[CONTRIBUTION FROM THE CHEMISTRY DIVISION, U. S. NAVAL RESEARCH LABORATORY]

The Structures of the Dialkyl Phosphonates and Some of their Salts

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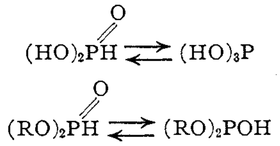
Infrared spectra of several dialkyl phosphonates, $(RO)_2P(O)H$, their solutions in proton-accepting solvents, and the salts obtained by replacing the hydrogen in the phosphonate with a metal atom are presented for the 670 to 5000 cm.$^{-1}$ region. No evidence was found in the spectra of the phosphonates for a keto-enol equilibrium, $(RO)_2P(O)H \rightleftarrows (RO)_2POH$, which has been postulated by some investigators to explain the chemical reactions of the phosphonates. All the salts have similar absorption spectra and lack any absorption bands which would indicate the presence of the phosphoryl group. The covalent structure which most closely represents the state of bonding in these salts is the one in which the metal atom is bonded to the phosphorus through the oxygen atom.

Introduction

The possibility of a tautomeric equilibrium in phosphorous acid and dialkyl phosphonates according to the equations



$$(HO)_2P(=O)H \rightleftarrows (HO)_3P$$

$$(RO)_2P(=O)H \rightleftarrows (RO)_2POH$$

I II

has been discussed in the literature since the early 1900's.[1-3] Raman[4] and infrared[5] spectral data on the dialkyl phosphonates and such chemical properties as their inability to undergo the usual addition reactions or the addition of sulfur[6] indicate that structure I predominates in the dialkyl phosphonates. However, recent work by Kabachnik and Golubeva[7] indicates that the dialkyl phosphonates can add sulfur in dioxane solution. The mechanism proposed for this reaction is based on a keto-enol equilibrium in which the dioxane, due to its basic properties, shifts the position of the equilibrium in favor of the enol form which then adds the sulfur.

It was of interest, therefore, to review the spectroscopic work to determine whether, under more favorable conditions, one could detect structure II in the dialkyl phosphonates.

Materials and Apparatus

The dialkyl phosphonates were obtained from commercial sources[8] and distilled at reduced pressure before use. Sodium, potassium and lithium derivatives were obtained by the reaction of the metal with the phosphonates in cyclohexane solution. However, the spectra of the alkali metal salts of dimethyl phosphonate were not included in this study since about half of the theoretical amount of the metal remained after the reaction had ceased. Silver derivatives were prepared by several methods: the dimethyl derivative, by adding silver acetate to a methyl alcohol solution of dimethyl phosphonate; the diethyl derivative, by refluxing silver oxide with a benzene solution of diethyl phosphonate; and the dibutyl derivative, by adding silver acetate to an ammoniacal solution of dibutyl phosphonate with subsequent neutralization of the ammonia. In the last procedure, the presence of ammonia prevented discoloration of the precipitate by free silver.

In order to reduce the possibility of hydrolysis, the spectra of the alkali metal salts were observed in the medium used in their preparation, *i. e.*, cyclohexane. However, due to the low solubility of the salts of diethyl phosphonate in cyclohexane and the consequent weak absorption spectra, slurries of the salts in their saturated cyclohexane solutions were used. The spectra of the silver salts were obtained using the finely ground solids or mulls made with petrolatum or fluorocarbon oil.

The infrared spectra were observed in the 670 to 5000 cm.$^{-1}$ region using a Perkin-Elmer model 21 spectrophotometer. Sealed absorption cells of the usual design were used for studying the liquid dialkyl phosphonates, and the cyclohexane solutions and slurries of the salts. The temperature was controlled by using an assembly similar to the one described by Lord, McDonald and Miller.[9]

Results

Investigation of the Keto-Enol Equilibrium.—It was found that the infrared spectrum of a solution of equal volumes of dioxane and di-*n*-butyl phosphonate in a cell 0.1 mm. thick was the same as the spectrum of a combination of matched cells of 0.05 mm. thickness each, one of which was filled with pure dioxane and the other with di-*n*-butyl phosphonate. Any change in the equilibrium ratio of keto to enol forms as proposed by Kabachnik and Golubeva must, therefore, be below the sensitivity limits of this method.

