

## Protonation Equilibria of Ketones in Aqueous Sulfuric Acid

Arrigo Levi, Giorgio Modena, and Gianfranco Scorrano\*

*Contribution from Centro C.N.R. Meccanismi di Reazioni Organiche, Istituto di Chimica Organica, 35100 Padova, Italy. Received April 2, 1974*

**Abstract:** The protonation equilibria of a few ketones have been studied in aqueous sulfuric acid. Different solvation requirements, as numerically expressed by the Bunnett and Olsen  $\phi$  parameter, are found when groups with different abilities to conjugate with a positive charge are linked to the carbonyl function. Therefore different acidity functions are required for different ketones. It is shown that this is not a peculiar case of this class of bases. Most of the families of bases so far studied are classified according to  $\phi$  values and it is suggested that  $\phi$  values, and hence acidity functions, might be predicted for compounds not yet investigated by taking into account the nature of the atom undergoing protonation and of the groups linked to it.

**E**valuation of the basicity of carbonyl compounds has attracted much interest since the very beginning of the attempts to measure the strength of weak bases.<sup>1</sup> Several papers have been published dealing, for instance, with protonation equilibria studies of acetophenones,<sup>2</sup> benzaldehydes,<sup>3</sup> diaryl ketones,<sup>4-6</sup> and  $\alpha,\beta$ -unsaturated aldehydes and ketones.<sup>7</sup> Other pertinent references are found in Arnett's review<sup>8</sup> and in two recent books on acidity functions.<sup>9,10</sup>

This large body of data notwithstanding, the behavior of carbonyl bases in aqueous acids has not been unambiguously described. Beside some experimental difficulties, which often arise in the interpretation of ultraviolet spectra of these compounds in acids, the main problem in the evaluation of  $pK_{XH^+}$  values is the definition of the kind of acidity function which the base obeys (see eq 1).<sup>11</sup>

$$pK_{XH^+} = \log \frac{c_{XH^+}}{c_X} - \log \frac{a_{H^+}f_X}{f_{XH^+}} = \log \frac{c_{XH^+}}{c_X} + H_X \quad (1)$$

In the earlier days it was believed that carbonyl compounds would behave as Hammett bases, that is that their activity coefficient ratios  $f_X/f_{XH^+}$  respond to changing medium as those of nitroanilines do.

However, slopes of  $\log I$  vs.  $-H_0$  very different from unity, the value required for an Hammett base, have been found.<sup>6,7</sup> Therefore, most of the  $pK$  values reported in earlier investigations are not true thermodynamic values but represent  $H_0$  values for half-protonation. In order to obtain true thermodynamic values, i.e.,  $pK_{XH^+}$  referred to dilute aqueous solution as standard state, we have used, in connection with studies

(1) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932); L. A. Flexser, L. P. Hammett, and A. Dingwall, *ibid.*, **57**, 2103 (1935); L. A. Flexser and L. P. Hammett, *ibid.*, **60**, 885 (1938).

(2) R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, **80**, 6355 (1958).

(3) K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 644 (1959).

(4) A. Fischer, B. A. Grigor, J. Packer, and J. Vaughan, *J. Amer. Chem. Soc.*, **83**, 4208 (1961).

(5) R. Stewart, M. R. Granger, R. B. Moodie, and J. J. Muenster, *Can. J. Chem.*, **41**, 1065 (1963).

(6) T. G. Bonner and J. Phillips, *J. Chem. Soc. B*, 650 (1966).

(7) R. I. Zalewski and G. E. Dunn, *Can. J. Chem.*, **46**, 2469 (1968).

(8) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(9) M. Liler, "Reaction Mechanisms in Sulphuric Acid," Academic Press, London, 1971.

(10) C. H. Rochester, "Acidity Functions," Academic Press, London, 1970.

