hydration should be greater for anions than for cations. The argument involves the orientation of water molecules and the possibility of additional motions. An additional energetic argument could be based on the fact that the center of positive charge in a dipolar water molecule is closer to the surface than is the center of negative charge, and the interaction with a negative ion will be stronger than with a positive ion.

The extreme entropy differences apparently involve additional configurational effects that undoubtedly are also reflected in the enthalpy values. Thus the anions plotted in Fig. 5 show irregular behavior not at all like that of the cations. These irregularities cannot be explained by uncertainties in electron affinities even though these quantities are known less well than the ionization energies needed for the cation data.

The discrete structure of solvent will be involved in any interpretation of these irregularities. One of the more surprising consequences of this work is the observation that data for cations with an inert gas structure fall so nicely on a smooth curve despite a six-fold change in radius. The water molecules around a cation extend their protons outward, and apparently ions having a wide range of sizes lead to configurations that adapt themselves to the surrounding water structure. Anions require the hydrogens of the water molecules to be directed inward, and it may be that the possible configurations of the inner hydration spheres are more sharply dependent on the size of the central ion.

Acknowledgment.—This work was supported in part by the National Science Foundation under Grants NSF-G-7330 and NSF-G-19646. Professor Henry S. Frank of the University of Pittsburgh made some very helpful comments that led to improved understanding of the entropy values.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK]

Deuterium Isotope and Solvent Effects on the Kinetics of the Keto-enol Interconversion of 2-Acetylcyclohexanone[1]

BY T. RILEY[2] AND F. A. LONG

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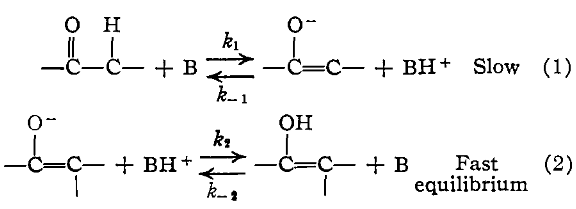
The rate of enolization of 2-acetylcyclohexanone, as measured by its rate of bromination, exhibits general base catalysis (only) with a Brønsted β of 0.60. The datum for water as a base fits well with the data for other bases. The relative reactivity of the 2-monodeuterated ketone leads to a kinetic isotope effect of $k_{KH}/k_{KD} \simeq 5$ for reaction of the ketones with either of the catalysts water or acetate ion. For reactions of the ordinary ketone in the solvents H_2O and D_2O, $(k_{KH}{}^H/k_{KH}{}^D)_{OAc^-} = 1.2$, and $(k_{KH}{}^H/k_{KH}{}^D)_{water} = 1.4$, leading to the conclusion that the base strengths of the species H_2O and D_2O are in the ratio 1.2, *i.e.*, not significantly different. Measurements of the keto–enol equilibrium and of the acid strength of the enol in the solvents H_2O and D_2O permit calculation of the relative rates of the reverse reactions. For the over-all ketonization, the relative rates k_H/k_D are again about 5 for the various catalysts. For the slow step, the attack of acid on the enolate ion, the ratios are $(k_{E^-}{}^H/k_{E^-}{}^D)_{H_3O^+} = 1.7$ and $(k_{E^-}{}^H/k_{E^-}{}^D)_{HOAc} = 5.9$. Both ratios are close to those for methyl acetylacetone, and it is concluded that the solvated proton is only about 1.5 times a better acid than is the solvated deuteron. Finally, these data, along with similar results for hydroxide ion, lead to the conclusion that the species H_2O is about a 5-fold stronger acid than is D_2O.

