

# Kinetic Acidity of Carbon Acids in Water/Dimethyl Sulfoxide Mixtures. I. Localized and Delocalized Carbanions as Reaction Intermediates

Alpo Kankaanperä, Markku Lahti and Pirketta Scharlin

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

Kankaanperä, Alpo, Lahti, Markku and Scharlin, Pirketta, 1986. Kinetic Acidity of Carbon Acids in Water/Dimethyl Sulfoxide Mixtures. I. Localized and Delocalized Carbanions as Reaction Intermediates. – Acta Chem. Scand. A 40: 387–391.

It has been shown that the localization or delocalization of the negative charge in the carbanion formed in a proton transfer reaction of a carbon acid does not alone predict the susceptibility to solvent basicity in water/dimethyl sulfoxide mixtures. Relatively low rate acceleration is, however, observed when negative charge is distributed between oxygen and carbon atoms as in oxo-carbanion intermediates. This behavior can be explained in terms of differences in structure-making ability of the hydroxide ion and of the transition state on the solvent.

It is well known<sup>1</sup> that the susceptibility of the rate of proton transfer to solvent basicity in water/dimethyl sulfoxide (DMSO) mixtures can be very different with different carbon acids. The slopes of the plots of  $\log(k/s^{-1})$  against  $H_-$  of the medium have been reported to vary between 0.4 and 1.0.<sup>1</sup> Since the factors generating these differences are still obscure, the behavior of structurally different carbon acids was studied in this work paying particular attention to carbon acids which produce either localized or delocalized carbanions. In these proton transfer reactions, differences in susceptibility to solvent basicity are expected on the basis of previous kinetic data. Ritchie<sup>2</sup> has stated that those carbon acids, the conjugate bases of which have localized charge, are predicted to have proton transfer rates considerably greater than the acids of the same thermodynamic strength with delocalized charge. Recently Koch<sup>3</sup> has stated that one should not predict the behavior of localized carbanions from model compounds which generate delocalized carbanions.

In this work, triphenyl methane and chloroform were taken as model compounds for kinetic measurements because they are structurally related. First, both are hydrocarbons. Second, in the transition state of their detritiation reactions,

the proton is transferred almost entirely to the solvent; in the detritiation of chloroform,  $\beta$  values are about unity;<sup>4,5</sup> in the detritiation of triphenyl methane,  $\beta$  values near unity are expected on the basis of the Hammond principle.<sup>6</sup> Third, the molecules of both of these compounds are relatively large. The anions, however, are not necessarily structurally similar. Chloroform produces a carbanion with the negative charge localized on the carbon atom.<sup>7</sup> In the case of triphenyl methane, the decision in favour of a localized or delocalized anion is not as straightforward. Phenyl substitution of one or more hydrogens of methane lowers the  $pK_a$  value by about 20 units.<sup>8,9</sup> This can be explained by delocalization of the negative charge in the  $\pi$  electron system of one of the phenyl rings. On the other hand, results with methanol as solvent suggest that triphenylmethyl anion behaves like a localized ion.<sup>3,10</sup> This controversy is discussed below on the basis of present kinetic data.

For the sake of comparison, some ketones were also subjected to kinetic studies in water/dimethyl sulfoxide mixtures. These carbon acids produce delocalized carbanions like triphenyl methane, but, by contrast, negative charge is also distributed to the heteroatom. The role of solvent reorganization is important in proton trans-

fer reactions of carbon acids.<sup>11</sup> The differences in type of charge delocalization may thus be reflected in solvent effects in water/dimethyl sulfoxide mixtures. Recently, Bernasconi<sup>12</sup> has favoured the principle of imperfect synchronization instead of solvent reorganization.

### Experimental

The labelling of carbon acids, ketones,<sup>13</sup> triphenyl methane<sup>13</sup> and chloroform,<sup>5</sup> has been performed previously. Dimethyl sulfoxide was purified by distillation over calcium hydride. The rate coefficients of detritiation were determined at 298.15 K in water/DMSO mixtures. Tetramethyl ammonium hydroxide was used as the catalyst. The methods of the kinetic measurements have been described earlier.<sup>14</sup> The mole fraction of DMSO varied in the kinetic experiments between 0 and 0.9. With chloroform, the measurements could be extended to mixtures in which the mole fraction of DMSO was lower than 0.15 only due to the high reactivity of the substrate. By contrast, the detritiation of triphenyl methane could be followed conveniently only when  $x(\text{DMSO})$  was higher than 0.5 due to the low reactivity of this carbon acid.

