THE USE OF TERTIARY-BUTYL HYPOCHLORITE FOR NON-AQUEOUS OXIDATIONS

By

Clayton Edward Van Hall

A THESIS

Submitted to the School of Advanced Graduate Studies of Michigan
State University of Agriculture and Applied Science in
partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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VITA

Name: Clayton Edward Van Hall

Born: April 24, 1924 in Grand Rapids, Michigan

Academic Career: Grand Haven High School, Grand Haven, Michigan
(1938-1942)

Hope College, Holland, Michigan
(1946-1949)

Michigan State University, East Lansing, Michigan
(1952-1956)

Degrees Held: A. B. Hope College (1949)

M. S. Michigan State University (1954)

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ABSTRACT

The use of tert-butyl hypochlorite for non-aqueous oxidations has been investigated and found suitable for the determination of a limited number of organic compounds.

Solutions of tert-butyl hypochlorite in glacial acetic acid were reasonably stable and decomposed at the rate of about 0.1 per cent a day. The solutions could be standardized accurately by adding an aliquot to aqueous potassium iodide solution and titrating the iodine with thiosulfate solution using starch indicator.

The indirect determination of unsaturation was not possible using an excess of tert-butyl hypochlorite solution alone or as a source of chlorine. Reaction rate studies in glacial acetic acid with several unsaturates established that with the hypochlorite alone the reactions were too slow and an excess of reagent was consumed. Reaction rate studies in glacial acetic acid using an excess of the hypochlorite and lithium chloride as a source of chlorine established that the addition of chlorine was rapid but that an excess of chlorine was consumed.

The direct titration of unsaturates with tert-butyl hypochlorite was not possible due to the slow reaction rate. Using the hypochlorite as a source of chlorine it was possible to titrate unsaturates amperometrically or potentiometrically in glacial acetic acid. With the exception of styrene all unsaturates tested yielded high results due to substitution or low results due to slow reaction rates. The results

obtained with styrene agreed with those obtained by an acid-catalyzed bromination method.

Efforts to improve the titration results were unsuccessful. High results were obtained with titrations at low temperatures using acetic acid containing 10 per cent water or 20 per cent carbon tetrachloride as solvents. The use of mercuric chloride as a catalyst also failed to improve the results.

Sodium oxalate could be determined accurately in 80 per cent acetic acid using an excess of the reagent and determining the excess. Phenol could be titrated amperometrically in 90 per cent acetic acid but the accuracy was poor. The determination was slow and limited to small samples. Hydroquinone could be titrated amperometrically with hypochlorite alone or as a source of chlorine but high results were obtained in both titrations. Benzaldehyde could not be determined directly or indirectly because the reaction was too slow.

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I INTRODUCTION

I INTRODUCTION

Although non-aqueous solvents have received much attention in their applications to acid-base titrations, little work has been reported on the use of non-aqueous solvents as media for direct volumetric determinations with oxidizing and reducing agents. This is due primarily to the lack of reagents that can be used in non-aqueous solvents.

Previous reported work concerns the use of inorganic oxidizing and reducing agents. Tomecek and Heyrovsky (37) investigated the use of a number of such oxidants in glacial acetic acid. These were bromine, chromic acid, and sodium permanganate. Tomecek and Valcha (38) extended this work to include the use of iodine, iodine monochloride, iodine monobromide, and lead tetraacetate. Hinsvark (20) has used glacial acetic acid solutions of ceric nitrate for the determination of simple oxygenated organic compounds.

The number of reducing agents that have been used in non-aqueous solvents is fewer. Hinsvark and Stone (21) have recommended ferrous perchlorate in glacial acetic acid as a reducing agent. Novotny (26) has reported the use of vanadyl acetate in glacial acetic acid and Freedman (12) has investigated the use of sulfur dioxide in pyridine for the determination of organic compounds containing positive halogens. Tomecek and Heyrovsky (37) have also reported the use of glacial acetic acid solutions of titanous chloride.

Most of the inorganic reagents investigated thus far have two disadvantages. Solutions of the reagents in non-aqueous solvents are unstable and their low solubilities limit the concentrations obtainable. Another prominent reason for the slow progress in this field is the excessive cost and disagreeable properties of the solvents themselves.

An organic oxidizing agent which may prove adaptable for use in volumetric analytical determinations in non-aqueous solvents is tert-butyl hypochlorite. This compound has found some use in preparative organic chemistry. Many of its reactions are characterized by high yields obtained rapidly with moderate conditions.

The purpose of this work was to investigate the use of tert-butyl hypochlorite as an oxidizing agent for analytical determinations of organic compounds in non-aqueous solvents. Glacial acetic acid was used as the solvent because of its high purity, stability, and moderate cost.

II HISTORICAL

II HISTORICAL

A. The Properties of Alkyl Hypochlorites

The alkyl hypochlorites are organic esters. They are pale yellow liquids, immiscible with water, with very irritating odors similar to chlorine. The primary and secondary alkyl hypochlorites are very unstable and decompose explosively when exposed to bright light. Even in darkness they decompose rapidly liberating sufficient heat to cause boiling. The tertiary alkyl hypochlorites are very stable. tert-Butyl hypochlorite can be distilled without change and kept for months with very little decomposition provided light is excluded. B.P. = 79.6°C/ 750 mm., d_4^{18} = 0.9583 (6). tert-Amyl hypochlorite does decompose on distillation, but it may be kept at room temperature with little change. When exposed to sunlight, both the tert-butyl and tert-amyl hypochlorites decompose quietly with the evolution of heat. The stability of the tertiary alkyl hypochlorites is attributed to the absence of a tertiary hydrogen atom which necessitates the breaking of a carbon-carbon bond for decomposition to occur.

The products of the decomposition of alkyl hypochlorites vary with the type (6). Primary hypochlorites decompose to form hydrogen chloride and aldehydes. Secondary hypochlorites form hydrogen chloride and ketones, and tertiary hypochlorites form methyl chloride and ketones. These reactions are illustrated by the following equations:

Primary $RCH_2OCl \longrightarrow RCHO + HCl$

Secondary $R_2CHOCl \longrightarrow R_2CO + HCl$

Tertiary $R_3COCl \longrightarrow R_2CO + RCl$

$R = CH_3$

The products of decomposition listed are principal products. Small amounts of other materials are obtained also.

B. The Preparation of Alkyl Hypochlorites

The alkyl hypochlorites can be prepared by several methods. The most widely used method is to pass chlorine into an aqueous alkaline solution of the alcohol. The reaction may be represented by the equation:

$$ROH + Cl_2 + NaOH \longrightarrow ROCl + NaCl + H_2O$$

The alkyl hypochlorites rise to the surface forming a layer that may be separated and dried with anhydrous calcium chloride or sodium sulfate. The stable tert-butyl hypochlorite may be purified further by distillation at atmospheric pressure in an all-glass apparatus. This method was was used by Sandmeyer (30,31) to prepare methyl and ethyl hypochlorites, and also by Chattaway and Backeberg (6) to prepare n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, and tert-amyl hypochlorites. Hanby and Rydon (19) substituted calcium carbonate for sodium hydroxide in this method.

Other methods have been used for the preparation of various alkyl hypochlorites. Anbar and Dostrovsky (2) prepared tert-butyl hypochlorite by adding an excess of tert-butyl alcohol to chlorine monoxide in carbon tetrachloride:

$$Cl_2O + 2\ ROH \longrightarrow 2\ ROCl + H_2O$$

The same authors prepared carbon tetrachloride solutions of tert-butyl hypochlorite by shaking an aqueous acid solution of hypochlorous acid with a carbon tetrachloride solution of tert-butyl alcohol. With this same method they prepared solutions of 3,3,3-trichloro-1-methylpropyl hypochlorite and ethyl and tert-butyl hypobromites.

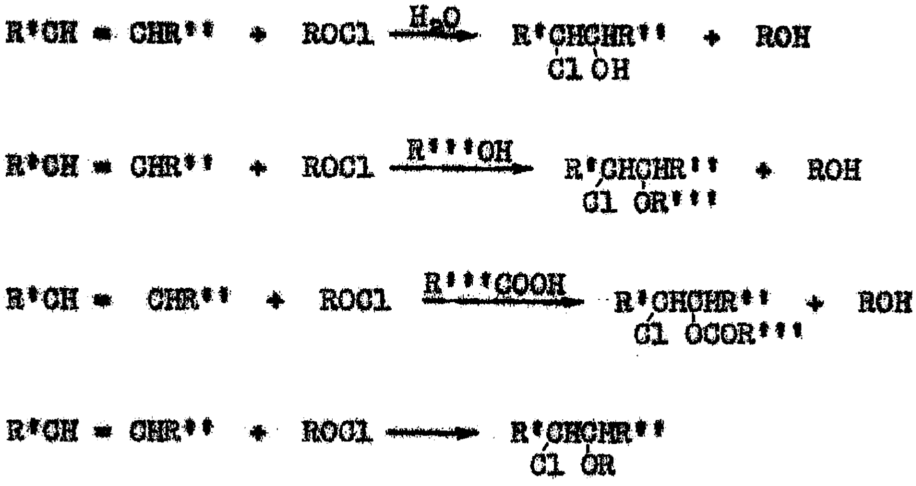
With many of the preceding methods yields up to 100 per cent were reported.

C. The Reactions of Alkyl Hypochlorites

With only a few exceptions (14,25) all of the reported work on the reactions of alkyl hypochlorites is concerned with the use of tert-butyl hypochlorite.

In 1931 Clark (7) reported that tert-butyl hypochlorite reacted with hydrocarbons, phenols, amines, alcohols, aldehydes, amides, ketones, esters, and ethers with some exceptions within the various classes of compounds. Acids and nitriles were unreactive.

Irwin and Hennion (22) found that the addition product formed in the reaction of tert-butyl hypochlorite with simple olefins depended on the solvent employed. Halohydrins, haloethers, and haloesters were produced by chlorination of olefins in the presence of water, alcohols, and acids respectively. In an inert solvent such as carbon tetrachloride or in the absence of a solvent, the tert-butoxy ether was formed. The following equations illustrate these reactions:



$$R'CH = CHR'' + ROCl \xrightarrow{H_2O} R'\underset{Cl}{C}H\underset{OH}{C}HR'' + ROH$$

$$R'CH = CHR'' + ROCl \xrightarrow{R'''OH} R'\underset{Cl}{C}H\underset{OR'''}{C}HR'' + ROH$$

$$R'CH = CHR'' + ROCl \xrightarrow{R'''COOH} R'\underset{Cl}{C}H\underset{OCOR'''}{C}HR'' + ROH$$

$$R'CH = CHR'' + ROCl \longrightarrow R'\underset{Cl}{C}H\underset{OR}{C}HR''$$

Emling, Vogt, and Hennion (11) extended this work to ethylenic compounds containing a reactive group. Some of the compounds studied were allyl chloride, allyl alcohol, cinnamic acid, cinnamaldehyde, and crotonaldehyde. Methanol was used as the solvent.

Other unsaturates that have received independent study are styrene (19), isoprene (27), methyl and ethyl acrylates (28), α-pinene (29), cholesterol (17), and vegetable oils (35).

Ginsburg (15) has investigated the reaction of tert-butyl hypochlorite with a number of aromatic aldehydes. He found that hydroxyl, methoxyl, and dimethylamino groups activated the nucleus resulting in nuclear chlorination, whereas hydrogen, chlorine, and methyl groups activated the aldehyde group resulting in the formation of acid chlorides. Benzoic acid, p-toluic acid, p-nitrobenzoic acid, m-nitrobenzaldehyde and p-nitrobenzaldehyde were unreactive. Excellent yields were obtained in many reactions using carbon tetrachloride, glacial acetic acid, and 90 per cent acetic acid as solvents.

In a similar study with phenols Ginsburg (16) found that tert-butyl hypochlorite reacted with phenols in carbon tetrachloride to form o-chlorophenols.

Grob and Schmid (18) found that tert-butyl hypochlorite oxidized primary alcohols to esters of the corresponding acids. Primary aromatic benzyl alcohol yielded benzaldehyde. Secondary alcohols were oxidized to ketones with mandelic acid being simultaneously decarboxylated to yield benzaldehyde. Good yields were obtained using carbon tetrachloride as the solvent.

Audrieth, Colton, and Jones have studied the formation of hydrazine from the reaction of tert-butyl hypochlorite with ammonia (3) and urea (8). Zimmer and Audrieth (42) have reported the use of tert-butyl hypochlorite as an N-chlorinating agent.

III EXPERIMENTAL

III EXPERIMENTAL

A. Apparatus

A Sargent Potentiometer (4 volt span) was used for the potentiometric titrations in glacial acetic acid. The indicator electrode consisted of a 2 cm. 18 gauge platinum wire. Two reference electrodes were used: a saturated calomel electrode of the fiber type, and a silver-silver chloride electrode. The latter was prepared by electrolyzing a solution of dilute hydrochloric acid using 1 cm. of 16 gauge silver wire as the anode.

A Fisher Elecdropode (sens. = 0.025 μa./scale div.) equipped with 2 cm. 18 gauge platinum wire electrodes was used for the amperometric titrations.

A Sargent Model III Manual Polarograph (sens. = 0.0064 μa./mm.) equipped with a twin inlay platinum electrode, Beckman #19031, was also used for amperometric titrations.

A Fisher Titrimeter equipped with a platinum wire indicator electrode and a saturated calomel reference electrode was used for some potentiometric titrations in aqueous solutions.

A 50 ml. amber buret equipped with a Nylon stopcock assembly was used in titrations with glacial acetic acid solutions of tert-butyl hypochlorite. All other titrations were performed using a 50 ml. calibrated Exax buret.

Small samples of liquid unsaturates were weighed using a 0.5 ml. hypodermic syringe. Larger samples were weighed with a weight buret.

B. Reagents and Solutions

The sodium oxalate and ansenious oxide used in this work were primary standard grade. All other inorganic reagents were either reagent grade, analytical reagent grade, or analyzed grade chemicals. Baker's C. P. Analyzed lithium chloride was assayed by the Fajans method for chloride and found to contain 89.9 per cent lithium chloride (39).

The organic chemicals used in this work were the best grades available commercially. The purity of several of these chemicals was determined by accepted procedures.

Merck Reagent phenol was assayed by a bromination method using standard bromate-bromide solution according to the procedure of Stone (32). It was found to be 99.8 per cent phenol.

Eastman hydroquinone was assayed by the procedure of Furman and Wallace in which the hydroquinone was titrated potentiometrically with ceric sulfate (13). Its purity was found to be 100.5 per cent.

Many of the unsaturates used in this work were assayed by the acid-catalyzed bromination method of Byrne and Johnson (5). The results of these determinations are found in the section entitled "Determination of Unsaturation".

Dupont glacial acetic acid (99.7%) was used exclusively throughout this work.

Glacial acetic acid free from reducing substances was prepared by refluxing 1 liter of glacial acetic acid with 20 g. (2%) of chromium trioxide for two hours in an all-glass apparatus. The acid was then distilled and 500 ml. of the middle fraction collected for use.

Anhydrous acetic acid was prepared by refluxing 1 liter of glacial acetic acid with 50 ml. of acetic anhydride (5% by volume) for four hours in an all-glass apparatus. The acid was then distilled and 500 ml. of the middle fraction collected for use.

Anhydrous acetic acid free from reducing substances was prepared by refluxing 1 liter of glacial acetic acid, 20 g. of chromium trioxide, and 50 ml. of acetic anhydride for four hours in an all-glass apparatus. The acid was then distilled and 500 ml. of the middle fraction collected for use.

tert-Butyl hypochlorite was prepared in 1 mole quantities according to the method of Teeter and Bell (36). The crude hypochlorite was purified by distillation at atmospheric pressure in an all-glass apparatus. The purified material was stored in amber glass-stoppered bottles in a refrigerator. Yields of 77 g. (71%) and 89 g. (82%) were obtained with two preparations. The purity of the hypochlorite was determined by breaking weighed ampules of the hypochlorite under 100 ml. of 5 per cent aqueous potassium iodide solution acidified with 25 ml. of glacial acetic acid. The liberated iodine was titrated with standard thiosulfate solution using starch indicator. The first preparation was found to contain 96.3 per cent tert-butyl hypochlorite. After eight months it contained 95.4 per cent. The second preparation contained 88.6 per cent hypochlorite.

