THE STRUCTURE AND PROPERTIES OF THE DIALKYL PHOSPHONATES

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I. INTRODUCTION

The dialkyl phosphonates or dialkyl phosphites, compounds possessing the structure $(RO)_2P(O)H$, are versatile chemical reagents which undergo a wide variety of reactions in which the phosphorus acts as either a nucleophilic or an electrophilic center. A summary of the reactions of these compounds is given in diagrammatic form in a recent pamphlet (1). Excellent reviews (34; 57, pp. 180–210) of the chemistry of these compounds have been published in recent years. Since these compounds are readily available in relatively large quantity, they serve as the starting materials for a number of important industrial compounds; they also possess important industrial applications in their own right.

The structure of the dialkyl phosphonates, as well as that of the parent acid, was a subject of considerable controversy in the early days of phosphorus chemistry, but there is now substantially complete agreement among chemists that both the acid and its diesters exist largely, if not entirely, in the phosphonate form, $(RO)_2P(O)H$. However, there are many reactions of the dialkyl phosphonates which are difficult to explain without assuming the existence of the equilibrium:

$$(RO)_2P(O)H \rightleftharpoons (RO)_2POH$$

This implies that a finite amount of the ester, however small, exists in the phosphite form. In recent years modern physical methods have been employed in an effort to establish the existence of this tautomer, and a number of papers have been published on this subject. There has also been controversy as to whether these compounds are monomolecular or associated. It is the purpose of this review to summarize the evidence for the existence of the dialkyl phosphonates in two tautomeric forms as well as data related to the association of these compounds. The chemical literature through February, 1960, has been covered in this respect. The chemical reactions of the dialkyl phosphonates have been reviewed only in those instances where they relate to the structure of these compounds.

Nomenclature

Since the compounds under discussion are esters of phosphorous acid, it is only natural that they should be named "dialkyl phosphites," and indeed such is the common terminology. Esters of phosphorous acid, however, exist in two different chemical forms. The trialkyl phosphites, $(RO)_3P$, are derived from one form of the acid and the dialkyl phosphonates, $(RO)_2P(O)H$, from the other. It becomes a question as to whether the chemical names employed should distinguish between these two forms or whether greater clarity is attained by naming both types of compounds as derivatives of phosphorous acid. In a report (2) brought in by the Advisory Committee on the Nomenclature of Organic Phosphorus Compounds (a special committee of the Division of Organic Chemistry of the American Chemical Society) compounds of the type $(RO)_2P(O)H$ are named dialkyl phosphonates, though the name phosphorous acid is retained for the parent compound. This nomenclature has been adopted by *Chemical Abstracts* and is required for all papers in the *Journal of the Chemical Society.* There has been, however, very severe criticism (63; 108, pp. 387–9) of this system, and it has not been widely used except in the United States and Great Britain.

Although this new nomenclature system for phosphorus compounds has faults, it is the opinion of the present authors that it represents a vast improvement over systems previously in use. Thus, until its adoption, it was almost impossible for an American chemist to follow British publications dealing with organophosphorus chemistry when only the names of the compounds were given. Unfortunately, conferences between British and American chemists failed to effect any compromise between the various systems then in use, and radical changes were necessary in order to bring about an agreement. The authors believe that the new system deserves consideration, and it will be used throughout the present review.

II. ASSOCIATION OF DIALKYL PHOSPHONATES

A. Raman and infrared spectra

Arbuzov, Batuev, and Vinogradova (4) were apparently the first to study the vibrational spectra of dialkyl phosphonates; the compounds used included the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, and diisobutyl phosphonates. In the Raman spectrum of each compound they observed a broad intense band near 2435 cm.$^{-1}$ which they ascribed to the P—H bond. The broad nature of this band and the fact that earlier workers (114) had reported a Raman frequency for the P—H bond in liquid phosphine at 2306 cm.$^{-1}$ led the Russian workers to conclude that the dialkyl phosphonates are associated into dimers or trimers through P—H···P or P—H···O bonds. The phosphoryl (P=O) band in these compounds occurred at about 1260 cm.$^{-1}$ and was weaker and more diffuse than the 1295 cm.$^{-1}$ band observed in phosphorus oxychloride. The decrease in intensity and the diffuseness were explained by the participation of the phosphoryl group in hydrogen bonding. Independently of the Russian workers, Meyrick and Thompson (69) in 1950 came to similar conclusions after observing a broad band near 2435 cm.$^{-1}$ in both the infrared and the Raman spectra of dimethyl, diethyl, and diisopropyl phosphonates.

In contrast to the above results, Daasch and Smith (29) found *sharp* infrared bands near 2400 cm.$^{-1}$ for diethyl and dibutyl phosphonates as well as for five other compounds containing the P—H bond (in phosphine, the fundamental stretching vibrations of the P—H bonds appear at 2327 and 2421 cm.$^{-1}$) (47). Sharp bands in the 2400 cm.$^{-1}$ region were found in the spectra of diethyl, dibenzyl, and dineopentyl phosphonates by Bellamy and Beecher (20), who concluded that there was no evidence of hydrogen bonding in these compounds.

In 1955 Serra and Malatesta (95) reëxamined the infrared spectrum of dimethyl phosphonate and noted that the P—H band was less diffuse than had been reported by Meyrick and Thompson; in other respects the results of the two groups of workers are in good agreement. On heating this compound for 10 hr. at 180°C., it was found that the infrared bands corresponding to the P—H and P=O groups were appreciably broadened and that the phosphoryl band was displaced from 1266 cm.$^{-1}$ to about 1230 cm.$^{-1}$; furthermore, the cryoscopic molecular weight of the heated material was changed. From these results it was concluded that heating dimethyl phosphonate transforms it into a hydrogen-bonded dimer. Unpublished work from the laboratory of the reviewers (36) has shown that heating dimethyl phosphonate causes profound changes in its constitution. This work is discussed in greater detail in Section II,D.

During the last decade numerous workers (21, 22, 25, 28, 32, 49, 65, 68, 70, 106) have investigated the infrared absorption of dialkyl phosphonates and have reported a band in the region near 2400 cm.$^{-1}$; in almost all cases the band was found to be sharp. It has also been found (28) that the position and intensity of the P—H absorption band of a dialkyl phosphonate are constant over the temperature range −100°C. to +70°C.; this fact strongly suggests that there is little or no hydrogen bonding between molecules of dialkyl phosphonates (32, p. 4). Further evidence for this conclusion is the fact that the P=O absorption of these compounds occurs in the expected region for the free, i.e., not hydrogen-bonded, phosphoryl group (19). In addition the P—H and the P=O absorption bands in dialkyl phosphonates are not appreciably shifted when the compounds are dissolved in dioxane (28), carbon disulfide (70), or triethylamine (28). It must be concluded, therefore, that the infrared spectra provide no evidence that dialkyl phosphonates are associated through hydrogen bonds.

B. Parachors

Although the original suggestion that dialkyl phosphonates are associated was based on Raman spectral data (4), a principal argument advanced by Arbuzov and his coworkers is derived from parachor studies. For this reason it is necessary to consider the parachor results in some detail.

In 1946 Arbuzov (6) published the first of an extensive series of papers devoted to the parachor. In these papers, the rather complicated formulas derived by Gibling (38, 39, 40, 41) were employed. Gibling believed that even minor changes in structure produced significant changes in parachor values and that in order to achieve accurate results it was necessary to apply a number of correction factors. With the use of these correctio nshe achieved excellent agreement between theoretical and observed values; he also employed parachor values in the interpretation of molecular structure. Gibling's work has been reviewed by Quayle (87), who, in spite of the accuracy of Gibling's results, still prefers the simpler system of atomic and structural constants.

As an example of Gibling's calculations, the method used for deriving the theoretical parachor for tripropyl phosphate is given below:

Three CH_3 groups (3 × 55.2)	165.6
Three —CH_2— groups (3 × 39.8)	119.4
Three —CH_2—(O) groups (3 × 37.4)	118.2
One PO_4 group	119.8
	523.0

From this sum is subtracted a correction of 10.8 calculated as follows: (*1*) a β-correction of 4.2 (3 × 1.4) attributed to the interaction of each β-carbon atom with an oxygen atom and (*2*) a correction of 6.6 (3 × 2.2) attributed to interaction between the three parallel chains. (This latter correction is applied to all carbon atoms beyond the β-carbon atom.) With this correction the value of 512.2 is obtained, which is termed the standard value (S.V.) for the parachor of tripropyl phosphate. To this, however, must be further added an expansion correction (E.C.) of 2.6 [E.C. = (S.V.)f^n, where f is an empirical constant, 1.0004165, and n is the total number of carbon and oxygen atoms in the side chains]. The final calculated parachor value is 514.8, which compares very well with the observed value of 515.9. Similar calculations were used for the methyl, ethyl, and butyl phosphates. In a somewhat similar manner the parachors of dialkyl sulfites and sulfates were calculated. In these cases, however, the correction due to interaction between parallel chains was applied to carbon atoms in only *one* chain, in contrast to the phosphates, where it was applied to carbon atoms in all three chains. No reason was advanced for this difference in the method of calculation, except that it produced better agreement between theoretical and observed values.

