

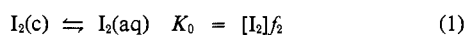
# Thermodynamics of Iodine Solubility and Triiodide Ion Formation in Water and in Deuterium Oxide

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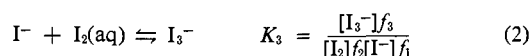
Contribution from Carleton College, Northfield, Minnesota. Received June 28, 1965

The solubility of iodine in water and in deuterium oxide has been determined in the range 5–50° using packed-column techniques, and the thermodynamic results are compared for the two solvents. The solubility of iodine in very dilute potassium iodide solutions leads inherently to apparent values of the triiodide formation constant which are higher than those obtained by precise spectrophotometric work at exceedingly low concentrations. The difference is explained in terms of the species  $I_5^-$ . For the reaction,  $I_3^- + I_2 \rightleftharpoons I_5^-$ , the formation constant is about 9 at 25°.

The complexing of aqueous iodine by iodide ion has long been of major interest, and studies have used solubility,<sup>1</sup> distribution,<sup>2,3</sup> and potentiometric,<sup>4</sup> conductimetric,<sup>5</sup> and spectrophotometric<sup>6,7</sup> techniques. It is widely accepted that in saturated solutions of iodine in the presence of iodide ion the principal equilibria are



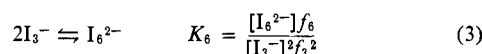
and



where the brackets indicate molarities and the  $f$  values are activity coefficients.

It has been common practice to assume that  $f_2 = 1$  and that  $f_3 = f_1$ , an approximation which is reasonable at low ionic strengths but highly questionable<sup>1</sup> at higher concentrations.

Another complication, revealed by a distribution study<sup>2</sup> at high concentrations, is the dimerization of triiodide ion



This effect has been ignored in all studies at low concentrations of iodine and iodide.

In spite of the interest in reaction 2, the serious divergence of thermodynamic results in the literature has not been given critical evaluation. It is clear from Figure 1 that both free energy and enthalpy changes have seemed dependent upon the particular technique used.

The object of the present work was to carry out an accurate solubility study over a range of temperatures, at ionic strengths lower than previously used, in an attempt to eliminate error both in the activity coefficient assumption and deviations caused by reaction 3. Also, it was desired to study the system in deuterium

oxide because there is a scarcity of thermodynamic information in this solvent. Finally, we shall seek to explain the differences among various experimental results.

## Experimental Section

Saturated solutions of iodine were obtained by slow passage of the solvent through 15 cm. of resublimed, finely ground iodine contained in a Pyrex tube of 4-mm. inside diameter. The tube had a drawn-out tip which contained a tight Pyrex wool plug. The portion of the tube above the plug was jacketed by water circulated from a bath controlled to within 0.05° of the recorded temperatures, which were determined with a thermometer certified by the National Bureau of Standards.

When the solvent was changed, the column was first rinsed several times, and determinations of iodine concentration were repeated until results were reproducible. Samples for analysis were taken quickly, with the column tip very close to the receiving solution to minimize any loss of iodine to the air. All potassium iodide solutions were prepared just before use, using water redistilled from alkaline permanganate. All solutions passed through the column contained  $10^{-4} M$  perchloric acid to prevent the hydrolysis of iodine.

The analytical procedure was as follows. A weighed test tube containing  $V$  ml. (by calibrated pipet) of 0.100  $M$  potassium iodide was used to receive  $m$  g. (mass by difference) of the column output solution. After rapid and thorough mixing the absorbance,  $A$ , at 353  $m\mu$  (absorption maximum for triiodide ion) was determined with a Beckman B spectrophotometer, using 1-cm. Pyrex cells with the same 0.100  $M$  potassium iodide solution as the reference. In a typical experiment,  $V$  was 10 ml. and  $m$  was 0.2 g., but, because of the variations of iodine solubility with conditions, these quantities were adjusted to make the absorbance fall into the optimum range of 0.4–0.5.