(11) X and  $XH^+$  represent the free and protonated base, whereas  $c$ ,  $a$ , and  $f$  are concentration, activity, and activity coefficient of the indicated species.

of other weak bases, like sulfoxides,<sup>12</sup> sulfides,<sup>13</sup> phosphoryl group containing bases,<sup>14</sup> and ethers,<sup>15</sup> the Bunnett and Olsen approach.<sup>16</sup>

This approach is based on the empirically observed correlation<sup>16</sup> between the logarithms of equilibrium quotients ( $Q = c_{XH^+}/c_X c_{H^+}$ ) which, as shown in Hammett's book,<sup>17</sup> may be expressed in terms of acidity functions as in eq 2, where  $1 - \phi$  is an arbitrary choice of slope parameter.

$$H_X + \log c_{H^+} = (1 - \phi)(H_0 + \log c_{H^+}) \quad (2)$$

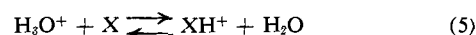
By substituting in eq 1 the value for  $H_X$  found through eq 2 and rearranging, one can easily obtain the Bunnett and Olsen equation<sup>16</sup>

$$\log (c_{XH^+}/c_X) + H_0 = \phi(H_0 + \log c_{H^+}) + pK_{XH^+} \quad (3)$$

From eq 3 the thermodynamic  $pK_{XH^+}$  of a base can be evaluated even in the case where  $H_X$  is not known. Moreover, by expressing  $H_X$  and  $H_0$  in terms of activity coefficients eq 2 becomes<sup>15</sup>

$$\log f_{H^+} - \log (f_{XH^+}/f_X) = (1 - \phi)(\log f_{H^+} - \log (f_{BH^+}/f_B)) \quad (4)$$

By definition,<sup>18,19</sup> activity coefficients of this type are proportional to the free energy change in transferring 1 mol of the indicated species from dilute aqueous solution to acid solution at a given concentration. Hence, eq 4 links the free energy change of transfer of equilibrium 5 to that of the similar equilibrium involving the



reference Hammett type base B. Thus, eq 4, and hence eq 2 and 3, is another example of a free energy relationship and the slope parameter  $\phi$  might assume a diagnostic meaning as  $\rho$  in the classical Hammett equation.

(12) (a) D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, **91**, 6703 (1969); (b) G. Scorrano, *Accounts Chem. Res.*, **6**, 132 (1973).

(13) P. Bonvicini, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 2267 (1972).

(14) R. Curci, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 531 (1973).

(15) P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J. Amer. Chem. Soc.*, **95**, 5960 (1973).

(16) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899 (1966).

(17) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1970.

(18) R. H. Boyd, "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969.

(19) K. Yates and R. A. McClelland, *Progr. Phys. Org. Chem.*, in press.

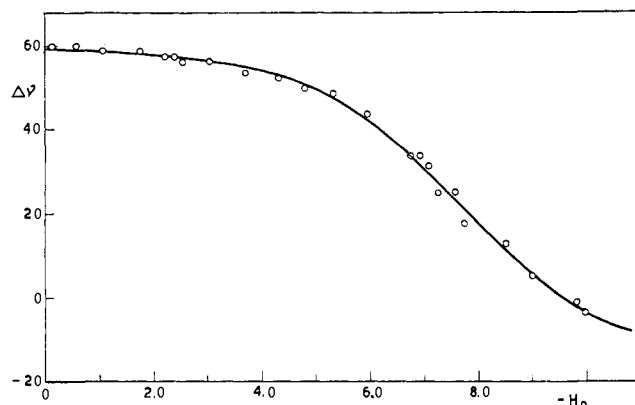


Figure 1. Calculated curve and experimental points for the protonation equilibrium of acetone.

Indeed, as discussed in previous papers,<sup>12-15</sup>  $\phi$  values depend on the solvation requirements of the protonation equilibrium and, consequently, they must be different for different classes of bases, say ketones and anilines, with that defining different acidity functions.

In this paper, the ionization ratio of a few ketones has been measured by the nmr technique, which allows minimization of experimental errors,<sup>20</sup> and these results, together with others from the literature, were treated on the basis of eq 3 to obtain thermodynamic  $pK_{XH^+}$  and  $\phi$  values.