The reversible base-catalyzed transformation of β-diketones into their enolic forms is a reaction whose mechanism is well established[3,4]



The rate of the forward reaction 1 can be conveniently measured by the rate of halogen uptake from solution since the enolate ion (E^-), once formed, reacts almost instantaneously with halogen. It is known that the enolization reaction is subject to general base catalysis[5–7] and that for β-diketones no acid catalysis occurs.[8,9] A summary of the previous studies on hydrogen isotope effects for these has been given recently by Bell.[10] The evidence points to a general solvent effect which alone will cause the reaction to be 20–40 % slower in D_2O than in H_2O. If one neglects this effect, which is superimposed on all comparisons of rates in H_2O and D_2O, then H_2O appears to be 20–30 % more effective as a base than D_2O. Conversely OH^- (in H_2O) is 30–40 % less effective as a base than OD^- (in D_2O).[10,11] Long and Watson[12] concluded from a study similar to the present one that the acid strengths of the species H_3O^+ and D_3O^+ are almost identical. These facts taken together with the

(1) (a) Work supported by a grant from the Atomic Energy Commission. (b) Presented in part at 139th Meeting of the American Chemical Society, St. Louis, Missouri, April 1961.

(2) King's College, London University, London, W.C. 2, England.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Ch. IV.

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Ch. X.

(5) H. M. Dawson, C. R. Hoskins and J. E. Smith, *J. Chem. Soc.*, 1884 (1929).

(6) K. J. Pedersen, *J. Phys. Chem.*, **38**, 999 (1934).

(7) R. P. Bell and co-workers, *Proc. Roy. Soc. (London)*, **A255**, 214 (1960), and earlier.

(8) R. P. Bell and O. M. Lidwell, *ibid.*, **A176**, 88 (1940).

(9) R. G. Pearson and J. M. Mills, *J. Am. Chem. Soc.*, **72**, 1692 (1950).

(10) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, New York, 1959, Ch. XI.

(11) Y. Pocker, *Chem. and Ind. (London)*, 1383 (1959).

(12) F. A. Long and D. Watson, *J. Chem. Soc.*, 2019 (1958).

known difference in the ion products of H_2O and D_2O suggest that H_2O is a much stronger acid than D_2O.[11,12] In view of the considerable uncertainty which has existed about the relative acid–base properties of the various species from water and in view of the importance of a knowledge of this for the understanding of acid–base reactions in the two solvents, it has seemed useful to do a further more extensive study. Use of the keto–enol transformation offers the additional point that, since the reaction exhibits general catalysis, comparisons can be made of the deuterium solvent isotope effect for other catalysts.

2-Acetylcyclohexanone is a suitable substrate for a study of this nature because it has only one hydrogen atom which can be replaced by bromine or deuterium. It also permits easy investigation of the over-all keto–enol equilibrium constant and of the acid dissociation constant of the enol. Knowledge of these enables the rates of the reverse reactions (*i.e.*, enol to ketone, and enolate ion to ketone) to be calculated. Hence one can obtain direct kinetic evidence on both the relative strength of water, as base, and of the solvated lyonium ions as acids. A further point of interest is that one may study the reactions of both monoprotonated and monodeuterated ketone in either solvent and thus obtain information on kinetic isotope effects as well.

Experimental

Materials.—2-Acetylcyclohexanone was prepared in an over-all yield of 57% from acetyl chloride and the morpholine complex of cyclohexanone[13] and had a boiling point of 74° (4 mm.). Eastman material used for part of the experiments had the same boiling point. Bromine titration indicated that the material from both sources was pure within experimental error and that only monobromination occurred.

Methylacetylacetone was prepared from the potassium salt of acetylacetone and methyl iodide[14] and had a boiling point of 57–58° (12 mm.). Both ketones were stored in the dark under refrigeration.

Acetic Acid.—Reagent grade material was used. A deuteriated sample (*i.e.*, AcOD) was obtained by dilution of the light material with D_2O (99.5%). **Glycolic acid** was reagent grade material recrystallized three times from ether, and melted at 81°. **Chloroacetic acid** was Eastman material. Titration against standard sodium hydroxide established that both glycolic acid and chloroacetic acid were > 99% pure. All acid solutions used were standardized against the same standard sodium hydroxide solution.

Sodium Hydroxide.—B.D.H. standard solution was diluted as required. **Sodium deuteroxide** solution was prepared by adding sodium to a mixture of toluene and D_2O in a separatory funnel. Dry carbon dioxide-free air was passed vigorously through the aqueous layer to remove traces of toluene. Solutions of sodium hydroxide and sodium deuteroxide were standardized against potassium hydroxide and sodium deuteroxide were standardized against potassium hydrogen phthalate.