Solutions of 0.1 N tert-butyl hypochlorite in glacial acetic acid were prepared by adding the required amount (5.4 g.) to 1 liter of glacial acetic acid. The solutions were stored in amber glass-stoppered bottles under a hood and protected from direct sunlight. The standardization of these solutions is discussed in the section entitled "Standardization of Glacial Acetic Acid Solutions of tert-Butyl Hypochlorite". Other standard solutions used in this work were prepared by accepted procedures. These include standard solutions of sodium thiosulfate (41), ceric sulfate (40), silver nitrate (39), bromate-bromide (32), and the bromination solution used for the determination of unsaturation (5). The ceric ammonium sulfate and the ferroin indicator used in the preparation of a standard ceric sulfate solution were obtained from the G. Frederick Smith Chemical Company. Standard procedures were used for the preparation of dichlorofluorescein (39) and starch indicators (41).

C. Standardization of Glacial Acetic Acid Solutions of tert-Butyl Hypochlorite

This work was undertaken to investigate the analytical applications of tert-butyl hypochlorite in glacial acetic acid. Therefore, it was of prime importance to establish an accurate method for the standardization of such solutions.

1. Iodine-Thiosulfate Method

Several investigators (1,6,34,35) have stated that tert-butyl hypochlorite liberates iodine quantitatively from an aqueous solution of potassium iodide acidified with acetic acid according to the reaction:

$$CH_3\overset{CH_3}{\underset{CH_3}{C}}-O-Cl + 2HI \longrightarrow CH_3\overset{CH_3}{\underset{CH_3}{C}}-OH + HCl + I_2$$

The iodine can be titrated with a standard thiosulfate solution and thus the purity or concentration of tert-butyl hypochlorite determined. This is the only method reported for the assay of tert-butyl hypochlorite.

In this reaction 1 mole of tert-butyl hypochlorite liberates 2 equivalents of iodine and the normality of a hypochlorite solution would be based on an equivalent weight equal to one-half of the molecular weight of tert-butyl hypochlorite.

Although this reaction appeared suitable and adaptable for a standardization procedure, several factors had to be investigated before it could be adopted as a method of standardization. The rapidity of the reaction and the effect of air oxidation had to be determined. The stoichiometry of the reaction had to be established also.

To determine the rapidity of the reaction and the effect of air oxidation the following experiment was performed.

Twenty-five ml. aliquots of tert-butyl hypochlorite solution were added to iodine flasks containing 50 ml. of water and 3 g. of potassium iodide. The flasks were stoppered and allowed to stand for varying time intervals and then titrated with standard thiosulfate solution to a starch endpoint. Three to 4 ml. of 0.5 per cent starch solution was added just prior to the disappearance of the yellor iodine color. Twenty-five ml. aliquots of glacial acetic acid were added to each of a second series of iodine flasks containing 50 ml. of water and 3 g. of potassium iodide. These flasks were allowed to stand for similar time intervals and the iodine then titrated in the same manner. The data from this experiment are contained in Table I.

TABLE I

EFFECT OF AIR OXIDATION AND REACTION TIME ON THE STANDARDIZATION PROCEDURE

Standing Time, Min.	Ml. ROCl	Ml. $Na_2S_2O_3$*			N ROCl
		Sample	Blank	Corrected	
2	24.97	22.89	0.00	22.89	0.0904
7	24.97	22.91	0.02	22.89	0.0904
15	24.97	22.92	0.03	22.89	0.0904
30	24.97	22.94	0.06	22.88	0.0904
45	24.97	22.96	0.08	22.88	0.0904
60	24.97	22.99	0.09	22.88	0.0904

*Normality = 0.0986

Although the required volume of thiosulfate increased with time, it was apparent from the data that this increase was caused by air oxidation. When corrected for the effect of air oxidation, the results showed good precision indicating that tert-butyl hypochlorite liberated iodine instantaneously from an acidified aqueous potassium iodide solution. If the iodine was titrated within a few minutes, no correction for air oxidation was necessary. The data also established the reproducibility of this method.

2. Excess Oxalate Method

Although the preceding data indicated that the iodine-thiosulfate method might be satisfactory from the point of time and precision, it was still necessary to establish that the liberation of iodine by tert-butyl hypochlorite was quantitative. The only way that this could be confirmed was to find an alternate method of standardization, a method using some standard material but not involving a thiosulfate titration of iodine.

a. Selection of Standard

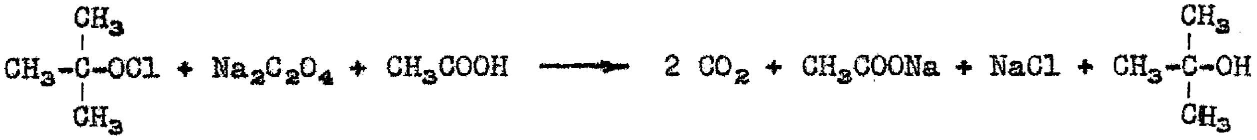
Two primary standard materials, sodium oxalate and arsenious oxide, were considered for this alternate method of standardization. There is no reported work on the reaction of tert-butyl hypochlorite with either of these two substances. Sodium oxalate (20) has been found suitable for the standardization of glacial acetic acid solutions of ceric nitrate and Tomecek and Heyrovsky (37) have titrated arsenious oxide with glacial acetic acid solutions of bromine.

The use of both of these substances was limited by their low solubility in non-aqueous solvents. Initial tests with arsenious oxide proved that this substance was impractical because of its low solubility, even in aqueous mixtures of acetic acid. Sodium oxalate also was insoluble in glacial acetic acid. However, by dissolving sodium oxalate in a small amount of water and then adding glacial acetic acid, solutions up to 0.04 N in 80 per cent acetic acid could be prepared.

b. Reaction Rate of tert-Butyl Hypochloride with Excess Sodium Oxalate

Any method of standardization using sodium oxalate that would not involve a thiosulfate titration would have to utilize an excess of sodium oxalate with subsequent determination of the excess. Therefore it was first necessary to determine if tert-butyl hypochlorite could be quantitatively consumed by excess oxalate in 80 per cent acetic acid, and if the excess oxalate could be determined under the experimental conditions.

It was expected that tert-butyl hypochlorite would react with sodium oxalate according to the following equation:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OCl + Na_2C_2O_4 + CH_3COOH \longrightarrow 2\ CO_2 + CH_3COONa + NaCl + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

In this reaction 1 mole of sodium oxalate would consume 1 mole of tert-butyl hypochlorite. Sodium chloride would be one of the products and as hypochlorites react with chlorides to form chlorine, it was expected that some chlorine would be formed in the course of the reaction. Since the hypochlorite is a volatile liquid and chlorine is a gas, frequent shaking would be necessary to cause complete consumption of these substances.

To determine if tert-butyl hypochlorite would be consumed quantitatively by excess oxalate, the following experiment was performed.

Twenty-five ml. aliquots of approximately 0.1 N hypochlorite solution were added to 0.2680 g. (4 meq.) samples of sodium oxalate dissolved in 20 ml. of water and 55 ml. of glacial acetic acid in 500 ml. iodine flasks. The flasks were stoppered and allowed to stand for various time intervals with frequent shaking. One hundred ml. of 3 per cent aqueous potassium iodide solution was then added and the liberated iodine titrated with standard thiosulfate solution. The percentage of hypochlorite consumption was calculated from the amount of thiosulfate solution necessary to titrate the iodine. If all of the hypochlorite was consumed, no iodine would be liberated. A blank was run to determine if any decomposition of the hypochlorite occurred under the experimental conditions. No chloride was added to the blank. The data from this experiment are contained in Table II.

From the data in Table II it was apparent that the hypochlorite was completely consumed in one hour and that no decomposition of the hypochlorite occurred under the experimental conditions specified. It was shown later that when chlorine was formed in a reaction and water was present that some decomposition did occur. In this particular case where the reaction proceeded very rapidly, it was unlikely that much chlorine was formed and that which was formed was probably consumed by oxalate before it could decompose.

TABLE II

REACTION RATE OF tert-BUTYL HYPOCHLORITE WITH EXCESS SODIUM OXALATE

Meq. $Na_2C_2O_4$	Meq. ROCl	Reaction Time, Min.	Ml. $Na_2S_2O_3$*	Meq. ROCl		Per Cent Consumed
				Left	Consumed	
0	2.230	0	22.63	2.230	0.0	0.0
0	2.230	60	22.63	2.230	0.0	0.0
4	2.230	15	0.27	0.0266	2.203	98.8
4	2.230	30	0.20	0.0197	2.210	99.1
4	2.230	45	0.02	0.0020	2.228	99.9
4	2.230	60	0.02	0.0020	2.228	99.9
4	2.230	60	0.00	0.000	2.230	100.0

*Normality = 0.0986

c. Determination of Sodium Oxalate with Ceric Sulfate

It was also necessary to determine if sodium oxalate could be titrated successfully in the solvent being used. The preceding experiment was run in 100 ml. of 80 per cent acetic acid. The products of the reaction included tert-butyl alcohol and chloride. Neither of these substances was present in an amount sufficient to be expected to cause interference. However, it was decided that it would be necessary to dilute the solution as much as practical to minimize any difficulties from the acetic acid. The oxalate was titrated with standard ceric sulfate solution using ferroin indicator.

The following procedure was used for this determination.

Accurately weighed samples of sodium oxalate (about 0.26 g., 4 meq.) were dissolved in solutions consisting of 30 ml. of concentrated hydrochloric acid, 5 ml. of 0.005 M. iodine monochloride solution, 80 ml. of glacial acetic acid, 0.2 ml. of tert-butyl alcohol, and 140 ml. of distilled water in 500 ml. iodine flasks. These solutions were then heated to 50°C and titrated with ceric sulfate solution using 2 drops of ferroin indicator. Several blanks were run in an identical manner with the sodium oxalate omitted. The results of this experiment are contained in Table III.

This experiment established conclusively that sodium oxalate could be determined accurately under the experimental conditions.

TABLE III

DETERMINATION OF SODIUM OXALATE WITH CERIC SULFATE

Ml. $Ce(SO_4)_2$*	g. Sodium Oxalate	
	Taken	Found
41.37	0.2717	0.2719
40.44	0.2660	0.2658
38.33	0.2518	0.2519
39.90	0.2622	0.2622

*Normality = 0.0981
Blank = 0.09 ml., Ave. of 3 results

d. Standardization Procedure

Having established that an excess of sodium oxalate completely consumed tert-butyl hypochlorite in one hour and that sodium oxalate could be accurately determined in the solvent being used, the following procedure was run as an alternate method of standardization.

Weighed samples of sodium oxalate of approximately 0.26 g. were dissolved in 20 ml. of distilled water in 500 ml. iodine flasks and then 55 ml. of glacial acetic acid was added to each flask. Twenty-five ml. aliquots of tert-butyl hypochlorite solution were added to these flasks and the flasks allowed to stand at least one hour with frequent shaking. To each flask was then added 120 ml. of distilled water, 30 ml. of concentrated hydrochloric acid, and 5 ml. of 0.005 M iodine monochloride solution. The solutions were then heated to 50°C and titrated with standard ceric sulfate solution using 2 drops of ferroin indicator.

The number of meq. of sodium oxalate consumed was calculated from the original sample weights and the amount remaining as found by the ceric sulfate titration. The normality of the hypochlorite solution was then calculated from the amount of sodium oxalate consumed and the volume of hypochlorite solution used. The results of these determinations are found in Table IV. The normality of the hypochlorite solution was determined by the iodine-thiosulfate method also. These results are tabulated in Table V.

The data in Tables IV and V verified the stoichiometry of the reaction of tert-butyl hypochlorite with potassium iodide. Therefore, this method was used exclusively throughout this work. The very close agreement of results between the two methods inferred that no decomposition of hypochlorite occurred in the excess oxalate method.

TABLE IV

STANDARDIZATION OF HYPOCHLORITE SOLUTION BY EXCESS OXALATE METHOD

$Na_2C_2O_4$ Taken		Ml.	Ml.	Meq. $Na_2C_2O_4$		N ROCl
G.	Meq.	ROCl	$Ce(SO_4)_2$*	Left	Consumed	
0.2660	3.970	24.97	17.84	1.750	2.220	0.0889
0.2686	4.009	24.97	18.20	1.785	2.224	0.0891
0.2825	4.217	24.97	20.35	1.996	2.221	0.0890

*Normality = 0.0981   Ave. = 0.0890

TABLE V

STANDARDIZATION OF HYPOCHLORITE SOLUTION BY IODINE-THIOSULFATE METHOD

Ml. ROCl	Ml. $Na_2S_2O_3$*	N ROCl
24.97	22.52	0.0889
24.97	22.52	0.0889
24.97	22.51	0.0889
24.97	22.53	0.0890

*Normality = 0.0986   Ave. = 0.0889

D. The Stability of Acetic Acid Solutions of tert-Butyl Hypochlorite

An important property of any solution is its stability. Practically all acetic acid solutions of oxidizing and reducing substances are unstable to some degree. In most cases this is due to the presence of impurities in the acetic acid. In many cases it is necessary to purify the acid before solutions of reasonable stability can be obtained.

Several factors were expected to have some effect on the stability of solutions of tert-butyl hypochlorite in acetic acid. These factors were the amount of water in the acetic acid, the presence of reducing substances, the presence of acids and bases, and the light sensitivity of tert-butyl hypochlorite.

1. Effect of Water

Since tert-butyl hypochlorite is an ester, it would be subject to hydrolysis according to the equation:

$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OCl + H_2O \longrightarrow CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH + HOCl$$

The amount of water present in the acetic acid would be expected to have some effect on this reaction. Whether or not the hydrolysis would have any effect on the amount of available chlorine would depend on the further decomposition of hypochlorous acid.

To determine the effect of water the stability of hypochlorite was studied in the following solutions: glacial acetic acid that was 99.7 per cent acid according to the label, acetic acid that was 10 per cent water by volume, and anhydrous acetic acid prepared by refluxing glacial acetic acid with an excess of acetic anhydride. These stability studies were carried out by the following procedure:

Approximately 0.1 N solutions of the hypochlorite in the desired solvent were prepared and placed in amber glass-stoppered bottles. The solutions were stored at room temperature under a hood and protected from direct sunlight. Twenty-five ml. aliquots of these solutions were assayed at specific time intervals by the iodine-thiosulfate method.

As these standard solutions were prepared individually, they had different concentrations. To facilitate comparison of the effects studies, the data were arranged so that all of the stability curves would have a common origin. This was accomplished by calculating the results on the basis of the percentage of hypochlorite remaining, the percentage at the time of preparation being 100.0 per cent. The results of these studies are represented graphically in Figure I, and the data are found in the Appendix.

Curve A in Figure I illustrates the stability of tert-butyl hypochlorite in commercial 99.7 per cent acetic acid. This solution decomposed at a rate of approximately 1 part per 1000 per day with a more rapid decomposition occurring during the first few days. Curve B represents the stability of hypochlorite in 90 per cent acetic acid. The increase in water content has approximately doubled the rate of decomposition. The general shape of curve B is similar to that of curve A. Curve C in Figure I represents the stability of the hypochlorite in anhydrous acetic acid. The very marked decrease in stability of this solution was due apparently to the presence of reducing substances in the acetic anhydride. This was verified in a later experiment. The presence of reducing substances in the acetic anhydride made it impossible to prepare an anhydrous acetic acid solution that could be used without interferences from the reducing substances. With either the 99.7 per cent or the 90 per cent acetic acid the amount of decomposition was negligible over a period of several hours. Daily standardization would be sufficient with glacial acetic acid solutions, but more frequent standardization would be necessary for 90 per cent acetic acid solutions.

