New Information on the Aqueous Hydrolysis of Tertiary Butyl Chloride

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Summary Aqueous hydrolysis of t-butyl chloride at concentrations in the range 10^{-5} to 10^{-3} mol dm^{-3} does not conform to simple first order kinetics with respect to the rate of production of hydrogen ions and is pH dependent.

LITERATURE results[1] on the aqueous hydrolysis of tertiary butyl chloride, Me_3CCl, may be combined and fitted to the transition state equation

$$k_r = (k\mathrm{T}/h)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT)$$

to yield the following pseudo-thermodynamic activation parameters: $\Delta H^*_{285\cdot65}$ 99,353 ± 79 J mol^{-1} = 23,746 ± 19 cal mol^{-1}; $\Delta S^*_{285\cdot65}$ 59·509 ± 0·276 J K^{-1} mol^{-1} = 14·223 ± 0·066 cal K^{-1}; $\Delta C_p{}^*_{285\cdot65}$ $-384\cdot1 \pm 5\cdot4$ J K^{-1} mol^{-1} = $-91\cdot8 \pm 1\cdot3$ cal K^{-1} mol^{-1}; $\mathrm{d}\Delta C_p{}^*/\mathrm{d}T - 40\cdot79 \pm 0\cdot25$ J K^{-2} mol^{-1} = $-9\cdot75 \pm 0\cdot06$ cal K^{-2} mol^{-1}

$\Delta C_p{}^*$ is unusually large and has a marked temperature dependence, suggesting a mechanism more complex than simple two-stage. We present new results showing that the reaction does not obey simple first-order kinetics with respect to the rate of production of hydrogen ions at concentrations below 10^{-3} mol dm^{-3}.

Most recent work has been at concentrations of approximately 10^{-3} mol dm^{-3}, using conductometric methods under conditions such that the early stages of the reaction were not observed. Further, the initial pH of the solvolysing medium was not controlled. We have followed the reaction with a rapid-response glass electrode, at concentrations as low as 5×10^{-6} mol dm^{-3}, and at initial pH values ranging from 6 to 8. A solution of Me_3CCl in acetone is added to a stirred vessel containing the solvolysing medium. The combined mixing plus response time is approximately-2 s. Adjustment of the initial pH is effected with dilute potassium hydroxide and hydrochloric acid, to a final chloride ion concentration of about 10^{-4} mol dm^{-3}. The

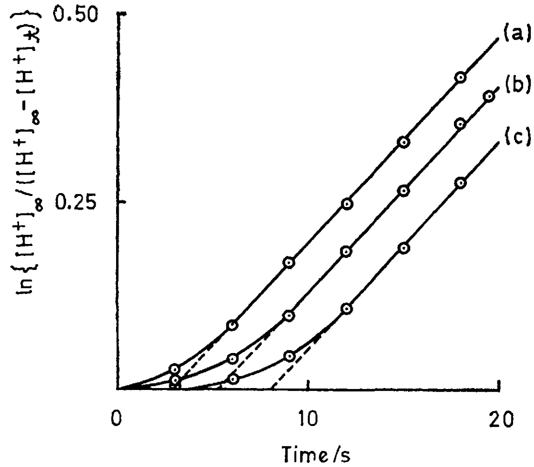

FIGURE. Variation in induction period with initial pH at constant [Me_3CCl] (= *ca.* 2×10^{-4} mol dm^{-3}). (a) Initial pH = 6·50, (b) 7·00, (c) 7·50.

amount of acetone used is too small ($\pm 5 \times 10^{-2}$ mol dm^{-3}) to affect the rate constant to a measureable extent.

At Me_3CCl concentrations of approximately 1×10^{-3} mol dm^{-3} at $pH_{init.} = 7$, the reaction follows normal first-order kinetics from the onset, with $k_r = 0{\cdot}0293$ s^{-1} at 298 K, in agreement with the literature.[1] As the concentration is reduced, at $pH_{init.} = 7$, however, the reaction exhibits an 'induction' period during which the rate of reaction is much slower. The induction period is as long as 30 s at a concentration of 2×10^{-5} mol dm^{-3}. Following the induction period, the slope of the first-order plot tends towards the accepted value of about 0·03 s^{-1}.

If the substrate concentration is maintained approximately constant at 2×10^{-4} mol dm^{-3} and the initial pH is varied, the induction period is found to increase in duration with increasing pH. The relevant results are plotted in the Figure.

At the very low concentrations at which we have been working, water exerts a buffering action and the observed hydrogen ion concentrations have to be corrected for this effect in order to determine the true rate of production of hydrogen ions by the reaction.

The results were unaffected by substitution of nitric acid for hydrochloric acid and likewise by substitution of dimethylformamide or dioxan for acetone, and also by change of reaction vessel from glass beaker to plastic beaker. The same kinetic behaviour is displayed when the hydrolysis in conductivity water is examined conductometrically at a Me_3CCl concentration of 5×10^{-5} mol dm^{-3}.

The dependence of the induction period on the initial hydrogen ion concentration implies that hydrogen ions play a definite role in the overall reaction mechanism.

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[1] E. A. Moelwyn Hughes, R. E. Robertson, and S. Sugamori, *J. Chem. Soc.*, **1965**, 1965; W. J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, 1969, **65**, 980.