

[CONTRIBUTION FROM THE ISOTOPE DEPARTMENT, WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

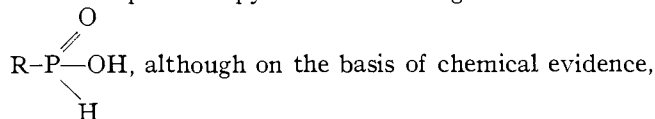
Deuterium Exchange between Phenylphosphonous Acid and Water

BY J. REUBEN, DAVID SAMUEL, AND BRIAN L. SILVER

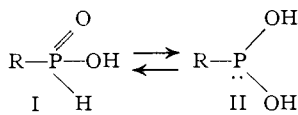
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The phosphorus-bonded hydrogen of phenylphosphonous acid undergoes isotopic exchange with deuterium in both acidified ethanol-water mixtures and in aqueous alkaline solution. The kinetics of the acid- and base-catalyzed exchange was studied utilizing nuclear magnetic resonance spectroscopy. Oxygen-18 exchange between phenylphosphonous acid and solvent water was not detectable under the conditions in which hydrogen exchange was measured.

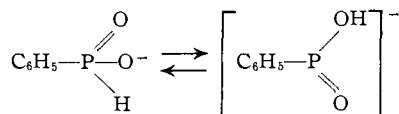
Phosphonous acids have been shown by n.m.r. and infrared spectroscopy¹ to have the general structure



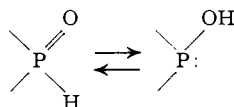
Frank² has suggested that these compounds are a mixture of tautomers, form I being the overwhelmingly predominant species.



Recently Quin and Dysart³ observed a lack of reactivity of phenylphosphonous acid with diazomethane and concluded that the anion of this acid is not tautomeric, *i.e.*, there is no equilibrium of the type



The hydrogen atom bound to phosphorus in related compounds has been shown to undergo isotopic exchange with deuterium (or tritium) from the solvent, *e.g.*, in dialkyl phosphonates,⁴⁻⁸ monoalkyl phosphonates,⁴ phosphorous acid,^{9,10} and hypophosphorous acid.¹¹ It was suggested that in each case this exchange is due to the tautomerism of the general type



We have found that phenylphosphonous acid also undergoes exchange with solvent deuterium in both acidified ethanol-water mixtures and in aqueous alkaline solution. The rate of this exchange was followed by observing the changes of intensity in the proton magnetic resonance spectra of the reaction solution.

Experimental

Phenylphosphonous acid (Hopkins and Williams) was recrystallized twice from hot water; m.p. 70–71°, lit.¹² 71°.

Phenylphosphonous Acid-*d*.—Phenylphosphonous acid (0.5 g.) was dissolved in ethanol-*d* (2 ml.) and 7.6 *N* DCl in D₂O

(1) J. R. Van Wazer, "Phosphorus and its Compounds," Interscience Publishers, Inc., New York, N. Y., 1958, p. 368.

(2) A. W. Frank, *J. Org. Chem.*, **26**, 850 (1961).

(3) L. D. Quin and M. R. Dysart, *ibid.*, **27**, 1012 (1962).

(4) P. R. Hammond, *J. Chem. Soc.*, 1365 (1962).

(5) R. B. Fox and W. J. Bailey, Division of Organic Chemistry, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958; R. B. Fox, *J. Org. Chem.*, **28**, 531 (1963).

(6) Z. Luz and B. Silver, *J. Am. Chem. Soc.*, **83**, 4518 (1961).

(7) Z. Luz and B. Silver, *ibid.*, **84**, 1095 (1962).

(8) B. Silver and Z. Luz, *ibid.*, **84**, 1091 (1962).

(9) R. B. Martin, *ibid.*, **81**, 1574 (1959).

(10) B. Silver and Z. Luz, *J. Phys. Chem.*, **66**, 1356 (1962).

(11) W. A. Jenkins and D. M. Yost, *J. Chem. Phys.*, **20**, 538 (1962); A. Fratiello and E. W. Anderson, *J. Am. Chem. Soc.*, **85**, 519 (1963).

