

Application of Acidity Function Method to the Determination of pK_a Values of Trihalomethanes. I. Trichloromethane

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The equilibrium acidity of trichloromethane has been studied at 298.15 K by means of the acidity function method in different H_2O –DMSO mixtures with a fixed hydroxide ion concentration. The measured pK_a values were found to vary systematically from 14.6 at $H_- = 13.40$ to 16.0 at $H_- = 15.13$. The observed trend was considered to indicate the invalidity of the Hammett activity coefficient postulate in this case. Application of the Bunnett-Olsen method to the extrapolation of the measured pK_a values to the aqueous state gave a value of 13.6 for the pK_a of trichloromethane.

In a previous paper,¹ the fractionation factors of trichloromethane, bromodichloromethane and tribromomethane in H_2O – D_2O solvent system have been reported. The studies concerning these trihalomethane homologues have been extended to clear up the correlation between fractionation factors and acid strengths of trihalomethanes for which the pK_a values of trihalomethanes are needed. The values found in the literature cannot, however, be utilized here because of their great discordance. For trichloromethane and tribromomethane, for instance, pK_a values between 15–24 and 9–13, respectively, can be found.^{2–5} The present work was undertaken in the hope of getting useful information about the acidities of trihalomethanes in the aqueous solvent system in which the fractionation factor measurements have been performed.

Experimental

Materials. Tritiation of methyl phenyl ketone (Fluka AG, puriss p.a) was carried out as described in Ref. 6. In liquid scintillation counting (LKB-Wallac 81000 Liquid Scintillation Counter), 1 mm³ of the product gave an activity of about 96000 cpm.

Trichloromethane (Merck, pro analysi) was used without purification.

Dimethyl sulphoxide, DMSO (Merck, pro analysi), was stirred with powdered calcium hydride for 2–3 days in a vessel protected from atmospheric moisture. After this treatment, DMSO was distilled over calcium hydride under reduced pressure keeping the temperature below 333 K and discarding the first and the last 15 % of the distillate. The distilled DMSO was stored under nitrogen atmosphere.

A 10 % aqueous solution of tetramethyl ammonium hydroxide (Merck) was used without further purification.

Preparation of solutions. A 0.5 mol dm⁻³ stock solution of tetramethyl ammonium hydroxide was prepared from the 10 % solution by dilution with degassed distilled water. The base concentration of the stock solution was determined by titration with a known acid solution. The H_2O –DMSO mixtures with the hydroxide ion concentration of 0.0110 mol dm⁻³ were prepared by weight from purified DMSO, degassed distilled water and the known tetramethyl ammonium hydroxide stock solution. The solutions were stored under a nitrogen atmosphere.

pK_a determinations. For trichloromethane, the RH and R^- equilibrium concentrations at 298.15 K were determined kinetically, following

the rates of detritiation of methyl phenyl ketone (standard acid) in a series of different H₂O–DMSO solutions, then repeating the procedure in the presence of a known concentration of trichloromethane. The method has been described in detail in Refs. 7 and 8.

On the basis of the definition of the acidity function H_- , eqn. (1) can be written for the calculation of pK_a .

$$pK_a = H_-(\text{eq}) - \log \left[\frac{c(\text{R}^-)}{c(\text{RH})} \right]_{\text{eq}} \quad (1)$$

The H_- (initial) values used for H₂O–DMSO mixtures with the hydroxide ion concentration of 0.0110 mol dm⁻³ were those determined by Dolman & Stewart.⁹

