is actually only about one-fifteenth the values for the other two salts. The explanation doubtless lies in the fact that the model, upon which the expectation of a high K value accompanying low mobility is based, assumes only the presence of coulomb forces between the ions.[13] In the case of silver iodide there are additional forces present which make K less than predicted when coulomb forces alone are involved. These forces are of the acid–base type.[3,4] The amphoteric nature of the iodide ion is well known[14] and is here substantiated. The results for silver nitrate and potassium iodide indicate that both silver and iodide ions are acting as acids in their association with the highly basic solvent. But toward the acidic silver ion the iodide ion acts as a base, tending to donate a pair of electrons to give partial covalent character[15] to the bond between the two ions. The presence of these additional forces decreases K to a value far below that expected from the low value of Λ_0.

IV. Summary

The conductances of three salts, potassium iodide, silver iodide, and silver nitrate in ethylenediamine have been measured, at concentrations low enough to permit calculation of Λ_0 and K. The best solvent that could be obtained had a conductance of 9×10^{-8} mho. An explanation based on the electronic theory of acids and bases is offered for the extraordinarily low value of K for silver iodide.

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[14] R. B. Sandin, *Chem. Rev.*, **32**, 249 (1943).

[15] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

BOSTON, MASS. RECEIVED OCTOBER 8, 1943

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Isomerization of Tri-alkyl Phosphites

BY GENNADY M. KOSOLAPOFF

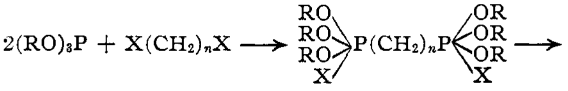
The isomerization of tri-alkyl phosphites in the course of the reaction with alkyl halides, according to the scheme

$$(RO)_3P + R'X \longrightarrow (RO)_3PR'X \longrightarrow RX + R'P(O)(OR)_2 \quad (1)$$

was first studied rather extensively by Arbuzov,[1] who utilized this reaction as an elegant method of preparation of a number of phosphonic acid esters.

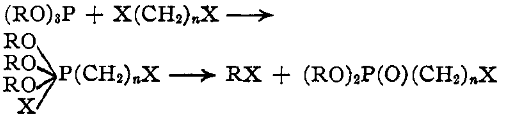
Usually the reaction is carried out by heating the reagents in a sealed tube, followed by distillation of the products. Under these conditions there are usually formed varying, and sometimes considerable, amounts of $RP(O)(OR)_2$, apparently formed through interaction of RX with either unreacted $(RO)_3P$ or the intermediate $(RO)_3PR'X$. It was felt that if the RX formed in the reaction were to be removed as rapidly as possible from the reaction mixture, not only should the course of the reaction be cleaner, but the measurement of RX evolved should offer a ready method for following the course of the reaction.

It was also felt that a technique employing the above principle could be utilized in obtaining additional information on the course of the reaction between tri-alkyl phosphites and paraffin dihalides. This reaction may be expected to follow both of the possible courses



$$2(RO)_3P + X(CH_2)_nX \longrightarrow \begin{matrix}RO\\RO\\RO\\X\end{matrix}\!\!>\!P(CH_2)_nP\!<\!\!\begin{matrix}OR\\OR\\OR\\X\end{matrix} \longrightarrow 2RX + (RO)_2P(O)(CH_2)_nP(O)(OR)_2 \quad (2)$$

and



$$(RO)_3P + X(CH_2)_nX \longrightarrow \begin{matrix}RO\\RO\\RO\\X\end{matrix}\!\!>\!P(CH_2)_nX \longrightarrow RX + (RO)_2P(O)(CH_2)_nX \quad (3)$$

Actually, the literature data are rather meager as to information on the course of this reaction. Thus, Arbuzov and Kushkova[2] isolated from the reaction of methylene iodide and triethyl phosphite only the iodomethanephosphonic acid diethyl ester, *i. e.*, the product of reaction (3), among other substances. More recently, Parfent'ev and Shafiev[3] investigated the reaction of triethyl phosphite and trimethylene bromide, obtaining a product corresponding to the γ-bromopropanephosphonic acid diethyl ester, which could not be distilled without decomposition, and was apparently formed according to reaction (3). Nylen[4] studied the reaction between sodium diethylphosphite and methylene chloride, ethylene bromide and trimethylene bromide, obtaining $CH_2(PO(ONa)(OEt)_2)_2$, ethylene and tetraethyl trimethylenediphosphonate, respectively, as the identifiable reaction products.

From consideration of the available information it was evident that a further study of this reaction was desirable with variation of the proportions of the reactants as a means of influencing the predominance of either reaction (2) or (3).

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[1] A. E. Arbuzov, "On the Structure of Phosphorous Acid," N. Alexandria, 1905.

[2] Arbuzov and Kushkova, *J. Gen. Chem.* (U. S. S. R.), **6**, 283 (1936).

[3] L. N. Parfent'ev and M. Kh. Shafiev, *Trudy Uzbesksk. Gos. Univ.. Sbornik Rabot Khim.*, 87–94 (1939).

[4] P. Nylen, "Studien über organische Phosphorverbindungen," Upsala, 1930.

