresponded to transitions characteristic of the chromyl linkage while the peak in the vicinity of 350 mμ results from the dichromate bridge.

Each siloxanylchromate exhibited one absorption maximum in the ultraviolet region occurring between 240-270 mμ and one plateau between 450 and 500 mμ in the visible region.

The absorption peak in the ultraviolet region shown by phenylsiloxanylchromates resulted from the phenyl groups and it masked the chromyl absorption which also occurred at these wavelengths. The ultraviolet chromyl absorption in 3,3,3-trifluoropropylmethylsiloxychromates was observed because the organic substituents did not absorb in this region. The absence of phenyl resolution in phenylsiloxanylchromates has been attributed to interaction of the chromium with the phenyl groups (5). This decrease in fine structure could also result from "double-absorption" within a specific range. The chromyl

absorptions in the visible range exhibited shifts which were related to the number of atoms within the ring. The cyclic dimer of diphenylsiloxanylchromate(VI) showed a chromyl transition plateau at 460 mμ while the cyclic trimer absorbed at 480 mμ. Both chromyl absorptions of cyclo-bis and cyclo-tris[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)] showed corresponding shifts to lower wavelengths (498 to 480 mμ and 250 to 243 mμ). Cyclo-bis[di-3,3,3-trifluoropropyldimethyl-disiloxanylchromate(VI)] extended this shift in the visible region even further (465 mμ). These shifts suggest that interactions between the chromyl group and some other substituents in the molecule did exist because as the ring size became smaller, thereby increasing the proximity of intramolecular substituents to the chromyl linkages, the wavelengths of the absorption became longer. This chromyl interaction most likely takes place with the phenyl (128) and the trifluoropropyl groups.

These spectral shifts mentioned above are also indicative of the cyclic structure of the compounds prepared during this investigation.

B. <u>Infrared Spectra</u>. The infrared spectra of the compounds prepared and used during this investigation were recorded in carbon disulfide, carbon tetrachloride solutions, and in potassium bromide pellets. The spectra in the sodium chloride region were obtained with a double-beam Perkins-Elmer Model 21

spectrophotometer using both sodium chloride and potassium
bromide cavity cells. The spectra in the cesium iodide
region were recorded with a double-beam Beckman IR-7 spec-
trophotometer and potassium bromide cells.

Most of the fine points concerning the infrared spectra
of the materials prepared during this study have been dis-
cussed at some length in the preceeding section.

Because of the qualitative nature of the Cr-O-Si vibra-
tional assignments, these assignments should be considered
tentative. Hare (5) assigned the 11 to 12 μ absorption to
the Cr-O-Si stretching vibration using a process of elimina-
tion and comparisons of the wavelengths to literature values
for transition metal-oxygen-silicon vibrational assignments.
His characterization of the vibrational mode was substantiated
during this study by similar means. The absorption appearing
between 20.6 and 21.4 μ was also assigned to Cr-O-Si vibra-
tions by means of a process of elimination and by comparisons
of the peak intensities shown by bis(triphenylsilyl)chromate(VI)
and cyclo-bis[tetraphenyldisiloxanylchromate(VI)]. The struc-
ture of these compounds had been previously established (5, 11).
The assignment of the absorption modes as stretching vibrations,
and more specifically as asymmetric and symmetric stretching
vibrations, was performed by comparing the absorption posi-
tions and appearances with the previously assigned Si-O-Si
asymmetric and symmetric stretching frequencies (113, 115).

The cesium iodide spectra of the phenylchlorosilane reactants are recorded in Table XIII (p. 99).

The silicon-fluorine asymmetric deformation mode which should be present in the spectrum of diphenylchlorofluorosilane was masked by the stronger silicon-chlorine asymmetric stretching mode. The shifts to shorter wavelengths by the phenyl-silicon out-of-plane ring bending modes are caused by the presence of fluorine in the molecule (115).

C. **Proton Magnetic Resonance Spectra.** All measurements were performed with a Varian A-60 spectrometer employing a sweep width of 500 c.p.s. The solvents used were carbon tetrachloride, diethylether, methylene chloride, and carbon tetrachloride-carbon tetrabromide solvent mixture. The standard was tetramethylsilane.

D. **X-Ray Diffraction Data.** The interatomic spacings for silver chromate and silver dichromate were calculated from x-ray diffraction patterns obtained with a Siemens Kristalloflex-4 diffractometer using copper, K_α radiation. The atomic spacings for cyclo-tris[diphenylsiloxanylchromate(VI)] were obtained from chromium K_α powder diffraction film using a North American Philips powder diffraction unit with a Debye-Scherrer camera.

TABLE XIII

INFRARED SPECTRA OF PHENYL-HALOSILANE REACTANTS (15-29 μ)

Peak No.	Reference Absorption (μ)	Assignment	Ref.	triphenylchlorosilane (μ)	I	diphenyldichlorosilane (μ)	I	diphenyldifluorosilane (μ)	I	diphenylchlorofluorosilane (μ)	I
1	16.0-16.2	Ph-Si in-the-plane ring bending	113	16.0	w	16.2	m	15.2	w	16.1	w
2	17.3-18.0	Si-Cl asymmetric stretch	113	18.1	vs	17.3	vs			17.6	vs
3		Si-F asymmetric deformation	113					17.6	s		
4	18.5	Si-Cl symmetric stretch	113			18.5	vs				
5	19.8-20.7	Ph-Si out-of-plane ring bending	113	19.85	vs	20.7	s	19.4	vs	20.0	vs
6		Si-F symmetric deformation	113					20.0	m		
7	22.4-23.5	Ph-Si antisymmetric stretch	113	23.2	m	22.4	w	20.8	w	23.2	w

E. <u>Vapor Phase Chromatography</u>. Vapor phase chromato-
grams were obtained with a Beckman GC-2 recording chromato-
graph and a twenty percent silica column. The flash plate
was maintained at maximum temperature (220° C.) A carrier
gas of helium was passed through the system at positive
pressures and the analyses were performed using samples of
approximately two microliters of the non-diluted liquid
silane.

Analytical Methods.

The following methods were found to be satisfactory
for silicon and chromium analyses. Carbon, hydrogen, and
chlorine analyses were carried out by Spang Microanalytical
Laboratory, Ann Arbor, Michigan and by Alfred Bernhardt
Microanalytical Laboratory, Mulheim, Germany.

<u>Chromium Analysis</u>: The decomposition of thirty to
fifty milligram samples took place in platinum crucibles
with a flux of approximately ten grams of sodium bicarbonate.
The crucibles were heated with a steam bath for several hours.
After cooling, the solid residue was dissolved in two hundred
milliliters of water and carefully neutralized with sulfuric
acid. A slight excess of acid was added and the solution was
diluted to four hundred milliliters. After the addition of
an electrolyte (ten grams of concentrated potassium chloride),

the chromate was titrated with a ferrous sulfate solution
which had been previously standardized against potassium
dichromate. The titration was followed amperometrically
using a rotating platinum electrode and a calomel cathode.
A recording ammeter plotted changes in the diffusion current
with increased ferrous sulfate concentration and the equiva-
lence point was obtained by extrapolation of the post-
equilibrium curve to the pre-equilibrium curve.

The fluorine substituent in bis(diphenylfluorosilyl)-
chromate(VI) appeared to interfere with the determination.
Therefore, ten grams of calcium nitrate were added and the
neutralized solution was left standing overnight. After
filtration, the above procedure was followed.

Silicon Analysis: Oxidation of fifty to one hundred
milligrams of the unknown sample was accomplished by the
addition of ten milliliters of concentrated sulfuric acid
to the material in a one hundred and fifty milliliter beaker.
The contents were heated to relatively high temperatures for
several hours followed by the careful addition of an excess
of ammonium peroxydisulfate (50 g.). The solution was heated
for approximately three more hours, cooled, and diluted to
four hundred milliliters. The insoluble silica was removed
by filtration through ashless paper and ignited in platinum
crucibles. The silicon dioxide content was determined by
weight difference.

It was predicted that the fluorine substituents present in several of the siloxanylchromates would interfere in the above analytical procedure. However, for reasons unknown to this investigator the suspected interference did not occur.

Fluorine Analysis: Several classical analytical procedures for the determination of fluorine were investigated, however none were found to be satisfactory. Fluorine analyses of diphenyldifluorosilane, diphenylchlorofluorosilane, and 3,3,3-trifluoropropylmethyldichlorosilane were performed by the Spang Microchemical Laboratory. Alfred Bernhardt determined the fluorine content of cyclo-bis and cyclo-tris-[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)] and bis-(diphenylfluorosilyl)chromate(VI). The fluorine and oxygen content of bis(diphenylfluorosilyl)chromate(VI) were also determined with activation analyses by the Dow Chemical Company. The activation analyses followed procedures described by Anders (129, 130).

Molecular Weight: Cryoscopic molecular weight determinations were performed with benzene solutions. Current variations resulting from temperature changes in the area of a thermister were fed through a Wheatstone bridge whose corresponding out-put was received by a Sargent Model XXI Polarograph and the cooling curves of the benzene solutions were automatically plotted on this current-time recorder.

Variations in temperature could be measured to 0.002° C.

The freezing point of solutions were obtained by extrapolation of the freezing curve to the cooling curve. The procedure consisted of determining the freezing point of the pure benzene, addition of weighed pellets of the unknown to the solution, dissolution, and then multiple determinations of the resulting lower freezing points. Weighed pellets of hexachlorobenzene were then added to the solution and five freezing curves were recorded. Averages of the above measurements were made and the freezing point depressions were expressed in terms of chart divisions, $\triangle D$ (mm), which correlated directly to $\triangle T$. The molecular weight of the unknown samples were calculated from the following relationship:

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

M-molecular weight of unknown.

M_2-molecular weight of hexachlorobenzene.

$\triangle T_1$-freezing point depression of the unknown solution.

$\triangle T_2$-freezing point depression of the hexachlorobenzene solution.

W_1-sample weight of the unknown.

W_2-sample weight of hexachlorobenzene.

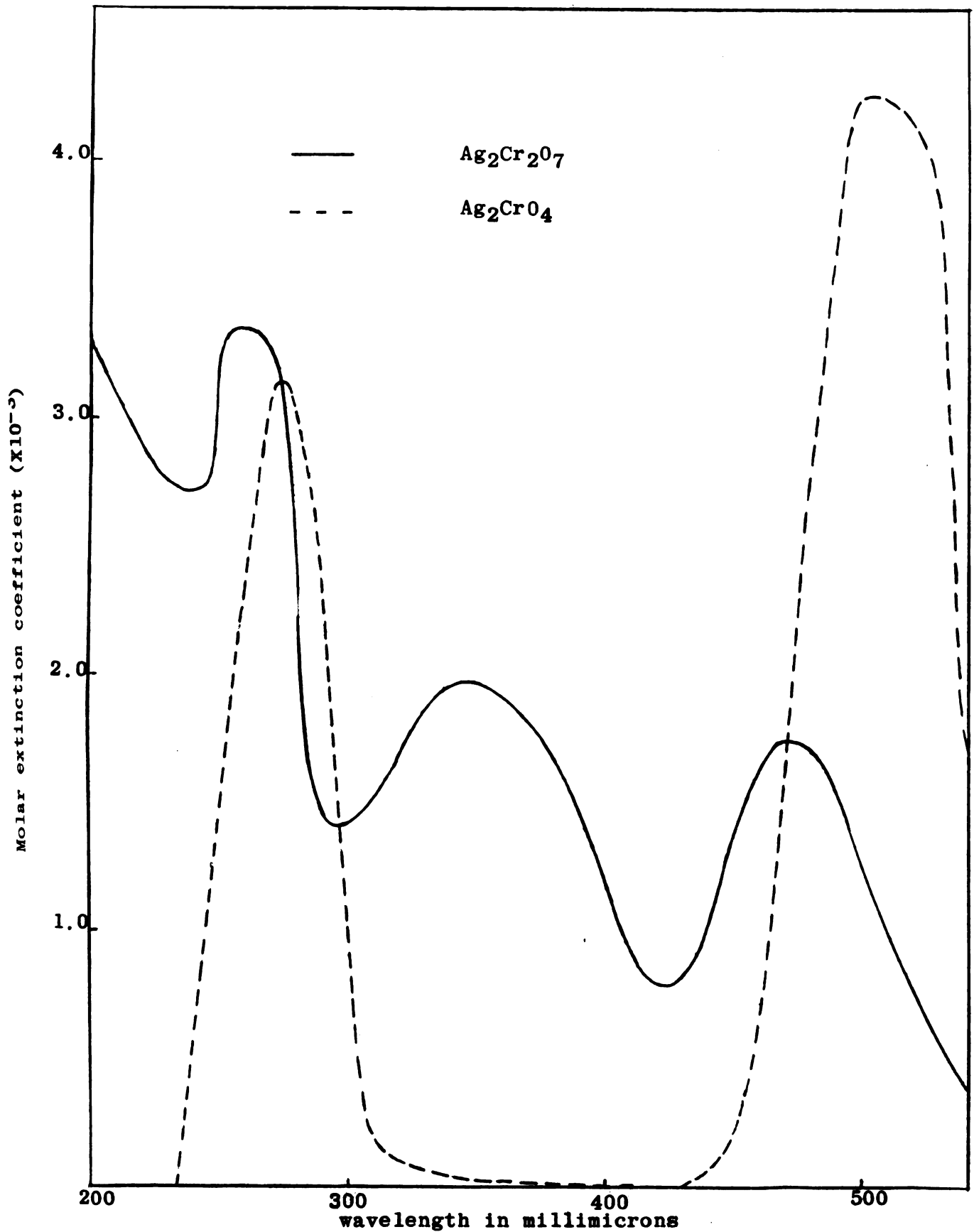The above procedure is described in greater detail by Skelcey (131).

Figure 5. Ultraviolet and visible spectra of silver chromate and silver dichromate.
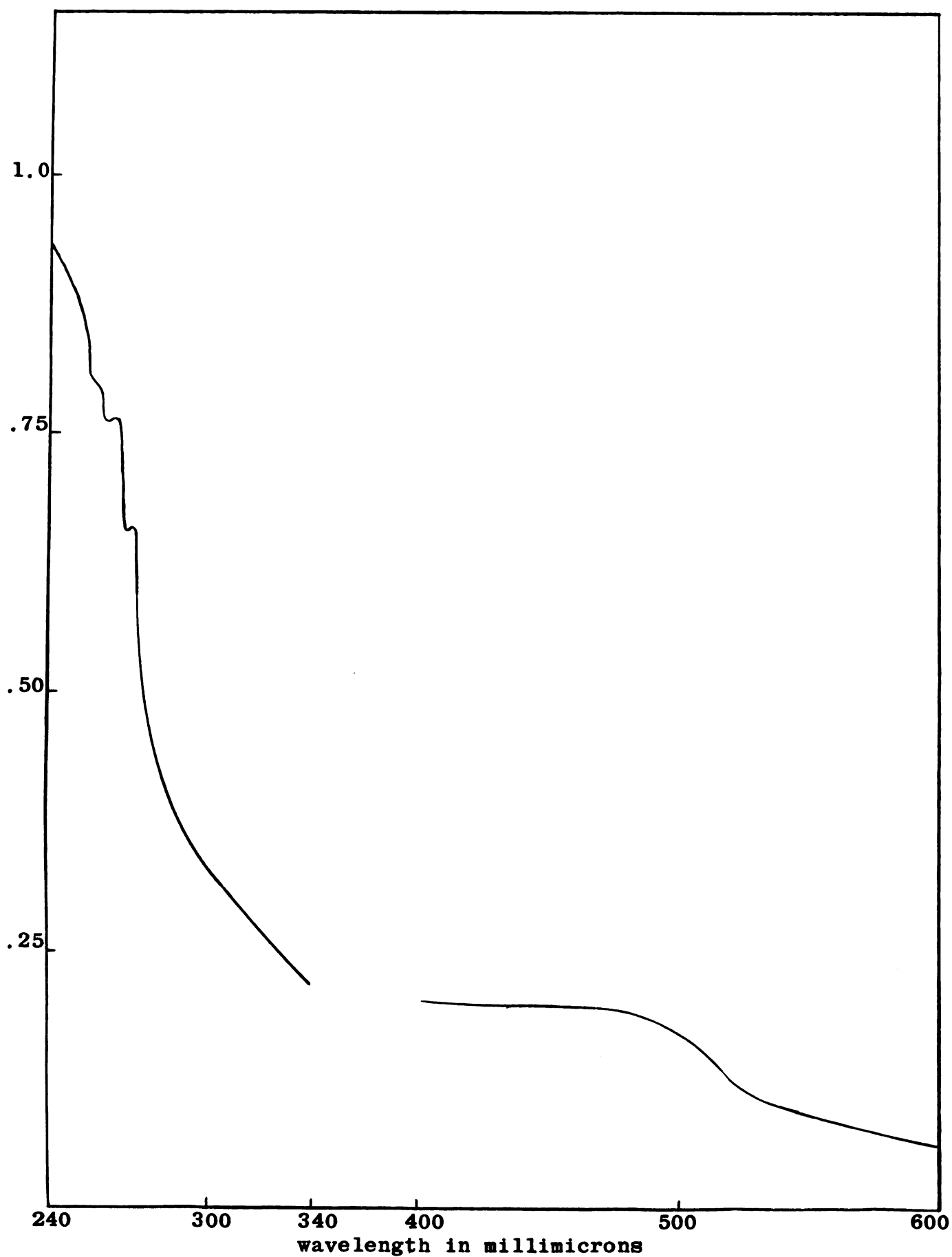
.50

.25

24

E

Figure 6. Ultraviolet and visible spectrum of bis(diphenylfluoro-silyl)chromate(VI).
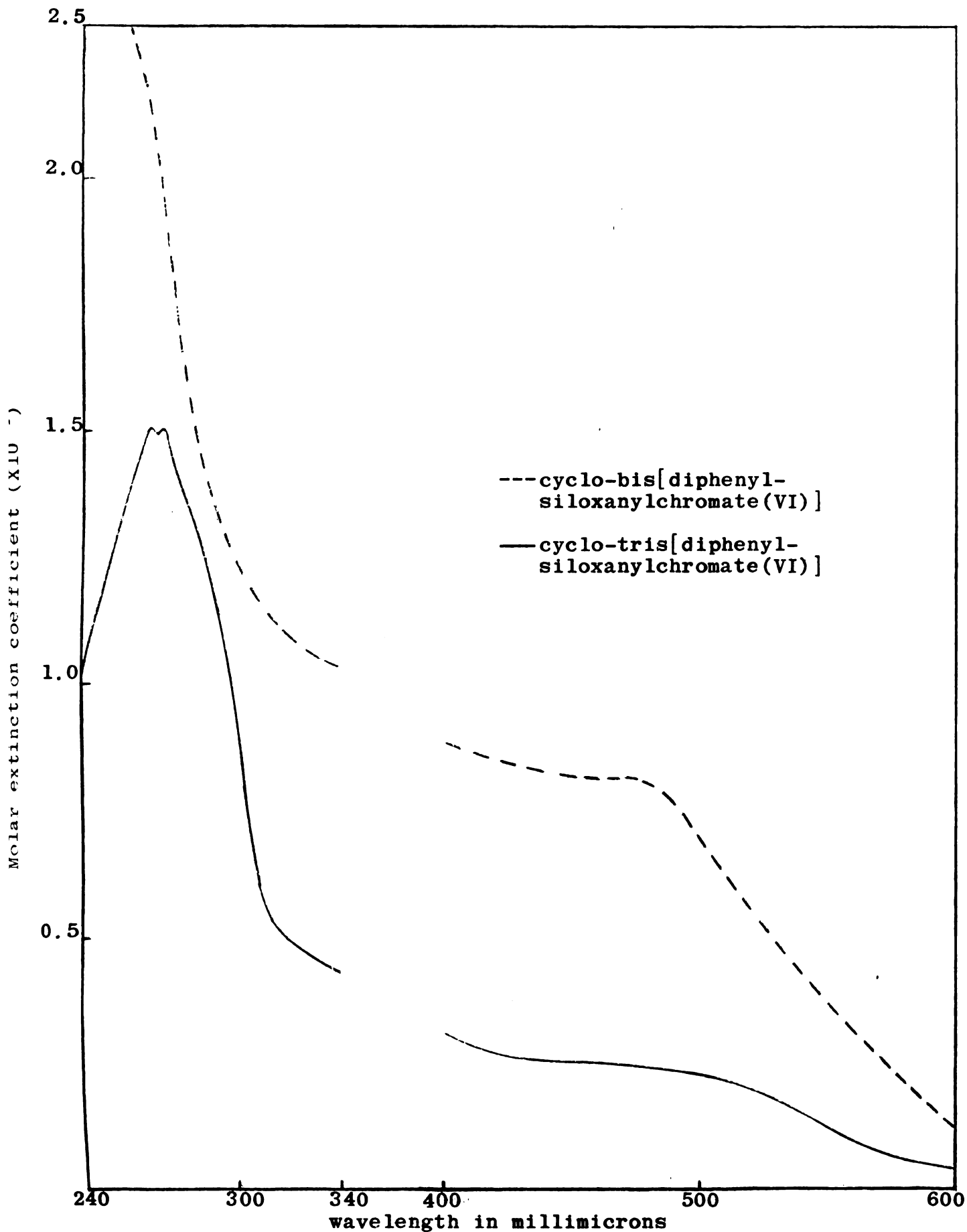
Figure 7. Ultraviolet and visible spectra of cyclo-bis[diphenyl-siloxanylchromate(VI)] and cyclo-tris[diphenylsiloxanyl-chromate(VI)].
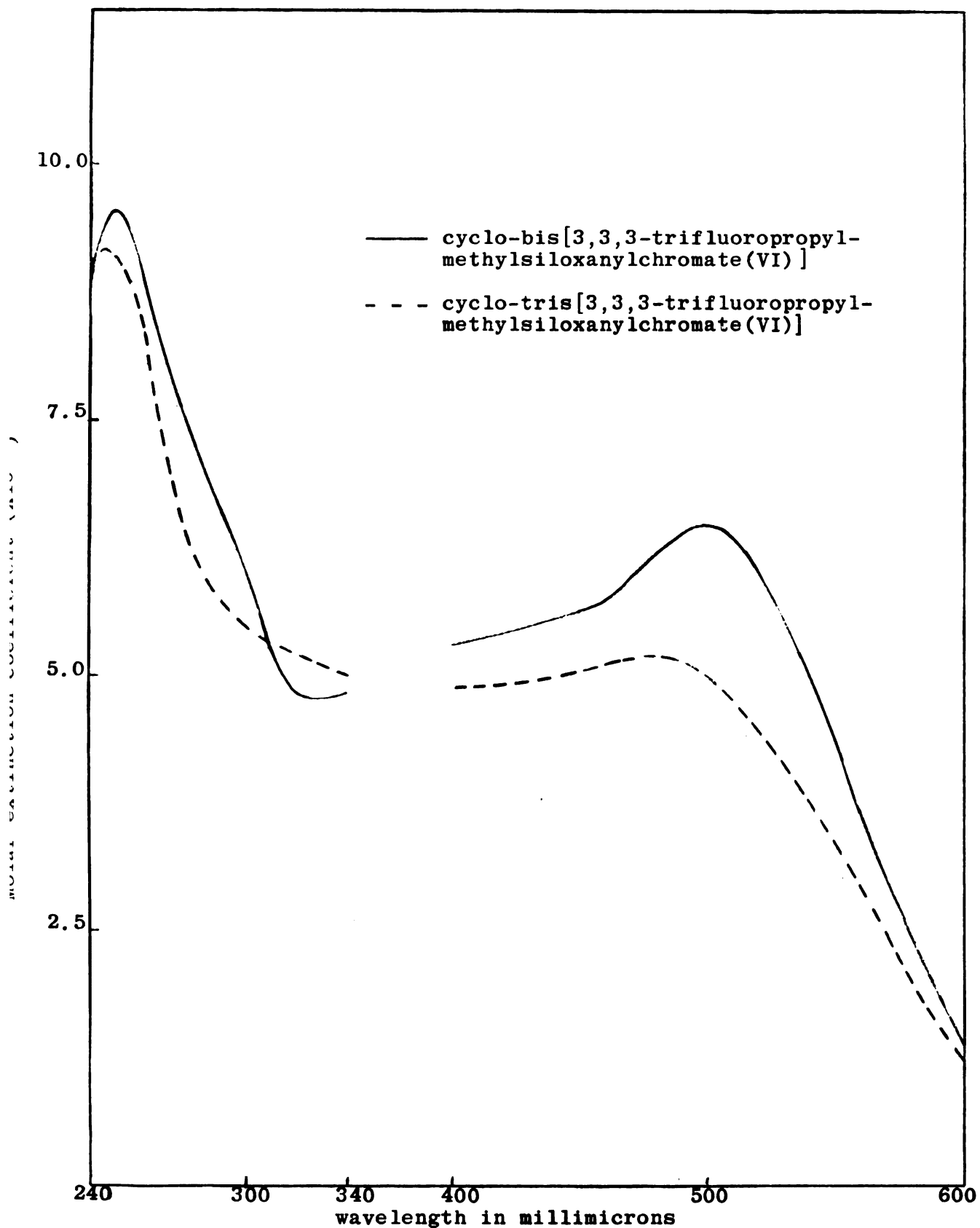
Figure 8. Ultraviolet and visible spectra of cyclo-bis[3,3,3-tri-fluoropropylmethylsiloxanylchromate(VI)] and cyclo-tris [3,3,3-trifluoropropylmethylsiloxanylchromate(VI)].
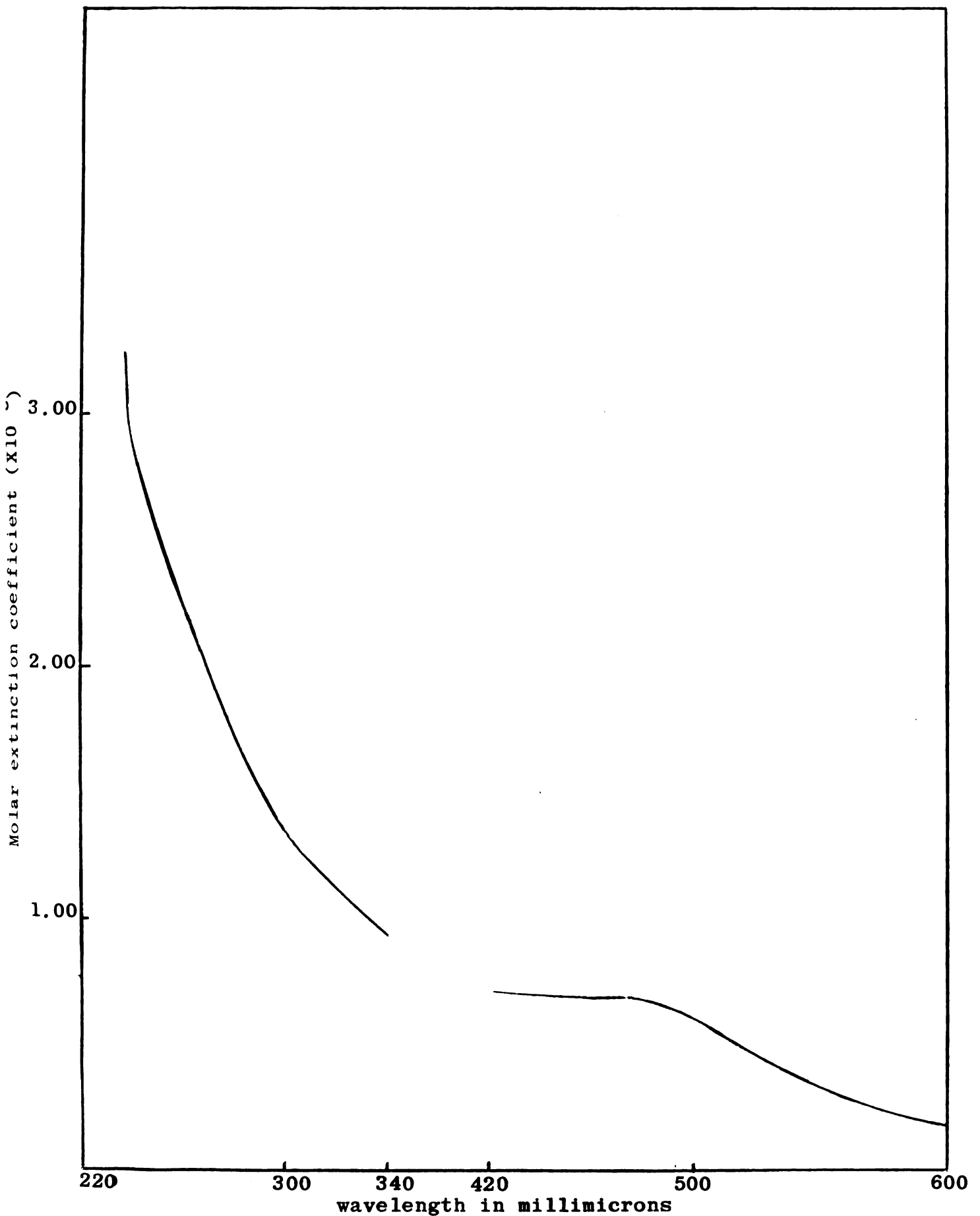
Figure 9. Ultraviolet and visible spectrum of cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)].

