The Role of Transitory Charge-transfer Complexes in the Bromination of Olefins

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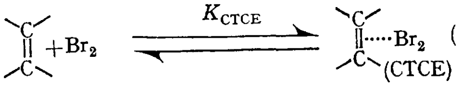
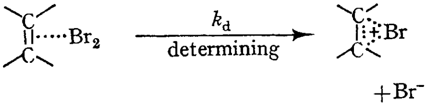
BY the use of spectroscopy we have demonstrated the rapid equilibrium formation of transitory 1 : 1 charge transfer complexes (or CTCE) between bromine and olefins during the bromination of the latter.[1] The physicochemical properties of these complexes agree with the role of kinetic intermediate shown in equation (1),[2] as often postulated in electrophilic addition reactions.[3] We now discuss the form of the rate-determining step.

Starting from the complex, bromination requires the rupture of the Br–Br bond and the nucleophilic attack by an anion N^- or a hydroxylic solvent molecule ROH. These two processes may be either simultaneous or consecutive and correspond to two distinct mechanisms which differ in the molecularity of the rate-determining step:

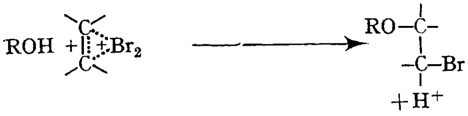
Ad_E C 1 : electrophilic addition involving a CTCE which ionises in a unimolecular rate-determining step



(1)

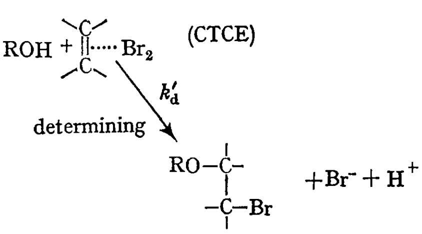


(2)



(3)

Ad_E C 2 : electrophilic addition involving a CTCE, which reacts with a nucleophile in a bimolecular rate-determining step: equation (1), followed by (2′)



(2′)

In order to differentiate between these two mechanisms, we shall consider solvent effects on reactivity. By the use of a spectrokinetic apparatus described elsewhere,[1] we have determined, for pent-1-ene in 9 solvents, the overall rate constant, $k_{\mathrm{Br_2(obs)}} = k_{\mathrm{CTCE}} \times k'_d$ which corresponds to zero bromide-ion concentration.[4] As shown on the Table, $k_{\mathrm{Br_2(obs)}}$ varies by a factor of 2×10^7.

The equilibrium constant K_{CTCE}, although unknown, should be almost insensitive to solvent effects.[5] Hence the large solvent effect observed on $k_{\mathrm{Br_2(obs)}}$ should essentially represent the solvent sensitivity of k_d of k'_d. In fact these steps (2) and (2′) are very distinct: the transition state involved in the rate-determining step (2), an S_N1-like unimolecular ionisation, is less bulky and more polarised and therefore more sensitive to solvation than the corresponding S_N2-like transition state in the rate-determining step (2′). The solvent effect on reactivity is expected to be very different for the two mechanisms, and assuming an analogy

TABLE

Rate constants [$k_{\mathrm{Br_2(obs)}}$ *in* l. mole^{-1} min.$^{-1}$] *for pent-1-ene in various solvents at* 25°

Solvent	log $k_{\mathrm{Br_2(obs)}}$	Δlog $k_{\mathrm{Br_2(obs)}}$	Y‡
H_2O	9·15	0·15	3·493
MeOH	4·36	0·05	−1·090
MeOH-H_2O (7 : 3)†	6·77	0·05	0·961
MeOH-H_2O (1 : 1)†	7·74	0·05	1·972
EtOH	2·89	0·10	−2·033
Pr^{i}OH	2·15	0·10	−2·73
Bu^{t}OH	1·90	0·10	−3·26
AcOH	2·84	0·10	−1·675
HCO_2H	7·80	0·15	2·054

† Volume ratio before mixing; ‡ A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770.

with S_N1 and S_N2 reactions one would expect a linear relationship between log k_d or log k_d' and the ionising power Y of the solvent, with a slope near unity for the mechanism Ad_E C 1 and only 0·3 for the mechanism Ad_E C 2.[6]

Using linear regression program on a computer, we determined the form of the function log $k_{Br_2(obs)}$ = f (Y):

$$\log k_{Br_2(obs)} = 1{\cdot}16\ Y + 5{\cdot}42$$

The very satisfactory linearity, $R = 0{\cdot}993$, and the value obtained for the slope, $m = 1{\cdot}16$, argue strikingly for the unimolecular mechanism of ionisation Ad_E C 1.

Obviously this mechanism represents only a limiting case in the bromination of olefins: the interaction of a bromine molecule and an olefin molecule. Due to the great complexity of this reaction, we intentionally isolate this principal reaction pathway in order to determine its profile. By taking into account specific interactions with the medium, we now hope to be able to elucidate the reaction scheme in more detail.

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[2] J. E. Dubois and F. Garnier, *Tetrahedron Letters*, 1966, 3047.
[3] R. H. Boyd, R. W. Taft, A. P. Wolf, and D. R. Christman, *J. Amer. Chem. Soc.*, 1960, **82**, 4729.
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[6] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, 1964, p. 419.