The reaction between sulfur and dialkyl phosphonates in dioxane solution reported by Kabachnik and Golubeva[7] was not apparent, but the reaction took place quite vigorously in triethylamine solution. It would appear that if a shift toward the enol form is responsible for the addition of sulfur, more basic solvents such as triethylamine or ammonia would engender an even greater shift to this form. If the enol form is acidic enough it would then form a salt, *e. g.*, $(RO)_2PO^-HN(C_2H_5)_3^+$; or, if it is not sufficiently acidic to form a salt, the phosphonate might form a loosely bound complex which would be spectroscopically apparent through a new equilibrium ratio of enol to keto forms. However, no appreciable changes occurred in the spectrum of diethyl phosphonate as the molar ratio of triethylamine to diethyl phosphonate was changed from 0.0 to 1.5. No absorption bands due to free or bonded hydroxyl groups appeared, and the decrease in intensity of the P-H band could be explained on the basis of simple dilutions, that is,

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(1) A. E. Arbuzov, "On the Structure of Phosphorous Acid and Its Derivatives," Dissertation, St. Petersburg, Russia, 1905.

(2) T. Milobendzki, *Ber.*, **45**, 298 (1912).

(3) P. Nylen, "Studien uber organische Phosphorverbindungen," Almqvist and Wiksells, Uppsala, Sweden, 1930.

(4) A. E. Arbuzov, M. I. Batuev and V. S. Vinogradova, *Doklady Akad. Nauk, SSSR*, **54**, 599 (1946).

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

(6) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 196.

(7) M. I. Kabachnik and E. I. Golubeva, *Doklady Akad. Nauk, SSSR*, **105**, 1258 (1955).

(8) Oldbury Electro-Chemical Co. supplied the diisoöctyl phosphonate and Virginia-Carolina Chemical Co. supplied the dimethyl, diethyl and dibutyl phosphonates.

(9) R. C. Lord, R. S. McDonald and F. A. Miller, *J. Opt. Soc. Amer.*, **43**, 149 (1952).

the data followed Beer's law. Furthermore, the matched cell technique as described above showed no change in the spectrum of diethyl phosphonate when in a 50% by volume solution with Et_3N. The addition of sulfur to dialkyl phosphonates also takes place when gaseous ammonia is bubbled through a mixture of sulfur and a phosphonate, but the infrared spectrum of dimethyl phosphonate was not affected by bubbling ammonia through the phosphonate for a period of over an hour.

Since the reaction with sulfur is quite rapid, it seems unlikely that equilibrium conditions would not have been reached previous to the time interval required to obtain a spectrum. However, in order to facilitate the attainment of equilibrium, a solution having a molar ratio of triethylamine to diethyl phosphonate of 1.5 was heated to about 70°, but again the spectrum was not affected. These results indicate that, within the sensitivity of the method, neither salt formation nor changes in the equilibrium ratio of enol to keto forms occurs when triethylamine is added to diethyl phosphonate or when ammonia is added to dimethyl phosphonate.

Another method of investigating isomeric equilibria is to observe the infrared or Raman spectrum of the sample as its temperature is changed.[10] If the equilibrium between structures I and II is real, a temperature change should produce changes in the relative amounts of the two forms of the phosphonate according to the thermodynamic equation

$$\ln C_{II}/C_{I} = \Delta S/R - \Delta H/RT$$

where ΔH is the change in heat content, ΔS the entropy difference between the two forms whose concentrations are C_I and C_{II}, R the gas constant and T the absolute temperature. Whether one can follow the changes in C_{II}/C_I by changes in the infrared spectrum depends on the relative and/or absolute values of ΔH and ΔS and the sensitivity of the method.

