The infrared spectrum (chloroform) indicates the absence of alcohol bands. The n.m.r. spectrum (carbon tetrachloride) contains two sharp peaks at τ 6.81 and 5.56, and an unresolved multiplet centered at about τ 3.0. The relative integrated intensities are 1.9, 1.0 and 7.8, respectively.[14]

Reduction of 3,3-dibenzylphthalide with a 1:1 molar mixture of lithium aluminum hydride–aluminum chloride in ether[7] led to a mixture of 1,1-dibenzylphthalan (6) and dibenzyl-*o*-(hydroxymethylphenyl)carbinol (5). A 0.73-g. sample of this mixture was converted by treatment with zinc dust and hydrochloric acid to 0.20 g. of 6 (m.p. 87.5–89.0°) whose infrared spectrum (chloroform) was identical with that of the phthalan obtained above.

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(14) This spectrum was measured at the University of New Hampshire with a Varian Model A-60 instrument.

Mercaptan Oxidations. VII. Oxidative Desulfurization of Benzyl Mercaptan, Benzyl Disulfide, and Related Species

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The base-catalyzed oxidation of benzyl mercaptan and benzyl disulfide was studied in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) at 23.5° and 80° in the presence of potassium *t*-butoxide, sodium methoxide, and potassium hydroxide. Oxidative desulfurization of the mercaptan and disulfide to benzoic acid was the predominant reaction observed in the presence of the alkoxide bases. The reaction path proposed involves the formation of peroxide ions which can rearrange to alkoxide ions that are unstable and decompose to benzaldehyde and α-toluenethiosulfinate ions ($C_6H_5CH_2S(O)S^-$). Apparently, the aldehyde and acid salt are oxidized rapidly to benzoic acid. The latter is substantiated by the fact that potassium α-toluenesulfonate could be oxidized rapidly to benzoic acid in quantitative yields. In the presence of potassium hydroxide, the main oxidation product was potassium α-toluenesulfonate. This is due apparently to the decreased basicity and increased sulfur nucleophilicity of the hydroxide ion. The oxidation of α,α′-dimercapto-*p*-xylene also was investigated. This compound was oxidized to terephthalic acid in 30 to 84% yield depending on the particular reaction conditions employed.

Previous studies in these laboratories have established that dipolar solvents markedly accelerate the base-catalyzed oxidation of mercaptans (thiols) by molecular oxygen.[1] If these reactions are allowed to proceed to completion, both alkyl and aryl mercaptans can be oxidized to their corresponding sulfonic acid salts.[2,3] The latter finding represents a new base-catalyzed oxidation reaction since the predominant product from the base-catalyzed oxidation of a mercaptan is usually the disulfide.[4] The present investigation is an extension of our previous studies on solvent effects in the base-catalyzed oxidation of sulfur compounds and is concerned with the oxidation of benzyl mercaptan, benzyl disulfide, and some related species. These compounds contain benzylic hydrogens which should be fairly acidic in a polar medium. Thus, it seemed worthwhile to determine if oxidation to the sulfonic acid or oxidative desulfurization to carboxylic acids would be the predominant course of reaction in mercaptans and disulfides of this general type.

Results

The base-catalyzed oxidation of benzyl mercaptan, benzyl disulfide, potassium α-toluenesulfonate, and α,α′-dimercapto-*p*-xylene has been studied at a constant oxygen partial pressure of one atmosphere at 23.5° and 80°. Reactions were carried out in dimethyl sulfoxide (DMSO, 80%)-*t*-butyl alcohol (20%)[5] using potassium hydroxide, sodium methoxide (NaOMe), and potassium *t*-butoxide (KO-*t*-Bu) as the bases. The ratio of base to reactant varied from 3 to 6 depending on the particular benzyl compound oxidized. Specific reaction conditions employed and product yields obtained under these conditions are summarized in Table I. In the presence of KO-*t*-Bu at 80°, benzyl mercaptan, benzyl disulfide, and potassium α-toluenesulfonate were converted to benzoic acid in 74 to 100 mole % yields. The mercaptan also formed benzyl disulfide and stilbene, the disulfide apparently being oxidized as it was formed. Stilbene was also a by-product of the disulfide oxidation. The initial rates of oxidation are shown in Fig. 1 for the system KO-*t*-Bu–DMSO–*t*-C_4H_9OH at 80°. All rates of oxygen consumption were extremely rapid. The acid salt consumed 2 moles oxygen/mole acid in 25 min. The mercaptan and disulfide were less reactive than the acid, consuming 0.75 and 0.45 mole oxygen/mole reactant, respectively, in 25 min. All rates of oxidation decreased in the latter stages of reaction since water and alcohols are formed, and the base is consumed by the acid products that are formed.

