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MECHANISTIC IMPLICATIONS OBTAINED FROM DIFFERENT DEGREES OF INTRAMOLECULAR HYDROGEN TRANSFER REACTIONS ON COMPETING METASTABLE TRANSITIONS OF GASEOUS ORGANIC CATIONS. THE CASE OF ETHYL BENZOATE.*

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Mass spectrometric studies of deuterated organic compounds have shown that hydrogen migration within the ionised species becomes pronounced in ions of lower internal energies and longer lifetimes, such as those formed at low electron voltages and those decomposing in the first and second drift regions of a double focussing mass spectrometer.[1] However, the use of stable isotope labelling techniques in general mass spectrometric studies is not precluded, since, in the 70 eV spectra, the loss of positional identity of the atoms involved is usually absent, or takes place only to a slight extent; this situation being peculiar to fragmentation processes involving simple bond cleavages.[1] We now report the use of the different degrees of hydrogen migration by which mechanistic inferences on tautomeric reacting precursors in competing unimolecular decompositions can be derived from the spectra of deuterated analogues.

In metastable transitions, where fragmentation occurs after 10^8 vibrations in ions normally characterised by a sufficiently narrow band of internal energies to discount variations in the energy distribution[2], we have found that ethyl benzoate molecular ions (1) show nine unimolecular decompositions[3] experimentally ascertained by the DADI analysis[4] using a reversed-geometry double-focussing mass spectrometer. Deuterium labelling experiments establish that 1 undergoes intramolecular hydrogen migration prior to some of the fragmentation reactions observed. The experimental data for $C_6H_5COOC_2D_5$ (2), labelled analogue of 1, are reported in the figure. This

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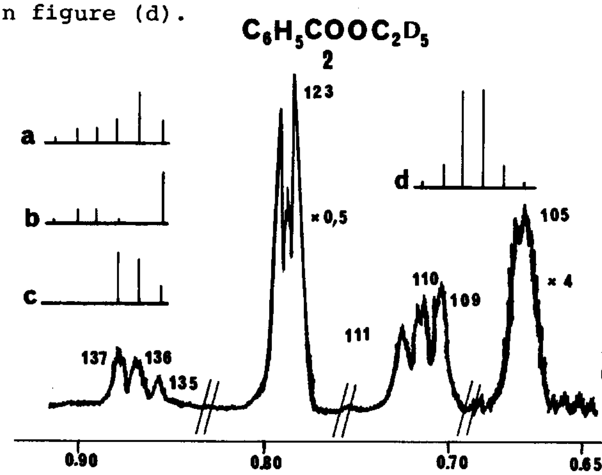
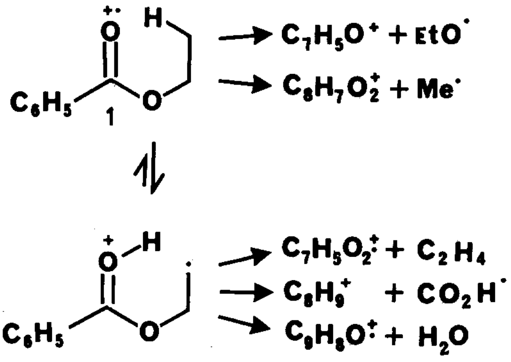
* *Electron Impact Induced Rearrangements of Organic Ions.IX. For part VIII in this series see ref. 3.*

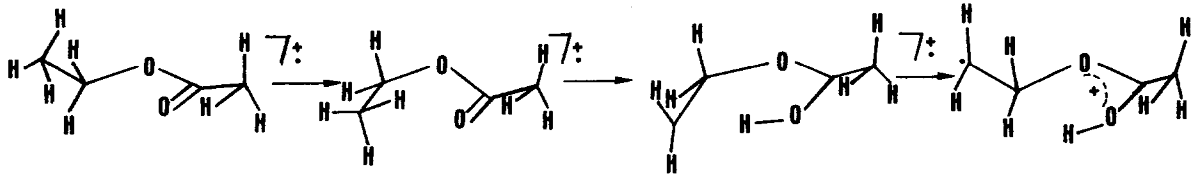
figure refers to the processes of choice together with the calculated spectra obtained assuming that H and D may or may not eventually participate equivalently in the unimolecular decompositions reported. For example, in the case of methyl and water loss from ions m/e 155, i.e. peaks 137, 136 and 135 in the DADI spectrum, the H and D atoms of 2 (a) might participate in both processes in an equivalent manner, (b) might, in the case of methyl expulsion, be randomly lost and, in that of water elimination according to proposed mechanism for the latter process^5, be specifically lost and (c) viceversa. Furthermore, a similar situation can be found in the case of the metastable transition yielding ethoxy radicals and probably deuterated ethoxy radicals also; the calculated relative abundance of the peaks for the process is reported in figure (d).