2. Effect of Reducing Substances

The effect of reducing substances on the stability of acetic acid solutions of tert-butyl hypochlorite was quite apparent from the previous study. To determine the effect of reducing substances the stability of hypochlorite was studied in the following solutions:

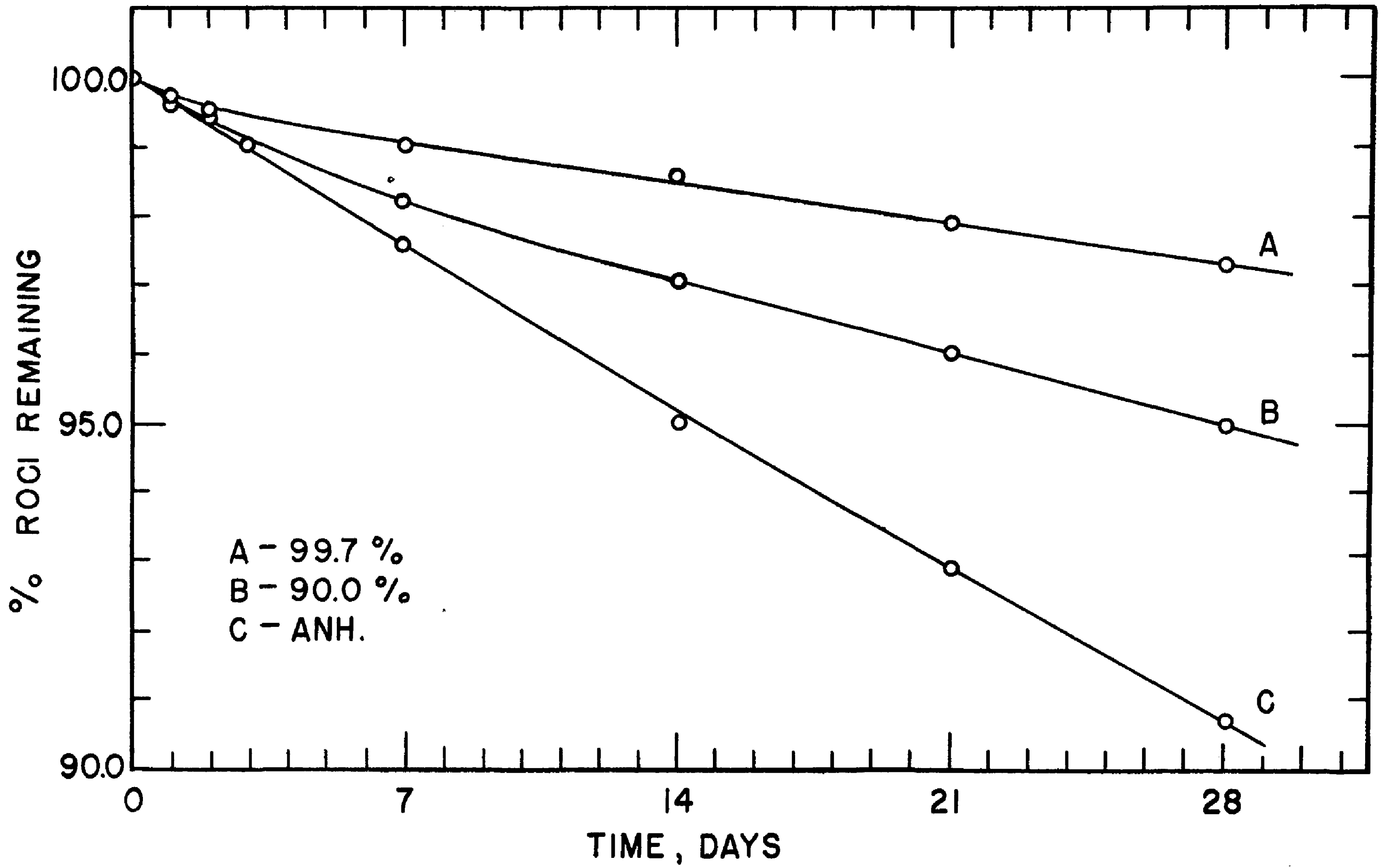


FIGURE I. EFFECT OF WATER ON THE STABILITY OF ACETIC ACID SOLUTIONS OF TERT-BUTYL HYPOCHLORITE glacial acetic acid freed from reducing substances but not anhydrous, and anhydrous acetic acid that was freed from reducing substances. These studies were carried out in the same manner as the previously described stability studies and the data were treated in the same manner also. The results are illustrated in Figure II and the data are contained in the Appendix. For comparison the stability curve for 99.7 per cent glacial acetic acid has been included in Figure II.

Curve B in Figure II represents the stability of tert-butyl hypochlorite in anhydrous acetic acid freed from reducing substances. This curve has a different shape than those of solutions not freed of reducing substances. When compared with curve A, which represents the stability of 99.7 per cent acetic acid, it is seen that the initial rapid decomposition has not occurred. However, the over-all rate of decomposition was slightly greater than that of the hypochlorite in commercial acetic acid. Curve C represents the stability of the hypochlorite in acetic acid freed from reducing substances but not anhydrous. The stability of this solution was similar to that of the anhydrous solution with the rate of decomposition slightly less. Both solutions freed from reducing substances showed an over-all rate of decomposition greater than that of the commercial untreated acid. The reason for this was not apparent.

The preceding stability studies indicated that no advantage would be gained in treating commercial acid to make it anhydrous or to remove reducing substances. Therefore, the commercial acid was used in the

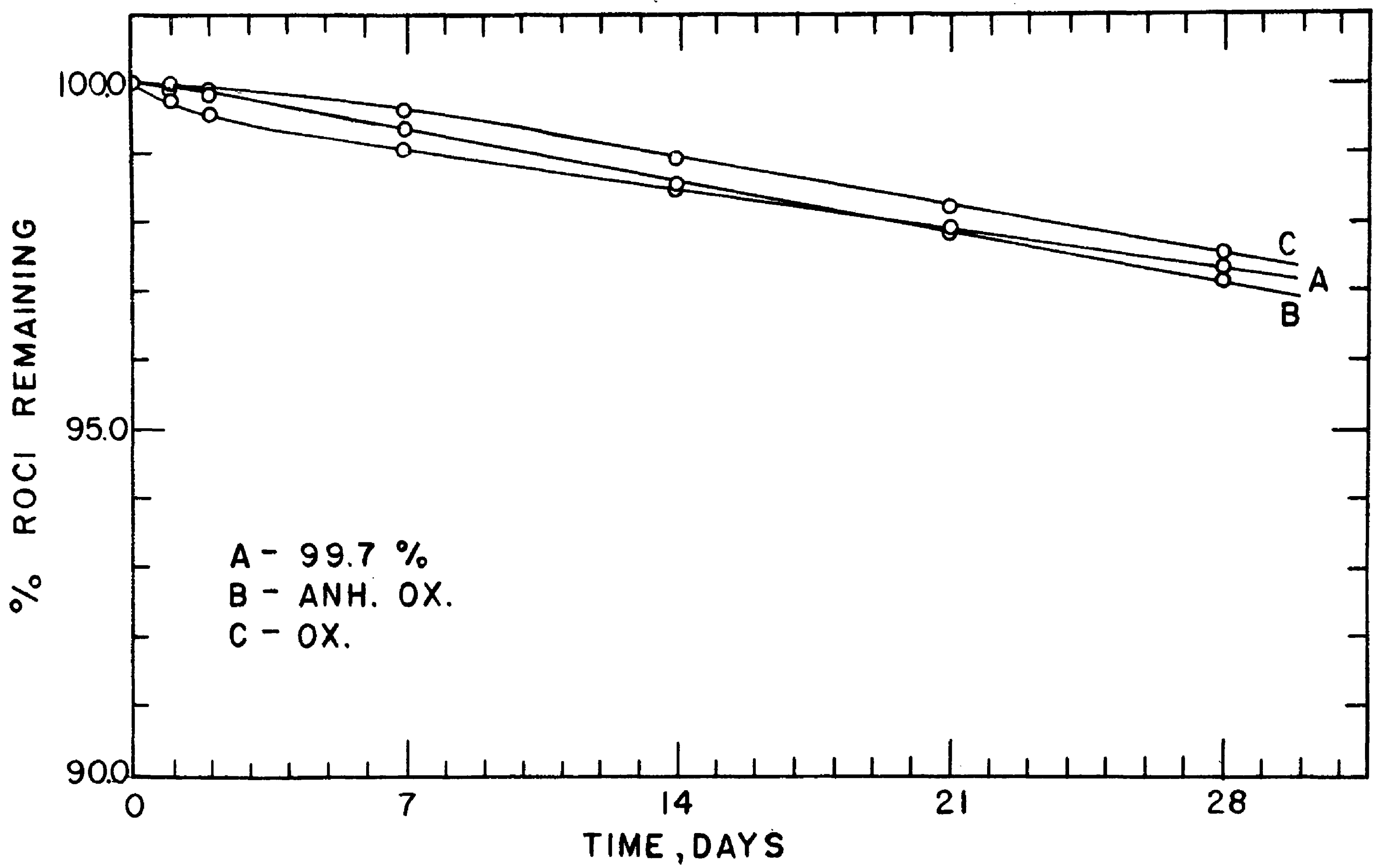


FIGURE II. EFFECT OF REDUCING SUBSTANCES ON THE STABILITY OF ACETIC ACID SOLUTIONS OF TERT-BUTYL HYPOCHLORITE preparation of all standard solutions of tert-butyl hypochlorite and as a solvent for titrations.

3. Acid-Base Catalyzed Decomposition

Anbar and Androvsky (1) have studied the effect of acids and bases on the hydrolysis of tert-butyl hypochlorite in aqueous solutions. They found that the decomposition was acid-base catalyzed and that the minimum rate occurred at a pH of 4.4.

Whether or not this acid-base catalyzed decomposition would occur in acetic acid solutions of tert-butyl hypochlorite had to be determined. The stability of hypochlorite was investigated in 0.1 N solutions of perchloric acid in acetic acid, hydrochloric acid in acetic acid, paratoluenesulfonic acid in acetic acid, and sodium acetate in acetic acid.

The following procedure was used for these stability studies. Twenty-five ml. aliquots of tert-butyl hypochlorite solution were added to flasks containing 75 ml. of glacial acetic acid and sufficient acid or base to make the final concentration 0.1 N. These flasks were allowed to stand for specific times and then 100 ml. of 3 per cent aqueous potassium iodide solution was added to each flask. The liberated iodine was then titrated in the usual manner. Reaction times of 15 and 60 minutes were used in this study. The percentage of decomposition was calculated by the following expression:

$$\text{Percent decomposition} = \frac{\text{Ml. } Na_2S_2O_3\text{(blank)} - \text{Ml. } Na_2S_2O_3\text{(sample)}}{\text{Ml. } Na_2S_2O_3\text{ (blank)}} \times 100$$

The data are found in Table VI.

TABLE VI

ACID-BASE CATALYZED DECOMPOSITION**

Ml. ROCl	Reaction Time, Min.	Ml. $Na_2S_2O_3$* Blank	Ml. $Na_2S_2O_3$* Sample	Ml. $Na_2S_2O_3$* Difference	Per Cent Decomposition
		<u>0.1 N Perchloric Acid</u>			
24.97	15	23.16	18.29	4.87	21.0
24.97	60	23.16	0.20	22.96	99.1
		<u>0.1 N p-Toluenesulfonic Acid</u>			
24.97	15	23.16	13.16	10.00	43.2
24.97	60	23.16	3.76	19.40	83.8
		<u>0.1 N Hydrochloric Acid</u>			
24.97	15	23.16	21.61	1.55	6.70
24.97	60	23.16	19.94	3.22	13.9
		<u>0.1 N Sodium Acetate</u>			
24.97	15	23.16	23.09	0.07	0.30
24.97	60	23.16	23.02	0.14	0.60

---

*Normality = 0.0986

**By comparison, 0.1 N solutions of tert-butyl hypochlorite in acetic acid decomposed approximately 0.1 per cent per day.

Perchloric acid is an apparent strong acid in glacial acetic acid whereas hydrochloric acid is an apparent weak acid. Para-toluenesulfonic acid has been investigated as this acid has been used as a catalyst for the addition of tert-butyl hypochlorite to olefins (11,22). The use of sodium acetate provided an apparent basic solution.

The solution of tert-butyl hypochlorite in 0.1 N perchloric acid in acetic acid was almost completely decomposed in one hour whereas the solution that was 0.1 N in hydrochloric acid had decomposed much less. However, an exact comparison between these two acids was impossible due to the formation of chlorine in the solution containing hydrochloric acid. The decomposition observed with the solution containing para-toluenesulfonic acid was similar to that observed with perchloric acid. In the case of the solution of sodium acetate, the decomposition was very slight but still of some consequence. As a result of this experiment it was obvious that care would have to be exercised in the use of tert-butyl hypochlorite, and that certain limitations were placed on the types of solvents that could be used.

4. Light Sensitivity

The effect of light on the stability of glacial acetic acid solutions of tert-butyl hypochlorite was determined in the following manner. An approximately 0.1 N solution of tert-butyl hypochlorite in 99.7 per cent acetic acid was prepared. One-half of this solution was placed in a clear glass-stoppered bottle and one-half was placed in an amber glass-stoppered bottle. Both bottles were stored side by side under a hood with normal exposure to laboratory radiation but protected from direct sunlight. At various time intervals the solutions were analyzed by the iodine-thiosulfate method. The results of this experiment are contained in Table VII.

TABLE VII

LIGHT SENSITIVITY OF tert-BUTYL HYPOCHLORITE IN GLACIAL ACETIC ACID

Time, Days	Clear			Amber		
	Ml. ROCl	Ml. $Na_2S_2C_3$*	N_{ROCl}	Ml. ROCl	Ml. $Na_2S_2O_3$*	N_{ROCl}
0	10.00	9.43	0.0942	10.00	9.43	0.0942
3	10.00	9.30	0.0929	10.00	9.32	0.0931
7	10.00	9.15	0.0914	10.00	9.20	0.0919
14	10.00	8.95	0.0894	10.00	9.04	0.0903
21	10.00	8.71	0.0870	10.00	8.88	0.0887
28	10.00	8.44	0.0843	10.00	8.71	0.0870

*Normality = 0.0999

The data contained in Table VII illustrate the light sensitivity of tert-butyl hypochlorite in glacial acetic acid.

E. Endpoint Detection

Several indicators are available for acid-base titrations in glacial acetic acid, but no indicators have been developed for redox titrations in this solvent. Electrometric methods of endpoint detection are the only methods available. Both amperometric and potentiometric methods have been used successfully with glacial acetic acid. Hinsvark and Stone (21) have used an amperometric method of endpoint detection in titrations with sodium permanganate in glacial acetic acid. Tomecek and Heyrovsky (37) and Tomecek and Valcha (38) employed a potentiometric method of endpoint detection using several inorganic oxidants in glacial acetic acid. Both amperometric and potentiometric methods were investigated in this work.

1. Potentiometric

Two electrode systems that have been used successfully for potentiometric redox titrations in glacial acetic acid are a saturated calomel-platinum electrode pair (37,38) and a silver-silver chloride-platinum electrode pair (20). These two electrode systems were used in this work.

Using either a saturated calomel-platinum or a silver-silver chloride-platinum electrode pair, no potential was observed when tert-butyl hypochlorite was added to glacial acetic acid. This was attributed to the low conductivity of glacial acetic acid. When sodium acetate was added to glacial acetic acid, potentials were observed with both electrode systems. With the calomel-platinum system one drop (0.03 ml.) of hypochlorite solution caused a change from 220 mv. to 721 mv. With the silver-silver chloride and platinum electrodes a potential change from 246 mv. to 850 mv. occurred with the addition of one drop.

The same approximate potential changes were observed when lithium chloride was used as the electrolyte. Potential changes of from 229 mv.

to 826 mv. and from 150 mv. to 910 mv. were observed with the calomel and silver-silver chloride electrodes respectively. The changes were very rapid. When lithium chloride was used as the electrolyte, the potential changes were due to the presence of chlorine and not hypochlorite. The observed potentials were unsteady and not reproducible. For example, potential changes of 653 mv. to 946 mv. and from 611 mv. to 842 mv. were observed using the silver-silver chloride and calomel electrode systems respectively under the same experimental conditions.

The potential changes observed with an excess of hypochlorite indicated that the potentiometric method of endpoint detection might be applicable in titrations with this reagent.

2. Amperometric

The amperometric method of endpoint detection employs two platinum electrodes connected to a potential source and a galvanometer. In the presence of a redox couple a current flows when a potential is applied to the electrodes. Several variations are possible with this method and they are discussed in the appropriate places.

