Steric Effects on the Proton Transfer Rates of Formic Acid Solutions of Methylamines

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Summary Deprotonation of monomethylammonium ion in formic acid involves exclusively the formate anion as the reacting base, in contrast with di- and tri-methylamine solutions.

Grunwald *et al.*[1] have measured the rate of deprotonation of ammonium salts in a protic solvent SH. They have established that the acidic proton of ammonium ion BH^+ can be removed by the conjugate base, either of BH^+ (B) or SH (S^-) according to:

$$BH^+ + S^- \xrightarrow{k_1} B + HS \quad (I)$$

$$BH^+ + B \xrightarrow{k_2} B + HB^+ \quad (II)$$

$$BH^+ + SH + B \xrightarrow{k_3} B + HS + HB^+ \quad (III)$$

Measuring the mean lifetime τ of BH^+ and SH by means of n.m.r. spectroscopy allows one to calculate k_1, k_2, and k_3, in water, where the kinetic laws as a function of the pH are consistent only with mechanisms (II) and (III) (*cf.* Table) for mono-, di-, and tri-methylammonium ions, respectively.

We have studied the same substrates in anhydrous formic acid, using a procedure already described for *N*-methylpiperidine:[2] for solutions of pure amines (0·3—1·2 M) the desired proton-transfer rate is obtained, as a function of the total amount of formate anion, through analysis of the line-shapes of their n.m.r. spectrum between 70 and 100°. The rate constants at 25° have been obtained by extrapolation to allow a comparison with Grunwald's results in aqueous solution[1] (Table). We observe values of the same order of magnitude in both solvents for k_2 and k_3 (except for $MeNH_3^+$; *cf.* below), using[6] pK_A (HCO_2H) $= pK_A$ (H_2O) + 5·3, as one would expect, since the reacting base is $MeNH_2$. The k_1 values may seem very low in formic acid, but it must be realized that huge quantities of formate ion (as compared with hydroxide ion in water) are present, so that the actual percentages of deprotonation of $MeNH_3^+$, $Me_2NH_2^+$, and Me_3NH^+ through reaction (I) are considerable: *ca.* 100, 70, and 32%, respectively, at 80° (against *ca.* 0% in water). The 100% value found for $MeNH_3^+$ does not mean that k_2 and k_3 are exactly zero; rather they become smaller than experimental errors (2—4%), for k_1 increases 12-fold at 80° from Me_2NH to

Kinetic constants at 25° for deprotonation of methylammonium ions in water (ref. 1; upper numbers) and formic acid (this work; lower numbers).

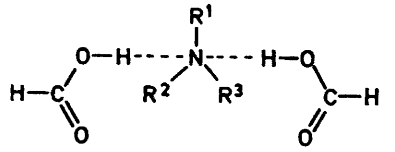
	$MeNH_3^+$	$Me_2NH_2^+$	Me_3NH^+
k_1 (s^{-1})	*ca.* 10^{11}	*ca.* 10^{11}	*ca.* 10^{11}
	7×10^{-2}	$1{\cdot}2 \times 10^{-3}$	$7{\cdot}7 \times 10^{-4}$
$10^{-7} \times k_2$ ($M^{-1}s^{-1}$)	25	4	neglig.
	neglig.	1·3	0·03
$10^{-7} \times k_3$ ($M^{-1}s^{-1}$)	34	56	31
	neglig.	13	1·2

$MeNH_2$, bringing its percentage from 70 to 97% for unchanged k_2 and k_3.

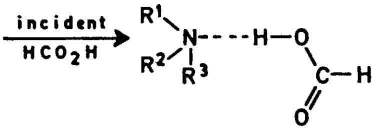
The major phenomenon is the widely separated order: $MeNH_3^+ >> Me_2NH_2^+ > Me_3NH^+$ for a mechanism fitting the kinetic law:

$$\frac{d[MeNH_3^+]}{dt} = k_1[MeNH_3^+][HCO_2^-]$$

Such a sequence cannot be accounted for by pK_A effects, nor, as in t-butyl alcohol by inactive hydrogen-bonded ion pairs;[3] it is rather reminiscent of S_N2 reactions of the analogous carbon compounds, and suggests the possibility of a symmetrical transition state:



resulting from the attack by a HCO_2H molecule of an internally hydrogen-bonded ion pair:



itself in equilibrium with the free ions $MeNH_3^+$ and HCO_2^-. This scheme has been envisaged by Grunwald and Price[4] for acetic acid solutions of $MeNH_3^+$, but rejected precisely for lack of steric effects. This "push–pull" mechanism, probably valid for $MeNH_3^+$ only, should be accompanied by a Walden-type inversion of nitrogen bonds, which could be evidenced only by a hypothetical amine where the *same* process would bring some change in the n.m.r. spectrum [as it would be the case with 1,2,6-trimethylpiperidine,[5] if it did not conform exclusively[2] to mechanisms (II) and (III)] This is the first evidence that such deprotonations may not always occur by a front attack of the base without configuration inversion.

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