Enthalpies of Activation in Solvolysis Reactions

By W. J. ALBERY* and J. S. CURRAN

(*Physical Chemistry Laboratory, South Parks Road, Oxford* OX1 3QZ)

Summary New data for the rate of solvolysis of $PhCH_2Cl$ at 0 and 4 °C fit on the same Arrhenius plot as data at higher temperatures contradicting the sharp change in activation parameters reported by Hills and Viana; the solvent isotope effect at 4 °C is normal and changes in the aqueous solvent between 0 and 4 °C produce no marked effect on the reaction rate of either $PhCH_2Cl$ or CMe_3Cl.

HILLS AND VIANA[1] have claimed to have found that at 1 atm. pressure, as the temperature is varied from 10 to 0 °C, the enthalpy of activation of reaction (1) changes sign

$$PhCH_2Cl + H_2O \rightarrow PhCH_2OH + HCl \qquad (1)$$

from a normal positive value to a negative value. They suggest that this surprising behaviour is caused by changes in the H_2O solvent in this temperature range and that their results are evidence for proton tunnelling in the transition state. They argue that this behaviour is unlikely to be a special property of benzyl chloride but may be a general one for reactions in H_2O.

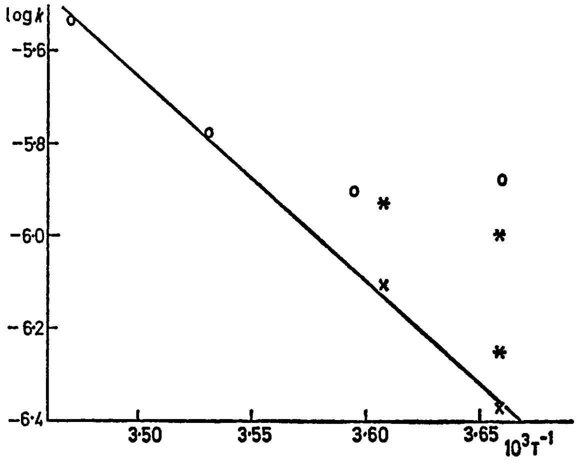

FIGURE. *Arrhenius plot for solvolysis of* $PhCH_2Cl$ *between* 0 *and* 15 °C; ○, *Hills and Viana*[1] *results*; ×, *this work*; *, *this work*, (Hg *added to the cell*).

Rate constants for the solvolysis of benzyl chloride in H_2O *at* 1 *atm.*

Temperature (°C)	Observed k (Ms⁻¹)	Calculated k from eq. (2) (Ms⁻¹)
3·98	0·77 ± 0·02	0·72
0·10	0·424 ± 0·004	0·411

We have studied the solvolysis of benzyl chloride in H_2O by measuring the change in the conductivity of the solution.[2] Data collected for at least 20 days (*ca.* 2 half lives) gave straight lines when plotted by Guggenheim's method.[3] The Figure shows a normal Arrhenius plot obtained using our results and those of Hills and Viana.[1] We can also compare our results with those of Robertson and Scott.[4] They fitted their data (obtained between 15 and 65 °C) to an equation of the form of equation (2).

$$\log k = A/T + B \log T + C \qquad (2)$$

Using their values of A, B, and C, we have calculated values of k at temperatures used by us (see Table). Considering that our points lie outside their temperature range, the agreement is satisfactory. The data in the Figure and the agreement with equation (2) suggest that the Arrhenius plot is in fact curved and that $PhCh_2Cl$ exhibits the usual negative $\Delta C_p^{\ddagger}$ right down to 0 °C.

The Figure also shows results obtained when mercury was deliberately introduced into the conductivity cell. A considerable enhancement in rate was observed; the mercury catalysed route would be likely to have a lower (and possibly even negative) enthalpy of activation compared to the ordinary route. We cannot tell whether this explains the difference between our results and those of Hills, but the results with mercury do show the difficulty of measuring very low rate constants.

The solvent isotope effect at 4 °C was obtained as equation (3).

$$k_{D_2O}/k_{H_2O} = 0.78 \pm 0.04 \qquad (3)$$

This is a normal result for a solvolysis reaction,[5] and does not indicate evidence for proton tunnelling or a drastic shift in the nature of the transition state. It is also in reasonable agreement with the value[5] of 0·82 at 41 °C for the same reaction.

Accurate results have been obtained by two independent groups[2,6] for the solvolysis of t-butyl chloride in H_2O and D_2O[7,8] in this temperature range. The results from the two groups are in agreement for k_{H_2O}, $\Delta H^{\ddagger}$, $\Delta C_P^{\ddagger}$, and k_{D_2O}/k_{H_2O}. There are no surprising changes in any of these parameters between 0 and 10 °C; the trends observed at higher temperatures continue smoothly down to 0 °C. In particular the differential method measures $\Delta H^{\ddagger}$ directly as a function of T and the results show that $\Delta H^{\ddagger}$ in fact increases as T decreases.[2] Our results for benzyl chloride, although less accurate because of the slowness of the reaction, show the same type of behaviour as those for t-butyl chloride. We therefore conclude that there are no special effects in this temperature region and that Hills and Viana's results[1] at 1 atm. and low temperature are in error.

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