Effect of Hydrogen Peroxide on the Rate of Hydrolysis of t-Butyl Chloride

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Summary An increase in the first-order rate constant for the hydrolysis of t-butyl chloride in water is observed when hydrogen peroxide is added, whereas a decrease is usually observed when organic co-solvents are added.

AT fixed temperature and ambient pressure, the first-order rate constant for the hydrolysis of t-butyl chloride in water decreases when ethyl alcohol,[1] isopropyl alcohol,[1] t-butyl alcohol,[1] tetrahydrofuran,[2] or acetonitrile[2] is added. Analysis of these solvent effects in the context of the thermodynamic[3] and ultrasonic absorption[4] properties of binary aqueous mixtures prompted us to measure the rate constant for the hydrolysis of t-butyl chloride when hydrogen peroxide was added.

The kinetic data were obtained by measuring the dependence of conductivity on time for at least three half-lives. The rate constants were calculated using a previously described method,[5] but with the computer programme (ALGOL) modified slightly. Slow decomposition of hydrogen peroxide occurred at the electrodes although analysis of the solutions after kinetic runs showed negligible change in the mole fraction of hydrogen peroxide. The data are summarised in the Table.

TABLE. *Ratio of first-order rate constant for the hydrolysis of t-butyl chloride at* 278·16K *in water and hydrogen peroxide mixture, k, to that in water, k_W; x_2 is the mole fraction of* H_2O_2

x_2	0	0·03	0·10	0·19
k/k_W	1	1·30	2·16	2·95

Arnett[6] and Robertson and Sugamori[1,2] have shown that, for t-butyl chloride in water, the effects of added co-solvent on the initial state of t-butyl chloride in water may be more important than those on the transition state. If this is correct then, in the present context, it is significant that hydrogen peroxide and water are nearly isodielectric[7] (see also ref. 8) and that the excess Gibbs function of mixing, G^E, is negative.[9] The latter feature of this system is, we suggest, extremely important, bearing in mind that for the other systems mentioned above, G^E is positive.[10]

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[1] R. E. Robertson and S. E. Sugamori, *J. Amer. Chem. Soc.*, 1969, **91**, 7254.

[2] R. E. Robertson and S. E. Sugamori, *Canad. J. Chem.*, 1972, **50**, 1353.

[3] F. Franks in 'Hydrogen-Bonded Solvent Systems,' eds. A. Covington and P. Jones, Taylor and Francis, London, 1968, p. 31.

[4] M. J. Blandamer and D. Waddington, *Adv. Mol. Relax. Proc.*, 1970, **2**, 1.

[5] P. Moore, *J.C.S. Faraday I*, 1972, **68**, 1890.

[6] E. M. Arnett, 'Physico-Chemical Processes in Mixed Aqueous Solvents,' Heinemann, London, 1967, p. 105.

[7] W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, 'Hydrogen Peroxide,' Reinhold, New York, 1955, p. 262.

[8] A. K. Covington, K. E. Newman, and M. Wood, *J.C.S. Chem. Comm.*, 1972, 1234.

[9] G. Scatchard, G. M. Kavanagh, and L. B. Ticknor, *J. Amer. Chem. Soc.*, 1952, **74**, 3715.

[10] For alcohols, see F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1; For H_2O + MeCN, see A.-L. Vierk, *Z. anorg. Chem.*, 1950, **261**, 283; For H_2O + tetrahydrofuran, see C. Treiner, J.-F. Bocquet, and M. Chemla, *J. Chim. phys.*, 1973, **70**, 72.