viously[8,10] that the twisted form would involve a decoupling of the π electrons and that consequently process 2 would require an activation energy of the order of the barrier height in ethylene, 61 kcal/mole.[13] However, an analysis of the symmetry properties of the two twisted molecules reveals that one deals here with two entirely different cases. In twisted ethylene, as in the planar molecule, the $2p\pi$ orbitals of the carbons do not mix with the orbitals of σ type. When the twist angle is 90°, the π bonding and the π antibonding molecular orbitals become degenerate. In diimide, on the contrary, owing to the different symmetry of the molecule, this degeneracy does not appear. The C_2 point group, to which the twisted molecule belongs, enables the mixing of the $2p\pi$ nitrogen orbitals with the 2s and $2p\sigma$ orbitals. The destabilization due to the decrease in π overlap is compensated to a certain extent by the appearance of some σ bonding in the molecular orbital which describes the π bond in the planar molecule.

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Hydrated Electron Reactions in View of Their Temperature Dependence

Sir:

The rates of reaction of hydrated electrons with hundreds of reactants, organic and inorganic, have been determined,[1,2] and it has been shown that the reactivity of e_{aq}^- toward a series of homologous reactants may be correlated with the electron deficiency of a functional reactive group.[1] It is obvious that any deeper understanding of the nature of e_{aq}^- reactivity requires information on the energy and entropy of activation of these reactions.

The energy of activation of e_{aq}^- reactions has been measured in a limited number of cases;[3-5] moreover, some of the values published are open to criticism. For the $e_{aq}^- + H_3O^+$ reaction $\Delta E = 3.2$ kcal/mole was determined[3] and a comparable value of 3.8 kcal/mole was obtained by another group of investigators.[5] $\Delta E = 2.0$ kcal/mole was estimated[4] for the $e_{aq}^- + C_6H_5CH_2COO^-$ reaction, based on the competition with CCl_3COO^-. This result is most probably erroneous in view of the complications involved in reactions of e_{aq}^- with polyhalo aliphatic compounds.[6] Baxendale, *et al.*,[5] have found $\Delta E = 4.2$ kcal/mole for the $e_{aq}^- + Co(NH_3)_6^{+3}$ reaction and $\Delta E = 5.7$ and 7.7 kcal/mole for the reactions of e_{aq}^- with Co^{+2} and Mn^{+2}, respectively.

We have measured the temperature dependence of a number of reactions of e_{aq}^- with reactants of different chemical nature, the reactivity of which ranges from 3×10^5 to 6×10^{10} M^{-1} sec^{-1}. The relative rate constants of the different reactants were determined by competition kinetics *vs.* nitrate ions[7] or *p*-bromophenol (PBP). It has been shown that *p*-bromophenol undergoes debromination by e_{aq}^- and by H atoms. In the presence of 0.1 *M* 2-propanol (added as a H-atom scavenger) $G(Br^-) = 2.6 \pm 0.2$ is obtained in deaerated solutions for doses up to 3.7×10^8 ev g^{-1} (Co^{60} γ rays, dose rate 3.7×10^{17} ev^{-1} g^{-1} min^{-1}). The specific rate constants at 20° were calculated from values of $k_{e_{aq}^- + NO_3^-} = 1.1 \times 10^{10}$ M^{-1} sec^{-1},[3] and $k_{e_{aq} + PBP} = 1.2 \times 10^{10}$ M^{-1} sec^{-1}. From the relative rates measured at 20, 45, and 70°, the difference between the activation energies of the reactants and the reference compounds, $\Delta(\Delta E)$, was calculated. The experimental error amounted to 0.5 kcal/mole.