Sodium Chloride.—Reagent grade material was dried at 100° before use.

Hydrochloric Acid.—Reagent material was used. Deuterium chloride solutions were prepared from concentrated hydrochloric acid and D_2O. These solutions were standardized against a standard sodium hydroxide solution.

Bromine.—Reagent grade material was used.

All solutions were made up from distilled water boiled to remove carbon dioxide, or from D_2O freed from carbon dioxide by flushing with dry carbon dioxide-free air. Because of occasional slight dilution effects it should be assumed that the phrase "D_2O as solvent" really refers to a solvent containing from 0.99 to 0.995 atom fraction deuterium. No attempt to correct data to values for pure D_2O has been made.

Procedure. (a) Enol Content of Ketone Solutions.—Known weights of ketone dissolved in H_2O and D_2O were left to equilibrate at 25° for approximately one day. The enol content of each was then determined by indirect bromine titration of the chilled aqueous solution.[15]

(b) Acid Dissociation Constants of the Ketones.—The gross pK_G values of the ketones in H_2O and D_2O were determined by measuring the *p*H of their solutions, partially neutralized (20–80%) by sodium hydroxide and sodium deuteroxide respectively. The ionic strength of the solutions was maintained at 0.01 *M* throughout by addition of sodium chloride. The solutions, magnetically stirred, were thermostated at 25° and dry nitrogen was passed over their surface as *p*H readings were taken. A Cambridge Research *p*H meter and a glass electrode assembly were used, and the *p*H scale was calibrated against standard buffers. For studies with D_2O as solvent the correction of Glasoe and Long[16] was used.

(c) Rates of Bromination.—The rate of bromination of the β-diketone was measured spectrophotometrically with a Beckman DU spectrophotometer by observing the absorption band of bromine at 3900 Å. Reactions were carried out in optical cells of 1 cm. path length thermostated at 25.00 ± 0.04°, and readings of optical density were taken at timed intervals. Ionic strengths of the solutions were maintained at 0.10 *M* throughout by addition of sodium chloride and for the experiments on base catalysis the *p*H of the solutions was kept within the range 4–6. Solutions for investigation of the catalysis by basic anions were prepared from standard solutions of sodium hydroxide (or sodium deuteroxide) and the appropriate acid. Corrections to the calculated concentration of basic anion were made (a) for the *p*H of the solution, and (b) for the amount of hydrobromic acid (or deuterobromic acid) liberated into solutions as reaction proceeded.[17] The effect of the presence of a varying concentration of strong acid on the "spontaneous" or water rate was also determined to establish whether or not catalysis by acids was detectable.

The ketone concentrations in the reaction cell initially were of the order 4×10^{-3} *M* after allowing for the instantaneous bromination of the enol content, and the initial bromine concentrations were usually a little less than this, *i.e.*, for the most part reactions were run with a slight excess of the ketone. The reaction as expected was first-order in ketone concentration and was independent of the bromine concentration. Good first-order plots were obtained with no indication of any side reactions.

When reactions of 2-acetylcyclohexanone-2-*d* were studied, this compound was made in solution by leaving a solution of the light material in D_2O for about one day before use.

An indication both of the accuracy of the experiments and of the methods of calculation is given in Table I which lists results for reaction of ordinary 2-acetylcyclohexanone (KH) in the solvent H_2O, in one case with no added base catalyst and in the second case with the catalyst glycolate ion. In these tables $k_{obsd.}$ is the observed first order constant in sec.$^{-1}$ and k_B (*i.e.* k_{H_2O} or k_{OG^-}) the second order velocity constant in l. mole^{-1} sec.$^{-1}$, using 55.5 for the molar concentration of water for the "spontaneous" reaction.

The studies with other catalysts and solvents were done in similar detail and led to results of comparable accuracy.