(12) V. M. Plets, *Zh. Obshch. Khim.*, **6**, 1198 (1936).

(2 ml.). After 1 hr. at room temperature the solvent and DCl were removed under high vacuum. The residue was recrystallized from hot D₂O; m.p. 70–71°. The n.m.r. spectrum in D₂O was identical with that of the normal compound except for the reduced intensity of the P–H resonance line.

Ethanol-*d*.—EtOD was made by hydrolyzing diethyl oxalate with D₂O and fractionally distilling the product¹³; b.p. 78.3–78.5°.

NaOD solution was made by dissolving sodium in D₂O.

DCl solution was made by passing DCl gas (from benzoyl chloride and D₂O¹⁴) into D₂O.

Procedure.—Proton magnetic resonance spectra were obtained on a Varian 4300 B high resolution spectrometer operating at 56.4 Mc./sec.

The proton magnetic resonance spectrum of phenylphosphonous acid in ethanol-water solution consists of resonance lines due to the phenyl group, to the solvent, and a doublet due to the phosphorus-bonded hydrogen with a spin-spin coupling constant of ~700 c.p.s. The progressive replacement of the phosphorus-bonded hydrogen results in a corresponding decrease in the intensity of the P–H doublet.

The change in intensity observed in the P–H resonance line of phenylphosphonous acid in deuterated solvents is due to an exchange reaction. Oxidation or other chemical reactions are ruled out by the observation that the spectrum of phenylphosphonous acid in 4 *N* NaOH and in 4 *N* HCl (containing 50% ethanol) is stable for at least 4 hr. In addition, the spectrum of

the deuterated substrate $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5-\text{P}-\text{OH} \\ | \\ \text{D} \end{array}$ in normal acid solution

shows a small P–H line which increases with time, following first-order kinetics (Table I).

TABLE I

ACID-CATALYZED HYDROGEN EXCHANGE OF PHENYLPHOSPHONOUS ACID IN ETHANOL-*d*-D₂O SOLUTION AT 23 ± 1°

[PPA], mole l. ⁻¹	[EtOD], % v./v.	[D ⁺], moles l. ⁻¹	k ₁ , min. ⁻¹ × 10 ²
0.7	50	0.5	2.22
.7	50	0.97	3.33
.7	50	1.0	3.18
.7	50	1.94	5.59
.7	50	2.95	7.36
.7	50	3.88	9.32
.28	50	2.95	8.74
1.00	50	2.95	6.99
0.7	25	1.94	4.82
0.7	75	1.94	8.32
1.0	50	2.95	4.13 ^a

^a For phenylphosphonous acid-*d*.

Owing to the limited solubility of phenylphosphonous acid in water, weighed quantities were dissolved in equal volumes of ethanol-*d* and DCl-D₂O solution. The intensity of one component of the P–H doublet was measured as a function of time for different concentrations of DCl and phenylphosphonous acid. The intensity of the P–H doublet as estimated by the peak height is directly proportional to the concentration of the phosphorus-bonded hydrogen.¹⁵

In previous studies^{7,10} on another n.m.r. spectrometer the intensity was taken arbitrarily as the ratio of the height of the P–H line to the height of an internal standard. However, the stability of the present instrument for periods up to an hour is

(13) J. Beersman and J. C. Jungers, *Bull. soc. chim. Belges*, **56**, 72 (1947).

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

(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 19.

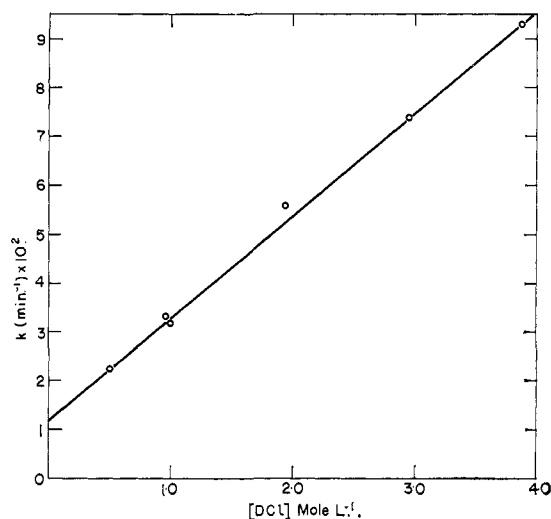


Fig. 1.—Observed first-order rate constants for hydrogen exchange in 0.7 *M* solutions of phenylphosphonous acid as a function of DCl concentration; solvent, ethanol-*d*-D₂O (1:1 by vol.); temp. 23 ± 1°.