Parachors were also obtained for diisopropyl and diisobutyl sulfates, but the observed values were not in agreement with the calculated values. Gibling states that the necessary "interference corrections are not calculable from present data." However, the values for diisopropyl, diisobutyl, and diisoamyl sulfites do agree with the theoretical provided that the calculations in the case of the isopropyl derivative are made in a different manner from that employed for the isobutyl and isoamyl derivatives.

It would appear to the reviewers that the various corrections used by Gibling are applied arbitrarily, largely to make the calculated values fit the data, and that by proper choice of correction factors it is possible to obtain almost any theoretical value desired. For this reason they believe that the parachor, as used by Gibling, can have very little value in the determination of chemical structure. Other workers have concluded that the parachor is unreliable in the solution of structural problems (91, 98, 107).

Arbuzov and Vinogradova (7, 8) applied Gibling's method to the calculation of the parachor of a series of dialkyl phosphonates, the straight-chain compounds, methyl through octyl, as well as the isopropyl and isobutyl compounds. The value of 115.45 was assigned to the —PO_3H group, calculated from the observed value of dimethyl phosphonate by subtracting the value for the two methyl groups. The authors also applied both the so-called β-correction and parallel-chain corrections in a manner similar to that used by Gibling for the dialkyl sulfites and sulfates. The observed values for the methyl, ethyl, propyl, and isopropyl compounds agree well with the calculated values, but with the remaining members there is an error which varies between 0.7 and 1.2 per cent. Accordingly, Arbuzov and Vinogradova calculated the values based on a dimeric structure. They suggested that in the dimer there is interaction between all four chains, and that the factor of 2.2 for interaction between parallel chains should thus be multiplied by four (for each carbon atom beyond the β-carbon atom). There is of course a further change in the calculated parachor, since the E.C. value depends on the total number of atoms in the chains. With these corrections, the maximum error in the straight-chain compounds is reduced to 0.4 per cent.

In a later paper Arbuzov and Vinogradova (9) modified their earlier viewpoint. They pointed out that the interaction of all four chains in the dimerized dialkyl phosphonates is difficult to understand on the basis of the geometry of the molecule. Since the deviations between observed and calculated parachors increase with increasing molecular weight, they suggested that the results might be explained on the assumption that the lower members of the series are dimeric and that the degree of association decreases with increasing molecular weight. They then determined molecular weights of the dimethyl, diisopropyl, and dioctyl phosphonates cryoscopically in benzene. The results obtained (see Section I,D) were interpreted to indicate that dioctyl phosphonate was monomolecular, whereas dimethyl phosphonate, except in dilute solution, was bimolecular. Then, by assuming that the observed parachors of the dioctyl and dimethyl compounds represented the true values for the monomer and dimer, respectively, Arbuzov and Vinogradova calculated the per cent association of the dipropyl, dibutyl, and diisobutyl phosphonates from the deviation for the value calculated for the dimer. The dihexyl and diheptyl compounds gave values corresponding to the monomer.

The authors do not believe that the results of Arbu-

TABLE 1

The parachors of dialkyl phosphonates calculated on the basis of monomeric and dimeric forms

R in $(RO)_2P(O)H$	P (Calculated by Doak and Freedman)	P (Observed)	Error	P (Calculated by Arbuzov and Vinogradova)	P (Observed)	Error
			per cent			*per cent*
C_2H_5	302.3	302.6	0.1	607.9	605.3	0.4
C_3H_7	378.4	378.9	0.1	760.3	758.0	0.3
C_4H_9	454.2	454.7	0.1	912.3	909.4	0.3
C_6H_{13}	606.2	607.5	0.2	1220.7	1216.0	0.4
C_7H_{15}	682.4	686.0	0.5	1375.1	1372.0	0.2
C_8H_{17}	758.4	764.0	0.7	1530.0	1528.0	0.1

zov and Vinogradova support, in any manner, the thesis that the dialkyl phosphonates are associated. Arbuzov and Vinogradova referred to Gibling as "establishing the influence of association (of fatty acids) on the parachor." Actually Gibling (39) considered only fatty acids which were completely dimerized and showed that his calculations confirmed the dimeric structure. Since Sugden (104) has pointed out that the experimental parachor of associated liquids varies with temperature, it is regrettable that the Russian authors did not determine parachor values as a function of temperature.

In his calculation of the parachor of the trialkyl phosphates, Gibling uses a correction factor of 6.6 (3 × 2.2) for each carbon atom beyond the β-carbon atoms, i.e., he considers that the parallel-chain correction applies to all three chains. It would seem therefore that in the dialkyl phosphonates the parallel-chain corrections should be applied to two chains. The authors have recalculated the theoretical parachor on this basis. The results, compared with Arbuzov's calculations based on a dimeric form, are given in table 1. The average of the errors by both methods of calculation is identical (0.3 per cent). The parachor data, therefore, do not justify any assumption that the dialkyl phosphonates are associated.

C. *Viscosity measurements*

The information obtained by Arbuzov and his associates on the structure of various organic phosphorus compounds has been supplemented by viscosity data (10, 11). Viscosities of the following dialkyl phosphonates were determined in either benzene or carbon tetrachloride solution: dibutyl, dihexyl, dicyclohexyl, dioctyl, dinonyl, didecyl, and dihexadecyl. Three different concentrations of each compound were employed, and the experimental results were then used to calculate $\eta^{20}_{sp}(1.4\%)$. This quantity is defined as the specific viscosity of a 1.4 per cent solution. (A second function, Z_η, was also calculated from the experimental results. This function was defined as the specific viscosity of a 0.1 per cent solution; as used by Arbuzov, Z_η is merely one-fourteenth the value of $\eta^{20}_{sp}(1.4\%)$. It should be noted that this use of Z_η apparently differs from that defined by Staudinger, Bier, and Lorentz (100).) According to Staudinger (99), it is possible to calculate theoretical values of the specific viscosity by the relationship

$$\eta^{20}_{sp}\,(1.4\%) = ny$$

where n is the number of methylene groups in the chain and y is a constant which depends only on the solvent. Although the above equation is applied by Staudinger only to hydrocarbons, the Russian authors count phosphorus, oxygen, and hydrogen-bridge atoms as equivalent to a methylene group; only the longest chain is considered in the evaluation of n.

Their results indicate that the experimental values are in better agreement with the theoretical values for the monomers than for the dimers. However, even for the monomers the difference between experimental and theoretical values is so large as to render doubtful any conclusions as to the degree of association of these compounds. The authors claim that somewhat better agreement is obtained if the equivalent viscosity, $\eta_{sp(\ddot{a}qu)}$, is used. The equivalent viscosity is the specific viscosity of a solution the concentration of which, in grams per liter, equals M/n, where M is the molecular weight and n is again the number of atoms of the longest chain. Theoretical values for the equivalent viscosity may be calculated, according to Staudinger, from the relationship

$$\eta_{sp(\ddot{a}qu)} = K_{\ddot{a}qu} \times M$$

where $K_{\ddot{a}qu}$ is a constant which depends only on the solvent.

It is difficult to assess the value of the results reported for the equivalent viscosities. There are, in the first place, a number of arithmetical errors in the calculations which tend to bias the results in favor of the monomeric form. The authors have recalculated the equivalent viscosities from the data given; their results are listed in table 2. The data still favor the monomeric form, although for several compounds the difference between calculated and found values is so large as to cast doubt on the results. There would seem to be little justification for drawing any conclusions as to the structure of dialkyl phosphonates from these viscosity measurements.