This method of attack was applied to the postulated isomerization of dialkyl phosphonates. During a temperature change of over 150° most of the absorption bands in the spectra were slightly affected in intensity or frequency, some key bands such as the P–H absorption around 2400 cm.$^{-1}$ were not affected at all, and no new absorption bands which might indicate the presence of the enol form appeared (Fig. 1).[11] Data of this type were obtained for diethyl phosphonate, di-*n*-butyl phosphonate and diisoöctyl phosphonate. Dibutyl phosphonate solidified near −75° at which point dramatic changes occurred in the infrared spectrum (Fig. 2). The interpretation of these changes in terms of structure is not clear at this time.

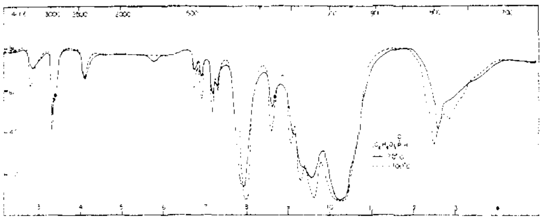


Fig. 1.—Infrared spectrum of diethyl phosphonate at 70° (—) and −100° (---).

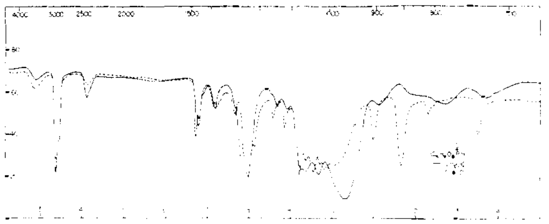
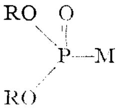


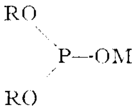
Fig. 2.—Infrared spectra of di-*n*-butyl phosphonate in liquid (—) and solid (---) states.

Apparently one of three situations exists: (1) there is no keto–enol equilibrium; (2) if ΔS is small for the equilibrium reaction, ΔH is large; (3) if ΔS is so large that the amount of one form of the molecule is not detectable in the infrared spectrum, then one cannot separate the effects of the factors $\Delta S/R$ and $-\Delta H/RT$, and the data give no indication of the magnitude of ΔH but show only that the amount of enol form is not detectable under the present experimental conditions.

Structure of the Metal Salts.—Unlike the case of a mixture of triethylamine and dialkyl phosphonate there is no doubt about the existence of the metal salts since they have been isolated as solid crystalline materials. It was of interest, therefore, to correlate their infrared spectra with the possible structures of the salts, as



A



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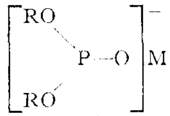
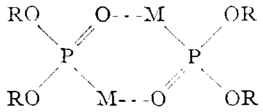


C



D

The ionic structure C which may be obtained from either the keto or enol covalent forms and the intermolecularly metal bonded structure D similar to that proposed by Rodinov[12] for alkoxides circumvent the choice between the enol and keto structures for the salts.

Shown in Fig. 3 are the infrared spectra of the sodium and silver salts of diethyl phosphonate and di-*n*-butyl phosphonate. The spectra of the lithium and potassium salts of di-*n*-butyl phosphonate and the silver salt of dimethyl phosphonate are roughly similar. The absence of absorption near the P=O absorption frequency[5,13] for all the silver salts and for the sodium salt of dibutyl phosphonate and the large decrease in intensity of this band in the other salts indicate that the best approximation for the hybrid is not structure A. Some residual P=O ab-

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(10) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954.

(11) The band at about 3450 cm.$^{-1}$ in the spectra of the phosphonates is not due to the enol form because it is not affected in either frequency or intensity by the addition of triethylamine which we assume would form a salt with any enol present.

(12) A. Rodinov, D. Shigorin, T. Talalaeva and K. Kosheshkov, *Isvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 120 (1958).

(13) J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, THIS JOURNAL, **76**, 5185 (1954).