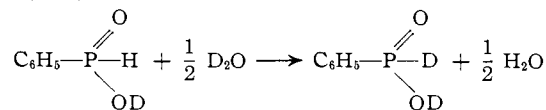
such that there was no significant difference between rate constants estimated from either absolute or arbitrary peak heights and most runs were based directly on absolute measurements of peak heights. Runs were followed to over 75% completion, an average of 30–40 points being taken per run. The temperature of the reaction solution was 23 ± 1°.

Runs in NaOD, in which the substrate is ionized, were carried out in the absence of methanol, since sodium phenylphosphonate is sufficiently soluble in water. The runs in alkaline solution were slower than those in acid solution, necessitating the use of an arbitrary peak height to allow for instrumental instability. The ratio of heights of the phenyl resonance line and one component of the P–H doublet was taken as a measure of the intensity of the P–H resonance line.

Calculation of Kinetic Results.—First-order kinetics are to be expected¹⁶ for any isotopic exchange reaction in which one of the isotopes is present in low concentration.

In the present case the concentration of exchangeable protons was never more than 3% and first-order kinetics were in fact observed.

The rate law for the replacement of the proton of phenylphosphonous acid by a deuterium in the large excess of deuterated solvent, *i.e.*, for



can be taken as

$$\frac{d}{dt} ([\text{C}_6\text{H}_5 \cdot \text{PHOOD}]_t - [\text{C}_6\text{H}_5 \cdot \text{PHOOD}]_\infty) = -k_1 ([\text{C}_6\text{H}_5 \cdot \text{PHOOD}]_0 - [\text{C}_6\text{H}_5 \cdot \text{PHOOD}]_\infty)$$

where the concentration terms refer to the concentrations of the hydrogen form of phenylphosphonous acid at zero time, time *t*, and at equilibrium (infinity). The very rapid exchange of the proton on the hydroxyl by deuterium is not measurable by this technique. Since the concentration of the hydrogen form at equilibrium may be neglected in the present case it follows that

$$k_1 = -\frac{1}{t} \ln \frac{[\text{C}_6\text{H}_5 \cdot \text{PHOOD}]_t}{[\text{C}_6\text{H}_5 \cdot \text{PHOOD}]_0}$$

A logarithmic plot of $\left[\text{C}_6\text{H}_5-\text{P}(\text{OH})_2 \right]_t$ against time should be

linear. In practice, the intensity of the P–H line was plotted on semi-log paper and excellent linear plots were obtained. The slopes were obtained by visually fitting a straight line through the experimental points. The pseudo-first-order rate constants obtained from the slopes of these plots are given in Tables I and II and plotted as functions of DCl and NaOD concentration in Fig. 1 and 2. Since the ratio of the hydrogen to deuterium in this system is of the order of 0.03, there is an uncertainty in the results of the order of 10%.

(16) G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951).

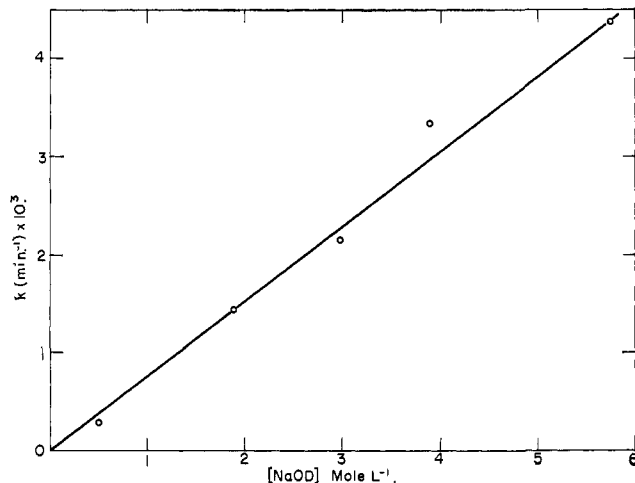


Fig. 2.—Observed first-order rate constant for hydrogen exchange in 0.7 *M* solutions of phenylphosphonous acid in D₂O, as a function of NaOD concentration; temp. 23 ± 1°.

