A Generalized Mechanism for Mass Spectral Reactions

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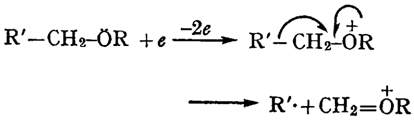
AN early approach to the mechanisms involved in forming mass spectra called for the localization in the molecular ion of the missing electron (lost in ionization by electron impact) at favoured sites, such as at nitrogen, oxygen, or other hetero-atoms.[1] This localized positive charge was viewed as being capable of triggering subsequent decomposition reactions leading to the fragment ions observed in the mass spectrum, *e.g.*, Reaction 1.



$$R'{-}CH_2{-}\ddot{O}R + e \xrightarrow{-2e} R'{-}CH_2{-}\overset{+}{\dot{O}}R \longrightarrow R'\cdot + CH_2{=}\overset{+}{O}R \qquad (1)$$

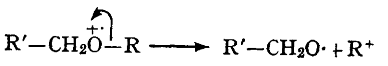
Such mechanisms have been developed further and used with considerable success in a number of extensive studies, particularly the substantial contributions of Djerassi and his co-workers[2] and of Shannon.[3] However, inadequacies in the localized charge concept, such as pointed out by Spiteller,[4] have limited its acceptance.[5]

There is now considerable evidence that mass spectral mechanisms should parallel those of organic solution chemistry; in fact, mass spectral substituent effects for certain benzoyl compounds correlate with Hammett σ-constants in a quantitative fashion.[6] Here we propose that a more generally satisfactory approach involves the *separate* consideration of the effect of the positive ion and radical sites in light of their known behaviour in condensed systems. It is important to recognize that the specific reactions possible for each are markedly different and characteristic. Among the most important of these are:

Radical site: Formation of an *additional* bond to an adjacent atom through donation of the unpaired electron plus transfer of another electron (half-arrow, or "fish-hook") of the adjacent atom; or formation of a *new* bond from the radical site to some other atom by rearrangement.[7]

Cation site: Transfer of an electron pair (full arrow) to move the site of the positive charge; or cleavage of a bond to the charged site by formation of a new bond to an attacking atom or group.[8]

Some examples may clarify this approach. For many single bond cleavages, the positive charge and the radical are localized on the same site. For Reaction 1, above, the driving force would be visualized as the donation of the unpaired electron to form a new bond to the hetero-atom. On the other hand, for another common fragmentation of ethers (Reaction 2) the driving force can be viewed as the positive charge acting to attract an adjacent pair of bonding electrons. In amines Reaction 1 is enhanced while 2 is depressed, as nitrogen is a better electron donor, but has a lower electronegativity, as compared to oxygen.

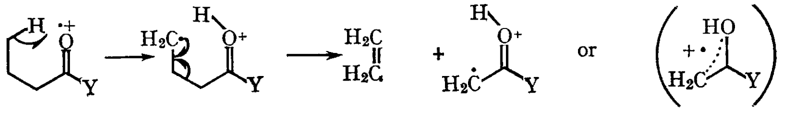


$$R'{-}CH_2\overset{+\cdot}{O}{-}R \longrightarrow R'{-}CH_2O\cdot + R^+ \qquad (2)$$

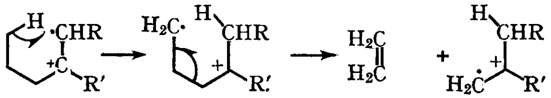
Many mechanisms have been advanced for the rearrangement of a hydrogen atom through a six-membered ring transition state[9] (often referred to [2,3,5] as the "McLafferty" rearrangement). In Reaction 3 the radical site of (I) can be viewed as providing the initial driving force through an abstraction rearrangement[10] to form a new bond to the oxygen atom. The observed specificity for rearrangement of the γ-H-atom[2] is in line with steric requirements for overlap with the highly directional orbital of the unpaired electron.[11,12] New bond formation to the radical site in (II) produces a stable molecule (III) with an accompanying entropy gain. Ionic product (IV) is isoelectronic with the allyl radical, stabilizing the final site of the radical.

In alkenes this abstraction rearrangement (Reaction 4) competes with allylic cleavage (Reaction 5). Reaction 4 predominates in 2-methylalkenes, indicating inductive stabilization of the charge at this site by $R = H$, $R' = Me$; allylic cleavage (5) predominates when $R' = H$, $R = Me$.[13] In the consecutive ("double hydrogen") rearrangement of ketones,[14] (Reaction 6, $Y = CH_2$), resonance stabilization of the ionic site in (I″) can similarly account for the abundant product (IV″). For esters ($Y = O$), the abundance of ion (IV″) is greatly reduced, in keeping with the higher stability expected for (II″) in this case. The decomposition of the alternative, favoured resonance form of (II″) (charge on the ether oxygen atom) would involve vinylic cleavage.

