

Evaluation of pK_a Values for Bromodichloromethane, Chlorodibromomethane and Tribromomethane from Kinetic Acidities

Pirketta Scharlin

Department of Chemistry, University of Turku, SF-20500 Turku, Finland

Scharlin, P., 1987. Evaluation of pK_a Values for Bromodichloromethane, Chlorodibromomethane and Tribromomethane from Kinetic Acidities. – Acta Chem. Scand., Ser. A 41: 480–483.

The rate-coefficients for the detritiation of trichloromethane, bromodichloromethane, chlorodibromomethane and tribromomethane in water at 298.15 K have been determined. The equilibrium acidities of bromodichloromethane, chlorodibromomethane and tribromomethane have been evaluated from the kinetic acidities of these trihalomethanes using the pK_a value of 13.6 for trichloromethane as reference. With the assumptions that the internal return mechanism is operative in the base-catalyzed hydrogen exchange of the trihalomethanes and that the diffusion rate-coefficient has the same value for each of the trihalomethane homologues, the values 12.9, 12.3 and 11.8 were obtained for the pK_a 's of bromodichloromethane, chlorodibromomethane and tribromomethane, respectively.

A survey of the literature shows that the pK_a values reported for a certain carbon acid can vary widely depending on the method and medium used for the determination. For trichloromethane and tribromomethane, for instance, pK_a values from 15 to 24 and from 9 to 14, respectively, can be found.¹⁻⁴ Previous studies concerning deuterium isotope fractionation between trichloromethane, bromodichloromethane, chlorodibromomethane, tribromomethane and water^{5,6} have been extended to elucidate the correlation between deuterium fractionation factors and equilibrium acidities of these trihalomethane homologues. The pK_a values reported in the literature are of no value for this purpose because of their great discordance. The work described in the present paper is a sequel to the previous study dealing with the equilibrium acidity of trichloromethane.⁷ The aim of this work was to evaluate the pK_a values for bromodichloromethane, chlorodibromomethane and tribromomethane in the aqueous solvent system in which the fractionation factor measurements have been performed.

Experimental

Materials. Tritium labelling of trichloromethane (Merck), bromodichloromethane (EGA Chemie), chlorodibromomethane (EGA Chemie) and tribromomethane (Fluka AG) was performed as described earlier.⁸ A 0.1 mol dm⁻³ stock solution of sodium hydroxide was prepared from a standard Dilut-it® solution (Baker Chemical Co.) by dilution with CO₂-free distilled water. Solutions of suitable NaOH concentration for kinetic measurements were prepared from the stock solution by dilution with CO₂-free distilled water just before carrying out the experiments.

Kinetics. Kinetic measurements were performed in water at 298.15 K with sodium hydroxide as catalyst. With tribromomethane-*t*, additional measurements in water at 283.15 K, 288.15 K and 293.15 K were made in order to determine the activation entropy for the detritiation of tribromomethane-*t*. The NaOH concentrations in the reaction mixtures were 0.001, 0.0025, 0.005 and

Table 1. Rate-coefficients for the detritiation of trihalomethanes in water at 298.15 K.

Substrate	<i>k</i> /mol ⁻¹ dm ³ s ⁻¹ ^a
Cl ₃ CH*	0.1670(18)
Cl ₂ BrCH*	0.7579(68)
ClBr ₂ CH*	3.023(26)
Br ₃ CH*	10.132(63)

^aMean values of five determinations with standard errors of mean.

0.01 mol dm⁻³ for the detritiation of tribromomethane-*t*, chlorodibromomethane-*t*, bromodichloromethane-*t* and trichloromethane-*t*, respectively. Tritiated substrate was dissolved in H₂O-NaOH solution thermostatted to the desired temperature. 5.0 cm³ samples were taken from the reaction mixture at suitable intervals and transferred to 50 cm³ glass cylinders containing enough dilute hydrochloric acid to stop the reaction. Exactly 10 cm³ of cyclohexane was added, the cylinders were shaken, and the layers were allowed to separate overnight. A 5.0 cm³ sample was withdrawn from each organic layer and diluted in 10 cm³ of scintillation liquid [5 g of 2,5-diphenyloxazole and 1 g of *p*-bis(*o*-methylstyryl) benzene per 1 dm³ of toluene]. The activity of the samples was counted in an LKB-Wallac 81000 liquid scintillation counter.