Results and Discussion

Table II summarizes the second order rate coefficients obtained in this study. The data for aqueous solutions of the ordinary ketone with various catalysts clearly show the expected general base catalysis. Figure 1 is a conventional Brønsted plot of these data. They lead to a β-value, *i.e.* slope of log k_B *vs.* log K_B, of 0.60, about as expected. [The data for catalysis in deuterium oxide are less complete and are not included in Fig. 1 but they lead to the closely similar β of 0.6.] The data for

(13) *Cf.* S. Hünig, E. Benzing and E. Lücke, *Ber.*, **90**, 2833 (1957).

(14) W. H. Perkin, *J. Chem. Soc.*, **61**, 848 (1892).

(15) M. L. Eidinoff, *J. Am. Chem. Soc.*, **67**, 2073 (1945).

(16) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

(17) R. P. Bell and H. L. Goldsmith, *Proc. Roy. Soc.* (*London*), **A210**, 322 (1952).

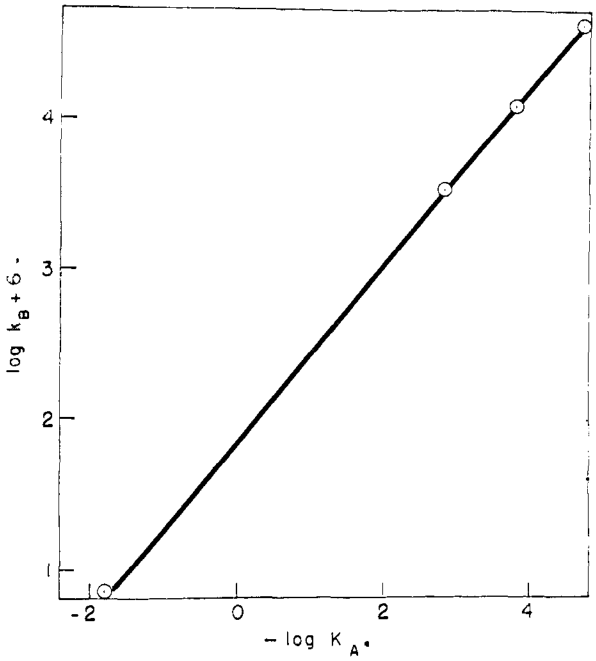


Fig. 1.—Brønsted plot for general base catalyzed enolization of 2-acetylcyclohexanone.

water as catalyst fit the line of the plot very well. This result has been noted before for β-diketones[7] and in this and other respects the present data fit well with the related extensive studies of Bell and co-workers.[7,18] In particular Bell[18] has shown that there is a relationship between the pK_G of the ketone, and the values of log R and β for a series of structurally related β-diketones (R is the catalytic constant $\equiv k_B$ for the anion of a hypothetical acid of pK 4). Another parameter which shows a similar trend is the water rate, log $k_{obsd.}^{H_2O}$, for the same series of compounds.[19] The present data for 2-acetylcyclohexanone (log $k_{obsd.}^{H_2O} = -3.40$, $\beta = 0.60$, log $R = -1.68$, $pK = 9.85$) fit in well between ethyl-2-carbethoxy-cyclohexanone[17] (log $k_{obsd.}^{H_2O} = -5.01$, $\beta = 0.67$, log $R = -2.76$, $pK = 10.94$) and ethylacetoacetate[20] (log $k_{obsd.}^{H_2O} = -3.22$, $\beta = 0.59$, log $R = -1.06$, $pK = 10.68$), except that the value of pK seems slightly low. Bell and McDougall[21] have recently measured the extent of hydration of some ketones in aqueous solution, and it is pointed out by Bell and Hansson[7] that this factor must be taken into account in the present type of analysis. No data on the extent of hydration, if any, of 2-acetylcyclohexanone are at hand and so the effect cannot be determined.

The data of Table II show the expected kinetic and solvent isotope effects. Thus for the reaction of KH and acetate ion in the two solvents

$$\left(\frac{k_{KH}^H}{k_{KH}^D}\right)_{OAc^-} = \frac{4.44}{3.69} = 1.2$$

where the superscripts H and D are used to denote

(18) Ref. 10, Chapter X.

(19) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(20) R. P. Bell, E. Gelles and E. Möller, *Proc. Roy. Soc. (London)*, **A198**, 310 (1949).