## Results

We have monitored, as a function of the acidity of the medium, the chemical shift of the methyl group of acetone (1), methyl cyclopropyl ketone (2), acetophenone (3), and *p*-methoxyacetophenone (4), relative to that of the trimethylammonium ion as internal standard ( $\Delta\nu = \nu - \nu_{ref}$ , in Hz, at 90 MHz).<sup>12-15, 20a</sup>

The evaluation of the ionization ratios requires the knowledge of the chemical shifts of the free ( $\Delta\nu_X$ ) and protonated ( $\Delta\nu_{XH^+}$ ) base.

$$I = (\Delta\nu_X - \Delta\nu)/(\Delta\nu - \Delta\nu_{XH^+}) \quad (6)$$

Since in the case of 1 and 2 it is impossible to obtain directly the  $\Delta\nu_{XH^+}$  (plateau at high acidity in the plot  $\Delta\nu$  vs.  $-H_0$ ), we have computed  $\Delta\nu_{XH^+}$  values as described in a previous paper.<sup>15</sup>

The chemical shifts of the unprotonated and protonated forms of compounds 1-4 are collected in Table I. Figure 1 illustrates the experimental points and the

Table I. Chemical Shifts of Unprotonated ( $\Delta\nu_X$ ) and Protonated ( $\Delta\nu_{XH^+}$ ) Methyl Ketones ( $CH_3-CO-R$ ) in Aqueous Sulfuric Acid<sup>a</sup>

| R                         | $\Delta\nu_X$ | $\Delta\nu_{XH^+}$ |
|---------------------------|---------------|--------------------|
| $CH_3$                    | +59.7         | -16.8 <sup>b</sup> |
| Cyclo- $C_3H_7$           | +61.4         | +15.3 <sup>b</sup> |
| $C_6H_5$                  | +22.5         | -29.0              |
| <i>p</i> - $OCH_3-C_6H_4$ | +30.0         | -11.7              |

<sup>a</sup> Values of chemical shifts (in Hz at 90 MHz) are relative to  $(CH_3)_3NH^+$  and measured at  $25 \pm 1^\circ$ . Positive values indicate upfield shifts. <sup>b</sup> Evaluated from computer analysis of data at lower acidities than required for complete protonation (see text for details).

(20) (a) P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967); (b) G. C. Levy, J. D. Cargioli, and W. Racela, *J. Amer. Chem. Soc.*, **92**, 6238 (1970).

curve calculated, on the basis of eq 3 and the  $\Delta\nu_X$  and  $\Delta\nu_{XH^+}$  of Table I, for the protonation equilibrium of acetone.

The ionization ratios are then easily evaluated (eq 6) and used to calculate the  $pK_{XH^+}$  and  $\phi$  values (eq 3) collected in Table II.

Data in the literature<sup>2, 20b</sup> for compounds 1, 2, and 4 cannot be directly compared with ours. Acetophenone has been studied by several authors<sup>1, 2, 7, 20, 21</sup> and the results are in fair agreement with ours (see for an example Table III).

Protonation ratios for acetophenone,<sup>1</sup> 3-methyl-3-penten-2-one (5), 2-cyclohexen-1-one (6),<sup>7</sup> 4-dichloromethyl-4-methylcyclohexa-2,5-dienone (7),<sup>22</sup> and several substituted benzophenones<sup>6</sup> have been treated according to eq 3 and the results are reported in Table III.

In Tables II and III are also collected the values of  $H_0$  at half-protonation,  $(H_0)_{1/2}$ , and the slopes ( $m$ ) of the plots  $\log I$  vs.  $-H_0$ .

## Discussion

Different relative basicities among the four ketones studied are found if one considers the thermodynamic  $pK_{XH^+}$ , referred to dilute solution in water, or the  $(H_0)_{1/2}$  evaluated in more concentrated acids. This clearly shows the importance of defining the effect of changing medium on the protonation equilibrium or, in other words, of defining the acidity functions followed.

An immediate way of defining acidity functions is through the  $\phi$  values. Since several  $\phi$  values are so far available (see Table IV), it is important to seek whether they can be ordered in a rational way and used to predict  $\phi$  values not yet measured.