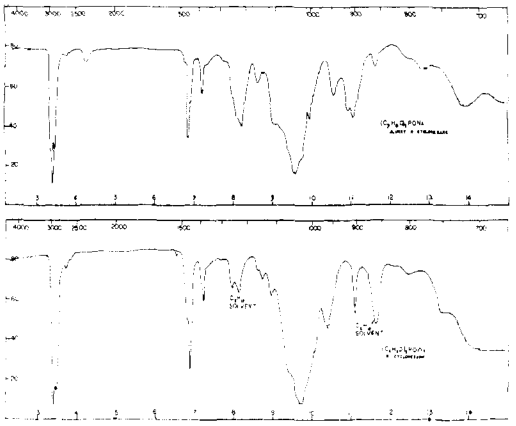

Fig. 3a.—Infrared spectra of the sodium salts of diethyl phosphonate (slurry in cyclohexane, upper figure) and di-*n*-butyl phosphonate (in cyclohexane, lower figure).

sorption in the alkali metal salts is believed to be due to hydrolysis of the salts which probably took place during the necessary transfers of the samples (note the P–H absorption in these spectra). In all the spectra there is a strong band in the 1050 cm.$^{-1}$ region where characteristic absorption for ionized P–O bonds is found.[14a,b] Unfortunately, the P–O–R groups in the dialkyl phosphonates also have a characteristic absorption band in this region, and the presence of the 1050 cm.$^{-1}$ band in the spectra of the salts does not necessarily indicate that structure C is predominant. In fact, the moderate solubility of these salts in organic solvents and calculations of 70 to 75% covalent character for the metallic bonds[15] would indicate that the ionic structure does not make the major contribution to the structure.

Conclusions

No evidence for the enol form in dialkyl phosphonates has been found in the infrared spectra of the pure compounds or in solutions of them in proton-accepting solvents. If there is a keto–enol equilibrium, it is displaced to the keto side to such an extent that the quantity of enol form is below

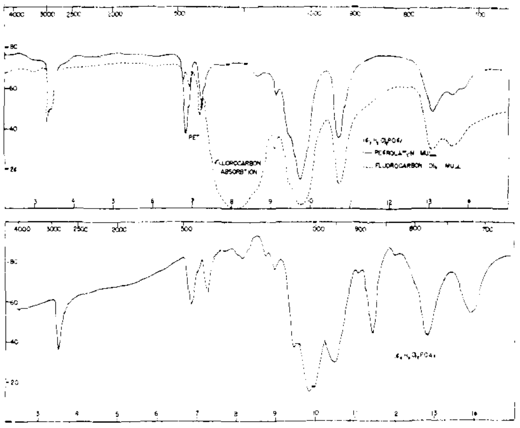

Fig. 3b.—Infrared spectra of the silver salts of diethyl phosphonate (—, petrolatum mull; ---, fluorocarbon oil mull, upper figure) and di-*n*-butyl phosphonate (lower figure).

the limits of detectability of the methods used here. Attempts to shift this supposed equilibrium by dissolution in basic media and by changes in the temperature of the sample failed to reveal the enol form. If the conversion from keto to enol form is responsible for such reactions as the addition of sulfur to dialkyl phosphonates, the combined change in entropy and internal energy for the keto–enol conversion must be large.

The infrared spectra give no indication that the structures of the dialkyl phosphonates change when they are added to proton-accepting solvents such as triethylamine. Therefore, the amount of salt formation that occurs must be very small.

The similarity of the infrared spectra of the sodium, potassium and silver salts of several dialkyl phosphonates indicates that they have similar structures. The absence of the characteristic phosphoryl group absorption band shows that, between the two possible covalent structures, the favored structure is the one in which the metal atom is bonded to the phosphorus through the oxygen atom.

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(14) (a) L. J. Bellamy, "Infra-red Spectra of Complex Molecules," John Wiley and Sons Inc., New York, N. Y., 1954, p. 266; (b) L. W. Daasch, "Infrared Spectra of Some Salts of Organophosphorus Acids," to be published.

(15) L. Pauling, "Nature of the Chemical Bond and the Structure of Molecules and Crystals," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940.