from the data of Latimer[13] is 1.05×10^{-18}, and in 4 M bromide solution 0.3% of 10^{-5} M cupric ion solution is in the cuprous state. The true extent of reduction of cupric ion is probably even greater because of still more extensive complexing of the cuprous ion. Since the *p*-nitro group favors the Sandmeyer reaction with cuprous chloride greatly[14] and since reactions with bromide are faster than those with chloride, as shown by competition experiments,[15] this Sandmeyer reaction should be very fast at 75°, and might well be important even at 10^{-5} M total copper.

An alternative mechanism to the nucleophilic attack of bromide ion on carbon is the kinetically indistinguishable series

$$ArN_2^+ + Br^- \rightleftarrows Ar—N=N—Br \qquad (15)$$

$$ArN_2Br \longrightarrow ArBr + N_2 \qquad (16)$$

with (15) rapid and reversible, and (16) rate determining. Reactions analogous to (15) have often been written, and the small alteration of the ultraviolet absorption spectrum of *p*-nitrobenzenediazonium ion in solutions of high bromide ion concentrations may be due to the presence of covalent diazobromides.[16] There are, however, no well-established analogies to reaction (16), and there is no justification for the acceptance of this mechanism in preference to the straightforward attack of bromide ion on carbon. It is possible that the tarry materials are partly derived from the free-radical scission of the covalent diazobromide of reaction (15).

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(13) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 53, 169, 170, 171.

(14) W. A. Cowdrey and D. S. Davies, *J. Chem. Soc.*, S48 (1949).

(15) H. H. Hodgson, *Chem. Revs.*, **40**, 251 (1947).

(16) Unpublished work of J. J. Cole, formerly of this Laboratory.

HOUSTON, TEXAS RECEIVED JUNE 2, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Kinetics and Stereochemistry of the Decomposition of Secondary Alkyl Chlorosulfites[1]

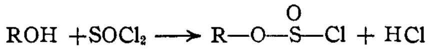
BY EDWARD S. LEWIS AND CHARLES E. BOOZER

The thermal decompositions of some secondary alkyl chlorosulfites have been studied kinetically and stereochemically with the aim of elucidating the mechanism of the formation of alkyl halides from alcohols and thionyl chloride. In dilute solution the decompositions of 2-butyl, 2-pentyl and 2-octyl chlorosulfites in dioxane are first-order reactions, yielding olefin and alkyl chloride as the principal products. The chloride has the same configuration as the alcohol from which it was derived and is only slightly racemized. When the chlorosulfite is decomposed in "isoöctane" solution or in the absence of solvent, the chloride has the opposite configuration from the alcohol.

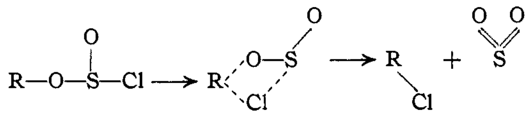
Introduction

The mechanism of nucleophilic displacement reactions has been extensively studied, but much experimental evidence is lacking concerning the cases in which the product has the same stereochemical configuration as the starting material. These cases can be classified in two groups: the first contains all the cases where the stereochemical result is determined by a neighboring group effect,[2] and the second contains the remaining examples in which no participation of a neighboring group can be considered.

Some of the reactions of thionyl chloride with alcohols belong in this latter group; for example, α-phenylethanol, cholestanol, methylcyclohexylcarbinol[3,4] and various closely related compounds react under suitable conditions to give a chloride of unaltered configuration. Hughes, Ingold and co-workers[5] have proposed a mechanism for this reaction involving the intermediate formation of a chlorosulfite[6] followed by loss of sulfur dioxide from the chlorosulfite and simultaneous formation of the carbon–chlorine bond at the point where the oxygen had previously been attached, presumably by way of a cyclic transition state



$$ROH + SOCl_2 \longrightarrow R—O—\overset{O}{S}—Cl + HCl$$



They call this the S_Ni reaction, and believe that it applies in essence to all nucleophilic displacement reactions resulting in retention of configuration not otherwise explained.