With the amperometric method of endpoint detection no current was observed when tert-butyl hypochlorite solution was added to glacial acetic acid. Potentials up to 3 volts did not produce a current flow. When sodium acetate was added to glacial acetic acid, small currents were observed. Larger currents were observed when lithium chloride was present. Bromides and iodides also produced currents with the magnitudes dependent on the applied potential, the concentration of the electrolyte, and the concentration of the hypochlorite. Bromides and iodides also yielded the corresponding halogen when hypochlorite was added. The observed currents were very steady.

This method also appeared applicable to titrations using tert-butyl hypochlorite.

F. tert-Butyl Hypochlorite as a Source of Chlorine

Frequent mention has been made of the formation of chlorine from the reaction of tert-butyl hypochloride with chlorides, a reaction that is very rapid. If a substance that reacted rapidly with chlorine were titrated with a tert-butyl hypochlorite solution in the presence of a chloride it would react with the chlorine as fast as it were formed. When this reaction was complete, the excess chlorine could be detected potentiometrically or amperometrically. Thus tert-butyl hypochlorite would act as a source of chlorine with the amount conveniently controlled by the amount of hypochlorite solution added.

This type of titration looked very promising and was investigated further.

Lithium chloride was selected as the source of chloride because of its solubility in glacial acetic acid. Other salts such as sodium chloride and potassium chloride were only slightly soluble in this solvent. Figure III illustrates the galvanometer deflection obtained with varying applied potentials when 0.1 ml. of tert-butyl hypochlorite solution was added to 100 ml. of glacial acetic acid containing various concentrations of chloride salts.

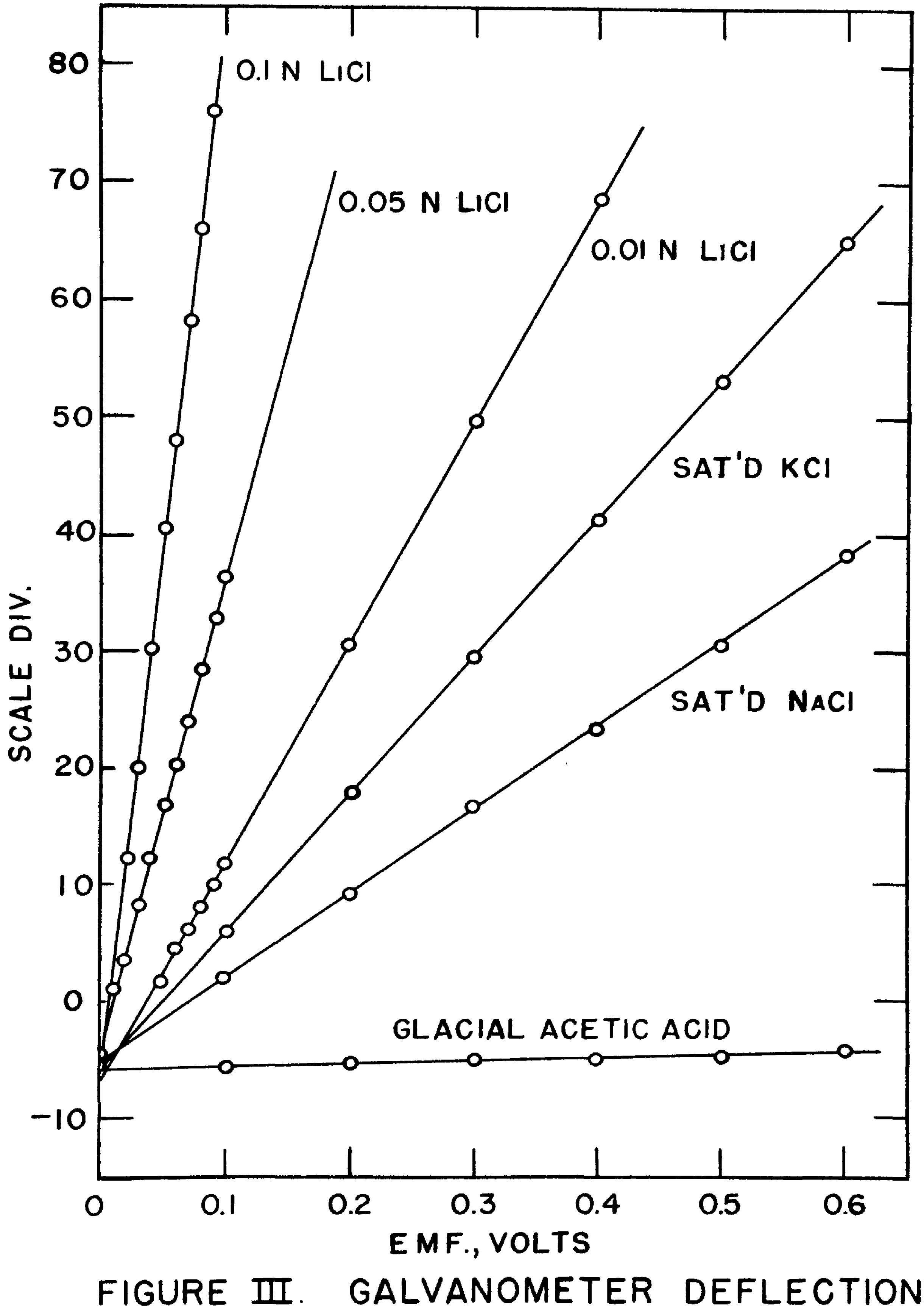


FIGURE III. GALVANOMETER DEFLECTION WITH VARIOUS CHLORIDE CONCENTRATIONS IN GLACIAL ACETIC ACID

From Figure III it is apparent that the greatest sensitivity is obtained with a 0.1 N solution of lithium chloride. The galvanometer deflections were very steady indicating that little or no loss of chlorine occurred either by volatility or chlorination of the solvent.

G. Determination of Unsaturation

Much emphasis in this investigation was placed on the application of tert-butyl hypochlorite for the determination of unsaturation, particularly because of the lack of good methods for the determination of this type of compound. The accepted mechanism of addition of either tert-butyl hypochlorite or chlorine to unsaturates is the same as that of the usual reagents for unsaturation such as bromine and iodine monochloride. Some of the types of unsaturates with which the usual methods fail are conjugated dienes, conjugated unsaturated esters, acids, and carbonyls. It is likely that these types would also present difficulties in this work.

As mentioned earlier, the products resulting from the reaction of tert-butyl hypochlorite and an unsaturate depend on the solvent composition. However, for quantitative purposes, this is of little importance as the consumption of tert-butyl hypochlorite would be the same regardless of whether a halohydrin, haloether, or haloester were formed. The solvent would be expected to have some effect on the rate of reaction however.

Three general methods for the determination of unsaturation were investigated. These were:

1. An indirect method in which the unsaturate was allowed to react with an excess of tert-butyl hypochlorite in glacial acetic acid and the excess hypochlorite determined by the iodine-thiosulfate method.

2. An indirect method in which the unsaturate was allowed to react with an excess of chlorine in glacial acetic acid and the excess chlorine determined by the iodine-thiosulfate method. The chlorine was provided by addition of lithium chloride to the solution of tert-butyl hypochlorite.

3. The direct titration of unsaturates in glacial acetic acid using tert-butyl hypochlorite and lithium chloride as a source of chlorine.

1. Excess Hypochlorite Method

Many methods for the determination of unsaturation involve the use of an excess of reagent with subsequent determination of the excess reagent. With such methods it is necessary to establish the optimum reaction time and this can be accomplished by performing reaction rate studies. Rate studies of the reaction of tert-butyl hypochlorite with several unsaturates were performed to determine if this method of determination would be feasible. Several unsaturates representing different types of unsaturation were selected for these rate studies.

The rate studies were performed according to the following procedure.

A glacial acetic acid solution of each unsaturate was prepared. These solutions were of such concentration that a 10 ml. aliquot contained approximately 1 to 1.5 meq. of unsaturation. The exact concentration of the unsaturate was determined by the acid-catalyzed bromination method. Ten ml. aliquots of the solution of unsaturate were added to 250 ml. iodine flasks containing a 25 ml. aliquot of approximately 0.1 N tert-butyl hypochlorite solution. The flasks were stoppered and allowed to stand at room temperature for specific time intervals with occasional shaking. Then 35 ml. of 5 per cent aqueous potassium iodide solution was added to each flask and the liberated iodine titrated immediately with thiosulfate solution to the disappearance of the yellow iodine color. Starch indicator was not used in the rate studies because of the rate at which the iodine color reappeared. A blank was run with the unsaturate sample omitted to determine the amount of hypochlorite present in the 25 ml. aliquot. Starch indicator was used for this determination. The data for these rate studies are contained in the Appendix.

The reaction rate curves for the various unsaturates are illustrated in Figure IV. In these curves, the ratios of meq. of unsaturation found by the hypochlorite method to the number of meq. found by the bromination method are plotted as a function of time. The ratio is designated by the symbol R in the figure. This allowed a more direct comparison of the several rate studies. The meq. of unsaturation found by the hypochlorite method were the number of meq. of hypochlorite consumed. These were calculated using the equation:

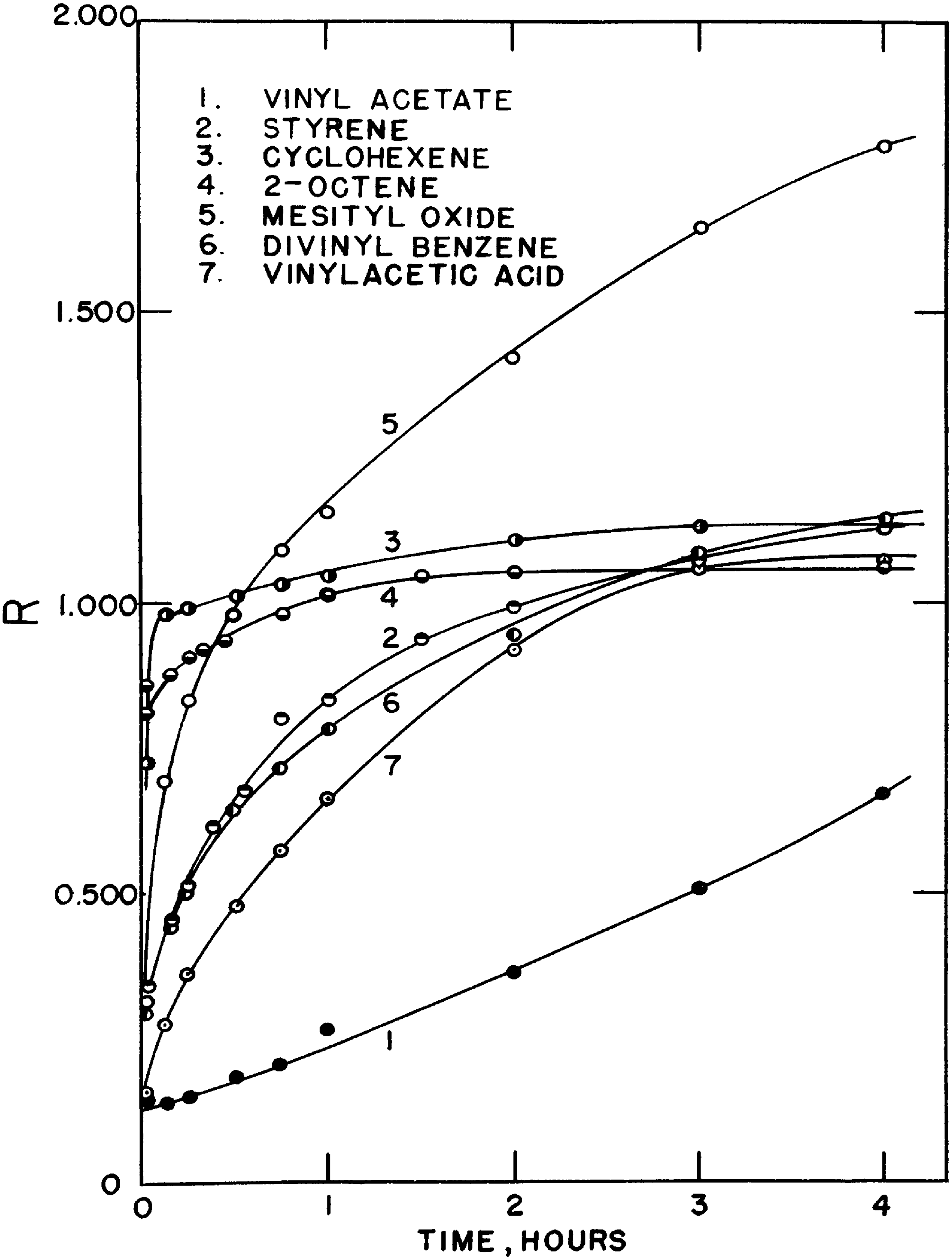


FIGURE IV. REACTION RATES OF SEVERAL UNSATURATES WITH TERT-BUTYL HYPOCHLORITE

meq. = [ml. $Na_2S_2O_3$(blank) - ml. $Na_2S_2O_3$(sample)] x $N_{Na_2S_2O_3}$

With the exception of vinyl acetate, all unsaturates studied consumed an excess of hypochlorite. The study of vinyl acetate was not completed due to the slowness of the reaction. The time for complete reaction varied with the different unsaturates with 2-octene requiring the shortest time of two hours. All rate studies indicated that the reaction of tert-butyl hypochlorite with unsaturates was too slow for analytical use.

It would be possible to develop analytical methods for individual unsaturates using empirical factors to correct for the high results. Such methods, however, would have no advantages over existing methods for unsaturation.

2. Excess Chlorine Method

A study of the reaction of unsaturates with chlorine was undertaken primarily to provide a comparison with the reaction of unsaturates with tert-butyl hypochlorite. This investigation, in the form of reaction rate studies, was accomplished using the same general procedure followed in the previous reaction rate studies involving tert-butyl hypochlorite. The reaction of tert-butyl hypochlorite with lithium chloride was used to provide the chlorine. The solutions of unsaturates in glacial acetic acid that were used in the preceding rate studies were used in this study also. They were assayed again by the bromination method.

The rate studies were performed using the following procedure. Twenty-five ml. aliquots of approximately 0.1 N tert-butyl hypochlorite solution were added to 250 ml. iodine flasks. To each flask was added approximately 0.5 g. of lithium chloride and a 10 ml. aliquot of the solution of the unsaturate. The flasks were stoppered and allowed to stand at room temperature for specific time intervals with occasional shaking. Then 35 ml. of 5 per cent aqueous potassium iodide solution was added to each flask and the liberated iodine titrated immediately with thiosulfate solution to the disappearance of the yellow iodine color. Starch indicator was not used in these rate studies except in titrations of the blanks. A blank was run with the unsaturate sample omitted to determine the amount of hypochlorite present in the 25 ml. aliquot. A second blank was run to determine if any change occurred in the amount of available chlorine after standing for a period of time. The data for these rate studies were treated in the same manner as the data of the previous rate studies and are contained in the Appendix. The reaction rate curves for the various unsaturates are illustrated in Figure V.