### Results and discussion

The kinetic data are collected in Table 1. When log of these rate coefficients was plotted against  $H_-$  values<sup>15,16</sup> of the solvent, nearly linear correlations were observed with the following slopes (Fig. 1): chloroform 1.08(2), triphenyl methane 0.80(1), acetophenone 0.433(4), methyl styryl ketone 0.435(3) and *tert*-butyl methyl ketone 0.384(9). On the basis of these slopes, it is evident that the localization or delocalization of the negative charge in the intermediate carbanion cannot be the only structural feature which determines the sensitivity to solvent basicity. The observed rate increase is highest in the detritiation of chloroform and triphenyl methane, although the former generates localized and the latter delocalized carbanions. Markedly lower accelerating effect is observed in the detritiation of ketones where delocalized carbanions are formed. To explain these differences, the kinetic results can be considered in terms of transition state theory.

Proton extraction from a carbon acid by hy-

Table 1. Rate constants for the detritiation of different carbon acids in water/dimethyl sulfoxide mixtures at 298.15 K.  $[\text{OH}^-] = 0.011 \text{ mol dm}^{-3}$ .

Carbon acid	$x(\text{DMSO})$	$H_-^a$	$k/10^{-4} \text{ s}^{-1}$
Chloroform	0	12.04	18.9 <sup>b</sup>
	0.0271	12.29	36.6
	0.0590	12.63	75.1
	0.0932	12.97	194
	0.1270	13.34	480
Triphenyl methane	0.554	18.02	0.000928
	0.698	19.49	0.0155
	0.746	19.99	0.0408
	0.750	20.03	0.0348
	0.758	20.09	0.0492
	0.800	20.58	0.103
	0.826	20.90	0.215
	0.834	21.00	0.235
	0.861	21.36	0.510
	0.871	21.51	0.680
	0.875	21.57	0.707
<i>Tert</i> -butyl methyl ketone	0	12.04	0.1063 <sup>c</sup>
	0.118	13.24	0.270
	0.224	14.53	0.802
	0.366	16.08	3.24
	0.555	18.03	21.1
Acetophenone (methyl phenyl ketone)	0	12.04	0.631 <sup>c</sup>
	0.118	13.24	2.05
	0.127	13.34	2.28
	0.206	14.31	5.38
	0.223	14.51	6.48
	0.284	15.21	13.96
	0.331	15.70	22.8
	0.366	16.08	33.5
	0.402	16.45	51.2
0.555	18.03	246	
Methyl styryl ketone	0	12.04	0.391 <sup>c</sup>
	0.118	13.24	1.34
	0.224	14.53	4.59
	0.366	16.08	23.6
	0.555	18.03	157

<sup>a</sup>Ref. 15, 16.

<sup>b</sup>Calculated from measurements in 0.1 mol dm<sup>-3</sup> NaOH.

<sup>c</sup>Ref. 14, calculated for  $[\text{OH}^-] = 0.011 \text{ mol dm}^{-3}$ .

droxide ion is described by eqn. (1). The reaction rate is given by eqn. (2) which, on integration, gives expression (3) for the observed first order rate coefficients. Since hydroxide ion concen-