(21) R. P. Bell and A. O. McDougall, *Trans. Faraday Soc.*, **56**, 1281 (1960).

TABLE I

RATE OF BROMINATION OF 2-ACETYLCYCLOHEXANONE IN WATER AT 25°

$[H^+]$	$10^4 k_{obsd.}$	$10^6 k_{H_2O}$
(a) Spontaneous reaction; added hydrochloric acid		
0.01	3.97	7.15
.02	3.96	7.14
.05	3.91	7.05
.10	3.99	7.19

$k_{H_2O} = 7.13 \times 10^{-1}$ l. mole^{-1} sec.$^{-1}$

$10^3[B]$	$10^4 k_{obsd.}$	$10^4(k_{obsd.} - k_{obsd.}^{H_2O})$	$10^2 k_B$
(b) Reaction with glycolate ions, B = OG$^-$			
5.99	4.65	0.69	1.15
15.99	5.96	2.00	1.25
21.25	6.64	2.68	1.26
30.00	7.69	3.73	1.24
39.10	8.85	4.89	1.25

$k_{OG^-} = 1.23 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$

TABLE II

RATES OF ENOLIZATION AT 25° AND IONIC STRENGTH OF 0.1

Substrate	Solvent	Catalyst	$10^2 k_B$
KH	H_2O	H_2O	7.13×10^{-3}
KH	H_2O	Acetate ion	44.4
KH	H_2O	Glycolate ion	12.4
KH	H_2O	Chloroacetate ion	3.38
KH	D_2O	D_2O	5.08×10^{-3} [a]
KH	D_2O	Acetate ion	36.9 [a]
KD	D_2O	D_2O	1.13×10^{-3}
KD	D_2O	Acetate ion	6.72
KD	D_2O	Glycolate ion	2.87

[a] Values corrected to 99% D_2O as solvent; the actual experiments were performed in 95% D_2O and led to rate coefficients of 5.17×10^{-6} and 3.72×10^{-2}, respectively.

the two solvents H_2O and D_2O. Since for this reaction both the substrate and the catalyst are identical, the entire departure of the ratio from unity must be attributed to a general solvent effect. The corresponding ratio for catalysis by water is

$$\left(\frac{k_{KH}^H}{k_{KD}^D}\right)_{water} = \frac{7.13}{5.08} = 1.4$$

It is reasonable to assume that the general solvent effect is the same here as for the acetate ion reaction. If so, then the relative base strengths of H_2O (in H_2O) to D_2O (in D_2O), for reaction with a weak carbon–hydrogen acid, are in the approximate ratio of 1.4/1.2 or 1.2. Within the accuracy of the data one can thus conclude that the base strengths of these two are virtually identical, a conclusion also supported by the studies with methylacetylacetone.[12]

The data of Table II also lead to the following ratios for the *kinetic isotope effect* for reaction of the ketone with bases

$$\left(\frac{k_{KH}^D}{k_{KD}^D}\right)_{D_2O} = \frac{5.08}{1.13} = 4.5; \quad \left(\frac{k_{KH}^D}{k_{KD}^D}\right)_{OAc^-} = \frac{36.9}{6.72} = 5.5$$

These large ratios are much as expected, both in terms of general principles and of previous experiments with ketones.[22] The reason for the higher ratio for acetate ion relative to water is not known,

(22) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955), summarizes the information on both points.

but a similar result has been found in previous related studies.[12,23]

In order to discuss the relative rates for the reverse, enol to ketone reaction, it is necessary to have information both on the equilibrium constant for the reaction and on the acid strength of the enol. Tables III and IV summarize data. In every case the listed numbers are averages of at least four measurements which agreed well with each other. Also included in Table IV are data on pK_{EH} for methylacetylacetone in H_2O and D_2O since these were not previously measured.[24]

TABLE III

ENOL CONTENT OF EQUILIBRATED KETONE SOLUTIONS AT 25°

Ketone	Solvent	Enol, %	K_{eq}[a]
2-Acetylcycloyexanone	H_2O	29.2[b]	0.41
2-Acetylcyclohexanone-2′-D	D_2O	25.9	.35
Methylacetylacetone	H_2O	3.3[c]	.034[c]
Methylacetylacetone-3′-D	D_2O	2.4[c]	.025[c]