The reaction rate studies established that the reaction of chlorine with unsaturation was very rapid. With the exception of divinylbenzene and mesityl oxide the reaction was complete in one or two hours. In all cases, however, the final value of R was over 1.000 indicating that too much chlorine was consumed. The blanks established that there was only a negligible decrease in the amount of available chlorine after an hour of standing. This loss amounted to less than 0.1 per cent

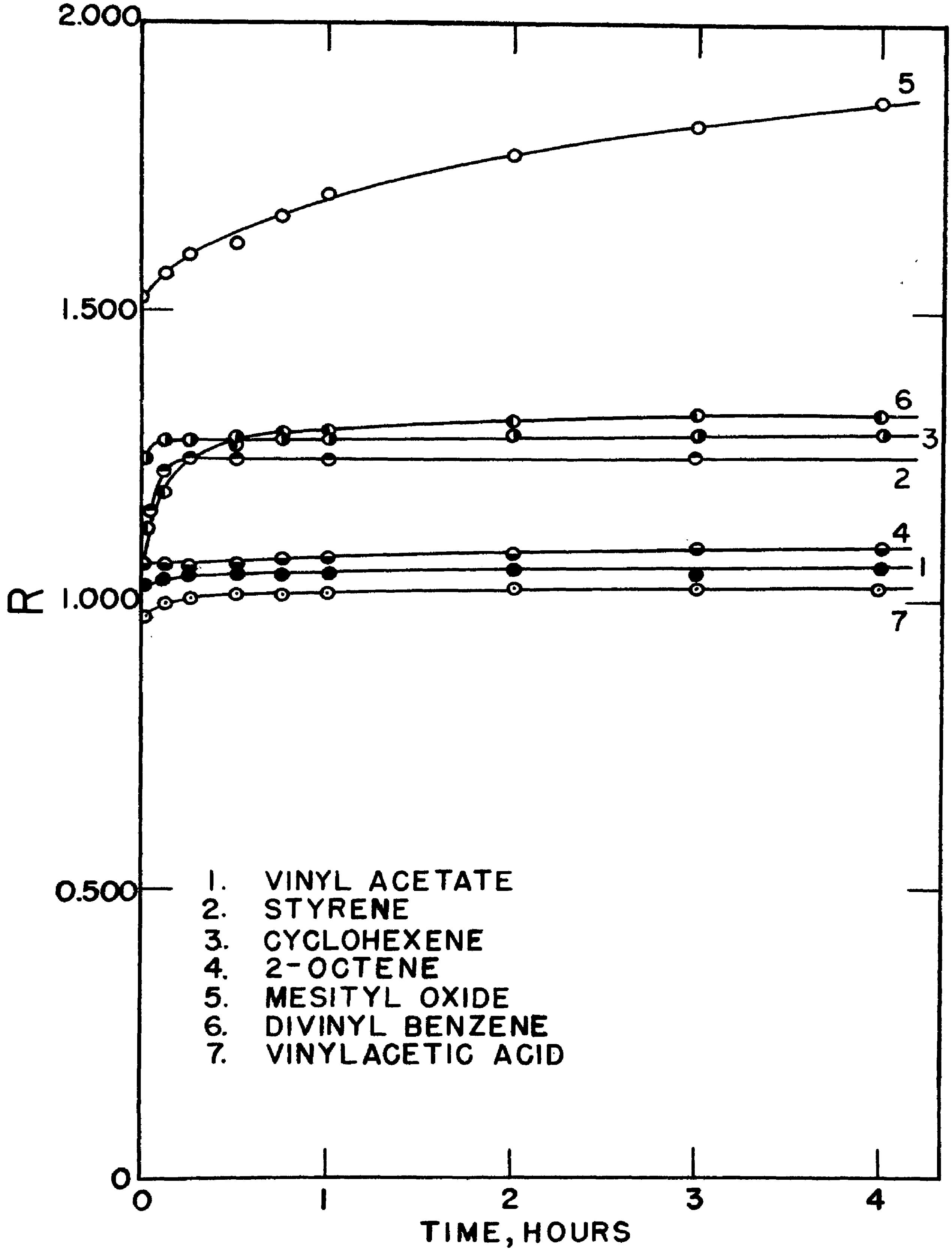


FIGURE V. REACTION RATES OF SEVERAL UNSATURATES WITH CHLORINE and it is possible that it occurred when the potassium iodide solution was added. Therefore the high results must be attributed to substitution effects. In this method where a large excess of chlorine was present the possibility of substitution was very likely.

3. Direct Titration with tert-Butyl Hypochlorite as a Source of Chlorine

The reaction of tert-butyl hypochlorite with unsaturates was too slow to permit a direct titration. Using potentiometric endpoint detection large potential changes were observed when hypochlorite solution was added to a solution of styrene in glacial acetic acid containing sodium acetate. The potentials drifted slowly and required several minutes to return to a stable value. This indicated that the reaction was slow and was supported by the previous reaction rate data. The same behavior was observed using amperometric endpoint detection.

From reaction rate data it appeared that the rate of reaction of chlorine with unsaturates was rapid enough so that a direct titration would be feasible using tert-butyl hypochlorite and lithium chloride as a source of chlorine.

a. Potentiometric Titration of Styrene

To determine if this type of titration was possible, a sample of styrene was titrated potentiometrically with a standard tert-butyl hypochlorite solution. The sample was weighed by hypodermic syringe into 100 ml. of glacial acetic acid containing 0.5 g. of lithium chloride. A Sargent Potentiometer equipped with platinum and silver-silver chloride electrodes was used. Figure VI illustrates a typical

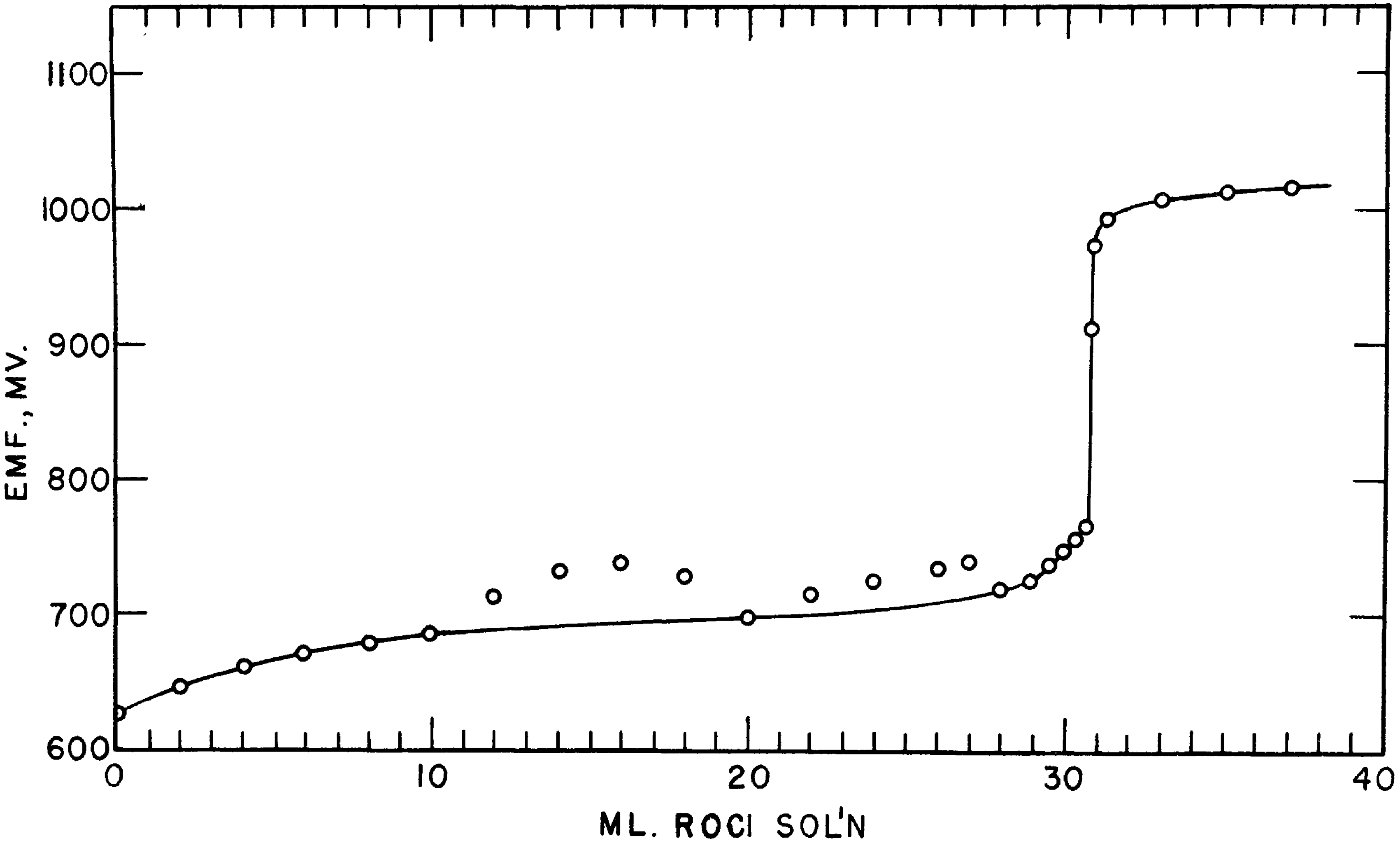


FIGURE VI. POTENTIOMETRIC TITRATION OF STYRENE WITH TERT-BUTYL HYPOCHLORITE AS A SOURCE OF CHLORINE potentiometric titration curve. The data for this curve are contained in the Appendix. Equilibrium was reached very rapidly after each addition of reagent and a well-defined potential change of approximately 200 mv. occurred at the endpoint in the titration.

Similar titration results were obtained when a calomel reference electrode was used. This electrode system, however, did not respond as rapidly as that using the silver-silver chloride electrode, and the titration was difficult to follow.

The erratic potential values observed during the titration were characteristic of all potentiometric titrations performed in this work. Several samples of styrene were titrated using potentiometric endpoint detection. The results of these titrations are contained in Table VIII.

TABLE VIII

POTENTIOMETRIC TITRATION RESULTS OF STYRENE

Electrode System	Ml. ROCl	N_{ROCl}	g. Styrene Taken	g. Styrene Found	Per Cent Styrene
Std. Cal.-Pt.	36.10	0.0922	0.1738	0.1733	99.7*
Ag-AgCl-Pt.	41.40	0.0921	0.1990	0.1985	99.8*
Ag-AgCl-Pt.	30.80	0.1033	0.1678	0.1657	98.7**

*99.5% by Bromination
**98.9% by Bromination

The potentiometric titration results agreed very well with the bromination results.

b. Amperometric Titration of Styrene

Several samples of styrene were titrated using amperometric end-point detection. A Sargent Manual Polarograph equipped with platinum electrodes was used. Fifty mv. was selected for the applied potential. The method of weighing and the solvent were the same as in the potentiometric titrations. Prior to the addition of the sample the galvanometer was adjusted to zero. The hypochlorite solution was added rapidly until a current was observed. This first current was unsteady and decreased rapidly to zero. The hypochlorite solution was then added slowly until one drop caused a steady current. The results of the titrations are contained in Table IX.

TABLE IX

AMPEROMETRIC TITRATION RESULTS OF STYRENE

Ml. ROCl	N_{ROCl}	g. Styrene Taken	g. Styrene Found	Per Cent Styrene*
38.13	0.0965	0.1918	0.1916	99.9
38.94	0.0964	0.1959	0.1955	99.8
37.43	0.0978	0.1912	0.1907	99.7
32.60	0.1033	0.1757	0.1753	99.8
42.80	0.1008	0.2256	0.2246	99.6
39.90	0.1014	0.2113	0.2106	99.7
41.51	0.0916	0.1989	0.1980	99.5

*99.5% by Bromination Method

Ave.= 99.7

The results obtained using this method agreed very well with both the potentiometric and bromination results.

There was a titration blank as some hypochlorite had to be added to cause a current to indicate the endpoint. This amounted to approximately 0.02 ml. of hypochlorite solution. The blank was neglected as it was less than 1 part per 1000.

The platinum electrodes used in the titrations showed no physical evidence of attack by chlorine and no change was noticed in the sensitivity of the electrodes. As a precaution the electrodes were stored in sulfuric acid-chromic acid cleaning solution when not in use.

The amperometric method of endpoint detection was much more convenient to perform than the potentiometric method. As the same results were obtained with both methods the amperometric method was used almost exclusively throughout this work.

c. Amperometric Titration of Other Unsaturates

A large number of unsaturates were titrated to determine the applicability of the method.

The following procedure was adopted as the standard titration procedure for these titrations.

The sample of unsaturate, 3 to 4 meq., was weighed by hypodermic syringe into a 250 ml. beaker containing 100 ml. of glacial acetic acid in which 0.5 g. of lithium chloride was dissolved. Stirring was accomplished using a magnetic bar stirrer. The galvanometer was adjusted to zero with a 50 mv. potential applied across the platinum electrodes. tert-Butyl hypochlorite solution was then added from the amber buret until one drop caused a steady deflection of several scale divisions. With most unsaturates the titrant could be added rapidly to within a few ml. of the endpoint without causing a galvanometer deflection. It was necessary then to add small increments and wait until the galvanometer returned to zero before further addition. The titration results are contained in Table X.

TABLE X

AMPEROMETRIC TITRATION RESULTS OF SEVERAL UNSATURATES

Unsaturate	Ml. ROCl	N ROCl	g. Unsaturate		Per Cent	Per Cent by Br_2	Per Cent Error
			Taken	Found			
Cyclohexene	46.40	0.0983	0.1594	0.1873	117.5	96.5	+21.0
Oleic acid	36.23	0.0925	0.4653	0.4733	101.7	96.6	+ 5.1
Methyl undecylenate	40.84	0.0912	0.3600	0.3693	102.6	94.4	+ 8.2
Allyl alcohol	46.35	0.0909	0.1797	0.1224	68.1	63.6	+ 4.5
Mesityl oxide	48.37	0.0909	0.1974	0.2158	109.3	73.9	+35.4
Cinnamyl alcohol	34.47	0.0913	0.2571	0.2111	82.1	89.8	- 7.7
Allyl acetate	39.40	0.0912	0.1753	0.1800	102.7	98.2	+ 4.5
Vinylacetic acid	34.30	0.0912	0.1479	0.1350	91.3	96.4	- 5.1
1-Octene	41.80	0.1008	0.1920	0.2364	123.1	98.1	+25.0
2-Octene	37.60	0.1013	0.2264	0.2137	94.4	90.0	+ 4.4
3-Heptene	37.50	0.1008	0.2084	0.1856	89.0	86.0	+ 3.0
2,5-Dimethylhexadiene-1,5	53.20	0.0912	0.0880	0.1337	145.0	101.7	+43.3
Vinyl acetate	40.60	0.1004	0.1793	0.1755	97.9	95.8	+ 2.1
Divinylbenzene	32.10	0.0996	0.1470	0.1030	70.0	69.6	+ 0.4
Divinylbenzene	36.30	0.0873	0.1462	0.1031	70.6	69.6	+ 1.0
Divinylbenzene	31.15	0.0868	0.1256	0.0880	70.1	69.6	+ 0.5

Several unsaturates that could not be titrated by this method are listed below.

Maleic acid
Cinnamic acid
Cinnamaldehyde
Crotonic acid
Methyl acrylate
Allyl chloride
Crotonaldehyde
Butynediol
2,5,-Dimethyl-3-hexyne-2,5-diol

Allyl chloride and crotonaldehyde did react slowly but the other unsaturates were unreactive.

Of all the unsaturates studied, only styrene gave good results with this method. The results obtained with divinylbenzene were fair. Low results were obtained with cinnamyl alcohol and vinylacetic acid. With these compounds the titration became so slow that it was discontinued. The titration results were high with all other unsaturates where a reasonably rapid titration was possible. This was attributed to substitution of the unsaturate being determined or substitution of the impurities in the sample.

d. Effect of Temperature

Du Bois and Skoog (10) in their method for unsaturation utilized low temperatures to reduce substitution effects. This technique was studied in this work also.

As glacial acetic acid freezes at approximately 17°C., it was necessary to find other solvents to study this effect. Two solvents were found that were suitable for titrations below 10°C: acetic acid containing 10 per cent water by volume which freezes at 5°C and acetic acid containing 20 per cent carbon tetrachloride by volume which freezes at 4°C. Pure carbon tetrachloride could not be used as a solvent due to the very low solubility of lithium chloride in it. The initial volumes of solvent were prepared in such a manner that the final volumes at the endpoint would be either 10 per cent water in acetic acid or 20 per cent carbon tetrachloride in acetic acid. Forty ml. was allowed for the reagent.

Samples of styrene were titrated in both of these solvents at room temperature and at a low temperature. For the low temperature titrations the temperature in the titration vessel was maintained between 5 and 10°C by means of an ice bath. The titrations were performed in the usual manner using the amperometric method of endpoint detection. The titration results are contained in Table XI.