Under less vigorous conditions of oxidation (NaOMe at 23.5°) benzyl mercaptan and benzyl disulfide were still oxidized readily to benzoic acid, but the yield of disulfide from the mercaptan was increased by a factor of 2.5. Both reactions yielded a small quantity of stilbene. When the weak base, potassium hydroxide, was used, the mercaptan and disulfide yielded potassium α-toluenesulfonate as the main oxidation product at 23.5°. In the protic solvent methanol, oxidation of the mercaptan beyond the disulfide stage did not occur

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(1) T. J. Wallace, A. Schriesheim, and W. Bartok, *J. Org. Chem.*, **28**, 1311 (1963), and references therein.

(2) T. J. Wallace and A. Schriesheim, *Tetrahedron Letters*, 1131 (1963).

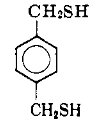
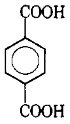
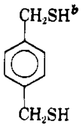
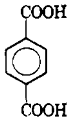
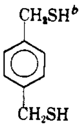
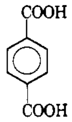
(3) T. J. Wallace and A. Schriesheim, paper to be submitted for publication.

(4) For a recent review of this area, see A. A. Oswald and T. J. Wallace, "The Anionic Oxidation of Mercaptans and the Co-Oxidation of Mercaptans with Olefins," Organic Sulfur Compounds, Vol. II, N. Kharasch, Ed., Pergamon Press, New York, N. Y., in press.

(5) This mixture has been employed as a solvent medium for the anionic oxidation of acidic hydrocarbons by Russell and co-workers [see Preprints, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 25, 1961].

TABLE I

SUMMARY OF BENZYL MERCAPTAN AND α,α'-DIMERCAPTO-*p*-XYLENE OXIDATION STUDIES IN DMSO-*t*-BUTYL ALCOHOL

Reactant (mole)	Base (mole)	Temp., °C.	Product	Yield, mole %[a]	% conversion of reactant	Time, hr.
$C_6H_5CH_2SH$	KO-*t*-Bu	80	$(C_6H_5CH_2)_2S_2$	10.0	100	23
(0.05)	(0.15)		C_6H_5COOH	85		
			$C_6H_5CH{=}CHC_6H_5$	3.4		
$(C_6H_5CH_2)_2S_2$	KO-*t*-Bu	80	C_6H_5COOH	70	90	18
(0.025)	(0.15)		$C_6H_5CH{=}CHC_6H_5$	18.4		
$C_6H_5CH_2SO_3K$	KO-*t*-Bu	80	C_6H_5COOH	~100	100	25
(0.05)	(0.15)					
$C_6H_5CH_2SH$	NaOMe	23.5	$(C_6H_5CH_2)_2S_2$	26.2	90	23
(0.05)	(0.15)		C_6H_5COOH	60.4		
			$C_6H_5CH{=}CHC_6H_5$	1.8		
$(C_6H_5CH_2)_2S_2$	NaOMe	23.5	C_6H_5COOH	90	99	28
(0.025)	(0.15)		$C_6H_5CH{=}CHC_6H_5$	3.0		
$C_6H_5CH_2SH$	KOH	23.5	$(C_6H_5CH_2)_2S_2$	8.0	92	14.5
(0.05)	(0.15)		C_6H_5COOH	29.5		
			$C_6H_5CH_2SO_3H$	50		
$(C_6H_5CH_2)_2S_2$	KOH	23.5	C_6H_5COOH	31	99	19
(0.025)	(0.15)		$C_6H_5CH_2SO_3H$	61		
			$C_6H_5CH{=}CHC_6H_5$	0.5		
 (.05)	KO-*t*-Bu (0.20)	80		84	100	29
 (0.025)	NaOMe (0.10)	23.5		84	99	23
 (0.025)	KOH (0.10)	23.5		30	71	21
$C_6H_5CH_2SH$	NaOMe[c]		$(C_6H_5CH_2)_2S_2$	84	90	23
(0.05)	(0.20)					

[a] Moles of product produced/theoretical moles × 100. [b] A polymeric disulfide of undetermined structure was produced also. [c] NaOMe–MeOH was employed as the base–solvent system.

