

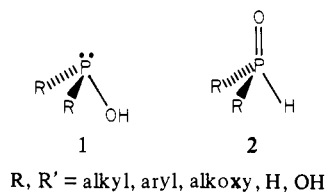
Tautomerization of Dimethyl Phosphonate

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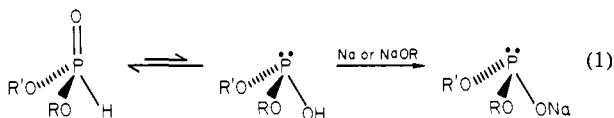
Abstract: The enthalpy of deuterium abstraction from protonated dimethyl phosphonate- d_1 has been determined by pulsed ion cyclotron double resonance spectroscopy to be 6.5 kcal mol⁻¹ higher than that corresponding to proton abstraction (i.e., proton affinity of dimethyl phosphonate). When the small effects resulting from differences in isotopic substitution are ignored, this difference is a direct measure of the relative thermochemical stabilities of dimethyl phosphonate and its tautomer dimethylphosphorous acid.

Although it was once believed that the lower oxy acids of phosphorus existed primarily in tautomeric forms (**1**), in which the central atom is trivalent, it is now well established that the vast majority of such compounds prefer instead structures (**2**) that incorporate formally tetravalent phosphorus. The infrared spectra



for all but one of the known phosphorus oxy acids show strong absorptions corresponding to P=O and P—H bond stretches and, except for R = R' = OH, show no evidence at all for characteristic OH stretches! Only the bis(trifluoromethyl) compound (R = R' = CF₃) is currently established to exist as tautomer **1**.²

Even though the oxy acid tautomers (**1**) of all other phosphonates (R = R' = alkoxy), phosphinates (R = alkoxy; R' = allyl, aryl) and secondary phosphine oxides (R = R' = alkyl, aryl) have never been directly observed, reaction mechanisms necessitating the tautomerization, **2** ⇌ **1**, have often appeared in the chemical literature.³ For example, while the alkali metal and silver salts of dialkyl phosphonates exhibit no P=O stretching band in the infrared, indicating that they are in fact derivatives of phosphorous acid, their preparation from the corresponding dialkyl phosphonates (the first step in the Michaelis-Becker reaction) requires intervention of the unstable oxy acid tautomer.⁵



There is also considerable evidence from kinetic experiments supporting the notion of facile interconversion between phosphonate and phosphorous acid tautomers. Representative are studies involving the iodination of dialkyl phosphonates,⁵ its reactions with α -chloro ketones,⁶ and its exchange of deuterium.⁷ The proposed mechanisms for reaction of secondary phosphine oxides with phenyldisulfide⁸ and of phosphonic acid with dialkyl

orthoformates⁹ also involves the intermediacy of the respective high-energy tautomers. Finally, the unstable phosphinous acid tautomers of both dimethyl- and diphenylphosphine oxides have been trapped by coordination to molybdenum pentacarbonyl.¹⁰

In view of the importance which has been attached to this general class of tautomerizations, it is perhaps surprising to note that not much attention has been directed toward the determination of its thermochemistry. Indeed, the only available data appear to be values given by Van Wazer¹¹ for tautomerization of hydrophosphoric acid and estimates given by Guthrie¹² of the equilibrium constants for tautomerization involving phosphorous acid and its mono- and diethyl esters. These latter data, although valuable in that they have been obtained in a consistent manner for a series of related compounds, are subject to considerable uncertainty.

We¹³ and others¹⁴ have recently demonstrated that pulsed ion cyclotron double resonance spectroscopy may be used to determine the thermochemical stabilities of many highly reactive or otherwise short-lived neutral molecules. Among the more interesting systems studied to date in our laboratory are methyleneimine,^{13a} *o*- and *p*-xylylene,^{13b} *o*-benzynes,^{13c} and 1,1-dimethylsilaethylene,^{13d} as well as the unstable proton tautomers of acetone,^{13e} hydrogen cyanide,^{13f} and formaldehyde.^{13g} We now report the successful application of the experimental technique to the determination of the relative gas-phase thermochemical stabilities of dimethylphosphorous acid (**1**, R = R' = OMe) and dimethyl phosphonate (**2**, R = R' = OMe).

Results and Discussion

Two series of experiments were performed. In the first, free energies for the gas-phase proton-transfer equilibria (reaction 2), where B is CF₃HCON(Me)₂, (*t*-Bu)₂CO, and (*i*-Pr)₂O, were measured with standard equilibrium ICR methods.^{15,16} These

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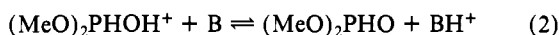
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Table I. Observation by Ion Cyclotron Double Resonance Spectroscopy of Deuteron Abstraction from Protonated Dimethyl Phosphonate-*d*₁ (2) Formation of Dimethylphosphorous Acid

abstracting base B	PA of B rel to 2, ^a kcal mol ⁻¹	is double resonance with BD ⁺ obsd?
(<i>i</i> -Pro) ₂ O	1.6	no
(<i>t</i> -Bu) ₂ CO	0.7 ^b	no
CF ₃ HCON(Me) ₂	0.0 ^c	no
2-F-py	-4.2	no
(MeO) ₃ PO	-6.1 ^d	no
<i>m</i> -MeC ₆ H ₄ NH ₂	-6.8	yes
3-Cl-py	-8.3	yes
EtNH ₂	-10.1	yes
<i>n</i> -ProNH ₂	-11.5	yes
py	-14.5	yes

^a Unless otherwise noted data are from: R. W. Taft in "Proton Transfer Equilibria", E. F. Caldin and V. Gold, Eds., Wiley-Halstead, New York, 1975, p 31. The published gas-phase basicities have been slightly modified in view of higher ambient temperatures in the ICR spectrometer than previously believed. ^b Data are from: C. Lebrilla, unpublished work. ^c Data are from: M. Berthelot, unpublished work. ^d Data are from: T. Gramstad, unpublished work.