Results and discussion

The acidity function method employed in this work has previously been used, e.g. to determine the pK_a values of some nitrogen acids⁷ and a series of *p*-substituted methyl phenyl ketones.¹⁰ The implication of eqn. (1) is that the Hammett activity coefficient postulate¹¹ is obeyed. According to eqn. (1), the plot of $\log [c(\text{R}^-)/c(\text{RH})]_{\text{eq}}$ versus $H_-(\text{eq})$ should be a straight line with unit slope. For methyl phenyl ketone, the variation of $\log [c(\text{R}^-)/c(\text{RH})]_{\text{eq}}$ with $H_-(\text{eq})$ has been found to be linear with a slope of 0.95(5).¹¹ The behaviour of methyl phenyl ketone with regard to this aspect must thus be very similar to the anilines and diphenylamines used to set up the H_- scale of Dolman & Stewart.⁹ The substituted methyl phenyl ketones probably also respond to basicity changes similarly to these scale indicators. This behaviour, however, cannot be generalized to all carbon acids. Measurements with trichloromethane show that large deviations from the ideals of the acidity function concept can exist. For trichloromethane, the variation of $\log [c(\text{R}^-)/c(\text{RH})]_{\text{eq}}$ with $H_-(\text{eq})$ is linear with a slope of 0.23(3) instead of a slope close to unity implied by the Hammett activity coefficient postulate. The pK_a values calculated for trichloromethane from eqn. (1) and listed in Table 1 show a systematic trend with $x(\text{DMSO})$ indicating the invalidity of eqn. (1) for calculation of pK_a in this case.

In the carbanion formed from trichloromethane, the charge is localized to the carbon atom, whereas in the carbanions formed from methyl

phenyl ketones, the charge is delocalized also to the oxygen atom and aromatic ring. Respecting the charge delocalization within a heteroatom and aromatic ring, the carbanions from methyl phenyl ketones resemble the anions formed from diphenylamines used as H_- scale indicators, and probably are affected by the basicity changes in a similar manner, the activity coefficient behaviour also being much the same.

Since on the basis of the measurements with trichloromethane, it is evident that the activity coefficients of trichloromethane, the corresponding carbanion, scale indicator acids and of corresponding anions do not cancel, the pK_a of trichloromethane should be calculated using eqn. (2) instead of eqn. (1). The behaviour of activity coefficients, however, is not known and some sort of assumption has to be made. Several methods for dealing with the activity coefficient term have been reported in the literature.¹²

$$pK_a = H_-(\text{eq}) - \log \left[\frac{c(\text{R}^-)}{c(\text{RH})} \right]_{\text{eq}} + \log \left[\frac{y(\text{In}^-)y(\text{RH})}{y(\text{InH})y(\text{R}^-)} \right]_{\text{eq}} \quad (2)$$

Table 1. Apparent pK_a values for trichloromethane measured in different H₂O–DMSO solutions at 298.15 K

$x(\text{DMSO})$	$H_-(\text{eq})$	$pK_a(\text{app})^a$
0.134	13.40	14.55(8)
0.151	13.60	14.63(5)
0.165	13.77	14.92(5)
0.175	13.90	15.00(7)
0.186	14.04	15.07(12)
0.192	14.11	15.07(5)
0.211	14.34	15.30(3)
0.221	14.46	15.30(6)
0.238	14.65	15.46(4)
0.256	14.84	15.61(7)
0.271	14.99	15.66(10)
0.283	15.13	15.96(5)
0.292	15.23	15.84(4)

^a Mean values of 4–6 determinations with standard deviations. In each H₂O–DMSO solution, $c(\text{HO}^-)$ was 0.110 mol dm⁻³. The H_- scale used was that of Dolman & Stewart.⁹

The widely used extrapolation technique is the Bunnett-Olsen method.^{13,14} In this treatment, it is assumed that there is a linear correlation between the term $\log [y(\text{R}^-)/y(\text{RH})y(\text{HO}^-)]$ for an acid RH and the term $\log [y(\text{In}^-)/y(\text{InH})y(\text{HO}^-)]$ for a set of indicator acids InH defining the acidity function. This is less strict than the Hammett assumption that the activity coefficient terms cancel. In basic H₂O–DMSO media, the Bunnett-Olsen eqn. (3) can be derived for calculation of pK_a of trichloromethane.

