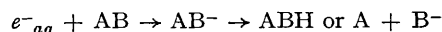


The Activation Energy of Reactions of Hydrated Electrons

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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}



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.



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 [$k(\text{CCl}_3\text{CO}_2^- + e^-_{aq}) = 8.5 \times 10^9 \text{ mole}^{-1} \text{ l. sec.}^{-1}$]⁶ and phenylacetate ions [$k(\text{PhCH}_2\text{CO}_2^- + e^-_{aq}) = 1.4 \times 10^7 \text{ mole}^{-1} \text{ l. sec.}^{-1}$]⁷ were irradiated in neutral deaerated aqueous solutions (pH = 7-8) by ⁶⁰Co- 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.

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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 compound⁹ and $G(\text{Cl}^-) = G(e^-_{aq}) = 2.8 \pm 0.1$ was obtained. The ratio $\text{PhCH}_2\text{CO}_2^-/\text{CCl}_3\text{CO}_2^-$ was then increased in order to determine the relative reactivity of the two electron scavengers. At 25° $R = k(e^-_{aq} + \text{CCl}_3\text{CO}_2^-)/k(e^-_{aq} + \text{PhCH}_2\text{CO}_2^-) = 950 \pm 50$ 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 $\text{PhCH}_2\text{CO}_2^-$, which is the less reactive substrate, decreases with temperature. A difference of 1.6 ± 0.1 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 $(e^-_{aq} + \text{CCl}_3\text{CO}_2^-)$ reaction is higher by 1.6 Kcal./mol. than that of $\text{PhCH}_2\text{CO}_2^-$. The $(\text{CCl}_3\text{CO}_2^- + e^-_{aq})$ reaction, the rate of which is very close to a diffusion-controlled rate (8.5×10^9 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 $(\text{H}_3\text{O}^+ + e^-_{aq})$ 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 $\text{CCl}_3\text{CO}_2^-$ reaction has an activation energy higher than 3.5 Kcal./mole, it must be concluded that ΔE of the $\text{PhCH}_2\text{CO}_2^-$ 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 $K = \text{AB}'/\text{AB}$. 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.

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