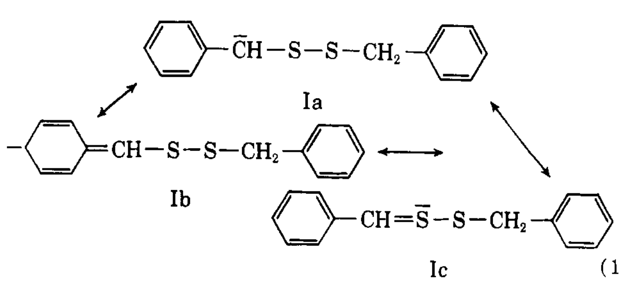
at room temperature and the disulfide showed no tendency to oxidize over a 20-hr. period.

The last phase of these oxidation studies were carried out with α,α'-dimercapto-*p*-xylene. This compound was oxidized rapidly under all conditions employed. As shown in Fig. 1, 2 moles oxygen/mole dimercaptan was consumed in 21 min. using potassium hydroxide in DMSO-*t*-C_4H_9OH at 23.5°. This is comparable to the rate observed with potassium benzyl sulfonate in the presence of KO-*t*-Bu at 80°. Terephthalic acid was the acidic product identified in all reactions, the yield varying from 30 to 84 mole % depending on the base and temperature used. Polymeric disulfides also were found, but no attempt to elucidate the structure of these disulfides or any other intermediates was made. Further, no attempt to determine the final fate of the sulfur moiety in any of these reactions was made.

Discussion

The results obtained in the present study indicate that benzyl mercaptan is initially oxidized to benzyl disulfide which, in the presence of excess base, is unstable and decomposes by several competing reaction paths to give ultimately benzoic acid and stilbene. Possible mechanistic paths by which these transformations proceed are of interest since they represent the first examples in which a mercaptan and disulfide of this general type are oxidatively desulfurized in the presence of base and oxygen at such a rapid rate.

The initial oxidation of the mercaptide ion ($C_6H_5CH_2S^-$) to the disulfide proceeds rapidly. In the presence of excess base, the resulting disulfide apparently undergoes α-proton abstraction to form a resonance-stabilized carbanion (Ia, b, and c). The resulting carbanion can rearrange to a 1,2-diphenylethyl mercaptide ion which in the presence of base is unstable and eliminates sulfide ion (S_2^{-2}) to give stilbene. This reaction previously was observed in the absence of oxygen with



(1)

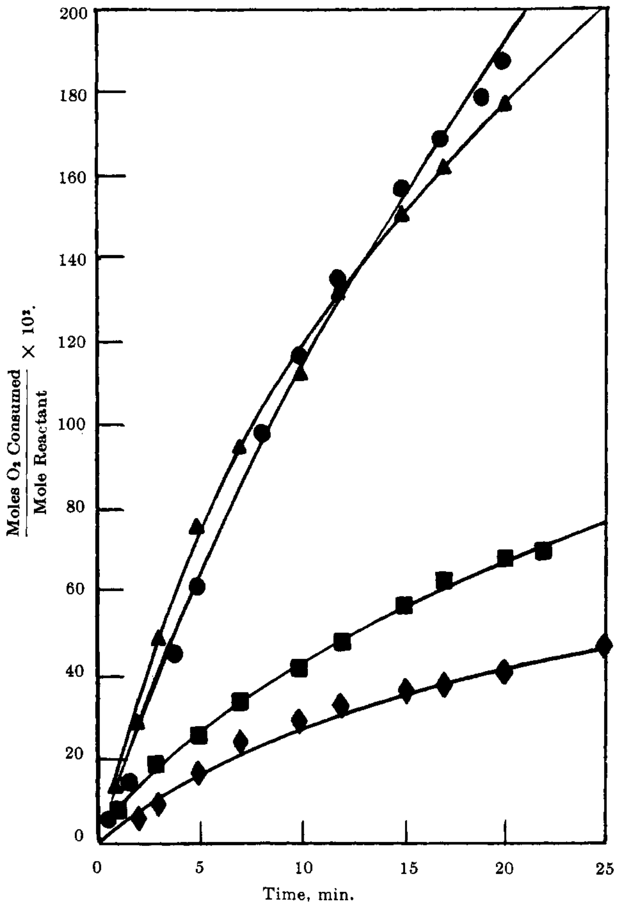
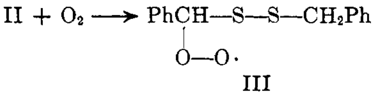