The molar solubility,  $S'$ , is then calculated by the equation

$$S' = \frac{A(Vd + m)}{\epsilon'm} \quad (4)$$

where  $d$  is the density of the saturated solution taken from the column, and  $\epsilon'$  is the apparent molar absorptivity at 353  $m\mu$  of the  $I_2$ – $I_3^-$  mixture in the final solution (0.100  $M$  iodide causes about 99% conversion to triiodide). The molal solubility,  $S$ , is simply equal to  $S'/d$  in the very dilute solutions used. The densities of these solutions do not differ by more than 0.1% from that of water (or heavy water), and this nominal correction was used throughout.

The apparent absorptivity was determined through measurements similar to those used for the solubility determinations, but using iodine solutions standardized vs. arsenous oxide. For the potassium iodide molarity

- (1) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **77**, 5814 (1955).
- (2) M. Davies and E. Gwynne, *ibid.*, **74**, 2748 (1952).
- (3) E. Rengevich and E. Shilov, *Ukr. Khim. Zh.*, **28**, 1080 (1962); *Chem. Abstr.*, **59**, 4590 (1963).
- (4) G. Jones and B. B. Kaplan, *J. Am. Chem. Soc.*, **50**, 1845 (1928).
- (5) W. C. Bray and C. M. MacKay, *ibid.*, **32**, 914 (1910).
- (6) A. D. Awtry and R. E. Connick, *ibid.*, **73**, 1842 (1951).
- (7) G. Daniele, *Gazz. chim. ital.*, **90**, 1068 (1960).

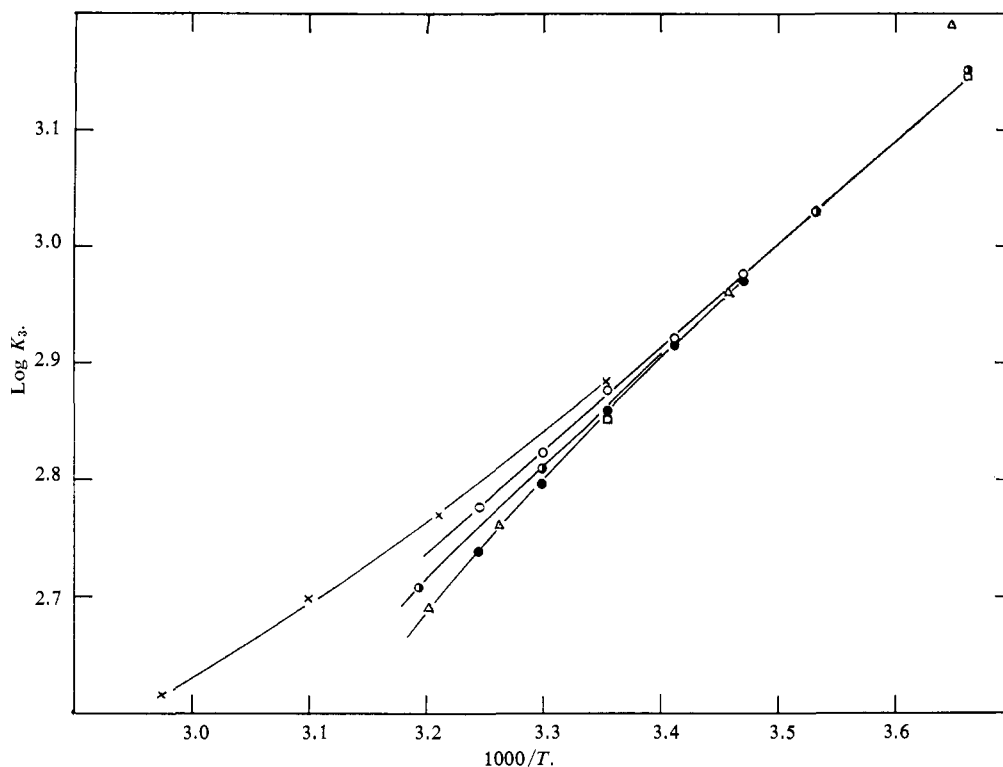


Figure 1. Variation of  $K_3$  and  $K_3'$  with temperature: ○, present work, solubility; ●, Daniele, spectrophotometric; △, Awtrey and Connick, spectrophotometric; ×, Davies and Gwynne, distribution; □, Jones and Kaplan, potentiometric; ⊙, Rengevich and Shilov, distribution.

