The Activation Energy of Reactions of Hydrated Electrons

By M. ANBAR and P. NETA

(The Weizmann Institute of Science and the Soreq Nuclear Research Centre, Rehovoth, Israel)

REACTIONS of hydrated electrons with a great number of organic and inorganic compounds have been investigated in the last three years.[1–9] The difference in the reactivity of different chemical species with e^{-}_{aq} has been attributed to the availability of a vacant orbital which may accommodate an additional electron on interaction with e^{-}_{aq}.[5,6,8]

$$e^{-}_{aq} + AB \rightarrow AB^{-} \rightarrow ABH \text{ or } A + B^{-}$$

The formation of AB^{-} as an intermediate could be demonstrated practically in all cases investigated.[10] The latter conclusion implies that no cleavage of chemical bonds is involved in the rate-determining step. In view of the diffuse nature of e^{-}_{aq},[11] it is not very likely that the polarization of the substrate molecule by the approaching hydrated electron is involved in the rate-determining step. Thus it must be concluded that the electron transfer from its aquated form to an orbital on the substrate molecule comprises the rate-determining step. Such an electron transfer takes place probably within $< 10^{-13}$ sec. Although many of the e^{-}_{aq} reactions were shown to be diffusion-controlled, in agreement with this assumption, the majority of reactions investigated proceed at much lower rates.[9]

It was suggested therefore that the reactions with e^{-}_{aq} which are not diffusion-controlled involve a pre-equilibrium between a reactive and a non-reactive form of the substrate molecule, where the former, which contains a localized electrophilic centre, reacts with e^{-}_{aq} at a diffusion-controlled rate.

$$AB \rightleftharpoons AB' \qquad AB' + e^{-}_{aq} \rightarrow AB^{-}$$

From the standpoint of entropy it is expected that AB′ with a localized charge should be favoured at lower temperatures. If our assumptions are correct the activation energy involved in all e^{-}_{aq} reactions should be that of a diffusion-controlled process, after correcting for the small and negative temperature effect on the pre-equilibrium involved.

To test these assumptions we have determined the relative rates of a fast and a slow reaction of e^{-}_{aq} with two organic compounds at different temperatures and thus measured the difference between their energies of activation.

Trichloroacetate ions [$k(CCl_3CO_2^{-} + e^{-}_{aq}) = 8{\cdot}5 \times 10^{9}$ mole^{-1} l. sec.$^{-1}$][6] and phenylacetate ions [$k(PhCH_2CO_2^{-} + e^{-}_{aq}) = 1{\cdot}4 \times 10^{7}$ mole^{-1} l. sec.$^{-1}$][7] were irradiated in neutral deaerated aqueous solutions (pH = 7–8) by ^{60}Co-γ-rays (dose rate = 6600 r/min.) at 0°, 25° and 90°C. The yield of chloride ions formed was determined coulometrically. Non-irradiated identical samples were analyzed in parallel, after identical time intervals, to correct for thermal dechlorination.

---

[1] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Amer. Chem.Soc.*, 1963, **85**, 1375.

[2] S. Gordon, E. J. Hart, and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 1262.

[3] J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, 1964, **68**, 1524.

[4] J. H. Baxendale, E. M. Fielden, C. Capellos, J. M. Francis, J. V. Davies, M. Ebert, C. W. Gilbert, J. P. Keene, E. J. Land, A. J. Swallow, and J. M. Nosworthy, *Nature*, 1964, **201**, 468.

[5] M. Anbar and E. J. Hart, *J. Amer. Chem. Soc.*, 1964, **86**, 5633.

[6] M. Anbar and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 271.

[7] A. Szutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 289.

[8] M. Anbar and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 973.

[9] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1965, **16**, 227.

[10] M. Anbar, "Reactions of Hydrated Electrons," "Advances in Chemistry" Series, American Chemical Society, 1965 (in press).

[11] J. Jortner, *Radiation Res.*, 1964, Suppl. **4**, 24.

Trichloroacetate ions 5×10^{-4}—10^{-3}M were irradiated in the presence of 10^{-2} M-phenylacetate. Under these conditions all OH and H radicals were completely scavenged by the aromatic compound[9] and $G(\mathrm{Cl}^-) = G(e^-_{aq}) = 2{\cdot}8 \pm 0{\cdot}1$ was obtained. The ratio $\mathrm{PhCH_2CO_2^-/CCl_3CO_2^-}$ was then increased in order to determine the relative reactivity of the two electron scavengers. At 25° $R = k(e^-_{aq} + \mathrm{CCl_3CO_2^-})/k(e^-_{aq} + \mathrm{PhCH_2CO_2^-}) = 950 \pm 50$ was obtained, in satisfactory agreement with the value of 610 ± 200 calculated from the values of k determined by pulse radiolysis.[6,7] At 0° and 90°, values of $R = 750 \pm 30$ and 1570 ± 20 respectively were obtained.

From the experimental results it is evident that the relative reactivity of $\mathrm{PhCH_2CO_2^-}$, which is the less reactive substrate, decreases with temperature. A difference of $1{\cdot}6 \pm 0{\cdot}1$ Kcal./mole between the activation energies of the two scavengers was calculated. The change in reactivity with temperature cannot be due to a change in the ionic strength of the medium as both reactants are equally negatively charged. Our results mean that the activation energy of the $(e^-_{aq} + \mathrm{CCl_3CO_2^-}$ reaction is higher by 1·6 Kcal./mol. than that of $\mathrm{PhCH_2CO_2^-}$. The $(\mathrm{CCl_3CO_2^-} + e^-_{aq})$ reaction, the rate of which is very close to a diffusion-controlled rate ($8{\cdot}5 \times 10^9$ mole^{-1} l. sec.$^{-1}$), is expected to have an activation energy of about 3·5 Kcal./mole. This value of ΔE, which has been observed for the $(\mathrm{H_3O^+} + e^-_{aq})$ reaction,[3] is characteristic for diffusion-controlled processes in aqueous solutions.[12] An increase of ΔE above this value would imply a collision frequency higher than the theoretical Z. As it is unlikely that the $\mathrm{CCl_3CO_2^-}$ reaction has an activation energy higher than 3·5 Kcal./mole, it must be concluded that ΔE of the $\mathrm{PhCH_2CO_2^-}$ reaction is of the order of 2 Kcal./mole, a value which cannot be explained unless a pre-equilibrium with a negative temperature coefficient is involved. In the absence of a pre-equilibrium a minimum value of 6·5 Kcal./mole would be expected for this reaction. Our assumptions on the nature of the e^-_{aq} reactions are thus corroborated.

Following this argument it may be implied that the ratio between the specific rate of a given slow reaction with e^-_{aq} and the diffusion-controlled rate is a direct measure of $K = \mathrm{AB'/AB}$. In other words the reactivity of a given substrate toward e^-_{aq} is a quantitative measure of electronic configurations which involve vacant electron orbitals. This has obviously far-reaching implications for the quantitative evaluation of chemical reactivity. The values of e^-_{aq} reaction rates should thus not be considered merely as a prerequisite for the understanding of radiolytic processes in aqueous solutions but rather as crucial chemical information.

(*Received, June 23rd,* 1965; *Com.* 390.)

---

[12] M. Eigen and L. de Maeyer, *Naturwiss*, 1955, **42**, 413.