TABLE XI

EFFECT OF TEMPERATURE ON TITRATION RESULTS

Solvent	Temp. °C.	Ml. ROCl	N ROCl	g. Styrene Taken	g. Styrene Found	Per Cent*
90% HAc, 10% H_2O	25	35.40	0.1033	0.1853	0.1904	102.8
90% HAc, 10% H_2O	< 10	44.00	0.1008	0.2273	0.2309	101.6
80% HAc, 20% CCl_4	25	41.20	0.0927	0.1981	0.1989	100.4
80% HAc, 20% CCl_4	< 10	44.07	0.0927	0.2126	0.2127	100.1

*99.5% by bromination
99.7% in glacial acetic acid

The reduction in temperature improved the titration results with both solvents. However, with both solvents at normal and reduced temperatures, the results were considerably high in comparison with the bromination results and the titration results obtained with glacial acetic acid. The high results using 90 per cent acetic acid were probably due partially to decomposition of the reagent. The reason for the high results using 80 per cent acetic acid is unknown. The titrations at low temperatures could be performed just as rapidly as those at room temperature and no difference was observed in the nature of the endpoint.

e. Effect of Mercuric Chloride

As substitution can take place simultaneously with addition, the slower the addition reaction the higher will be the error due to increased opportunity for substitution to take place. Therefore, an effort was made to reduce this effect by accelerating the addition reaction. Acids (5) and heavy metals (4,23,24) have been used to catalyze addition reactions. The use of acids with tert-butyl hypochlorite was prohibited because the decomposition of the reagent was acid-catalyzed. Lucas and Pressman (24) and Lewis and Bradstreet (23) found that mercuric chloride was effective as a catalyst in bromination methods. This compound was selected for investigation in this work due to its solubility in glacial acetic acid.

Samples of styrene were titrated at room temperature and low temperatures in the same solvents used for the low temperature titrations.

The titration procedure was the same also except for the addition of 1 g. of mercuric chloride prior to the addition of the sample to the solvent. A sample of styrene was titrated in glacial acetic acid with mercuric chloride added also. The results of these titrations are found in Table XII. For comparison the results from Table XI have been included in Table XII. These are the titration results performed at both temperatures in the same solvents.

TABLE XII

EFFECT OF MERCURIC CHLORIDE ON TITRATION RESULTS

Solvent	Temp. °C.	Ml. ROCl	N ROCl	g. Styrene		Per Cent* Styrene	Per Cent Error
				Taken	Found		
gl HAc (Hg)	25	33.27	0.1032	0.1783	0.1788	100.3	+0.6
90% HAc,10% H_2O	25	35.40	0.1033	0.1853	0.1904	102.8	+3.1
90% HAc, 10% H_2O (Hg)	25	35.60	0.1033	0.1907	0.1915	100.4	+0.7
90% HAc, 10% H_2O	< 10	44.00	0.1008	0.2273	0.2309	101.6	+1.9
90% HAc, 10% H_2O (Hg)	< 10	42.10	0.1008	0.2208	0.2210	100.1	+0.4
80% HAc, 20% CCl_4	25	41.20	0.0927	0.1981	0.1989	100.4	+0.7
80% HAc, 20% CCl_4(Hg)	25	43.80	0.0873	0.1987	0.1991	100.2	+0.5
80% HAc, 20% CCl_4	< 10	44.07	0.0927	0.2126	0.2127	100.1	+0.4
80% HAc, 20% CCl_4(Hg)	< 10	42.10	0.1007	0.2210	0.2208	99.9	+0.2

*99.7% in glacial acetic acid at room temperature

The titration result obtained with mercuric chloride in glacial acetic acid at room temperature was high compared with the previous results obtained with mercuric chloride absent. This was probably due to decomposition caused by mercuric chloride. The extent of this decomposition could not be determined by rate studies due to interference from mercuric iodide formed in the usual procedure involving iodine and thiosulfate. The endpoints were very stable in titrations where mercuric chloride was present. The decomposition was probably very slow and occurred during the titration.

The presence of mercuric chloride improved the results obtained using the other solvents at both temperatures although the results were again higher than those obtained using glacial acetic acid without mercuric chloride. The presence of mercuric chloride improved the actual titrations as they could be performed more rapidly with fewer unsteady deflections prior to the endpoint. This resulted in sharper endpoints.

With the exception of glacial acetic acid alone at room temperature, the best experimental conditions for the titration of unsaturates were low temperature, the presence of mercuric chloride, and glacial acetic acid containing 20 per cent carbon tetrachloride as the solvent. Several other unsaturates were titrated using these conditions and the results are found in Table XIII.

There was a definite improvement in the results with 1-octene and 2-octene. No change was obtained with vinyl acetate and 3-heptene yielded poorer results.

TABLE XIII

COMPARISON OF TITRATION RESULTS

Unsaturate	Ml.	N	g. Unsaturate		Per Cent Unsaturate		
	ROCl	ROCl	Taken	Found		*	**
1-Octene	28.20	0.1013	0.1515	0.1603	105.8	123.1	98.1
2-Octene	28.20	0.1013	0.1746	0.1603	91.8	94.4	90.0
3-Heptene	34.70	0.1012	0.1914	0.1724	90.1	89.0	86.0
Vinyl acetate	43.40	0.1004	0.1914	0.1876	98.0	97.9	95.6

*In glacial acetic acid alone
**By bromination method

H. Miscellaneous Oxidations

1. Sodium Oxalate

The reaction of tert-butyl hypochlorite with excess sodium oxalate as a means of standardization has been discussed previously. The use of tert-butyl hypochlorite for the determination of sodium oxalate was studied also. As with previous work it was necessary to use 80 per cent acetic acid as a solvent.

The direct titration of sodium oxalate using tert-butyl hypochlorite as a source of chlorine was too slow to be practical. When the usual titration procedure was used, the addition of hypochlorite solution caused a large current which decreased very slowly indicating a slow reaction. Therefore, indirect methods were investigated in which an excess of the hypochlorite was present.

To determine if an indirect method would be feasible, the following rate study was performed.

Twenty-five ml. aliquots of tert-butyl hypochlorite solution were added to 250 ml. iodine flasks containing 0.067 g. (1 meq.) of sodium oxalate dissolved in 20 ml. of water and 55 ml. of glacial acetic acid. The flasks were stoppered and allowed to stand for varying lengths of time with occasional shaking. Then 100 ml. of 3 per cent aqueous potassium iodide solution was added to each flask and the iodine titrated immediately with thiosulfate solution to a starch endpoint. A blank with the oxalate omitted was run to determine the number of meq. of hypochlorite present in the 25 ml. aliquot. The number of meq. of hypochlorite consumed for each sample was calculated from the equation:

$$\# \text{ meq.} = [\text{Ml. } Na_2S_2O_3 \text{ (blank)} - \text{Ml. } Na_2S_2O_3 \text{ (sample)}] \times N\ Na_2S_2O_3$$

The results of this study are found in Table XIV.

TABLE XIV

REACTION RATE OF SODIUM OXALATE WITH EXCESS tert-BUTYL HYPOCHLORITE

Reaction Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Found
	Blank	Sample	Difference	
1	22.76	13.61	9.15	0.902
5	22.91	12.79	10.12	0.998
15	22.94	12.80	10.14	1.000
30	22.91	12.75	10.16	1.002
45	22.94	12.79	10.15	1.001
60	23.07	12.90	10.17	1.003
90	22.94	12.76	10.18	1.004

*Normality = 0.0986

It appeared that the reaction of tert-butyl hypochlorite with sodium oxalate was quantitative with a reaction time of 15 minutes. The high results obtained with longer reaction times pointed to the possible decomposition of chlorine. The chlorine would be formed by the reaction of the excess tert-butyl hypochlorite with the chloride formed as one of the products in the oxidation of sodium oxalate.

To determine if the high results were due to this decomposition, a rate study was performed on the decomposition of chlorine in 80 per cent acetic acid. In the previous rate study there were approximately 1 meq. of excess tert-butyl hypochlorite and 1 meq. of chloride. Therefore, the rate study was carried out using their quantities of reagents. The procedure used in this rate study was identical with the previous reaction rate study except for the quantities of reagents used.

Ten ml. aliquots of hypochlorite solution were added to 250 ml. iodine flasks containing 0.0585 g. (1 meq.) of sodium chloride dissolved in 20 ml. of water and 70 ml. of glacial acetic acid. The flasks were stoppered and allowed to stand for varying lengths of time with occasional shaking. Then 100 ml. of 3 per cent aqueous potassium iodide solution was added to each flask and the iodine titrated immediately with standard thiosulfate solution using starch indicator. For the blank a 10 ml. aliquot of hypochlorite solution was added to 90 ml. of glacial acetic acid containing no sodium chloride. The data are contained in Table XV. The percent decomposition has been calculated on the basis of the volumes of thiosulfate solution used in the titrations.

$$\text{Percent decomposition} = \frac{\text{Ml. } Na_2S_2O_3\text{(blank)} - \text{Ml. } Na_2S_2O_3\text{(sample)}}{\text{Ml. } Na_2S_2O_3\text{(blank)}} \times 100.$$

TABLE XV

DECOMPOSITION OF CHLORINE IN EIGHTY PER CENT ACETIC ACID

Reaction Time, Min.	Ml. $Na_2S_2O_3$* Blank	Ml. $Na_2S_2O_3$* Sample	Difference	Per Cent Decomposition
1	8.52	8.52	0.00	0.00
5	8.52	8.52	0.00	0.00
15	8.52	8.52	0.00	0.00
30	8.52	8.51	0.01	0.12
45	8.52	8.50	0.02	0.23
60	8.52	8.49	0.03	0.35
90	8.52	8.48	0.04	0.47

*Normality = 0.0986

The data in Table XV verifies the decomposition of chlorine in 80 per cent acetic acid and accounts for the high results obtained. If the reaction time were limited to 15 minutes, the decomposition would be negligible.

Several samples of sodium oxalate were determined using this procedure with a 15 minute reaction time. The results are found in Table XVI.

The results in Table XVI indicate that this method is applicable for the determination of sodium oxalate.

TABLE XVI

DETERMINATION OF SODIUM OXALATE WITH EXCESS tert-BUTYL HYPOCHLORITE

Ml. $Na_2S_2O_3$*			g. $Na_2C_2O_4$	
Blank	Sample	Difference	Taken	Found
22.82	11.98	10.84	0.0716	0.0716
22.82	11.52	11.30	0.0746	0.0747
22.82	13.19	9.63	0.0635	0.0636
22.82	5.91	16.91	0.1119	0.1117
22.82	10.61	12.21	0.0807	0.0807

*Normality = 0.0986

2. Benzaldehyde

The reaction of tert-butyl hypochlorite with benzaldehyde and substituted benzaldehydes has been studied by Ginsburg (15). He found that excellent yields of the corresponding acids or acid chlorides were obtained. The reactions were rapid at room temperature in 90 per cent acetic acid, tert-butyl alcohol, and carbon tetrachloride.

The high yields and moderate conditions reported by Ginsburg prompted an investigation into the analytical possibilities of the reaction of tert-butyl hypochlorite with benzaldehyde.

The direct titration of benzaldehyde using tert-butyl hypochlorite as a source of chlorine was too slow. When the usual titration procedure was used the addition of hypochlorite solution caused a large current flow which remained steady indicating a very slow reaction.

Indirect methods were tried using both excess hypochlorite and excess chlorine. Samples of benzaldehyde were added to 250 ml. iodine flasks containing 25 ml. aliquots of tert-butyl hypochlorite solution. One flask had 0.5 g. of lithium chloride added. The flasks were allowed to stand one hour with frequent shaking and then the excess hypochlorite or chlorine was determined in the usual manner. The results of this experiment are contained in Table XVII.

TABLE XVII

OXIDATION OF BENZALDEHYDE

Sample	Ml. $Na_2S_2O_3$*			g. Benzaldehyde		Per Cent Found
	Blank	Sample	Difference	Taken	Found	
Hypochlorite	21.73	21.52	0.21	0.0750	0.0011	1.46
Chlorine	21.73	21.52	0.21	0.1037	0.0011	1.06

*Normality = 0.0986

The results indicated that the oxidation of benzaldehyde was very slight under the experimental conditions and no further investigations were made with benzaldehyde.

3. Phenol

Ginsburg (16) and Clark (7) have investigated the reaction of tert-butyl hypochlorite with phenols. The reactions were very rapid at room temperature resulting in excellent yields of the corresponding ortho-substituted chlorophenols. With a large excess of hypochlorite various polysubstituted chlorophenols were obtained.

Samples of phenol were titrated amperometrically in glacial acetic acid using tert-butyl hypochlorite as a source of chlorine. The first additions of hypochlorite solution caused small deflections which returned rapidly to zero. Subsequent additions of reagent caused larger deflections that returned to zero slower. Finally a point was reached in the titration where the deflection was almost steady. This occurred beyond the volume of reagent corresponding to monosubstitution of phenol. It was apparent from this that chlorine was too reactive to be used in the determination of phenol.

The amperometric titration of phenol with hypochlorite solution alone was investigated using several solvents. When the reagent was added to a solution of phenol in glacial acetic acid no deflection was observed. With sodium acetate present the addition of reagent did cause a deflection which decreased slowly indicating a slow reaction. The same behavior was observed with acetic acid containing 5 per cent water and no salts. The titrations using both of these solvents were too slow for practical use. In acetic acid containing 10 per cent water and no salts the titration was more rapid and additions of reagent caused deflections which returned to zero in one or two minutes. Near the endpoint corresponding to monosubstitution the deflections became larger and returned slower. Past the equivalence point the deflections decreased very slowly indicating that further substitution was taking place. However, the titration could be performed by reading the galvanometer deflection at a predetermined time after each addition and then plotting the observed deflections versus ml. of reagent. Figure VII

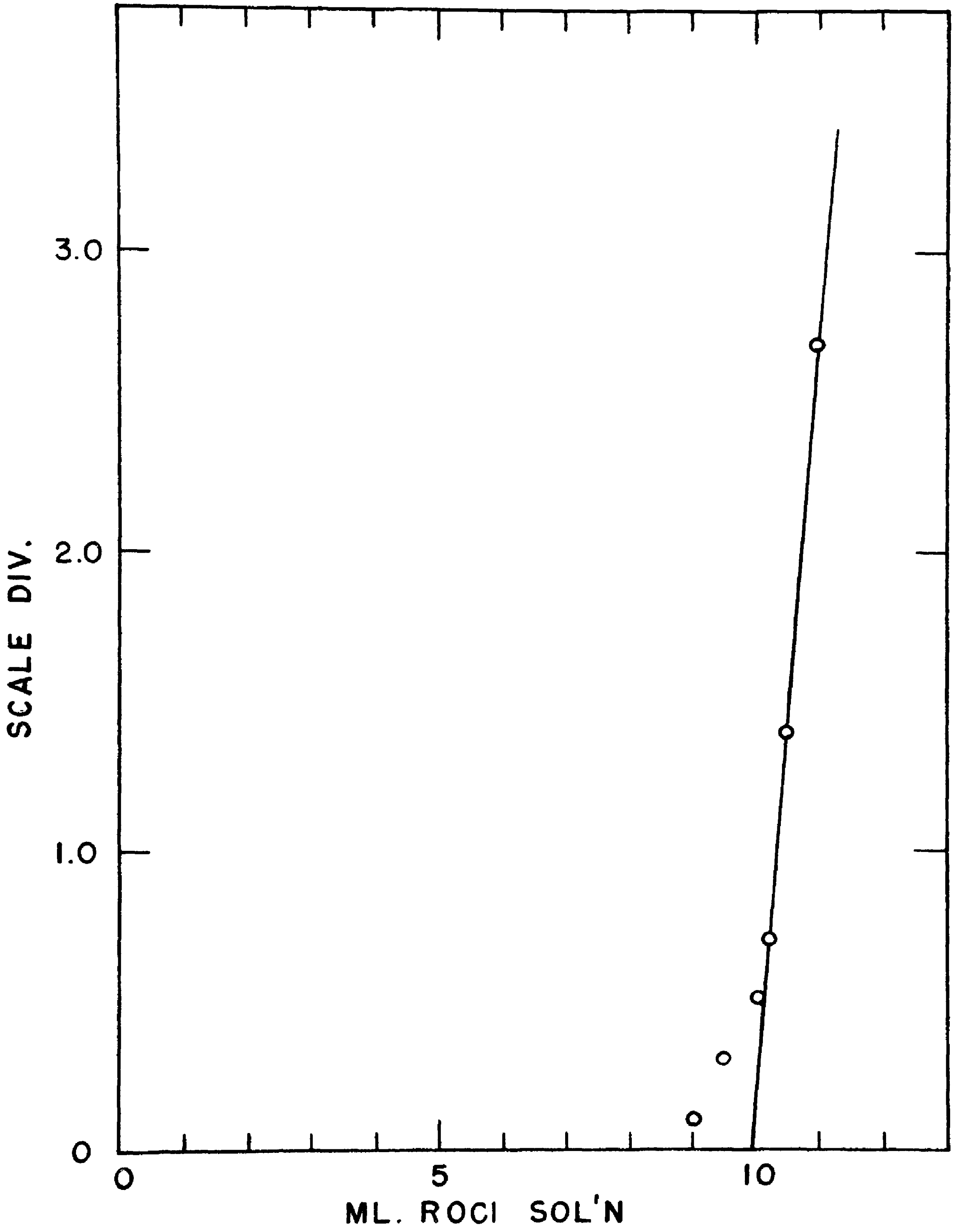


FIGURE VII. AMPEROMETRIC TITRATION OF PHENOL WITH TERT-BUTYL HYPOCHLORITE is a plot of titration results using a 90 seconds interval after each addition before reading the deflection. The data for this Figure are found in the Appendix. The volume of reagent was determined by drawing a line through the deflection points beyond the endpoint and finding its intercept on the reagent axis.