of 0.100, the value of  $\epsilon'$  was found to be 25,900 l./mole cm. The absorptivity, correcting for the incomplete conversion to triiodide, is then 26,200, in close agreement with previously reported values.<sup>6,7</sup>

The corrected absorptivity (determined with a Cary Model 15 spectrophotometer) at 353  $m\mu$  was found to be a linear function of iodide concentration, expressed by  $\epsilon = 26,000 + 2200[I^-]$  in the range up to 1  $M$  iodide. At 287  $m\mu$ , the other triiodide absorption maximum, the absorptivity decreased with iodide concentration, approximately in the relationship,  $\epsilon = 39,700 - 3600[I^-]$ . Such effects have been noted before,<sup>8</sup> and, since the shifts are in different directions, they may be qualitative evidence for the formation of a new species, possibly  $I_4^{2-}$ . French and Effenberger<sup>9</sup> have also concluded that the species  $I_4^{2-}$  exists as well as other species.

The equations for the temperature dependence of equilibrium constants were established by the method of least squares using an IBM 1620 computer. The Fortran program, which also calculated all thermodynamic results, is available from the authors.

#### Comments on Previous Work

Figure 1 shows that there has been a lack of good agreement at 25° and a more serious divergence at both lower and higher temperatures. The various slopes of the  $\log K_3$  vs.  $1/T$  plots have led to reported values of  $\Delta H^\circ$  for reaction 2 ranging from -3300 to -5100 cal./mole.

(8) Y. Chia, Thesis, University of California at Berkeley, UCRL 8311, 1958.

(9) French and Effenberger, Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3-8, 1961, p. 25T.

The two spectrophotometric studies gave values of  $K_3$  which not only were lower but which are best described by a downward curve. Solubility results are higher and give a linear plot. The results of one distribution study are still higher and the plot is an upward curve.

*Spectrophotometric.* The inherent advantage in a spectrophotometric approach is the suitability of very low concentrations of both iodine and iodide ion. This eliminates activity coefficient problems and avoids any appreciable formation of higher complexes. It is noted that extremely careful potentiometric measurements,<sup>4</sup> which also used very low concentrations, gave a result at 25° which was even slightly lower than the spectrophotometric values.

In the case of solubility measurements, however, even using 0.01  $M$  potassium iodide, the free iodine concentration is about 100 times that used in the spectrophotometric work, and the triiodide concentration is about 1000 times as large. If these conditions lead to the significant formation of higher polyiodide species, the  $K_3$  values calculated on the basis of the simple model of eq. 1 and 2 only would be too high. If the effect increases with temperature, the  $\log K$  vs.  $1/T$  plots would tend to become linear with smaller slopes.

The most recent determination of  $K_3$  is the work of Daniele,<sup>7</sup> whose spectrophotometric measurements were carried out at both absorption maxima, using a wide variation of very low iodine and iodide concentrations, with very closely agreeing results for about 80 measurements at each of five temperatures. We recommend the adoption of this excellent study as the standard of reference for the discussion of other work. The values of  $K_3$  ( $t^\circ$ ) obtained by Daniele are 935 (15.0), 824 (20.0), 723 (25.0), 626 (30.0), and 547 (35.0),

and are described with an average deviation of less than 0.2% by the equation

$$\log K_3 = 2.8580 - 1.170 \times 10^{-2}(t - 25) - 3.77 \times 10^{-5}(t - 25)^2 \quad (5)$$

The corresponding thermodynamic quantities at 25° are then:  $\Delta F^\circ = -3900$  cal./mole,  $\Delta H^\circ = -4760$  cal./mole, and  $\Delta S^\circ = -2.88$  cal./deg. mole. The calculated value of  $\Delta C_p$  is  $-63$  cal./deg. mole, but this is sensitive to slight variations in the  $K_3$  values used in obtaining the fit. Equation 5 gives 721 as the best value of  $K_3$  at 25°.