$\Delta(\Delta E)$ of $e_{aq}^- + H_3O^+$ and $e_{aq}^- + NO_3^-$ was found to be 0.4 ± 0.4 kcal/mole. The corresponding $\Delta(\Delta E)$ of $e_{aq}^- + H_3O^+$ and $e_{aq}^- +$ PBP was 0.0 ± 0.4 kcal/mole. It was concluded that the activation energies of these three reactions are equal within the experimental error. These and other $\Delta(\Delta E)$ determined in this study are summarized in Table I. The values of the specific rate constants obtained agree within the experimental error with the rate constants obtained directly by pulse kinetics. The energies of activation of the different reactions studied, derived from the experimental $\Delta(\Delta E)$ and the measured ΔE of the $e_{aq}^- + H^+$ reaction,[3] range between 3.0 and 3.9 kcal/mole. The specific rates of these reactions range over *five* orders of magnitude, and no correlation whatsoever could be found between ΔE and $k_{e_{aq}^- + X}$. It could be tentatively stated therefore that $e_{aq}^- + X \rightarrow X^-$ reactions have an over-all activation energy of 3.5 ± 0.4 kcal/mole. This value is equal to the activation energy of diffusion in aqueous solution,[8,9] *i.e.*, 3.5 kcal/mole at 45°.[9] This means that e_{aq}^- reactions, irrespective of their specific rates, take place without any energy of activation in excess of the energetic requirements of diffusion. The entropies of activation, $\Delta S^{\ddagger}$, are listed in the last column of Table I.

The statement that all $e_{aq}^- + X \rightarrow X^-$ reactions have $\Delta E \simeq 3.5$ kcal/mole does not exclude the possibility of finding experimental $\Delta E \neq 3.5$ kcal/mole for reactions of e_{aq}^- with certain reactants. This may occur if the $e_{aq}^- + X$ reaction is preceded by a preequilibrium $Y \rightleftarrows X$ where $k_{e_{aq}^- + X}$ differs significantly from $k_{e_{aq}^- + Y}$. Acid–base preequilibria are the best

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Table I. Activation Energies of Reactions of Hydrated Electrons

		Relative to e_{aq}^- + NO_3^- (20°)		Relative to e_{aq}^- + PBP (20°)					
Reactant (X)	pH	$k_{e_{aq}^-+X}$, M^{-1} sec^{-1}	$\Delta(\Delta E)_{NO_3^-}$, kcal/mole	$k_{e_{aq}^-+X}$, M^{-1} sec^{-1}	$\Delta(\Delta E)_{PBP}$, kcal/mole	$\Delta(\Delta E)_{av}$, kcal/mole	$\Delta E_{e_{aq}^-+X}$, kcal/mole	$\Delta S^{\ddagger}$,[b] cal $mole^{-1}$ deg^{-1}	Specific rate constant (lit.)
H_3O^+	3	4.0×10^{10}	+0.4	2.5×10^{10}	0.0	+0.2	3.2[a]	−2.2	2.36×10^{10}[c]
NO_2^-	5.5–6	..	...	3.4×10^9	0.0	0.0	3.4	−6.2	$3.5–8.1 \times 10^9$,[d]
$[Co(NH_3)_5H_2O]^{+3}$	5.5–6	5.8×10^{10}	0.0	4.6×10^{10}	+0.5	+0.2	3.2	−0.7	$6.1–7.6 \times 10^{10}$[e]
NO_3^-	5.5–6	..	...	1.1×10^{10}	−0.5	−0.5	3.9	−3.85	$8.2–11 \times 10^9$[f]
2-Aminopyrimidine	5.5–6	1.4×10^{10}	−0.5	1.3×10^{10}	−0.2	−0.3	3.7	−3.4	..
p-Bromophenol	5.5–6	1.2×10^{10}	+0.4	..	...	+0.4	3.0	−3.7	....
Cyclohexanone	5.5–6	8×10^9	−0.1	7.8×10^9	−0.4	−0.2	3.6	−4.5	....
Phthalate ion	7	4.5×10^9	0.0	4.6×10^9	+0.5	+0.2	3.2	−5.7	6.2×10^9[g]
Benzoate ion	7	3.6×10^9	−0.4	2.7×10^9	0.0	−0.2	3.6	−6.3	3.1×10^9[g]
Pyridine	5.5–6	3×10^9	−0.5	4.6×10^9	−0.5	−0.5	3.9	−6.0	$1–3.7 \times 10^9$[h]
Benzenesulfonate ion	7	1.15×10^9	−0.6	8×10^8	+0.4	−0.1	3.5	−8.6	4×10^9[i]
Chloroacetate ion	7	1.1×10^9	−0.4	..	...	−0.4	3.8	−8.5	$1.2–3.8 \times 10^9$[j]
Benzyl alcohol	5.5–6	1.9×10^8	−0.1	1.8×10^8	−0.5	−0.3	3.7	−12.0	1.3×10^8[i]
Phenylalanine	7	1.6×10^8	−0.4	1.35×10^8	+0.3	0.0	3.4	−12.3	$8.8–15 \times 10^7$[k]
Acetamide	5.5–6	4×10^7	−0.2	3.0×10^7	0.0	−0.1	3.5	−15.1	1.7×10^7[l]
Formamide	5.5–6	3.8×10^7	+0.2	..	...	+0.2	3.2	−15.25	4.2×10^7[l]
Phenyl acetate ion	7	3.1×10^7	+0.3	3.3×10^7	−0.4	0.0	3.4	−15.6	$1.4–5.1 \times 10^7$[g]
Urea	5.5–6	2.7×10^5	0.0	..	...	0.0	3.4	−25.1	3×10^5[l]