Table XVII contains the results of several titrations performed using this procedure.

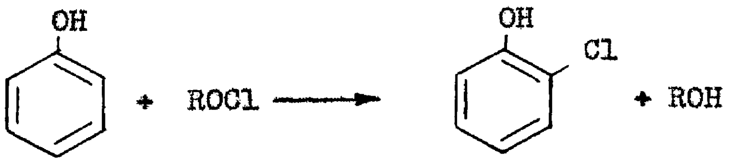
TABLE XVIII

AMPEROMETRIC TITRATION RESULTS OF PHENOL

Ml. ROCl	N_{ROCl}	g. Phenol Taken	g. Phenol Found	Per Cent*
7.75	0.0993	0.0360	0.0362	100.6
5.52	0.0993	0.0258	0.0258	100.0
9.95	0.0890	0.0421	0.0417	97.1**

*99.8% by bromination
**From Figure VII

It appeared from the results obtained that the reaction proceeded according to the equation:



This titration procedure was not practical with larger samples of phenol because of the time involved in performing the titration. This procedure also failed when sodium acetate was added to the 90 per cent acetic acid solvent. In this case the titration resembled that in which the hypochlorite was used as a source of chlorine. Indirect methods for the determination of phenol were not investigated because phenol reacts with iodine thus interfering with the general method.

4. Hydroquinone

The reaction of tert-butyl hypochlorite with hydroquinone has not been investigated previously. It was studied in this work primarily because the hydroquinone-quinone system is one of the few organic redox systems available for investigation (9).

When hydroquinone was titrated amperometrically using only glacial acetic acid as a solvent, no deflection was observed with applied potentials up to 3 volts. A rapid oxidation did take place, however, as the solution turned yellow when the reagent was added. Hydroquinone could be titrated in glacial acetic acid using tert-butyl hypochlorite as a source of chlorine. Figure VIII illustrates the resulting titration curve. The data for this figure are found in the Appendix. The titration curve in Figure VIII is characteristic for redox systems in which both the oxidized and reduced forms govern the current flow (33).

Throughout most of the titration, equilibrium was attained rapidly. When the endpoint was approached additions of reagent caused large deflections which returned slowly to steady values. The endpoint should have been indicated by a large steady deflection caused by the formation of chlorine. However, an endpoint could not be obtained due to the unsteady deflections which returned to zero.

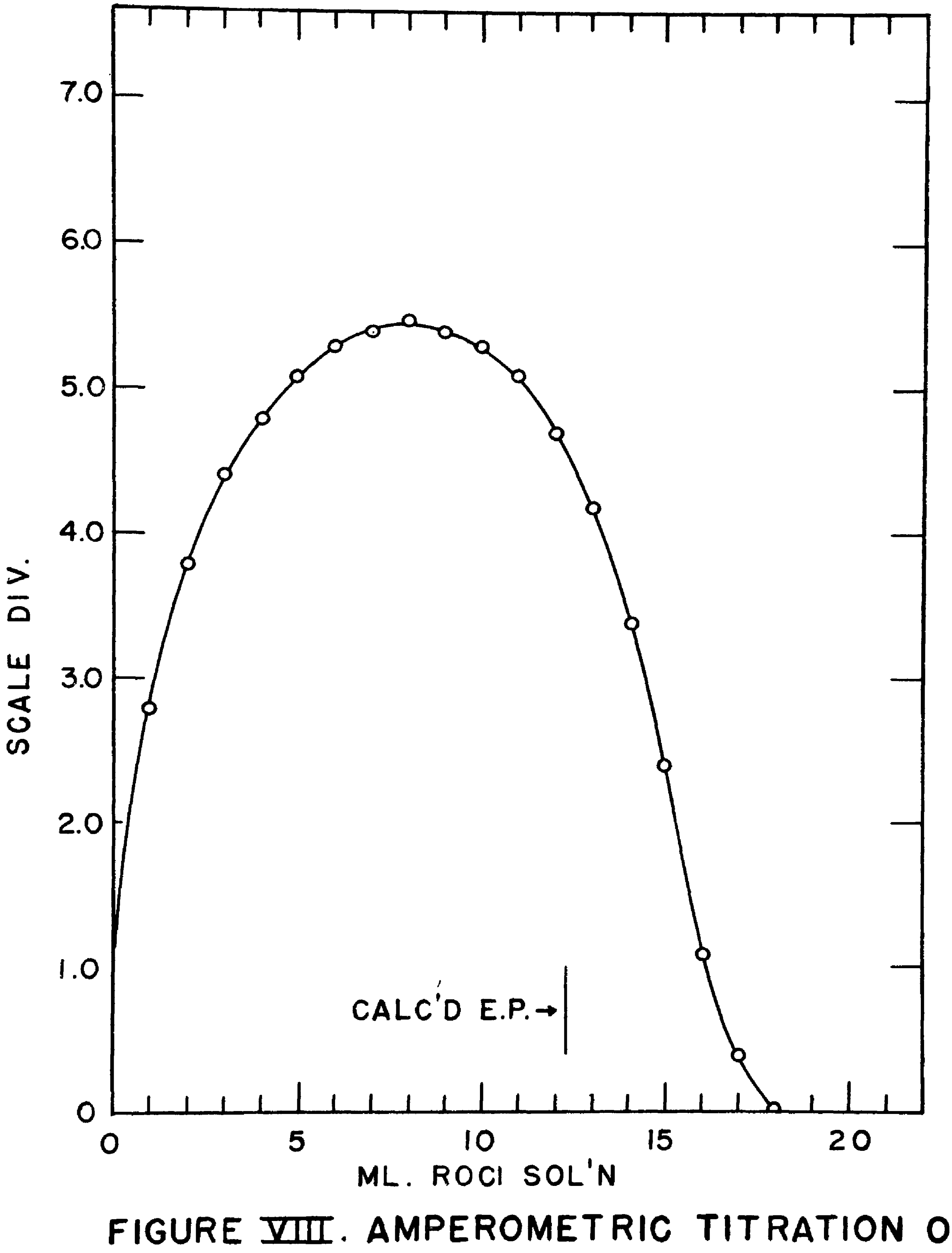
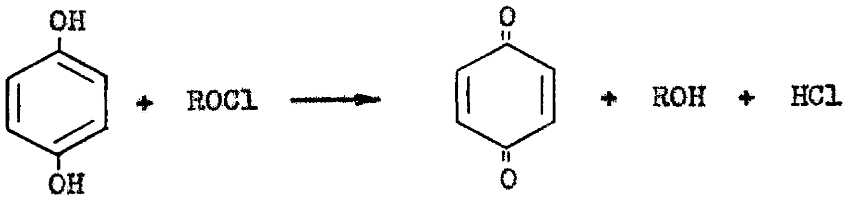


FIGURE VIII. AMPEROMETRIC TITRATION OF HYDROQUINONE WITH TERT-BUTYL HYPOCHLORITE AS A SOURCE OF CHLORINE

The titration was not stoichiometric and a large excess of reagent was used. Similar titration results were obtained when hydroquinone was titrated in acetic acid containing 10 per cent water.

Hydroquinone was also titrated using glacial acetic acid containing sodium acetate. The addition of the sample to the solvent caused a large deflection that remained steady. This was not observed in the titration using lithium chloride but it was observed using 90 per cent acetic acid as a solvent. In the latter case the titration curve was similar to that obtained using lithium chloride. When hydroquinone was titrated in glacial acetic acid containing sodium acetate, a different titration curve was obtained. This is illustrated in Figure IX. The data are found in the Appendix. Equilibrium was reached rapidly throughout the titration and the endpoint was steady. The titration results were still high but much better than in previous titrations using other solvents.

The oxidation of hydroquinone by tert-butyl hypochlorite can be represented by the following equation:



A similar equation could be written for the reaction in which the hypochlorite is used as a source of chlorine. It is probable that some chlorine was formed during the titration of hydroquinone with tert-butyl hypochlorite alone and that the high results were due to the

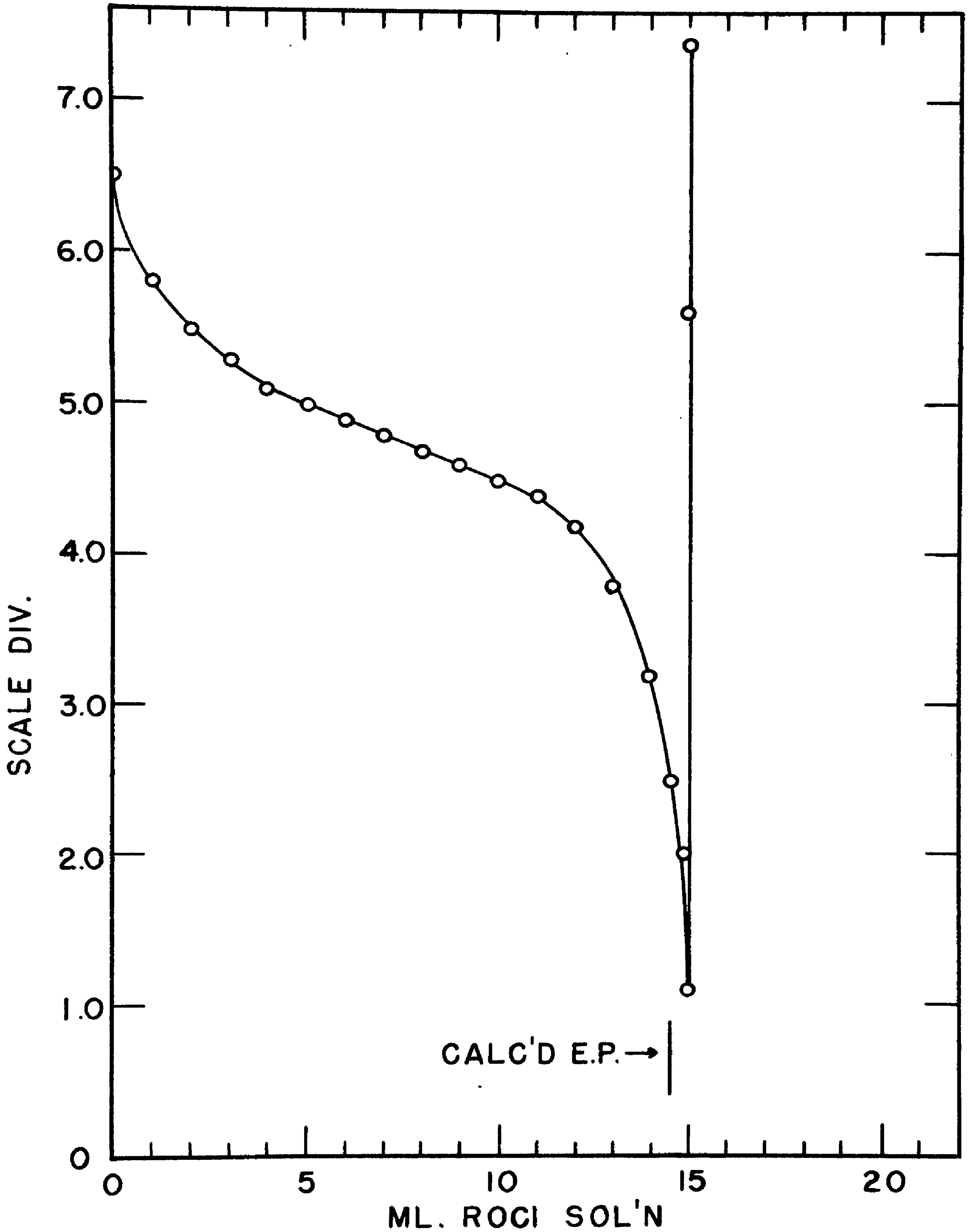


FIGURE IX. AMPEROMETRIC TITRATION OF HYDROQUINONE WITH TERT-BUTYL HYPOCHLORITE chlorination of quinone. The much larger error observed with titrations in which the hypochlorite was used as a source of chlorine supports the fact that it was chlorine and not hypochlorite that was responsible for the high results.

The explanation for the titration curve obtained using glacial acetic acid containing sodium acetate was not apparent.

IV SUMMARY

IV SUMMARY

Tertiary butyl hypochlorite can be used as an analytical reagent for the determination of a limited number of organic compounds in non-aqueous solvents.

Solutions of tert-butyl hypochlorite in glacial acetic acid are reasonably stable and decompose at the rate of 0.1 per cent a day. The solutions can be standardized easily and rapidly.

The indirect determination of unsaturation was not possible using an excess of tert-butyl hypochlorite solution either alone or as a source of chlorine. Reaction rate studies with several unsaturates established that with tert-butyl hypochlorite the reactions were too slow and an excess of reagent was consumed. Reaction rate studies using an excess of tert-butyl hypochlorite as a source of chlorine established that the addition was rapid but that an excess of chlorine was consumed.

The direct titration of unsaturates with tert-butyl hypochlorite was not possible due to slow reaction rates. Using the hypochlorite as a source of chlorine it was possible to titrate unsaturates amperometrically or potentiometrically. Good results were obtained with styrene and fair results were obtained with divinylbenzene when glacial acetic acid was used as the solvent. With all other unsaturates tested the results were either high due to substitution or low due to slow reaction rates.

Efforts to improve the titration results were unsuccessful. High results were obtained with titrations at low temperatures using acetic acid containing 10 per cent water or 20 per cent carbon tetrachloride as solvents. The use of mercuric chloride as a catalyst also failed to improve the results.

Sodium oxalate could be determined accurately in 80 per cent acetic acid using an excess of tert-butyl hypochlorite and determining the excess. Phenol could be titrated amperometrically in 90 per cent acetic acid but the determination was limited to small samples and was not very accurate. Hydroquinone could be titrated also but an excess of reagent was used yielding high results. Benzaldehyde could not be determined directly or indirectly because the reaction was too slow.

