

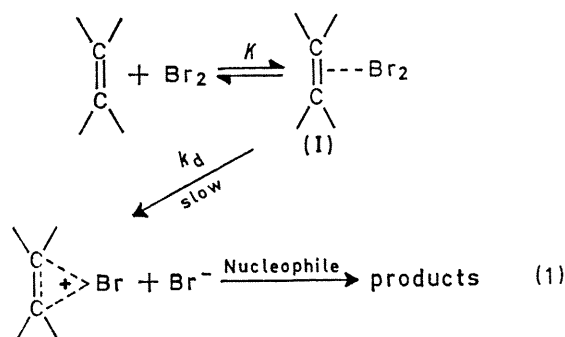
Reactivity of Ethylenic Compounds: Bromination Reaction. Solvation and Charge Development in the Transition State of $Ad_E C1$ Mechanism in Hydroxylic Solvents

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Summary An analysis of the secondary solvent isotope effect and of the solvent effect in methanol-water mixtures on the rate of bromination of pent-1-ene indicates that the transition state for this reaction is highly polarized and essentially solvated through hydrogen bonding.

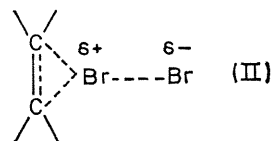
A SPECTROKINETIC analysis of the bromination of alkenes has led us to suggest an $Ad_E C1$ mechanism for this reaction in hydroxylic solvents (reaction 1).¹



In this reaction, the slow step involves the unimolecular ionisation, k_d , of the intermediate charge transfer complex (I). The observation of a large solvent effect, correlated by the equation $\log k/k_0 = 1.16Y^\dagger$ was shown to be consistent with a highly polarized transition state (II).

In order to confirm this hypothesis and to clarify the role of the solvent in the stabilization of the transition state, we

have analysed the kinetic behaviour of a typical alkene, regarding its relation to (i) a secondary solvent isotope effect, to determine the importance of hydrogen bonding in the solvation of the transition state; (ii) a kinetic solvent effect, a comparison of which with the thermodynamic effect of these solvents on the free energy of solvation of a bromide ion Br^- may allow us to specify the degree of charge development in the transition state.

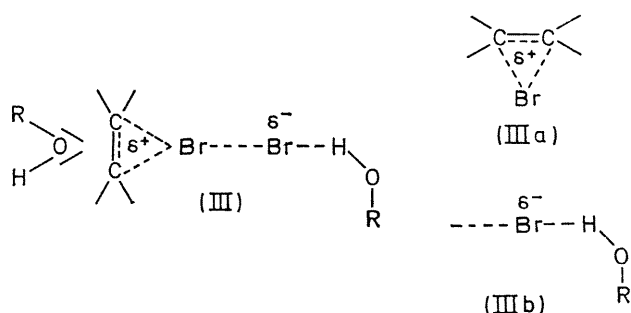


The solvent isotope effect on the rate of bromination of pent-1-ene in methanol (MeOH) and deuteriated methanol (MeOD) has been determined. In each solvent, the rate constant $k(Br_2)$ associated with the addition of a bromine molecule to an alkene molecule has been obtained by a series of experiments using different concentrations of bromide ion. The results obtained at 25 °C, $k(Br_2, MeOH) = (0.39 \pm 0.04) \times 10^3$, $k(Br_2, MeOD) = (0.28 \pm 0.02) \times 10^3$ l mol⁻¹s⁻¹, show a secondary solvent kinetic isotope effect, $k(Br_2, MeOH)/k(Br_2, MeOD) = 1.40 \pm 0.20$.

We attribute this exceptionally high value, the highest so far reported in the literature, to the marked importance of hydrogen bonds in the solvation of the transition state, for which we suggest structure (III). Such a high secondary solvent isotope effect, in solvolysis reactions has been interpreted by Swain and Pègues² and by Bunton and Shiner³ as being due to an "ion-solvent" interaction between

* Y is defined as the measure of the ionizing power of the solvent; A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **1956**, **78**, 2770.

a highly polarized transition state and the solvent molecules organized as shown in (III). As a consequence of the localisation of the charge δ^- on the departing bromine atom and of the distribution of the charge δ^+ on the three centres C,C,Br [see (IIIa)], the major contribution to solvation should be assigned to hydrogen bonding between the anionic part of the transition state and the solvent [see (IIIb)].



Feakins⁴ has determined the free energies of solvation of potassium bromide in methanol-water, and has expressed them as free energies of transfer, $\Delta G^0(\text{KBr})$. These values represent a measure of the solvation energy of a bromide ion in these hydroxylic solvents. We have compared this thermodynamic effect to the kinetic effect of these solvents on the free energy of activation $\Delta G^\ddagger(\text{Br}_2)$ for the bromination of pent-1-ene.

As shown in the Figure, the function $\Delta G^\ddagger(\text{Br}_2) = f[\Delta G^0(\text{KBr})]$ yields an acceptable linear correlation, correspondin

† R is the correlation coefficient.

¹ F. Garnier and J. E. Dubois, *Bull. Soc. chim. France*, 1968, 3797.

² C. G. Swain and E. E. Pègues, *J. Amer. Chem. Soc.*, 1958, **80**, 812.

³ C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 3207.

⁴ D. Feakins, 'Physicochemical Processes in Mixed Aqueous Solvents,' Heinemann, London, 1967, p. 71.

to the equation $\Delta G^\ddagger(\text{Br}_2) = 0.86 \Delta G^0(\text{KBr}) + 12.3$ ($R = 0.997$ †).

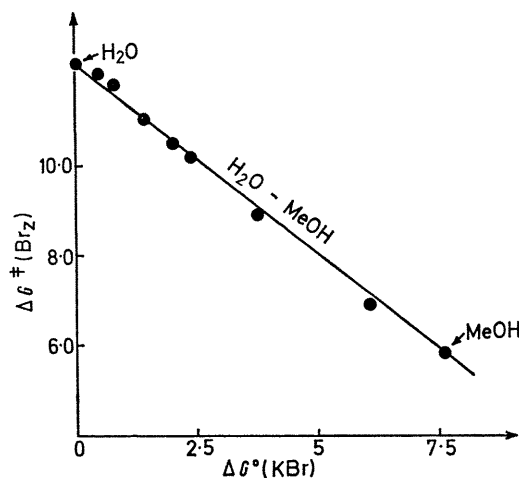


FIGURE. Linear relationship between free energy of activation $\Delta G^\ddagger(\text{Br}_2)$ and free energy of transfer in methanol-water mixtures.

The calculated slope, 0.86, indicates that the charge development in the transition state is similar to that on a bromide ion. This result leads us to conclude that the heterolytic fission of the Br---Br bond is very advanced, and that the structure of the transition state is very similar to that of the bromonium ion produced by the rate-determining step.

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