Two experimentally verifiable conditions are required by this mechanism: first, that a chlorosulfite results from the reaction of thionyl chloride and the alcohol, and, second, that this chlorosulfite decomposes by a unimolecular reaction to give a chloride with retention of configuration. It has never been shown that these conditions are met. No chlorosulfites have been prepared of any of the alcohols which give retention of configuration in the reactions with thionyl chloride, and none of the many chlorosulfites which have been prepared have given rise to chlorides of the same configuration on decomposition. No kinetic measurements on chlorosulfite decompositions have shed light on the order of this reaction. Nevertheless, the mechanism of Hughes and Ingold[5] has experimental foundation in the parallel work on the reactions of the chlorocarbonates, in which the analogous conditions have both been met.[7] It therefore seemed

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(1) From the Masters Thesis of C. E. Boozer, The Rice Institute, May, 1951.

(2) S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2780 (1942).

(3) J. Kenyon, A. G. Lipscomb and H. Phillips, *J. Chem. Soc.*, 415 (1930).

(4) P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **75**, 587 (1927).

(5) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1196 (1937).

(6) The English workers refer to these esters as chlorosulfinates. We prefer the term chlorosulfite because it carries no implication of a carbon–sulfur bond.

(7) A. H. J. Houssa and H. Phillips, *J. Chem. Soc.*, 108, 1232 (1932).

possible to meet them in at least some cases in the thionyl chloride system, and we selected first cases in which preparation of chlorosulfites was known to be possible.

Experimental

Materials.—The chlorosulfites were prepared by adding a solution of the alcohol in petroleum ether over a period of two hours to a stirred solution of excess thionyl chloride in petroleum ether at −20°. At the end of this addition most of the resulting hydrogen chloride was removed under vacuum. After allowing the solution to stand at room temperature for several hours, the petroleum ether and excess thionyl chloride were removed at room temperature with the water pump, and the residue was vacuum distilled. This procedure differs only slightly from that of Gerrard.[8] There was appreciable decomposition in this distillation, and in case of the octyl compound it was sometimes omitted, since the product before distillation was usually quite pure. Products of this decomposition were collected in a cold trap, and the alkyl chloride recovered from this trap is the material elsewhere described as the product of decomposition without solvent.

The boiling points of the chlorosulfites were: for 2-butyl, 47.0° at 10 mm.; for 2-pentyl, 37–38° at 2.4 mm.; and for 2-octyl 63–64° at 0.18 mm. The butyl compound was analyzed by hydrolysis in alkali, and conventional analyses for sulfur dioxide and chloride were applied to the resulting solution. *Anal.* Calcd. for $C_4H_9SO_2Cl$: SO_2, 40.8; Cl, 22.8. Found: SO_2, 40.0; Cl, 22.6. The other two were characterized by their ultraviolet adsorption spectra which were indistinguishable from that of the butyl compound, and by the near quantitative yield of sulfur dioxide on decomposition.

When 2-butanol $[\alpha]^{25}\text{D}$ −12.5° was used, the chlorosulfite had the opposite sign of rotation: $[\alpha]^{25}\text{D}$ +7.6°, *c* 8.4 in isoöctane and $[\alpha]^{25}\text{D}$ +10.7, *c* 18 in dioxane.

All the chlorosulfites decomposed fairly rapidly in the pure state, but could be kept virtually unaltered in solution in dioxane or isoöctane for a week or two.

The alcohols used were Eastman Kodak Co. white label grade, further purified by fractional distillation. Butanol-2 and octanol-2 were resolved by the methods of Pickard and Kenyon.[9] Our sample of *l*-butanol-2 was nearly optically pure, with $[\alpha]^{25}\text{D}$ −12.5°, instead of the value $[\alpha]^{20}\text{D}$ 13.87°, reported by these authors. The samples of octanol-2 used were less optically pure, having $[\alpha]^{20}\text{D}$ +5.12° and −6.2°. The highest rotation reported, on which the calculations of optical purity were based, is 9.9°.

Isoöctane was Phillips "pure" grade 2,2,4-trimethylpentane. It was used without further purification, and was a satisfactory spectrophotometric solvent.