It is evident from the linearity of these plots that the dependence of exchange on hydrogen ion and hydroxide ion concentration is first order. The positive intercept in Fig. 1 is a measure of the uncatalyzed "water reaction" of the unprotonated species. There is no significant intercept obtained on extrapolating to zero hydroxide concentration the results of base-catalyzed exchange. No significant exchange was detected after 3 days at room temperature in runs carried out in sodium acetate solution.

From Tables I and II it may be seen that there is less than 15% variation in the rate for concentrations of phenylphosphonous acid in the range 0.4–1.0 *M*, which indicates that the exchange reaction is also first order in phosphonous acid. It should be noted that the "acidic" hydrogen of phosphonous acid has³ *pK*_a 1.75 and therefore any contribution to the acidity of the DCl solutions due to this hydrogen may be neglected in the range of acidity studied.

TABLE II
BASE-CATALYZED HYDROGEN EXCHANGE OF PHENYLPHOSPHONOUS ACID IN D₂O AT 23 ± 1°

Concn. of phenylphosphonate, mole l. ⁻¹	[OD] ⁻ , moles l. ⁻¹	k ₁ , min. ⁻¹ × 10 ²
0.7	0.5	0.30
.7	1.9	1.46
.7	2.98	2.15
.7	3.9	3.33
.7	5.74	4.37
1.0	5.75	4.52
0.28	5.74	4.18
Sodium phenylphosphonate, mole l. ⁻¹	Sodium acetate, mole l. ⁻¹	
0.7	0.12	
.7	.25	No detect. exch.
.7	.38	in 72 hr.
.7	.5	

The dependence of rate on ethanol concentration is shown by the last three results in Table I. The small difference in rate in going from 25% to 50% ethanol justifies qualitative comparisons between the results of the present study and previous data obtained for dialkyl phosphonates in aqueous solution.

Oxygen-18 Experiments.—To determine whether phenylphosphonous acid undergoes oxygen exchange with the solvent under the conditions used to study hydrogen exchange, samples of phenylphosphonous acid were dissolved in solvents containing water enriched in oxygen-18. After times corresponding to over 4 half-lives for hydrogen exchange in the same solvent, the solvent was partially evaporated in the case of acidic solvents and the first crop of crystals was filtered, washed with a little water, and dried for 3 hr. on a high vacuum line. The recovered phenylphosphonous acid (m.p. 70–71°) was analyzed for oxygen-18 by the method of Anbar and Guttman.¹⁷

The alkaline reaction solution was neutralized with HCl solution and the phenylphosphonous acid extracted with ethyl

(17) M. Anbar and S. Guttman, *Intern. J. Appl. Rad. Isotopes*, **4**, 233 (1959).

TABLE III

¹⁸O EXCHANGE BETWEEN PHENYLPHOSPHONOUS ACID AND WATER AT 23 ± 0.1°

Solvent	Atom %	Time, hr.	Atom %
	excess ¹⁸ O in solvent		excess ¹⁸ O in recovd. substr.
H ₂ O-EtOH (1:1)	1.75	1	0.008
H ₂ O-EtOH (1:1) 1.2 N HCl	1.94	1	.006
7.9 N NaOH	1.83	4	.020