Figure 10. Infrared spectrum of triphenylchlorosilane in the sodium chloride region.

Figure 11.   Infrared spectrum of triphenylchlorosilane in the
cesium iodide region.

Figure 12. Infrared spectrum of diphenyldichlorosilane in the sodium chloride region.
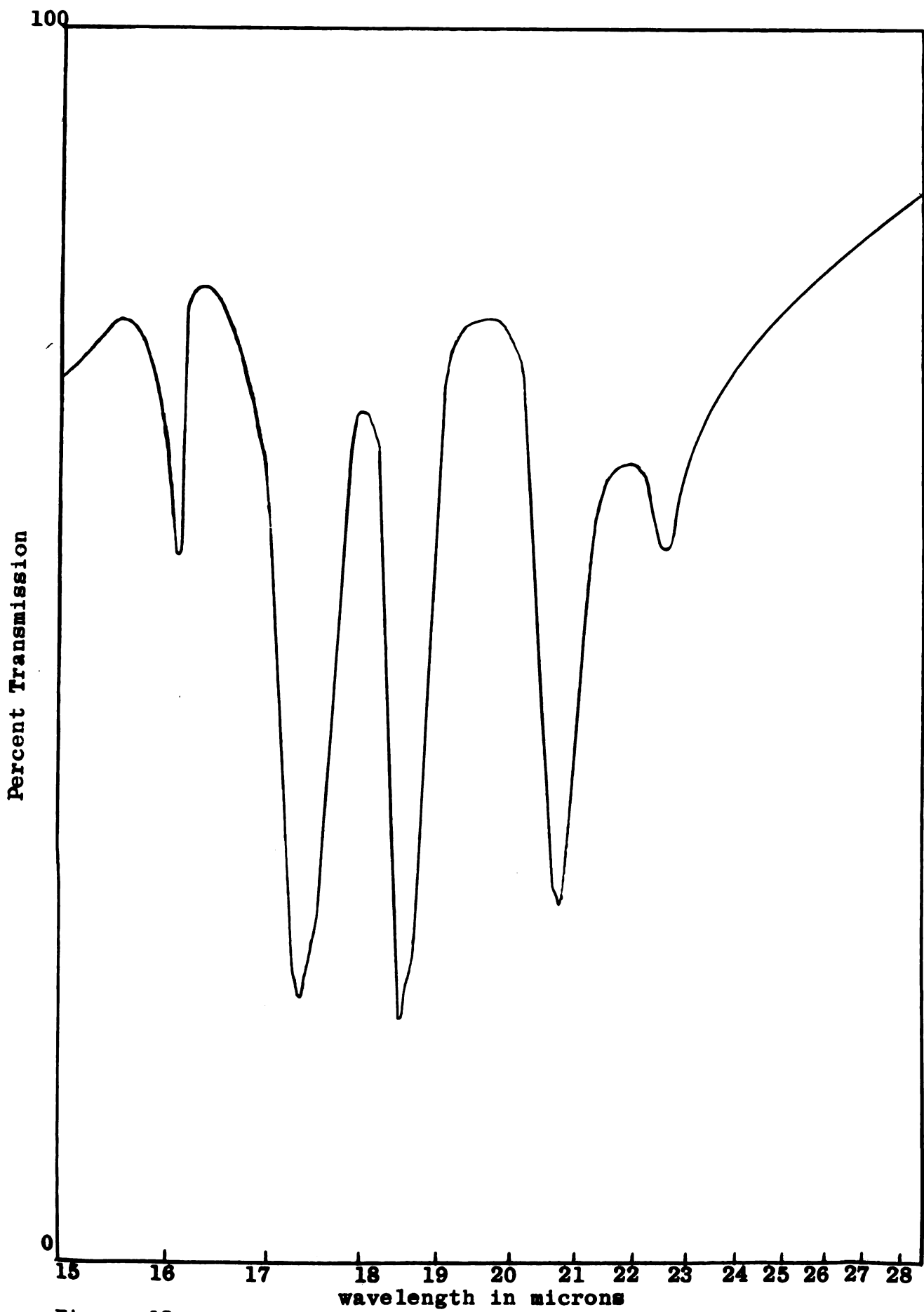
Figure 13.   Infrared spectrum of diphenyldichlorosilane in the cesium iodide region.
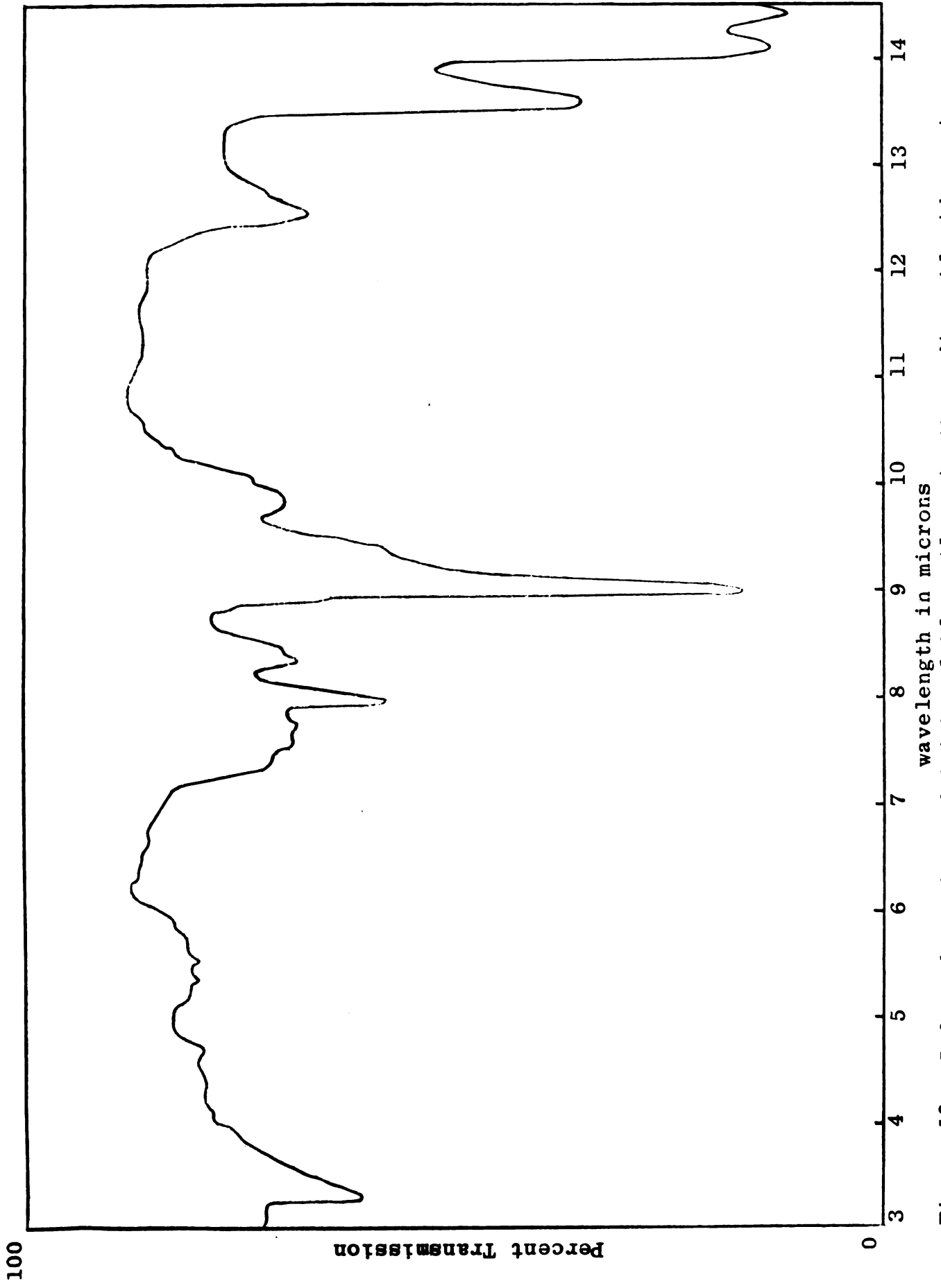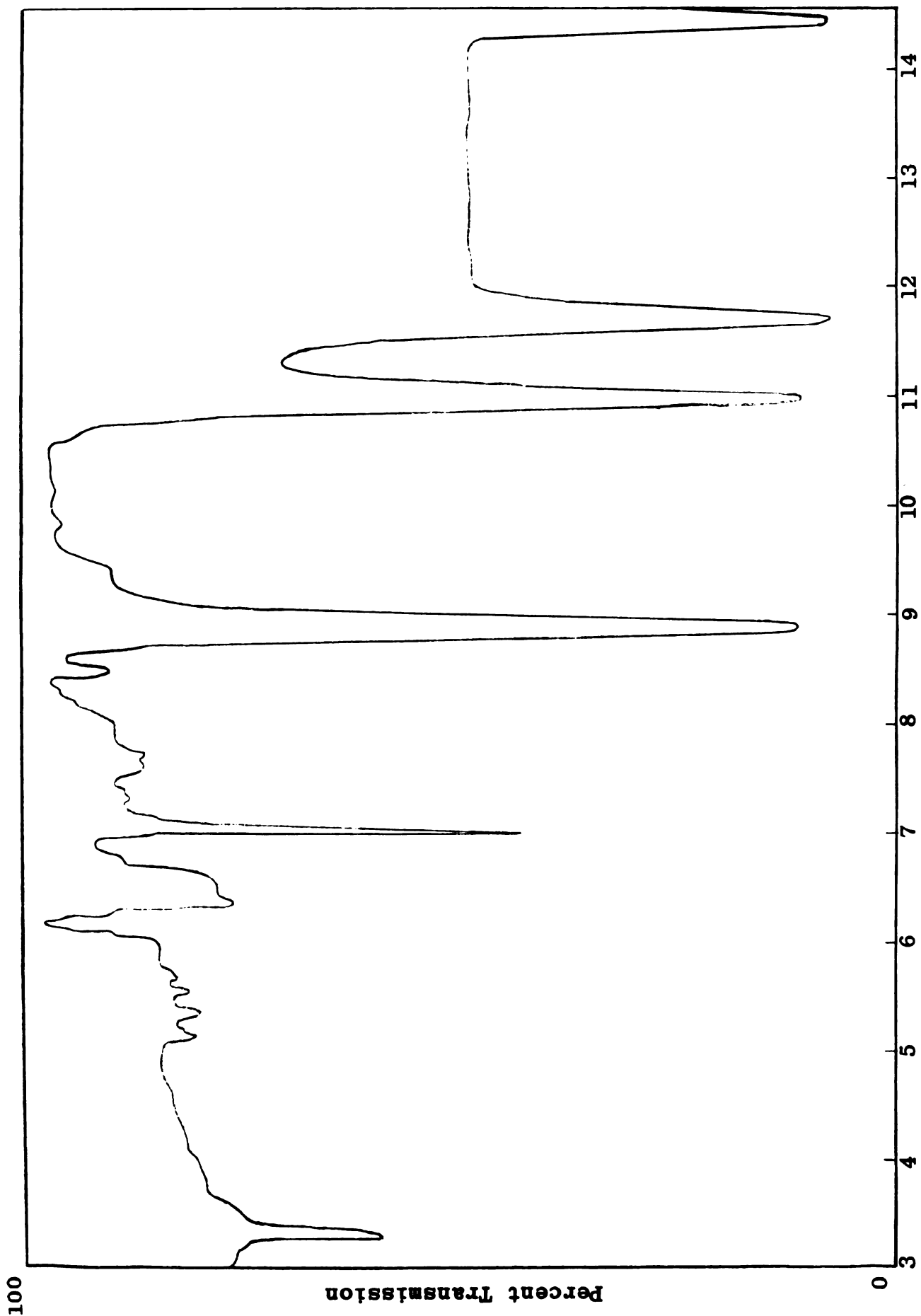
Figure 14. Infrared spectrum of diphenyldifluorosilane in the sodium chloride region.
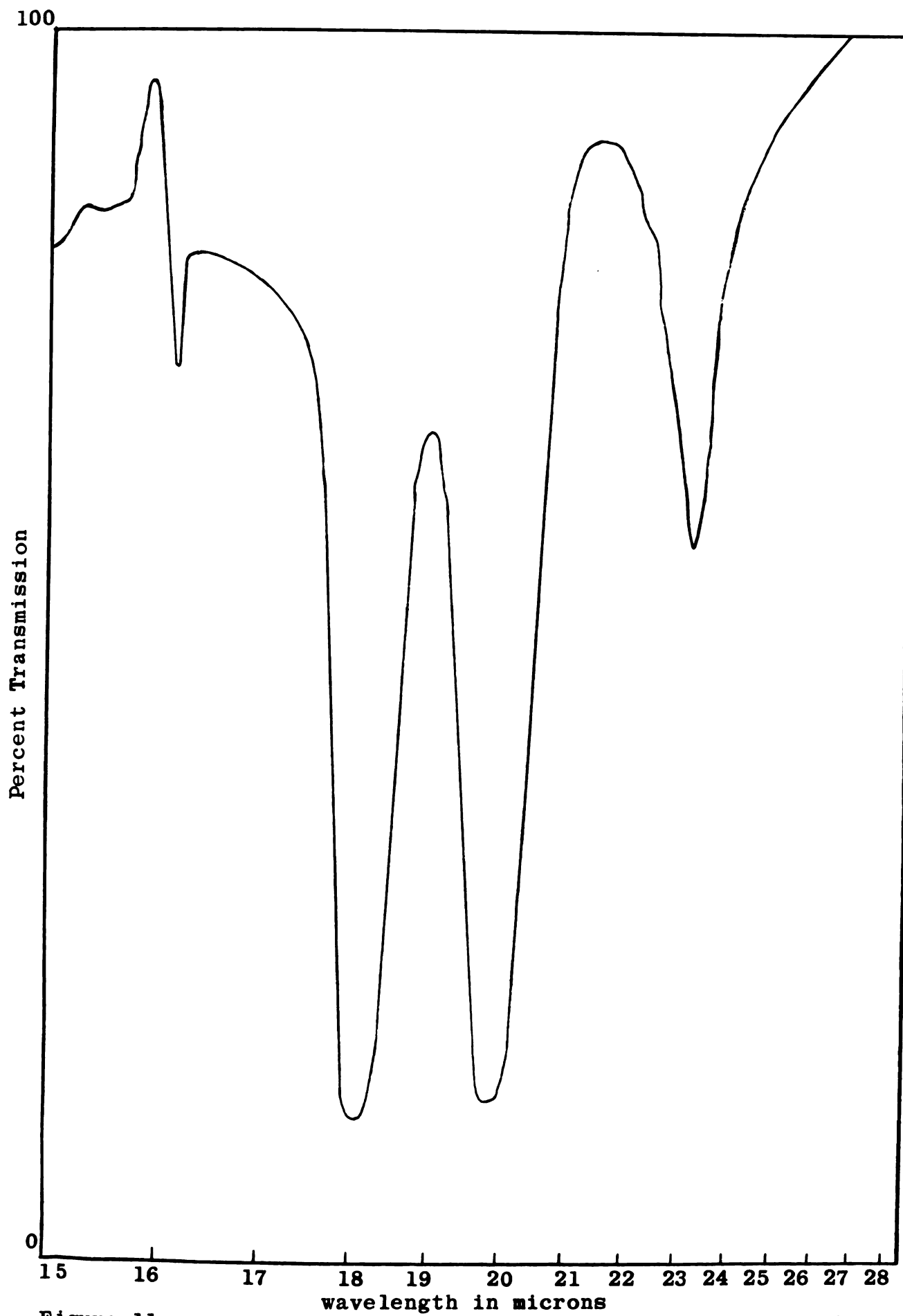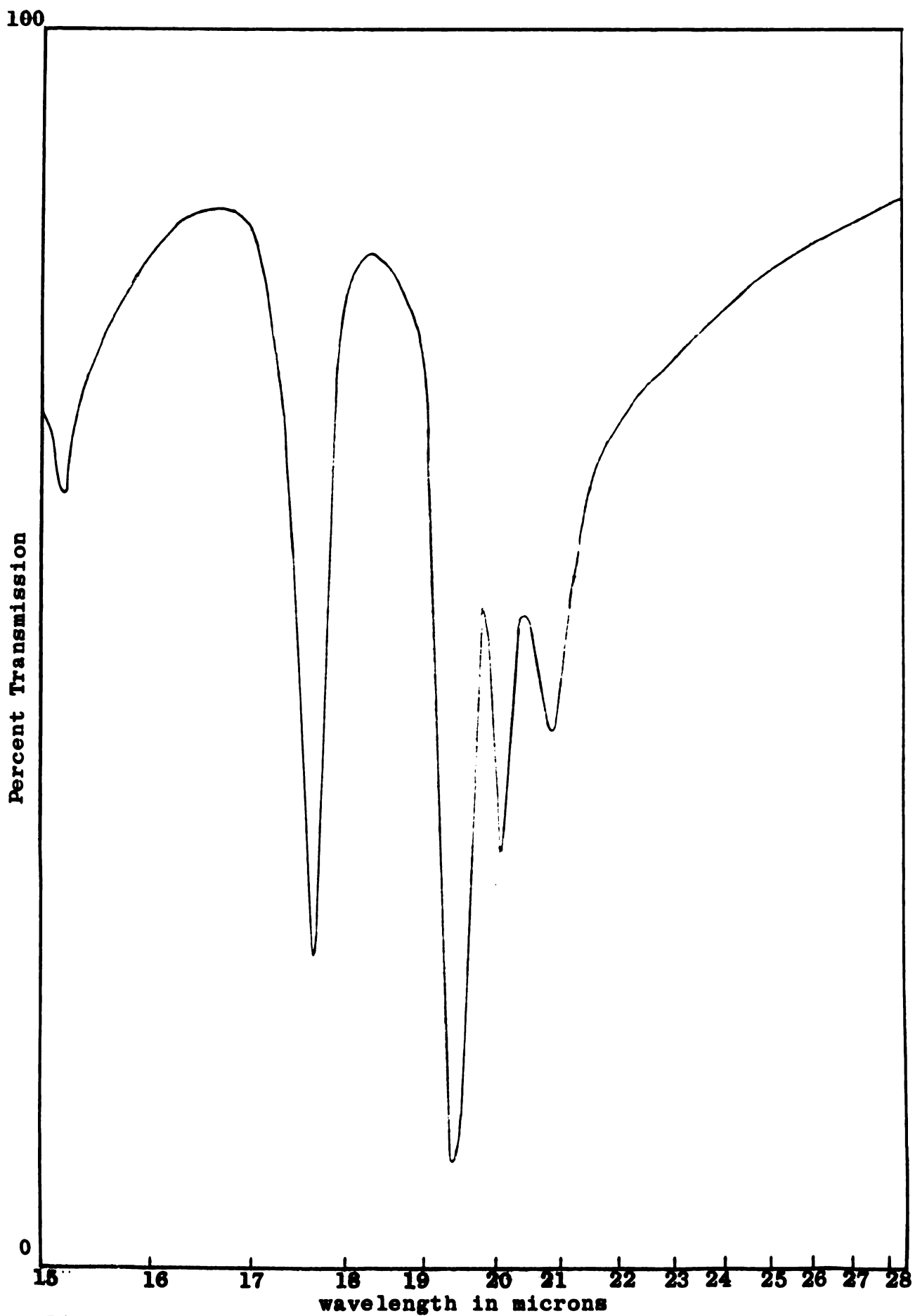
Figure 15.   Infrared spectrum of diphenyldifluorosilane in the
cesium iodide region.