According to eq 4,  $1 - \phi$  is the slope of the free energy relationship linking the protonation equilibrium of a base X to that of a reference Hammett base B. From recent activity coefficients measurements<sup>18, 19</sup> we know that the activity coefficients vary almost always<sup>18, 19</sup> in the order  $f_{H^+} > f_{XH^+} > f_X$ . Therefore the left hand part of eq 4 must be positive, with the actual magnitude depending on the ratio  $f_{XH^+}/f_X$ . Two extreme situations may be considered. (i)  $f_{XH^+}$  is much greater than  $f_X$ . This situation is found<sup>19</sup> in those cases where the introduction of a positive charge greatly enhances the differences between the two species, X and  $XH^+$ , that is, when the proton is bound to a small and not polarizable molecule. In these cases the ratio  $f_{XH^+}/f_X$  will be large since the differences in solvation, and therefore in free energy of transfer, are large. Hence the difference  $\log f_{H^+} - \log f_{XH^+}/f_X$  tends to be smaller than  $\log f_{H^+} - \log f_{BH^+}/f_B$  and  $\phi$  values positive ( $1 - \phi$  smaller than unity). (ii)  $f_{XH^+}$  is of similar magnitude of  $f_X$ . This is found when the positive charge is buried into a large and polarizable molecule and the interactions with the solvent are therefore not much different for the base and its conjugate acid. In this case the ratio  $f_{XH^+}/f_X$  is small and the  $\phi$  values are negative.

These predictions are clearly verified by the  $\phi$  values measured for oxonium, ammonium, sulfonium, and carbonium ion bases which are in the order expected, if

(21) C. G. Greig and C. D. Johnson, *J. Amer. Chem. Soc.*, **90**, 6453 (1968), see also A. A. El-Anani, C. C. Greig, and C. D. Johnson, *Chem. Commun.*, 1024 (1970).

(22) V. P. Vitullo, *J. Org. Chem.*, **34**, 224 (1969).

Table II. Acid-Base Equilibria of Ketones<sup>a</sup>

| Compd                         | $pK_{XH}^{+b}$   | $\phi^b$         | $(H_0)_{1/2}^c$  | $m^c$           |
|-------------------------------|------------------|------------------|------------------|-----------------|
| Acetone                       | $-2.85 \pm 0.05$ | $+0.75 \pm 0.01$ | $-7.86 \pm 0.06$ | $0.29 \pm 0.01$ |
| Methyl cyclopropyl ketone     | $-3.27 \pm 0.07$ | $+0.55 \pm 0.01$ | $-5.96 \pm 0.06$ | $0.48 \pm 0.01$ |
| Acetophenone                  | $-4.36 \pm 0.17$ | $+0.40 \pm 0.03$ | $-6.50 \pm 0.04$ | $0.63 \pm 0.03$ |
| <i>p</i> -Methoxyacetophenone | $-3.39 \pm 0.14$ | $+0.37 \pm 0.04$ | $-4.81 \pm 0.04$ | $0.65 \pm 0.04$ |

<sup>a</sup> In aqueous sulfuric acid at 25°. <sup>b</sup> Evaluated as slope ( $\phi$ ) and intercept ( $pK_{XH}^{+}$ ) from least-square, analysis of  $(\log I + H_0)$  vs.  $(H_0 + \log c_{H^+})$  plots. <sup>c</sup> Evaluated from least-squares analysis of  $\log I$  vs.  $-H_0$  plots;  $m$  are slopes and  $(H_0)_{1/2}$  the values for  $\log I = 0$ .

