

The Mechanism of Solvolysis of Organic Halides in Formic Acid

By J. R. FOX and G. KOHNSTAM

(Chemistry Department, South Road, Durham)

It has often been considered that the solvolysis of organic halides and sulphonates is much more likely to occur by the unimolecular mechanism, S_N1 , in formic acid than in aqueous solvents. The present results for the reactions of substituted benzyl bromides with formic acid containing 0.5% water provide information about the validity of this hypothesis. Comparison of the relative rates (k_X/k_H) at 80.17° (I) with those for the S_N1 solvolysis of substituted 4'-nitrodiphenylmethyl chlorides in 85% aqueous acetone at 0° (II) show that electron-releasing substituents accelerate both reactions similarly but that electron-attracting groups retard reaction (I) much less than reaction (II) (see below). This suggests that the less reactive benzyl bromides do not undergo S_N1 solvolysis in formic acid, a conclusion which could also have been reached from the highly curved plots of $\log k$ against σ^+ (not shown).

A more precise indication of mechanism can be obtained from the entropies of activation, ΔS^\ddagger , which are virtually independent of the nature of 4-substituents (apart from alkoxy-groups) in S_N1 solvolysis.² This does not apply to the present systems where the results are consistent with a bimolecular reaction by the parent compound and an increasing tendency to react by mechanism S_N1 as the facility for donating electrons to the reaction centre is increased.²⁻⁴ The fact that the accelerating effect of 4-fluoro- and 4-phenyl-substituents is accompanied by an increase in the energy of activation supports this conclusion.

Substituent (X) ..	4-F	4-Me	4-Ph
$\Delta S^\ddagger_X - \Delta S^\ddagger_H$, 80.17°			
(cal. deg. ⁻¹) ..	1.82	4.10	8.15

These considerations suggest that, at best, benzyl bromides will only undergo S_N1 solvolysis

Substituent (X)	4-MeO	4-Me	4-Ph	4-F	3-Cl	4-NO ₂
(I)	5.24×10^5	39.9	22.6	1.61	0.114	1.31×10^{-2}
k_X/k_H	(II) 5.28×10^5	72.8	19.9	3.59	0.010*	1.17×10^{-4}

* Calculated from results for the $\alpha\alpha$ -dimethylbenzyl chloride.¹

¹ H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

² G. Kohnstam, "The Transition State," Chem. Soc. Special Publication, No. 16, 1962, p. 179.

³ (a) G. R. Cowie, J. R. Fox, M. J. H. Fitches, K. A. Hooton, D. M. Hunt, G. Kohnstam, and B. Shillaker, *Proc. Chem. Soc.*, 1961, 222; (b) G. Kohnstam and D. Tidy, *Chem. and Ind.*, 1962, 1193.

⁴ L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 1.

in formic acid when a 4-phenyl group or a better electron-donor is present.** In more aqueous solvents a better electron-releasing group than 4-methyl is required⁵† and it can therefore be concluded that, contrary to widely held views, mechanism S_N1 does not always operate at a much earlier stage in a series of increasing electron accession to the reaction centre for solvolysis in formic acid than for solvolysis in more aqueous

media. It must be stressed that the present conclusions only apply to entirely S_N1 solvolysis; there is ample evidence⁶ that the importance of bond-breaking (" S_N1 character") in bimolecular solvolysis is greater in formic acid than in more aqueous solvents. A more detailed discussion of the differences between the two solvent systems will be presented at a later date.

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** The entropies of activation suggest that the solvolysis of the 4-phenyl compound proceeds *via* a transition state which is closer to that required by mechanism S_N1 than the slightly faster solvolysis of the 4-methyl derivative. If the two compounds react *via* different transition states, the rates may not reflect the polar properties of the substituents. Our observations may therefore reflect the greater ability of the highly polarisable phenyl group to respond to the strongly electron-demanding situation of S_N1 solvolysis in formic acid.

† This has only been established for the chlorides^{3a} and toluene-*p*-sulphonates^{3b} but there is no reason to believe that the bromides will behave differently (*cf.* ref. 5).

⁵ G. R. Cowie, H. J. M. Fitches, and G. Kohnstam, *J. Chem. Soc.*, 1963, 1585.

⁶ For example, L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 1940, 945.