[a] K_{eq} = [EH]/[KH] for water or [ED]/[KD] for D_2O as solvent. [b] Schwarzenbach and Felder[25] give a value of 29.1% at 20°. [c] Values from Long and Watson.[12]

TABLE IV

THERMODYNAMIC ACID IONIZATION CONSTANTS IN H_2O AND D_2O, 25°

pK_G is gross dissociation constant of substrate: pK_E is ionization constant of enol form, *i.e.* $K_E/K_G = K_{eq}/(1 + K_{eq})$

Substrate	pK_G^H	pK_G^D	pK_{EH}^H	pK_{ED}^D
2-Acetylcyclohexanone	9.85[a]	10.44	9.47	9.98
Methylacetylacetone	10.82[b]	11.35	9.35	9.75

[a] Ref. 25 lists 10.01 for this. [b] Given as 10.82 by Pearson and Mills[2] and as 11.06 in ref. 25.

In terms of the mechanism given earlier for the keto–enol transformation one can write for the second, equilibrium step 2, $k_{-2}/k_2 = K_{EH}/K_{BH^+}$ where K_{EH} and K_{BH^+} are acid ionization constants for enol and for the conjugate acid of the catalyst, respectively. (Our conventions lead for water as catalyst to $K_{BH^+} = 55.5$.) Then for the equilibrium, defined as in Table III

$$K_{eq} = \frac{[EH]}{[KH]} = \frac{k_1}{k_{-1}}\frac{K_{BH^+}}{K_{EH}} = \frac{k_1}{k_r}$$

where k_r is simply the second order rate coefficient for the over-all reaction between enol and base catalyst. The data of Tables III and IV (combined with available ionization constants for the catalysts) now permit us to calculate both k_r and k_{-1}. The latter is of particular interest since it is the rate coefficient for the slow *acid catalyzed* reaction of the enolate ion. Tables V and VI summarize the results.

If we look first at the over-all base catalyzed reaction, it is noteworthy that for the true equilibrium reaction (substrates KH or EH in water and KD or ED in D_2O) the change to the deuterium system causes a roughly five-fold decrease in rate in either direction. Furthermore there is little indication of a significant effect of strength of the catalyst base, at least as between the species water and acetate ion, independent of whether the reaction involves a direct slow proton removal or a pre-equilibrium. These results as well as those next to be discussed for acids agree with the general predictions of Long and Bigeleisen.[26]

TABLE V

BASE CATALYZED CONVERSION OF ENOL TO KETONE

Reaction	Solvent	$10^5 k_r$, l. m.$^{-1}$ s.$^{-1}$	k_r^H/k_r^D
EH + H_2O	H_2O	0.73	5.3
ED + D_2O	D_2O	0.33	
EH + OAc^-	H_2O	10800	5.6
ED + OAc^-	D_2O	1920	
EH + OG^-	H_2O	3020	3.7
ED + OG^-	D_2O	820	

TABLE VI

ACID CATALYZED REACTION OF ENOLATE, μ = 0.1

Reaction	Solvent	$10^{-3}k_{-1}$, l. m.$^{-1}$ s.$^{-1}$	k_{-1}^H/k_{-1}^D
$E^- + H_3O^+$	H_2O	1780	1.66
$E^- + D_3O^+$	D_2O	1070	
E^- + HOAc	H_2O	5.75	5.9
E^- + DOAc	D_2O	0.98	
E^- + HOG	H_2O	11.5	3.4
E^- + DOG	D_2O	3.4	

For the slow attack of acids on the enolate ion, the situation is very different. The strong acid species H_3O^+ leads to a k_{-1}^H/k_{-1}^D value of 1.7 whereas with acetic acid as reactant the value is 5.9. When Long and Watson made similar calculations for the enolate ion of methylacetylacetone their results were uncertain because of a lack of the value for pK_{ED}^D. Using the value for this from Table VI, a recalculation of their data leads to k_{1-}^H/k_{-1}^D values of 1.3_5 and 6.9 for the solvated proton and acetic acid respectively. It thus appears from these enolate ion reactions that H_3O^+ (in H_2O) is roughly 1.5 times a stronger acid than is D_3O^+ (in D_2O). Put another way, the large effects predicted by a conventional zero point energy argument and found for the weak acid acetic do not show up for the solvated proton.