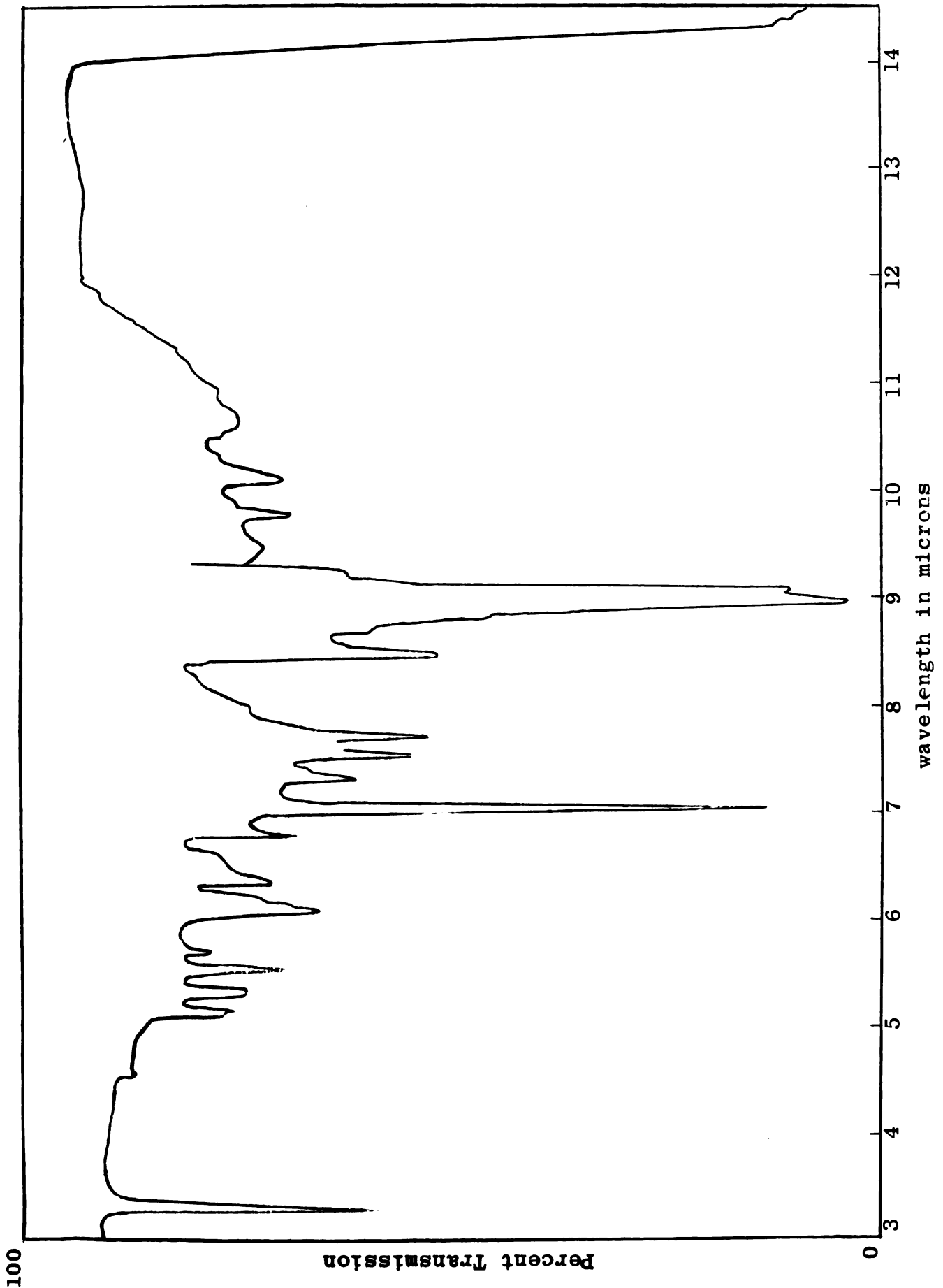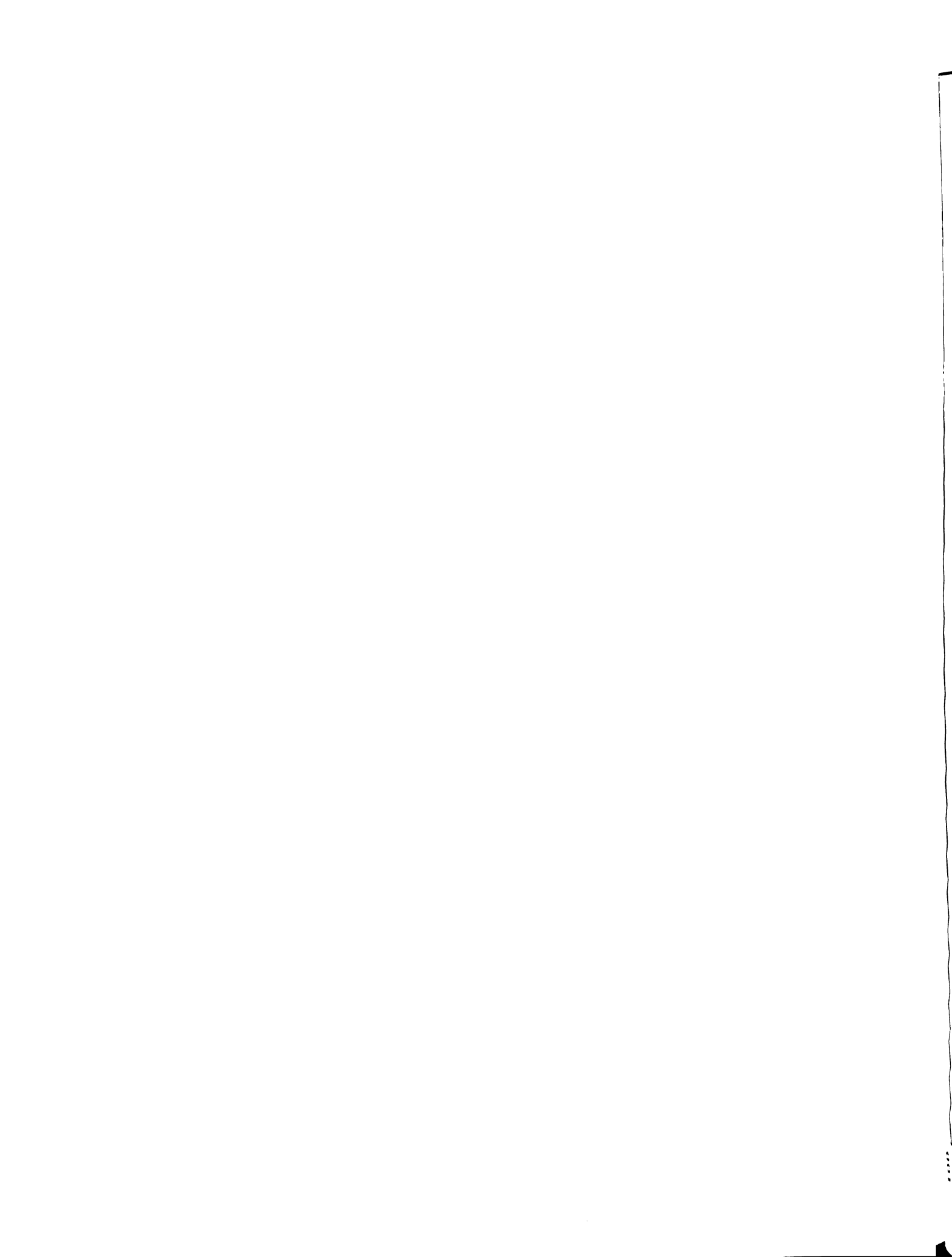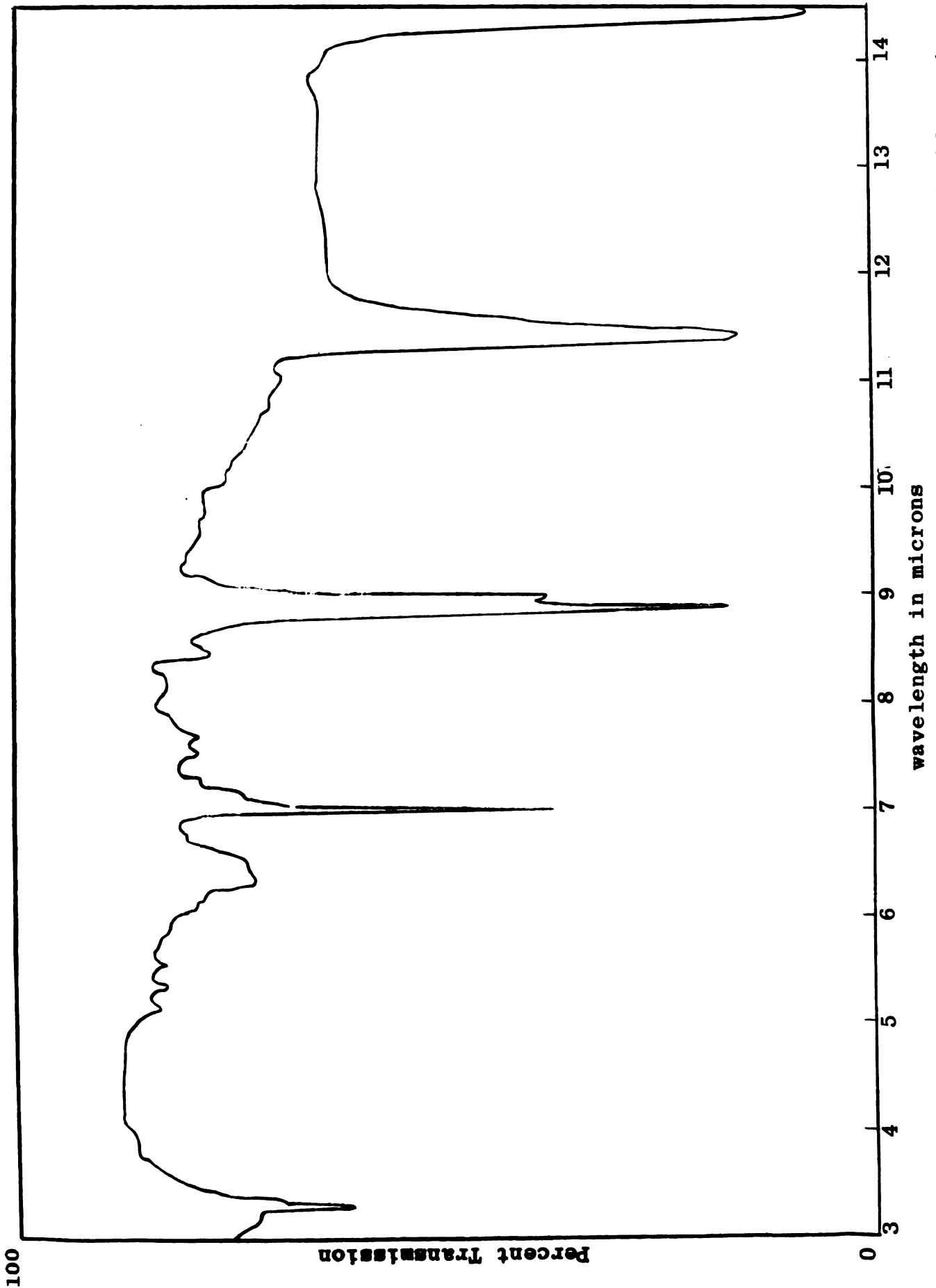Figure 16. Infrared spectrum of diphenylchlorofluorosilane in the sodium chloride region.
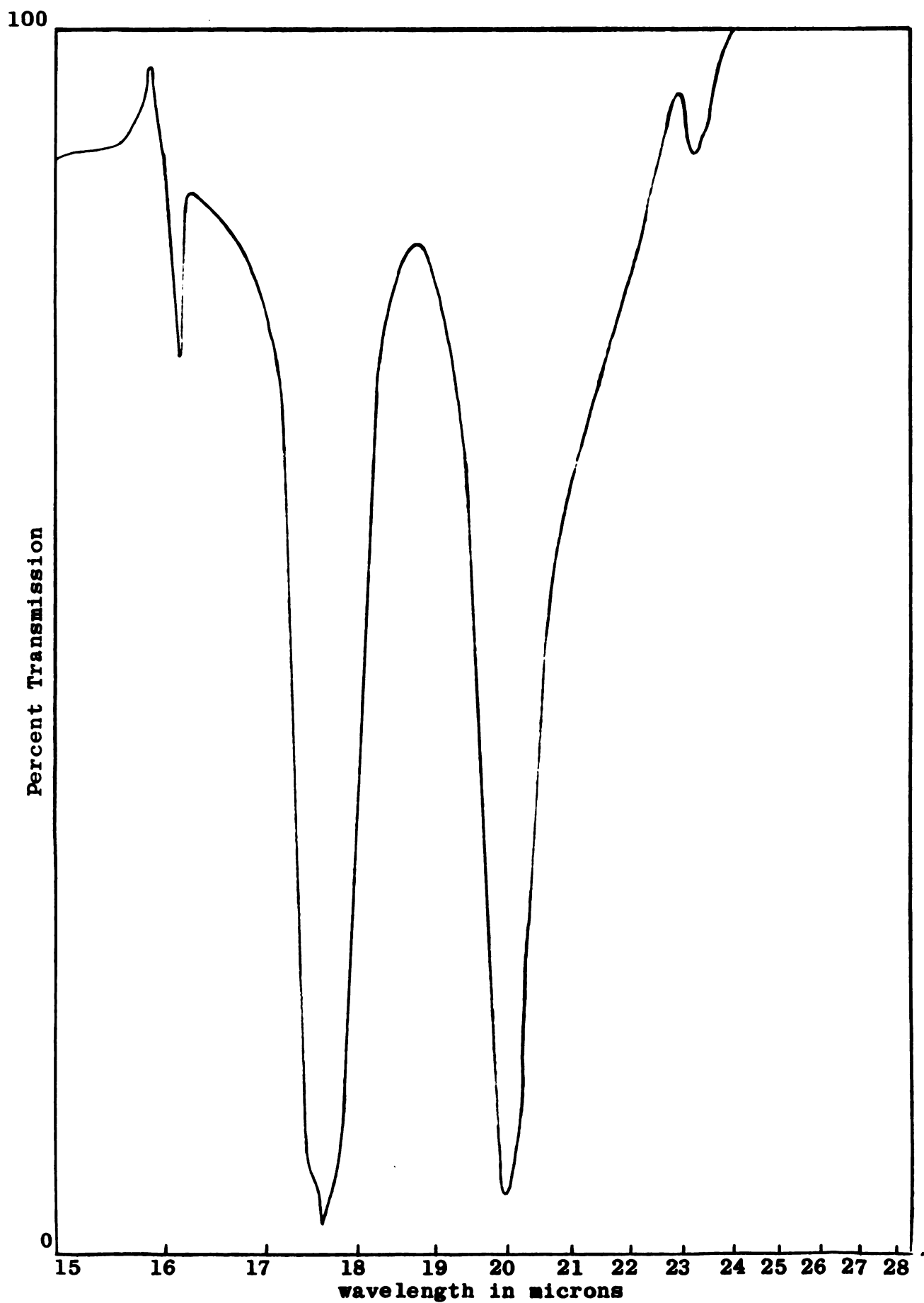
Figure 17.   Infrared spectrum of diphenylchlorofluorosilane in
            the cesium iodide region.
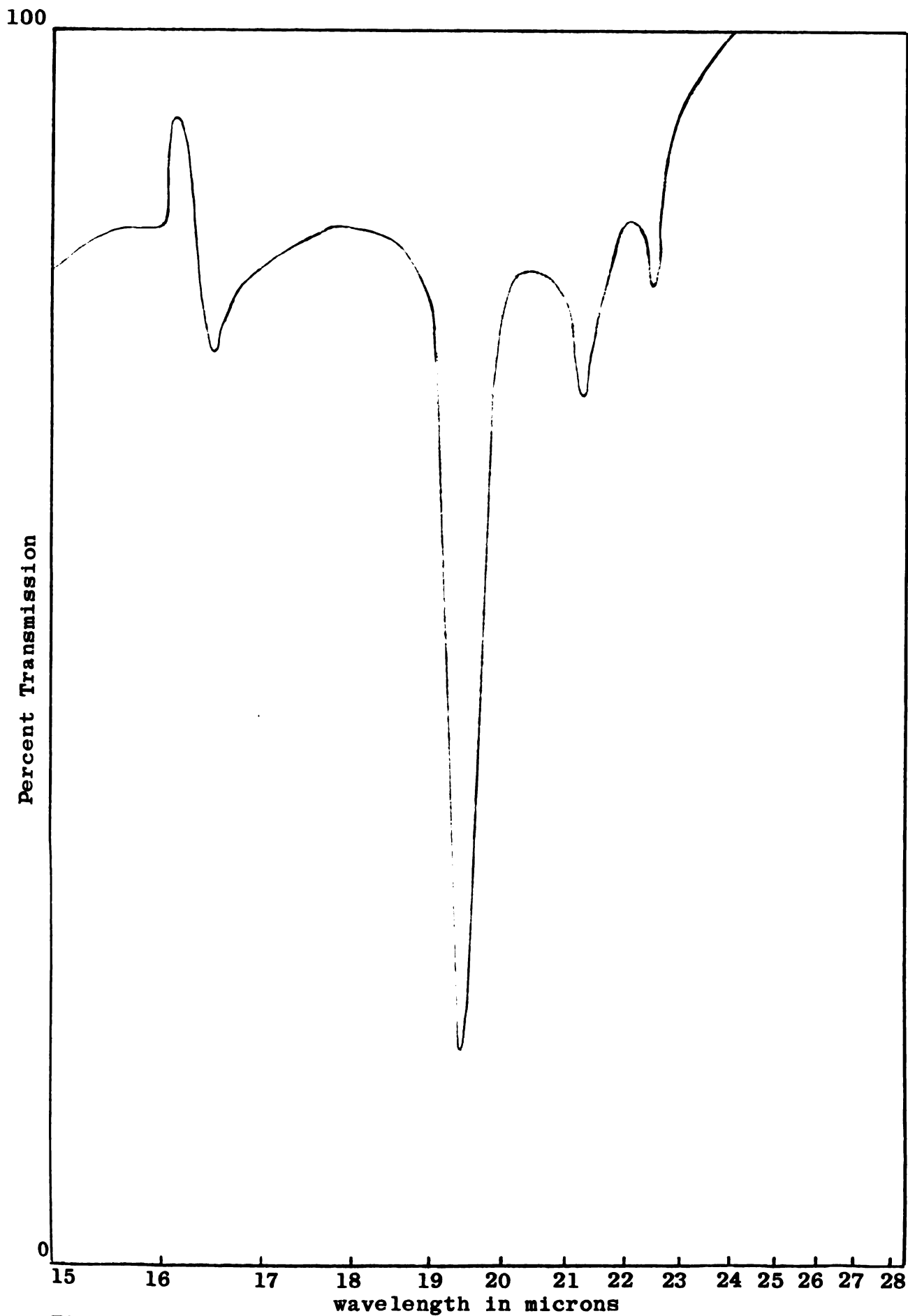
Figure 18.   Infrared spectrum of bis(triphenylsilyl)chromate(VI) in the cesium iodide region.