TABLE 2

The equivalent viscosity of dialkyl phosphonates calculated for the monomeric and dimeric forms

R in $(RO)_2P(O)H$	$\overset{20}{\eta}\mathrm{sp}$(äqu) × 10^{-3} for the Monomer		Difference	$\overset{20}{\eta}\mathrm{sp}$(äqu) × 10^{-3} for the Dimer		Difference
	Found (mean ± standard deviation)	Calculated		Found (mean ± standard deviation)	Calculated	
			per cent			*per cent*
C_4H_9	15.9 ± 1.47	21.0	24.4	24.9 ± 2.28	41.9	40.6
C_6H_{13}	26.4 ± 2.47	27.0	2.1	44.0 ± 4.14	54.1	18.6
C_8H_{17}	27.1 ± 0.95	33.1	17.8	46.7 ± 1.75	66.2	29.5
C_9H_{19}	33.1 ± 3.89	36.1	8.3	57.9 ± 6.79	72.2	19.8
$C_{10}H_{21}$	35.7 ± 2.26	39.1	8.7	63.2 ± 3.96	78.3	19.6
$C_{16}H_{33}$	60.3 ± 0.93	57.3	4.9	111.4 ± 1.70	114.6	2.8

D. Molecular weights

Evidence for the association of dialkyl phosphonates based on spectral measurements, parachor values, etc., is largely a question of interpretation of data and can obviously lead to equivocal results. This should not be the case, however, with the cryoscopic determination of molecular weights, which for many years has been a satisfactory method for demonstrating association through hydrogen bonding (64). One restriction imposed in such determinations is that the solutions used should be sufficiently dilute that Raoult's law applies (42). Several determinations of molecular weights of dialkyl phosphonates have been made; where the above rule has been considered, the results are in complete agreement with the monomolecular structure.

The first attempt to determine the molecular weight of dialkyl phosphonates cryoscopically was apparently made by Arbuzov and Vinogradova (9). These authors used benzene as the solvent and obtained the following results: with dimethyl phosphonate in concentrations of 0.632 to 27.439 moles per cent, the molecular weight ranged from 117.6 to 222.8; with diisopropyl phosphonate in concentrations of 0.397 to 20.88 moles per cent, the molecular weight ranged from 160.0 to 202.4; with dioctyl phosphonate in concentrations of 0.951 to 12.637 moles per cent the molecular weight actually decreased from 305.9 to 278.1. From these data the authors concluded that the dimethyl and diisopropyl compounds are associated, the former as a dimer, whereas the dioctyl compound exists only as the monomer. The authors (12) also reported that compounds of the type RP(OR)(O)H are monomolecular in solution.

Kosolapoff and Powell (60) independently determined the molecular weights of several dialkyl phosphonates in nonpolar solvents. Diethyl phosphonate gave molecular-weight values of 138–141 (theoretical 138) at molalities of 0.05 to 0.13 in naphthalene solution. Similarly, dibutyl phosphonate showed no significant deviation from the monomeric molecular-weight value in the same solvent (molalities not stated). In a note added in proof Kosolapoff and Powell are critical of the molecular-weight results obtained by Arbuzov and Vinogradova, because of the concentrated solutions employed. In another paper, Kosolapoff and Powell (59) report that the values found for the molecular weight of diethyl phosphonate in benzene (molalities not given) are in essentially perfect agreement with the calculated value of the monomer. They suggest that the presence of a true hydroxyl group is essential for association and that the dialkyl phosphonates and similar compounds possessing the =P(O)H grouping do not associate, at least in benzene solution.

Serra and Malatesta (95) have also determined the molecular weight of dimethyl phosphonate cryoscopically in benzene solution; the values found were 135 and 132, for a theoretical value of 110. No molalities or other experimental details are given, and it is difficult to draw conclusions from the meager data listed.

A more complete study of the molecular weights of these compounds has recently been reported by Page and Purnell (83). The dimethyl, diethyl, and dipropyl phosphonates were unequivocally monomolecular in camphor at all concentrations studied (mole fractions of approximately 0.01 to 0.15 as judged from the published graphs). The dipropyl compound was also monomolecular in benzene over a wide range of concentration. With the diethyl compound, one point deviated a few per cent from the calculated value for the monomer when the freezing-point depression was approximately 3°C. With the dimethyl compound, there were two points which indicated a slight degree of association. Both points were obtained with freezing-point depressions in excess of 2°C. At a concentration of 0.05 mole fraction, the amount dimerized was calculated as 13 per cent, from which, by extrapolation, a value of 75 per cent dimerization for the pure ester was obtained.

From this evidence Page and Purnell (83) conclude that their cyroscopic measurements substantiate the general claims of Arbuzov and his coworkers. It is difficult to follow this argument. Thus, Page and Purnell's evidence clearly indicates that the dipropyl compound is monomeric, whereas the Russian authors claim that this compound is 40 per cent dimerized. The cryoscopic evidence for the association of the diethyl ester is so slight as to be negligible, whereas the Russian workers claim that this compound is almost completely (88 per cent) associated. Since the actual figures are not given by Page and Purnell, it is difficult to assess the deviations from the monomeric values observed for dimethyl phosphonate. The maximum deviation of 13 per cent is larger than the experimental error usually found, although when the depressions did not exceed 1° there was no evidence of association. At least one standard text (31) on physical chemistry warns that for an accurate determination of molecular weight, the depression should not exceed 0.5°C. The authors are inclined to attribute the small deviations obtained by Page and Purnell to experimental error. In this connection some results recently reported (23) for trioctylphosphine oxide are of interest. This compound, which cannot be associated by hydrogen bonding, gives cryoscopic molecular weights in benzene which are 10 per cent higher than the theoretical.

An interesting and unexpected result was obtained by Serra and Malatesta (95) in the work referred to above. These authors discovered that when dimethyl phosphonate was heated for 10 hr. in a dry atmosphere the molecular weight of the resulting compound apparently increased from 132–135 to 218–220. They attributed this to dimerization through hydrogen bonding, a conclusion which is difficult to understand. Accordingly, the authors have repeated some of the work of the Italian investigators, obtaining results which may be summarized as follows (36): When dimethyl phosphonate is heated in an inert atmosphere for periods of 10 hr. or longer, a series of complicated reactions occurs and a number of products can be isolated. Phosphine is evolved as the temperature rises. At the completion of the heating period, vacuum distillation gave a volatile acidic fraction and a thick undistillable residue. The volatile fraction consisted principally of dimethyl methylphosphonate, admixed with methylphosphonic acid or methyl hydrogen methylphosphonate, or, most probably, both. The undistillable residue could be hydrolyzed to phosphoric and methylphosphonic acids and undoubtedly consisted of mixed anhydrides of these two acids. The thermal rearrangement of dimethyl methylphosphonate has also been reported by other workers (17, 18, 93). There would seem to be no justification for the claim of Serra and Malatesta that dimethyl phosphonate dimerizes on heating.

E. Boiling points and the possibility of dipole–dipole association

It must be concluded from the data reviewed in the above sections that there is no convincing evidence that dialkyl phosphonates are associated through hydrogen bonds. Indeed, it is hard to understand why this type of association has been seriously considered. An essential requirement for hydrogen bonding is that the hydrogen atom be attached to a strongly electron-attracting element, e.g., fluorine, oxygen, or nitrogen (13, 50, 55; 84, p. 286; 110). Phosphorus has an electronegativity value of 2.1 and is, accordingly, less electron-attracting than sulfur, iodine, or carbon (84, p. 64). As one would expect from the low electronegativity of phosphorus, phosphine is a very weak acid (pK_a about 29) and is not associated in the liquid state (82). It does not seem likely, therefore, that the P—H group can behave as a proton donor in hydrogen bonding.

An important fact relevant to the question of association in dialkyl phosphonates appears to have been ignored by previous writers on this subject. This fact is that dialkyl phosphonates have abnormally high boiling points (*cf.* table 3). For example, dipropyl phosphonate has a boiling point 44° higher than that of triethyl phosphite, although both compounds have the same molecular weight. Even more striking is the case of dimethyl phosphonate, which has a lower molecular weight than trimethyl phosphite but boils about 60° higher. By contrast, the boiling points of dialkyl phosphonates are almost the same as the boiling points of dialkyl alkylphosphonates of equal molecular weight. Thus, dipropyl phosphonate and diethyl ethylphosphonate have virtually identical boiling points (203°C. vs. 198°C.). Van Wazer (108, p. 377) has pointed out that "isomers in which the phosphorus is triply connected to its neighboring atoms are found to have uniformly lower boiling points," but no explanation for this phenomenon has been explicitly given. It is obvious that there is no possibility of hydrogen bonding in the dialkyl alkylphosphonates. However, these compounds as well as the dialkyl phosphonates contain the phosphoryl group, which possesses a moderately large permanent dipole moment (5, 85, 97). It seems reasonable, therefore, to attribute the abnormally high boiling points of phosphonate esters to dipole–dipole

TABLE 3

Boiling points of some phosphites and phosphonates

Alkyl Group	Trialkyl Phosphite	Dialkyl Phosphonate	Dialkyl Alkylphosphonate
	°C.	*°C.*	*°C.*
Methyl	111[a]	170.6[d]	181[a]
Ethyl	159[a]	190.0[d]	198[a]
Propyl	206[b]	203.0[d]	126 at 18 mm.[e]
Butyl	127 at 18 mm.[c]	230.3[d]	160 at 20 mm.[f]

[a] Taken from reference 108, p. 376.