Table III. Acid-Base Equilibria of Aromatic and Alicyclic Ketones<sup>a</sup>

| Compd                        | $pK_{XH}^{+b}$   | $\phi^b$         | $(H_0)_{1/2}^c$  | $m^c$           | Ref      |
|------------------------------|------------------|------------------|------------------|-----------------|----------|
| 5                            | -2.87            | +0.56            | -5.24            | 0.48            | <i>d</i> |
| 6                            | -3.02            | +0.55            | -5.44            | 0.49            | <i>d</i> |
| 7                            | $-3.53 \pm 0.05$ | $+0.44 \pm 0.01$ | $-5.51 \pm 0.02$ | $0.59 \pm 0.01$ | <i>e</i> |
| Acetophenone                 | $-4.02 \pm 0.17$ | $+0.44 \pm 0.03$ | $-6.33 \pm 0.04$ | $0.58 \pm 0.03$ | <i>f</i> |
| Benzophenone                 | $-4.03 \pm 0.20$ | $+0.47 \pm 0.03$ | $-6.68 \pm 0.07$ | $0.55 \pm 0.03$ | <i>g</i> |
| Substituted benzophenones    |                  |                  |                  |                 |          |
| 4,4'-Dichloro-               | $-5.29 \pm 0.14$ | $+0.37 \pm 0.02$ | $-7.71 \pm 0.03$ | $0.65 \pm 0.02$ | <i>g</i> |
| 3-Chloro-                    | $-5.55 \pm 0.04$ | $+0.28 \pm 0.01$ | $-7.31 \pm 0.01$ | $0.73 \pm 0.01$ | <i>g</i> |
| 4-Chloro-                    | $-5.10 \pm 0.15$ | $+0.34 \pm 0.02$ | $-7.12 \pm 0.03$ | $0.68 \pm 0.02$ | <i>g</i> |
| 3-Chloro-4-methoxy-          | $-4.16 \pm 0.11$ | $+0.40 \pm 0.02$ | $-6.27 \pm 0.03$ | $0.62 \pm 0.02$ | <i>g</i> |
| 4-Chloro-4'-methoxy-         | $-3.80 \pm 0.11$ | $+0.42 \pm 0.02$ | $-5.81 \pm 0.03$ | $0.60 \pm 0.02$ | <i>g</i> |
| 4-Hydroxy-                   | $-4.26 \pm 0.11$ | $+0.27 \pm 0.02$ | $-5.46 \pm 0.03$ | $0.74 \pm 0.02$ | <i>g</i> |
| 4-Methoxy-                   | $-4.18 \pm 0.10$ | $+0.26 \pm 0.02$ | $-5.32 \pm 0.02$ | $0.75 \pm 0.02$ | <i>g</i> |
| 2,4-Dihydroxy-               | $-3.89 \pm 0.23$ | $+0.25 \pm 0.06$ | $-5.00 \pm 0.04$ | $0.76 \pm 0.05$ | <i>g</i> |
| 4-Hydroxy-3,3',4'-trimethoxy | $-3.55 \pm 0.06$ | $+0.29 \pm 0.02$ | $-4.60 \pm 0.01$ | $0.73 \pm 0.01$ | <i>g</i> |
| 4,4'-Dimethoxy-              | $-3.68 \pm 0.11$ | $+0.23 \pm 0.03$ | $-4.45 \pm 0.03$ | $0.79 \pm 0.03$ | <i>g</i> |
| 2,4,4-Trimethoxy-            | $-3.89 \pm 0.11$ | $-0.11 \pm 0.04$ | $-3.58 \pm 0.02$ | $1.10 \pm 0.03$ | <i>g</i> |
| 2,2',4,4'-Tetramethoxy-      | $-3.59 \pm 0.08$ | $-0.07 \pm 0.03$ | $-3.41 \pm 0.01$ | $1.06 \pm 0.02$ | <i>g</i> |

<sup>a-c</sup> See footnotes in Table II. <sup>d</sup> Reference 7. <sup>e</sup> Reference 22. <sup>f</sup> The ionization ratios have been calculated from data of ref 1 by using differences in optical densities at 290 and 240 nm. <sup>g</sup> Reference 6.

Table IV.  $\phi$  Values for Several Bases in Sulfuric Acid

| Acidity function | Base                                 | $\phi^a$                          | Ref          |
|------------------|--------------------------------------|-----------------------------------|--------------|
| $H_R$            | Triarylcarbinol/triarylcarbonium ion | -1.02 to -1.59                    | <i>b</i>     |
| $H_I$            | Indoles                              | -0.26 to -0.46 and -0.67 to -0.85 | <i>c</i>     |
| $H_C$            | Azulenes, diphenylethylenes          | -0.70                             | <i>e</i>     |
| $H_0'''$         | Tertiary anilines                    | -0.33 to -0.48                    | <i>f</i>     |
| $H_T$            | Thioamides                           | -0.36 <sup>d</sup>                | <i>g</i>     |
| $H_S$            | Dialkyl sulfides                     | -0.26 to -0.29                    | 13           |
| $H_0$            | Primary anilines                     | 0                                 | 1            |
| $H_A$            | Amides                               | +0.42 to +0.55                    | <i>h</i>     |
| $H_{ROB}$        | Dialkyl Ethers                       | +0.75 to +0.82                    | 15           |
| $H_{ROH}$        | Alcohols                             | +0.85                             | 15, <i>i</i> |
| $H_{H_2O}$       | Water                                | +1.00                             | 15           |

