The Acid Catalyzed Exchange of Phosphorus Bonded Hydrogen in Aqueous Solutions of Dialkyl Phosphonates, Studied by Nuclear Magnetic Resonance

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The exchange of the phosphorus-bonded hydrogen with deuterium in D_2O has been studied for dimethyl-, diethyl- and di-n-propylphosphonate.[1] The kinetics was followed by means of intensity measurements on the proton magnetic resonance spectra of these compounds. The exchange was found to be acid-catalyzed, the rate law for the reaction being: rate = k_H[phosphonate][H^+] + k_w[phosphonate]. From a comparison of the data obtained with those found for the oxidation of the same compounds, it is suggested that the phosphite[1] form of the dialkyl phosphonates serves as a common intermediate for both the exchange and oxidation reactions.

Introduction

Little work has been done on the exchange of phosphorus bonded hydrogen. Martin[2] used Raman spectroscopy to study the exchange of deuterium with phosphorous acid and Fox[3] used infrared spectroscopy to follow the exchange of deuterium with dibutylphosphonate in butyl alcohol-d. However in neither case was it possible to make an exact kinetic analysis of the exchange reaction. Jenkins and Yost[4] used tritium labelling to study the exchange reaction in hypophosphorous acid and gave a detailed kinetic analysis of their results.

In the present work a study was made of the exchange of phosphorus bonded hydrogen in dimethyl-, diethyl- and di-n-propylphosphonate. Use was made of the fact that the intensity of a proton magnetic resonance line is proportional to the concentration of the relevant proton in the sample studied.[5]

Interpretation of Spectra.—The nuclear magnetic resonance spectra of the dialkyl phosphonates consist of a group of lines due to the alkyl groups and a doublet due to the phosphorus bonded hydrogen, with a spin–spin interaction of about 700 cycles.[6] The components of the doublet (hereafter referred to as the P–H lines) are isolated from the other lines of the spectrum. If H_2O is present, its absorption line appears near those of the alkyl groups. The intensities of the P–H lines are directly proportional to the concentration of the phosphorus bonded hydrogen in the observed sample. The progressive replacement of this hydrogen by deuterium results in a corresponding decrease in the intensity of the P–H lines, due to the fact that the deuterium resonance in the same field is at a much lower frequency.

The facts outlined above form the basis for a method of following the kinetics of hydrogen exchange in the dialkyl phosphonates. The method is applicable only if several spectra can be recorded during the half-life of the reaction.

Experimental

Dialkyl Phosphonates.—Dimethyl- and di-n-propylphosphonates were made from the corresponding alcohols and phosphorus trichloride.[7] Diethylphosphonate was obtained commercially (Albright and Wilson). All phosphonates were doubly distilled before use: b.p. dimethyl-, 57–58° (9 mm.)(lit.[8] 56–58° (10 mm.)), diethyl-, 72° (9 mm.)(lit.[9] 72–73° (9 mm.)), di-n-propyl-, 93° (9 mm.)(lit.[10] 91° (9–10 mm.)).

DCl Solution.—A stock solution of 3.64 N DCl was prepared by passing DCl gas into D_2O. DCl was prepared[11] from benzoyl chloride and D_2O.

Spectrometer.—The n.m.r. spectrometer has been described previously.[12]

Procedure.—Preliminary experiments on solutions of dialkyl phosphonates in D_2O showed that the exchange rate increased with increasing acidity. In order to study the kinetics quantitatively the following general procedure was adopted. Solutions of dialkyl phosphonate in D_2O (~99%) containing varying amounts of DCl (0.2–1.0 M) were prepared, the recording of spectra being commenced as soon as possible after the preparation. The exchange process was followed by observing the decrease in intensity of one component of the P–H doublet (see Fig. 1). Since a change in the radio frequency (r.f.) intensity will in itself result in a change in the absolute intensity of a resonance line, use was made of an arbitary measure of intensity, viz., the ratio of the heights of the P–H line to one of the lines of the alkyl groups recorded immediately afterwards. This ratio, giving the relative intensity of the P–H line, is independent of any long term variations in the r.f. field, since the intensity of the alkyl lines is unaffected by the exchange reaction. The reactions were followed till at least the half-life. The experimental error in estimating the relative intensity varied between 5–15% depending on the absolute intensity of the P–H line.