[b] Taken from reference 57, p. 203.

[c] Taken from reference 57, p. 204.

[d] Taken from reference 83. The values given are the computed boiling points at 1 atm. and were derived from experimental results obtained at lower pressures.

[e] Taken from reference 57, p. 149.

[f] Taken from reference 57, p. 150.

association of the phosphoryl groups. A similar type of explanation has been used to account for the boiling points of nitriles (78, p. 250), carbonyl compounds (78, p. 197), and nitro compounds (78, p. 455). The possibility of dipole–dipole association due to the phosphoryl group (in compounds other than the dialkyl phosphonates) has been previously discussed in the literature (14, 70). It may be concluded, therefore, that dialkyl phosphonates are probably associated *in the liquid state*, but that hydrogen bonding has nothing to do with this association. A similar conclusion concerning the structure of dibenzyl phosphonate has been reached from dielectric constant measurements, which indicate that this compound does not exhibit a dimeric structure but rather a type of association similar to that of ketones and nitrobenzene (81).

III. THE TAUTOMERIC EQUILIBRIUM $(RO)_2P(O)H \rightleftharpoons (RO)_2POH$

A. Chemical evidence

The dialkyl phosphonates are neutral substances which do not react with aqueous bases to form salts. In contrast to the trialkyl phosphites, in which the phosphorus must be trivalent, the dialkyl phosphonates are resistant to oxidation and do not form addition compounds with cuprous halides. Consideration of these properties led A. E. Arbuzov (3) to formulate these compounds as possessing the structure $(RO)_2P(O)H$.

In some of their reactions, the dialkyl phosphonates behave as typical electrophilic reagents. Thus they react with an excess of the Grignard reagent to form the dialkyl- or diarylphosphine oxides (111):

$$(RO)_2P(O)H \xrightarrow{R'MgX} R'_2P(O)H$$

This is a typical electrophilic attack of phosphorus on the carbanion of the Grignard reagent.

Dialkyl phosphonates in organic solvents react with alkali metals, with the evolution of hydrogen and the formation of the corresponding salts. Sodium salts can also be prepared by using sodium alkoxides. Silver salts are prepared when the esters, in aqueous solution or suspension, are treated with ammoniacal silver nitrate and the resulting solution carefully neutralized with nitric acid. Other metallic salts of dialkyl phosphonates are also known.

Daasch (28) has investigated the infrared spectra of the lithium, sodium, potassium, and silver salts of several dialkyl phosphonates. In the majority of salts studied there was a complete absence of the phosphoryl frequency. (The slight absorption found in a few cases was attributed to hydrolysis by atmospheric moisture during transfer of the samples.) This result is sufficient evidence, Daasch believes, for ruling out the phosphonate structure for these salts. All salts studied exhibited strong absorption at 1050 $cm.^{-1}$, which is characteristic for both the $P—O^-$ and the $P—O—R$ groups, so that direct evidence for the structure $[(RO)_2PO]^-Na^+$ could not be obtained. In fact, Daasch favors a structure containing a covalent oxygen–metal bond. This reasoning is based on the remarkable solubility of the alkali metal salts in nonpolar solvents (e.g., the sodium salt of dibutyl phosphonate is readily soluble in petroleum ether) and on "calculations of 70 to 75% covalent character for the metallic bonds." It is unfortunate that x-ray diffraction studies of these salts have not been undertaken, since valuable information would probably be obtained.

It has been argued (52, 71, 79) that the formation of metallic salts, which must exist in the trivalent form, is evidence for the phosphonate–phosphite equilibrium. However, since phosphine itself, as well as primary and secondary phosphines, will form metallic salts, and since the anion of the dialkyl phosphonate is the same regardless of whether it is derived from the phosphonate or from the phosphite form, the above argument is not valid.

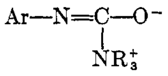
The alkali metal salts of the dialkyl phosphonates are powerful nucleophilic reagents and react with a wide variety of substances which contain electrophilic centers. This fact is in accord with the phosphite structure of these salts. The dialkyl phosphonates themselves also undergo a variety of reactions in which the ester acts as a nucleophile. The majority of these reactions are base catalyzed. Fox (32, p. 1) has stated that over two hundred papers have been published in the last ten years on the base-catalyzed condensation of dialkyl phosphonates with unsaturated compounds. An excellent review of this subject has recently been published (86). Mechanisms which involve the removal of a proton by the base to form the anion, $(RO)_2PO^-$, have been suggested by a number of workers (32, p. 13; 35, 67, 82, 101). The base-catalyzed reaction, from this viewpoint, is similar to the reactions of the salts themselves.

Kabachnik (52, 53, 54) has suggested that the phosphonate–phosphite equilibrium, which in a medium S may be represented thus:

$$(RO)_2P(O)H + S \rightleftharpoons (RO)_2PO^- + HS^+ \rightleftharpoons (RO)_2POH + S$$

is affected by the basicity of the solvent. Accordingly, Kabachnik and Golubeva (52) studied the addition of sulfur to diethyl phosphonate in alcohol, toluene, ether, and dioxane as well as in the absence of a solvent. Only in the most basic solvent, dioxane, did the reaction give a satisfactory yield of diethyl phosphorothionate. Daasch (28), however, was unable to confirm the above results in dioxane, although the reaction did proceed readily in triethylamine. Furthermore, he was unable to show any change in the infrared spectra of dialkyl phosphonates when dissolved in basic solvents. From this latter evidence he concluded that any shift of the equilibrium in such solvents must be less than that which could be detected by the use of infrared spectroscopy. It should be noted, however, that the sensitivity of infrared spectroscopy is such that several per cent of the ester could be in the phosphite form without being detected by this technique.

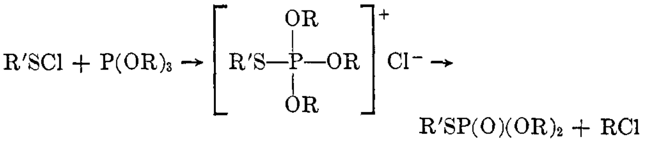
The failure to obtain any change in the infrared spectrum of dialkyl phosphonates in basic solution has led Fox and Venezky (35) to postulate an alternative mechanism for the base-catalyzed addition of these esters to isocyanates. By analogy with the base-catalyzed reaction between alcohols and isocyanates, which has been shown (15, 16) to involve a complex of the type



$$\mathrm{Ar{-}N{=}\underset{\displaystyle NR_3^+}{\underset{|}{C}}{-}O^-}$$

Fox and Venezky (35) suggest an initial attack of the tertiary amine on the isocyanate, followed by a reaction of the resulting complex with the dialkyl phosphonate. No careful kinetic study of the base-catalyzed addition of dialkyl phosphonates to unsaturated compounds has been published, and it seems futile to speculate on the mechanism until this has been done. It should also be noted that at elevated temperatures dialkyl phosphonates react with isocyanates in the absence of a catalyst (89, 90).

Although the base-catalyzed addition of dialkyl phosphonates does not offer concrete evidence for the phosphonate–phosphite equilibrium, other chemical evidence which is somewhat more convincing has been advanced. Morrison (75) has shown that trialkyl phosphites react with sulfenyl halides to give trialkyl phosphorothiolates:



$$\mathrm{R'SCl + P(OR)_3 \rightarrow \left[R'S{-}\overset{\displaystyle OR}{\overset{|}{\underset{\displaystyle OR}{\underset{|}{P}}}}{-}OR \right]^+ Cl^- \rightarrow R'SP(O)(OR)_2 + RCl}$$

This reaction represents a nucleophilic displacement of chloride, followed by elimination of alkyl chloride. Morrison (76) has recently demonstrated that dialkyl phosphonates undergo a similar reaction, with the elimination of hydrogen chloride and formation of trialkyl phosphorothiolates. He also found that trialkylphosphines react with sulfenyl chlorides, but that the reaction stops at the intermediate phosphonium stage:

$$[\mathrm{R_3PSR'}]^+\mathrm{Cl}^-$$

This offers strong proof for the suggested mechanism of the reaction. It seems probable that the dialkyl phosphonates react with the sulfenyl chlorides by a mechanism which involves the phosphite form of the ester.

