152.5 – 153.5 °C (dec.). Anal. $C_{16}H_{18}IO_2P$: C, H, I. NMR [(CD$_3$)$_2$SO]: δ_P 25.6; δ_H 4.72 (CH_2COOH, $^2J_{PH}$ 13.7 Hz).

(Ethoxycarbonylmethyl)diphenylethylphosphonium iodide. The compound was prepared as above and had m.p. 129.5 – 130 °C (from 2-PrOH). Anal. $C_{18}H_{22}IO_2P$: C, H, I. NMR [(CD$_3$)$_2$SO]: δ_P 26.0; δ_H 4.88 (CH_2COOEt, $^2J_{PH}$ 14.2 Hz).

(Carbamidomethyl)diphenylethylphosphonium iodide. The compound was prepared as above, m.p. 165 – 167 °C (from H$_2$O). Anal. $C_{16}H_{19}INOP$: C, H, N, I. NMR [(CD$_3$)$_2$SO]: δ_P 26.4; δ_H 4.57 (CH_2CONH$_2$, $^2J_{PH}$ 14.2 Hz).

(N,N-Dimethylcarbamidomethyl)diphenylethylphosphonium iodide. The compound was prepared as above, m.p. 235 – 237 °C (dec.; from EtOH). Anal. $C_{18}H_{23}INOP$: C, H, N, I. NMR [(CD$_3$)$_2$SO]: δ_P 26.3; δ_H 4.97 (CH_2CONMe$_2$, $^2J_{PH}$ 13.3 Hz).

Acknowledgements. We thank Mrs. Eva Asmussen for obtaining the kinetic data and the Danish Scientific Research Council for the purchase of the photoelectron spectrometer.

1. Davies, W. C. and Lewis, W. P. G. *J. Chem. Soc.* (1934) 1599.
2. Henderson, W. A., Jr. and Buckler, S. A. *J. Am. Chem. Soc. 82* (1960) 5794.
3. Mastryukova, T. A. and Kabacknik, M. I. *Russ. Chem. Rev. 38* (1969) 795.
4. Dahl, O. and Jensen, F. K. *Acta Chem. Scand. B 29* (1975) 863.
5. Dahl, O. *Acta Chem. Scand. B 30* (1976) 799.
6. Issleib, K. and Thomas, G. *Chem. Ber. 93* (1960) 803.
7. Lappert, M. F., Pedley, J. B., Wilkins, B. T., Stelzer, O. and Unger, E. *J. Chem. Soc. Dalton Trans.* (1975) 1207.
8. Klopman, G. *Chemical Reactivity and Reaction Paths,* Wiley, New York 1974, p. 60.
9. Taft, R. W., Jr. In Newman, M. S. *Steric Effects in Organic Chemistry,* Wiley, New York 1956, pp. 591, 595 and 619.
10. Stevenson, G. W. and Williamson, D. *J. Am. Chem. Soc. 80* (1958) 5943.
11. *Beilsteins Handbuch der Organischen Chemie,* Springer, Berlin 1920, Bd. 2.
12. Debies, T. B. and Rabalais, J. W. *Inorg. Chem. 13* (1974) 308.
13. Hewertson, W., Shaw, R. A. and Smith, B. C. *J. Chem. Soc.* (1964) 1020.
14. Issleib, K. and Thomas, G. *Z. Anorg. Allg. Chem. 330* (1964) 295.
15. Kopecký, J. and Šmejkal, J. *Chem. Ind. London* (1966) 1529.

Received January 13, 1977.

Tropylium Ions. Part VIII.[1] General Base Catalysis in the Reaction of Phenyltropylium Ions with Water

P. O. I. VIRTANEN and E. HAKALA

Department of Chemistry, University of Oulu, SF-90100 Oulu 10, Finland

There are divided opinions about the occurrence [2-4] and importance [5] of general base catalysis in the reaction of carbonium ions with water and consequently also of general acid catalysis in the reverse dissociation reaction. Direct observations have earlier been reported for reactions of triarylmethyl cations [2-5] and for the hydration of N-substituted iminolactones.[6-7] In this paper we wish to report our observations about general base catalysis in the reaction of a representative of another cation system, phenyltropylium cations.

When dissolved in aqueous B – BH+ buffer solution, phenyltropylium cations undergo the reactions

$$Tr^+ + 2H_2O \rightleftharpoons TrOH + H_3O^+ \tag{1}$$

$$Tr^+ + OH^- \rightleftharpoons TrOH \tag{2}$$

and if general base catalysis by B contributes, the one-step reaction

$$Tr^+ + H_2O + B \rightleftharpoons TrOH + BH^+ \tag{3}$$
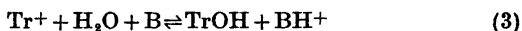
The observed pseudo first-order rate constant can be written as

$$k_{obs} = k_{H_2O} + k_{OH^-}[OH^-] + k_B[B] \tag{4}$$

where k_B is the second-order rate constant for catalysis by the base B. At constant buffer ratio (more exactly, at constant pH) the slope of the plot of k_{obs} vs. [B] gives k_B, and the intercept $k^{B=0}$ is $k_{H_2O} + k_{OH^-}[OH^-]$. If the intercepts $k^{B=0}$ measured at different buffer ratios are plotted as a function of [OH$^-$], the values of k_{H_2O} and k_{OH^-} at zero concentration of buffer are obtained.