Rate-coefficients were calculated as slopes of plots of ln (C_t-C_∞) as a function of time (C = counts per minute). Weighted least-squares analysis with weighting factor (C_t-C_∞) was used in the calculations. The standard errors of the slopes of these plots were less than 1%. Second-order rate-coefficients were obtained by dividing the calculated first-order rate-coefficients by the concentration of base catalyst. The results are listed in Tables 1 and 2.

Discussion

The acidity function method⁹ applied to the determination of the pK_a value for trichloromethane⁷ proved to be unsuitable for the determination of pK_a values for bromodichloromethane, chlorodibromomethane and tribromomethane

Table 2. Rate-coefficients for the detritiation of tribromomethane in water at different temperatures.

T/K	<i>k</i> /mol ⁻¹ dm ³ s ⁻¹
283.15	1.520 ^a
288.15	2.987 ^a
293.15	5.457 ^a
298.15	10.132 ^b

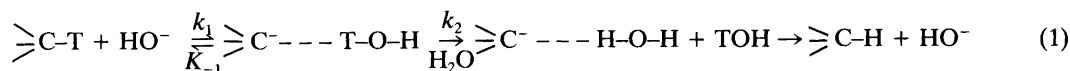
^aMean value of two determinations. ^bMean value of five determinations.

because of the disturbingly rapid base hydrolysis of these trihalomethanes in H₂O-DMSO mixtures. For Cl₂BrCH, ClBr₂CH and Br₃CH it is possible, however, to evaluate the pK_a values on the basis of the pK_a value for trichloromethane and the rates of detritiation of trichloromethane-*t*, bromodichloromethane-*t*, chlorodibromomethane-*t* and tribromomethane-*t*.

The base-catalyzed hydrogen exchange in trichloromethane has been shown to be of the internal return type^{3,4} (eqn. 1).

A positive entropy of activation and a primary kinetic isotope effect near unity are characteristic of internal return.^{3,10,11} For the detritiation of trichloromethane-*t* in water at 298.15 K a value of 64.9 J K⁻¹ mol⁻¹ can be calculated for the activation entropy.³ Using the *k_D* value of Hine *et al.*¹² and the *k_T* value obtained in this work, a value of 1.18 is obtained for *k_D*/*k_T* for trichloromethane. For the detritiation of tribromomethane-*t* in water at 298.15 K a value of (62.4 ± 3.2) J K⁻¹ mol⁻¹ was obtained for the activation entropy from the kinetic results of Table 2, and a value of 1.48 for *k_D*/*k_T* can be calculated from the *k_D* value of Hine *et al.*¹³ and the *k_T* value obtained in this work. These values indicate that the internal return mechanism is operative also in the detritiation of tribromomethane-*t*. For the detritiation of chlorodibromomethane-*t*, a value of 1.29 for *k_D*/*k_T* can be calculated from the existing data.¹³ On the basis of the results for trichloromethane and tribromomethane it is reasonable to assume that the same mechanism is operative in hydrogen exchange in bromodichloromethane and chlorodibromomethane.

The expression for the rate-coefficient for the



total reaction (1) reduces to eqn. (2), where K is the equilibrium constant for the first stage in the internal return mechanism.

$$k(\text{obs}) = \frac{k_1}{k_{-1}} k_2 = K \cdot k_2 \quad (2)$$

For the reactions of two related compounds eqn. (3) can be written as

$$\frac{k(\text{obs})}{k'(\text{obs})} = \frac{K}{K'} \cdot \frac{k_2}{k'_2} \quad (3)$$

If the diffusion rate-coefficient k_2 has the same value for each of a series of related compounds, the last term in eqn. (3) reduces to unity and the ratio of the observed rates is directly equal to the ratio of the equilibrium acidities.^{10,11} With this assumption the kinetic acidities measured in this work (Table 1) can be used to evaluate the equilibrium acidities of bromodichloromethane, chlorodibromomethane and tribromomethane from the equilibrium acidity of trichloromethane determined in previous work.⁷ Hydrogen exchange in trihalomethanes takes place via the internal return mechanism, the primary kinetic isotope effect being near unity.^{3,11} The k_H/k_D and k_D/k_T values are likely to be quite similar in this homologous series. Therefore, in the evaluation of the pK_a values for trihalomethanes it is reasonable simply to use the k_T values which can be determined more accurately than the k_H values. The results together with values found in the litera-

ture are listed in Table 3. In this table the pK_a estimations of Ref. 1 are based on kinetic acidity data for isotopic exchange in 2-substituted 1,1,1,3,3,3-hexafluoropropanes, 1,1,1-trifluoroethanes and trihalomethanes at 310.15 K, employing $\text{CF}_3\text{CH}(\text{C}_6\text{H}_5)\text{CF}_3$ and $(\text{CF}_3)_3\text{CH}$ as standards. The solvent system used in kinetic studies was 50:50 mole % DMSO–methanol. The values of Ref. 2 were obtained by a polarographic method using anhydrous dimethylformamide as solvent. The method of estimation of the pK_a value given in Ref. 3 remains obscure.