Dioxane was purified by boiling with concentrated hydrochloric acid under reflux for 24 hours, followed by fractionation to remove water, further boiling under reflux with metallic sodium for 3 days, and finally fractionation through a three-foot column packed with glass helices. The fraction b.p. 101.0–101.1° was used, although impurity was still present, as shown by absorption in the ultraviolet region below 250 mμ. Greater transparency could be attained by further purification by fractional freezing, but this was usually omitted.

Kinetic Measurements.—A flask was fitted with a gas inlet tube, a thermometer and a small reflux condenser. The appropriate solvent was placed in the flask, and dry nitrogen was bubbled through the solvent. It passed out of the apparatus through the top of the condenser into water, which trapped soluble and volatile reaction products. A measured quantity of a solution of the chlorosulfite in the solvent was added and samples were withdrawn frequently. These samples were immediately cooled by dilution with isoöctane, and the concentration of chlorosulfite was determined by measuring the optical density of the diluted solutions at 234 mμ. Rate constants were determined from the slopes of straight lines resulting from a plot of the logarithm of optical density against time. Several of the rate constants were also determined from the slopes of straight lines resulting from a plot of the logarithm of the change in concentration in a given time interval against time, according to Guggenheim.[10] Both methods gave essentially the same results, but the latter was especially useful when minor side reactions produced absorbing by-products. In early work, the reaction flask was cleaned with chromic acid cleaning solution, then rinsed with water and dried. On several occasions first-order plots gave curved lines, and two of these cases gave good straight lines when the reciprocal of the concentration was plotted against time. In subsequent work the cleaning was extended by adding an ammonia rinse, followed by a second water rinse before drying; all reactions since this cleaning method was adopted were well fitted only by first-order equations.

Titration of hydrogen chloride and of sulfur dioxide trapped by water from the nitrogen stream from the reaction vessel gave an indication of reaction rate, but the rate of collection of gases at this point was not equal to the rate of formation of these gases, because they were not immediately liberated from solution. Both evolution of sulfur dioxide and hydrogen chloride were first-order as measured by this method, but the data appears to be neither very significant, nor reproducible. However, over-all yields of sulfur dioxide and hydrogen chloride were accurately measured by this method.

The stream of nitrogen did remove sulfur dioxide rapidly enough to prevent interference with the spectrophotometric determinations. However, the evaporative cooling lowered the temperature by as much as 2° below the thermostat temperature. The temperatures reported are those in the reaction flask, but they could not be read very accurately, and much of the error in rate constants may have arisen from this source. The control of temperature in any one run was probably good to about 0.1°, and since the energy of activation of the reaction is only 18 kcal./mole, this variation does not cause much difficulty.

Product Analysis.—The reactions were allowed to proceed in the flask used for the kinetic runs, or a similar one cleaned in the same way. About 10–25 g. of chlorosulfite was used instead of about 50 mg. of material used for most of the kinetic runs. After sufficient time for completion of the reaction, the solution was fractionally distilled through a three-foot column packed with glass helices. Fractions not consisting largely of solvent were refractionated to give fairly pure olefins and alkyl halides. The olefin from 2-pentyl chlorosulfite boiled at 37–38° and was therefore practically exclusively pentene-2. Since the boiling point of 2-chloropentane is only four degrees below that of dioxane, this separation was accomplished by washing dioxane out of the sample with water. The run using active 2-butyl chlorosulfite gave amounts of 2-chlorobutane too small to obtain in a pure state with the available equipment. Rotations were therefore taken on solutions of 2-chlorobutane in isoöctane and dioxane. All optical rotations were measured with sodium D light in a 2-decimeter tube using an O.C. Rudolf precision polarimeter, and are accurate to at least 0.01°.

Discussion of Results

In dioxane solution the decomposition of 2-butyl, 2-pentyl and 2-octyl chlorosulfites followed a first-order course out to at least 80% completion. In isoöctane solution the reaction was much slower and was not always followed as far, but the reaction was still apparently first-order. The difference in rate of the reactions for the different chlorosulfites in dioxane was experimentally undetectable. The reactions were followed spectrophotometrically, taking advantage of an intense absorption of the chlorosulfites at 234 mμ not shared by the likely contaminants. The spectrum of 2-butyl chlorosulfite together with those of the corresponding sulfite, thionyl chloride, and sulfur dioxide is shown in Fig. 1. Table I shows the first-order rate constants under various conditions in both dioxane and isoöctane.

