Formation and Stabilization of Intermediate Ion–Neutral Complexes in Radical Cation Dissociation Reactions

Steen Hammerum

Department of General and Organic Chemistry, University of Copenhagen, The H.C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

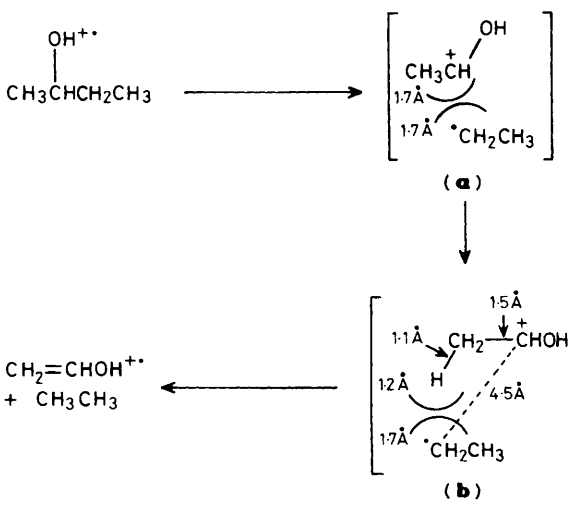
Intermediate ion–neutral complexes arising when radical cations dissociate will be only moderately stabilized by polarization forces, inasmuch as the distance between the components of the complex cannot be less than the sum of their van der Waals radii; reactions *via* such complexes are primarily important for systems where the critical energy for simple cleavage is low.

Suggestions that unimolecular dissociation reactions of isolated radical cations could have discrete intermediates (ion–neutral complexes) were originally advanced by Morton,[1] by Longevialle and Botter,[2] and by Bowen and Williams,[3] following work on even-electron systems by the last-named authors.[4] It has been suggested[1–5] that a variety of intriguing reactions can be rationalized in terms of models that assume the intermediacy of ion–neutral complexes, wherein the incipient fragments are bonded predominantly by electrostatic forces (ion-dipole or ion-induced dipole interactions), rather than by valence forces. Models of this nature are being used increasingly to describe the detailed course of the low-energy fragmentation of radical cations, but *a priori* criteria to indicate when a reaction would be complex-mediated have not been suggested, nor have the models provided independently testable predictions.

The dearth of compelling experimental evidence to verify the presence of stable complexes in the course of radical cation dissociation is seemingly related to uncertainty concerning the properties expected of intermediate ion–neutral complexes, in particular with regard to the lifetime and the energetics of formation and stabilization. Some of these problems have been addressed by Longevialle and Botter,[2] whose results strongly suggest the intermediacy of such complexes for certain reactions in steroid systems. The evidence advanced for simple radical cations has been predominantly inferential, some apparently successful rationalizations notwithstanding. Similar problems concerning criteria and verification exist with regard to intermediate ion–neutral complexes suggested for reactions of even-electron ions. However, the stabilization of ion–neutral complexes relative to the separated fragments can be assessed on the assumption that their dimensions are bounded by the van der Waals radii of the components. With this simple addition to the usual description of an ion–neutral complex it becomes possible to delineate the conditions for reaction of saturated radical cations *via* intermediate complexes. Experimental evidence confirming the intermediacy of complexes in the dissociation reactions of alcohol and ether radical cations is presented in the accompanying communication.[6]

An ion–neutral complex existing as an intermediate in a radical cation dissociation reaction consists of an intimate pair of the incipient fragments, bonded by electrostatic forces arising from ion–dipole or ion–induced dipole interactions rather than by covalent bonds. The minimum inter-species distance is dictated by the van der Waals radii of the components of the complex. The complex must exist as a non-dissociating entity considerably longer than required for physical reorganization and chemical reaction to take place.

The physical separation of the two components of a complex distinguishes complex-mediated processes from transformations within covalently bonded ions. Simple addition of the van der Waals radii[7,8] shows that the minimum inter-



(1)

$$\begin{tikzcd}
(CH_3)_3CCH_2OH^{+\bullet} \arrow[r] & {[(CH_3)_3C^{+} \quad {}^{\bullet}CH_2OH]} \arrow[d, dash] \\
C_4H_8^{+\bullet} + CH_3OH & {} \arrow[l]
\end{tikzcd} \tag{2}$$

species distance is 3.4 Å for a complex intermediate formed by attempted dissociation of an aliphatic radical cation such as that of butan-2-ol [equation (1)]; this probably constitutes a lower limit in the general case also. If reaction between the two species (at its simplest, hydrogen transfer) is to occur, then the separation needs to be greater, to allow the necessary reorganization. Following Benson,[7] we can calculate that the distance between the (formal) charge and the alkyl radical carbon must be more than 4.5 Å for hydrogen abstraction to be possible [(**b**) in equation (1)], if we assume a C–H–C angle of over 150°. The ion-induced dipole interaction is at this distance less than 2 kcal mol^{-1} for the butan-2-ol example.† In general, small ion–neutral complexes capable of inter-species reaction will be stabilized by polarization forces of less than 3—4 kcal mol^{-1} relative to the separated fragments. The stabilization of reacting complexes with a methyl (or methane) component will only be around 1 kcal mol^{-1}; hence such complexes should rarely intervene. This is presumably the reason why loss of methane from low-energy aliphatic radical cations occurs much less frequently than does loss of other alkanes.[10] The electrostatic interactions in a complex can be somewhat stronger if the neutral species has an appreciable dipole moment. The interaction between the hydroxymethyl radical and the *t*-butyl cation [equation (2)] at a distance of 4.5 Å is estimated to be about 6 kcal mol^{-1}.‡

The classical expressions[9] for ion–dipole and polarization interactions require that the charge can be treated as a point charge; the polarization forces in particular decrease noticeably if the charge in the ionic fragment is significantly delocalized. This will influence the actual stabilization of intermediate ion–neutral complexes and could, in turn, give rise to differences amongst complex-mediated reactions of various classes of compound, since the charge distribution in the initial ionic fragments as well as in those formed by inter-species reaction can vary substantially. The orientation of the neutral species with respect to the charge centre may influence the reactions within complexes considerably, since the optimum orientation for stabilization may be quite different from that required for reaction.