Figure 19. Infrared spectrum of cyclo-bis [tetraphenyldisilox-anylchromate(VI)] in the cesium iodide region.
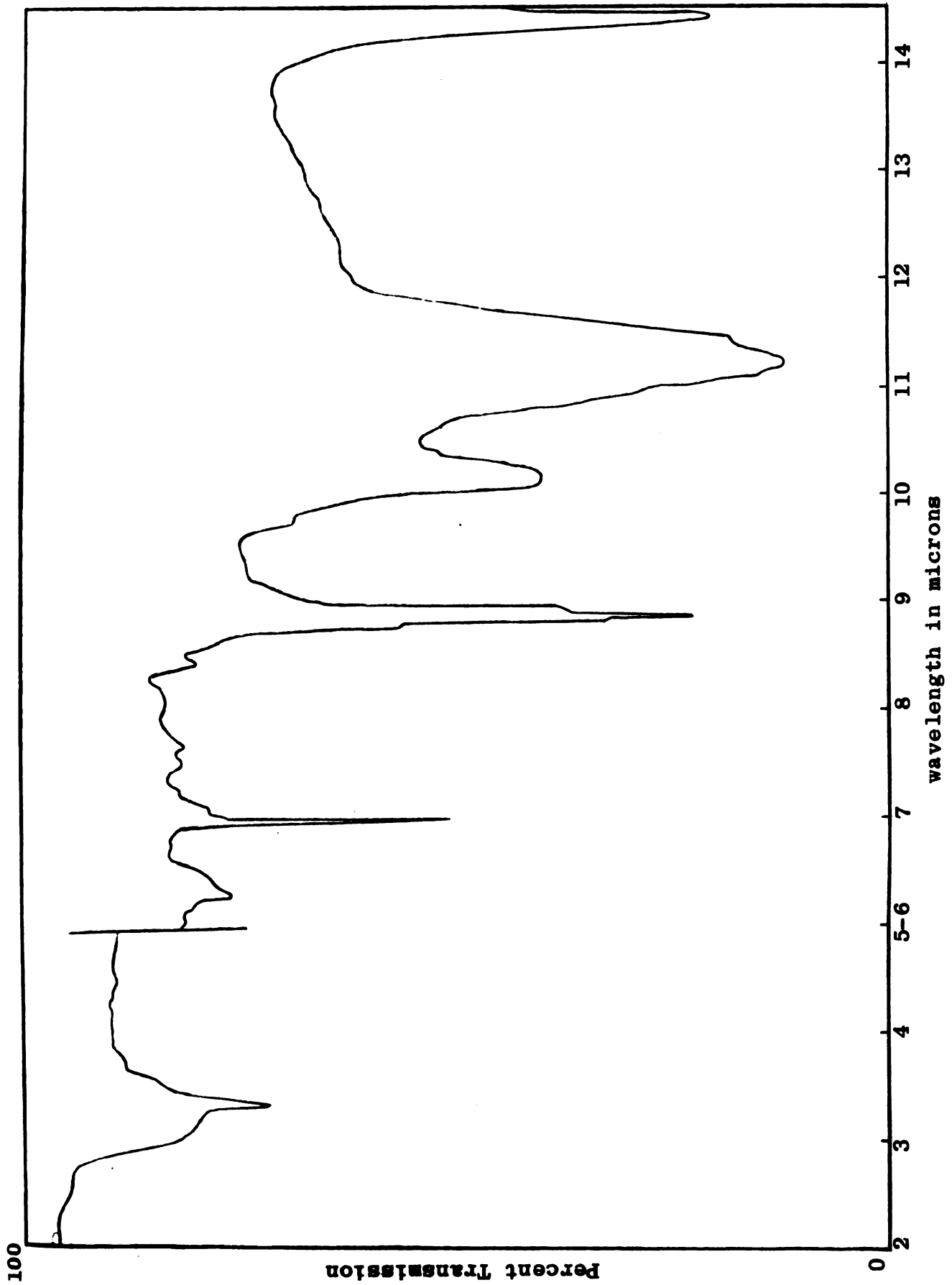
Figure 20. Infrared spectrum of bis(diphenylfluorosilyl)chromate(VI) in the sodium chloride region.
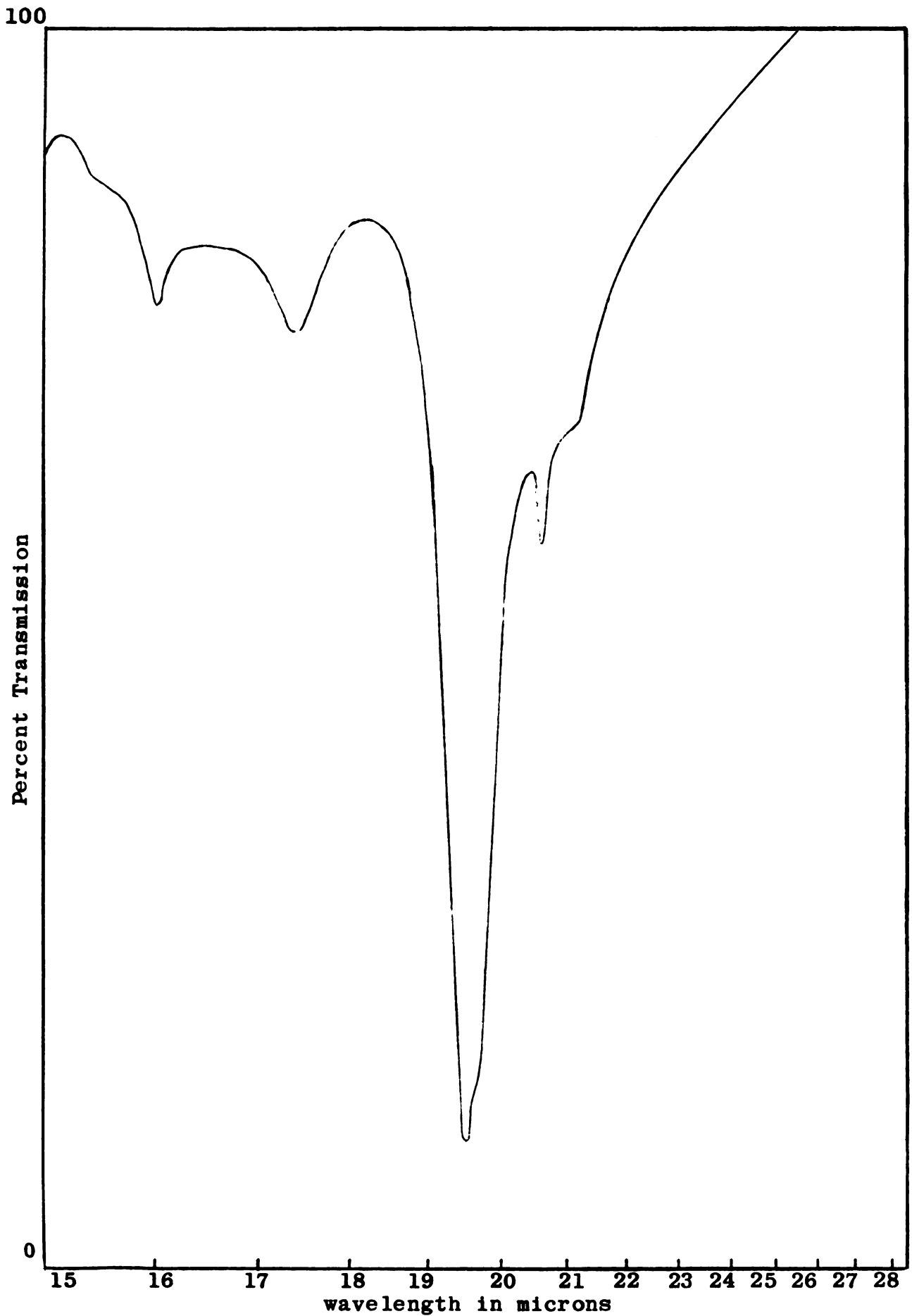
Figure 21.   Infrared spectrum of bis(diphenylfluorosilyl)-
chromate(VI) in the cesium iodide region.
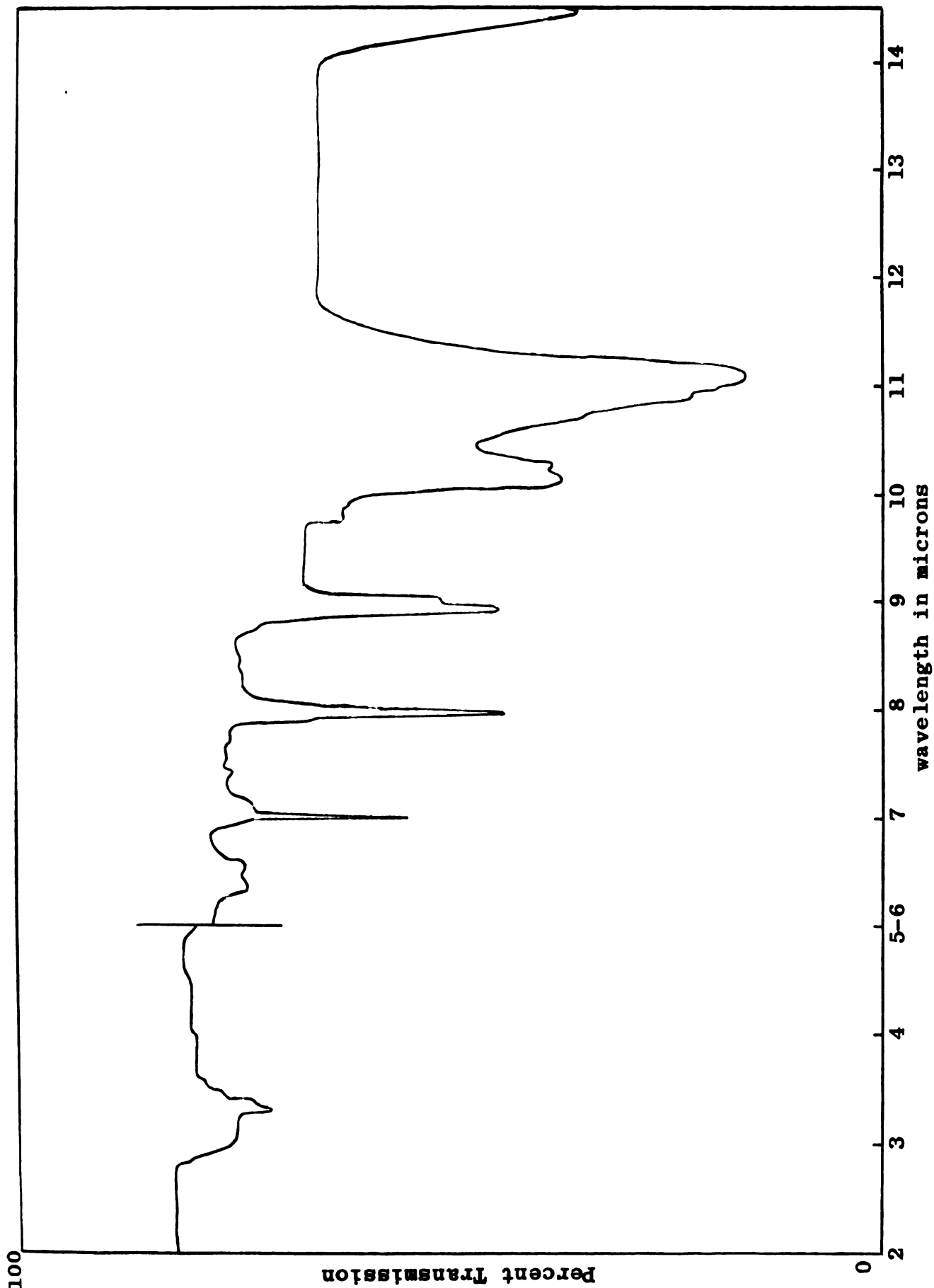
Figure 22. Infrared spectrum of cyclo—bis[diphenylsiloxanylchromate(VI)] from Ag_2CrO_4 in the sodium chloride region.
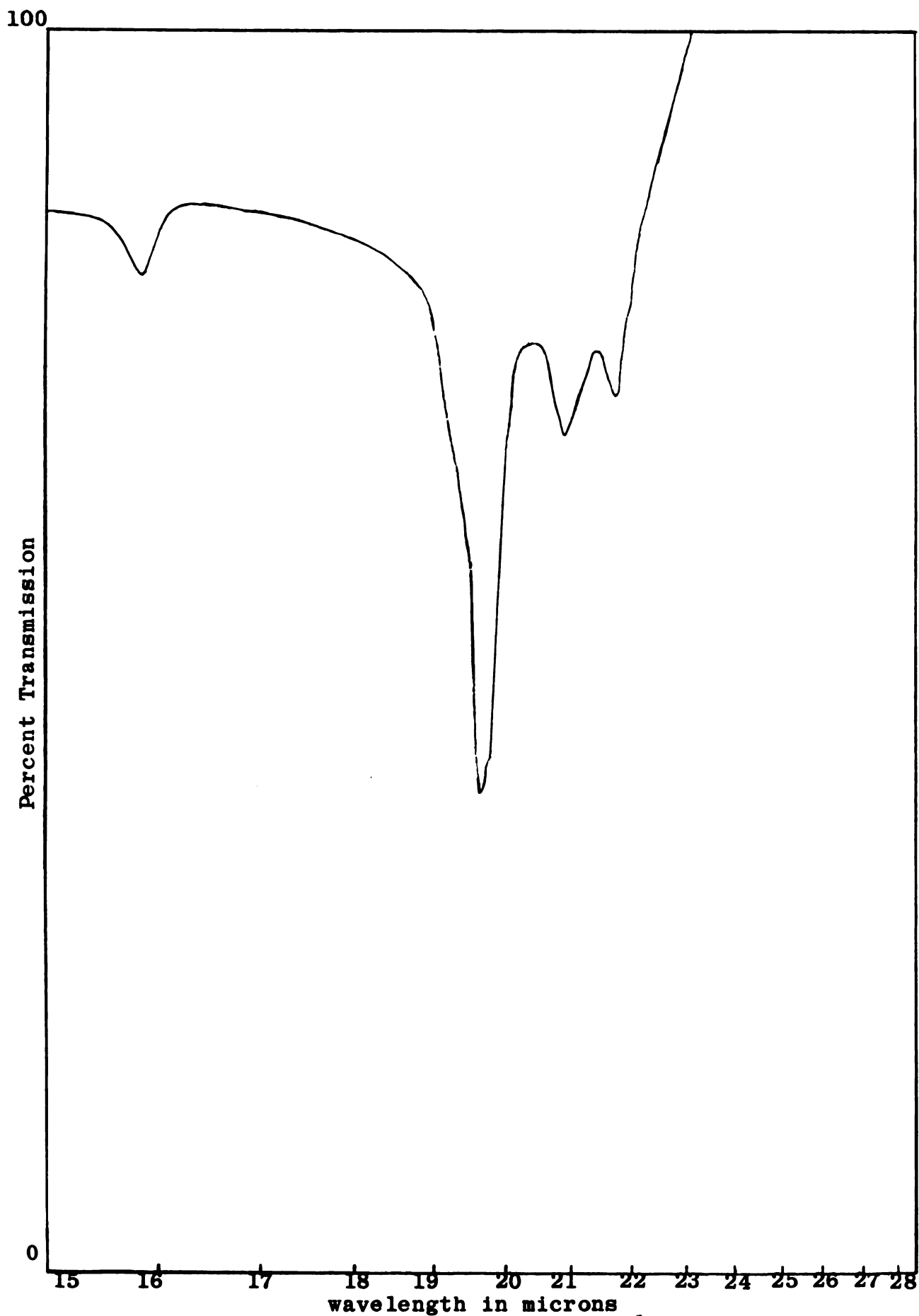
Figure 23.   Infrared spectrum of cyclo-bis[diphenylsiloxanyl-
chromate(VI)] from Ag_2CrO_4 in the cesium iodide
region.
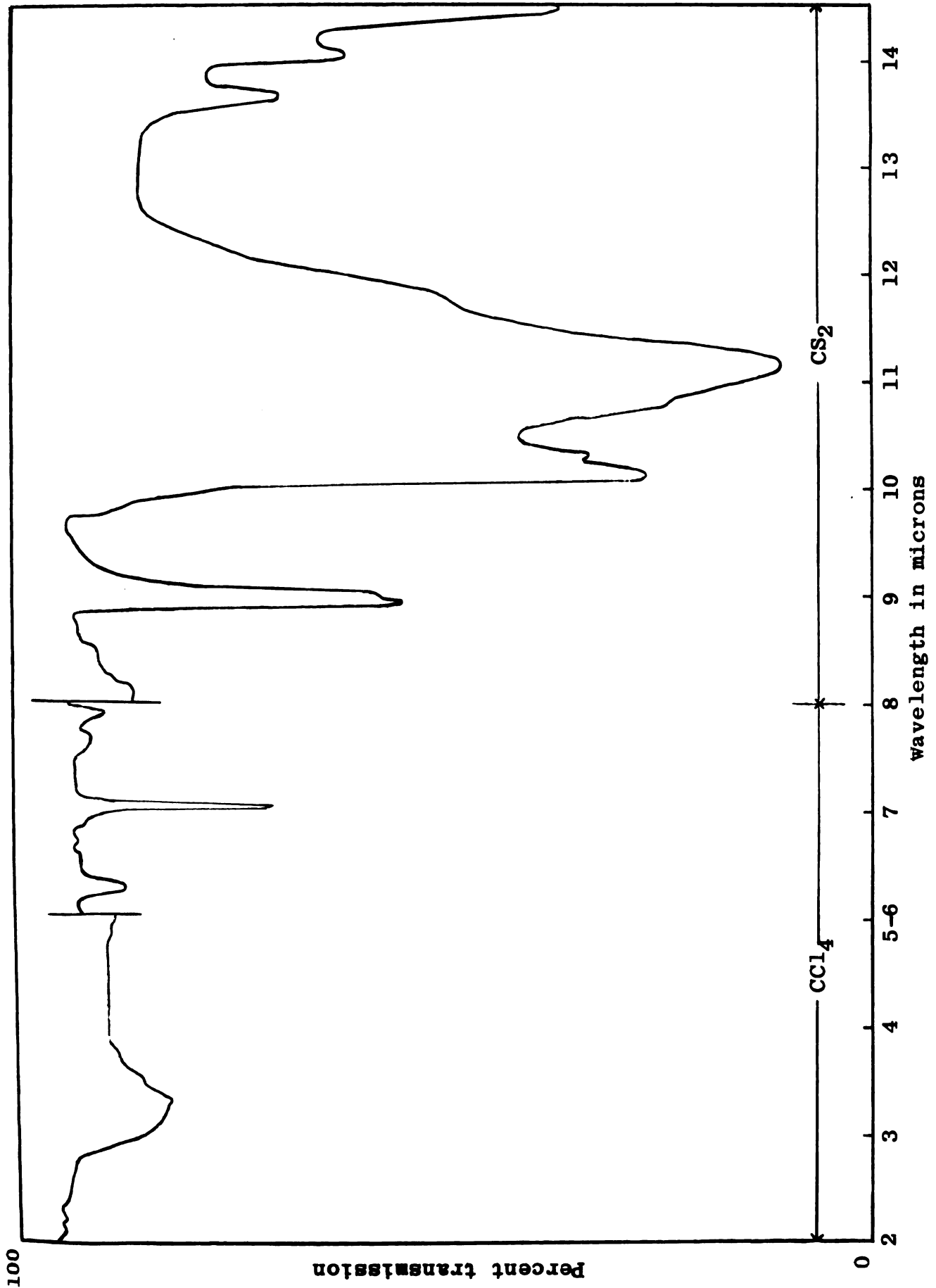
Figure 24. Infrared spectrum of cyclo-tris[diphenylsiloxanylchromate(VI)] in the sodium chloride region.
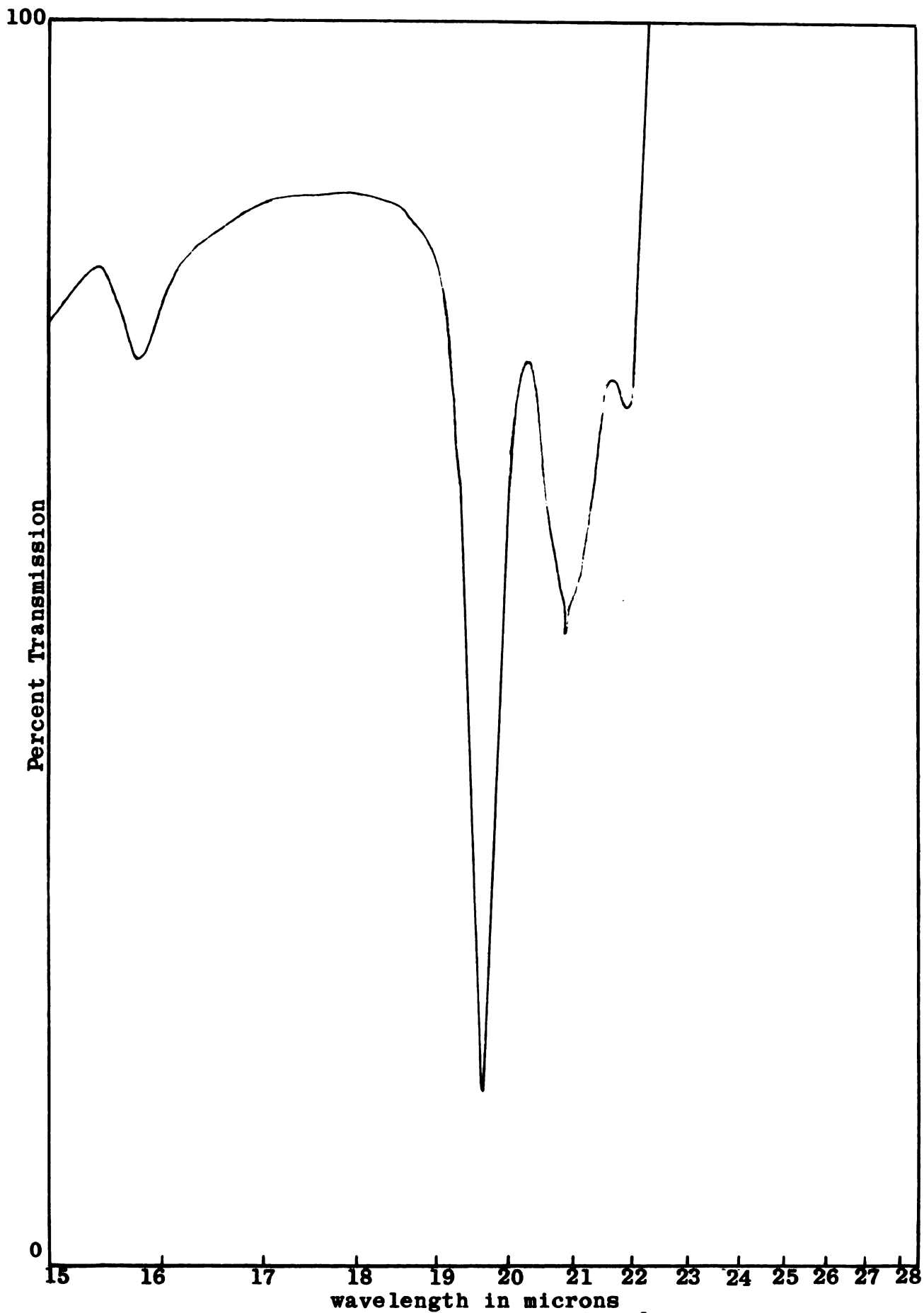
Figure 25.   Infrared spectrum of cyclo-tris[diphenylsiloxanyl-
chromate(VI)] in the cesium iodide region.
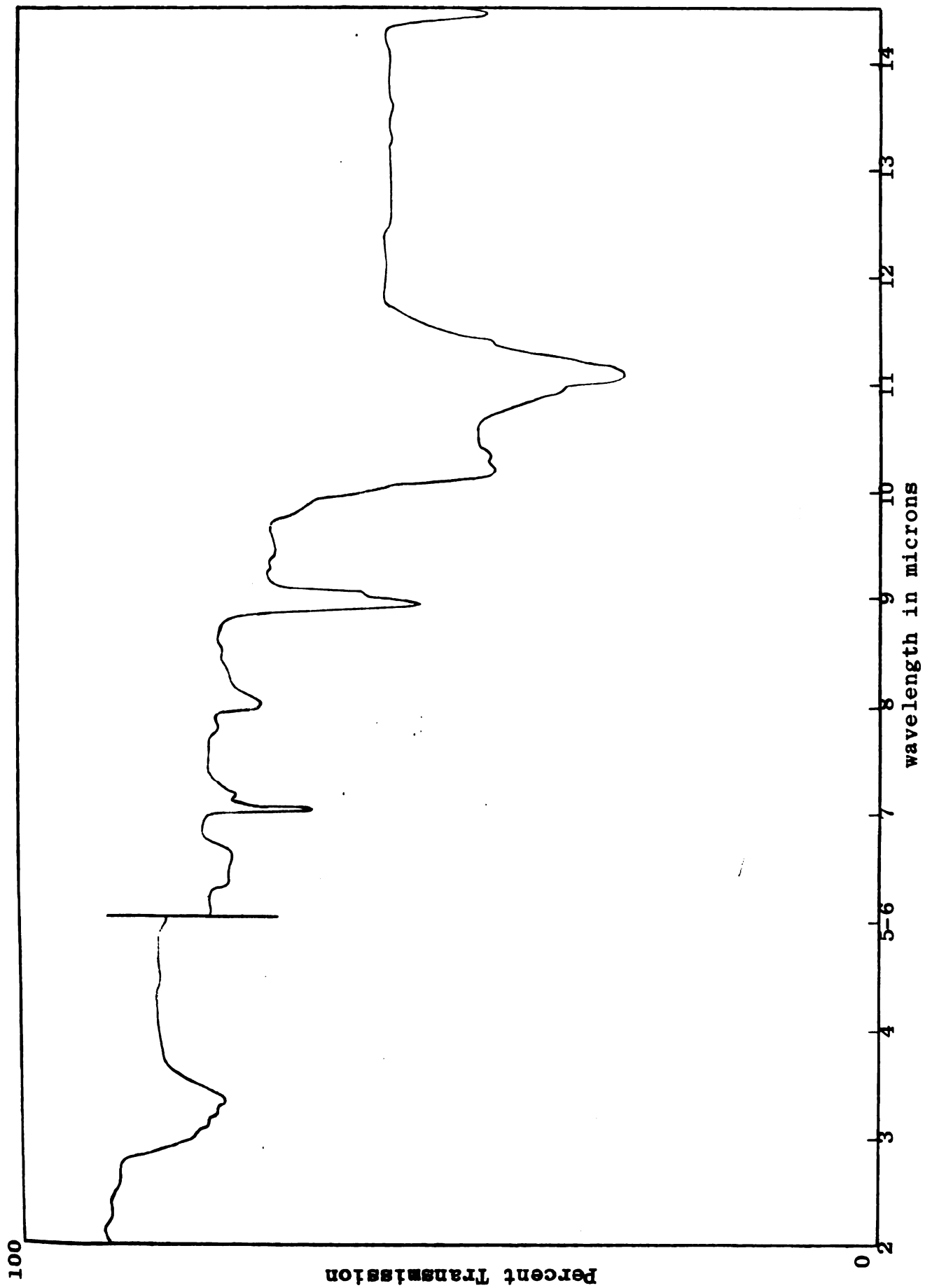
Figure 26. Infrared spectrum of cyclo-bis[diphenylsiloxanylchromate(VI)] from $Ag_2Cr_2O_7$ in the sodium chloride region.
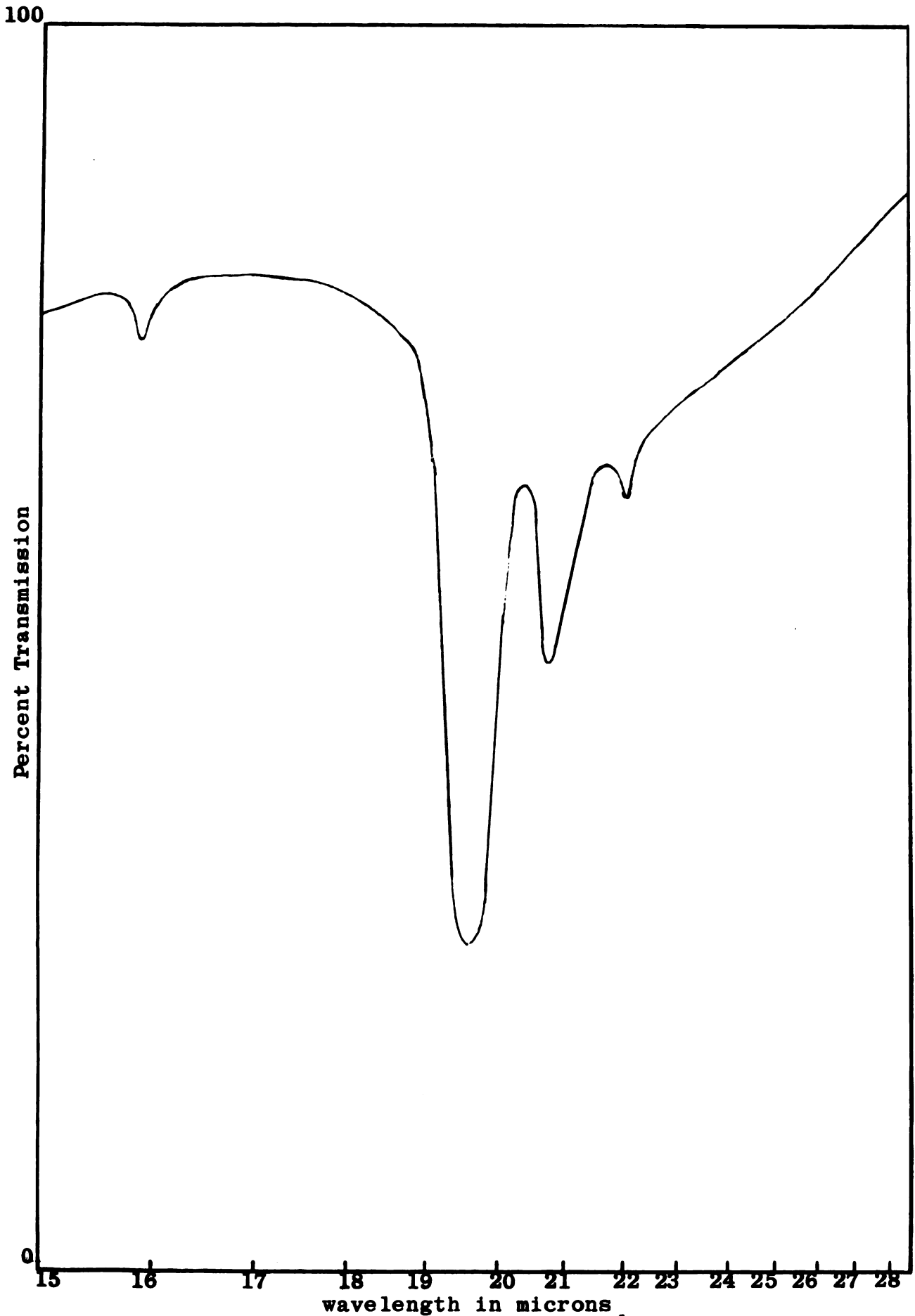
Figure 27.   Infrared spectrum of cyclo-bis[diphenylsiloxanyl-
chromate(VI)] from $Ag_2Cr_2O_7$ in cesium iodide region.
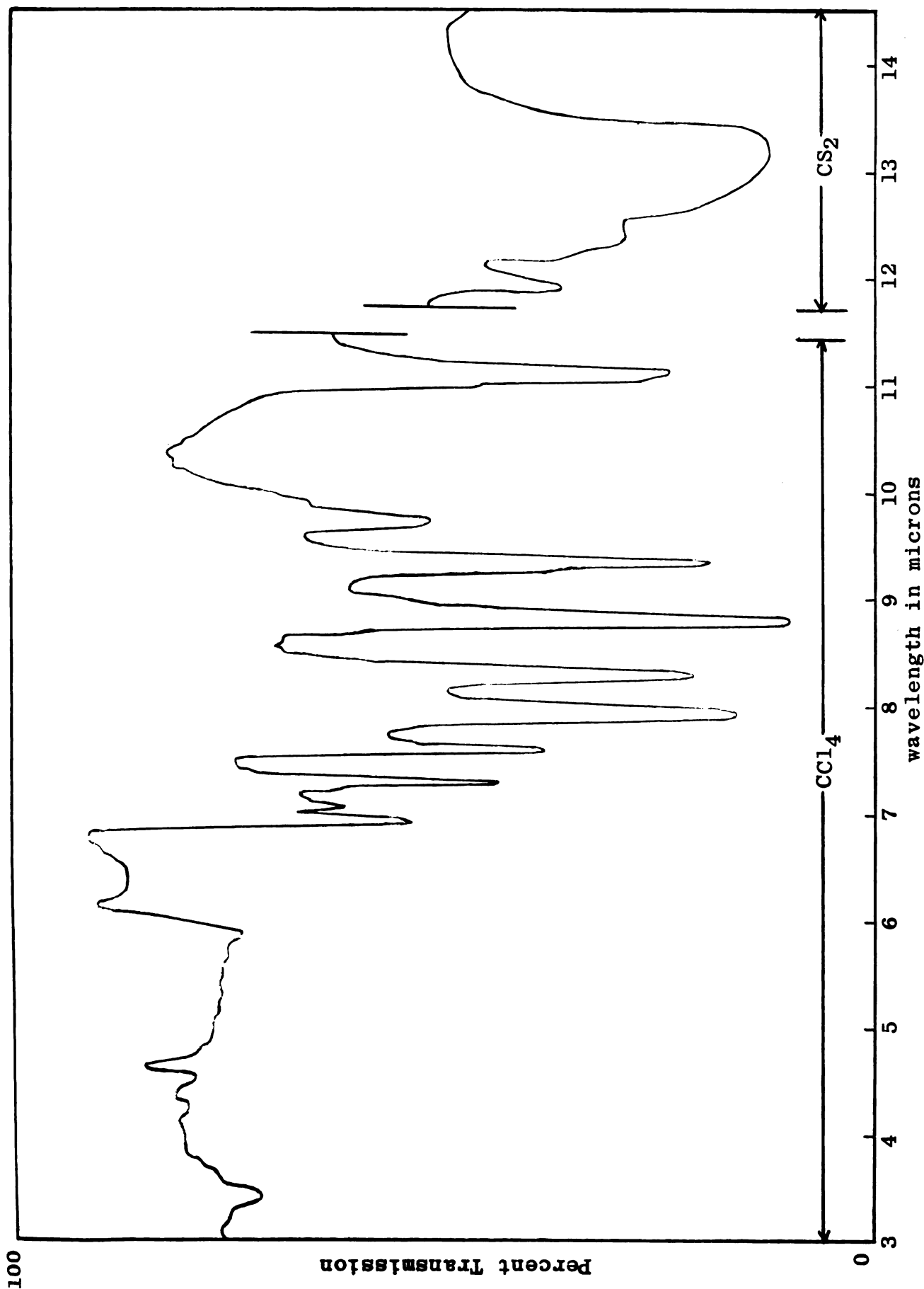
Figure 28. Infrared spectrum of 3,3,3-trifluoropropylmethyldichlorosilane in the sodium chloride region.
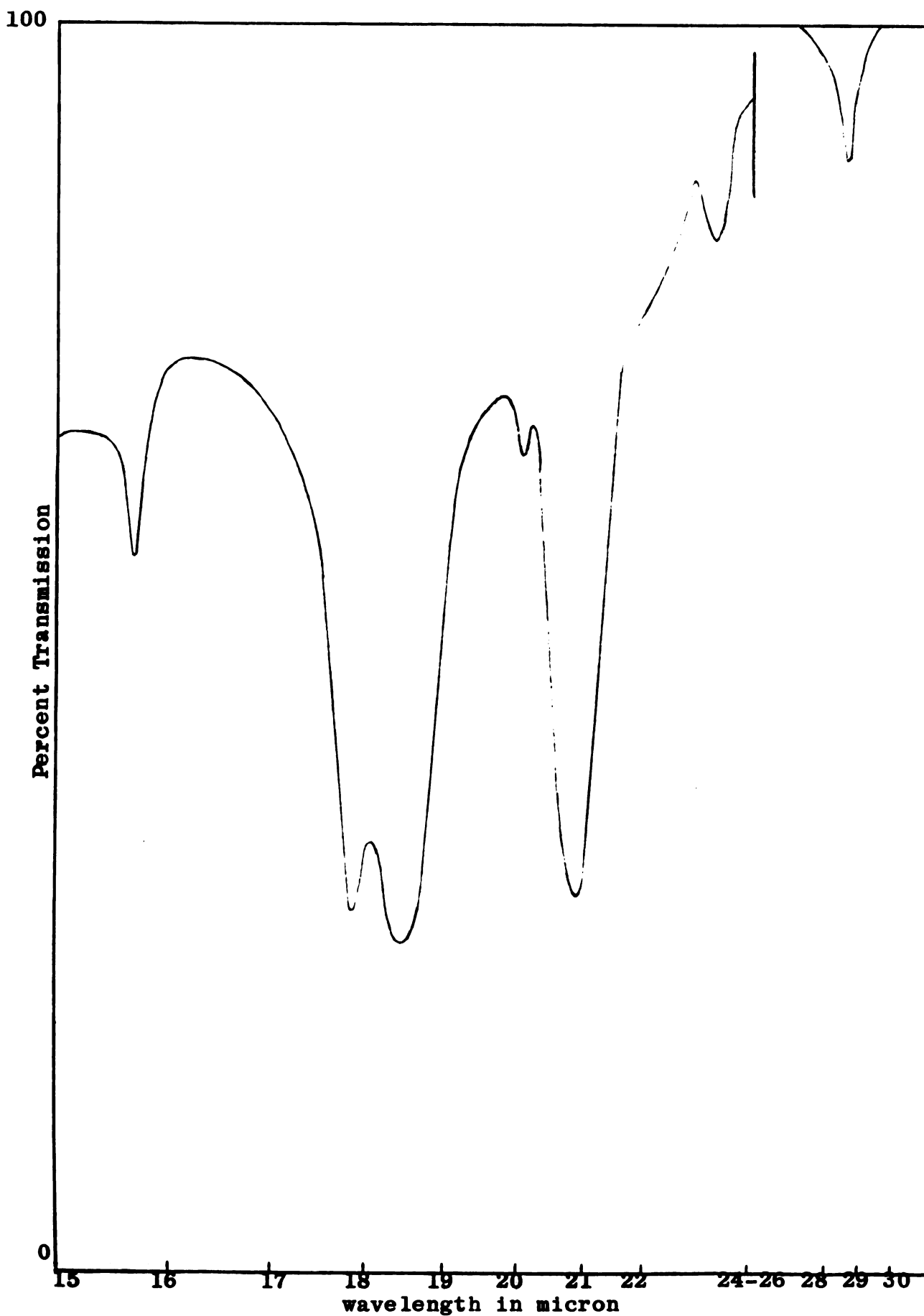
Figure 29.   Infrared spectrum of 3,3,3-trifluoropropylmethyldi-
chlorosilane in the cesium iodide region.
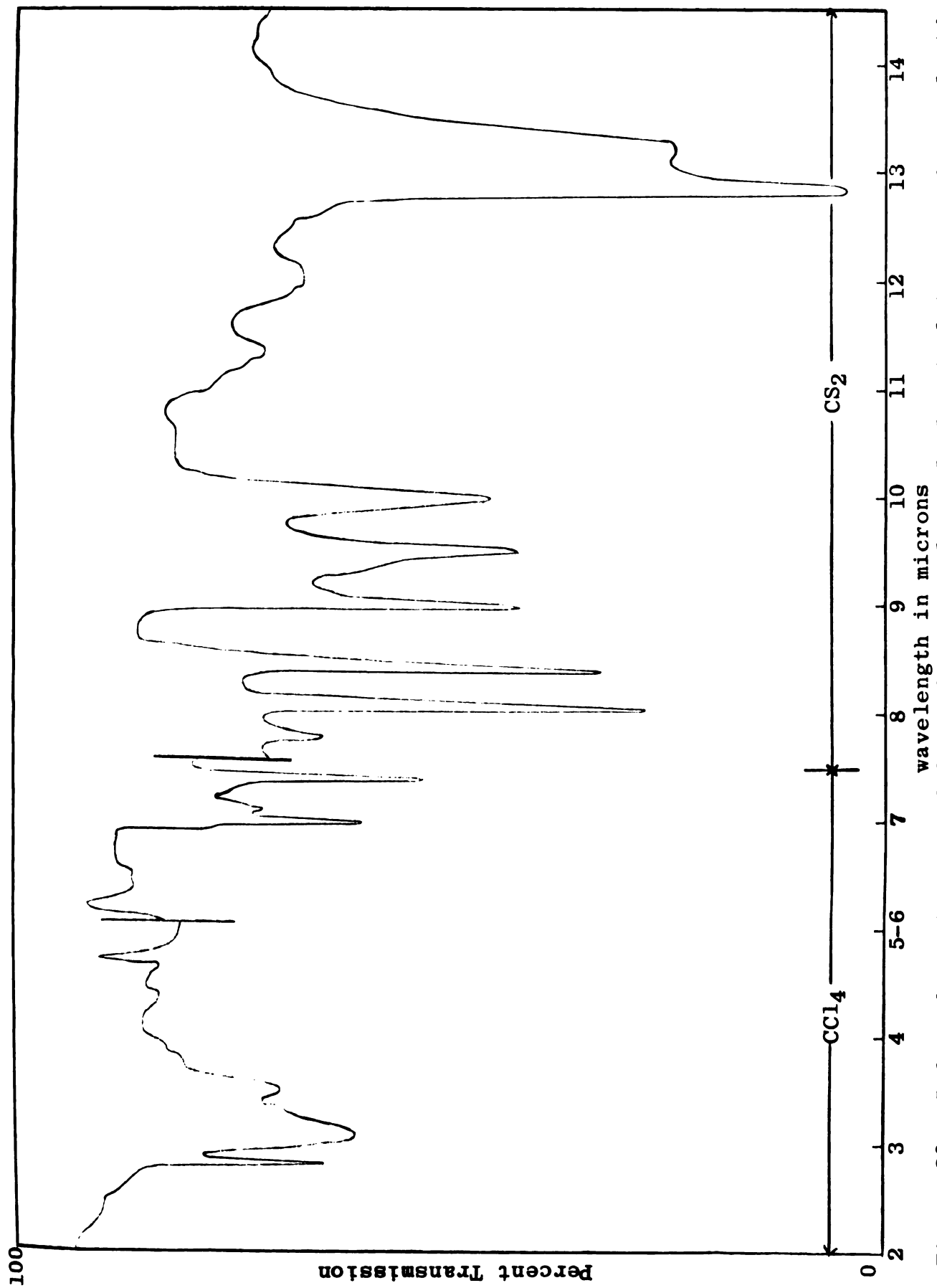
Figure 30. Infrared spectra of 3,3,3-trifluoropropylmethylsilanediol in the sodium chlcride region.
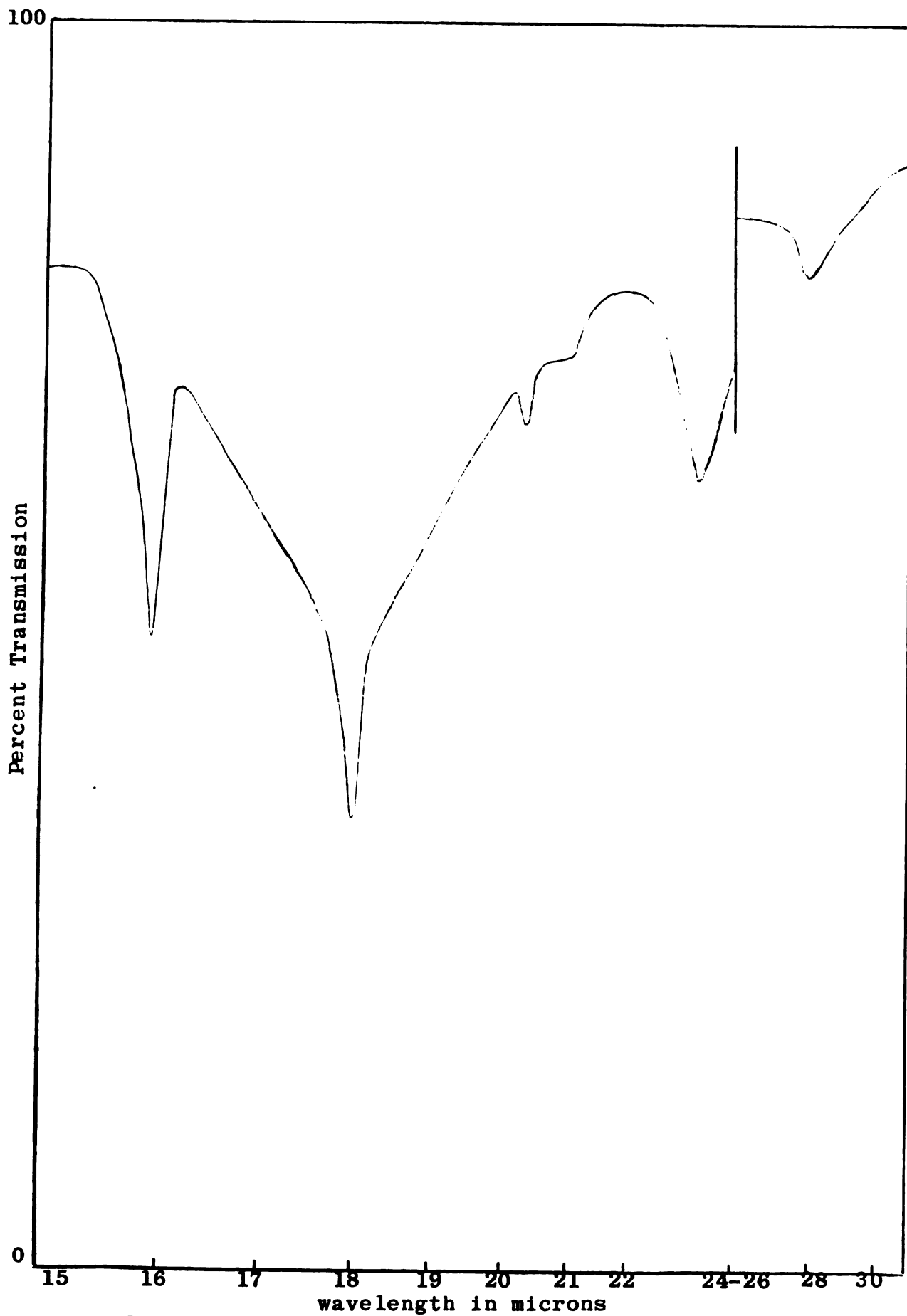
Figure 31.   Infrared spectrum of 3,3,3-trifluoropropylmethylsil-
anediol in the cesium iodide region.
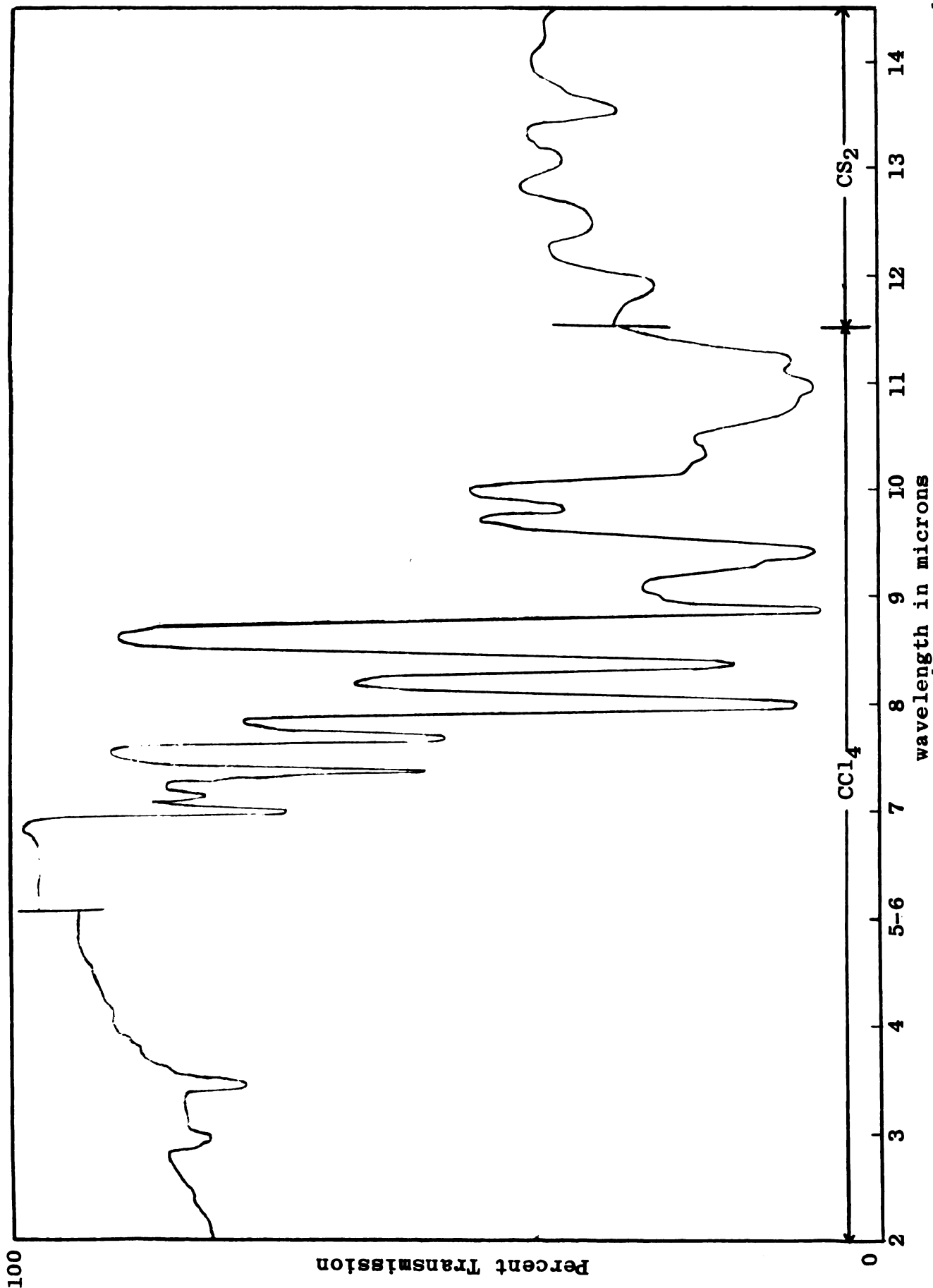
Figure 32. Infrared spectrum of cyclo-bis[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)] in the cesium iodide region.
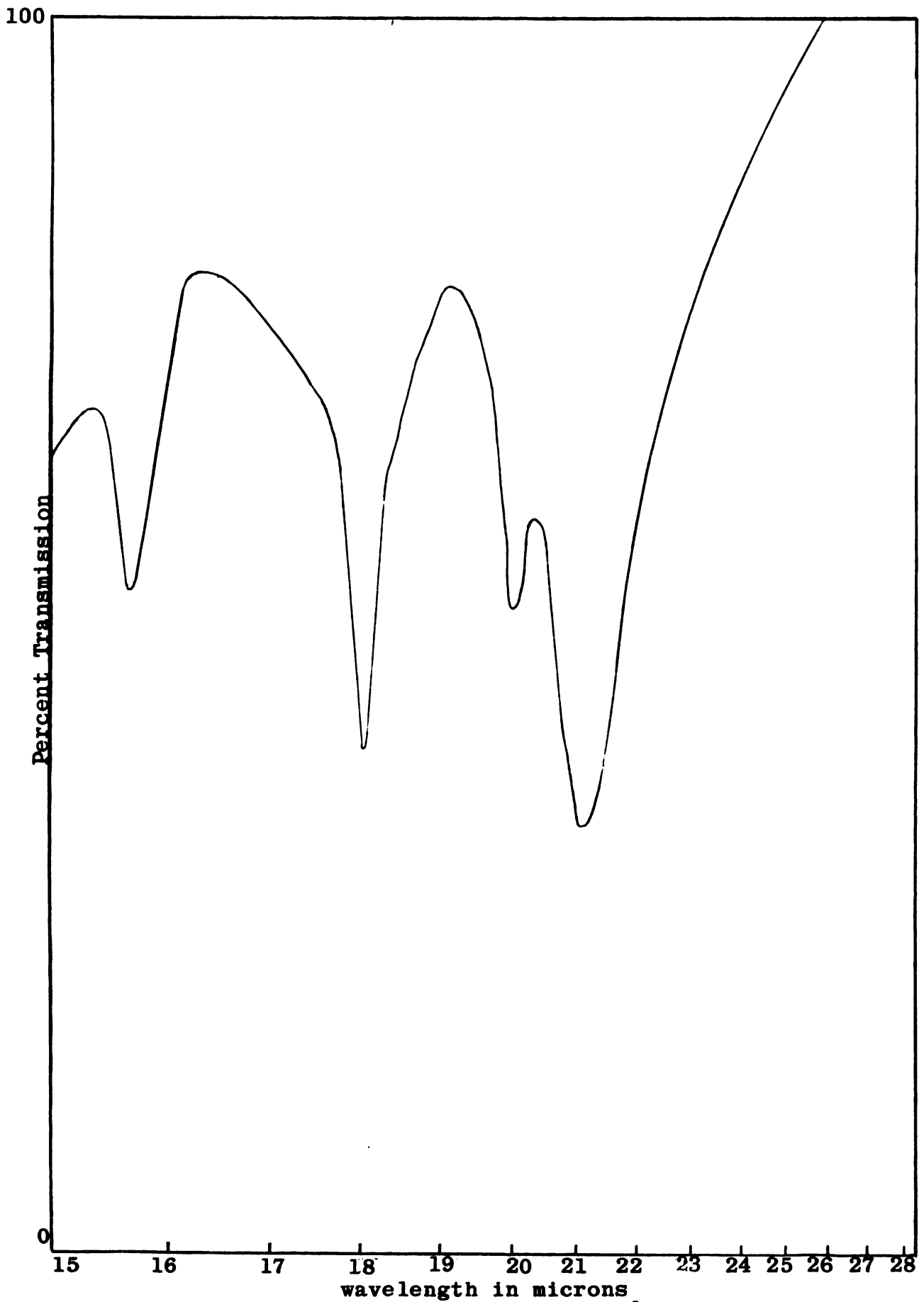
Figure 33.   Infrared spectrum of cyclo-bis[3,3,3-trifluoropro-
             pylmethylsiloxanylchromate(VI)] in the cesium
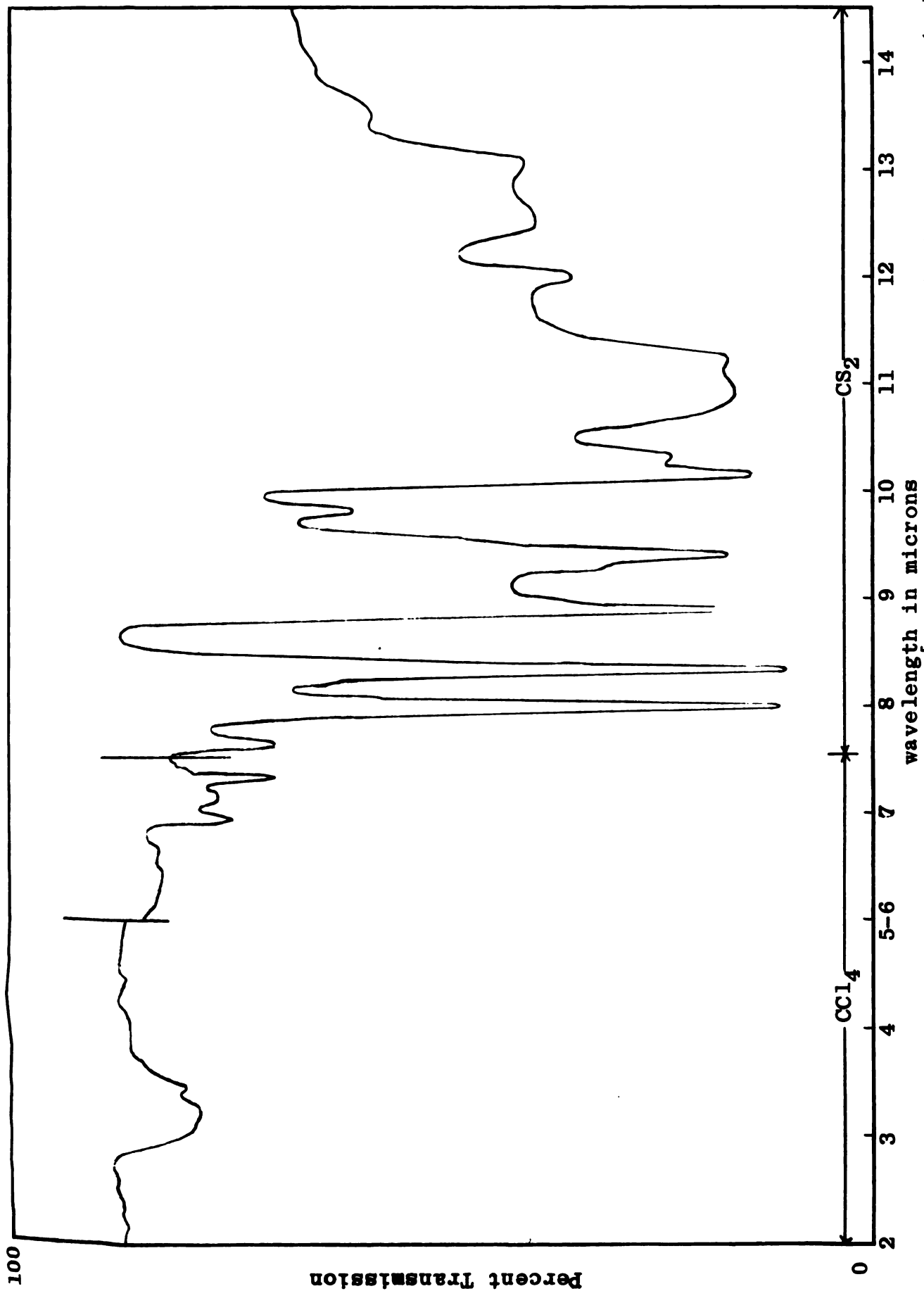
Figure 34. Infrared spectrum of cyclo-tris[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)] in the sodium chloride region.
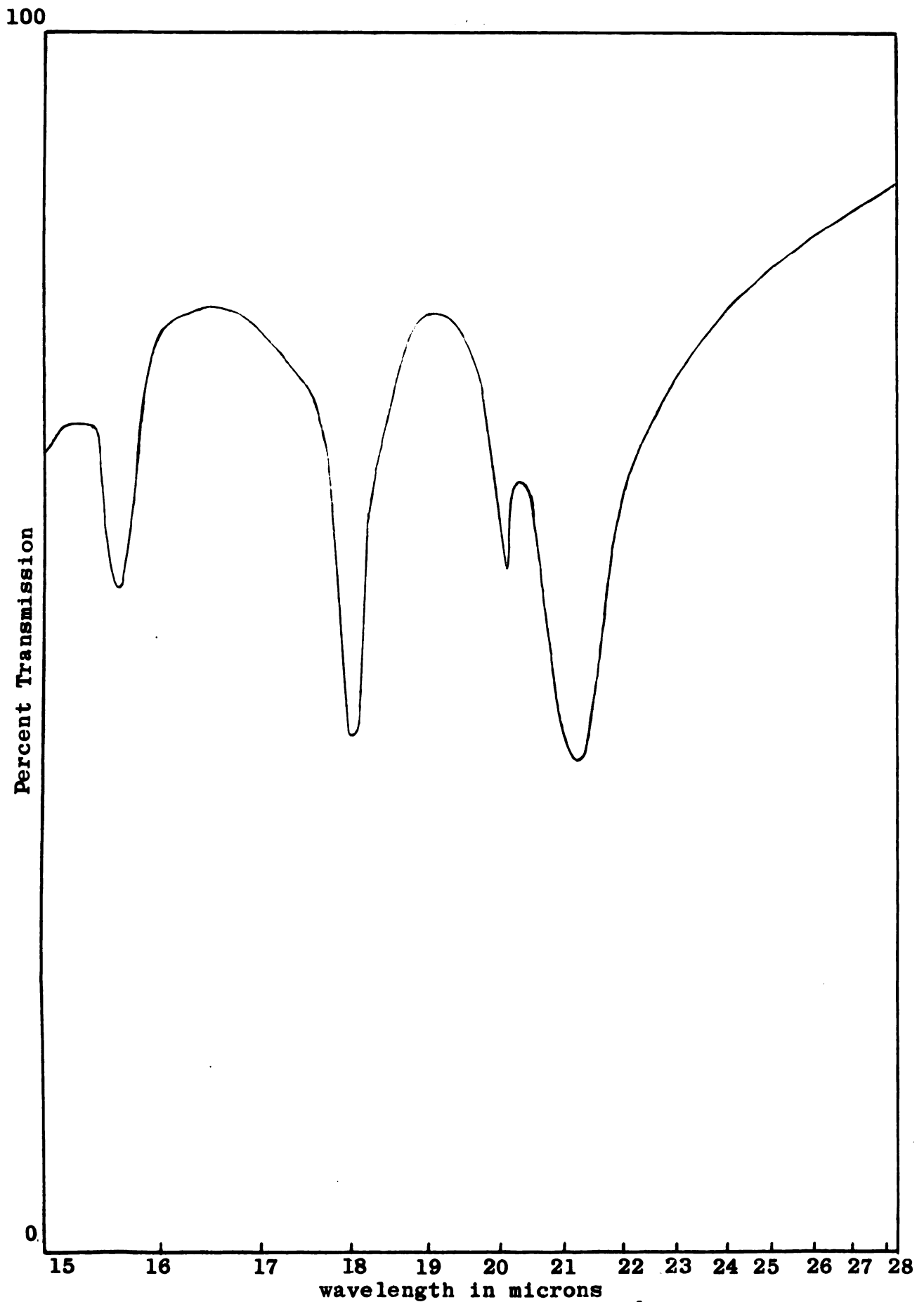
Figure 35.   Infrared spectrum of cyclo-tris[3,3,3-trifluoropro-
pylmethylsiloxanylchromate(VI)] in the cesium iodide
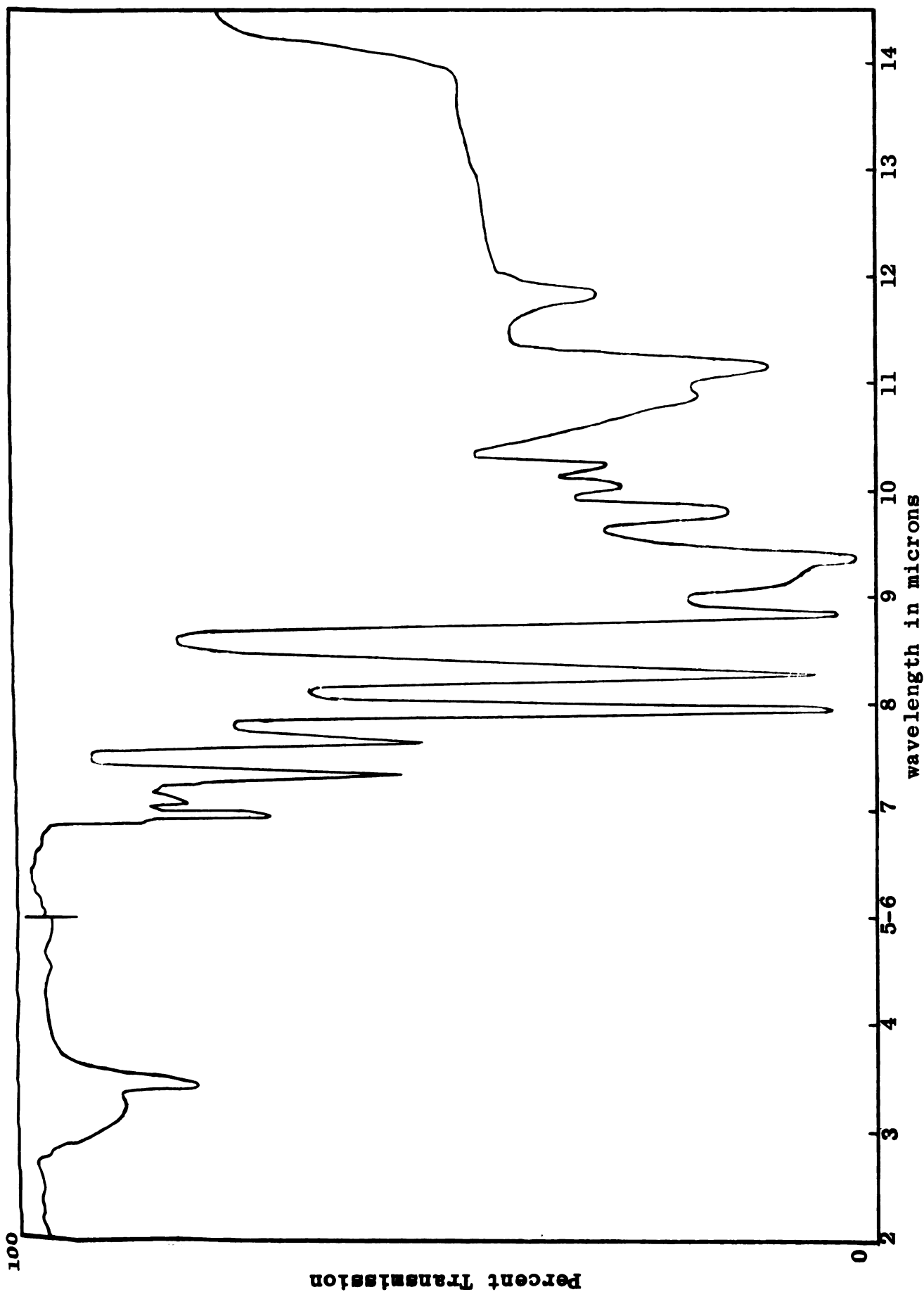
Figure 36. Infrared spectrum of cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanyl-chromate(VI)] in the sodium chloride region.
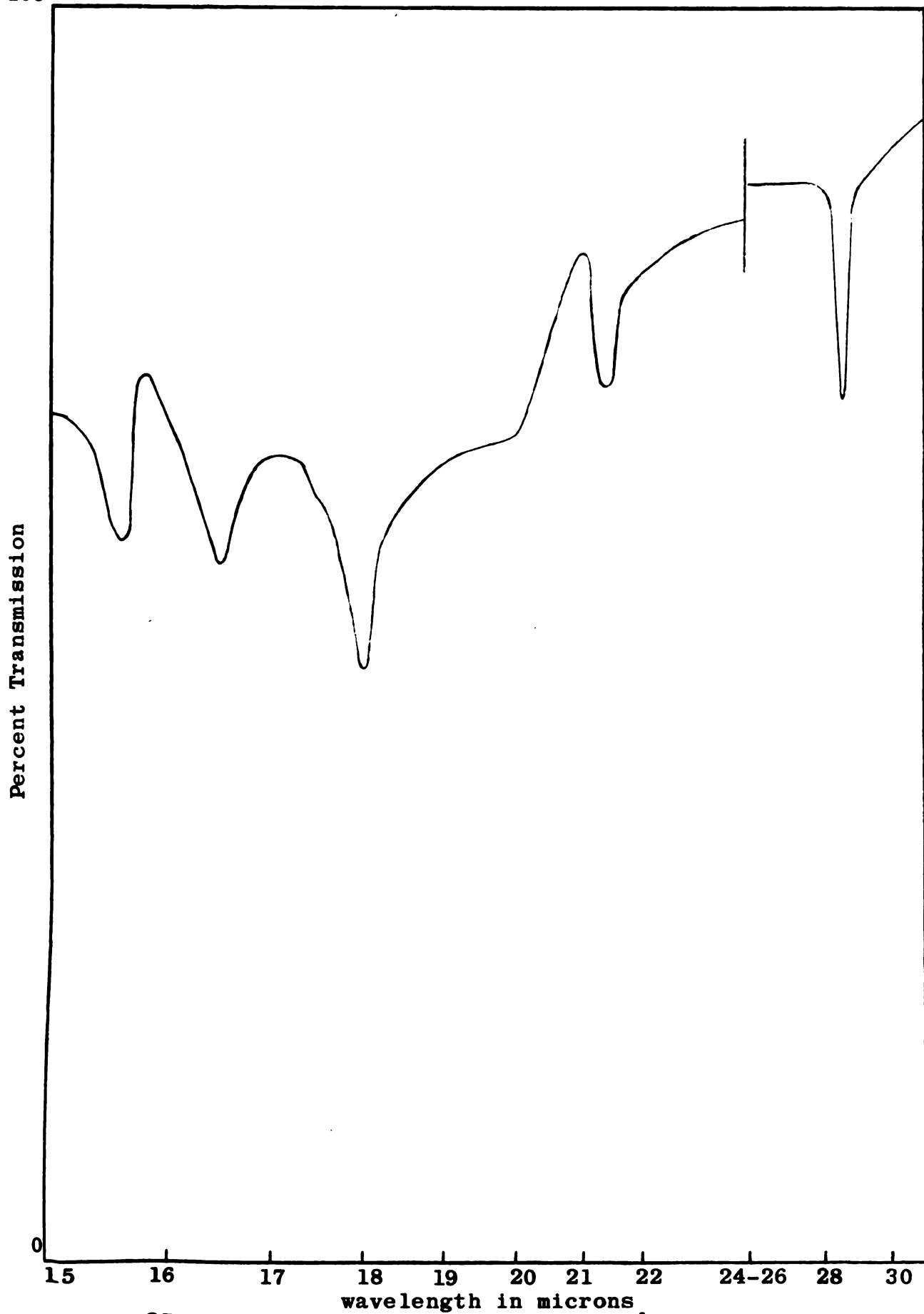
Figure 37.   Infrared spectrum of cyclo-bis[di-3,3,3-trifluoro-propyldimethyldisiloxanylchromate(VI)] in the cesium iodide region.