As noted earlier,[12] these various results also permit a comparatively unambiguous assessment of the relative *acid* strengths of the species H_2O and D_2O. The ratio of ion products for these two is 1/6.5,[27] and this can be expressed as

$$\frac{K_w^H}{K_w^D} = \frac{1}{6.5} = \frac{R_{H_3O^+}{}^A \times R_{OH^-}{}^B}{R_{H_2O}{}^A \times R_{H_2O}{}^B}$$

where $R_{H_3O^+}{}^A$ is the relative acid strength of H_3O^+ and D_3O^+ etc. From the present study $R_{H_3O^+}{}^A = 1.5$ and $R_{H_2O}{}^B = 1.4$, where for consistency we use observed values of the ratios in every case, *i.e.*, we include the "medium effect." Taking the value $R_{OH^-}{}^B = 0.7$ from the work of Pocker[11] on the rate of reaction of acetone with OH^- and OD^-, we have

(23) R. P. Bell, J. A. Fendley and J. R. Hulett, *Proc. Roy. Soc.* (*London*), **A235**, 453 (1956).

(24) It is worth noting that the ratios K_{EH}^H/K_{ED}^D for ionization of the enols in the two solvents are only 3.2 and 2.5 for acetylcyclohexanone and methylacetylacetone, respectively. These values are considerably smaller than expected for acids with pK values near 10. The explanation undoubtedly involves the fact that there is strong intramolecular hydrogen bonding in the enol form and that the extent of this differs for the H and D cases. See G. Dahlgren, Jr., and F. A. Long, *J. Am. Chem. Soc.*, **82**, 1303 (1960) and A. O. McDougall and F. A. Long, to be published.

(25) G. Schwarzenbach and E. Felder, *Helv. chim. acta*, **27**, 1701 (1944).

(26) F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **55**, 2077 (1959).

(27) R. W. Kingerly and V. K. LaMer, *J. Am. Chem. Soc.*, **63**, 3256 (1941).

$$\frac{1}{6.5} = \frac{1.5 \times 0.7}{R_{H_2O}{}^A \times 1.4}$$

or

$$R_{H_2O}{}^A = 5$$

This value is in good agreement with the fact that weak acids ROH are normally stronger than ROD by factor of from 3 to 6 and also with the experimental conclusion of Pocker that in 50–50 H_2O–D_2O, neutralization of an anion by H_2O is roughly 6-fold faster than by D_2O.[11] This result implies that for a reaction subject only to general acid catalysis the rate of the "solvent" reaction should be five-fold faster for H_2O than for D_2O.

All of the above R ratios derive from data for reaction with particular acidic and basic species and their values can be expected to vary somewhat as strengths of these reference species change. However, these variations should not be large, probably no larger than the uncertainty in the present ratios themselves.

[CONTRIBUTION FROM THE WM. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

The Relative Acidities of Iodine Monochloride, Bromine and Sulfur Dioxide toward N,N-Dimethylacetamide

BY RUSSELL S. DRAGO AND DONALD A. WENZ[1]

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The relative acidities of ICl, Br_2 and SO_2 are compared by evaluating the heats of formation of the adducts formed with N,N-dimethylacetamide. This series of acids, and iodine, provides an interesting variation in dipole moment and polarizability. The relative order of acidity obtained is: ICl > I_2 > SO_2 > Br_2. The dipole moments of the compounds in this series are: SO_2, 1.6 Debye; ICl, 1.3 Debye; Br_2 and I_2, zero Debye. The observed order of acidity cannot be explained by simply considering the dipole moment of the acid. It is concluded that polarizability must be a very important factor contributing to acidity. The structure of the complexes and a description of the bonding is discussed qualitatively.