<sup>a</sup> From  $(\log I + H_0)$  vs.  $(H_0 + \log c_{H^+})$  plots, if not otherwise indicated. <sup>b</sup> N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955). <sup>c</sup> R. L. Hinman and J. Long, *ibid.*, **86**, 3796 (1964). <sup>d</sup> From  $(H_X + \log c_{H^+})$  vs.  $(H_0 + \log c_{H^+})$  plots. <sup>e</sup> M. T. Reagan, *J. Amer. Chem. Soc.*, **91**, 5506 (1969). <sup>f</sup> E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964). <sup>g</sup> C. Tissier and M. Tissier, *Bull. Chem. Soc. Fr.*, 2109 (1972). <sup>h</sup> K. Yates, J. B. Stevens, and A. R. Katritzky, *Can. J. Chem.*, **42**, 1957 (1964). <sup>i</sup> D. J. Lee and R. Cameron, *J. Amer. Chem. Soc.*, **93**, 4724 (1971).

one takes into account the atom undergoing protonation and the kind of molecule which it is part of.

It is interesting to consider what happens within the series of oxonium ions. The  $\phi$  values decrease going from alcohols to dialkyl ethers to amides following, therefore, the ability of the oxonium ion to disperse the positive charge into a larger molecule. The more de-

localized the positive charge is, the weaker will be the hydrogen bond between the oxonium ion and water. Therefore, a less effective solvation is expected, and found, as the  $\phi$  values show.

With this in mind we may return to the case of protonated ketones. The charge dispersion depends on the nature of the residues linked to the carbonyl group and in fact the  $\phi$  values clearly follow the ability of the methyl ( $\phi = +0.75$ ), cyclopropyl ( $\phi = +0.62$ ), and phenyl ( $\phi = +0.40$ ) groups to delocalize the positive charge.<sup>23</sup>

This hypothesis also agrees with data from the literature (see Table III). The  $\phi$  value found for acetone is substantially decreased for  $\alpha,\beta$ -unsaturated ketones (+0.55) and for dienones (0.44). Even more striking is what is observed in substituted benzophenones. Although some variations of individual  $\phi$  values are not easily explained, there is a very clear trend of decreasing  $\phi$  values with the increase of electron donor groups in the benzene rings. The tri- and tetramethoxy substituted benzophenones have negative  $\phi$  values (-0.11 and -0.07)!

In conclusion,  $\phi$  values from +0.7 to -0.1 are found for ketones by changing the nature of the group linked to the C=O. This is a clear indication that there is not a single ketone acidity function.

The same behavior is found in other carbonyl compounds as for instance esters and amides (see Table V).

Although the set of data so far available does not allow such a firm conclusion as for ketones, also in these cases different  $\phi$  values seem to be found when an alkyl

(23) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

Table V. Acid-Base Equilibria of Esters and Amides<sup>a</sup>

| Compd                | $pK_{XH^+}$ <sup>b</sup> | $\phi$ <sup>b</sup> | $(H_0)_{1/2}$ <sup>c</sup> | $m$ <sup>c</sup> | Ref      |
|----------------------|--------------------------|---------------------|----------------------------|------------------|----------|
| Ethyl acetate        | -4.61                    | +0.40               | -6.98                      | 0.62             | <i>d</i> |
| Methyl benzoate      | -7.05                    | +0.17               | -8.28                      | 0.81             | <i>d</i> |
| <i>n</i> -Butyramide | -0.74                    | +0.59               | -1.24                      | 0.56             | <i>e</i> |
| Benzamide            | -1.50                    | +0.42               | -2.15                      | 0.66             | <i>f</i> |

<sup>a-c</sup> See footnotes in Table II. <sup>d</sup> C. A. Lane, M. F. Cheung, and G. F. Dorsey, *J. Amer. Chem. Soc.*, **90**, 6492 (1968). <sup>e</sup> V. C. Armstrong and R. B. Moodie, *J. Chem. Soc. B*, 275 (1968). <sup>f</sup> K. Yates and J. B. Stevens, *Can. J. Chem.*, **43**, 529 (1965).

or aryl group is linked to the group undergoing protonation.