Although Arbuzov (3) used the fact that trialkyl phosphites form addition compounds with cuprous salts whereas dialkyl phosphonates do not, as an argument for the phosphonate structure of the latter compounds, it has been shown (44) that the dialkyl phosphonates will serve as ligands to tetracovalent platinum under certain conditions. Thus, when triethyl phosphite reacts with potassium chloroplatinate, two compounds are formed:

$$[\mathrm{Pt\{P(OC_2H_5)_3\}_4}][\mathrm{PtCl_4}]$$

and

$$[\mathrm{Pt\{P(OC_2H_5)_2OH\}_2\{PO(OC_2H_5)_2\}_2}]$$

The dialkyl phosphonate arises from partial hydrolysis of the triester. The formation of the second complex has been advanced as an argument for the existence of the phosphite form of the diester. It has also been shown (43) that dimethyl phosphonate hydrolyzes at a different rate from the platinum complex,

$$[\mathrm{Pt\{P(OCH_3)_2OH\}_2\{PO(OCH_3)_2\}_2}]$$

This result has been taken to indicate that in the platinum complex the ester exists in the phosphite form. The argument would seem to have no bearing on the structure of the dialkyl phosphonates in the free state.

Kabachnik (54) has considered that the phosphonate–phosphite equilibrium is an acid-base equilibrium and that substitution of an electron-attracting group such as phenyl for the alkyl groups in the dialkyl phosphonates would increase the probability that the oxygen would accept a proton. Although diphenyl phosphonate does not show the infrared absorption characteristic of the hydroxyl group, many other properties characteristic of the phosphite form were found for this ester. Thus, it reacted with phenyl azide in the cold to form diphenyl phenylphosphoramidate; with sulfur, in the absence of a solvent, to form diphenyl phosphorothionate; and with diazomethane to form diphenyl methyl phosphite. It also formed an addition compound with cuprous chloride. All of these properties, Kabachnik believes, suggest that diphenyl phosphonate exists to a greater extent in the phosphite form than do the dialkyl esters.

B. Infrared and ultraviolet spectra

A number of papers on the vibrational spectra of dialkyl phosphonates have been discussed in Section II,A. All of these studies show the presence of the P—H group and the absence of the O—H group. Daasch (28) has made a determined effort to demonstrate the existence of a "keto–enol" type of equilibrium in dialkyl phosphonates. However, after observing that the infrared spectra of dialkyl phosphonates are virtually unaffected by changes in solvent or temperature, he has concluded that either there is no such equilibrium in these compounds or that the amount of phosphite form is too small to be detected by infrared measurements. In a paper by Sass and Cassidy (92) a statement is found that an unpublished investigation of the infrared (and nuclear magnetic resonance) spectrum of dimethyl phosphonate provides evidence for a phosphonate-phosphite equilibrium in which the amount of phosphite form is about 10 per cent. However, a personal communication from Dr. Sass indicates that subsequent physical measurements in his laboratory have failed to confirm the existence of the phosphite form. Other workers (27) have also referred to unpublished infrared results which suggest that certain dialkyl phosphonates contain a significant proportion of the phosphite form. Fox (32, p. 5) has suggested that this conclusion may have been prompted by the observation of a weak band at about 3400 cm.$^{-1}$ which is in the region of the O—H stretching vibration; this weak band, he believes, may be due to the presence of a small amount of hydrolytic impurities or it may be due to an overtone of some other band.

In marked contrast to all other work on this subject, it was reported in a preliminary note (112) that the infrared spectra of esters of the type $(C_6H_5O)(RO)P(O)H$ (where R is an alkyl group) indicated that these compounds exist largely, if not entirely, in the phosphite form. Recently, however, it has been reported from the same laboratory that the preliminary work was performed on impure compounds; the spectra of the pure esters are consistent with the phosphonate structure. Another paper (48) from this laboratory reports that the infrared spectra of diaryl phosphonates contain a broad band near 3340 cm.$^{-1}$ which can be ascribed to the associated O—H group. However, Houalla and Wolf (48) are careful to point out that this band may be due to impurities, and hence that the spectral results do not prove the existence of the phosphite form of diaryl esters of phosphorous acid. Other workers (54) have reported that the infrared spectrum of diphenyl phosphonate shows a sharp band (at 2420 cm.$^{-1}$) characteristic of the P—H group and a sharp band (at 1280 cm.$^{-1}$) characteristic of the phosphoryl group; no noticeable absorption was found which could be ascribed to the hydroxyl group.

Although phosphorous and phosphoric acids do not absorb in the ultraviolet above 210 mμ (24) and although alkyl groups are not chromophores, it has been reported (46, 94) that several dialkyl phosphonates show selective absorption in the region around 260 mμ. These results, it has been concluded, are consistent with the phosphonate (rather than the phosphite) structure. Earlier workers (73, 74), however, had demonstrated that pure esters of phosphorous acid do *not* absorb in the ultraviolet; the absorption sometimes observed (72) was shown to be due to traces of impurities introduced during the preparation of the esters. More experimental data are needed to settle the question of the nature and significance of the ultraviolet absorption of dialkyl phosphonates.

C. *Nuclear magnetic resonance*

Since the discovery by Knight (56) of chemical shifts in the nuclear magnetic resonance (NMR) of P^{31}, a number of investigators have found that nuclear magnetic resonance spectroscopy can furnish invaluable information about the structure of phosphorus compounds. Phosphorus NMR measurements on dialkyl phosphonates have unequivocally confirmed the generally accepted structure of these compounds and have provided no evidence for the existence of the phosphite form (26, 31, 77, 109). The magnitude of the phosphorus chemical shift is consistent with the assumption that the dialkyl phosphonates contain the phosphoryl group, i.e., there must be a total of four atoms attached to the phosphorus by covalent bonds. Furthermore, the resonance peak is split into a doublet, which shows that one hydrogen atom is attached directly to the phosphorus. (No splitting due to spin-spin coupling is observed in the P^{31} spectra of compounds containing the P—O—H group.) In addition, the P^{31} spectra of the dialkyl phosphonates do not contain peaks in the region where resonance is observed for the trialkyl and triaryl phosphites. It has been estimated (26) from this fact that the phosphite form of the dialkyl phosphonates cannot be present to the extent of as much as 5 per cent. The nuclear magnetic resonance data for phosphorus also show that the "acidic" proton of the dialkyl phosphonates does not readily undergo exchange, whereas there is considerable exchange whenever a hydrogen atom is bonded to an oxygen atom. Proton magnetic resonance measurements on dialkyl phosphonates (66) are in complete agreement with the conclusions reached in the P^{31} studies. In summary, it may be said that neither infrared nor NMR spectroscopy has been able to demonstrate that dialkyl phosphonates exist as mixtures of tautomeric forms.

It is of interest that NMR spectroscopy has confirmed the fact that phosphorous acid (45) is also a tetracovalent derivative of phosphorus.

D. *Miscellaneous physical measurements*

The dipole moments of several dialkyl phosphonates have been determined by Arbuzov and Rakov (5) and are given in table 4. It is seen that the dialkyl phos-

TABLE 4

Dipole moments of some phosphites and phosphonates in carbon tetrachloride

Alkyl Group	Trialkyl Phosphite	Dialkyl Phosphonate	Dialkyl Alkylphosphonate
Methyl	1.83	2.94	2.86
Ethyl	1.96	3.08	2.91
Propyl	1.99	3.15	2.92
Isopropyl	1.98	3.08	2.91
Butyl	1.92	3.17	2.90

phonates have considerably higher moments than the trialkyl phosphites; by contrast, the dialkyl phosphonates and dialkyl alkylphosphonates have very similar moments. These results are not surprising, since the phosphoryl group (which is, of course, absent in the trialkyl phosphites) has a moderately large moment (85, 97). It was also found that the dipole moment of diethyl phosphonate varies slightly as the solvent is changed. This variation, the Russian workers concluded, is due to changes in the ratio of phosphite to phosphonate forms. However, the dipole moment in general varies with the solvent even in the absence of tautomerism (96). Accordingly, the dipole moment data on dialkyl phosphonates give us no information concerning the existence or nonexistence of the phosphite form.

The attempted use of parachor data for investigating the possibility of association in dialkyl phosphonates has been discussed in Section II,B. Parachors have also been consiedred in connection with the question of tautomerism in these compounds (8). Samuel (91) has proposed a set of atomic parachors in which different values are used for different valence states of the same element. Using Samuel's values, Arbuzov and Vinogradova (8) calculated theoretical parachors for both phosphonate and phosphite forms. Table 5 lists these values as well as the values actually observed. It is seen that in every case the observed parachor is closer to the theoretical value for the phosphonate form. Unfortunately, however, the difference between the calculated values for the two forms is so small (2.9 units) that these parachor data are unable to provide any useful information concerning the structure of the dialkyl phosphonates.