Introduction

In a previous article the thermodynamic data for the formation of an addition compound between N,N-dimethylacetamide (DMA) and iodine were reported.[2] In an attempt to gain information concerning the nature of such interactions, free energies and enthalpies of formation were measured for the 1:1 adducts formed by DMA with ICl, Br_2 and SO_2. These acids all react with DMA to form compounds whose solubilities permit use of the solvent carbon tetrachloride. This feature simplifies the interpretation of the enthalpy data obtained.

Since the bonding in the adduct depends upon contributions from covalency, dispersion forces and electrostatic interactions, the heat of formation of the adduct should be enhanced by an acid with a large polarizability and a high dipole moment. The polarizabilities[3] decrease in the order $I_2 > ICl > Br_2 >> SO_2$. The dipole moments of I_2 and Br_2 are zero while the moments of ICl and SO_2 are 1.2 and 1.6 Debye,[4] respectively. An interesting variation in these two parameters is provided by this series of acids. Information on the relative acid strengths should provide an insight into the nature of the bonding forces in these complexes.

This study represents the first evaluation of the enthalpy of formation of adducts of all three of these acids with a single reference base. The following order of acidity[5] derived from the magnitude of the equilibrium constant for the benzene complexes has been reported

$$Cl_2 < SO_2 < Br_2 < I_2 < ICl$$

Iodine monochloride has been studied extensively. The equilibrium constants with benzene,[6–8] substituted benzenes,[7–8] acetic acid,[9,10] propionitrile[9,10] dioxane,[11,12] pentamethylenetetrazole[13] and acetonitrile[14] have been reported. In all instances K and ΔH values for the formation of the ICl adducts were found to be larger than those for the corresponding iodine addition compound. Enthalpy measurements were carried out only on some substituted benzene donors.[8] The data available on bromine are limited to equilibrium constant determinations of the complexes formed with some benzene derivatives[15,16] and t-butyl alcohol.[16] Again, enthalpy data are lacking.

Sulfur dioxide has been investigated as a Lewis acid toward a number of aromatics,[5,17,18] olefins[18] and ethyl alcohol.[19] A large discrepancy exists in the heat of formation reported for the benzene complex[17,18] ($-\Delta H$ = 7.8 or 1.0 kcal./mole).

It was of interest to evaluate the acidity as indicated by enthalpy measurements of these Lewis

(1) Abstracted in part from the Ph.D. thesis of D. A. Wenz, University of Illinois (1961).

(2) R. S. Drago, R. L. Carlson, N. J. Rose and D. A. Wenz, *J. Am. Chem. Soc.*, **83**, 3572 (1961).

(3) Landolt–Börnstein, "Zahlenwerte und Functionen," Vol. I, Pt. 3. J. Springer, Berling, 1951, p. 510; F. Fairbrother, *J. Chem. Soc.*, 847 (1936).

(4) J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 86.

(5) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **73**, 4169 (1951); R. L. Scott, *ibid.*, **75**, 1550 (1953).

(6) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

(7) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

(8) N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4204 (1955).

(9) R. E. Buckles and J. F. Mills, *ibid.*, **76**, 4845 (1954).

(10) R. E. Buckles and J. F. Mills, *ibid.*, **75**, 552 (1953).

(11) A. I. Popov, C. Castellani-Bisi and W. B. Person, *J. Phys. Chem.*, **64**, 691 (1960).

(12) L. S. Lilich and O. E. Presnikova, *Ser. Khim. Nauk*, **12**, 3 (1953); *Chem. Abstr.*, **49**, 5939g (1955).

(13) A. I. Popov, C. Castellani-Bisi and M. Craft, *J. Am. Chem. Soc.*, **80**, 6513 (1958).

(14) A. I. Popov and W. A. Deskin, *ibid.*, **80**, 2976 (1958).

(15) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950).

(16) R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 3561 (1953).

(17) P. A. D. DeMaine, *J. Chem. Phys.*, **26**, 1036 (1957).

(18) D. Booth, E. S. Dainton and K. J. Ivin, *Tran. Faraday Soc.*, **55**, 1293 (1959).

(19) P. A. D. DeMaine, *J. Chem. Phys.*, **26**, 1042 (1957).