The solvent used contained approximately 1% H_2O giving a corresponding absorption line. During the exchange reaction an increase in the intensity of this line is observed and in principle this increase could also be used to follow the exchange kinetics. However, because the relative changes in the water line are less than those in the P–H lines, this method was found to be much less sensitive and therefore was not used.

Results

Isotopic exchange reactions, in the absence of appreciable isotope effects, show first order kinetics as measured by the disappearance of one isotopic species from one of the reactants.[13] The expression

(1) The nomenclature in this article follows that used in a recent review by G. O. Doak and L. D. Freedman, *Chem. Revs.*, **61**, 31 (1961).

(2) R. Bruce Martin, *J. Am. Chem. Soc.*, **81**, 1574 (1959).

(3) R. B. Fox, "NRL Report," 5242, Jan. 8, 1959.

(4) W. A. Jenkins and D. M. Yost, *J. Inorg. Nuclear Chem.*, **11**, 297 (1959).

(5) J. A. Pople, W. C. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, Chap. 19.

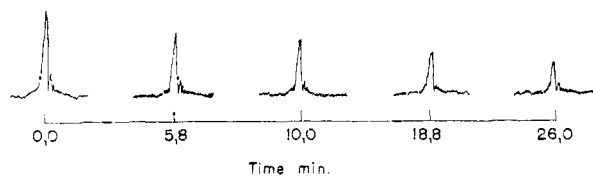(6) H. Finegold, *Ann. N. Y. Acad. Sci.*, **70**, (4), 885 (1958).

(7) H. McCombie, S. C. Saunders and G. J. Stacie, *J. Chem. Soc.*, 380 (1945).

(8) T. Milobendzki and A. Sachnowsky, *Chem. Polsk.*, **15**, 34 (1917).

(9) W. Strecker and R. Spitaler, *Ber.*, **59**, 1754 (1926).

(10) A. E. Arbuzov, *ibid.*, **38**, 1171 (1905).

(11) H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, **64**, 2223 (1942).

(12) E. Grunwald, A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 630 (1957).

(13) "Radioactivity Applied to Chemistry," Editors, A. C. Wahl and N. A. Bonner, John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 1.

Fig. 1.—Intensity of P–H lines in a 1.7 M solution of dimethylphosphonate in D_2O, containing 0.56 M DCl, as a function of time.

for the total rate of the reaction is

$$R = -\frac{1}{t} \cdot \frac{ab}{a+b} \ln(1 - F)$$

where a and b are the total concentrations of the exchanging species and F is the fraction-exchange value. In the present case the exchanging species are dialkyl phosphonate and water and since the water is present in large excess the rate equation reduces to the form

$$k = \frac{R}{[(RO)_2PO\cdot H)]} = -\frac{1}{t} \ln(1 - F)$$

where k is the specific rate of the reaction. From the above equation it follows that a plot of log $([(RO)_2PO\cdot H)]_t - [(RO)_2PO\cdot H]_{eq})$ versus time should be linear, where $[(RO)_2PO\cdot H]_t$ is the concentration of the hydrogen form of phosphonate at time t, and $[(RO)_2PO\cdot H]_{eq}$ is the concentration of the hydrogen form at equilibrium. As the mole fraction of hydrogen in the reaction solutions was less than 3% the term $[(RO)_2PO\cdot H_{eq}]$ can be neglected and therefore only the first term in the bracket need be considered. In practice the logarithm of the relative intensity of the P–H line was plotted against time since the line intensity is proportional to $[(RO)_2PO\cdot H]_t$. A linear dependence was in fact observed as shown for the case of diethylphosphonate in Fig. 2. The specific rates, k, for the different dialkyl phosphonates were obtained from the slopes of these plots. The slopes were obtained by visually fitting a straight line through the experimental points. To determine the order of the reaction with respect to the acid, sets of runs were carried out at constant phosphonate concentration and varying amounts of DCl. The results are given in Table I and plotted in Fig. 3. These plots are linear and have positive intercepts on the vertical axis, showing that the reaction is first order with respect to acid and that a spontaneous, acid-independent, exchange occurs.