The other important spectrophotometric study is by Awtrey and Connick,<sup>6</sup> who determined the temperature dependence of the absorbance of a single solution containing 0.002 *M* potassium iodide and approximately  $3 \times 10^{-6}$  *M*  $I_2 + I_3^-$ . To the inherent advantages of spectrophotometry, this approach adds the nicety that the solution is left undisturbed and unchanged throughout, thus permitting optimum internal precision. However, the interpretation of the data requires precise knowledge of the molar absorptivity (which the authors determined in separate experiments) and an assumed value for  $K_3$  at one of the temperatures used. Awtrey and Connick chose  $K_3 = 714$  at 25°, from the precise potentiometric work of Jones and Kaplan, and calculated the  $K_3$  values at other temperatures on this basis. Though it does not make a large difference, we have recalculated the results using the value  $K_3 = 721$  as obtained from Daniele's work. The results then are 1552 (1.0°), 917 (16.1°), 721 (25.0°), 577 (33.4°), and 491 (39.2°). These are the values plotted in Figure 1, and it is seen that the agreement with Daniele's values is excellent. However, the point at 1° is inconsistent with the trend and with earlier results at 0°. When it is included in a linear fit of the data,  $\Delta H^\circ = -5100$  cal./mole as reported by Awtrey and Connick. However, it seems preferable to omit this point and to describe the results by the quadratic equation

$$\log K_3 = 2.8587 - 1.168 \times 10^{-2}(t - 25) - 6.9 \times 10^{-6}(t - 25)^2 \quad (6)$$

This leads to the following values at 25°:  $K_3 = 722$ ,  $\Delta F^\circ = -3900$  cal./mole,  $\Delta H^\circ = -4750$  cal./mole,  $\Delta S^\circ = -2.85$  cal./deg. mole, and  $\Delta C_p = -37$  cal./deg. mole. Except for the  $\Delta C_p$  value, these results agree excellently with those from Daniele's data, and the thermodynamics of reaction 2 are thereby firmly established. Therefore the deviations of the solubility and distribution studies will be discussed in terms of interactions previously overlooked.

**Distribution.** In their study of the distribution of iodine between carbon tetrachloride and solutions up to 1 *M* in potassium iodide, Davies and Gwynne<sup>2</sup> calculated apparent values of  $K_3$  on the basis of the simple model of the molecular distribution of iodine and the formation of triiodide only, using the relationship

$$K_3' = \frac{C - [I_2]}{[I_2](C_K - C + [I_2])} \quad (7)$$

where *C* is the molar concentration of titratable iodine in the aqueous phase,  $[I_2]$  is the free iodine concentration calculated from the known distribution coef-

ficient and the determined molarity of iodine in the carbon tetrachloride phase,  $C_K$  is the initial concentration of potassium iodide, and the activity coefficients have been disregarded. The values of  $K_3'$  ranged up to over 1200 as the iodine concentration, and hence the triiodide concentration increased. Davies and Gwynne showed that the trend in  $K_3'$  values was better explained by postulating the formation of  $I_6^{2-}$  by reaction 3 than by the formation of the species  $I_5^-$ , and they calculated fairly consistent values of  $K_6 \approx 1$  at  $C_K = 1$ .

A more precise distribution study, at much lower potassium iodide concentrations, has recently been reported by Rengevich and Shilov.<sup>3</sup> The results are summarized in the equation

$$\log K_3 = +2.8613 - 1.074 \times 10^{-2}(t - 25) + 3.55 \times 10^{-5}(t - 25)^2 \quad (8)$$

It can be seen from Figure 1 that this work lies between the spectrophotometric and solubility studies. The value of  $\Delta H^\circ$  is calculated to be 4369 cal./mole at 25°.

Evidently the high ionic strengths employed by Davies and Gwynne do not permit accurate extrapolation to thermodynamic values for  $K_3'$ .

## Results and Discussion

It had been hoped, in the present work, that the accurate determination of solubilities in very dilute (0.01 *M*) potassium iodide solutions would lead to  $K_3$  values in better agreement with the spectrophotometric work. Thus, the low concentration of iodide would minimize  $I_6^{2-}$  formation and activity coefficient effects, and the use of the packed-column technique and direct spectrophotometry would achieve higher precision in the values of  $K_3$  over a wider temperature range than had previously been studied.