Fig. 1.—Rates of oxygen consumption for anionic oxidation in DMSO-t-C_4H_9OH: ●, $C_6H_5CH_2SO_3K$ (KO-t-Bu, 80°); ▲, p-$HSCH_2C_6H_4CH_2SH$ (KOH, 23.5); ■, $C_6H_5CH_2SH$ (KO-t-Bu, 80°); ◆, $(C_6H_5CH_2)_2S_2$ (KO-t-Bu, 80°).

several benzyl-type sulfur compounds.[6,7] Since oxygen is present in a large excess, it is not surprising that this reaction proceeds in low yield. Thus, the main reaction path involves oxidation of the α-carbanion. As shown in Table I, benzoic acid is formed in high yields in the presence of KO-t-Bu and NaOMe. Even at 23.5°, the yield of benzoic acid from benzyl mercaptan and benzyl disulfide varied from 60 to 90%. Thus, the intermediate products must be highly unstable in the presence of base and oxygen.

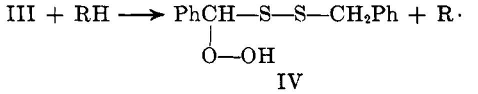
$$Ph\underset{-}{C}H—S—S—CH_2Ph + O_2 \longrightarrow PhCH—S—S—CH_2Ph + O_2 \quad (2)$$

II



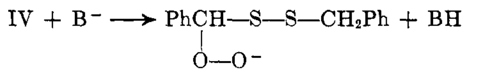
$$II + O_2 \longrightarrow Ph\underset{\displaystyle O—O\cdot}{\underset{|}{C}}H—S—S—CH_2Ph \quad (3)$$

III



$$III + RH \longrightarrow Ph\underset{\displaystyle O—OH}{\underset{|}{C}}H—S—S—CH_2Ph + R\cdot \quad (4)$$

IV

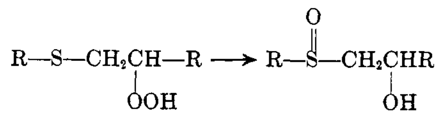


$$IV + B^- \longrightarrow Ph\underset{\displaystyle O—O^-}{\underset{|}{C}}H—S—S—CH_2Ph + BH \quad 5)$$

V

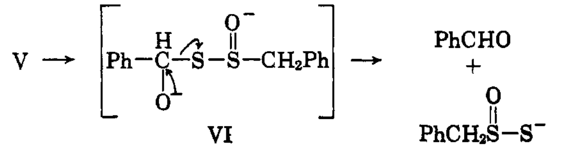
$$III + Ia \longrightarrow V + II \quad (6)$$

Intuitively, we feel that the carbanion is first oxidized to an unstable hydroperoxide ion (V) as shown. This species is analogous to the hydroperoxides formed during the co-oxidation of mercaptans with olefins. These intermediates are highly unstable and rearrange to β-hydroxy sulfoxides as shown.[4] In the present case,

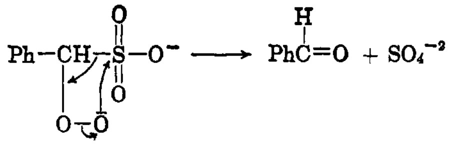


$$R—S—CH_2\underset{\displaystyle OOH}{\underset{|}{C}}H—R \longrightarrow R—\overset{\displaystyle O}{\overset{\|}{S}}—CH_2\underset{\displaystyle OH}{\underset{|}{C}}HR \quad (7)$$

a similar rearrangement of V would yield, presumably, an unstable alkoxide ion (VI) that could readily de-