$\Delta(\Delta E)_{NO_3^-} = \Delta E_X - \Delta E_{NO_3^-}$ $\Delta(\Delta E)_{PBP} = \Delta E_X - \Delta E_{PBP}$

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examples for such cases. The higher values of ΔE reported for e_{aq}^- + Mn^{+2} and e_{aq}^- + Co^{+2} reactions in neutral solution are probably due to preequilibria between aquo complexes at different degrees of hydrolysis. It has been shown[10] that the degree of hydrolysis has a significant effect on the rate of reaction of e_{aq}^- with transition metal ions. It remains to be demonstrated that these ions have a lower ΔE in acid solution. Another type of e_{aq}^- reaction which might have $\Delta E > 3.5$ kcal/mole are those which proceed by an atom-transfer mechanism,[11] $e_{aq}^- + X \rightarrow OH^- + HX$. $e_{aq}^- + H_2O$ is the most likely process to take place by this mechanism.

It has been suggested that e_{aq} reactions involve the incorporation of an electron into the orbitals of the substrate;[1] thus their rate depends primarily on the electron distribution of the latter. This distribution, which might be changed by electron excitation, is not expected to be affected by temperature up to 100°. What should therefore determine the rate of e_{aq}^- reactions is the probability of finding an electron vacancy on the substrate molecule; this probability which is represented by the entropy of activation is temperature independent in our range of temperatures. Our findings that $\Delta E^{\ddagger}$ for all $e_{aq}^- + X \rightarrow X^-$ reactions is equal to the energy of activation of diffusion in water corroborated these conclusions.

Slow $e_{aq}^- + X \rightarrow X^-$ reactions take place with polyatomic reactants only. These reactions involve a large number of collisions with substrate molecules having an unfavorable electronic configuration. An interaction of e_{aq}^- with a reactant molecule in a favorable electronic configuration results in the formation of an activated complex. Once an activated complex has been formed the electron transfer in it is expected to occur within $<10^{-14}$ sec according to the Frank–Condon principle.

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Conformational Aspects of Polypeptide Structure. XX. Helical Poly-N-methyl-L-alanine. Experimental Results[1]

Sir:

Considerable effort has been expended on the conformational analysis of poly-L-proline in solution.[2-9] Hydrogen bonding is impossible because the amide nitrogens are alkylated. Nevertheless, poly-L-proline can exist in two *ca.* threefold helical forms, poly-L-proline

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