**Results in the Absence of Iodide.** Our results for the intrinsic solubility (reaction 1) of iodine in slightly acidified water are summarized in Table I.

**Table I.** Intrinsic Solubility of Iodine in Water and in Heavy Water

Temp., °C.	$M \times 10^{-3}$	
	H <sub>2</sub> O	D <sub>2</sub> O
2	0.672	
5		0.613
11	0.856	
15		0.814
20	1.127	
25	1.326	1.088
30	1.537	
35	1.796	1.462
40.2	2.122	
44.9	2.470	1.965
49.1	2.850	
50.3		2.305

The molal values of  $K_0$  are accurately described by the equations

$$\log K_0(\text{H}_2\text{O}) = -2.8812 + 1.334 \times 10^{-2}(t - 25) + 2.520 \times 10^{-5}(t - 25)^2 \quad (9)$$

$$\log K_0(\text{D}_2\text{O}) = -2.9630 + 1.268 \times 10^{-2}(t - 25) + 8.592 \times 10^{-6}(t - 25)^2 \quad (10)$$

**Table II.** Molal Thermodynamic Quantities  $I_2(c) \rightleftharpoons I_2(aq)$  at 25°

	In H <sub>2</sub> O	In D <sub>2</sub> O	Change
$K_0$	1.315 × 10 <sup>-3</sup>	1.089 × 10 <sup>-3</sup>	
$\Delta F^\circ$ , cal./mole	+3930	+4042	+112
$\Delta H^\circ$ , cal./mole	+5426	+5157	-269
$\Delta S^\circ$ , cal./deg. mole	+5.01	+3.73	-1.48
$\Delta C_p$ , cal./deg. mole	+57	+42	-15

**Table III.** Iodine Solubilities in Water and Heavy Water Solutions of Potassium Iodide, and Apparent Values of  $K_3$ 

Temp., °C.	In water				In heavy water			
	10 <sup>2</sup> × M KI	No. of detrn.	S' × 10 <sup>3</sup>	$K_3'$	10 <sup>2</sup> × M KI	No. of detrn.	S' × 10 <sup>3</sup>	$K_3'$
15.0	0.999	7	5.76	949	1.002	10	5.30	870
20.1	1.008	4	6.00	828	1.002	9	5.49	768
20.0	1.000	3	6.00	842				
25.0	0.999	4	6.27	751	1.002	10	5.69	676
25.0	1.009	7	6.32	752				
30.0	1.000	3	6.58	666	1.002	9	5.98	608
35.0	0.993	3	6.97	601	1.002	9	6.31	548
35.0	0.999	2	6.93	593				

The standard interpretation of these temperature dependences gives the results shown in Table II.

The change in  $\Delta H^\circ$  in going from water to deuterium oxide is substantially negative, by itself tending to cause an increase in the solubility. However, the negative difference in the entropy change is more than sufficient to overcome the heat effect, and the free energy difference is therefore positive.

The standard entropy of solid iodine is given<sup>10</sup> as 27.76 cal./deg. mole at 25°. From the above results we conclude that the standard entropy of  $I_2(aq)$  is 32.8 in water and 31.5 in deuterium oxide.

From Daniele's work, the standard entropy change for reaction 2 is -2.88 cal./deg. mole. Since the standard entropy of aqueous iodide ion<sup>10</sup> is known from other work to be 25.3, we calculate the standard entropy for the aqueous triiodide ion to be 55.2 cal./deg. mole.

*Results in the Presence of Iodide.* What we now recognize as apparent values for  $K_3$  were calculated using solubility results in 0.01 M potassium iodide. Assuming reactions 1 and 2 only, the relationship is

$$K_3' = (S' - K_0)/K_0(C_K - S' + K_0) \quad (11)$$

where  $S'$  is the molar solubility in the presence of  $C_K$  molar potassium iodide, and molar  $K_0$  values are calculated from eq. 9 and 10 and the known densities. The data and results are shown in Table III.

The results of Katzin and Gebert<sup>1</sup> in the presence of 0.01 M perchloric acid agree closely with the above at 20 and 25° but are slightly higher at 30°.