Triethyl phosphite was selected as the alkyl phosphite while *n*-butyl bromide and *n*-hexyl bromide were selected as the alkyl halides for the study of reaction (1), while ethylene bromide was taken for the study of reactions (2) and (3).

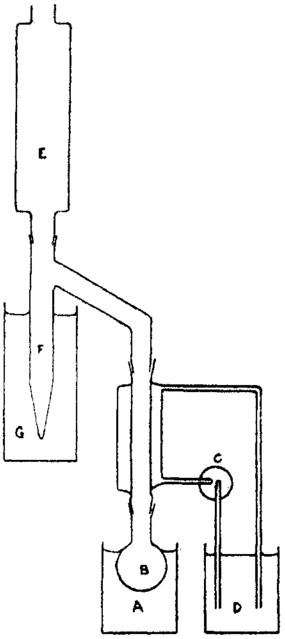

Fig. 1.—A, Oil-bath; B, reaction flask; C, circulating pump; D, heated water reservoir; E, reflux condenser; F, Stark-Dean trap; G, ice-water bath.

Experimental.—The reactants were heated, after mixing. in a small round-bottomed flask connected to an upright condenser, through the jacket of which water, heated to 50°, was circulated by a pump. The upper end of the condenser was connected to a Stark-Dean trap which was immersed in ice-water, while the exit from the trap was surmounted by an efficient spiral condenser. The reaction flask was heated by a thermostatically controlled oil-bath. The amount of ethyl bromide collected in the trap in the course of the reaction was read periodically. The apparatus is shown on Fig. 1.

***n*-Hexyl Bromide.**—Triethyl phosphite (16.6 g., 0.1 mole) and *n*-hexyl bromide (16.5 g., 0.1 mole) reacted at 133 and 150°. The results are shown in curves 1 and 2. respectively, of Fig. 2.

***n*-Butyl Bromide.**—Triethyl phosphite (16.6 g., 0.1 mole) and *n*-butyl bromide (13.7 g., 0.1 mole) reacted at 150°. The results are shown on curve 3, Fig. 2.

Ethylene Bromide.—Triethyl phosphite (16.6 g., 0.1 mole) reacted with the following amounts of ethylene bromide: 0.5 mole (94 g.), 0.2 mole (37.6 g.), 0.1 mole (18.8 g.) and 0.05 mole (9.4 g.) at 150°. The results are shown on curves 4, 5, 6 and 7, respectively, of Fig. 2. The reaction mixtures were subjected to vacuum distillation after completion of the runs. In the first three cases after distillation of excess ethylene bromide there was collected a very small amount of a liquid corresponding in boiling point to diethyl ethylphosphonate. Distillation from that point became impossible due to decomposition even at 1 mm. The last run, however, gave approximately 7 g. of diethyl ethylphosphonate. b. p. 50° at 1 mm., 194–198°.

Discussion of the Results.—In view of the fact that the over-all reaction in all of the cases studied must consist of at least two steps, *i. e.*, the formation of the intermediate addition compound, followed by thermal decomposition of the latter, it is not possible to calculate the reaction constants from our data. However, it is interesting to note the considerable effect of temperature upon both the induction period and the over-all reaction rate in case of *n*-hexyl bromide. The former is apparently the "accumulation" period of the phosphonium compound. The behavior of *n*-butyl bromide may be explained on a similar basis: while appreciable amounts of free butyl bromide exist in the mixture, the temperature of the latter is conditioned by the refluxing butyl bromide, while after the latter had combined substantially with the phosphite, the mixture attains bath temperature and the greater decomposition rate of the butyl phosphonium compound (in comparison with the hexyl compound) is evidenced by the generally steeper reaction curve.

In order to bring the reaction curve of the 0.05–0.1 molar mixture of ethylene bromide and triethyl phosphite to the same scale as that of the other three runs for more apparent visual comparison, the ordinates of curve 7 were multiplied by two and the resultant "hypothetical" curve is shown as curve 8, Fig. 2. It is evident that the suppression of di-substitution is sharply pronounced with greater excess of ethylene bromide. It is conceivable that the use of overwhelmingly large excess of the ethylene bromide may lead to almost complete suppression of di-

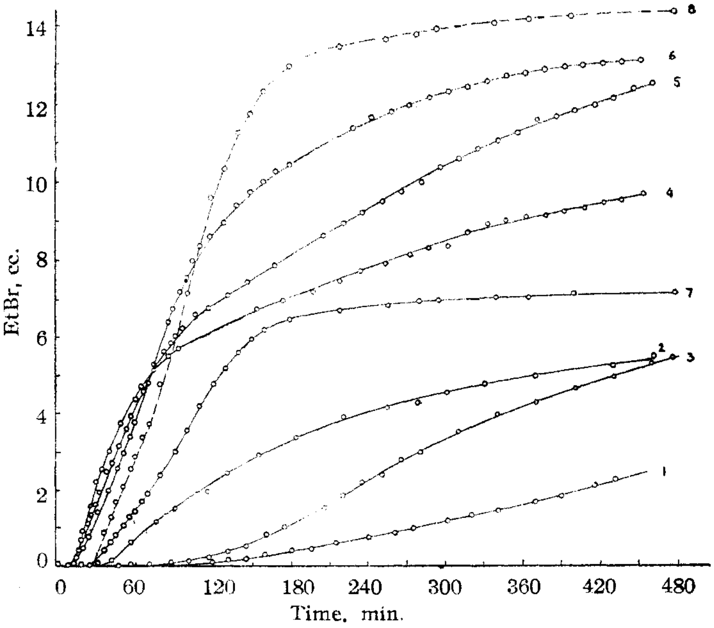

Fig.. 2.