TABLE I

SPECIFIC RATES OF HYDROGEN EXCHANGE IN DIALKYL PHOSPHONATES FOR DIFFERENT ACID CONCENTRATION
(TEMP. 23 ± 1°)

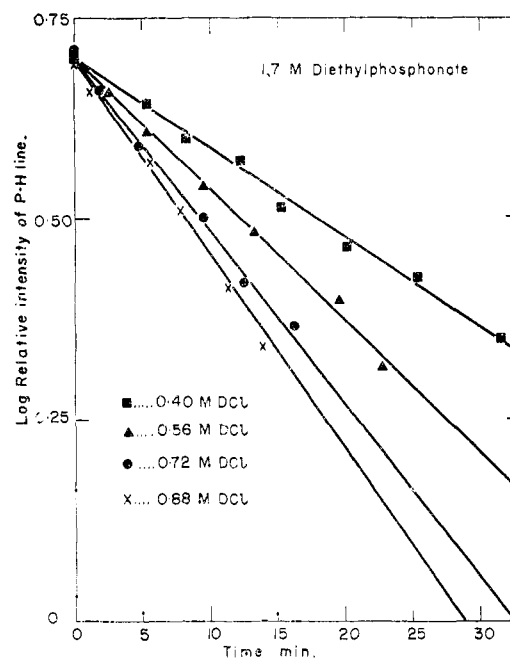|	DCl mole l.$^{-1}$	0.19	0.37	0.56	0.75
1.7 M dimethyl-	$k \times 10^2$ min.$^{-1}$	2.1	3.4	4.1	5.8
	DCl mole l.$^{-1}$	0.40	0.56	0.72	0.88
1.7 M diethyl-	$k \times 10^2$ min.$^{-1}$	2.6	3.6	4.9	5.5
1.0 M diethyl-	$k \times 10^2$ min.$^{-1}$	2.3	3.5	4.2	5.4
	DCl mole l.$^{-1}$	0.20	0.37	0.52	0.75
1.7 M di-n-propyl-	$k \times 10^2$ min.$^{-1}$	1.9	2.8	4.0	4.8

Fig. 2.—Plots versus time of the logarithm of the relative intensity of the P–H line of 1.7 M solutions of diethylphosphonate, at different concentrations of DCl. For clarity, the plots have been adjusted to pass through a common, arbitrary, intercept on the vertical axis (temp. 23 ± 1°).
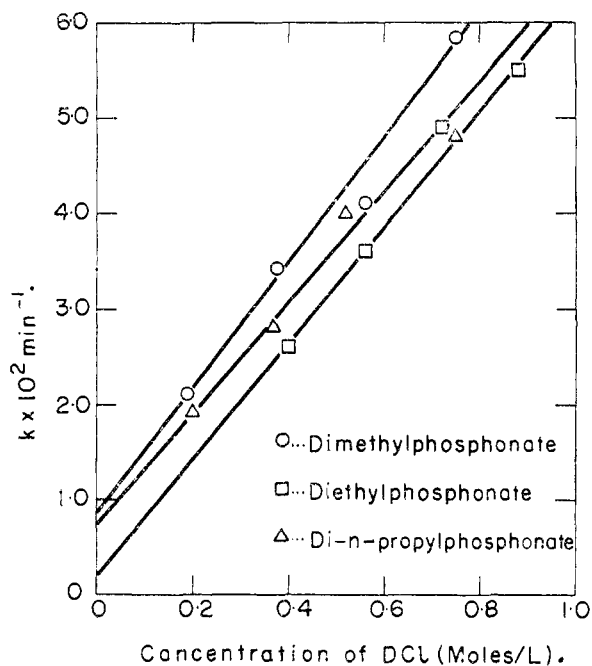

Concentration of DCl (Moles/L).

Fig. 3.—Specific rates of exchange, k, for different dialkyl phosphonates (1.7 M solutions), as a function of DCl concentration. Individual values are taken from Table I.