In a few experiments using 0.02 and 0.005 M potassium iodide we obtained agreeing results at 25° in water, but the precision was less with the more dilute solution.

The present values of  $K_3'$  are given by the equations  $\log K_3' (H_2O) = 2.8737 - 1.000 \times 10^{-2}(t - 25) + 2.834 \times 10^{-4}(t - 25)^2$  (12)

(10) K. K. Kelley and E. G. King, "Entropies of the Elements and Inorganic Compounds," U. S. Bureau of Mines, Bulletin 592, U. S. Government Printing Office, Washington, D. C., 1961.

$$\log K_3' (D_2O) = 2.8319 - 1.008 \times 10^{-2}(t - 25) + 7.506 \times 10^{-4}(t - 25)^2 \quad (13)$$

The apparent molal thermodynamic quantities which follow from these equations are presented in Table IV. The effects of change of solvent on the thermodynamic quantities for this reaction are so slight as to be within experimental error. The fairly high stability of the triiodide is due largely to the enthalpy change, with the entropy change playing a minor role.

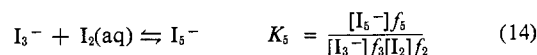
**Table IV.** Apparent Molal Thermodynamic Quantities for  $I_2(aq) + I^- \rightleftharpoons I_3^-$  at 25° Obtained from Solubility Measurements

	In water	In heavy water
$K_3'$ (molal)	748	753
$\Delta F^\circ$ , cal./mole	-3918	-3928
$\Delta H^\circ$ , cal./mole	-4066	-4097
$\Delta S^\circ$ , cal./deg. mole	-0.49	-0.59

It remains now to explain why the solubility method gives  $K_3'$  values which are too high, and a  $\Delta H^\circ$  value some 800 cal./mole less negative than those accepted from the spectrophotometric work.

*The Evidence for  $I_5^-$ .* Because the dimerization of triiodide ion was established by the distribution results discussed above, it is appropriate to try to invoke reaction 3 as an explanation for the solubility results. However, the algebraic result is similar to eq. 7 with  $[I_2]$  replaced by  $K_0$  since the solutions are saturated. This model would require  $K_3'$  to be a linear function of the iodide concentration. We found constant values for  $K_3'$  at potassium iodide molarities of 0.005, 0.01, and 0.02, while Katzin and Gebert found constant values in the range from 0.025 to 0.07 M. If we calculate  $K_6$  values anyway, we find  $K_6 \approx 5$  at 25°, although from activity coefficient considerations it should be lower than the value of  $K_6 = 1$  found by Davies and Gwynne in 1 M potassium iodide. Further, the apparent values of  $K_6$  at our several temperatures would lead to an abnormally high enthalpy change for such a reaction. Since the third term of eq. 8 seems negligible with the free iodide molarity equal to 0.005-0.04, we conclude that the value of  $K_6$  at these lower ionic strengths does not exceed 0.1.

Instead, the results seem better explained by the formation of  $I_5^-$



where, as in the case of reaction 3, activity coefficients will be neglected at low ionic strengths. The solu-

bility of iodine in iodide solutions is now expressed as

$$S' = [I_2] + [I_3^-] + 2[I_5^-] + 2[I_6^{2-}] \quad (15)$$

and the concentration of potassium iodide is

$$C_K = [I^-] + [I_3^-] + [I_5^-] + 2[I_6^{2-}] \quad (16)$$

From eq. 1, 2, 3, 14, 15, and 16 it follows that

$$S' = K_0 + K_0 K_3 [I^-] + 2K_0^2 K_3 K_5 [I^-] + 2K_0^2 K_3^2 K_6 [I^-]^2 \quad (17)$$

$$[I^-] = \frac{C_K - S' + K_0}{1 - K_0^2 K_3 K_5} \quad (18)$$

$$K_3' = \frac{K_3 + 2K_0 K_3 K_5}{1 - K_0^2 K_3 K_5} + \frac{2K_0 K_3^2 K_6 (C_K - S' + K_0)}{(1 - K_0^2 K_3 K_5)^2} \quad (19)$$