The moderate stabilization of intermediate complexes relative to the separated fragments implies that reorganization and chemical reaction within complexes will compete successfully with direct dissociation only when the reactant molecular ions have energies close to threshold. Intermediate complexes are thus unlikely to be important in fast reactions, unless the critical energy for the initial cleavage is very low. Dissociation of radical cations may in that case yield complexes that are more stable than the initial molecular ions.[6] The moderate stabilization also implies that reactions *via* complexes will be less likely to occur when the critical energy for simple cleavage is high, owing to the substantial excess energy required for reaction at the necessary rate.

The electrostatic interactions between the incipient fragments will influence the course of reaction mainly when the critical energy for simple cleavage is low. Expulsion of alkyl radicals from aliphatic radical cations often requires only *ca.* 10—15 kcal mol^{-1}, considerably less than the energy released if the cleavage products were brought from infinity to, say, a distance of 2 Å. This indicates that electrostatic interactions between the incipient fragments contribute significantly to the bonding in the intact molecular ion also, and that these interactions will be important in particular when the valence forces between the fragments diminish as the molecular ion approaches dissociation. In such systems it is possible that the intermediacy of an ion–molecule complex will open additional reaction pathways and influence the rates of reaction. It is suggested that ion–radical complexes capable of inter-species reaction can in general be expected close to threshold for simple cleavage reactions if the critical energy is less than the electrostatic attraction between the incipient fragments at a distance of 2.5—3 Å. This distance is not the inter-species separation in the ion–neutral complex, but is an estimate of the distance at which the polarization energy (or ion–dipole forces) must account for a major proportion of the bonding if complex-mediated reactions are to intervene.

Similar considerations of dimensions and energetics apply when the intermediacy of ion–neutral complexes is considered for reactions of even-electron ions and for reactions of rearranged radical cations. Stable complexes will rarely intervene after passage of energy barriers higher than the heat of formation of the final products.

Advice and constructive criticism from Drs. Aa. E. Hansen and T. Vulpius is gratefully acknowledged.

Received, 1st February 1988; Com. 8/00388B

References

1 T. H. Morton, *J. Am. Chem. Soc.*, 1980, **102**, 1596; T. H. Morton, *Tetrahedron*, 1982, **38**, 3195.

2 P. Longevialle and R. Botter, *J. Chem. Soc., Chem. Commun.*, 1980, 823; P. Longevialle and R. Botter, *Org. Mass Spectrom.*, 1983, **18**, 1.

3 R. D. Bowen and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 836.

4 R. D. Bowen, B. J. Stapleton, and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1978, 24; R. D. Bowen and D. H. Williams, *Int. J. Mass Spectrom. Ion Phys.*, 1979, **29**, 47; D. H. Williams, *Philos. Trans. Roy. Soc. London, A*, 1979, **293**, 117; R. D. Bowen and D. H. Williams, *J. Am. Chem. Soc.*, 1980, **102**, 2752.

5 D. G. Hall and T. H. Morton, *J. Am. Chem. Soc.*, 1980, **102**, 5686; H. W. Biermann, W. P. Freeman, and T. H. Morton, *ibid.*, 1982, **104**, 2307; J. F. Wendelboe, R. D. Bowen, and D. H. Williams, *ibid.*, 1981, **103**, 2333; *J. Chem. Soc., Perkin Trans. 2*, 1981, 958; P. Longevialle, *Org. Mass Spectrom.*, 1985, **20**, 644; R. D. Bowen and A. Maccoll, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1005; C. E. Hudson and D. J. McAdoo, *Int. J. Mass Spectrom. Ion Processes*, 1984, **59**, 325; M. Masur, A. Sprafke, and H.-F. Grützmacher, *Org. Mass Spectrom.*, 1987, **22**, 307; D. J. McAdoo and C. E. Hudson, *ibid.*, p. 615; J.-D. Shao, T. Baer, J. C. Morrow, and M. L. Fraser-Monteiro, *J. Chem. Phys.*, 1987, **87**, 5242; G. Bouchoux, Y. Hoppilliard, and P. Longevialle, *Rapid Comm. Mass Spectrom.*, 1987, **1**, 94.

6 S. Hammerum and H. E. Audier, following communication.

7 S. W. Benson, *Acc. Chem. Res.*, 1986, **19**, 335.

8 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960; A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

9 S. W. Benson, 'Thermochemical Kinetics,' 2nd edn., Wiley, New York, 1976.

10 S. Hammerum, K. F. Donchi, and P. J. Derrick, *Int. J. Mass Spectrom. Ion Phys.*, 1983, **47**, 347.

11 L. Radom, personal communication; S. Saebø, L. Radom, and H. F. Schaefer, *J. Chem. Phys.*, 1983, **78**, 845.

12 Landolt-Börnstein, 'Zahlenwerte und Funktionen,' Springer, Berlin, 1961, p. 510.

---

† Calculated[9] on the assumption that the charge is localized at the oxygen-bearing carbon atom and that the polarizability of the ethyl radical is close to that of ethane.

‡ Calculated[9] using μ = 1.5 D (ref. 11) and α = 3.2 $Å^3$ (the average polarizability of methanol[12]).