TABLE XIV

INTERATOMIC SPACINGS OF SILVER CHROMATE

(Cu K_α radiation, $\lambda = 1.5418\text{Å}$)

Line	θ (Degrees)	d_{hkl} (Å)	Relative Intensity
1	5.40	7.53	9
2	10.75	4.14	5
3	15.44	2.90	54
4	15.69	2.85	48
5	16.05	2.79	36
6	17.72	2.53	6
7	19.50	2.31	9
8	20.98	2.15	100
9	21.49	2.11	30
10	22.01	2.06	16
11	22.56	2.01	16
12	24.34	1.87	21
13	25.05	1.82	5
14	25.89	1.77	11
15	27.78	1.65	15
16	28.39	1.62	20
17	30.83	1.50	12
18	31.40	1.48	10

TABLE XV

INTERATOMIC SPACINGS OF SILVER DICHROMATE

(Cu K_α radiation, λ = 1.5418$\overset{\circ}{A}$)

Line	θ (Degrees)	d_{hkl} ($\overset{\circ}{A}$)	Relative Intensity
1	5.53	7.00	20
2	8.72	5.09	5
3	10.80	4.11	5
4	15.42	2.90	95
5	15.55	2.88	92
6	16.00	2.80	100
7	16.69	2.69	15
8	19.47	2.31	19
9	20.87	2.16	49
10	21.44	2.11	15
11	21.96	2.06	24
12	22.54	2.01	28
13	25.87	1.77	13
14	28.26	1.63	20
15	28.86	1.60	30
16	31.28	1.48	14
17	31.63	1.47	9

DISCUSSION

Hydrolytic - Stability.

Silyl and siloxanylchromates prepared prior to this study have shown very little stability in the presence of water. Cyclo-bis[tetraphenyldisiloxanylchromate(VI)] (5) decomposes very slowly in water but very quickly in wet organic solvents such as acetone or ether. Its slow reaction with pure water apparently results from the non-wetability of the crystalline solid. The hydrolytic stabilities shown by siloxanylchromates containing the trifluoropropyl groups were therefore somewhat surprising. McBee (109) found that 3,3,3-trifluoropropylmethyldichlorosilane and similar silanes are not only stable in the presence of water but do not hydrolyze with prolonged refluxing in the presence of forty percent potassium hydroxide. Clark, et al. (136) found diperfluoropropyldialkylsilanes to be impervious to water but unstable to fifty percent potassium hydroxide solutions. Haszeldine (65) has shown that the thermal and hydrolytic stabilities of polyfluoroalkylsiloxanes are dependent upon the position of the fluorines relative to the silicon. He found the following stability relationships: ɤ fluorine ≫ β > ⍺ .