To determine the order of the reaction with respect to the dialkyl phosphonate, three sets of runs were carried out at constant DCl concentration and varying concentrations of dimethylphosphonate. The results are given in Table II. The variation of the specific exchange rate, k, with the phosphonate concentration is a measure

of the order of the reaction with respect to phosphonate.[13] As may be seen from Table II, over the range of phosphonate concentration studied, k is practically constant for each acid concentration, indicating that the reaction is first order with respect to phosphonate. The values for k obtained at the highest phosphonate concentration are systematically slightly higher than the values at lower concentrations. A similar effect was observed for two sets of runs with diethylphosphonate shown in Table I. These results may be the consequence of a medium effect due to the relatively large percentage by volume of phosphonate.

Table II

Specific Rates of Hydrogen Exchange, k (Min.$^{-1}$), in Dimethylphosphonate (Temp. 20.5 ± 0.5°)

(CH₃O)₂PO·H concn.	DCl concn. 0.21 M	0.42 M	0.63 M
0.42 M	1.5×10^{-2}	2.6×10^{-2}	3.7×10^{-2}
0.63 M	1.5×10^{-2}	2.6×10^{-2}	3.6×10^{-2}
0.84 M	1.5×10^{-2}	2.5×10^{-2}	3.5×10^{-2}
1.25 M	1.5×10^{-2}	2.5×10^{-2}	3.7×10^{-2}
1.67 M	1.6×10^{-2}	2.9×10^{-2}	4.1×10^{-2}

It is known[14] that the hydrolysis of dialkyl phosphonates is acid catalyzed. Such hydrolysis was actually observed, showing itself by the appearance of lines due to monoalkyl phosphonates. From the relative intensity of these lines the amount of hydrolysis occurring during the time of the runs was seen to be small, and any correction to the value obtained for the specific rates of exchange, due to this hydrolysis, would have fallen within the experimental error of the measurements.

Discussion

From the above results the rate law for the exchange reaction can be deduced and may be written

$$\text{Specific rate} = k = \frac{R}{[(RO)_2PO\cdot H]} = k_H[H^+] + k_w \quad (1)$$

where k_H is the catalysis constant for the hydrogen (deuterium) ion and k_w the catalysis constant for the spontaneous, acid-independent exchange. Values for k_H and k_w for the different dialkylphosphonates may be derived, respectively, from the slopes and intercepts of the lines in Fig. 3 and are given in Table III.

Table III

Catalysis Constants for Exchange and Oxidation of Some Dialkyl Phosphonates

|	Exchange[a] k_H M^{-1} min.$^{-1}$	k_w min.$^{-1}$	Oxidation[b] k_H M^{-1} min.$^{-1}$	k_w min.$^{-1}$
Dimethyl-	6.6×10^{-2}	8×10^{-3}	3.2×10^{-2}	1.4×10^{-3}
Diethyl-	6.0×10^{-2}	2×10^{-3}	2.5×10^{-2}	0.4×10^{-3}
Di-n-propyl-	5.8×10^{-2}	7×10^{-3}	2.5×10^{-2}	0.2×10^{-3}

[a] Concentrations of phosphonates were 1.7 M. Estimated error for k_H values is ± 10%, for k_w values ± 30% (temp. 23 ± 1°). [b] Taken from ref. 15 (temp. stated. 20°).

It is of interest to compare our results with those obtained by Nylen[15] for the oxidation of dialkyl phosphonates by iodine in acid solution. Nylen found that above a certain ratio of iodine

(14) P. Nylen, Svensk. Kem. Tidssk., **49**, 29 (1937).
(15) P. Nylen, Z. Anorg. Allgem. Chem., **235**, 161 (1938).

to dialkyl phosphonate concentration, the oxidation rate was independant of iodine concentration, and under these conditions he obtained a rate law for the oxidation identical in form to that given in equation 1. The values obtained by Nylen for k_H and k_w[16] for dimethyl-, diethyl- and di-n-propylphosphonate, respectively, are shown in Table III, together with the values for k_H and k_w which were obtained for the exchange reaction.

The fact that the oxidation of the dialkyl phosphonates under the stated conditions follows an identical rate law with the exchange rate of the phosphorus bonded hydrogen, and the close correspondence between the respective catalytic constants, suggests that the rate determining step is the same for both reactions. Nylen suggested an equilibrium between the normal form of the dialkyl phosphonate and an active form. As a result of the present work we are able to define this equilibrium more specifically.