On several early occasions the course of the reaction in dioxane was poorly fitted by a first order equation, but fitted a second-order equation well.

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[8] W. Gerrard, *J. Chem. Soc.*, 218 (1940).

[9] R. H. Pickard and J. Kenyon, *ibid.*, **99**, 45 (1911).

[10] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

TABLE I

RATE CONSTANTS FOR THE DECOMPOSITION OF ALKYL CHLOROSULFITES

Chlorosulfite	Solvent	Temp., °C.	$k \times 10^4$, sec.$^{-1}$
2-Pentyl	Dioxane	72.5	4.17
2-Pentyl	Dioxane	73.0	4.44
2-Pentyl	Dioxane	99.8	60.0
2-Pentyl	Dioxane	99.0	54.4
2-Pentyl	Dioxane	99.6	56.3
2-Butyl	Dioxane	73.0	4.22
2-Octyl	Dioxane	98.5	61.6
2-Pentyl	Isoöctane	100.5	0.17
2-Pentyl	Isoöctane	101.3	0.20

These experiments have not been reproduced and may have resulted from an improperly cleaned reaction vessel.

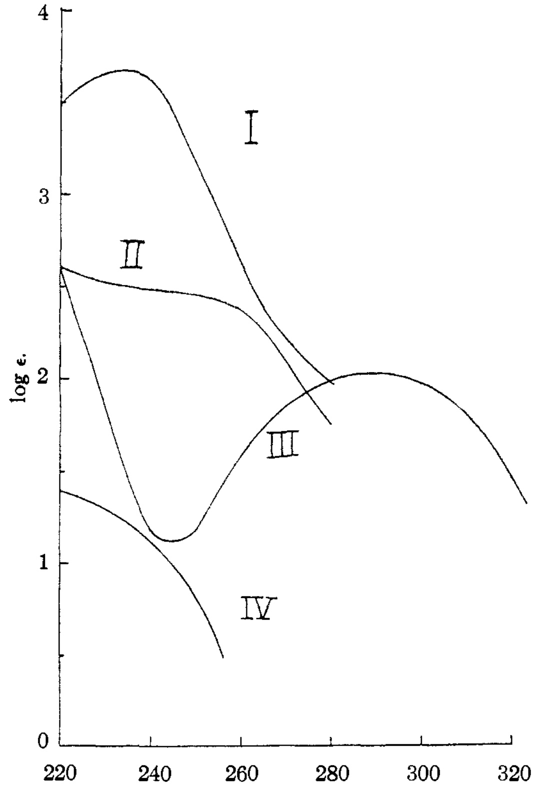

Fig. 1.—Absorption spectra in isoöctane: I, C_4H_4OSOCl; II, $SOCl_2$; III, SO_2; IV, $(C_4H_9O)_2SO$. Curve II is 0.88 unit too low.

Table II shows the yields of alkyl chloride and olefin in the three cases, determined by isolation of the product, except for butene. The yield of butene was estimated from the yield of hydrogen chloride presumably produced simultaneously. We have no explanation of the greater yield of olefin from the butyl compound when decomposed in dioxane than from the other two.

TABLE II

YIELDS OF PRODUCTS FROM CHLOROSULFITE DECOMPOSITIONS AT 100°

Chlorosulfite	Solvent	RCl, %	Olefin, %
2-Octyl	Dioxane	50	35
2-Pentyl	Dioxane	40	25
2-Butyl	Dioxane	40	60
2-Octyl	Isoöctane	80	10
2-Butyl	Isoöctane	60	

It is likely that both the reaction to give olefin and the one giving the chloride are first-order, otherwise the combination could hardly have been first-order, when the reactions are comparable in extent. Experimentally the evolution of hydrogen chloride from the octyl compound followed a first-order course; the observed rate constant at 97.5° was 6.5×10^{-4} sec.$^{-1}$. This was determined by titration of chloride in the gases swept from the solution by nitrogen and as the rate of evolution of hydrogen chloride from its solution in dioxane was not studied, the rate of formation need not be the same as the rate observed. It is evident, however, that the hydrogen chloride cannot arise from the 2-chlorobutane.