The hydrolysis of the silyl and siloxanylchromates quite possibly results from a nucleophilic attack on the

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silicon which has been given partial positive character by the electron-withdrawing organic substituents. The phenyl radicals in phenylsiloxanylchromates and the fluorine substituent of bis(diphenylfluorosilyl)chromate(VI) would therefore create favorable conditions for hydrolysis; however the 3,3,3-trifluoropropyl substituent would also enhance hydrolysis for it has been shown to have definite electronegative character (137). The fluoroorganic and methyl groups must in some manner inhibit the attack of the nucleophilic agent. Steric hinderence is not a likely explanation, for the phenyl substituents would afford more protection than the 3,3,3-trifluoropropyl and methyl groups. The silicon-oxygen bond could possibly be shielded from the nucleophilic agent by the strong polar environment established around the silicon by the 3,3,3-trifluoropropyl and methyl groups (85).

Thermal Stability.

The decomposition temperatures of several organosilyl-chromates prepared by Hare (5) indicated that the nature of the organic groups has a direct influence on the thermal properties of the compound. Molecules containing organo-silicon substituents with electron-withdrawing character are considerably more thermally stable than those with electron-releasing groups. Bis(trimethylsilyl)chromate(VI) is

explosive at room temperature; bis(diphenylmethylsilyl-chromate(VI) and bis(diphenyl-p-tolylsilyl)chromate(VI) decompose when warmed, while bis(triphenylsilyl)chromate(VI) is unaffected by temperatures below 300° C. (Figure 39, p. 151). Similar trends have been observed with organosiloxy-vanadates (138, 139) and organosiloxytitanates. Burg (140) reported that the thermal stability of resins with phosphorus-phosphorus bonding were greatly enhanced by the addition of the highly electronegative perfluoromethyl substituents. Andrianov (143, 159) found that the "oxidative destruction" of polyorganosiloxanes was dependent upon the nature of the organic radical. He established the following order of diminishing thermal stabilities:

$$C_6H_5 \quad > \quad CH_2 - CH_2 \quad > \quad CH_3 \quad > \quad C_2H_5.$$

Because of the apparent connection between greater thermal stability and highly electronegative substituents, it was felt that organosilyl and siloxy chromates containing fluorine and fluoroorganic radicals would show even better resistance towards thermal oxidation than had been seen previously. Fluorine was selected for several reasons. It is the most electronegative element (47) and is also believed to exert a greater electron-withdrawing tendency than any poly-elemental radical. The silicon-fluorine ionic bond energy of 143 kcal/mole (141) and the energy of homolytic

cleavage (135 kcal/mole) (6, 7) is the highest of any known silicon linkage. The silicon-oxygen bond which shows such phenomenal thermal properties in naturally occurring silicates has a considerably lower bond energy (89 kcal/mole). It should be noted that bond energies, although important, are not the only, or even the primary, influence upon thermal stabilities. Although the energy of the silicon-oxygen bond is more than twice as large as the silicon-carbon bond, linear polysiloxanes yield cyclic siloxanes upon heating, leaving the silicon-carbon bond intact. Explanations for this occurrence usually attribute it to reaction mechanisms in which bond rearrangement occurs through a transition state with a low energy barrier relative to that required for direct thermal rupture (51, 73). Fluorine also increases the thermal stability of the carbon-carbon bond. The decomposition temperature for tetrafluoroethylene polymers (510° C.) is one hundred degrees higher than for polyethylene (159, 142). Kriegsmann (53) examined the force constants for Si-X bonds (X = F, Cl, Br, I, O, S, N, C, and H) and found that a strengthening of the Si-X bond and neighboring bonds in the silicon occurred when X was a strongly electronegative element. He stated that the electronegative tendency imparted partial double bond character to the Si-X linkages.

The thermal properties of various silyl and siloxanyl-chromates were studied by differential thermal analysis (DTA).

The thermal effect for various physical and chemical type reactions are listed in Table XVI.

TABLE XVI

PHYSICAL AND CHEMICAL ENTHALPIC REACTIONS (145)

Reaction Type	Thermal Effect*
Physical	
Absorption	+
Adsorption	+
Crystalline transition	±
Desorption	-
Fusion	-
Second-order transition	-
Sublimation	-
Vaporization	-
Chemical	
Chemisorption	+
Decomposition	-
Dehydration	-
Desolvation	-
Oxidation in gaseous atmosphere	±
Oxidative degradation	±
Redox reaction	±
Reduction in gaseous atmosphere	±
Solid-state reaction	±

* + Exothermic reaction,   - Endothermic reaction

The analyses of the liquid organosiloxychromates were accomplished by mixing the liquid with alumina to form a thick paste, thereby preventing sample leakages or absorption into the ceramic holder. This technique also decreased the intensity of the thermogramic bands to convenient size for the recorder

being used. Crystalline materials were ground to fine pow-
ders before analysis to increase the definition of the result-
ing thermal peaks (144). All analyses were performed at a
temperature elevation rate of 10° C./min.

Thermograms obtained from analyses of organosiloxy-
chromates exhibited broad and intense endothermic peaks with
maxima lying between 300 and 500° C. Smaller endothermic
bands were always found at 532 ± 12° C. The crystalline com-
pounds showed sharp endotherms which occurred at temperatures
corresponding to their respective melting points. The liquid
siloxychromates containing methyl and 3,3,3-trifluoropropyl
radicals exhibited a third broad endotherm at 245 ± 10° C.

The intense bands occurring between 300 and 500° C. were
assigned to the decomposition temperatures of the various
organosiloxychromates and the following reaction was proposed:

$$- \overset{|}{\underset{|}{Si}} - O + \overset{O}{\underset{\underset{O}{\|}}{\overset{\|}{Cr}}} - O + \overset{|}{\underset{|}{Si}} \xrightarrow{\Delta} CrO_3 + -\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}}-$$
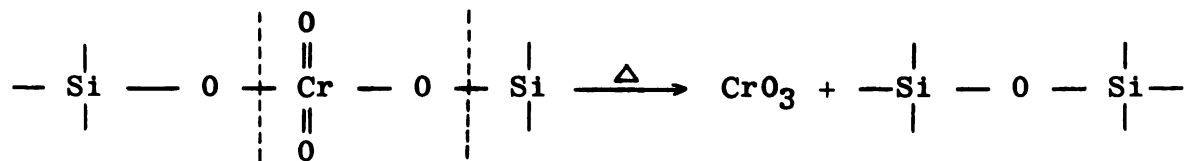
This reaction would, of course, include ring breaking as part
of the decomposition. The temperatures at which the bond
breaking occurred varied with the different organosiloxy-
chromates (Figures 38 - 41). The strongly electronegative
effect of the organic radicals gave partial positive character
to the silicon (137) which in turn possibly shifted the charge

from the oxygen toward the reaction site.

$$\geqslant Si^{\delta^+} \longleftarrow \bar{\ddot{O}} \longrightarrow \overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{Cr}}}} \longrightarrow O^- \longrightarrow \overset{\delta^+}{Si} \leqslant$$ This charge transfer
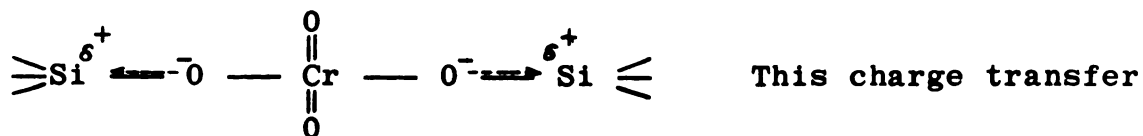
creates partial double bonding which strengthens the sili-

con-oxygen link. In phenyl-containing siloxychromates the

π-electrons of the benzene ring may partially overlap vacant d

orbitals of silicon to strengthen the silicon-oxygen bond

even further by partial conjugation with the phenyl rings

(53, 55, 146, 149, 150, 151, 152, 153, 154, 155).

The sample holder contained a green powdered residue

after each organosiloxychromate analysis. This high melting

solid was believed to be chromium(III) oxide (m. 1990° C.).

The endotherm which occurred consistantly at 532 ± 12° C.

was therefore attributed to the thermal reduction of chromium-

(VI) oxide.

$$4CrO_3 \xrightarrow{\Delta} 2Cr_2O_3 + 2O_2$$

Hare (5) in observing the melting points of crystalline

organosiloxychromates reported that bis(triphenylsilyl)-

chromate(VI) melted and immediately decomposed at 154° C. and

that cyclo-bis [tetraphenyldisiloxanylchromate(VI)] showed a

sharp decomposition point at 169° C. The sharp endothermic

DTA bands associated with these compounds and with cyclo-tris-

[diphenylsiloxanylchromate(VI)] indicated that the specific

temperatures produced fusion and not decomposition. The solid compounds were dissolved in methylene chloride after fusion and cooling, yielding orange solutions with no apparent insoluble decomposition products. It is possible that the black substance observed by Hare after melting the organosiloxychromates was actually deep orange in color. Some of the liquid organosiloxychromates appeared to be black because of their extremely intense orange color.

The endotherms appearing at 245 $\pm$ 10° C. with 3,3,3-trifluoropropylmethylsiloxanylchromates were believed to result from cleavage of the methyl-silicon linkage which is known to be quite unstable (159).

The relative thermal stabilities of several organosiloxychromates were compared by observing the temperatures at which bond breaking maxima occurred (Table XVII).

The replacement of a phenyl radical in bis(triphenylsilyl)chromate(VI) (Figure 38, p. 150) by the highly electronegative fluorine, yielding bis(diphenylfluorosilyl)chromate(VI), increased the thermal stability of the species by more than 60° C., thereby substantiating the original hypothesis.

The resistance to thermal degradation of diphenylsiloxychromates appeared to be slightly better than that of 3,3,3-trifluoropropylmethylsiloxychromates; thus cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)] decomposed at 25° C. below cyclo-bis [tetraphenyldisiloxanylchromate(VI)].

Cyclo-bis[3,3,3-trifluoropropylmethylsiloxanylchromate(VI)]
and cyclo-bis[diphenylsiloxanylchromate(VI)] degraded at
approximately the same temperature (375° C.). The greater
stability shown by the phenyl-containing siloxanylchromates
indicated that the combined electron-withdrawal of the two
phenyl radicals was slightly better than the 3,3,3-tri-
fluoropropyl-methyl combination; however, the phenylsilox-
anylchromates would have some added stability from the partial
double bond conjugation with the aromatic rings. It is be-
lieved that replacement of the methyl group by a more electro-
negative substituent such as fluorine, phenyl, or even another
3,3,3-trifluoropropyl group would result in compounds with
even greater thermal resistances.

The degree of electron-withdrawal was apparently not the
only factor influencing thermal stabilities for if this were
the case bis(triphenylsilyl)chromate (d. 390° C.) with three
phenyl radicals for each Si-0-Cr would show greater stability
than cyclo-bis[tetraphenyldisiloxanylchromate(VI)] (d. 425° C.)
with two phenyl groups per Si-0-Cr linkages. Probably the
cyclic structure accounts for the added stability (73).
Cyclo-bis (d. 375° C.) and cyclo-tris[diphenylsiloxanyl-
chromate(VI)] (d. 322° C.) with one phenyl group per Cr-0-Si
linkage degraded at even lower temperatures. The difference
between decomposition temperatures of these two compounds
indicated that the dimeric structure was the more stable form.

The thermal decomposition points of the above compounds further suggests a cyclic structure for the liquid dimer. Assuming that both compounds were linear, their decompositions should occur at approximately the same temperature and if the dimer were linear the decomposition point would have been lower than that of the crystalline trimer.

Reactions Mechanisms.

The heterogeneous reactions of organohalosilanes with silver chromate and dichromate did not yield the expected products; however, the data accumulated during the course of this investigation suggested routes which could possibly explain the formation of the compounds which were obtained.

The proposed mechanisms for the reaction of organohalosilanes with silver chromate and dichromate require as an initial step the dissolution of the salt in methylene chloride followed by the immediate establishment of a chromate-dichromate equilibrium. Reactions did not occur when either pentane or diethyl-ether was used as the solvent and proceeded at a much greater rate in methylene chloride than in carbon tetrachloride. If crystal dissolutions were considered as part of the over-all reaction then the necessity for a polar nonreactive solvent becomes apparent.

The possibility of a reaction at the crystal surface may be ruled out if the silver chloride by-product is

TABLE XVII

DIFFERENTIAL THERMAL ANALYSES OF ORGANOSILYL- AND SILOXANYLCHROMATES

Peaks	bis(triphenyl-silyl)chrom-ate(VI) (Figure 38)			bis(diphenyl-fluorosilyl)-chromate(VI) (Figure 38)			cyclo-bis-[tetra-phenyldi-siloxanyl-chromate(VI)] (Figure 39)			cyclo-bis-[diphenyl-siloxanyl-chromate-(VI)] (Figure 40)			cyclo-tris-[diphenyl-siloxanyl-chromate-(VI)] (Figure 40)			cyclo-bis-[3,3,3-tri-fluoropropyl-siloxanyl-chromate-(VI)] (Figure 41)			cyclo-bis-[di-3,3,3-trifluoro-propyldi-methyldi-siloxanyl-chromate(VI)] (Figure 41)		
	M.°C.	T.E.	I	M.°C.	T.E.	I	M.°C.	T.E.	I	M.°C.	T.E.	I	M.°C.	T.E.	I	M.°C.	T.E.	I	M.°C.	T.E.	I
Melting point	178	endo	m				185	endo	s, sp				103	endo	vs, sp						
SiCH$_3$ cleavage																235	endo	m, b	253	endo	m, b
unknown	300	endo	w, b																342	endo	sh, b
Bond breaking	390	endo	s, b	453	endo	s, b	425	endo	s, b	375	endo	s, b	322	endo	s, b	372	endo	s, b	400	endo	s, b
chromium reduction	530	endo	m, b	520	endo sh	m, b	533	endo	m, b	538	endo	m, b	523	endo	m, b	540	endo	m, b	544	endo	m, b

= strong; vs = very strong; m = medium; w = weak; sh = shoulder; b = broad; sp = sharp.
.°C. = maximum °C.; T. E. = Thermal Effect; I = intensity.
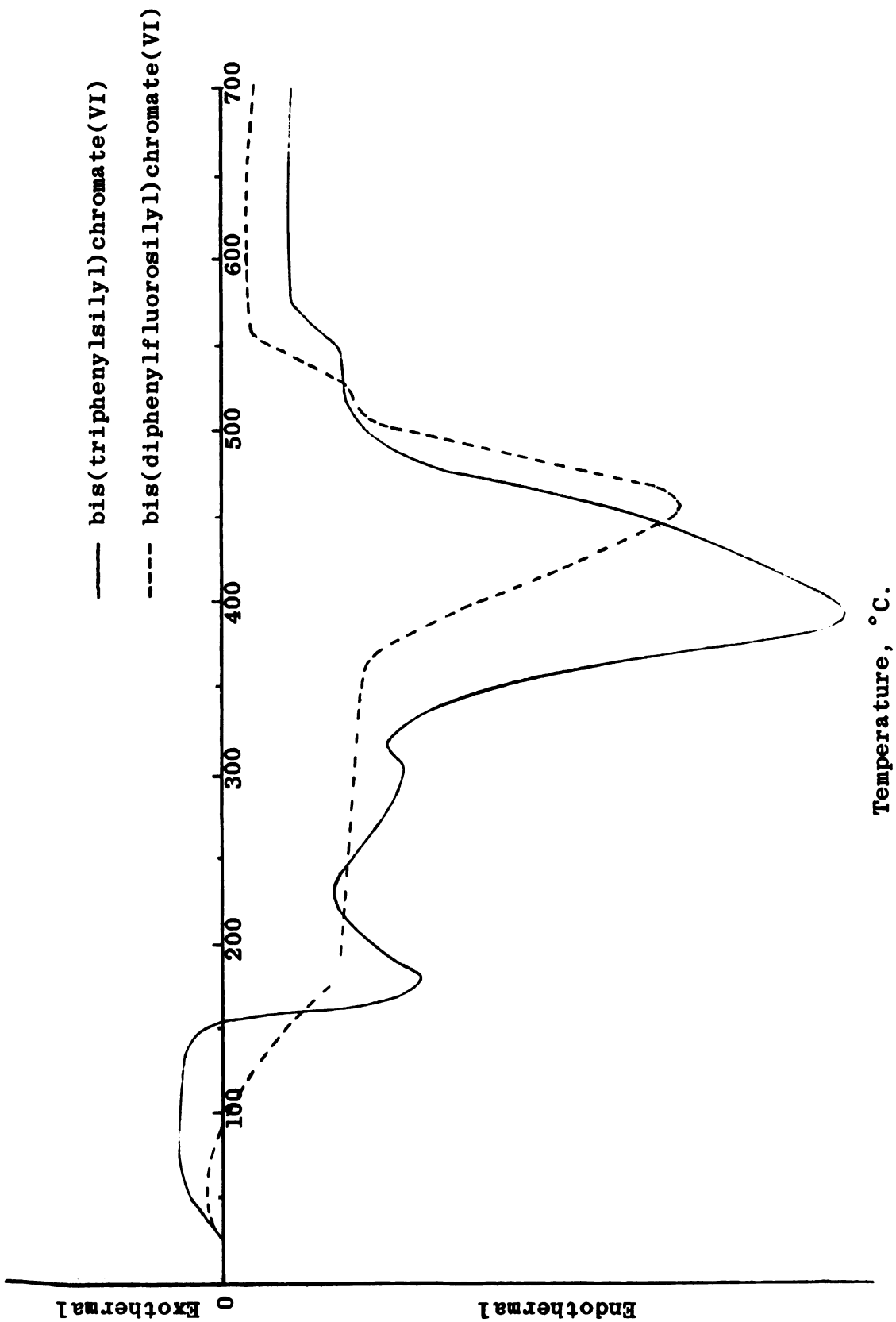
Figure 38. Differential thermal analyses of bis(triphenylsilyl)chromate(VI) and bis(diphenylfluorosilyl)chromate(VI).
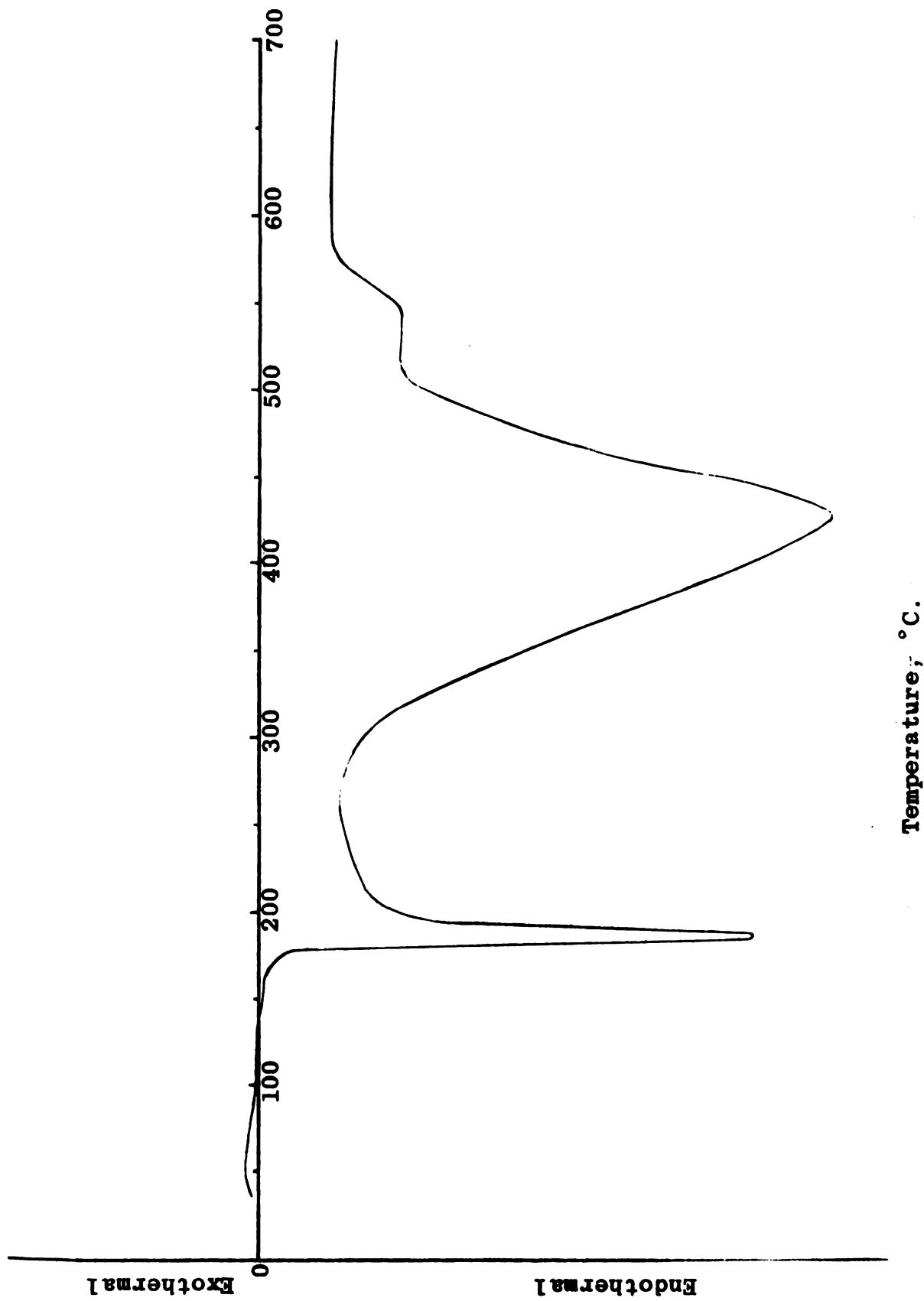
Figure 39. Differential thermal analysis of cyclo-bis[tetraphenyldisiloxanylchromate(VI)].
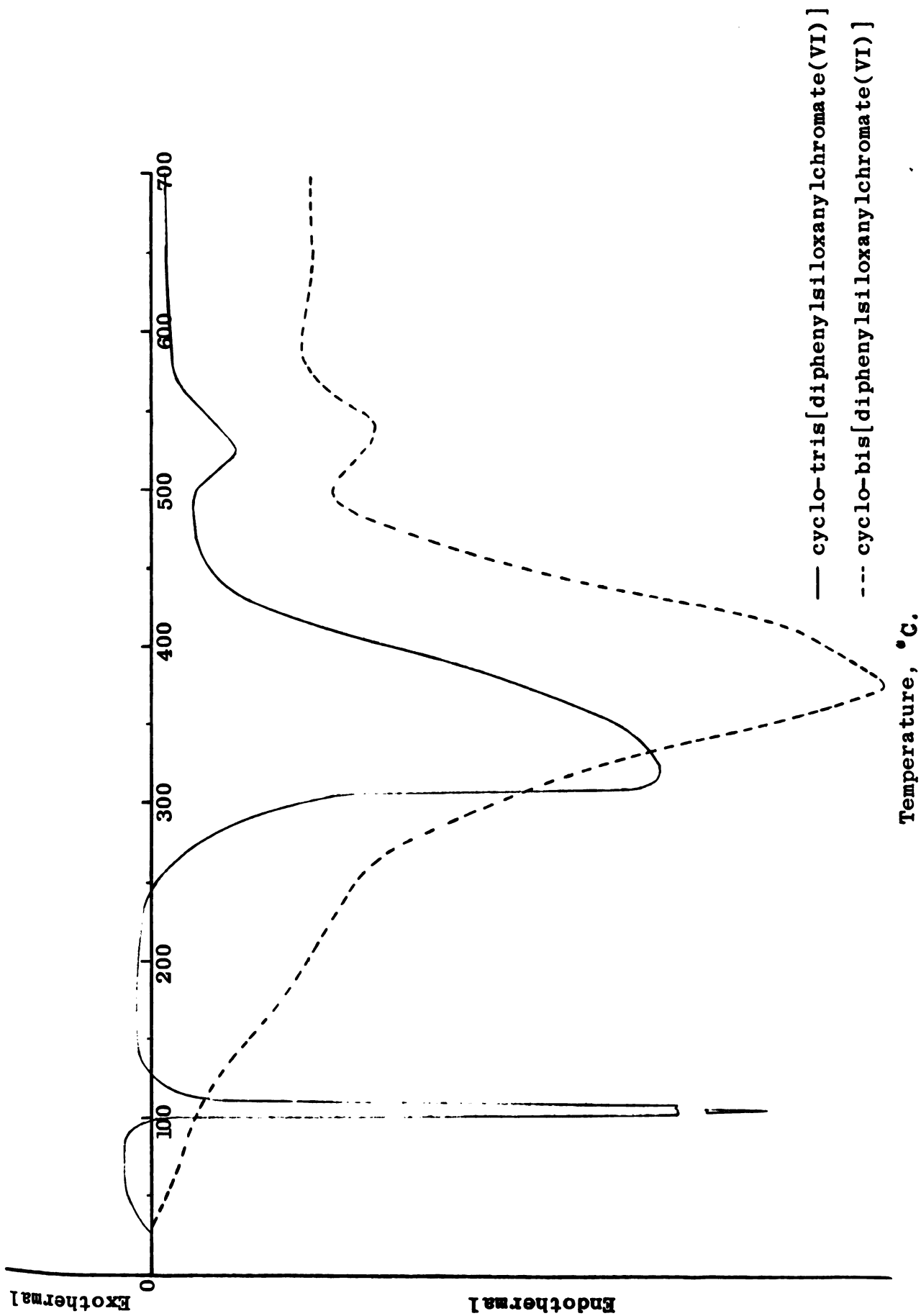
Figure 40. Differential thermal analyses of cyclo-bis[diphenylsiloxanylchromate(VI)] and cyclo-tris[diphenylsiloxanylchromate(VI)].
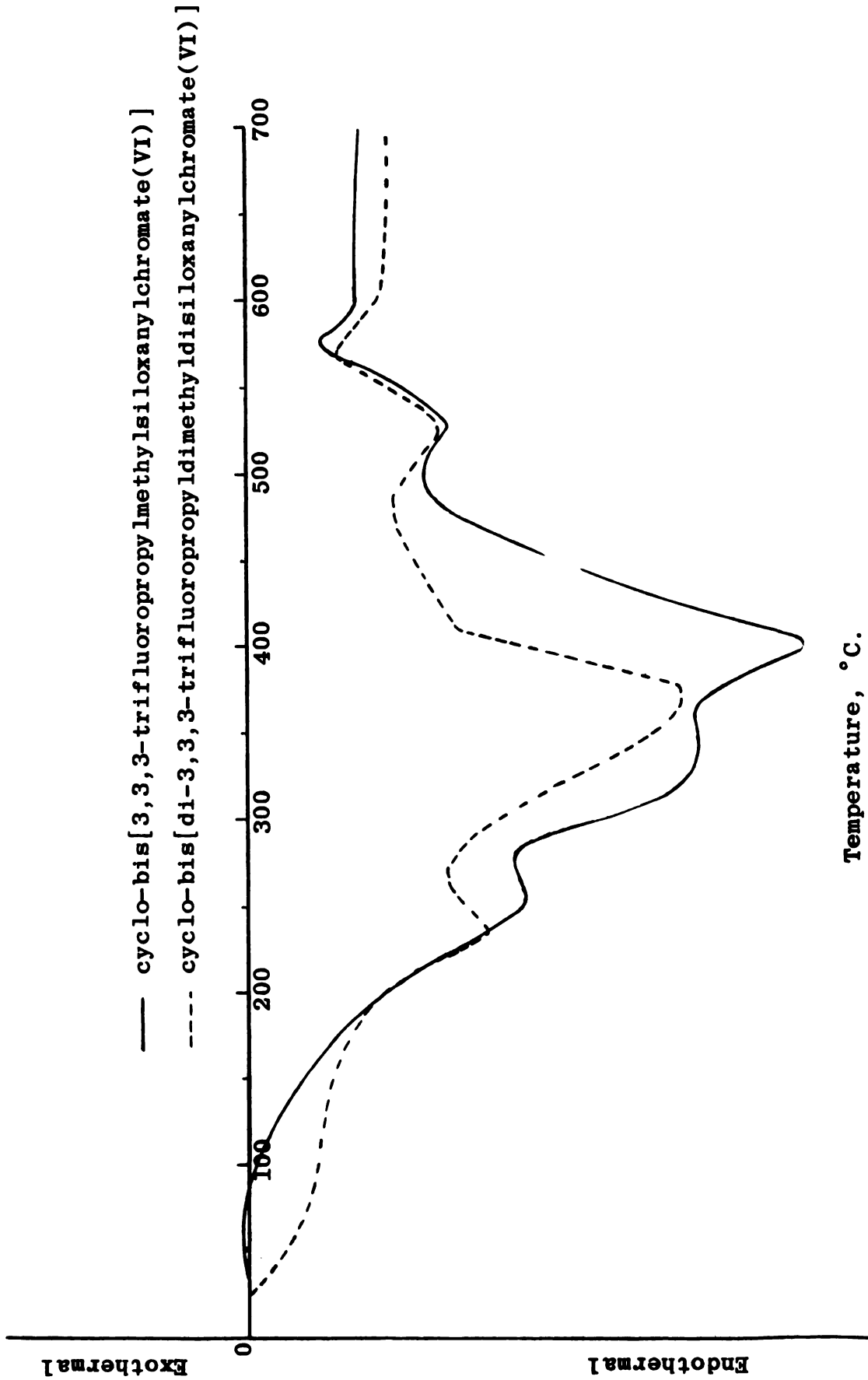
Figure 41. Differential thermal analyses of cyclo-bis[3,3,3-trifluoropropylmethyl-siloxanylchromate(VI)] and cyclo-bis[di-3,3,3-trifluoropropyldimethyl-disiloxanylchromate(VI)].

adsorbed by the crystal in such a way as to block the
surface rapidly. The absence of color in the silver chro-
mate or silver dichromate methylene chloride slurries
indicated that the salt was only very slightly soluble.
The definite and sharp melting point of silver dichromate
indicated that it was more ionic in nature than the chro-
mate, and their respective solubilities in water

$(Ag_2CrO_4, 7.5 \times 10^{-7}$ mole/l. ; $Ag_2Cr_2O_7, 1.9 \times 10^{-4}$ mole/l. ;

tended to substantiate this hypothesis. It was, therefore,
assumed that the salts were also slightly soluble in the
polar methylene chloride and that the dichromate was some-
what more soluble than the chromate.