TABLE 5

Comparison of the calculated and observed parachors of dialkyl phosphonates

Alkyl Group	Phosphonate Form	Phosphite Form	Observed Value
Methyl	225.0	227.9	226.3
Ethyl	303.0	305.9	302.6
Propyl	381.0	383.9	379.0
Isopropyl	381.0	383.9	377.8
Butyl	459.0	461.9	454.7
Isobutyl	459.0	461.9	453.1
Hexyl	615.0	617.9	608.0
Heptyl	693.0	695.9	686.0
Octyl	771.0	773.9	764.0

Stelling (102) has used x-ray absorption spectroscopy to investigate the structure of dialkyl phosphonates and their metallic derivatives. He found that the spectrum of the silver derivative of diethyl phosphonate was similar to that of the trialkyl phosphites, while the spectrum of the sodium derivative was similar to that of the free dialkyl phosphonate. From these results Stelling concluded that the silver derivative exists in the phosphite form, $(RO)_2POAg$, and that the sodium derivative exists in the form in which the phosphorus is connected to four neighboring atoms, with the sodium bound directly to the phosphorus. Although none of these measurements were performed on solutions, he suggested that in solution the diesters and their metallic derivatives are probably tautomeric mixtures containing trivalent and pentavalent phosphorus. Stelling's data are quite interesting, but they do not of course prove that dialkyl phosphonates can exist in a phosphite form.

In 1926 Strecker and Spitaler (103) determined the molar refraction (MR) values of diethyl phosphonate and other phosphorus compounds and concluded that these measurements indicated that the phosphorus atom was pentavalent in the diesters of phosphorous acid. Kosolapoff (58) has reported the molar refraction values of a number of dialkyl phosphonates and has found that excellent agreement between observed and theoretical values is obtained if the atomic refraction (AR) of phosphorus is taken as 4.44. This is a very reasonable value since the phosphorus in phosphates and pyrophosphates has an AR of 3.75, the phosphorus in phosphonic acid (RPO_3H_2) derivatives has an AR of 4.27, and the phosphorus in phosphinic acid (R_2PO_2H) derivatives has an AR of 4.79 (51, 61). By contrast the AR value of phosphorus in trivalent derivatives [such as $(RO)_3P$ or $ROPX_2$] has a value of 7.04. It is obvious, then, that these molar refraction data support the generally accepted structure of the dialkyl phosphonates but cannot be used to confirm or exclude the possible presence of a small amount of phosphite form. Very recently Quesnel and Mavel (88) have employed a bond refraction method (rather than the atomic refraction method) for the calculation of theoretical molar refractions of both the phosphonate and phosphite forms of seventeen dialkyl phosphonates. In every case the results indicated that the phosphonate form predominated. However, in fourteen of the seventeen cases the observed value was higher than theoretical for this form; the authors attributed this result to the presence of varying amounts of the phosphite tautomer, since the theoretical value for this form was 2.06 units higher than that for the phosphonate form. They then calculated that the amount of phosphite form present in the fourteen esters varied between 1 and 43 per cent. This procedure is open to criticism, since the error in the molar refraction values may be a significant fraction of 2.06 units. For example, the refraction value for the P—H bond used is uncertain by approximately 0.4 unit. It seems unwise therefore to rely on differences as small as 0.02 unit (as the authors have done) for determining the concentration of the phosphite form.

A study of the magnetic rotatory power of dialkyl phosphonates and related compounds has been reported by Gallais and Voigt (37). They found that the contribution of the phosphorus atom to the total magnetic rotatory power was virtually the same in phosphorous acid, dialkyl alkylphosphonates, and dialkyl phosphonates; the contribution of the phosphorus in trialkyl phosphites was much greater. The authors concluded, therefore, that phosphorous acid and its dialkyl esters are *not* trivalent derivatives of phosphorus but have a structure similar to that of the dialkyl alkylphosphonates. These results, in common with all other physical measurements so far reported, show that dialkyl phosphonates exist predominantly (but not necessarily completely) in the phosphonate form.

E. Kinetic evidence

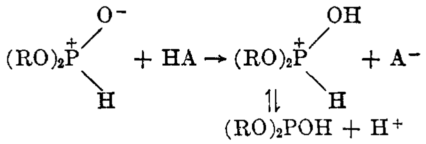
Kinetics have proved to be a valuable tool in the study of tautomeric equilibria. The classical studies of Lapworth (62) on the bromination of acetone may be said to have initiated the modern era of theoretical organic chemistry. Since the phosphonate–phosphite equilibrium bears at least a superficial resemblance to keto–enol tautomerism, it is to be expected that kinetics would be applied to this problem.

The first application of kinetics to the phosphonate–phosphite problem was reported by Nylén (79), who studied the iodination and bromination of diethyl phosphonate. The reactions were run in buffered solutions in the presence of potassium iodide (or bromide). The study was later extended to include the dimethyl, dipropyl, diisopropyl, and dibutyl esters (80). The rate of the reaction was found to increase with the concentration of phosphonate and was always first order with respect to the ester. With low concentrations of iodine, the reaction rate increased with increasing iodine concentration; but with an excess of iodine, the reaction rate depended only on the concentration of ester. The rate was independent of the halogen (iodine or bromine) used, and was subject to general acid–base catalysis. In acid solution, however, the kinetics were complicated by ester hydrolysis. When the concentration of iodide ion was increased, the rate was unaffected; from this result the author concluded that the reactive species was the triiodide ion.

The fact that the rate was independent of both the halogen used and its concentration, as well as the general acid–base catalysis, led Nylén to formulate a prototropic shift as the rate-controlling step of the reaction. He was led to this conclusion from a consideration of other chemical evidence for the phosphonate–phosphite equilibrium. Much of the evidence (discussed in Section III,A) is not convincing; however, there is no doubt that his kinetic results are best explained by postulating the existence of this equilibrium.

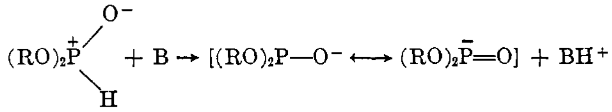
Kinetics of this reaction were extended to nonaqueous solution by Fox (33), who employed butyl alcohol as the solvent and dibutyl phosphonate as the ester. The reaction was complicated by the occurrence of several side reactions. In general, however, the rate was first order with respect to phosphonate when low iodine and high buffer concentrations were employed. The reaction appeared to be zero order with respect to iodine. Although subject to general acid–base catalysis, the order of the reaction with respect to either acid or base could not be established. In the absence of added acid or base the reaction was autocatalytic.

Fox suggests that the rate-controlling step of the acid-catalyzed reaction is the protonation of the phosphonate form of the ester:



$$(RO)_2\overset{+}{P}(O^-)(H) + HA \rightarrow (RO)_2\overset{+}{P}(OH)(H) + A^-$$
$$(RO)_2\overset{+}{P}(OH)(H) \rightleftharpoons (RO)_2POH + H^+$$

In the base-catalyzed reaction the usual removal of a proton is suggested as rate-controlling:



$$(RO)_2\overset{+}{P}(O^-)(H) + B \rightarrow [(RO)_2P{-}O^- \longleftrightarrow (RO)_2\bar{P}{=}O] + BH^+$$

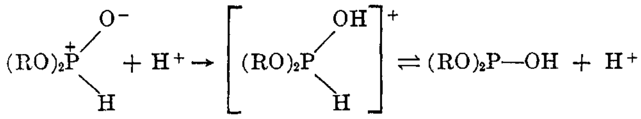
Near the neutral point there was considerable overlapping of the two pathways with the base-catalyzed reaction predominating. Thus, the kinetic results in butyl alcohol are in essential agreement with the earlier observations of Nylén and suggest that the actual species reacting with the halogen is the phosphite form.

Fox (32) has also studied the rate of deuterium exchange between dibutyl phosphonate and butyl alcohol-*d*, in the presence of acid and base as catalysts, and with and without a solvent. The reaction rate was followed by infrared spectroscopy in which the change of the absorbance of the O—H band at 2.9 μ was followed as a function of time.

