Reaction of the Hydrated Electron with Polychloro-compounds

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IN many cases, the rate constants of reactions of the hydrated electron determined by the pulse radiolysis (p.r.) technique are consistent with relative rate constants determined by competition studies. It has been discovered that considerable discrepancy may occur with polychloroalkanes, especially with compounds having two or more chlorine atoms attached to the same carbon atom.

Hydrated electrons were generated photochemically[1] from iodide ions in a solution which also contained known concentrations of nitrous oxide and of the chloro-compound, RCl. Where solubility permitted, as with $CHCl_3$, the concentration of the latter was varied over a wide range. The relative rate constant, $k(e^- + RCl)/k(e^- + N_2O)$ was obtained from the reciprocal plot and the values are: 0·17 ± 0·04 ($CHCl_3$), 0·08 ± 0·02 (CCl_4), 0·06 ± 0·02 (CH_3CHCl_2), 0·14 ± 0·02 ($CH_3{\cdot}CHCl{\cdot}CH_2Cl$) and 0·09 ± 0·02 ($Cl[CH_2]_3Cl$).

The values found for the dichloropropanes are in accord with the p.r. work[2] on the propyl chlorides, since they are a little higher than the ratio $k(e^- + Pr^nCl) : k(e^- + N_2O) = 0{\cdot}08$. But the most notable feature of these results is that the values for $CHCl_3$ and CCl_4 are smaller by factors of about 20 and 40 than the corresponding ratios of absolute rate constants. The explanation would seem to be that, by the two methods, the rates of different processes are being measured.

It was suggested[2] that the capture of an electron need not be followed immediately by the dissociation of $(RCl)^-$. If the following reaction scheme is assumed:

$$e^-_{aq} + RCl \underset{-1}{\overset{1}{\rightleftharpoons}} (RCl)^- \qquad (1)$$

$$(RCl)^- \xrightarrow{2} R + Cl^- \qquad (2)$$

$$e^-_{aq} + N_2O \xrightarrow{3} N_2 + O^- \qquad (3)$$

then the quantum yield of nitrogen is given by equation (4).

$$\phi(N_2) = \phi_{e^-} \frac{k_3[N_2O]}{k_3[N_2O] + k_1\left(\dfrac{k_2}{k_{-1} + k_2}\right)[RCl]} \qquad (4)$$

Thus the relation of $\phi(N_2)$ to solute concentrations is of the same form as in the case of straight competition, but slope/intercept of the reciprocal plot is actually a measure of $k_1k_2/k_3(k_{-1} + k_2)$. If, in the p.r. studies, the equilibrium in reaction (1) is not approached within the time over which the absorption due to the electron is used in calculating the rate constant, then the value obtained should be a close approximation to k_1. Large discrepancies between the relative rate constant and the ratio of the absolute rate constants would then be expected if $k_2 \ll k_{-1}$, but if, in addition the equilibrium constant for reaction (1) were unusually low, little discrepancy might be observed since the p.r. value could then be a measure of $k_1 k_2/(k_{-1} + k_2)$.

In the above interpretation, it is assumed that the entity $(N_2O)^-$ always dissociates to give $N_2 + O^-$. Negative-ion studies do not lead one to expect a significant difference between N_2O and CCl_4 after electron capture. Curran and Fox[3] found that the onset of the O^- and the Cl^- peaks are both at about 0·0 ev.

It has been reported[4] that the relative rate constant $k(e^- + Cl_3C{\cdot}CO_2^-)/k(e^- + PhCH_2{\cdot}CO_2^-)$, determined from competition studies, increases with increase in temperature. However, the moderate agreement at 25° with the ratio of the p.r. rate constants may be fortuitous and leaves open the possibility that, for both solutes, a reaction scheme of the above type is applicable with $k_{-1} \sim$ or $> k_2$. Thus the results hardly constitute a satisfactory basis for the evaluation of an activation energy.

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