The chromate-dichromate equilibrium in water has been
discussed on p. 8. The position of the equilibrium is
affected by the presence of an acid or a base and by the
concentration of the dissolved species. In very dilute
solution this equilibrium is far to the right

$$H_2O + \left[\begin{array}{c} O \\ \| \\ O - Cr - O - Cr - O \\ \| \quad\quad \| \\ O \quad\quad O \end{array} \right]^{--} \rightleftharpoons 2 \left[\begin{array}{c} O \\ \| \\ O - Cr - O \\ \| \\ O \end{array} \right]^{--} + 2H^+$$
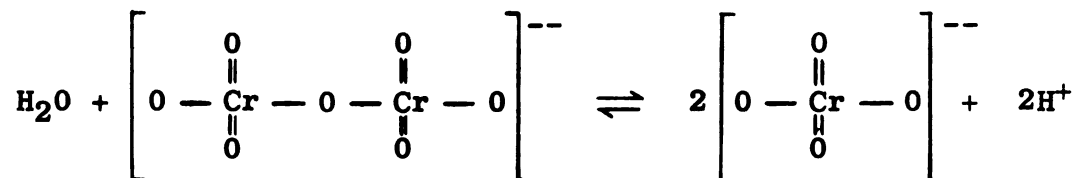
and as the solution becomes more concentrated, the solute
species begins to polymerize yielding first the dichromate,
then the trichromate and finally the tetrachromate ion
$[Cr_4O_{13}]^{--}$ at very high concentrations (27, 147, 148). It
would be expected that the dissolution of silver chromate in

methylene chloride would produce very little of the dichromate species for it would be unlikely that the highly purified solvent would contain any species which would shift the equilibrium towards the dichromate. The dissolution of silver dichromate in methylene chloride could possibly yield the above equilibrium; however, a complete reaction would require that water be present in amounts equivalent to or greater than the molar quantity of the organohalosilane reactant. The rather elaborate percautions taken to exclude water from the solvents, reactants, and apparatus suggest that the chromate species was not formed by the action of water. It is possible that the following equilibrium existed in methylene chloride.

$$\left[\begin{matrix} & O & & O & \\ & \| & & \| & \\ O- & Cr & -O- & Cr & -O \\ & \| & & \| & \\ & O & & O & \end{matrix}\right]^{--} \rightleftharpoons \left[\begin{matrix} & O & \\ & \| & \\ O- & Cr & -O \\ & \| & \\ & O & \end{matrix}\right]^{--} + CrO_3$$
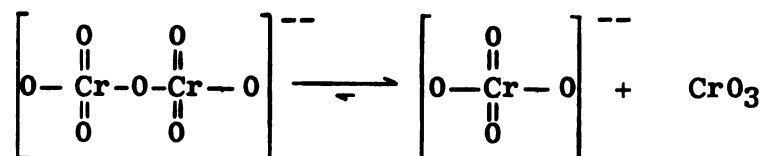
Chromium(VI) oxide, like the silver salts, is not very soluble in methylene chloride (5).

Once dissolution has occurred and the equilibrium favoring the chromate species established, reactions of organochlorosilanes with both the silver chromate and dichromate would follow the same path. Triphenylchlorosilane and diphenylchlorofluorosilane would be expected to react in much the same manner since the fluorine-silicon linkage of diphenylchlorofluorosilane was not cleaved with the reaction conditions

employed. Bimolecular displacement (S_n2) of chlorine from the organochlorosilane by the nucleophilic chromate ion appears to be the most likely process.

The mechanism is illustrated below:

Reaction Scheme A

$$Cl\text{------}\overset{\overset{R}{\underset{|}{\diagdown}}\overset{R}{\underset{|}{\diagup}}}{\underset{\underset{R'}{|}}{Si}}^{\delta+}\text{-------}O-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Cr}}-O^- \xrightarrow{-AgCl} R-\overset{\overset{R}{|}}{\underset{\underset{R'}{|}}{Si}}-O-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Cr}}-O^-$$

$-AgCl$

$R_2R'SiCl$

$$R-\overset{\overset{R}{|}}{\underset{\underset{R'}{|}}{Si}}-O-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Cr}}-O-\overset{\overset{R}{|}}{\underset{\underset{R'}{|}}{Si}}-R$$
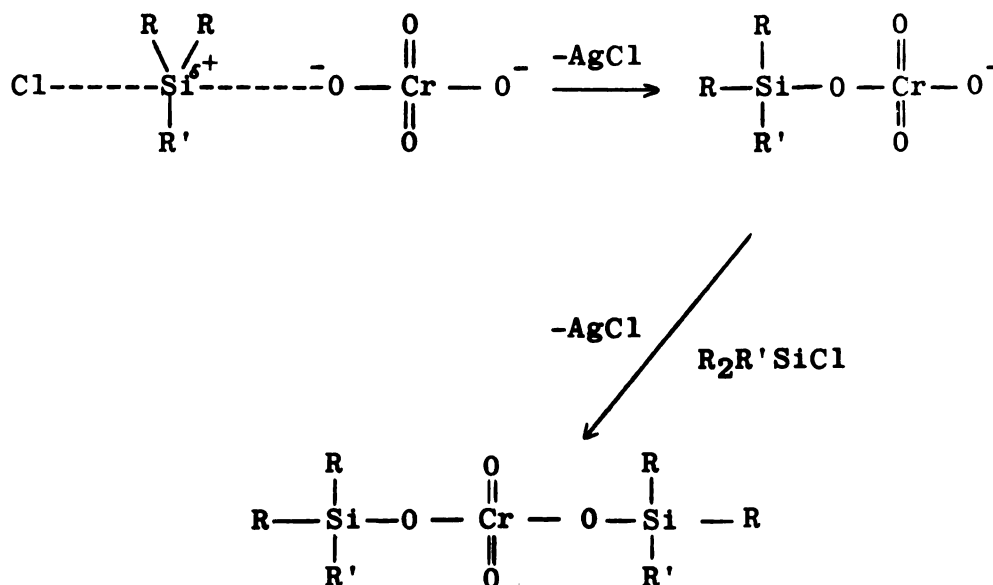
R-phenyl
R'-phenyl or fluoro

The formation of the very insoluble silver chloride could be considered as the driving force of the reaction. The silicon-oxygen bonding would be stabilized by the partial double bond character resulting from d π - p π interaction of a vacant silicon d orbital and a filled p orbital on the oxygen. The conjugation of the phenyl ring and silicon-oxygen double bonds would strengthen the bonding even

further. The above interactions would tend to lower the
energy required for bond formation, resulting in faster
rates with phenyl-containing halosilanes.

The mechanism for the reactions of organosilanes con-
taining two labile chlorines would in all liklihood follow
a similar procedure, i.e. consecutive bimolecular chain
building steps with ring closure as the termination process.
The reactions could take place in the following manner:

<div align="center">Reaction Scheme B</div>
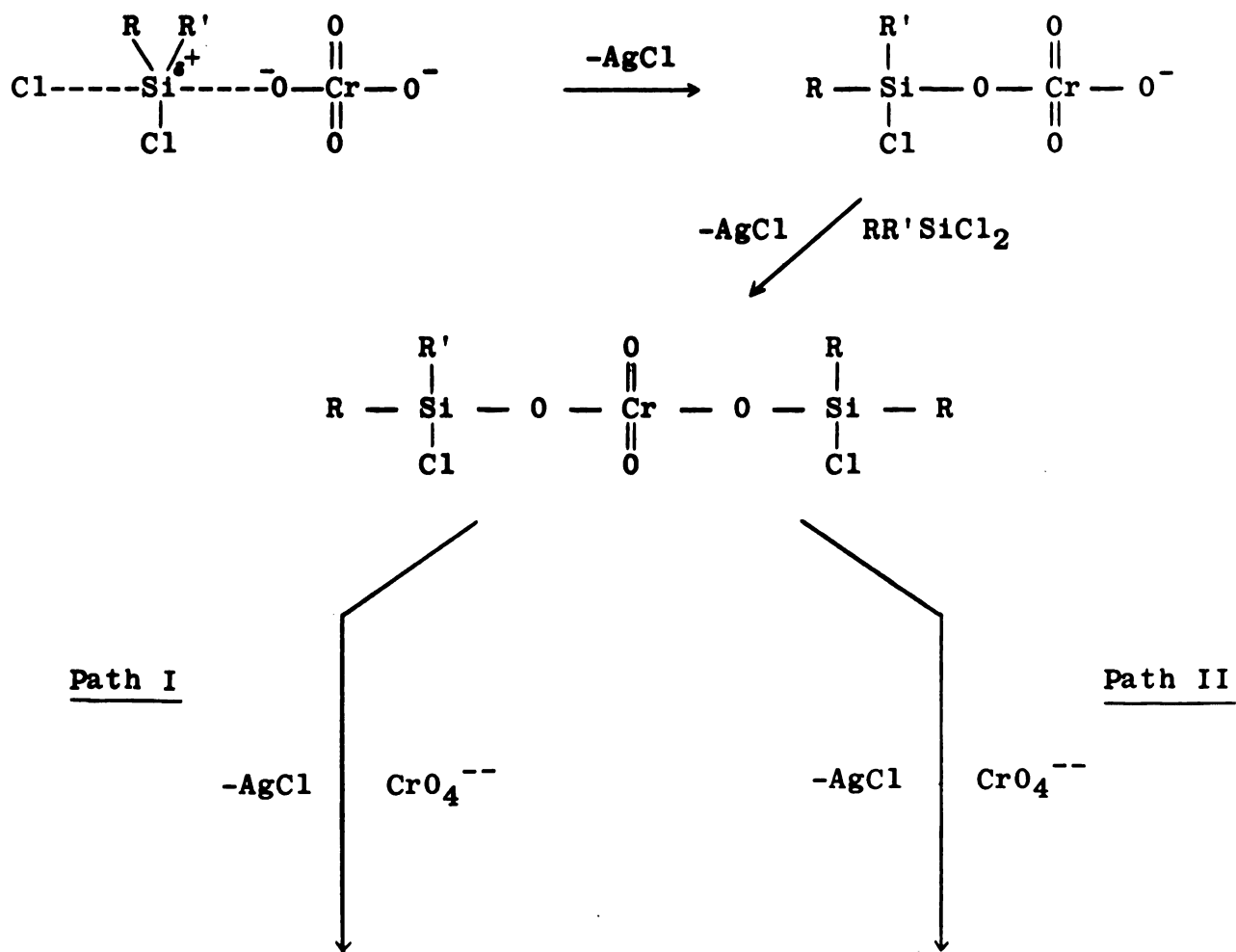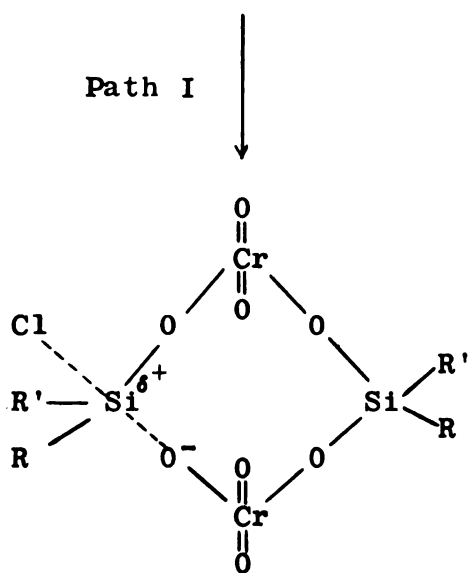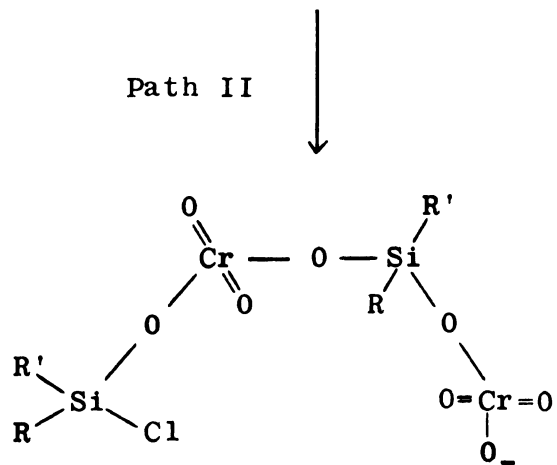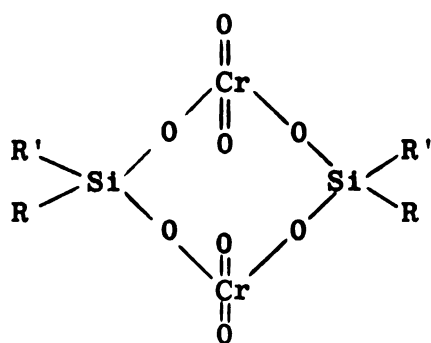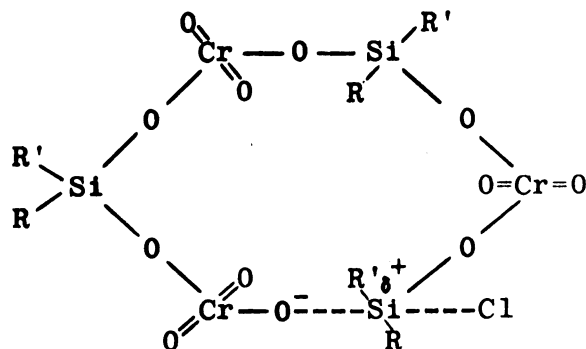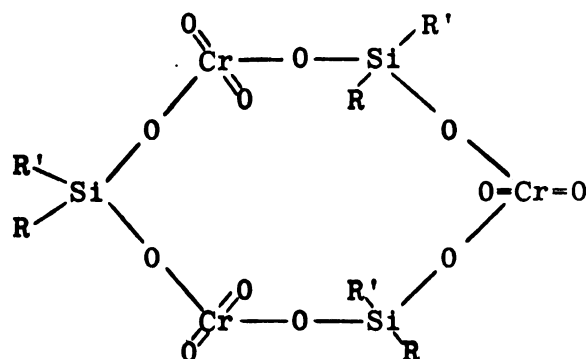
The structures of the compounds which resulted from the reactions of organodichlorosilanes with silver chromate and dichromate are not fully explained by the preceeding mechanism. The apparent inconsistencies can be explained by consideration of the chromate ion concentration and the relative ease of bond formation which in turn was influenced by the organo-silicon radicals. The reaction of diphenyldichlorosilane with small amounts of silver dichromate (two-fold excess) yielded only the cyclic dimer of diphenylsiloxanylchromate(VI) while similar amounts of silver dichromate and 3,3,3-trifluoropropylmethyl-dichlorosilane produced the cyclic trimer of 3,3,3-trifluoro-propylmethylsiloxanylchromate(VI). The relative solubilities of silver chromate and dichromate would suggest that the dichromate should yield greater concentrations of the nucleophilic agent CrO_4^{--} than an equal amount of chromate. The high electronegativity of the phenyl groups along with the double bond conjugation would tend to enhance bond forma-tion in phenylsiloxychromates. The termination or ring closure in reaction Scheme B would be dependent upon the con-centration of CrO_4^{--} and the ease of bond formation. Small amounts of CrO_4^{--} would tend to lead the reaction mechanism along Path I while larger concentrations would favor continua-tion of the chain building steps (Path II), while the stronger electrophilic nature of the phenyl-containing silicons would encourage ring closure at the dimer stage (Path I). The

formation of the various telomers and the probable mechanistic
influences are listed in Table XVIII.

TABLE XVIII

ORGANODICHLOROSILANE REACTIONS WITH SILVER CHROMATE

AND SILVER DICHROMATE

Reaction	CrO_4^{--} conc.	Mechanistic Path favored by		Actual Structure
		CrO_4^{--} conc.	Organic Radical Influence	
Ag_2CrO_4 + Ph_2SiCl_2	LC	Path I	Path I	Dimer
$Ag_2Cr_2O_7$ + Ph_2SiCl_2	MC	Path I or II	Path I	Dimer
$Ag_2Cr_2O_7$ + Ph_2SiCl_2	HC	Path II	Path I	Trimer(0.20) Dimer (0.80)
Ag_2CrO_4 +$(CF_3CH_2CH_2)(CH_3)SiCl_2$	LC	Path I	Path II	Dimer
$Ag_2Cr_2O_7$+$(CF_3CH_2CH_2)(CH_3)SiCl_2$	MC	Path I or II	Path II	Trimer

LC = Low concentration (two-fold excess of Ag_2CrO_4); MC = Medium
concentration (two-fold excess of $Ag_2Cr_2O_7$); HC = High concentra-
tion (ten-fold excess of $Ag_2Cr_2O_7$).

The equilibrium proposed for silver dichromate

$$2Ag^+ \; + \; \begin{bmatrix} & O & & O & \\ & \| & & \| & \\ O\!-\!\overset{\displaystyle \|}{\underset{\displaystyle \|}{Cr}}\!-\!O\!-\!\overset{\displaystyle \|}{\underset{\displaystyle \|}{Cr}}\!-\!O \\ & O & & O & \end{bmatrix}^{--} \rightleftharpoons Ag^+ + \begin{bmatrix} & O & \\ & \| & \\ O\!-\!\overset{\displaystyle \|}{\underset{\displaystyle \|}{Cr}}\!-\!O \\ & O & \end{bmatrix}^{--} + \; CrO_3 \; + \; Ag^+$$
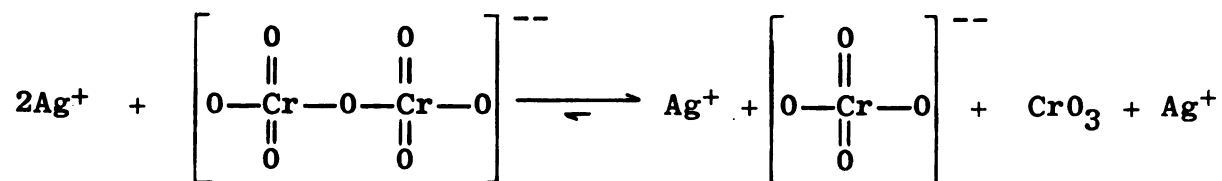
yields two species, one silver ion and chromium(VI) oxide, which were not consumed during the reactions. It was fairly unlikely that the unreacted species were completely removed by the crude purification techniques required for the liquid product resulting from the reaction of diphenyldichloro-silane with silver dichromate. Minimal amounts of the low molecular weight impurities could account for the large error observed in the molecular weight values of cyclo-bis[diphenyl-siloxanylchromate(VI)] (p. 75 and Table V).

The absence of disiloxanyl linkages in the products obtained from reactions of silver chromate and dichromate with organodichlorosilanes would tend to substantiate Hare's (5) hypothesis that these linkages resulted from the tendency of the diol reactants to undergo rapid self-condensation.

The synthesis of cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)] from chromyl chloride and 3,3,3-trifluoropropylmethylsilanediol in methylene chloride was analogous to Hare's reaction using diphenylsilandiol. Both reactions yielded two products; however, the liquid

product from the 3,3,3-trifluoropropylmethylsilanediol syn-
thesis was not characterized primarily because it occurred
in such small amounts. Hare proposed two mechanistic routes
(Reaction Scheme C) for the preparation of cyclo-bis [tetra-
phenyldisiloxanylchromate(VI)] which also gives an adequate
explanation for the synthesis of cyclo-bis[di-3,3,3-tri-
fluoropropyldimethyldisiloxanylchromate(VI)].

Reaction Scheme C

Path I

Path II

Path I   Path II

−HCl   RR'Si(OH)$_2$ (−HCl)   CrO$_2$Cl$_2$

R   O   R
| ‖ |
HO — Si —— Cr —— Si — OH
| ‖ |
R'   O   R'

Path II structure:

                    O
                    ‖
        R   O   Cr   O   R
         \ Si   Si /
        R' | | R'
            O   O
        R' | | R'
         \ Si   Si /
        R   O   O   O   R
                 ‖   δ+ δ−
                 Cr···O
                 | |
                 Cl   H
                 ‖
                 O

bimolecular
condensation
(−2H$_2$O)

−HCl

Final cyclic dimer structure:

                O
                ‖
        R   O   Cr   O   R
         \ Si   ‖   Si /
        R' | O | R'
            O   O
        R' | | R'
         \ Si   Si /
        R   O   O   O   R
                 ‖
                 Cr
                 ‖
                 O
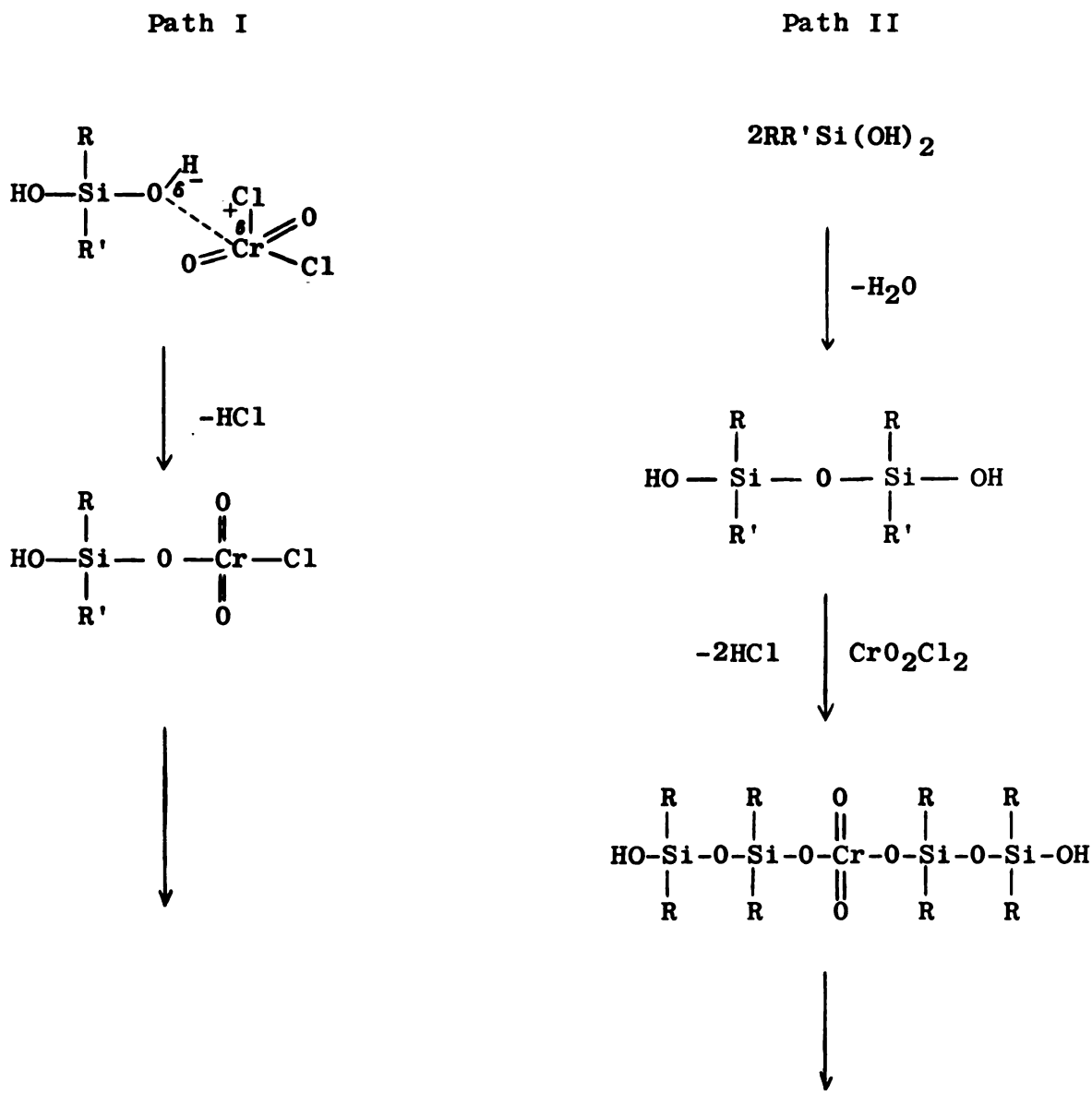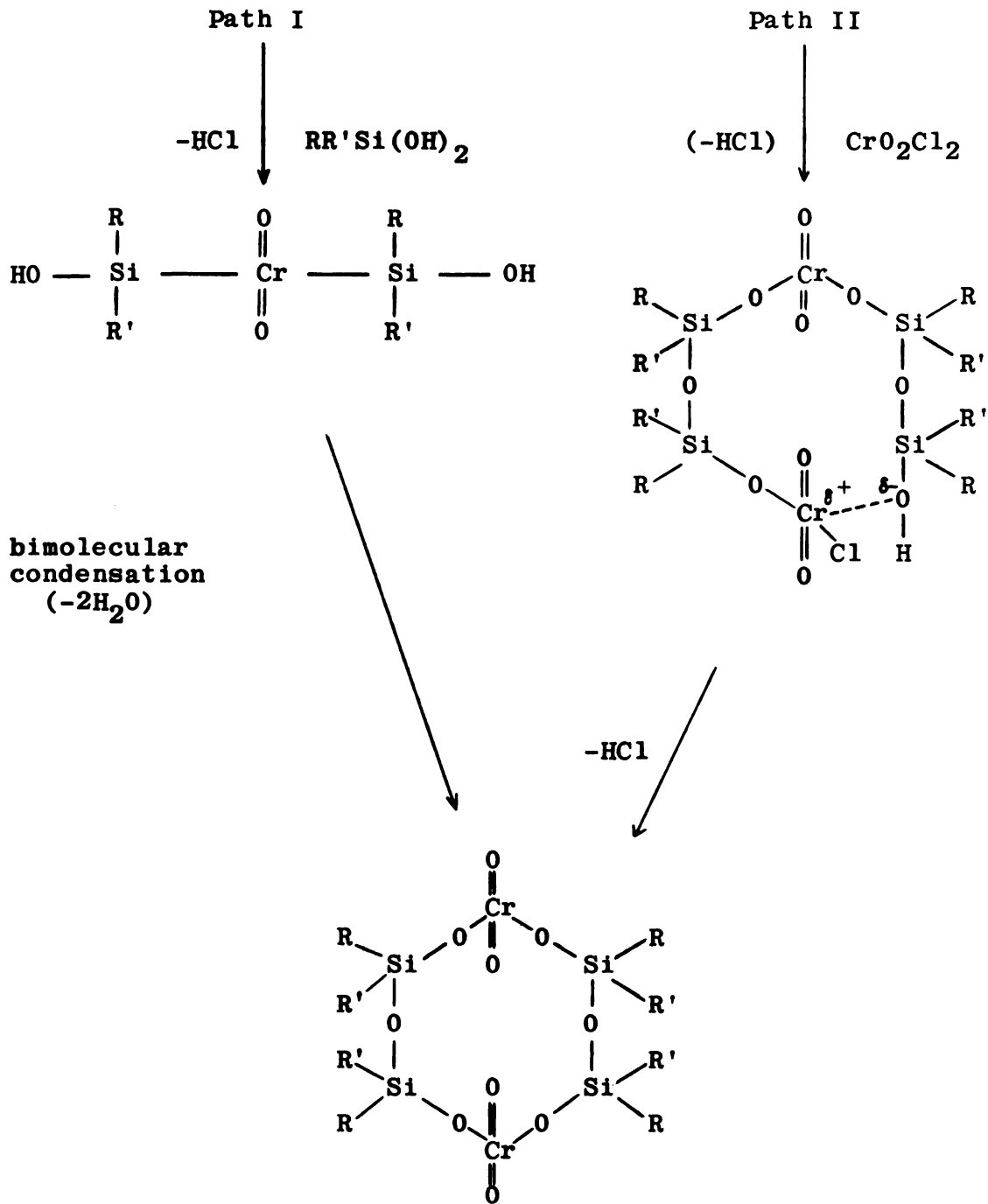
Hare explained the formation of the liquid reaction product
as being either the hydrolysis of the cyclic dimer followed
by cleavage of a chromate groups during the coupling of diphenyl-
hydroxosiloxy group or the initial condensation of diphenylsil-

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anediol to hexaphenyl-1,5-dihydroxotrisiloxane, which
attacked the chromyl chloride molecule to form bis(hexaphenyl-
6-hydroxotrisiloxanyl)chromate(VI).