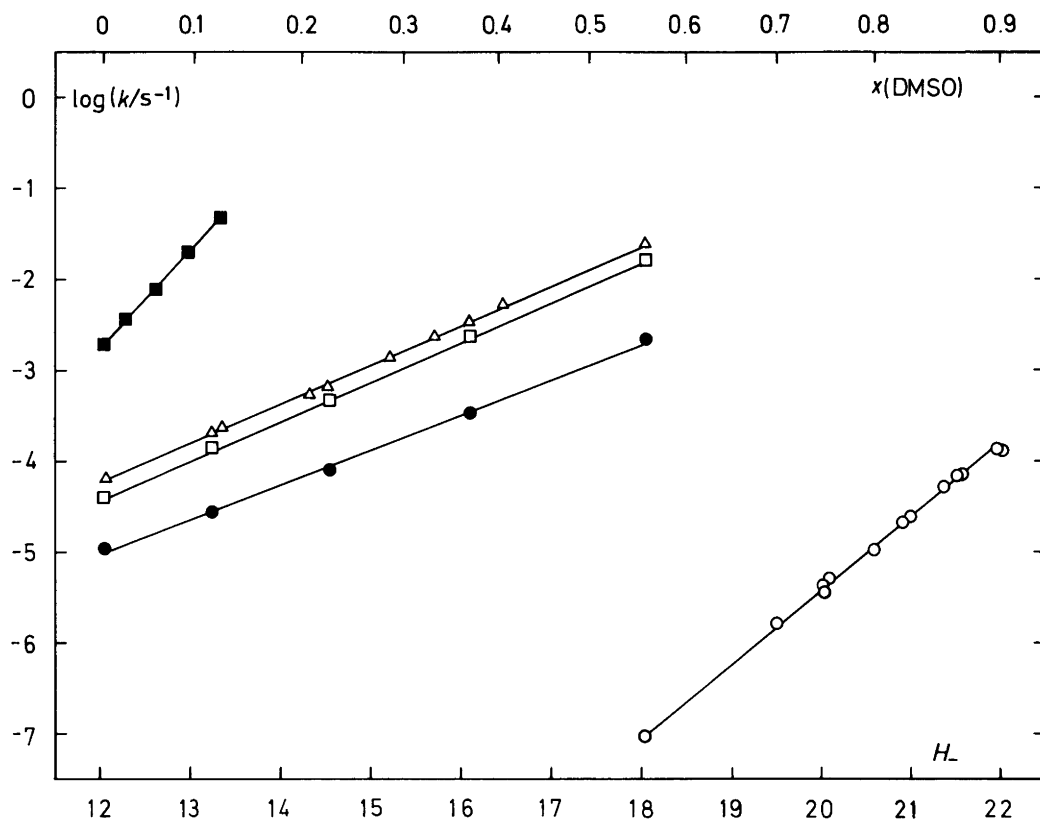


Fig. 1. Plots of  $\log(k/s^{-1})$  vs.  $H_-$  for the detritiation of different carbon acids in water/dimethyl sulfoxide mixtures. Notations: chloroform (■), acetophenone ( $\Delta$ ), methyl styryl ketone ( $\square$ ), *tert*-butyl methyl ketone (●) and triphenyl methane (○).



$$-\frac{d[SH]}{dt} = k^\ominus [SH][HO^-] \frac{y(HO^-) y(SH)}{y^*} \quad (2)$$

$$k(\text{obs}) = k^\ominus [HO^-] \frac{y(HO^-) y(SH)}{y^*} \quad (3)$$

tration is kept constant in the reaction medium, eqn. (3) can be written in the form  $k(\text{obs}) =$

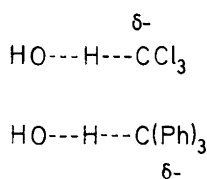
constant  $\cdot [y(HO^-) y(SH)/y^*]$ . When logs are taken for both sides of this equation, expression (4) is obtained. Thus the observed changes in

$$\log(k/s^{-1}) = \log \frac{y(HO^-) y(SH)}{y^*} + \text{constant}' = \log Y + \text{constant}' \quad (4)$$

$\log(k/s^{-1})$  give information on changes in activity coefficient quotient  $Y$ . When the observed differences in susceptibility to solvent basicity are discussed in terms of activity coefficients given in eqn. (4),  $y(SH)$  in quotient  $Y$  can be assumed to be nearly independent of the solvent since neutral species cannot introduce significant changes in solvent reorganization. Therefore, the observed rate increase when the amount of dimethyl sulfoxide is increased in the solvent must be mainly due to the increase in the activity coefficient ratio  $y(HO^-)/y^*$ . In this ratio  $y(HO^-)$ , which depends only on the solvent system, increases markedly with  $x(\text{DMSO})$  in water/DMSO mixtures as shown by the measured  $H_-$  values.<sup>15,16</sup> On the other hand, the solvent dependence of  $y^*$  may be different for different substrates, since, in water solution, the structure-making ability of

the transition state must be related to its structure.

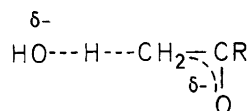
Let us first discuss the detritiation of chloroform and triphenyl methane in which the observed susceptibility to solvent basicity is highest. In the transition states of these reactions, the proton is transferred almost entirely to the hydroxide ion as stated above and, therefore, the negative charge must be mainly distributed to the hydrocarbon moiety either localized or delocalized (Scheme 1). The observed high susceptibility to solvent basicity reveals that  $y^\ddagger$  does not depend significantly on solvent composition; otherwise, the accelerating effect of  $y(\text{HO}^-)$  when going from water to water/dimethyl sulfoxide mixtures would be cancelled significantly. One explanation of this is that, although both of these transition states are ionic species, their structure-making ability on water may be considerably lower than that of the hydroxide ion, since the negative charge, either localized or delocalized, is in a carbon atom system. Thus the assumption, based on the measured  $pK_a$  values, that triphenyl methane forms a delocalized carbanion cannot be excluded on the basis of present kinetic data. In addition, it must be mentioned that, in methanol/dimethyl sulfoxide mixtures, the accelerating effect of DMSO on the proton transfer reaction of triphenyl methane<sup>17</sup> is comparable to that of fluorene<sup>1</sup> which produces a  $\pi$ -delocalized carbanion. Although in the above-mentioned cases it is



Scheme 1.