substitution (excess of the order of 20–1 molar ratio). Such a mixture, however, was not practicable for our experimental set-up due to the relatively large bulk of such a reaction mixture. The results obtained from the 0.05–0.1 molar mixture show, apparently, a somewhat different reaction course from the other three runs. The amount of ethyl bromide collected corresponds very closely to the theoretical for complete disubstitution (*i. e.*, 7.25 cc.) according to reaction (2), while the distillation of the reaction mixture yielded approximately one-half of the triethyl phosphite used in the form of diethyl ethylphosphonate. It appears that the amount of the bromoethyl ester formed is very small, but due to its ready decomposition, on attempted distillation, and evolution of hydrogen bromide, the tetraethyl ester, which apparently forms by a normally expected reaction (2), suffers decomposition, either *per se* or influenced by the hydrogen bromide, with diethyl ethylphosphonate being one of the decomposition products. The mechanism of this decomposition is obscure and appears to require a form of disproportionation. The results with ethylene bromide are in general accord with the above cited work of Nylen, who was able to isolate only decomposition products. It is curious to note that the methane member of the series yields a halomethyl product of some stability, as well as the di-substitution product (in modified form), as shown by Arbuzov (see above) and Nylen (see above). It is now shown that the ethane derivative apparently undergoes the normal reaction course for reactions (2) and (3), with the attendant complication of poor stability of the bromoethyl compound (not unexpected, by analogy with β-haloethyl carboxylic acid derivatives), making it impossible to isolate pure reaction products.

Summary

The reaction between triethyl phosphite, on one hand, and *n*-butyl bromide, *n*-hexyl bromide and ethylene bromide, on the other hand, was studied by following the rate of evolution of ethyl bromide. The latter reaction apparently follows the normally expected mono- and disubstitution courses, controllable by proportion of the reactants.

DAYTON, OHIO RECEIVED AUGUST 12, 1943

[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

The Relation of Starch–Iodine Absorption Spectra to the Structure of Starch and Starch Components[1]

BY R. R. BALDWIN, R. S. BEAR[2] AND R. E. RUNDLE

The activity of iodine in solution in the presence of starch has been shown to be a function of the nature of the starch, *i. e.*, of the proportion of amylose (or unbranched) component, the chain length of the amylose and the length of the free (or unbranched) portions of the amylopectin component.[3] Changes in starch-iodine color have long been known to accompany starch fractionation and starch degradation. It is to be expected that a more quantitative study of the absorption spectra of solutions of starch and its components should yield information, perhaps more detailed than that provided by the potentiometric study, concerning the structure of starch and its components.

Simerl and Browning made a spectrophotometric study of the iodine complex of a number of starches, dextrins, and starch components,[4] and Lampitt, Fuller and Goldenberg examined the absorption spectra of the starch–iodine complexes given by starch ground in a ball mill.[5] Both examinations were handicapped by the lack, at that time, of adequate methods of fractionating starch and characterizing the resultant fractions. Recent fractionation procedures and a rapid method of analysis of starch fractions[3] have overcome many of the previous difficulties.

Apparatus and Procedure.—Absorption spectra of the various solutions have been examined by means of a Coleman Model 10S double monochromator spectrophotometer, with an accompanying vacuum tube electrometer (Coleman pH meter) serving as an intensity measuring device. A slit selecting a 15 millimicron band of light was used for all transmission data. The solution to be examined was placed in a square cuvette, 13 mm. thick, and compared with a control solution in a matched square cuvette. The control solution contained a concentration of iodine equal to that used in preparing the starch–iodine solution. This procedure overcorrects for the iodine not involved in the complex, but the error is slight because of the negligible absorption of the very dilute iodine solutions used. For highly absorbing solutions a glass prism with optically parallel sides was placed in the cuvette to reduce the solution thickness from 13 to 1.63 mm. The temperature in all cases was kept at 23.0 ± 0.5°.

The perfectly clear solutions required for spectrophotometric work are possible only for very dilute starch solu-

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(1) Journal Paper No. J-1150 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 660. Supported in part by a grant from the Corn Industries Research Foundation. This paper is based on a thesis submitted by R. R. Baldwin to the Iowa State College.

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(3) F. Bates, D. French and R. Rundle, THIS JOURNAL, **65**, 142 (1943).

(4) L. Simerl and B. Browning, *Ind. Eng. Chem., Anal. Ed.*, **11**, 125 (1939).

(5) L. Lampitt, C. Fuller and N. Goldenberg, *J. Soc. Chem. Ind.*, **60**, 99 (1941).