As mentioned in the beginning, the acidity function method described in the previous paper⁷ for trichloromethane could not be employed in the determination of the pK_a 's for Cl_2BrCH , ClBr_2CH and Br_3CH because of the disturbingly rapid base hydrolysis of these trihalomethanes. The order of the rates of hydrolysis in H_2O –DMSO mixtures was found to be $\text{Cl}_2\text{BrCH} > \text{ClBr}_2\text{CH} > \text{Br}_3\text{CH} > \text{Cl}_3\text{CH}$. The same order in 66.7% dioxane–water solution has been reported earlier by Hine *et. al.*,¹⁶ the relative rates of hydrolysis at 298.45 K being 26:13:5:1. The hydrolysis of tribromomethane in H_2O –DMSO mixtures was slow enough, compared to the rate of detritiation of the standard carbon acid (methyl phenyl ketone), to make it possible to draw some conclusions about the magnitude of the pK_a for tribromomethane. The results obtained using the method of Ref. 7 are in favor of a pK_a value around 12–13, thus supporting the value of 11.8 estimated in this work for tribromomethane.

Acknowledgement. I thank professor Alpo Kankaanperä for helpful discussions throughout the course of this work.

Table 3. pK_a values for trihalomethanes.

Cl_3CH	Cl_2BrCH	ClBr_2CH	Br_3CH	Ref.
13.6 ^a	12.9	12.3	11.8	7, This work
15.5 ^b			13.7 ^b	1
15 ± 1			9 ± 1	2
24				3

^aThe value for trichloromethane was determined by the acidity function method⁹ in different H_2O –DMSO mixtures at 298.15 K applying the Bunnett-Olsen method¹⁴ to the extrapolation of the apparent pK_a values to the aqueous state. The H_- scale used was that of Dolman and Stewart.¹⁵ ^b310.15 K.

References

1. Klabunde, K. J. and Burton, D. J. *J. Am. Chem. Soc.* 94 (1972) 5985.
2. Reutov, O. A., Beletskaya, I. P. and Butin, K. P. *CH-acids*, Pergamon Press, Oxford 1978, p. 29.
3. Margolin, Z. and Long, F. A. *J. Am. Chem. Soc.* 95 (1973) 2757.
4. Lin, A. C., Chiang, Y., Dahlberg, D. B. and Kresge, A. J. *J. Am. Chem. Soc.* 105 (1983) 5380.
5. Scharlin, P. *Acta Chem. Scand., Ser. A36* (1982) 117.
6. Scharlin, P. *Unpublished results.*

7. Scharlin, P. *Acta Chem. Scand., Ser. A 40* (1986) 207.
8. Kankaanperä, A., Oinonen, L. and Salomaa, P. *Acta Chem. Scand., Ser. A 31* (1977) 551.
9. Earls, D. W., Jones, J. R., Rumney, T. G. and Cockerill, A. F. *J. Chem. Soc., Perkin Trans. 2* (1975) 54.
10. Streitwieser, A., Jr., Hudson, J. A. and Mares, F. *J. Am. Chem. Soc.* 90 (1968) 648.
11. Jones, J. R. *The Ionisation of Carbon Acids*, Academic Press, London 1973, p. 40.
12. Hine, J., Peek, R. C., Jr. and Oakes, B. D. *J. Am. Chem. Soc.* 76 (1954) 827.
13. Hine, J., Burske, N. W., Hine, M. and Langford, P. B. *J. Am. Chem. Soc.* 79 (1957) 1406.
14. Bunnett, J. F. and Olsen, F. P. *Can. J. Chem.* 44 (1966) 1899.
15. Dolman, D. and Stewart, R. *Can. J. Chem.* 45 (1967) 911.
16. Hine, J., Dowell, A. M., Jr. and Singley, J. E., Jr. *J. Am. Chem. Soc.* 78 (1956) 479.

Received June 29, 1987.