(8)

compose to benzaldehyde and a thiosulfinate ion (C_6H_5-$CH_2S(O)S^-$). The aldehyde would form benzoic acid readily. The acid could oxidize further to the thiosulfonate ($C_6H_5CH_2SO_2S^-$) or undergo concommitant proton abstraction at the α-benzyl position. The thiosulfonate also would form the anion readily. Based on our results with the α-toluenesulfonate ion, both carbanions should oxidize readily to another unstable peroxide ion that eliminates the sulfur moiety and ultimately gives benzoic acid.


(9)

Initial electron transfer between the carbanion and oxygen (eq. 2) is most reasonable since detailed studies by Russell[8] on the base-catalyzed autoxidation of acidic hydrocarbons indicate that this reaction does occur. The proposed intermediacy of benzaldehyde in these reactions is also reasonable since benzaldehyde and benzyl alcohol are highly unstable under the present reaction conditions.[9] Based on the results of our recent elimination studies on aliphatic sulfones and sulfoxides,[10,11] instability of intermediate VI under the present reaction conditions also would be expected. Rate studies have established that sulfinate ion (RSO_2^-) elimination from isopropyl sulfone in KO-t-Bu–DMSO is so rapid that accurate rate measurements cannot be obtained even at room temperature.

In the presence of potassium hydroxide at 23.5° both the mercaptan and disulfide react rapidly, but this base alters the reaction path to some extent since potassium α-toluenesulfonate is the predominant product. Our previous studies on the oxidation of mercaptide ions to sulfonic acids indicated that hydroxide

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(6) T. J. Wallace, *et al.*, *Proc. Chem. Soc.*, 137 (1963).

(7) It also has been determined that $C_6H_5CH_2SH$ and $C_6H_5CH_2SO_3K$ do not α-eliminate in these base–solvent systems.

(8) For a discussion see G. A. Russell, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p. 107, *et seq.*

(9) In the present system and in DMF, we have found benzaldehyde and benzyl alcohol are rapidly autoxidized at room temperature to benzoic acid in the presence of KOH, NaOMe, and KO-t-Bu; this is also true for acetophenone, see ref. 5.

(10) T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2739 (1963).

(11) J. E. Hofmann, T. J. Wallace, and A. Schriesheim, *ibid.*, in press.

ion was highly nucleophilic toward the disulfide linkage.[2,12] Thus, in addition to the above possible reaction path, preferential displacement on the disulfide linkage to form the mercaptide ion and a sulfenate ion (RSO^-) must occur. The sulfenate ion would, of course, be unstable[12] and could either disproportionate to the disulfide and sulfonic acid or be oxidized directly by oxygen. Since potassium hydroxide is a relatively weak base, proton abstraction from the α-toluenesulfonate ion does not occur as readily as with the alkoxide bases, hence the decreased yield of benzoic acid in the presence of this base.

$$3\,PhCH_2SO^- \longrightarrow (PhCH_2)_2S_2 + PhCH_2SO_3^- \qquad (10)$$

$$PhCH_2SO^- \xrightarrow{O_2} PhCH_2SO_3^- \qquad (11)$$

The oxidation of α,α′-dimercapto-*p*-xylene to terephthalic acid undoubtedly occurs by the above paths. Formation of the monocarboxylic acid should facilitate further oxidation at the α′-position. Since the intermediates were complex and their structures were not determined, further discussion is not warranted. However, the results demonstrate the generality of these reactions with mercaptans of this type.

Experimental

Reagent.—Benzyl mercaptan (Aldrich Chemical Co.) was purified by distillation through an 18-in. silvered column equipped with a tantalum wire spiral (b.p. 90° at 5 mm.). α,α′-Dimercapto-*p*-xylene (Evans Chemetics) was obtained as the reagent grade material (98% pure) and used without further purification. Both mercaptans were stored under nitrogen and handled in a nitrogen drybox. Benzyl disulfide (m.p. 70°) was prepared from the reaction of benzyl mercaptan with iodine according to the procedure outlined in Vogel.[13] Potassium α-toluenesulfonate was prepared from the reaction of benzyl bromide with potassium sulfite according to the method of Fromm.[14] Potassium *t*-butoxide was obtained from the Mine Safety Appliance Co. as the sublimed material and stored in a nitrogen drybox.