measurements indicate that the gas-phase proton affinity of dimethyl phosphonate is 2.4 kcal mol⁻¹ greater than that of the standard ammonia.¹⁷

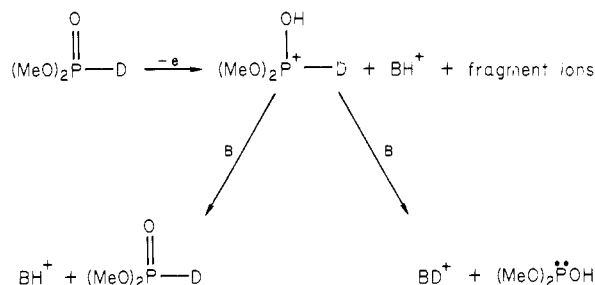


In the next series of experiments, outlined in the scheme below, a mixture of dimethyl phosphonate-*d*₁,¹⁸ some base B of known strength, and argon as a buffer gas (in approximate ratio 4:1:10 and total pressures of (5–10) × 10⁻⁶ torr) was added to the ICR spectrometer. Electron-impact-induced fragmentation of the labeled dimethyl phosphonate and of B effects protonation of both and (depending on the base) leads as well to formation of fragment ions of B. If B is sufficiently strong, it will be capable of proton abstraction from protonated dimethyl phosphonate-*d*₁, leading to the regeneration of the original tautomer and concurrently providing an additional source of BH⁺. If stronger still, it will be able to abstract deuterium, leading to the formation of BD⁺ and concurrently to the production of dimethylphosphorous acid, the unfavorable tautomer of dimethyl phosphonate. Therefore, by

(16) Measured: free energy of 2 for B = CF₃HCON(Me)₂, -0.1 kcal mol⁻¹; B = (*t*-Bu)₂CO, 0.5 kcal mol⁻¹; B = (*i*-Pro)₂O, 1.1 kcal mol⁻¹. Combined with free energies of protonation of CF₃HCON(Me)₂, (*t*-Bu)₂CO and (*i*-Pro)₂O, relative to the standard ammonia (-3.2 kcal mol⁻¹, -2.9 kcal mol⁻¹, and -2.0 kcal⁻¹, respectively), these data yield an average free energy of protonation of (MeO)₂PHO relative to ammonia of -3.2 kcal mol⁻¹ or a relative proton affinity (enthalpy) of -2.4 kcal mol⁻¹.

(17) The original value of 202.3 kcal mol⁻¹ for the proton affinity of the ammonia standard as derived from ICR spectroscopy (ref 15) has been revised upward to 205 kcal mol⁻¹ due to recent work: (a) 203.6 kcal mol⁻¹, S. T. Ceyer, P. W. Tiedmann, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, **70**, 14 (1979); (b) *Soc.*, **101**, 4067 (1979); (c) 209.2 kcal mol⁻¹, R. G. McLoughlin and J. C. Traeger, *ibid.*, **101**, 5791 (1979). Thus, the absolute proton affinity of dimethyl phosphonate is assigned a value of 207.4 kcal mol⁻¹.

(18) Prepared by the reaction of CH₃OD with PCl₃ in refluxing hexane. The compound was handled under dry nitrogen to prevent exchange of the label.



using a series of abstracting bases of known and increasing strength and by monitoring the onset of production of BD⁺, the enthalpy of dedeuteration (from phosphorus) of protonated dimethyl phosphonate-*d*₁ may be determined.¹⁹ Small effects due to isotopic substitution of the phosphonate tautomer will tend to be canceled by similar effects arising from deuteration of the abstracting base. The overall differential isotope effect, therefore, will be small (i.e., on the order of a few tenths of a kcal mol⁻¹) and has been ignored in our treatment. Relative to the previously established enthalpy of (oxygen) deprotonation (see above) this corresponds precisely to the difference in the heats of formation of the two tautomers. The experimental data are presented in Table I. Trimethyl phosphate (the proton affinity of which is 6.1 kcal mol⁻¹ greater than that of dimethyl phosphonate) was the strongest base considered for which deuteron abstraction was not observed; *m*-toluidine (the proton affinity of which is 6.8 kcal mol⁻¹ greater than that of dimethyl phosphonate) was the weakest base for which abstraction was confirmed. We assign the threshold for deuteron abstraction as the mean of these two values, 6.5 kcal mol⁻¹. This corresponds to the enthalpy of the dimethyl phosphorous acid tautomer relative to the ground-state dimethyl phosphonate form.

No other gas-phase data are available for this or closely related compounds. A 3-21G* level²⁰ calculation yields a larger energy separation of 11.1 kcal mol⁻¹ for the two tautomers.

The heat of tautomerization of neat ethyl phosphonate estimated by Guthrie¹² (9.8 kcal mol⁻¹) is higher than the gas-phase value for the dimethyl compound reported here. The difference may be rationalized on the basis of intermolecular association in the liquid. The dilution studies of Wolf, Houalla, and Mathis²¹ and of Gramstad and Snaprud²² have demonstrated the existence of hydrogen bonding between the phosphorus-bound proton and the phosphoryl oxygen in dimethyl phosphonate and other dialkyl phosphonates. Such interactions may further increase the stability of the alkyl phosphonate tautomer relative to the corresponding phosphorous acid form.

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Registry No. Dimethyl phosphonate, 868-85-9; dimethyl phosphonate-*d*₁, 6729-36-8.

(19) The possibility of deuterium scrambling can be ruled out if a distinct threshold for deuteron abstraction above that for proton abstraction is indeed found.

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