Proton Transfer in Methylammonium Salts: a Comparison of Water and Acetonitrile as Solvents

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Summary The rate of deprotonation of trimethylammonium ion by its conjugate base is 10^3 smaller in acetonitrile than in water.

RITCHIE points out, in a recent review,[1] that "reliable data for simple proton transfers in nonaqueous solvents are not plentiful". No comparison has been made of the rate of such a reaction in protic and aprotic solvents, with the same substrate and mechanism (or, at least, the same kinetic law). Such a comparison, however, is fundamental on account of the exceptional part played by protic solvents in these transfers, as evidenced by Grunwald, Loewenstein, and Meiboom[2] with methylammonium ions in water and, later on, in other hydroxylic solvents SH: MeOH[3] and Bu^{t}OH[4] (acetic acid[5] is omitted because the transfer is not promoted by the free amine in this case).

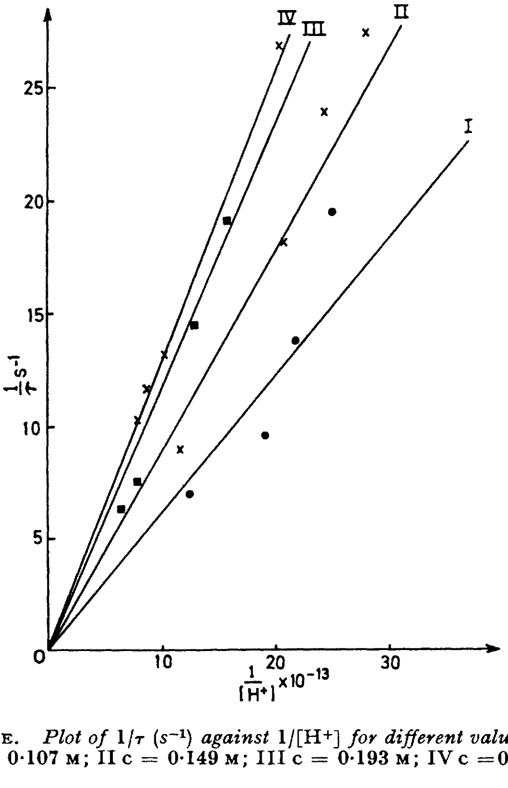

FIGURE. *Plot of* $1/\tau$ (s^{-1}) *against* $1/[H^+]$ *for different values of* c. (I c = 0·107 M; II c = 0·149 M; III c = 0·193 M; IV c = 0·223 M)

We report the first such experiment in a neutral solvent, anhydrous acetonitrile, for which the very low basicity[6] and autoprotolysis constant[7] (3×10^{-29}) rule out any assistance to the observed deprotonation of trimethylammonium (BH^+) chloride. The ^1H n.m.r. spectrum of the pure salt shows one singlet for BH^+, indicating a fast proton exchange on n.m.r. time-scale. This rate is made measurable by very small additions of anhydrous hydrochloric acid (*ca.* 10^{-4}—10^{-5} M). The pH of the solution (*ca.* 13·5—14·5) is determined using an indicator IH (Thymol Blue;[8] pK = 13·4), which is added progressively (10^{-5}—10^{-4} M), so as to obtain the pH by extrapolation to zero concentration of IH (this procedure is made necessary by the nearly equivalent quantities of free acid and indicator).

A plot of the reciprocal of the mean lifetime τ of BH^+ (between two transfers) against $1/[H^+]$ is made up of straight lines passing through the origin, one for each salt concentration c (Figure), whose slopes are themselves proportional to c: 0·59; 0·89; 1·17; and $1·33 \times 10^{-13}$ M s^{-1} respectively (according to a least-squares analysis; correlation coefficients: 0·954; 0·998; 0·991; 1·009). The accuracy is poor for low concentrations (points I, Figure). These results fit the following scheme:

$$BH^+ + B \xrightarrow{k} B + HB^+ \text{ (I), with } \frac{1}{\tau} = \frac{kK_Ac}{[H^+]} \qquad (1)$$

where K_A is the ionization constant of BH^+ (pK_A = 17·61 [9]). Equation (1) yields:

$$k = 2·41 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 20°.$$

Possibly, an intermediate $B \cdots H \cdots B^+$ could be involved[9,10] according to:

$$BH + B \underset{k'}{\overset{k}{\rightleftharpoons}} B \cdots H \cdots B \xrightarrow{k'} B + HB$$

which would be immaterial, except that the previously calculated value of k should be multiplied by 2.

Preliminary experiments with mono- and di-methylammonium ions show an analogous order of magnitude for k. These values may be compared with those relative to the same substrates[2–4] in different hydroxylic solvents SH, in which reaction (I) was subdivided into two parallel paths (yielding the same kinetic equation), namely (I) and (II):

$$BH^+ + SH + B \rightarrow B + SH^* + HB^+ \qquad (II).$$

The rate was, for either mechanism (I) or (II), about 10^8 M^{-1} s^{-1} ($3{\cdot}1 \times 10^8$ M^{-1} s^{-1} at 22° in water for Me_3NH^+), except in Bu^{t}OH for Me_3NH^+ (but not for $MeNH_3^+$ and $Me_2NH_2^+$), simply on account of an incomplete dissociation and the existence of tightly bonded ion pairs $BH^+ \cdots X^-$.

So we may conclude that the deprotonation rate of a methylammonium ion by its conjugate base is greatly increased by a protic solvent [even if it does not yield direct assistance as is the case in (II)]. This fact is presumably due to a greater proton mobility in a protic solvent and not to a change in the nucleophilicity of the reacting neutral free amine.[11]

(*Received, May 14th*, 1970; *Com.* 749.)

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[1] C. D. Ritchie, "Solute-Solvent Interactions," eds. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, p. 265.

[2] E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, 1956, **25**, 382.

[3] E. Grunwald, *J. Phys. Chem.*, 1967, **71**, 1846; E. Grunwald and M. Cocivera, *Discuss. Faraday Soc.*, 1965, **39**, 105.

[4] M. Cocivera, *J. Amer. Chem. Soc.*, 1966, **88**, 672.

[5] E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, 1964, **86**, 2965, 2970.

[6] Ref. 1, pp. 227 and 282.

[7] J. F. Coetzee, *Progr. Phys. Org. Chem.*, 1967, **4**, 45.

[8] I. M. Kolthoff, M. K. Chantooni, jun., and S. Bhowmik, *Analyt. Chem.*, 1967, **39**, 315.

[9] J. F. Coetzee and G. R. Padmanabham, *J. Amer. Chem. Soc.*, 1965, **87**, 5005.

[10] G. Charlot and B. Tremillon, "Les Réactions chimiques dans les Solvants et les Sels fondus," Gauthier Villars, Paris, 1963, p. 378.

[11] B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc.* (*B*), 1966, 152.