TABLE IV

CATALYSIS CONSTANTS FOR EXCHANGE OF PHENYLPHOSPHONOUS ACID, DIETHYL PHOSPHONATE, AND PHOSPHOROUS ACID

	k_{H^+} , mole ⁻¹ min. ⁻¹	k_w , min. ⁻¹	k_{OH^-} , mole ⁻¹ min. ⁻¹	k_{AcO^-} , mole ⁻¹ min. ⁻¹	$k_{PO_4^-}$, mole ⁻¹ min. ⁻¹
Phenylphosphonous acid	2.1×10^{-2a}	$1.2 \times 10^{-2a,d}$	0.77×10^{-3e}
Diethyl phosphonate (EtO) ₂ POH	6.0×10^{-2b}	2×10^{-3b}	7.0×10^{-2}	7.5×10^{-2}	2.1
Phosphorous acid, H ₃ PO ₃	1.8×10^{-3c}	0.5×10^{-3c}

^aEthanol-water solution (1:1 by volume), temp. 23 ± 1°. ^bAqueous solution, temp. 20° (ref. 6 and 7). Values of k_{OH^-} and $k_{PO_4^-}$ are oxidation catalysis constants taken from P. Nylen, *Z. anorg. allgem. Chem.*, **235**, 161 (1938). ^cAqueous solution, temp. 80 ± 0.2°, D. Samuel and B. Silver, unpublished results. ^dNeutral molecule. ^eMonoanion. ^fDianion.

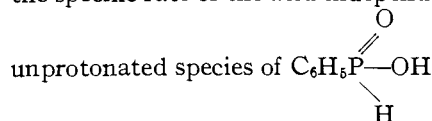
acetate. After removal of the solvent, phenylphosphonous acid was obtained, dried on the vacuum line, and analyzed for ¹⁸O. The results are given in Table III.

Discussion

The results show that in acidified 50% ethanol-water (v./v.) solution phenylphosphonous acid undergoes hydrogen exchange with the solvent, the rate being given by

$$\text{specific rate} = k_A = R \left/ \left[\text{C}_6\text{H}_5\text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{OH} \\ | \\ \text{H} \end{array} \right] \right. = k_H[\text{H}^+] + k_w$$

where R is the total rate of exchange, k_H is the catalysis constant for the hydrogen (deuterium) ion, and k_w the specific rate of the acid-independent exchange of the



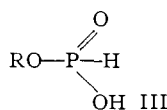
In sodium deuteroxide solutions in D₂O exchange also occurs, the specific rate being given by

$$k_B = R \left/ \left[\text{C}_6\text{H}_5\text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{O}^- \\ | \\ \text{H} \end{array} \right] \right. = k_{OH}[\text{OH}^-]$$

where k_{OH} is the catalysis constant for the hydroxide (deuteroxide) ion.

It may be seen from Table II that the exchange reaction is not catalyzed by acetate ion.

The above results indicate that under the experimental conditions, the neutral species, the protonated species, and the monoanion of phenylphosphonous acid are all involved in tautomeric equilibria. This is to be expected in view of the close structural relationship between the phosphonous acids (I) and monophosphonates (III) where hydrogen exchange with water is known⁴ to occur.



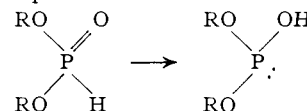
It is of interest to compare the rate constants for the hydrogen exchange of phenylphosphonous acid with the corresponding constants for a typical dialkyl phosphonate (diethyl phosphonate)^{7,9} and phosphorous acid.^{10,11} As may be seen from Table IV, the pre-

dominating influence on the exchange rate is the charge state of the substrate. Thus while exchange in diethyl phosphonate is catalyzed by cations (in the order $\text{OH}^- > \text{PO}_4^- > \text{AcO}^-$), phosphorous acid does not exchange in the presence of these ions, presumably owing to the electrostatic repulsion between the ions and the mono- and dianions of phosphorous acid. The behavior of phenylphosphonous acid falls between these extremes. The monoanion is not attacked by acetate or phosphate ions. In strong base, however, phenylphosphonous acid exists as the monoanion as compared to a dianion

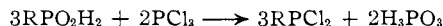
in the case of phosphorous acid. The lower negative charge results in an observable rate of exchange due to the attack of the strongly basic hydroxide ion.

Differences between the uncatalyzed and acid-catalyzed rates are probably more closely related to intramolecular electronic factors in the substrate. The presence of negative charged oxygen atoms in the anions of phenylphosphonous and phosphorous acid will strengthen the P-H bond by an inductive effect relative to the bond in dialkyl phosphonates.