evident that  $y^\ddagger$  does not depend significantly on solvent composition, this result cannot be generalized for proton transfer reactions of all carbon acids. The ketones studied in this work, for example, are exceptions. Their susceptibility to solvent basicity is much lower than that of chloroform and triphenyl methane. In terms of eqn. (4), this means that, in quotient  $Y$ , the activity coefficient of the transition state must increase markedly with mole fraction increase of dimethyl sulfoxide. The main reason for this increase is

that both of the oxygen atoms in the transition as shown in Scheme 2. The HO group is negatively charged as the proton transfer is not yet complete in the transition state of the reaction. This conclusion is based on Brönsted  $\beta$  values, which for proton transfer reactions of ketones are of the magnitude 0.6–0.9.<sup>18</sup> In water solution, the structure-making ability of this transition state may even be as great as that of the hydroxide ion. In dimethyl sulfoxide, the stabilizing effect is eliminated and, as a result,  $y^\ddagger$  will increase – in extreme cases, even as fast as  $y(\text{HO}^-)$ . Thus, the change of  $y(\text{HO}^-)$ , when going from water to water/dimethyl sulfoxide mixtures, will be compensated for, more or less completely, by the change of  $y^\ddagger$ . Therefore, the accelerating effect of dimethyl sulfoxide mixtures remains relatively lower than in the detritiation of chloroform and triphenyl methane.



Scheme 2.

The fact that, in the detritiation of *tert*-butyl methyl ketone, the slope of the plot  $\log(k/s^{-1})$  vs.  $H_-$  is, within the limits of experimental error, lower than that for the aromatic ketones studied is also in accord with the assumptions made above. In the transition state of detritiation of *tert*-butyl methyl ketone (Scheme 2, R = C(CH<sub>3</sub>)<sub>3</sub>), the electron density in the carbonyl oxygen is higher than, for instance, in the corresponding transition state of acetophenone due to the higher electron-releasing ability of the *tert*-butyl group. The higher the electron density in the oxygen atom, the higher is its structure-making ability on water. Again, when going to water/DMSO mixtures, this extra stabilization is partially reduced; in terms of activity coefficients, this means an increase in  $y^\ddagger$  values. When comparing the effects of  $y^\ddagger$  to rate coefficients in water/DMSO mixtures in the light of eqn. (4), it is evident that the accelerating effect of  $y(\text{HO}^-)$  is reduced more effectively in the detritiation of *tert*-butyl methyl ketone than in the detritiation of acetophenone.

On the basis of the present kinetic data, it is thus evident that the susceptibility to solvent bas-

icity cannot be predicted solely on the basis of the localization or delocalization of the negative charge in the carbanion formed in the reaction. However, if delocalized oxo-carbanion are formed in the reaction, relatively low accelerating effect is observed due to the negatively charged oxygen atom in the transition state of the reaction. On the contrary, in proton transfer reactions of hydrocarbon acids, the accelerating effect of dimethyl sulfoxide is in most cases relatively high, especially if the transition state has a product-like structure, which is typical for carbon acids of low acidity.

### References

1. Reutov, O. A., Beletskaya, I. P. and Butin, K. P. *CH-Acids*, Pergamon Press, London 1978. 183–189.
2. Ritchie, C. D. *J. Am. Chem. Soc.* 91 (1969) 6479.
3. Koch, H. F. *Acc. Chem. Res.* 17 (1984) 137.
4. Lin, A. C., Chiang, Y., Dahlberg, D. B. and Kresge, A. J. *J. Am. Chem. Soc.* 105 (1983) 5380.
5. Kankaanperä, A. and Oinonen, L. *Unpublished results*.
6. Hammond, G. S. *J. Am. Chem. Soc.* 77 (1955) 334.
7. Kresge, A. J. *Acc. Chem. Res.* 9 (1975) 354.
8. Streitwieser, A., Murdoch, J. R., Häfeli, G. and Chang, C. J. *J. Am. Chem. Soc.* 95 (1973) 4248.
9. Jaun, B., Schwarz, J. and Breslow, R. *J. Am. Chem. Soc.* 102 (1980) 5741.
10. Koch, H. F., Koch, J. G., Koch, N. H. and Koch, A. S. *J. Am. Chem. Soc.* 105 (1983) 2388.
11. Bernasconi, C. F. *Pure Appl. Chem.* 54 (1982) 2335.
12. Bernasconi, C. F. *Tetrahedron* 41 (1985) 3219.
13. Kankaanperä, A., Salomaa, P., Oinonen, L. and Mattsén, M. *Finn. Chem. Lett.* (1978) 25.
14. Kankaanperä, A., Oinonen, L. and Salomaa, P. *Acta Chem. Scand. A* 31 (1977) 551.
15. Cox, R. A. and Stewart, R. *J. Am. Chem. Soc.* 98 (1976) 488.
16. Dolman, D. and Stewart, R. *Can. J. Chem.* 45 (1967) 911.
17. Kollmeyer, W. D. and Cram, D. J. *J. Am. Chem. Soc.* 90 (1968) 1784.
18. Jones, J. R. *The Ionisation of Carbon Acids*, Academic Press, London, 1973, p. 136.

Received December 31, 1985.