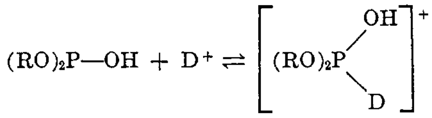
In acid solution the necessary catalysis was accomplished by adding *p*-toluenesulfonyl chloride, where the following interchange was assumed to go nearly to completion:

$$p\text{-}CH_3C_6H_4SO_2Cl + C_4H_9OD \rightarrow p\text{-}CH_3C_6H_4SO_2OC_4H_9 + DCl$$

The rate was independent of the concentration of butyl alcohol-*d* but dependent upon the amount of added *p*-toluenesulfonyl chloride. This suggests that the rate-controlling step in the acid-catalyzed reaction is protonation of the phosphonate molecule followed by rapid deuteration at the free electron pair of the phosphorus:

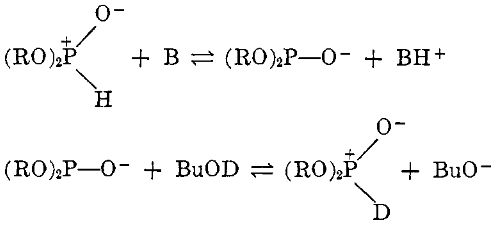


$$(RO)_2\overset{+}{P}(O^-)(H) + H^+ \rightarrow \left[(RO)_2P(OH)(H)\right]^+ \rightleftharpoons (RO)_2P{-}OH + H^+$$



$$(RO)_2P{-}OH + D^+ \rightleftharpoons \left[(RO)_2P(OH)(D)\right]^+$$

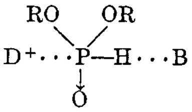
The base-catalyzed reaction is dependent on the concentration of both the base and the attacking reagent. Unfortunately, the accuracy of the data did not permit the determination of the order of the reaction. However, Fox considers that the data suggest one of two mechanisms. The first involves removal of a proton from the phosphonate molecule, followed by the reaction of the resulting conjugate base with the weak acid, butyl alcohol-*d*, with both reactions rate-controlling.



$$(RO)_2\overset{+}{P}(O^-)H + B \rightleftharpoons (RO)_2P{-}O^- + BH^+$$

$$(RO)_2P{-}O^- + BuOD \rightleftharpoons (RO)_2\overset{+}{P}(O^-)D + BuO^-$$

The second mechanism considered is a termolecular attack of base and deuterium ion on the phosphonate molecule:



$$D^+\cdots P(OR)_2(\rightarrow O){-}H\cdots B$$

This mechanism is based on the so-called push-pull mechanism of Swain (105) for explaining reactions which are catalyzed by both acid and base. However, in this case it is difficult to understand how the deuterium ion, which must be present in vanishing low concentrations in basic solution, can take part in the reaction.

Finally, in neutral solution, it was shown that the deuteration is slower by several orders of magnitude than either the acid- or the base-catalyzed reaction. From this result Fox concludes that, if the tautomeric phosphonate–phosphite equilibrium exists, the phosphite form can be present only in approximately the same concentration as the enol form of acetone in aqueous solution, i.e., about 10^{-4} per cent. This conclusion is consistent with other reactions of dialkyl phosphonates in neutral solution, such as the uncatalyzed reaction of these esters with sulfur, whch occurs to a small but definite amount in the absence of added base (52).

F. Conclusions

Both the chemical evidence (Section III,A) and the kinetic data (Section III,E) are best interpreted by assuming that a dialkyl phosphonate is in equilibrium with a phosphite form. The only reliable estimate of the amount of the latter form comes from the work of Fox (32), who suggested that dibutyl phosphonate contains about 10^{-4} per cent phosphite. All of the physical measurements are in agreement with the conclusion that dialkyl phosphonates exist predominantly in the phosphonate form; however, none of the methods employed would have detected even as much as 1 per cent of the phosphite form. It seems reasonable to conclude, therefore, that dialkyl phosphonates do exist as mixtures of tautomeric forms. Further work is necessary in order to determine the amount of phosphite form actually present.

IV. REFERENCES

(1) Albright and Wilson Ltd.: *Dialkyl Phosphites.* London (1958).
(2) Anon.: Chem. Eng. News **30,** 4515 (1952).
(3) Arbuzov, A. E.: Dissertation, Kazan (1905). The place listed for this dissertation is somewhat confusing. Kosolapoff (57, p. 194) gives Kazan; Fox (32, p. 16) gives New Alexandria, while Kabachnik and Polikarpov (54) give St. Petersburg. Dr. Kosolapoff has explained, in a personal communication, that Arbuzov received his undergraduate degree from Kazan University and his master's degree from New Alexandria. He selected Kazan as the site for the defense of his thesis. The actual printing of the thesis was done in St. Petersburg and Moscow.
(4) Arbuzov, A. E., Batuev, M. I., and Vinogradova, V. S.: Doklady Akad. Nauk S.S.S.R., **54,** 599 (1946).
(5) Arbuzov, A. E., and Rakov, P. I.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk **1950,** 237; Chem. Abstracts **44,** 8713 (1950).
(6) Arbuzov, B. A., and Vinogradova, V. S.: Doklady Akad. Nauk S.S.S.R. **54,** 787 (1946).
(7) Arbuzov, B. A., and Vinogradova, V. S.: Doklady Akad. Nauk S.S.S.R. **55,** 31 (1947).
(8) Arbuzov, B. A., and Vinogradova, V. S.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk **1947,** 617.
(9) Arbuzov, B. A., and Vinogradova, V. S.: Doklady Akad. Nauk S.S.S.R. **72,** 695 (1950).
(10) Arbuzov, B. A., and Vinogradova, V. S.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk **1952,** 507.
(11) Arbuzov, B. A., and Vinogradova, V. S.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk **1952,** 865.
(12) Arbuzov, B. A., and Vinogradova, V. S.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk **1954,** 622; Chem. Abstracts **49,** 11541 (1955).
(13) Badger, G. M.: Revs. Pure and Appl. Chem. (Australia) **7,** 55 (1957).
(14) Baes, C. F., Jr.: ORNL Report 2737, p. 7, July 2, 1959.
(15) Baker, J. W., and Gaunt, J.: J. Chem. Soc. **1949,** 9.
(16) Baker, J. W., and Holdsworth, J. B.: J. Chem. Soc. **1947,** 713.
(17) Beach, L. K.: U. S. patent 2,908,708 (October 13, 1959); Chem. Abstracts **54,** 3202 (1960).
(18) Beach, L. K., and Drogin, R.: U. S. patent 2,863,900 (December 9, 1958); Chem. Abstracts **53,** 9059 (1959).
(19) Bellamy, L. J.: *The Infrared Spectra of Complex Molecules,* 2nd edition, p. 320. John Wiley and Sons, Inc., New York (1958).
(20) Bellamy, L. J., and Beecher, L.: J. Chem. Soc. **1952,** 475.
(21) Bellamy, L. J., and Beecher, L.: J. Chem. Soc. **1952,** 1701.
(22) Bennett, F. W., Emeléus, H. J., and Haszeldine, R. N.: J. Chem. Soc. **1954,** 3598.
(23) Brown, K. B., Coleman, C. F., Crouse, D. J., and Ryon, A. D.. ORNL Report 2443, p. 12, September, 1957.
(24) Buck, R. P., Singhadeja, S., and Rogers, L. B.: Anal. Chem. **26,** 1240 (1954).

(25) Burger, L. L., and Wagner, R. M.: Chem. Eng. Data Ser. **3**, 310 (1958).

(26) Callis, C. F., Van Wazer, J. R., Shoolery, J. N., and Anderson, W. A.: J. Am. Chem. Soc. **79**, 2719 (1957).

(27) Cook, H. G., Ilett, J. D., Saunders, B. C., Stracey, G. J., Watson, H. G., Wilding, I. G. E., and Woodcock, S. J.: J. Chem. Soc. **1949**, 2923.

(28) Daasch, L. W.: J. Am. Chem. Soc. **80**, 5301 (1958).

(29) Daasch, L. W., and Smith, D. C.: Anal. Chem. **23**, 853 (1951).

(30) Findlay, A.: *Practical Physical Chemistry*, p. 120. Longmans, Green and Company, London (1923).

(31) Finegold, H.: Ann. N. Y. Acad. Sci. **70**, 875 (1958).

(32) Fox, R. B.: NRL Report 5242, January 8, 1959.

(33) Fox, R. B.: NRL Report 5335, July 24, 1959.

(34) Fox, R. B., and Lockhart, L. B.: "The Chemistry of Organo-Phosphorus Compounds," NRL Report C-3323, pp. 58–63, July 8, 1948.

(35) Fox, R. B., and Venezky, D. L.: J. Am. Chem. Soc. **78**, 1661 (1956).

(36) Freedman, L. D., and Doak, G. O.: To be published.

(37) Gallais, F., and Voigt, D.: Compt. rend. **226**, 577 (1948).

(38) Gibling, T. W.: J. Chem. Soc. **1941**, 299.

(39) Gibling, T. W.: J. Chem. Soc. **1942**, 661.

(40) Gibling, T. W.: J. Chem. Soc. **1943**, 146.

(41) Gibling, T. W.: J. Chem. Soc. **1944**, 380.

(42) Glasstone, S.: *Textbook of Physical Chemistry*, 2nd edition, pp. 646, 675. D. Van Nostrand Company, Inc., New York (1946).