The role of tautomerism in the reactions of phenylphosphonous acid is unknown. In the case of dialkyl phosphonates the rate of oxidation in aqueous halogen solution is known to be controlled by the rate of formation of the phosphite tautomer⁶⁻⁸

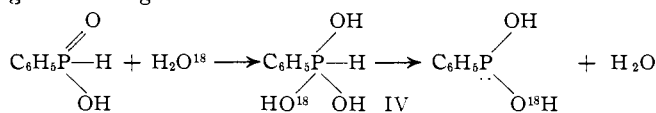


A similar situation appears to obtain in the acid-catalyzed oxidation of phosphorous acid¹⁰ and of hypophosphorous acid.¹¹ The present demonstration of the existence of tautomerism in hydroxylic solvents has no direct bearing on the reaction in nonhydroxylic solvents

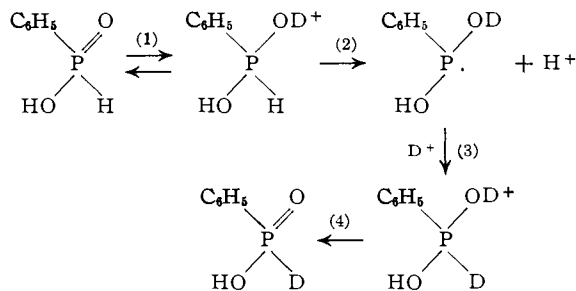


studied by Frank.² An unsuccessful attempt to find evidence of tautomerism³ was based on the fact that the titration curve of phenylphosphonous acid shows only one inflection. Arguments of this kind are invalidated when the potentially ionizable hydrogen is involved in a comparatively strong covalent bond such as the P-H bond in phenylphosphonous acid, dialkyl and monoalkyl phosphonates, phosphorous and hypophosphorous acids. A direct titration of the hydrogen of a P-H bond has only been possible in the case of trialkylphosphonium compounds.^{18,19}

The results of Table III show that oxygen-18 does not exchange significantly between phenylphosphonous acid and the given solvents within 1 half-life of the exchange of hydrogen with water. This result is evidence against a "hydration mechanism" for hydrogen exchange

(18) W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1622 (1937):(19) B. Silver and Z. Luz, *J. Am. Chem. Soc.*, **83**, 786 (1961).

since, if the hydroxyl groups of intermediate IV are equivalent, a path is available for oxygen exchange between substrate and solvent. The mechanism of hydrogen exchange are assumed to be the same as those presented for the dialkyl phosphonates.⁶⁻⁸ The acid-catalyzed exchange may be formulated as



The first step (1) involves a fast pre-equilibrium protonation, followed by the rate-determining step (2), the fission of the P-H bond to give the tricovalent tautomer, which subsequently picks up deuterium from the sol-

vent, step (3), and loses a proton from one of the hydroxyl groups, step (4). The hydroxide ion catalysis of exchange presumably proceeds by direct proton abstraction. There is no physical evidence for the tricovalent tautomer of phenylphosphonous acid. The

normal form $\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{P} \\ \diagdown \\ \text{H} \quad \text{OH} \end{array}$ is probably stabilized by conjugation of the phenyl and phosphoryl groups.²⁰ The tautomer $\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{P} \\ \diagdown \\ \text{OH} \end{array}$ will lose this stabilizing energy, but a partial compensation may be expected due to the conjugation of the phenyl group and the lone pair of the phosphorus atom, such as Jaffé²¹ has found in triphenylphosphine.

(20) M. I. Kabachnik, T. A. Mastryukova, and T. A. Melentiyeva, *Tetrahedron*, **17**, 239 (1962).

(21) H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSISSIPPI, UNIVERSITY, MISS.]