TABLE III

OPTICAL RESULTS OF DECOMPOSITIONS OF CHLOROSULFITES FROM OPTICALLY ACTIVE ALCOHOLS[a]

Alcohol	Solvent	$[\alpha]^{25}_D$ of chloride	Optical purity, %
l-Butanol-2	Dioxane	− 0.805	..
l-Butanol-2	Isoöctane	+ 0.994	..
l-Butanol-2	None	+ 3.3	11
l-Octanol-2	None	+30.6	85
d-Octanol-2	Dioxane	+30.4	84
d-Octanol-2	Isoöctane	−15.3	43
d-Octanol-2	None	−27.2	76

[a] The first two entries are observed rotations in dioxane and isoöctane solution, respectively. The remainder are specific rotations calculated on the basis of optically pure alcohol.

Table III shows the optical results when active alcohols were used as starting materials. The values given are specific rotations calculated on the basis of optically pure starting alcohol except for the two entries where only impure chloride was obtained, and the rotations are observed values in a two-decimeter tube at an unknown concentration in the solvent used for the reaction. The optical purity column is based on estimates of the maximum values of the rotations. These are 31.4° for 2-chlorobutane and 35.8° for 2-chlorooöctane,[5,11] but these values are not critical in the argument.

It has been shown previously that in these two cases the alcohol and chloride of the same configuration have the same sign of rotation,[5,7,12] It is also reasonable to suppose that the reaction to form the chlorosulfite from the alcohol does not affect the asymmetric center, and it has been shown that the hydrolysis of the chlorosulfite regenerates the original alcohol with unchanged activity.[13] Therefore, it can be said that the reaction in dioxane solution is a reaction with retention of configuration throughout, and the reactions in isoöctane and in the absence of solvent proceed with inversion (accompanied by more or less racemization).

The kinetics showed that a first-order reaction occurs both in dioxane and isoöctane, but the re-

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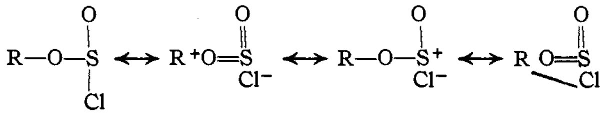
(11) R. L. Letsinger, L. G. Maury and R. L. Burwell, Jr., THIS JOURNAL, **73**, 2373 (1951).

(12) J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

(13) W. Gerrard, *ibid.*, 85 (1944).

action is much slower in the latter solvent. While it is not possible to say that the reaction to give retention of configuration is absent in isoöctane, it is certainly much slower in this solvent than in dioxane. If the reaction does indeed go by the mechanism of Hughes and Ingold,[5] then the reduction in rate on changing to the less polar solvent (unless due to a specific solvent effect) implies that the transition state has a higher dipole moment than the normal chlorosulfite, and contributions to the transition state from structures II and III



$$\mathrm{R{-}O{-}\overset{\overset{O}{|}}{\underset{\underset{Cl}{|}}{S}}} \longleftrightarrow \mathrm{R^{+}O{=}\overset{\overset{O}{\|}}{\underset{Cl^{-}}{S}}} \longleftrightarrow \mathrm{R{-}O{-}\overset{\overset{O}{|}}{\underset{Cl^{-}}{S^{+}}}} \longleftrightarrow \mathrm{R\;O{=}\overset{\overset{O}{\|}}{S}{\diagdown}Cl}$$

I II III IV

as well as I and IV should be considered. This view is consistent with the very rapid reaction of thionyl chloride with phenylcarbinols,[13] because of the further stabilization of structure II, and also with the apparent instability of chlorosulfites from tertiary alcohols, indicated by failures to obtain these compounds. We have not shown rigorously that the reaction is independent of impurities in the dioxane or isoöctane, but the careful purification of the dioxane coupled with reproducibility of rates using different batches indicates that the effect of impurities in this notoriously impure solvent is not large; the isoöctane was probably quite pure but our investigations were more limited than in dioxane, and we believe that the reproducibility of rates in this solvent may have been due partly to a reproducibility of experimental conditions, and may be influenced by factors such as surface or impurities.