Data for the reaction of p-dimethylaminophenyltropylium cation with water in Dabco (1,4-diazabicyclo[2.2.2]octane) – DabcoH+ and Et$_3$N – Et$_3$NH+ buffers are collected in Table 1. The rates were measured by stopped-flow technique at 25 °C and at constant ionic strength, regulated with potassium perchlorate.[8] Examination of the data gives the values of 1.4 dm^3 mol^{-1} s^{-1} and 2.3 dm^3 mol^{-1} s^{-1} for catalysis by Dabco and Et$_3$N, respectively, a value 0.8×10^{-2} s^{-1} for k_{H_2O} and a value 1.5×10^3 dm^3 mol^{-1} s^{-1} for k_{OH^-} at ionic strength 0.02 mol dm^{-3}, and a value 1.1×10^{-2} s^{-1} for k_{H_2O} and a value 1.3×10^3 dm^3 mol^{-1} s^{-1} for k_{OH^-} at ionic strength 0.1 mol dm^{-3}. Slightly

Table 1. Reaction of *p*-dimethylaminophenyltropylium fluoroborate in aqueous buffered solutions at 25 °C.

pH	$[OH^-]/$ mol dm^{-3} 10^{-4}	$k^{B=0}/$ s^{-1}	$k_{Dabco}/$ dm^3 mol^{-1} s^{-1}	$k_{Et_3N}/$ dm^3 mol^{-1} s^{-1}
Ionic strength 0.020 mol dm^{-3}				
9.33	0.214	0.0405	1.28	
9.36	0.229	0.0414	1.30	
9.49	0.309	0.0545	1.32	
9.65	0.447	0.0748	1.68	
Ionic strength 0.100 mol dm^{-3}				
9.80	0.631	0.0925		2.13
10.22	1.660	0.226		2.25
10.60	3.981	0.525		2.46

higher values, 2.0×10^{-2} s^{-1} and 1.7×10^3 dm^3 mol^{-1} s^{-1}, have earlier been reported for the two last-mentioned rate constants measured in borate and triethylamine buffers at ionic strength 0.01 mol dm^{-3} at 23 °C.[9] The slight increase in the values of k_B with increasing concentration of B may be an indication that a second amine molecule facilitates the reaction of a water molecule.

Nucleophilic catalysis is unlikely. At 23 °C the rate constant for the reaction of the *p*-dimethylaminophenyltropylium cation with diethylamine is 4.2×10^4 dm^3 mol^{-1} s^{-1} and with ethylamine 2.8×10^3 dm^3 mol^{-1} s^{-1}.[10] These values are much higher than the value 2.3 dm^3 mol^{-1} s^{-1} found for triethylamine and imply the unimportance of nucleophilic catalysis. We therefore believe that the reaction of phenyltropylium cations with water involves general base catalysis.

Ritchie has suggested that the value of the rate constant ratio k_{H_2O}/k_{Dabco} may be a useful criterion for distinguishing between general base and nucleophilic catalysis.[4] The ratio varies from 0.06 mol dm^{-3} to 0.20 mol dm^{-3} for triarylmethyl cations and is 0.13 mol dm^{-3} for *N*,*O*-trimethylenephthalimidium cation.[2,4,7] For acetate esters, which are observed to be subject to nucleophilic catalysis, the ratio is much smaller, from 1.2×10^{-4} mol dm^{-3} to 1.5×10^{-7} mol dm^{-3}.[11] For *p*-dimethylaminophenyltropylium ion the ratio is 1.0×10^{-2} mol dm^{-3}.

1. Virtanen, P. O. I. and Tolonen, Y. *Finn. Chem. Lett.* (1977). *In press.* Part VII.
2. Ritchie, C. D. *J. Am. Chem. Soc. 94* (1972) 3275.
3. Ride, J. N., Wyatt, P. A. H. and Zochowski, Z. M. *J. Chem. Soc. Perkin Trans. 2* (1974) 1188.
4. Ritchie, C. D., Wright, D. J., Huang, D. and Kamego, A. A. *J. Am. Chem. Soc. 97* (1975) 1163.
5. Hill, E. A. and Mueller, W. J. *Tetrahedron Lett.* (1968) 2565; Postle, M. J. and Wyatt, P. A. H. *J. Chem. Soc. Perkin Trans. 2* (1972) 474; Bunton, C. A. and Huang, S. K. *J. Am. Chem. Soc. 94* (1972) 3536; *96* (1974) 515.
6. Schmir, G. L. and Cunningham, B. A. *J. Am. Chem. Soc. 87* (1965) 5692.
7. Gravitz, N. and Jencks, W. P. *J. Am. Chem. Soc. 96* (1974) 489.
8. Virtanen, P. O. I. and Vaskuri, J. *Finn. Chem. Lett.* (1975) 159.
9. Ritchie, C. D. and Fleischhauer, H. *J. Am. Chem. Soc. 94* (1972) 3481.
10. Ritchie, C. D. and Virtanen, P. O. I. *J. Am. Chem. Soc. 95* (1973) 1882.
11. Jencks, W. P. and Gilchrist, M. *J. Am. Chem. Soc. 90* (1968) 2622.