The general scheme suggested for the acid catalyzed oxidation and exchange reactions is

(I)
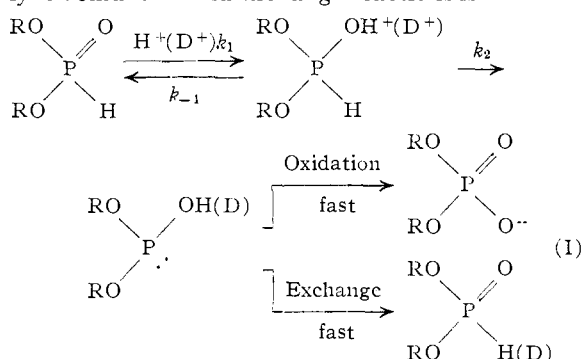
The first step shows a protonation of the phosphoryl group which is followed by the fission of the phosphorus hydrogen bond, resulting in the formation of the phosphite[1] form of the phosphonate. This phosphite form is assumed to be extremely reactive, an assumption supported by evidence from the reactions of analogous structures. For example, the trialkyl phosphites, $(EtO)_3P$, are amongst the most reactive organophosphorus compounds, being extremely easily oxidized and also undergoing facile rearrangement reactions to give tetracovalent compounds.[17] The tricovalent phosphorus atom in organic pyrophosphites and hypophosphites is also oxidized extremely rapidly by oxidizing agents.[18]

In the presence of excess oxidizing agent, under the conditions studied by Nylen, the phosphite form is oxidized rapidly into a dialkyl phosphate. In the absence of an oxidant, the phosphite form rapidly reverts to the phosphonate form by accepting a proton from a suitable donor. It follows that the acid catalyzed rate of oxidation and exchange should both be equal to the rate of formation of the phosphite form. From the observed data this rate is given by

$$\frac{d[\text{Phosphite}]}{dt} = k_H[\text{Phosphonate}][H^+] \quad (2)$$

(16) Given as $_ik_H$ and $_ik_w$ in Nylen's paper.
(17) G. Kosolapoff, "Organo-phosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 196.
(18) D. Samuel and B. Silver, Chem. and Ind. (London), 556 (1961).

Such a rate law is consistent with scheme I provided there is a pre-equilibrium between the phosphonate and its conjugate acid and that the degree of protonation is small.[19] Another possibility consistent with the rate law is a one-step mechanism, i.e., protonation of the phosphonate accompanied by a simultaneous fission of the phosphorus hydrogen bond.[19] No distinction can be made between the above alternatives from the present data. The detailed mechanism of the formation of the phosphite form is being investigated by a study of kinetic isotope effects.

The non-acid-catalyzed term, k_w, in equation 1 represents a spontaneous dissociation of the P–H bond, presumably favored by the high dielectric constant of water and its basic properties.

From Table III it is seen that the values of k_H and k_w for the exchange reaction are larger than the corresponding values for the oxidation reaction.

(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. 9.

This difference is partly due to the different temperatures at which the experiments were carried out. A further cause for the discrepancy may be due to differences in medium between the two sets of experiments. The dialkyl phosphonate concentration was less than 0.1% by volume in the case of the oxidation reaction mixtures studied by Nylen,[15] as compared to 15–25% by volume in the case of the exchange reaction. It should also be noted that the exchange was studied in D_2O solution and the oxidation results are for H_2O solutions. Considering the differences in the temperature and the nature of the medium, the agreement between the values of the catalytic constants obtained from both reactions is reasonably good.

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Some Reactions of Peroxydisulfuryl Difluoride

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The reactions of peroxydisulfuryl difluoride with several substances have been examined. Three new fluorosulfonates, octafluorobis-(fluorosulfonato)-cyclopentane $(C_5F_8(SO_3F)_2)$, tetrafluorobis-(fluorosulfonato)-ethane $(C_2F_4(SO_3F)_2)$ and tetrafluorobis-(fluorosulfonato)-sulfur (VI) $(SF_4(SO_3F)_2)$ were produced by direct combination of peroxydisulfuryl difluoride with perfluorocyclopentene (C_5F_8) and tetrafluoroethylene (C_2F_4) at room temperature and with sulfur tetrafluoride (SF_4) at 128° respectively. These new compounds have been characterized. Structures have been confirmed by mass, nuclear magnetic resonance and infrared spectra. A white solid, dioxobis-(fluorosulfonato)-molybdenum(VI) $(MoO_2(SO_3F)_2)$, was obtained with either molybdenum hexacarbonyl or molybdenum metal.