Solvent Effects on Charge-Transfer Complexes. I. The *s*-Trinitrobenzene-Naphthalene Complex in Carbon Tetrachloride, *n*-Heptane, *n*-Hexane, Cyclohexane, Chloroform, or Carbon Disulfide^{1a}

By C. C. THOMPSON, JR., AND P. A. D. DE MAINE^{1b}

RECEIVED MAY 13, 1963

Formation constants and absorptivities for the 1:1 *s*-trinitrobenzene-naphthalene complex in six *inert solvents* (CCl₄, *n*-hexane, cyclohexane, *n*-heptane, CHCl₃, or CS₂) were calculated with spectrophotometric data collected at fifteen wave lengths between 3300 and 4000 Å. at 20 and 45°. All data were processed with an IBM 1620-60 K computer using programs with the self-judgment principle, fail-safe procedure, error-analysis, and instructions for correcting concentrations for density-volume-temperature changes incorporated. Absorptivities (*a_c*) for the complex at the absorption maxima (near 3600 Å.) at 20° vary from 1294 (±22) for *n*-heptane to 1540 (±13) for *n*-hexane. As the temperature is increased from 20 to 45°, the absorptivities decrease by approximately 10% except in CHCl₃ systems where those between 3650 and 4000 Å. are unchanged. The formation constant (*K*) is independent of wave length at each temperature in all solvents except *n*-heptane where at 20° *K*, in moles/l. units, is 9.58 (±0.17) for wave lengths between 3300 and 3700 Å., and then gradually increases to 14.61 (±0.17) at 4000 Å. At 45°, *K* in *n*-heptane is 6.12 (±0.09) at wave lengths up to 3850 Å., then it increases to 8.27 (±0.09) at 4000 Å. Average values for *K* at 20° vary from 1.82 (±0.08) in CHCl₃ to 9.58 (±0.17) in *n*-heptane. However, the heat of complex formation appears to be independent of the inert solvent with a median value near -3.0 kcal. per mole except for cyclohexane where the value is -4.16 (±0.63) kcal. Recent developments in theories of complex formation are examined. Variations of *K* with wave length and of *a_c* with temperature are attributed to simultaneous higher order reactions.

Introduction

In the new computer method² preselected limits of experimental error are used in tests of data compatibility with a number of alternate equations or theories. The method yields precise information for each parameter, thereby completely removing ambiguities in reported results.

For the reaction, $A + B \xrightleftharpoons{K} C$, the Benesi-Hildebrand,^{3a} Ketelaar,^{3b} and Scott⁴ noniterative spectrophotometric methods can be used to calculate the equilibrium constant, *K*, and *a_c*, the absorptivity for C, only if [A] ≫ [B], *a_A* and *a_B* are known, and *a_A*, *a_B*, and *a_C* are independent of concentration. Recent computer work in our laboratories has shown that *a_A* and *a_B* are seldom completely independent of concentration and the use of constant values for *a_A* and *a_B*

(1) (a) Taken from the Ph.D. thesis of C. C. T., University of Mississippi, 1964. (b) Department of Chemistry, University of Illinois, Urbana, Ill.

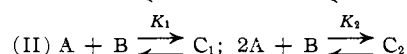
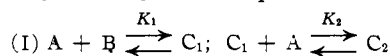
(2) P. A. D. de Maine and R. D. Seawright, "Digital Computer Programs for Physical Chemistry, Vol. I, The Macmillan Co., New York, N. Y., 1963.

(3) (a) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949); (b) J. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzubas, *Rec. trav. chim.*, **71**, 1104 (1952).

(4) R. L. Scott, *ibid.*, **75**, 787 (1956).

can result in erroneous conclusions. In the iterative method used in this work (see Data Processing Method) the restrictions on relative concentrations and the required concentration independence of *a_A* and *a_B* are removed.

For three systems researchers⁵⁻⁷ have reported that the values for *K* calculated for 1:1 complex formation vary with wave length. Such variations in *K* and non-linear Benesi-Hildebrand or Ketelaar plots have been attributed to the neglect of unsuspected higher order reactions. Recently⁸ there have been devised mathematically exact iterative methods for calculating *K*₁, *K*₂, *a_A*, *a_B*, *a_{C1}*, and *a_{C2}* for the equation sets



In these methods there are no restrictions on concentra-

(5) P. A. D. de Maine, M. M. de Maine, and C. Froese, *J. Mol. Spectry.*, **8**, 373 (1962).

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