The minimal amounts of liquid product obtained with
3,3,3-trifluoropropylmethylsilanediol suggested that the
reaction involving the formation of hexaphenyl-1,5-dihydroxo-
trisilane would be favored in the synthesis of bis(hexaphenyl-
6-hydroxotrisiloxanyl)chromate(VI) (5), for the phenyl radicals
with their higher electronegativities and double bond conjuga-
tion would tend to condense the diol to a greater degree than
the 3,3,3-trifluoropropylmethyl combination. These intra-
molecular interactions predict that 3,3,3-trifluoropropylmethyl-
silanediol would follow Path I for the preparation of the cyclic
dimer.

The synthesis of diphenylchlorofluorosilane from diphenyl-
dichloro- and diphenyldifluorosilane involved elemental exchange.
The reaction conditions required for the exchange indicated that
the reaction was one of unimolecular substitution. Reaction
Scheme D illustrates the probable steps.

Reaction Scheme D

$$\text{Ph} - \underset{\underset{Cl}{|}}{\overset{\overset{Ph}{|}}{Si}} - Cl \quad \xrightarrow[\Delta]{slow} \quad \text{Ph} - \underset{\underset{Cl}{|}}{\overset{\overset{Ph}{|}}{Si}}{}^+ + Cl^-$$

$$
\begin{array}{ccc}
\overset{\displaystyle Ph}{\underset{\displaystyle F}{\underset{\displaystyle |}{\overset{|}{Ph - Si - F}}}} & \xrightarrow[\text{slow}]{\triangle} & \overset{\displaystyle Ph}{\underset{\displaystyle F}{\underset{|}{\overset{|}{Ph - Si^{+} + F^{-}}}}}
\end{array}
$$

$$
\begin{array}{ccc}
\overset{\displaystyle Ph}{\underset{\displaystyle F}{\underset{|}{\overset{|}{Ph - Si^{+} + Cl^{-}}}}} & \xrightarrow{\text{fast}} & \overset{\displaystyle Ph}{\underset{\displaystyle F}{\underset{|}{\overset{|}{Ph - Si - Cl}}}}
\end{array}
$$

$$
\begin{array}{ccc}
\overset{\displaystyle Ph}{\underset{\displaystyle Cl}{\underset{|}{\overset{|}{Ph - Si^{+} + F^{-}}}}} & \xrightarrow{\text{fast}} & \overset{\displaystyle Ph}{\underset{\displaystyle Cl}{\underset{|}{\overset{|}{Ph - Si - F}}}}
\end{array}
$$
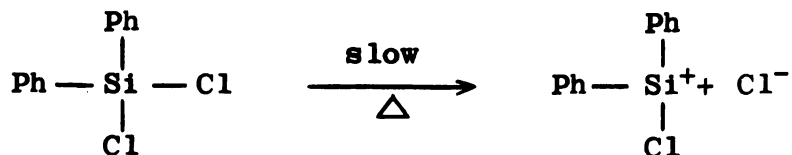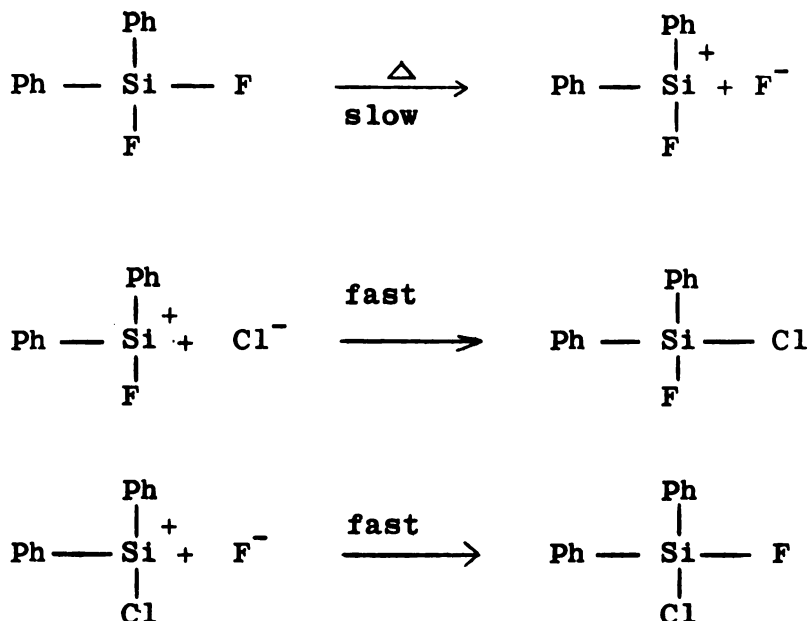
When equal molar quantities of the diphenyldihalosilanes were refluxed at 150° C. the exchange did not occur; however, refluxing at much higher temperatures (275° C.) yielded di-phenylchlorofluorosilane. The high temperature quite probably resulted in unimolecular heterolytic dissociation. If the mechanism had been a temperature dependent bimolecular sub-stitution, at least small amounts of the mixed halosilane would have been produced during the prolonged low temperature refluxing.

The composition of the refluxing mixture (275° C.) was checked by vapor phase chromatography at approximately ten-hour intervals over a period of one hundred and fifty hours.

A maximum yield of twenty percent diphenylchlorofluorosilane was reached at this point. Calculations involving molar quantities of the ionic species available for recombination predicted a yield of fifty percent for diphenylchlorofluorosilane and twenty five percent for each of the diphenyldihalosilanes. The diphenylfluorosilyl cation, because of the electronegativity of the fluorine radical, should possess greater electrophilic character than the diphenylchlorosilyl cation and should preferentially attract the more electronegative fluorides. Diphenyldifluorosilane should, therefore, be the most prevalent recombination product; however, because of the relative number of ions available, the final mixture contained equal molar quantities of diphenyldifluoro- and diphenylchlorosilane.

SUMMARY AND CONCLUSIONS

The previously known crystalline bis(triphenylsilyl)-chromate(VI) was prepared by the metathetical reaction of silver chromate and triphenylchlorosilane. A similar reaction using diphenylchlorofluorosilane yielded a deep orange liquid which was characterized as bis(diphenylfluorosilyl)-chromate(VI). The replacement of the phenyl group with the more electronegative fluorine increased the thermal stability of the silicon-oxygen-chromium linkage.

The reaction of diphenyldichlorosilane with silver chromate or silver dichromate gave mixtures of a cyclic dimer and trimer with alternating oxygen-chromium-oxygen-silicon linkages, cyclo-bis and tris[diphenylsiloxanylchromate(VI)]. The amounts of each cyclic species produced were dependent upon both the nature and amount of the silver salt reactant. The assignment of the cyclic structure to these molecules resulted from interpretation of their infrared spectra, shifts occurring with ultraviolet and visible absorption bands, proton magnetic resonance spectra, and thermal decomposition studies.

Similar cyclic A-B-C type monomers with 3,3,3-trifluoropropyl and methyl-silicon substituents were prepared from the reaction of 3,3,3-trifluoropropylmethyldichlorosilane with silver chromate and dichromate. These compounds were the

first siloxy-chromates containing fluoroorganic groups. Structural proofs were similar to those used for the cyclic phenyl-siloxanylchromates. It is believed that these four monomers are the first cyclic compounds with alternating oxygen-silicon-oxygen-metal linkages that have been isolated and identified.

The condensation of chromyl chloride with 3,3,3-trifluoro-propylmethylsilanediol yielded cyclo-bis[di-3,3,3-trifluoro-propyldimethyldisiloxanylchromate(VI)], a liquid at room temperature, which could be made to crystallize at lower temperatures. This compound contained silicon-oxygen-silicon linkages which resulted from the tendency of silanols to undergo self-condensation.

Attempts to prepare organosilyldichromate from the metathetical reaction of triorganochlorosilanes with silver dichromate were unsuccessful; regardless of the conditions, the reaction invariably led to the chromate product. The inability to obtain the predicted dichromate was attributed to the establishment, in methylene chloride, of a chromate-dichromate equilibrium where the chromate species was highly favored because of the extremely low concentrations involved.

The investigation of the thermal stabilities of the compounds prepared during this study was accomplished by means of differential thermal analysis. The peaks occurring in the thermograms were tentatively assigned to various thermal phenomena. The decomposition peaks for each of the organosiloxy-chromates were found to correlate fairly well with the relative

electronegativities of their respective silicon radicals, i.e.,
greater electronegativities or withdrawing effects resulted
in higher decomposition temperatures. In addition, hydrolytic
stabilities of the organosiloxychromates, which were observed
qualitatively, appeared to be a function of the electronegativ-
ity of the silicon substituent. Generally high electronega-
tive substituents facilitate hydrolysis. This concept was
somewhat belied by the apparent inert behavior of the fluoro-
organosiloxanylchromates toward water and alkaline solutions.
Here hydrolytic stability quite possibly resulted from screen-
ing of the silicon-oxygen-chromium linkage by both the fluorine
atoms and the methyl radicals.

Infrared spectroscopy was used extensively in the identi-
fication and structural characterization of reaction products.
The linkages contained in the organosiloxychromate molecules
absorbed in the region between 2 and 30 μ. The absorption of
Si-F, Si-R$_f$, Si-OH, Si-O-Si, and Si-O-Cr were of particular
importance. The silicon-oxygen-chromium vibrational modes
absorbing at 11-12 μ and 20.6-21.4 μ were tentatively assigned
to the respective asymmetric and symmetric stretching wave-
lengths.

RECOMMENDATIONS FOR FUTURE WORK

1. The preparation of organosiloxydichromates should be possible; however, this would entail the selection of a solvent which would favor the dichromate species in the chromate-dichromate equilibrium. The solvent should also be inert towards the silane reactant and organosiloxydichromate product.

2. The reaction mechanism discussed on p. 159 suggests that slower addition of diphenyldichlorosilane to the heterogenous methylene chloride solution of a large excess of silver dichromate would possibly give greater yields of the crystalline cyclo-tris[diphenylsiloxanylchromate(VI)]. A more thorough study of the temperature-dependence of all the reactions should be made.

3. The thermal behavior of the compounds prepared during this investigation indicated that the replacement of the methyl group in cyclo-bis[di-3,3,3-trifluoropropyldimethyldisiloxanyl-chromate(VI)] with a highly electronegative substituent such as fluorine, trifluoromethyl, phenyl, or another 3,3,3-trifluoropropyl group would yield a monomer with an outstanding resistance to thermal decomposition. The addition of fluorine or trifluoromethyl groups, however, might tend to make the resulting compounds less hydrolytically stable.

4. A quantitative study of the hydrolysis, both aqueous and alkaline, of the organosilyl- and siloxanylchromate compounds should yield significant information for future preparations.

5. The further polymerization of the cyclic siloxanyl-chromates should be attempted. This might possibly be attained by the use of a Lewis acid catalyst or possibly solid state irradiation of the crystalline cyclo-tris[diphenyl-siloxanylchromate(VI)].

6. Sulfur tetrafluoride reacts with metal-oxygen linkages to form difluoro-metal units in the following manner (64):

$$MO \text{ or } RMO + SF_4 \longrightarrow MF_2 \text{ or } RMF_2$$

Under the appropriate conditions the reaction of sulfur tetrafluoride with the chromium-oxygen linkage in silyl- and siloxy-anylchromates might yield substances having very interesting physical properties.

7. Structural isomers of the cyclic siloxanylchromates containing 3,3,3-trifluoropropyl and methyl linkages can be drawn. Cyclo-bis and tris[3,3,3-trifluoropropylmethylsilox-anylchromate(VI)] should have one cis and one trans isomer with the following structures:
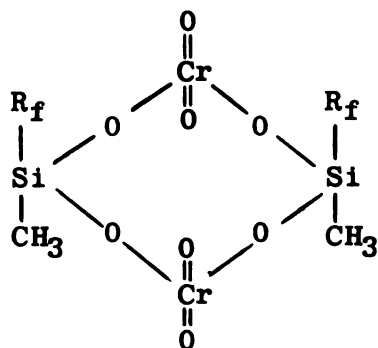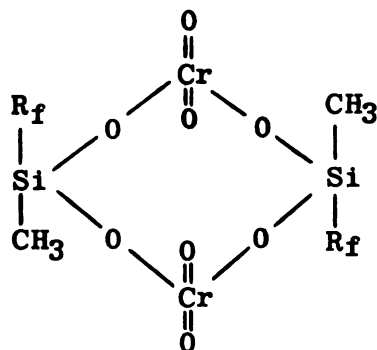
cis   trans

Six possible structural isomers can be postulated for cyclo-
bis[di-3,3,3-trifluoropropyldimethyldisiloxanylchromate(VI)].
Although difficult, the resolution and investigations of
these isomers should prove to be an interesting project.

APPENDIX

PREPARATION OF TRIS(TRIPHENYL)VANADATE(V)

Tris(triphenylsilyl)vanadate was first prepared
by Granchelli and Walker (10) in 1955 by treating
tris(n-butoxy)vanadate(V) with triphenylchlorosilane
in refluxing xylene. They obtained a thirty percent
yield of a pure white crystalline solid which melted
at 228-229° C. In 1958 Orlov, et al., (139) reported
the preparation of this solid (m. 228° C.) by the re-
action of tris(n-butoxy)vanadate(V) and triphenylsilanol
and in 1962 Chamberlain (160) obtained ninety-five percent
crude yields of the white tris(triphenylsilyl)vanadate(V)
(m. 225° - 6° C.) by the reaction of a benzene solution
of vanadium oxytrichloride with triphenylsilanol in the
presence of ammonia.

EXPERIMENTAL

Preparation of Vanadium Oxytrichloride.

One hundred grams of vanadium pentoxide (0.58 mole) and 130 ml. of thionyl chloride (1.1 moles) were refluxed for twenty hours on a steam bath. Pure vanadium oxytrichloride (b. 127° C.) was obtained from the reaction mixture by distillation.

Preparation of Sodium Triphenylsilanolate.

An excess of sodium metal was refluxed in 150 ml. of toluene for one hour followed by the addition of ten grams (3.6 x 10^{-2} mole) of triphenylsilanol. After continued refluxing for another three hours, the hot mixture was decanted from the sodium metal. White crystals of sodium triphenylsilanolate, which formed during cooling, were washed with hot ethanol and toluene.

Synthesis of Tris(triphenylsilyl)vanadate(V).

A slight excess of sodium triphenylsilanolate (4.97 g. or 1.67 x 10^{-2} mole) was slurried in 100 ml. of cyclohexane. The cyclohexane had been previously distilled into a two necked 300 ml. round bottom reaction flask. Additional cyclohexane (50 ml.) was distilled into a 100 ml. dropping funnel to which 0.87 gram (5.0 x 10^{-3} mole) of vanadium oxytrichloride

were added. The dropping funnel and a reflux condenser with a drying tube were connected to the reaction flask and the sodium triphenylsilanolate slurry was stirred with an internal magnet. The vanadium oxytrichloride solution was added rapidly to the excess sodium triphenylsilanolate and the reaction mixture was stirred at room temperature for twenty minutes.

The residue from the filtered reaction solution was subjected to x-ray diffraction and infrared spectral analysis and proved to be a mixture of sodium chloride and the excess sodium triphenylsilanolate. Light green crystals appeared when the filtrate was condensed to approximately twenty milliliters by rotary evaporation. Recrystallization of the product from fresh cyclohexane gave a seventy percent yield of pure white tris(triphenylsilyl)vanadate(V).

The white crystals had a metallic sheen and were soluble in either hot or cold aliphatic and aromatic hydrocarbons, alcohols, ethers, alkyl halides, organic acids, ketones, anhydrides, acetates, and all other organic solvents used. The solid was not wet by water and was either insoluble or decomposed in mineral acids.

The differential thermal analysis of a 1:1 mixture of tris(triphenylsilyl)vanadate(V) and α-alumina (Figure 43, p. 179) exhibited a sharp endothermic band at 230° C. which agreed with the value for the melting point determination (227.5° C.). The thermal decomposition has been assigned to the broad exothermic peak occurring at 400° C.

Elemental analyses and cryoscopic molecular weight determinations of the recrystallized product (Table XIX) agreed quite well with the calculated values for tris(triphenylsilyl)-vanadate (V).

TABLE XIX

ELEMENTAL ANALYSIS AND MOLECULAR WEIGHT OF TRIS(TRIPHENYLSILYL) VANADATE (V)

	Calculated (%)	Experimental (%)
Carbon	72.62	72.50
Hydrogen	5.08	5.28
Silicon	9.44	9.48, 9.56
Vanadium	5.70	5.67, 5.51
Molecular Weight	893	892, 889

The infrared spectrum between 2 and 15 μ for tris(triphenylsilyl)vanadate(V) (Figure 42, p. 178) was determined in carbon disulfide and gave the normal absorption associated with phenyl-silicon molecules. The peak occurring at 9.93 μ resulted from the stretching vibration of the vanadium-oxygen linkage (10). The strong broad maximum at 11.07 μ has been assigned to the V-O-Si asymmetric stretching vibration. This peak is quite similar in appearance and absorption wavelength to the Ti-O-Si (13, 131, 158) and Cr-O-Si (5, 157) (p. 6 and 97) asymmetric stretching modes.

The x-ray powder diffraction pattern of the white crystal-line solid was obtained with copper K_α radiation using a North American Philips powder diffraction unit and a Debye-Scherrer camera. The interatomic spacings are listed in Table XX.

TABLE XX

INTERATOMIC SPACINGS OF TRIS(TRIPHENYLSILYL)VANADATE(V)

(Cu K_α radiation, λ = 1.5418Å)

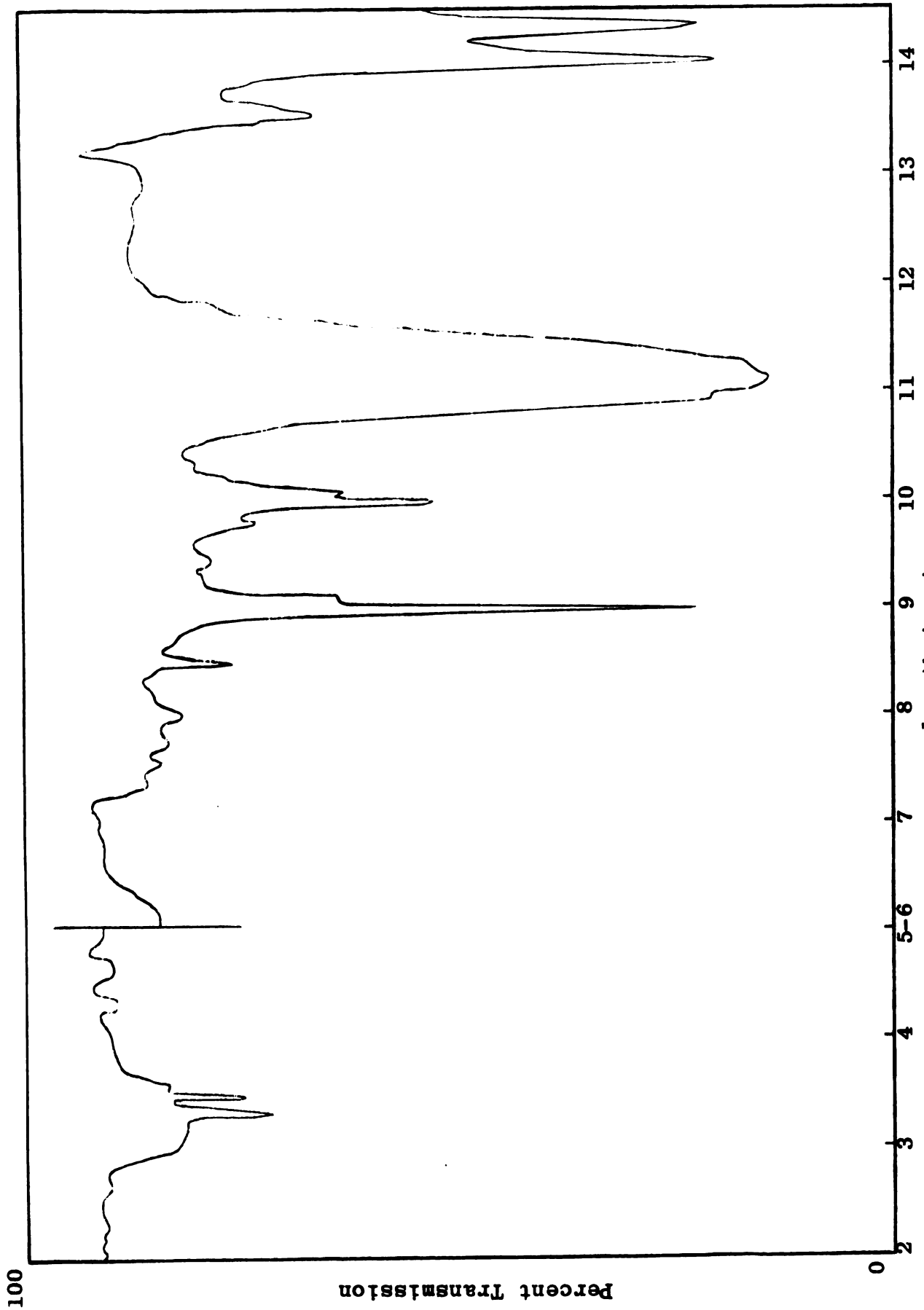| Line	θ (degrees)	d_{hkl} (Å)	Relative Intensity
1	27.7	1.66	3
2	26.2	1.75	1
3	23.9	1.90	1
4	22.7	2.00	1
5	16.8	2.67	2
6	15.8	2.83	1
7	13.5	3.30	1
8	12.8	3.48	2
9	11.7	3.80	2
10	11.3	3.94	1
11	10.6	4.91	2
12	10.2	4.35	6
13	9.9	4.48	9
14	9.7	4.58	7
15	9.1	4.87	6
16	8.2	5.41	3
17	6.9	6.42	3
18	6.2	7.14	4
19	5.6	7.90	3
20	5.0	8.84	10
21	4.9	9.30	2
22	4.3	10.09	8
23	3.8	11.63	10

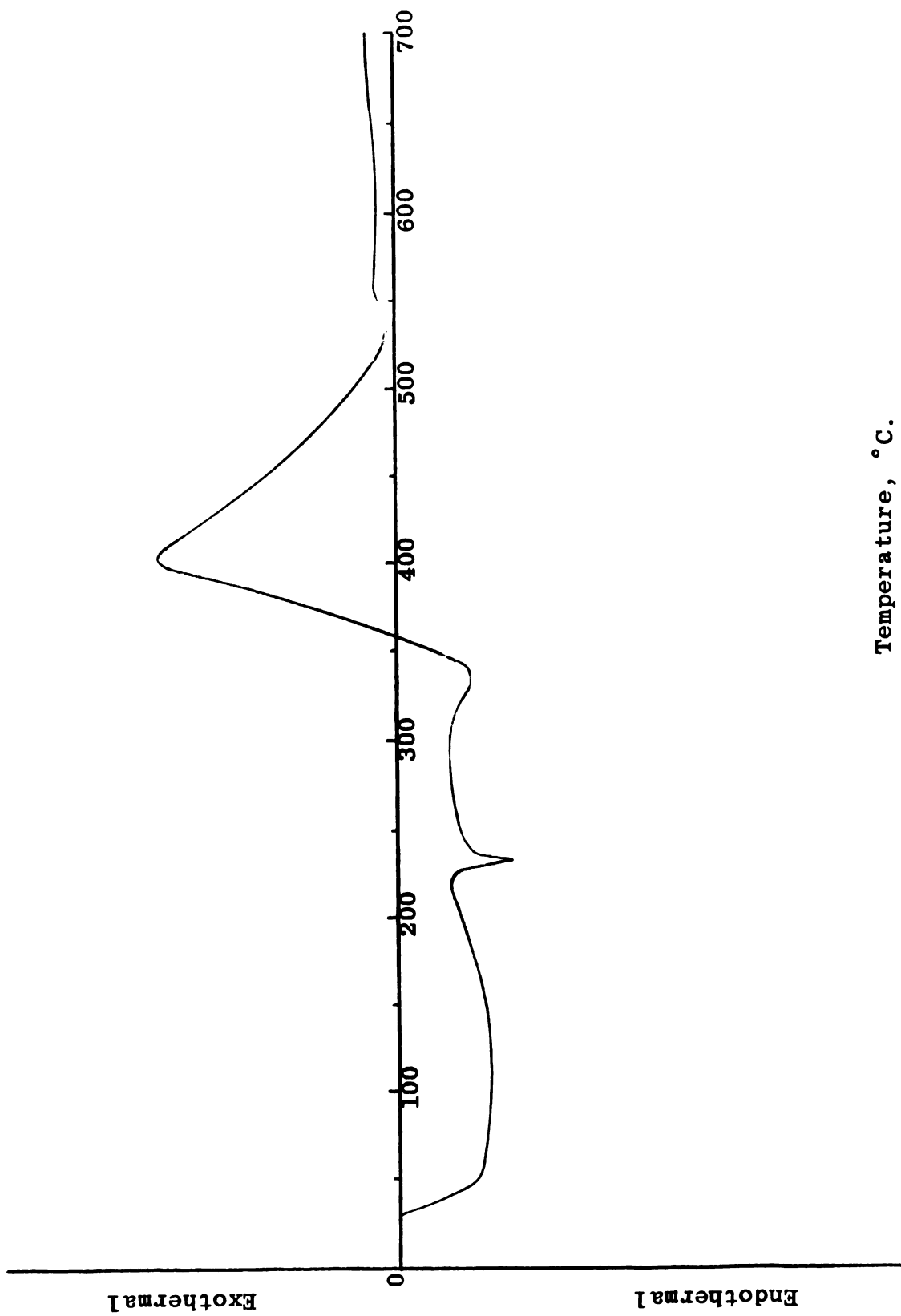Figure 42. Infrared spectrum of tris(triphenylsilyl)vanadate(V) in the sodium chloride region.

Temperature, °C.

Figure 43. Differential thermal analysis of tris(triphenylsilyl)vanadate(V).

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