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Hydrogen Randomisation in Alkyl Chains upon Electron Impact

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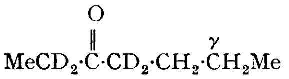
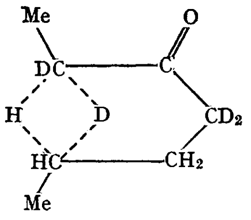
THE recent report[1] of H/D scrambling in the low-voltage spectra of specifically deuteriated ethyl pentyl ketones prior to the loss of an ethyl radical has led us to consider the extent of H/D scrambling in alkyl chains in relation to ion lifetimes. The observation that scrambling is much more evident in the fragment ions observed in low-voltage spectra indicates that the scrambling reactions have relatively low activation energies and low frequency factors.[2] For example, H/D exchange between alkyl chains of 2,2,4,4-$[^2H_4]$heptan-3-one (I) might be visualised in terms of the transition state (Ia) for the rearrangement.†. Let the rise of the unimolecular rate constant (k_r) for this rearrangement with internal energy occur as indicated in Figure 1 (this curve is typical of those computed on the basis of the quasi-equilibrium theory).[3] Consider also some fragmentation process with a higher energy of activation and higher-frequency factor, such that the curve representing the variation of the rate constant for fragmentation (k_f) with internal energy crosses the first curve (Figure 1) (as the internal energies tend to infinity, the rate constants tend to the frequency factors). Thus, for fragment ions formed with rate constants in the range 10^6—10^8 sec.$^{-1}$, H/D scrambling in the molecular ion will be rapid compared with fragmentation, whereas for fragment ions formed with rate constants $>10^8$ sec.$^{-1}$, scrambling will be slow compared to



$$\mathrm{MeCD_2{\cdot}\overset{\overset{\displaystyle O}{\|}}{C}{\cdot}CD_2{\cdot}CH_2{\cdot}\overset{\gamma}{C}H_2Me}$$

(I)



(Ia)

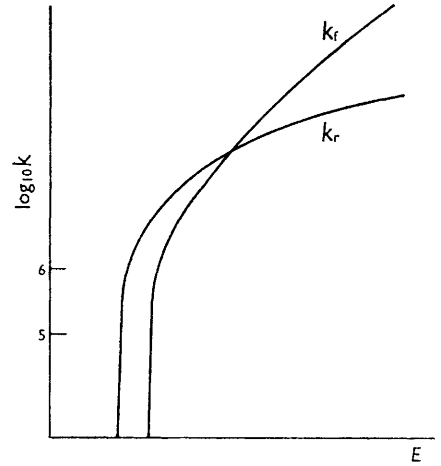


FIGURE 1

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† This need only be one of a number of similar transition states.

fragmentation (assuming only that the reactions occur as competing unimolecular processes). It follows that ions of relatively long lifetimes (low internal energies) will have scrambled most extensively prior to fragmentation, and that scrambling will be most evident in low-voltage spectra, as observed experimentally[1] in ethyl pentyl ketone. It follows further that for cases resembling the situation shown in Figure 1, scrambling will be even greater for metastable decompositions ($^{1}m^{*}$) occurring in the first field-free region of an MS 9 mass spectrometer (ln $k \cong$ 5—6),[4] and greatest (for observational purposes) for metastable decompositions ($^{2}m^{*}$) occurring in the second field region of the spectrometer (ln $k \cong 5$).

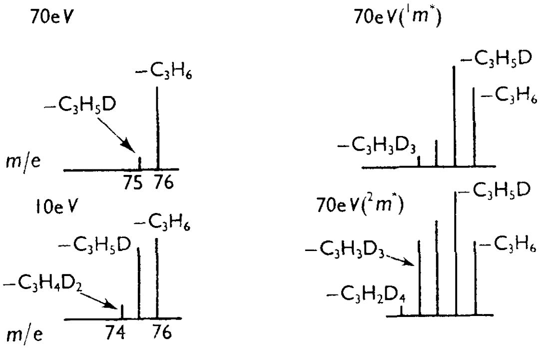

FIGURE 2

To test the above concepts, a number of specifically deuteriated ketones have been synthesised. The experimental data obtained are in accordance with the above generalisations and one example is given. The McLafferty rearrangement in dialkyl ketones is generally agreed to involve a site-specific γ-hydrogen rearrangement.[5] Accordingly, the 70 ev mass spectrum of (I) contains a large peak due to the loss of propene. However, even at 70 ev, there is a small peak due to loss of [$^{2}H_{1}$]propene.‡ At a nominal 10 ev the loss of [$^{2}H_{2}$]propene affords a peak which is of significant abundance relative to m/e 75 and 76, while transitions ($^{1}m^{*}$) observed in the first field-free region (with the aid of a metastable defocusser[4]) show additionally loss of [$^{2}H_{3}$]propene (Figure 2). Even a significant loss of [$^{2}H_{4}$]propene is observed for transitions ($^{2}m^{*}$) occurring in the second field-free region.

While significant cases of H/D scrambling in alkyl chains,[1,6] or between an alkyl chain and an aromatic nucleus,[7] have previously been noted, the relationship of the phenomenon to ion lifetimes possibly has extremely important relevance to the interpretation of deuterium-labelling results and isotope effects in general. The literature is replete with hydrogen rearrangement reactions for which (as a result of deuterium-labelling experiments) the rearranging hydrogen atom is assumed to originate from several different carbon atoms. Since fragment ions formed in rearrangement reactions may frequently be produced from precursor ions (not necessarily molecular ions) with relatively long lifetimes,[2] the possibility of extensive H/D scrambling prior to formation of the daughter ions should be seriously considered.[8] A number of previous observations on differences in the high and low ev spectra of deuteriated compounds, which have been rationalised in terms of energy-dependent isotope effects, might also be explained in terms of H/D randomisation.

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‡ The observation of such a phenomenon can depend critically on the residence time of ions in the source, which may vary not only from instrument to instrument, but also from source to source on the same instrument.

[1] W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, 1968, **90**, 160.

[2] R. G. Cooks and D. H. Williams, *Chem. Comm.*, 1968, 663; see also S. Meyerson, *Appl. Spectroscopy*, 1968, **22**, 30.

[3] *E.g.* M. L. Vestal, *J. Chem. Phys.*, 1965, **43**, 1356.

[4] K. R. Jennings in "Some Newer Physical Methods in Structural Chemistry", ed. R. Bonnett and J. G. Davies, United Trade Press, London, 1967, p. 105.

[5] For a recent review of pertinent references, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, 1967, p. 155.

[6] W. H. McFadden and A. L. Wahrhaftig, *J. Amer. Chem. Soc.*, 1956, **78**, 1572; S. Sample and C. Djerassi, *J. Amer. Chem. Soc.*, 1966, **88**, 1937; A. G. Harrison and E. G. Jones, *Canad. J. Chem.*, 1965, **43**, 960.

[7] A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Amer. Chem. Soc.*, 1965, **87**, 805.

[8] See W. Fenz and K. Biemann, *J. Amer. Chem. Soc.*, 1964, **86**, 2375.