Purification of Solvents.—*t*-Butyl alcohol (Matheson Coleman and Bell) and DMSO (Crown Zellerbach) were purified by distillation over Linde 13-X Molecular Sieves to remove any water that was present. The sieves were conditioned previously by calcination at 400° for 4 hr. All solvents were stored under a nitrogen atmosphere.

Oxidation Experiments.—All base–solvent systems were made up to the appropriate molarity under nitrogen in a heavy walled Pyrex flask equipped with a side arm. The reactant was added to the reaction flask, the flask was sealed under nitrogen, removed from the drybox, and transferred to the oxidation apparatus. Oxygen was stored in a polyethylene balloon under 1-atm. pressure and was passed through a wet-test meter, into a calcium chloride drying tower, through a water-cooled Friedrichs condenser, and into the reaction flask containing the reaction mixture. The system was flushed with oxygen through the flask side arm, the side arm was sealed, and an equilibrium pressure was established. The reaction was initiated by stirring at 1300 r.p.m. The volume of oxygen consumed as a function of time was determined from the wet-test meter which allows an estimation of the volume of gas consumed to within ±1 ml. With this method, a constant oxygen pressure of 1 atm. was maintained above the system. All reactions were allowed to proceed to completion. This oxidation technique has been described in greater detail elsewhere.[15]

Quantitative Determination of Reactants and Products.—Unchanged mercaptan was determined by potentiometric titration with standard silver nitrate solution. Unchanged disulfide or disulfide produced as an oxidation product was determined by reduction to the mercaptan in zinc–acetic acid and subsequent titration with silver nitrate. Blank samples containing mercaptan, disulfide, and a mixture of mercaptan and disulfide were subjected to these techniques, and the results indicated that the method was essentially quantitative (±1%). Analysis for the aromatic acids and stilbene was carried out according to the method of Pobiner, Wallace, and Hofmann.[16] Two methods can be employed. One involves an extraction–ion-exchange–infrared procedure and the other an extraction–ultraviolet procedure. Both rely on initial homogenization with water and subsequent extraction with cyclohexane to remove the starting material and nonacidic products. This removes any spectral interference during the determination of acidic products. The acidic products remain as their acid salts in the aqueous DMSO phase and are liberated subsequently by acidification with hydrochloric acid. If the acid is aromatic, it can be quantitatively determined directly by ultraviolet spectroscopy from standard curves. If the acidic material is aliphatic or presents a weak ultraviolet absorption, it is determined by the ion-exchange–infrared method. This involves treating the aqueous phase with Amberlite LA-2 anion-exchange resin. The free acid is extracted with carbon tetrachloride and quantitatively determined by infrared spectroscopy. These methods were accurate to within 95–99% for all products identified.

Other Methods of Identification.—In addition to the infrared and ultraviolet comparison to authentic samples, the products were isolated and identified by melting point at least once when separation was feasible. Thus, benzoic acid (m.p. 121–122°) and stilbene (m.p. 124°) were further substantiated. Terephthalic acid, which sublimes, had an infrared spectrum which was identical with an authentic sample. In the oxidation of α,α′-dimercapto-*p*-xylene, polymeric disulfides were formed but no attempt to determine the structures was made owing to the complexity of the material.

Acknowledgment.—We thank Mr. J. I. Haberman and Mr. F. T. Fitzsimmons for experimental assistance and the Esso Research and Engineering Co., especially the Process Research Division, for the privilege of publishing this research.

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(12) See also A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

(13) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans Green and Co., London, England, 1959.

(14) E. Fromm and J. S. Palma, *Ber.*, **39**, 3312 (1906).

(15) T. J. Wallace, W. Bartok, and A. Schriesheim, *J. Chem. Educ.*, **40**, 39 (1963).

(16) H. Pobiner, T. J. Wallace, and J. E. Hofmann, *Anal. Chem.*, **35**, 680 (1963).