It seems reasonable, at this point, to confirm earlier suggestions that each individual base requires its own acidity function.<sup>12b, 24</sup>

This brings up the question as to whether it is possible to measure any acidity function at all, since it is obvious we need several bases to cover the entire range of acid concentration.

Inspection of the literature<sup>16</sup> has shown that there are series of structural related bases with different basicities but with very similar solvation requirements. It is interesting that the best defined acidity functions, those which better obey the postulate of constancy in  $\log I$  differences between overlapping indicators, have been established for compounds with not very high resonance interactions between the protonation center and the residues linked to it. Once again,<sup>17</sup> the selection of nitroanilines to define the original Hammett acidity function has been proved to be the best possible.

Another consequence of differences in  $\phi$  values among different bases is the change in relative basicities going from dilute to concentrated acids. A recent example has shown<sup>15</sup> that ethers are more basic than sulfides in dilute and less basic in concentrated acid solutions. Because of the greater solvation requirements of ethers, which are associated with greater  $\phi$  values, their protonation is favored in the water rich medium. Solvation phenomena of the same type are also useful to explain "anomalous" basicity orders, in aqueous solutions, of alkylamines,<sup>25</sup> and of ethers and alcohols.<sup>15</sup>

(24) Table IV, footnote *f*.

Of course, inversion of basicity order may occur also within bases with the same functional group when structural factors cause large changes of  $\phi$  values. This is the case with, e.g., the pair acetone-cyclopropyl methyl ketone. The former has a more positive  $pK_{XH^+}$  but the half-neutralization occurs at a more negative  $H_0$ . The greater solvation of the acetone conjugate acid (greater  $\phi$ ) overwhelms, in water, the intrinsically greater basicity of the cyclopropyl methyl ketone, expected from the better electron releasing properties of the cyclopropyl group.

In conclusion, the behavior of weak bases in acids cannot be described only by their  $pK_{XH^+}$  values, being very different, the response of their acid base equilibria to changing acid concentration. The second necessary parameter is  $\phi$ . The knowledge of this value allows us, in fact, to extrapolate from the  $pK_{XH^+}$  values the degree of protonation in every acid solution and, through eq 4, to compare activity coefficient behavior of the various bases and their conjugate acids. This, hopefully, will be of great help in understanding solvent effects in organic chemistry.

### Experimental Section

The pmr spectra were taken on a Bruker HFX-10 spectrometer at 90 MHz. Sulfuric acid solutions were made up by dilution of concentrated acid and titrated with standard NaOH. The  $H_0$  values were obtained by interpolation of recently published data.<sup>26</sup> The compounds studied, commercially available, were purified by distillation.

**$pK_{XH^+}$  Measurements.** Solutions of bases (ca. 0.05 *M*) were made in sulfuric acid solution (0.5–18.5 *M*) containing  $Me_3NH^+$  (0.05 *M*) as reference. No decomposition occurs even in the more concentrated solutions and, by dilution with water, it is possible to reproduce the spectra of the freshly prepared less concentrated solution.

Protonation of compounds **1** and **2** is not complete even in pure sulfuric acid and therefore  $\Delta\nu_{XH^+}$  values had to be computed. The calculation was made on the basis of eq 3 by expressing  $\Delta\nu$  as a function of  $\Delta\nu_X$ ,  $H_0$ ,  $\log c_{H^+}$ ,  $\Delta\nu_{XH^+}$ ,  $\phi$ , and  $pK_{XH^+}$ . The last three terms were varied by 1% increments until the best fit between calculated and experimental  $\Delta\nu$  values was found through the least-squares analysis reported by Sillen.<sup>27</sup>

(25) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

(26) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, **91**, 6654 (1969).

(27) L. G. Sillen, *Acta Chem. Scand.*, **18**, 1805 (1964), and previous papers.