Scheme 1

In the DADI spectrum of ions from 2, the relative peak intensities for loss of water, CO_2H and CO_2D, i.e. peaks at m/e 137, 136, 135, 110 and 109, show that these processes are preceded by complete intramolecular H/D exchange within the molecular ions.^{3} However, the experimental data give unequivocal evidence for specific elimination of ethylene, methyl and ethoxy radical, i.e. CD_3(137), C_2D_4(123) and C_2D_5O(105). The question of the completely different degrees of intramolecular H/D migration found among the transitions observed, must be reconciled with the metastable ratios which provide qualitative measure of the activation energies for the unimolecular reactions. In fact the elimination of methyl and ethoxy radicals must be characterized by higher activation energies than those for loss of C_2H_4, CO_2H and H_2O (metastable ratio favouring the latter processes). Also in the light of the different entropy requirements for the decompositions, the first two reactions are homolythic single bond cleavages (more competition as regards short ion lifetimes) and the second group are rearrangements $^{3,6-7}$ (more competition in the drift regions). While it is plausible that the activation energy for intramolecular hydrogen transfer should fall between those for loss of C_2H_4 and loss of CO_2H and H_2O, as has been noted in similar cases,[8] it seems worth emphasizing that the situation regarding the specific elimination of methyl and ethoxy radicals is not straight forward. The two transitions show quite clearly that they occur at low rate constants (3 and ≃ 2% of the total ion current of the DADI spectrum) after approximately 10 μsecs of the molecular ion formation, but are more abundant in the normal ion spectrum[3]; therefore, we may exclude isolated electronic states giving rise to these decomposition reactions. Considering the above conclusion, the H/D intramolecular migration over the whole molecular ion must occur with a rate constant higher than that of H_2O and CO_2H losses in the metastable region and should compete effectively with the elimination of methyl and ethoxy radicals, if these processes truly occur from the same precursor ion structure. On the basis of these arguments, we are forced to the conclusion that loss of methyl and ethoxy radicals do not compete in the metastable region with the other transitions from the molecular ion having identical structure. If these specific radical eliminations, usually but not generally observed as such[9], do not compete directly with the other decompositions, then they must occur from the initial, not rearranged structure of the ethyl benzoate molecular ion, which undergoes the tautomeric isomerisation known as a part of the McLafferty rearrangement and reported in Scheme 1. Thus, competition occurs between direct loss of methyl and ethoxy radicals and the hydrogen transfer from the γ carbon atom of the alkyl chain to the oxygen atom of the carbonyl group. Thus, this isomeration process must be faster than the intramolecular exchange. In order to clarify the situation with regard to the relative stabilities of the initial and isomerized molecular ion 1, molecular orbital calculations have been performed on a model system, i.e. the ethyl acetate isomers I to IV (see Scheme 2), since the higher number of internal coordinates and basis functions of 1 would have been prohibitive timewise and costly. The energy of the radical cations I to IV has been obtained using a MINDO/3 SCF-LCAO scheme[10] with geometry optimization[11]. The theoretical data, i.e. the heat of formation of the radical cations reported in Scheme 2, point out that both I and II are less stable than III by 15.8 and 31.5 Kcal/mole respectively, while IV is more stable than III of 2.9 Kcal/mole. The physical origin of the process is therefore associated with the greater inherent stability of the carbon atom radical relative to the oxygen one. The energy profile of the isomerisation under study,[12] which preceeds some unimolecular dissociations, seems to confirm that the reactive ionic species may be different and also gives further theoretical proof that the McLafferty rearrangement proceeds through an intermediate, therefore involving a two step mechanism.[13]



I II III IV

Heat of formation (kcal/mole) 103.5 119.2 87.7 84.8

Scheme 2

The main conclusions reached in the present study are that the difference in the degree of H/D exchange appears to offer unique advantages in mechanistic studies, in spite of the well known source of ambiguity in using deuterium labelling experiments.[1] As a consequence of the above data there is new experimental and theoretical evidence to confirm that, even if not necessarily valid for all other systems, the McLafferty rearrangement proceeds in a stepwise fashion in the case of ethyl benzoate too.

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