$$\text{p}K_{\text{a}}(\text{app}) = -\varphi [H_{-} - \text{p}K_{\text{w}} - \log c(\text{HO}^-) + \log a(\text{H}_2\text{O})] + \text{p}K_{\text{a}} \quad (3)$$

Using the value of 13.996 for pK_w and the water activities calculated by Cox & Stewart¹⁴ for different H₂O–DMSO mixtures at 298.15 K, eqn. (4) is obtained by applying the method of linear least squares to values [pK_a(app), H₋(eq)] of Table 1. The intercept of the straight line (4) gives a value of 13.6 for the pK_a of trichloromethane.

$$\text{p}K_{\text{a}}(\text{app}) = 0.88(2) [H_{-}(\text{eq}) - \text{p}K_{\text{w}} - \log c(\text{HO}^-) + \log a(\text{H}_2\text{O})] + 13.56(5) \quad (4)$$

Another well-known extrapolation technique, the Marziano-Cimino-Passerini method^{15,14} or excess acidity method, gives the same value for the pK_a of trichloromethane.

During recent years, doubt has been cast on traditional methods for determining pK_a values. It has been pointed out that, instead of pK_a values, these methods give rather a quantity which is the sum of the true pK_a value and an indeterminate constant.^{16,17} It is clear that empirical pK_a values are complicated functions of solvent effects and intramolecular polar and spatial interactions. It is also obvious that in the acidity function approach, the necessary assumptions concerning the activity coefficient behaviour are not always valid. However, since many of the most interesting reactions occur in solutions, the empirical relative pK_a values are of great practical significance and in many cases the only useful ones when measurements are made in certain solvent systems. The limitations of any method used

for pK_a determinations should be recognized, and when employing the acidity function method, the scale used should also be always mentioned when the pK_a values are reported.

At this moment, the Bunnett-Olsen method still provides a reasonable means of estimating the pK_a values for weak acids which are structurally unrelated to aromatic amines used as H₋ scale indicators.

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References

1. Scharlin, P. *Acta Chem. Scand. A* 36 (1982) 117.
2. Klabunde, K. J. and Burton, D. J. *J. Am. Chem. Soc.* 94 (1972) 5985.
3. Reutov, O. A., Beletskaya, I. P. and Butin, K. P. *CH-acids*, Pergamon Press, Oxford 1978, p. 29.
4. Margolin, Z. and Long, F. A. *J. Am. Chem. Soc.* 95 (1973) 2757.
5. Lin, A. C., Chiang, Y., Dahlberg, D. B. and Kresge, A. J. *J. Am. Chem. Soc.* 105 (1983) 5380.
6. Kankaanperä, A., Oinonen, L. and Salomaa, P. *Acta Chem. Scand. A* 31 (1977) 551.
7. Earls, D. W., Jones, J. R., Rumney, T. G. and Cockerill, A. F. *J. Chem. Soc. Perkin II* (1975) 54.
8. Kankaanperä, A., Salomaa, P., Oinonen, L. and Mattsén, M. *Finn. Chem. Lett.* (1978) 25.
9. Dolman, D. and Stewart, R. *Can. J. Chem.* 45 (1967) 911.
10. Earls, D. W., Jones, R. and Rumney, T. G. *J. Chem. Soc. Perkin II* (1975) 878.
11. Hammett, L. P. and Deyrup, J. *J. Am. Chem. Soc.* 54 (1932) 2721.
12. Cox, R. A. and Yates, K. *Can. J. Chem.* 61 (1983) 2225.
13. Bunnett, J. F. and Olsen, F. P. *Can. J. Chem.* 44 (1966) 1899.
14. Cox, R. A. and Stewart, R. *J. Am. Chem. Soc.* 98 (1976) 488.
15. Marziano, N. C., Cimino, G. M. and Passerini, R. *C. J. Chem. Soc. Perkin II* (1973) 1915.
16. Wojcik, J. F. *J. Phys. Chem.* 86 (1982) 145.
17. Wojcik, J. F. *J. Phys. Chem.* 89 (1985) 1748.

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