(43) Grinberg, A. A., Itshovich, T. B., and Troitskaya, A. D.: Zhur. Neorg. Khim. **4**, 30 (1959).

(44) Grinberg, A. A., and Troitskaya, A. D.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk **1944**, 178; Chem. Abstracts **39**, 1604 (1945).

(45) Gutowsky, H. S., McCall, D. W., and Slichter, C. P.: J. Chem. Phys. **21**, 279 (1953).

(46) Hauss, J. L. de: Chim. anal. **34**, 248 (1952).

(47) Herzberg, G.: *Infrared and Raman Spectra*, p. 164. D. Van Nostrand Company, Inc., New York (1945).

(48) Houalla, D., and Wolf, R.: Compt. rend. **247**, 482 (1958).

(49) Houalla, D., and Wolf, R.: Bull. soc. chim. France **1960**, 129.

(50) Hunter, L.: Ann. Repts. on Prog. Chem. (Chem. Soc. London) **43**, 141 (1946).

(51) Kabachnik, M. I.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk **1948**, 219; Chem. Abstracts **42**, 5736 (1948).

(52) Kabachnik, M. I., and Golubeva, E. I.: Doklady Akad. Nauk S.S.S.R. **105**, 1258 (1955).

(53) Kabachnik, M. I., and Ioffe, S. T.: Doklady Akad. Nauk S.S.S.R. **91**, 833 (1953); Chem. Abstracts **48**, 1779 (1954).

(54) Kabachnik, M. I., and Polikarpov, Yu. M.: Doklady Akad. Nauk S.S.S.R. **115**, 512 (1957).

(55) Ketelaar, J. A. A.: *Chemical Constitution*, p. 425. Elsevier Publishing Company, Amsterdam (1958).

(56) Knight, W. D.: Phys. Rev. **76**, 1259 (1949).

(57) Kosolapoff, G. M.: *Organophosphorus Compounds.* John Wiley and Sons, Inc., New York (1950).

(58) Kosolapoff, G. M.: J. Am. Chem. Soc. **73**, 4989 (1951).

(59) Kosolapoff, G. M., and Powell, J. S.: J. Am. Chem. Soc. **72**, 4291 (1950).

(60) Kosolapoff, G. M., and Powell, J. S.: J. Chem. Soc. **1950**, 3535.

(61) Kosolapoff, G. M., and Watson, R. M.: J. Am. Chem. Soc. **73**, 4101 (1951).

(62) Lapworth, A.: J. Chem. Soc. **85**, 30 (1904).

(63) Larsson, L., Holmstedt, B., and Tjus, E.: Acta Chem. Scand. **8**, 1563 (1954).

(64) Lassettre, E. N.: Chem. Revs. **20**, 263 (1937).

(65) Maarsen, J. W., Smit, M. C., and Matze, J.: Rec. trav. chim. **76**, 713 (1957).

(66) Mavel, G.: Compt. rend. **248**, 3699 (1959).

(67) McConnell, R. L., and Coover, H. W., Jr.: J. Am. Chem. Soc. **79**, 1961 (1957).

(68) McIvor, R. A., Grant, G. A., and Hubley, C. E.: Can. J. Chem. **34**, 1611 (1956).

(69) Meyrick, C. I., and Thompson, H. W.: J. Chem. Soc. **1950**, 225.

(70) Miller, C. D., Miller, R. C., and Rogers, W., Jr.: J. Am. Chem. Soc. **80**, 1562 (1958).

(71) Milobedzki, T.: Ber. **45**, 298 (1912).

(72) Milobedzki, T., and Borowski, W.: Roczniki Chem. **18**, 725 (1938); Chem. Abstracts **33**, 6156 (1939).

(73) Milobedzki, T., and Borowski, W.: Roczniki Chem. **19**, 507 (1939); Chem. Abstracts **34**, 3986 (1940).

(74) Milobedzki, T., and Lewandowski, M.: Roczniki Chem. **19**, 509 (1939); Chem. Abstracts **34**, 3986 (1940).

(75) Morrison, D. C.: J. Am. Chem. Soc. **77**, 181 (1955).

(76) Morrison, D. C.: Abstracts of Papers Presented at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958, p. 87P.

(77) Muller, N., Lauterbur, P. C., and Goldenson, J.: J. Am. Chem. Soc. **78**, 3557 (1956).

(78) Noller, C. R.: *Chemistry of Organic Compounds*, 2nd edition. W. B. Saunders Company, Philadelphia and London (1957).

(79) Nylén, P.: Dissertation, Uppsala (1930).

(80) Nylén, P.: Z. anorg. u. allgem. Chem. **235**, 161 (1938).

(81) Oehme, F., Hermann, H., and Venner, H.: Chem. Ber. **90**, 772 (1957).

(82) Paddock, N. L.: Chem. & Ind. (London) **1955**, 900.

(83) Page, F. M., and Purnell, J. H.: J. Chem. Soc. **1958**, 621.

(84) Pauling, L.: *The Nature of the Chemical Bond*, 2nd edition. Cornell University Press, Ithaca, New York (1944).

(85) Phillips, G. M., Hunter, J. S., and Sutton, L. E.: J. Chem. Soc. **1945**, 146.

(86) Pudovick, A. N.: Uspekhi Khim. **23**, 547 (1954).

(87) Quayle, O. R.: Chem. Revs. **53**, 439 (1953).

(88) Quesnel, G., and Mavel, G.: Compt. rend. **248**, 695 (1959).

(89) Reetz, T.: U. S. patent 2,909,558 (October 20, 1959); Chem. Abstracts **54**, 3204 (1960).

(90) Reetz, T., Chadwick, D. H., Hardy, E. E., and Kaufman, S.: J. Am. Chem. Soc. **77**, 3813 (1955).

(91) Samuel, R.: J. Chem. Phys. **12**, 167 (1944).

(92) Sass, S., and Cassidy, J.: Anal. Chem. **28**, 1968 (1956).

(93) Schrader, G.: BIOS Final Report 714, p. 41, Feb. 17, 1959.

(94) Serra, M., and Malatesta, P.: Ann. chim. (Rome) **43**, 568 (1953).

(95) Serra, M., and Malatesta, P.: Ann. chim. (Rome) **45**, 911 (1955).

(96) Smith, J. W.: *Electric Dipole Moments*, p. 127. Butterworths Scientific Publications, London (1955).

(97) Smyth, C. P.: J. Am. Chem. Soc. **60**, 183 (1938).

(98) Spauschus, H. O., and Scott, J. M.: J. Am. Chem. Soc. **73**, 208 (1951).

(99) Staudinger, H.: *Hochmolekulare organische Verbindungen*, pp. 56–72. Julius Springer, Berlin (1932); Photolithoprint Reproduction, Edwards Brothers, Ann Arbor, Michigan (1943).

(100) STAUDINGER, H., BIER, G., AND LORENTZ, G.: Makromol. Chem. **3,** 251 (1949).

(101) STEINBERG, G. M.: J. Org. Chem. **15,** 637 (1950).

(102) STELLING, O.: Z. physik. Chem. **117,** 194 (1925).

(103) STRECKER, W., AND SPITALER, R.: Ber. **59,** 1754 (1926).

(104) SUGDEN, S.: *The Parachor and Valency,* p. 165. George Routledge and Sons, Ltd., London (1930).

(105) SWAIN, C. G.: J. Am. Chem. Soc. **72,** 4578 (1950).

(106) THOMAS, L. C.: Chem. & Ind. (London) **1957,** 198.

(107) THOMPSON, G. W.: *Physical Methods of Organic Chemistry,* edited by A. Weissberger, Vol. I, p. 207. Interscience Publishers, Inc., New York (1945).

(108) VAN WAZER, J. R.: *Phosphorus and its Compounds.* Vol. I. Interscience Publishers, Inc., New York (1958).

(109) VAN WAZER, J. R., CALLIS, C. F., SHOOLERY, J. N., AND JONES, R. C.: J. Am. Chem. Soc. **78,** 5715 (1956).

(110) WHELAND, G. W.: *The Theory of Resonance,* p. 46. John Wiley and Sons, Inc., New York (1944).

(111) WILLIAMS, R. H., AND HAMILTON, L. A.: J. Am. Chem. Soc. **74,** 5418 (1952).

(112) WOLF, R., MATHIS-NOËL, R., AND MATHIS, F.: Bull. soc. chim. France **1957,** 990.

(113) WOLF, R., MATHIS-NOËL, R., AND MATHIS, F.: Bull. soc. chim. France **1960,** 124.

(114) YOST, D. M., AND ANDERSON, T. F.: J. Chem. Phys. **2,** 624 (1934).