It has been shown that peroxydisulfuryl difluoride reacts with some substances to give fluorosulfonates.[2–3] The reactions of $S_2O_6F_2$ with several additional substances have now been studied, and it has been found that the peroxide acts in three ways: (1) as an oxygenating agent through the addition of oxygen to the central atom of the reacting species, e.g., with CO, PF_3, SOF_2, $COCl_2$, CCl_4 or S; (2) as a fluorosulfonating agent, e.g., with HgO, KCl, ICl, C_5F_8, C_2F_4, or SF_4; (3) as an oxygenating and fluorosulfonating agent by adding oxygen and fluorosulfonate groups to the central atom, e.g., SOClF, Mo or $Mo(CO)_6$. Pyrosulfuryl fluoride $(S_2O_5F_2)$ is obtained as a product of reactions of types 1 and 3.

Experimental

Preparation of Peroxydisulfuryl Difluoride.—Peroxydisulfuryl difluoride can be prepared by reaction of fluorine with an excess of sulfur trioxide at about 250°, by the combination of fluorine fluorosulfonate with sulfur trioxide at 300°[4] or by the electrolysis of fluorosulfonic acid.[5] The catalytic fluoronation of sulfur trioxide vapors by fluorine in the presence of a heated catalyst of copper ribbon coated

(1) Department of Chemistry, University of Idaho, Moscow, Idaho.

(2) John E. Roberts and George H. Cady, J. Am. Chem. Soc., **81**, 4166 (1959).

(3) John E. Roberts and George H. Cady, ibid., **82**, 352, 353 (1960).

(4) F. B. Dudley and G. H. Cady, ibid., **79**, 513 (1957).

(5) F. B. Dudley, Thesis, University of New England, Australia (1960).

with silver difluoride provided an easy and simple method to prepare the easily purified product.

Fluorination of sulfur trioxide carried by a stream of dry nitrogen with a slight excess of fluorine in the presence of a silver difluoride catalyst in a "catalytic reactor"[6] at 155° produced the $S_2O_6F_2$, which was purified by prolonged pumping at −78° to remove the contaminants silicon tetrafluoride, sulfuryl fluoride and fluorine fluorosulfonate. In a 15 hr. run using a nitrogen flow of 8 liters per hour and a catalyst contact time of about 15 minutes, a 96 g. sample of product was obtained. It contained 97% peroxydisulfuryl difluoride. In another run, 26.1 g. of sulfur trioxide yielded 31.6 g. of $S_2O_6F_2$ (yield, 97% theoretical).

Storage of the compound in a glass vessel at −78° was satisfactory. Although the glass container apparently was not attacked at room temperature, a nonvolatile oily material was slowly formed in the $S_2O_6F_2$. Apparently this did not introduce contaminants into the $S_2O_6F_2$ distilled from the vessel. The yellow oil was not identified.

Materials.—The Swarts reaction[7] provided a general method for the conversion of chlorides to the corresponding fluorides by reaction of the former with antimony(III) fluoride in the presence of antimony(V) chloride as a catalyst. Thionyl fluoride and thionyl chlorofluoride were obtained using thionyl chloride while phosphorus(III) fluoride was prepared from phosphorus(III) chloride. Tetrafluoroethylene was produced by the pyrolysis of Teflon (polytetrafluoroethylene) in an iron vessel at 550°. Sulfur tetrafluoride was used directly from a cylinder supplied by E. I. du Pont de Nemours and Co., Inc. All other materials were of reagent grade.

(6) K. B. Kellogg and G. H. Cady, J. Am. Chem. Soc., **70**, 3086 (1948).

(7) H. S. Booth and F. C. Mericola, ibid., **62**, 640 (1940).