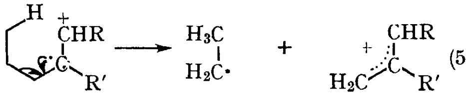
Another classic hydrogen rearrangement of quite different characteristics occurs in the decomposition of secondary even-electron ions formed from amines, ethers, and similar compounds.[15] Recent definitive papers by Djerassi and Fenselau[16] show, in contrast to the radical rearrangement (and to the original mechanism proposed[15]) that the rearranging hydrogen atom can originate from the α-, β-, γ-, or δ-positions. These results are consistent with the *absence* of a radical site—the rearrangement cannot involve a hydrogen abstraction. Such a *displacement* rearrangement (D) at the positive ion site (Reaction 7) must involve cleavage of a bond to the nitrogen atom *concurrent* with the formation of the new N–H bond (similar to an S_N2 reaction). The non-bonding orbital is *not* available for new bond formation, in keeping with the lack of specificity of the rearranging hydrogen atom.

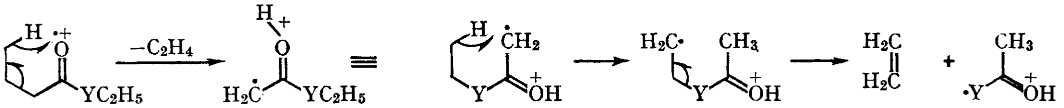

(3)

(I) (II) (III) (IV)

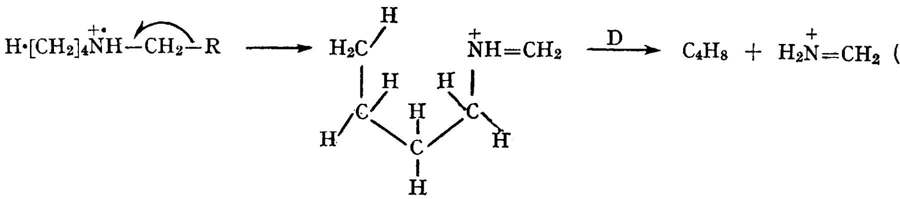

(4)

(I′) (II′) (III′) (IV′)


(5)


(6)

(I″) (II″) (IV″)


(7)

The hydrogen rearrangements of esters have been studied extensively, as summarized in a recent comprehensive paper.[17] Some of the anomalous results of deuterium-labelling can be explained by postulating several separate pathways of reaction at the radical- and charge-bearing sites. Attempts to devise similar mechanisms for many of the common reactions found in mass spectra have been encouraging.

It should be clear that the evidence marshalled here to support this generalized mechanism is not conclusive. Although this localized electron picture appears to be a useful approximation of the molecular orbital description for molecules with isolated functional groups, extension to more complex ions is not warranted without further study. The mechanism is presented in this preliminary form because of its apparent usefulness in interpreting mass spectral data, and because its critical examination by others in the field may hasten the clarification of these problems.[18]

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[1] F. W. McLafferty in "Determination of Organic Structures by Physical Methods", F. C. Nachod and W. D. Phillips, eds., p. 93, Academic Press, New York, 1962; F. W. McLafferty, "Mass Spectrometry of Organic Ions", p. 315, Academic Press, New York, 1963.

[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds"; Structure Elucidation of Natural Products by Mass Spectrometry, Vol. I and II; Holden-Day, San Francisco, 1964; A. M. Duffield, R. T. Aplin, H. Budzikiewicz, C. Djerassi, C. F. Murphy, and W. C. Wildman, *J. Amer. Chem. Soc.*, 1965, **87**, 4902, and previous references; many further references in press. I am deeply indebted to Prof. Djerassi for supplying copies of these papers in advance of publication.

[3] J. S. Shannon, *Austral. J. Chem.*, 1963, **16**, 683; S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, and J. S. Shannon, *ibid.*, 1965, **18**, 1539, and previous references.

[4] G. Spiteller and M. Spiteller-Friedmann, *Monatsh.*, 1964, **95**, 257.

[5] P. Bommer and K. Biemann, *Ann. Rev. Phys. Chem.*, 1965, **16**, 481.

[6] F. W. McLafferty, *Analyt. Chem.*, 1959, **31**, 477; M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, in the press.

[7] The latter is an abstraction reaction, and will be designated by the symbol A.

[8] The latter is a displacement reaction, and will be designated by the symbol D.

[9] F. W. McLafferty, *Analyt. Chem.*, 1959, **31**, 82.

[10] The radical site of (II) should be capable of re-abstracting the hydrogen atom to reverse this reaction, although the equilibrium should favour the more stable (II). Possibly such an equilibration could be observed in the mass spectrum of $CD_3{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3){=}CH_2$ to distinguish between this mechanism and the concerted mechanism proposed previously (Ref. 9.)

[11] This similarity to the Type II photoelimination of olefins from ketones is made even more striking by the recent communication of P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, 1965, **87**, 4009. Their results indicate that hydrogen abstraction can be accomplished by the radical site on oxygen in *either* the singlet or triplet $n \rightarrow \pi^*$ state of the carbonyl group.

[12] Similar abstractions by radical sites in bimolecular reactions are described by A. Padwa, *Tetrahedron Letters*, 1964, 3465, and by C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, 1965, **87**, 3361.

[13] F. W. McLafferty, *Analyt. Chem.*, 1959, **31**, 2072.

[14] A. G. Sharkey, Jr., J. L. Schultz, and R. A. Friedel, *Analyt. Chem.*, 1956, **28**, 934; H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, in the press.

[15] F. W. McLafferty, *Analyt, Chem.*, 1957, **29**, 1782.

[16] C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, 1965, **87**, 5747, 5752.

[17] C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, 1965, **87**, 5756.

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