In order to make sure that the reaction of *d*-2-octyl chlorosulfite in dioxane was not one of the anomalous second-order reactions previously noted, the disappearance of chlorosulfite was followed spectrophotometrically although the concentration was twenty to fifty times that used in the other kinetic runs. The similarity of rate constant as well as the observed first-order kinetics under these conditions confirms the unimolecular nature of the reaction in this solvent.

It can therefore be concluded that there is a first-order reaction of secondary alkyl chlorosulfites which goes with retention of configuration, but that this will occur only in favorable environments. In other environments inversion may predominate.

HOUSTON, TEXAS RECEIVED JULY 2, 1951

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

The Development of Crystallinity in Polychlorotrifluoroethylene

BY FRASER P. PRICE

Polychlorotrifluoroethylene on cooling from above its first-order transition point (205–210°) develops crystalline regions in the form of spherulites. The development of this crystallinity is accompanied by an increase in dielectric constant and loss, tensile strength, opacity and density. Spherulites appear only on cooling from above the melting point. Their growth rates are linear with time and depend on the growing temperature and the viscosity of the melt. Between 175–190° the number of spherulites does not increase with time and is determined by the highest temperature above the melting point to which the sheet was heated. Below 175° the number increases with time. These facts indicate heterogeneous nucleation above 175° and heterogeneous plus homogeneous nucleation below 175°. A sheet quenched to room temperature from above its melting point develops evidence of crystallinity only very slowly when heated to 150–190°. This is due to the very slow coalescing of microcrystalline regions to produce the gross effects of crystallinity. Density measurements have been made from 15–230° and thermal expansion coefficients calculated. It is proposed that spherulite growth is a consequence of the long chain structure of high polymers and that all crystallizable polymers will show this growth under the correct conditions.

Introduction

Crystalline regions in an amorphous polymer matrix are known to have profound effects on the mechanical, electrical and optical properties of the polymer mass.[1] This paper describes an investigation of the development of crystallinity in polychlorotrifluoroethylene and some of the effects of this crystallinity on the electrical, mechanical and thermodynamic properties of the polymer.

Microscopic study of a sheet of polychlorotrifluoroethylene cooling slowly from 250° reveals the growing spherulitic structures shown in Fig. 1. While similar type structures have been observed in polyethylene,[2] polyurethan[3] and polyamides,[4] it is believed that this is the first time that such well-defined structures in an organic high polymer have been observed and their behavior described.

Materials and Procedures

Polychlorotrifluoroethylene was obtained from the M. W. Kellogg Company under the trade name, KelF. Samples of two grades, KelF NST 300 (KelF Hi) and KelF NST 240 (KelF Lo), were used throughout this study. The former had a specific viscosity in a 1% solution at 140° in dichlorobenzyltrifluoride of 2.24, the latter had a specific viscosity under the same conditions of 0.86. The 15-mil sheets of polymer used in this investigation were obtained by pressing the white granular powder at 260° and 1000 p.s.i.

This polymer has a transition point analogous to a melting point, which it will henceforth be called, at about 210°. This is evidenced by a change from a bright to a completely dark field when observed between crossed Nicols under the microscope and by abrupt changes in electrical and thermodynamic properties.

The apparatus used to prepare samples for microscopic examination consisted of a tube oven, with its axis vertical, mounted over a silicone oil-bath. The oven temperature, T_1, constant to ±1°, was above the polymer melting point, while the bath temperature, T_2, was below the melting point and was held constant to ±0.2°. The polymer sheet,

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(1) T. Alfrey, Jr., "Mechanical Behavior of High Polymers," Interscience Publishers, Inc., New York, N. Y., 1948; R. E. Reinhardt, *Ind. Eng. Chem.*, **35**, 422 (1943).

(2) C. W. Bunn and T. C. Alcock, *Trans. Faraday Soc.*, **41**, 317 (1945).

(3) Von E. Jenckel and H. Wilsing, *Z. Elektrochem.*, **53**, 4 (1949).

(4) R. Gabler, *Naturwissenschaften*, **35**, 284 (1948).