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LITERATURE CITED

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APPENDIX

DATA FOR FIGURE I

Stability of tert-Butyl Hypochlorite in Glacial Acetic Acid

Time, Days	Ml. $Na_2S_2O_3$*	N_{ROCl}	Per Cent ROCl Remaining
0	24.60	0.0993	100.0
1	24.54	0.0991	99.8
2	24.49	0.0987	99.6
7	24.37	0.0984	99.1
14	24.26	0.0979	98.6
21	24.08	0.0972	97.9
28	23.94	0.0966	97.3

*Normality = 0.1008

Stability of tert-Butyl Hypochlorite in Ninety Per Cent Acetic Acid

Time, Days	Ml. $Na_2S_2O_3$*	N_{ROCl}	Per Cent ROCl Remaining
0	26.63	0.1075	100.0
1	26.54	0.1071	99.6
2	26.49	0.1069	99.4
7	26.15	0.1056	98.2
14	25.84	0.1043	97.0
21	25.59	0.1033	96.1
28	25.37	0.1021	95.0

*Normality = 0.1008

Stability of tert-Butyl Hypochlorite in Anhydrous Acetic Acid

Time, Days	Ml. $Na_2S_2O_3$*	N_{ROCl}	Per Cent ROCl Remaining
0	23.73	0.0949	100.0
1	23.63	0.0945	99.6
3	23.51	0.0941	99.1
7	23.17	0.0927	97.6
14	22.54	0.0902	95.0
21	22.05	0.0882	92.9
28	21.52	0.0861	90.7

*Normality = 0.0999

DATA FOR FIGURE II

Stability of tert-Butyl Hypochlorite in Anhydrous Acetic Acid Freed from Reducing Substances

Time, Days	Ml. $Na_2S_2O_3$*	N_{ROCl}	Per Cent ROCl Remaining
0	23.51	0.0941	100.0
1	23.48	0.0939	99.9
2	23.48	0.0939	99.9
7	23.35	0.0934	99.3
14	23.17	0.0927	98.6
21	23.01	0.0921	97.9
28	22.83	0.0913	97.1

*Normality = 0.0999

Stability of tert-Butyl Hypochlorite in Glacial Acetic Acid Freed from Reducing Substances

Time, Days	Ml. $Na_2S_2O_3$*	N_{ROCl}	Per Cent ROCl Remaining
0	24.16	0.0967	100.0
1	24.15	0.0966	100.0
2	24.14	0.0966	99.9
7	24.06	0.0963	99.6
14	23.90	0.0956	98.9
21	23.73	0.0949	98.2
28	23.57	0.0943	97.6

*Normality = 0.0999

DATA FOR FIGURE III

Galvanometer Deflection with Various Chloride Ion Concentrations in Glacial Acetic Acid

Applied Potential, Volts	Galvanometer deflection, scale divisions					
	gl. HAc	Sat'd KCl	Sat'd NaCl	0.01 N LiCl	0.05 N LiCl	0.1 N LiCl
0.0	-6.0	-5.8	-4.6	-6.0	-5.1	-5.7
0.01	—	—	—	-4.9	1.4	1.6
0.02	—	—	—	-2.4	3.8	12.2
0.03	—	—	—	-1.2	7.6	20.1
0.04	—	—	—	1.0	12.3	30.4
0.05	—	—	—	2.2	16.9	40.8
0.06	—	—	—	4.8	20.4	48.2
0.07	—	—	—	6.4	24.0	58.2
0.08	—	—	—	8.2	28.4	66.0
0.09	—	—	—	10.2	33.0	76.0
0.10	-5.6	6.1	2.2	11.9	36.4	86.0
0.2	-5.2	18.0	9.1	30.6	81.0	88x2
0.3	-5.0	29.6	16.7	49.8	62x2	57x5
0.4	-4.8	41.5	23.5	68.8	87x2	78x5
0.5	-4.7	53.2	31.0	88.2	46x5	52x10
0.6	-4.1	65.4	38.5	53x2	57x5	64x10
0.7	-3.9	77.8	46.2	63x2	68x5	76x10
0.8	-3.8	90.3	54.5	73x2	80x5	89x10
0.9	-3.6	51x2	62.5	82x2	91x5	52x20
1.0	-3.3	57x2	71.0	93x2	53x10	59x20

*0.10 ml. of 0.1 N hypochlorite solution added to 100 ml. of solvent.

DATA FOR FIGURE IV

Reaction Rate of Vinyl Acetate with tert-Butyl Hypochlorite

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
2	23.66	20.69	2.97	0.301	0.142
9	23.66	20.80	2.86	0.290	0.139
15	23.66	20.56	3.10	0.314	0.147
30	23.66	19.58	4.08	0.413	0.184
45	23.66	19.18	4.48	0.454	0.202
60	23.66	18.04	5.62	0.569	0.264
120	23.66	16.69	6.97	0.706	0.362
180	23.66	15.23	8.43	0.854	0.508
240	23.66	14.04	9.62	0.975	0.671

*Normality = 0.1013

**1.406 meq. found by bromination

Reaction Rate of Styrene with tert-Butyl Hypochlorite

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
2	28.38	23.40	4.98	0.505	0.343
9	28.38	21.61	6.77	0.686	0.466
15	28.38	20.89	7.49	0.759	0.516
23	28.38	19.42	8.96	0.908	0.617
33	28.38	18.46	9.92	1.005	0.683
45	28.30	16.97	11.33	1.148	0.780
60	28.30	16.16	12.14	1.230	0.836
90	28.30	14.65	13.65	1.383	0.939
120	28.30	13.81	14.49	1.468	0.997
180	28.35	12.65	15.70	1.590	1.081
240	28.35	11.94	16.41	1.662	1.129
300	28.35	11.91	16.44	1.665	1.131

*Normality = 0.1013

**1.472 meq. found by bromination

Reaction Rate of Cyclohexene with tert-Butyl Hypochlorite

Time, Min.	Ml. $Na_2S_2O_3$[*]			Meq. Unsaturate Found[**]	R
	Blank	Sample	Difference		
1	21.97	11.43	10.54	1.053	0.727
7	21.97	7.73	14.24	1.423	0.982
15	21.97	7.55	14.42	1.441	0.995
30	21.97	7.30	14.67	1.466	1.012
45	21.97	7.03	14.94	1.496	1.033
60	21.97	6.77	15.20	1.519	1.048
120	21.97	5.84	16.13	1.611	1.112
180	21.97	5.54	16.43	1.641	1.133
240	21.97	5.54	16.43	1.641	1.133
300	21.97	5.54	16.43	1.641	1.133
360	21.97	5.52	16.45	1.643	1.135

[*] Normality = 0.0999

[**] 1.449 meq. found by bromination

Reaction Rate of 2-Octene with tert-Butyl Hypochlorite

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
1	28.51	17.60	10.91	1.105	0.809
2	28.55	16.95	11.60	1.175	0.860
9	28.55	16.76	11.79	1.194	0.874
15	28.55	16.36	12.19	1.235	0.904
20	28.55	16.08	12.47	1.263	0.924
27	28.55	15.95	12.60	1.276	0.934
45	28.51	15.27	13.24	1.341	0.982
60	28.51	14.86	13.65	1.383	1.012
90	28.51	14.38	14.13	1.431	1.047
120	28.51	14.26	14.25	1.444	1.056
240	28.51	14.18	14.33	1.452	1.062

*Normality = 0.1013
**1.367 meq. found by bromination

Reaction Rate of Mesityl Oxide with tert-Butyl Hypochlorite

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
1	22.42	19.39	3.03	0.305	0.322
7	22.42	15.84	6.56	0.659	0.696
15	22.42	14.59	7.83	0.787	0.831
30	22.42	13.14	9.28	0.933	0.985
45	22.42	12.10	10.32	1.037	1.096
60	22.42	11.52	10.90	1.096	1.157
120	22.42	9.02	13.40	1.347	1.422
180	22.42	6.91	15.51	1.559	1.647
240	22.42	5.64	16.78	1.686	1.781
300	22.42	4.67	17.75	1.784	1.884
360	22.42	4.58	17.84	1.798	1.894

*Normality = 0.1005

**0.947 meq. found by bromination

Reaction Rate of Divinylbenzene with tert-Butyl Hypochlorite

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
1	22.71	19.19	3.52	0.354	0.301
7	22.71	17.48	5.23	0.526	0.442
15	22.71	16.82	5.89	0.592	0.503
30	22.71	15.18	7.53	0.757	0.644
45	22.71	14.34	8.37	0.841	0.715
60	22.71	13.55	9.16	0.921	0.783
120	22.71	11.64	11.07	1.113	0.946
180	22.71	10.12	12.59	1.265	1.076
240	22.71	9.29	13.42	1.349	1.147
300	22.71	8.66	14.05	1.412	1.201
360	22.71	8.53	14.18	1.425	1.212

*Normality = 0.1005

**1.176 meq. found by bromination

Reaction Rate of Vinylacetic Acid with tert-Butyl Hypochlorite

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
1	22.53	20.49	2.04	0.205	0.155
7	22.53	18.88	3.65	0.367	0.278
15	22.53	17.79	4.74	0.476	0.361
30	22.53	16.22	6.31	0.634	0.481
45	22.53	14.94	7.59	0.763	0.578
60	22.53	13.80	8.73	0.877	0.665
120	22.53	10.42	12.11	1.217	0.922
180	22.53	8.56	13.97	1.404	1.064
240	22.53	8.40	14.13	1.420	1.076
300	22.53	8.38	14.15	1.422	1.078
360	22.53	8.36	14.17	1.424	1.079

*Normality = 0.1005
**1.320 meq. found by bromination

DATA FOR FIGURE V

Reaction Rate of Vinyl Acetate with Chlorine

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
1	22.48	8.46	14.02	1.401	1.024
7	22.48	8.26	14.22	1.421	1.038
15	22.48	8.15	14.33	1.432	1.046
30	22.48	8.15	14.33	1.432	1.046
45	22.48	8.14	14.34	1.433	1.047
60	22.48	8.08	14.40	1.439	1.051
120	22.48	8.02	14.46	1.445	1.056
180	22.48	8.09	14.39	1.438	1.050
240	22.48	7.87	14.61	1.460	1.066
300	22.48	7.82	14.66	1.465	1.070
360	22.48	7.78	14.70	1.469	1.073

*Normality = 0.0999
**1.367 meq. found by bromination

Reaction Rate of Styrene with Chlorine

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
2	23.66	6.88	16.78	1.700	1.154
7	23.66	5.90	17.76	1.799	1.222
15	23.66	5.53	18.13	1.837	1.247
30	23.66	5.54	18.12	1.836	1.246
60	23.66	5.57	18.09	1.833	1.244
180	23.66	5.46	18.20	1.844	1.252

*Normality = 0.1013

**1.473 meq. found by bromination

Reaction Rate of Cyclohexene with Chlorine

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
1	23.21	5.17	18.04	1.802	1.245
7	23.21	4.68	18.53	1.851	1.279
15	23.21	4.72	18.49	1.847	1.276
30	23.21	4.68	18.53	1.851	1.279
45	23.21	4.65	18.56	1.854	1.281
60	23.21	4.57	18.64	1.862	1.286
120	23.21	4.51	18.70	1.868	1.290
180	23.21	4.50	18.71	1.869	1.291
240	23.21	4.44	18.77	1.875	1.295
300	23.21	4.37	18.84	1.882	1.300
360	23.21	4.34	18.87	1.885	1.302

*Normality = 0.0999

**1.448 meq. found by bromination

Reaction Rate of 2-Octene with Chlorine

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
1	22.04	7.72	14.32	1.431	1.060
7	22.04	7.64	14.40	1.439	1.066
15	22.04	7.71	14.33	1.432	1.061
30	22.04	7.72	14.32	1.431	1.060
45	22.04	7.55	14.49	1.448	1.073
60	22.04	7.49	14.55	1.454	1.077
120	22.04	7.35	14.69	1.468	1.087
180	22.04	7.24	14.80	1.479	1.096
240	22.04	7.27	14.77	1.476	1.093
300	22.04	7.25	14.79	1.478	1.095
360	22.04	7.29	14.74	1.473	1.091

*Normality = 0.0999

**1.350 meq. found by bromination

Reaction Rate of Mesityl Oxide with Chlorine

Time, Min.	Ml. $Na_2S_2O_3$[*]			Meq. Unsaturate Found[**]	R
	Blank	Sample	Difference		
1	23.16	8.74	14.42	1.440	1.523
7	23.16	8.36	14.80	1.479	1.563
15	23.16	8.05	15.11	1.510	1.596
30	23.16	7.87	15.29	1.528	1.615
45	23.16	7.36	15.80	1.578	1.668
60	23.16	7.03	16.13	1.611	1.703
120	23.16	6.34	16.82	1.679	1.775
180	23.16	5.92	17.24	1.722	1.821
240	23.16	5.50	17.66	1.764	1.865
300	23.16	4.94	18.22	1.820	1.924
360	23.16	5.03	18.13	1.811	1.914

[*] Normality = 0.0999

[**] 0.946 meq. found by bromination

Reaction Rate of Divinylbenzene with Chlorine

Time, Min.	Ml. $Na_2S_2O_3$* Blank	Sample	Difference	Meq. Unsaturate Found**	R
1	23.26	10.00	13.26	1.325	1.125
7	23.26	9.23	14.03	1.402	1.190
15	23.26	8.56	14.70	1.469	1.247
30	23.26	8.26	15.00	1.499	1.272
45	23.26	8.05	15.20	1.519	1.289
60	23.26	7.95	15.31	1.530	1.299
120	23.26	7.79	15.47	1.546	1.312
180	23.26	7.61	15.65	1.563	1.327
240	23.26	7.62	15.64	1.563	1.327
300	23.26	7.63	15.63	1.562	1.326
360	23.26	7.63	15.63	1.562	1.326

*Normality = 0.0999
**1.178 meq. found by bromination

Reaction Rate of Vinylacetic Acid with Chlorine

Time, Min.	Ml. $Na_2S_2O_3$*			Meq. Unsaturate Found**	R
	Blank	Sample	Difference		
1	22.85	9.87	12.98	1.296	0.975
7	22.85	9.57	13.28	1.327	0.998
15	22.85	9.47	13.38	1.337	1.005
30	22.85	9.40	13.45	1.344	1.011
45	22.85	9.35	13.50	1.349	1.014
60	22.85	9.30	13.55	1.354	1.018
120	22.85	9.22	13.63	1.362	1.024
180	22.85	9.16	13.69	1.368	1.029
240	22.85	9.19	13.66	1.365	1.026
300	22.85	9.19	13.66	1.365	1.026
360	22.85	9.14	13.71	1.370	1.030

*Normality = 0.0999
**1.130 meq. found by bromination

DATA FOR FIGURE VI

Potentiometric Titration of Styrene with tert-Butyl Hypochlorite as a Source of Chlorine

Ml. ROCl*	E.M.F.(mv.)	Ml. ROCl	E.M.F.(mv.)
0.0	627	26.0	736
2.0	647	27.0	741
4.0	663	28.0	721
6.0	672	29.0	728
8.0	680	29.5	738
10.0	688	30.0	748
12.0	714	30.4	757
14.0	734	30.6	764
16.0	740	30.8	915
18.0	729	30.9	975
20.0	698	31.3	994
22.0	716	33.0	1007
24.0	726	35.0	1013
		37.0	1017

*Normality = 0.1033

DATA FOR FIGURE VII

Amperometric Titration of Phenol with tert-Butyl Hypochlorite

Ml. ROCl*	Galv. Defl., Scale Div.	Ml. ROCl	Galv. Defl., Scale Div.
0.0	0.0	7.0	0.0
1.0	0.0	8.0	0.0
2.0	0.0	9.0	0.1
3.0	0.0	9.5	0.3
4.0	0.0	10.0	0.5
5.0	0.0	10.2	0.7
6.0	0.0	10.5	1.4
		11.0	2.7

*Normality = 0.0890
Sample weight = 0.0421
Calculated endpoint = 10.03 ml.

DATA FOR FIGURE VIII

Amperometric Titration of Hydroquinone with tert-Butyl Hypochlorite as a Source of Chlorine

Ml. ROCl*	Galv. Defl., Scale Div.	Ml. ROCl	Galv. Defl., Scale Div.
0.0	0.0	10.0	5.3
1.0	2.8	11.0	5.1
2.0	3.8	12.0	4.7
3.0	4.4	13.0	4.2
4.0	4.8	14.0	3.4
5.0	5.1	15.0	2.4
6.0	5.3	16.0	1.1
7.0	5.4	17.0	0.2
8.0	5.5	18.0	0.0
9.0	5.4		

*Normality = 0.0880
Sample weight = 0.0603 g.
Calculated endpoint = 12.40 ml.

DATA FOR FIGURE IX

Amperometric Titration of Hydroquinone with tert-Butyl Hypochlorite

Ml. ROCl*	Galv. Defl., Scale Div.	Ml. ROCl	Galv. Defl., Scale Div.
0.0	6.5	10.0	4.5
1.0	5.8	11.0	4.4
2.0	5.5	12.0	4.2
3.0	5.3	13.0	3.8
4.0	5.1	14.0	3.2
5.0	5.0	14.5	2.5
6.0	4.9	14.8	2.0
7.0	4.8	14.9	1.1
8.0	4.7	14.93	5.6
9.0	4.6	14.97	7.4

*Normality = 0.0839
Sample weight = 0.0667
Calculated endpoint = 14.51 ml.