Equation 19 shows that the apparent value for  $K_3$  would always be higher than the true value, even when the potassium iodide concentration approaches zero, or even if the effect of  $K_6$  is negligible. Assuming that the latter is true for our solutions, we may solve for  $K_5$  with the result

$$K_5 = \frac{K_3' - K_3}{K_0 K_3 (2 + K_0 K_3')} \quad (20)$$

By using eq. 12 for  $K_3'$  values, eq. 9 for  $K_0$  values, and eq. 5 for  $K_3$  values, we have calculated  $K_5$  as a function of temperature, with the result

$$\log K_5 \approx 0.954 + 0.0308(t - 25) \quad (21)$$

The thermodynamic values for 25° are:  $\Delta F^\circ = -1.3$  kcal./mole,  $\Delta H^\circ \approx +12$  kcal./mole, and  $\Delta S^\circ \approx 50$  cal./deg. mole, but little reliability can be placed on these values. The value of  $K_5$  at 25° is about 9.

The postulation of  $I_5^-$  also accounts qualitatively for the intermediate position of the distribution results for  $K_3'$ , since those studies involved intermediate concentrations of  $I_2$  and  $I_3^-$ .

Finally, we have determined that the inclusion of the  $I_5^-$  results in the interpretation of the distribution data does not materially affect the calculated values of  $K_6$ .

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## Properties of Bases in Acetonitrile as Solvent. IV. Proton Acceptor Power and Homoconjugation of Mono- and Diamines

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*Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213. Received June 30, 1965*

The dissociation constants of the conjugate acids of 31 amines of various structural types were measured in anhydrous acetonitrile as solvent by means of a glass electrode shown to respond reversibly to hydrogen ion activity in this solvent. The electrode was calibrated in a series of buffers containing picric acid and tetraethylammonium picrate, using the dissociation constant found for picric acid in a careful study by Kolthoff and Chantooni. All measurements were carried out at a constant and sufficiently low ionic strength to allow extrapolation of equilibrium constants to their limiting values. No simple, quantitative correlation was found between base strengths in acetonitrile and water. Although the  $pK_a$  values of the majority of the ammonium ions studied are from 7.2 to 7.9 units greater in acetonitrile than in water, several ions differ significantly from this "norm." Aromatic ions are considerably stronger acids in acetonitrile than would be predicted from the strengths of aliphatic ions. In the series of monoprotonated diamines,  $H_2N(CH_2)_nNH_3^+$ , the acids with  $n = 3$  and 4 derive considerable stability from intramolecular hydrogen bonding. Although acetonitrile is much more inert than water, its solvation of ammonium ions still exerts an important influence. Steric inhibition of solvation appears to be more important in acetonitrile than in water. A correlation exists between the base

strength of an amine,  $B$ , and its tendency to form homoconjugated complexes,  $B_nBH^+$ , in acetonitrile.

During recent years considerable evidence has been obtained for the hypothesis, originally proposed by Trotman-Dickenson<sup>3</sup> and others, that the relative hydration of an amine and its conjugate acid may influence the proton acceptor power of the amine in water to a marked extent. For example, this hypothesis adequately accounts for the fact that, in aqueous solution, secondary amines generally are the strongest and tertiary amines the weakest proton acceptors, while inductive effects alone would lead to an order of strengths increasing from the primary to the secondary to the tertiary amine. This and other consequences of the solvation hypothesis were discussed for a large number of amines by Hall.<sup>4</sup>

Much less is known about corresponding solvation effects in solvents other than water, with a few notable exceptions. Spectrophotometric studies by Davis and Hetzer<sup>5</sup> and by Pearson and Vogelsson<sup>6</sup> of the reaction of certain amines with reference (indicator) acids in low

(3) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

(4) H. K. Hall, Jr., *J. Am. Chem. Soc.*, 79, 5441, 5444 (1957).

(5) M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, 48, 381 (1952).

(6) R. G. Pearson and D. C. Vogelsson, *J. Am. Chem. Soc.*, 80, 1038 (1958).

(1) Address all correspondence to this author.

(2) From the Ph.D. Thesis of G. R. P., University of Pittsburgh, 1963.