Kinetics and Mechanisms of Unimolecular Gas-phase γ-Hydrogen Rearrangements of Aliphatic Aldehydes at Times of the Order of 10 Picoseconds and longer following Field Ionisation

By ROGER P. MORGAN and PETER J. DERRICK*

(*Department of Chemistry, University College, University of London, 20 Gordon Street, London* WC1H 0AJ)

Summary Evidence is presented that the γ-hydrogen transfer in the decomposition processes of aliphatic aldehydes referred to as McLafferty rearrangement occurs as a discrete step at times longer than *ca.* 20 ps following field ionisation.

RECENT kinetic results[1] obtained by the field ionisation kinetics (FIK) technique[2,3] revived the persistent question of whether the γ-hydrogen transfer in the decomposition processes of aldehydes[4] referred to as McLafferty rearrangement[5] occurs as a discrete step or in concert with subsequent β-cleavage. We report preliminary results from an FIK study of 3-methylpentanal which elucidate this and related mechanistic questions. An FIK study of hexanal has been described.[6]

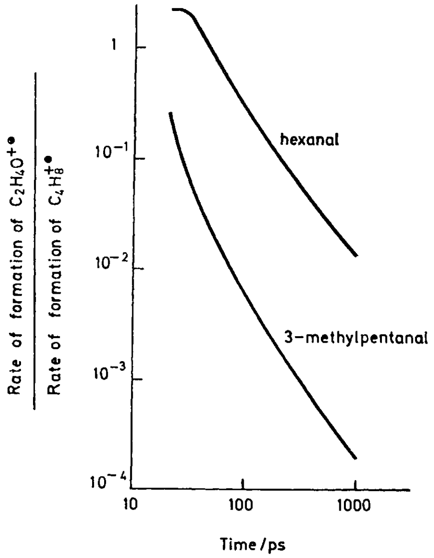
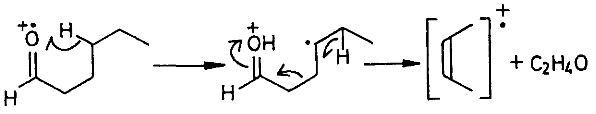


FIGURE. The relative rates of formation of $\mathrm{C_2H_4O^{+\cdot}}$ and $\mathrm{C_4H_8^{+\cdot}}$ from 3-methylpentanal and from hexanal following field ionisation (FI).

The apparatus[7] and the experimental method[8] have been described. 3-Methylpentanal and hexanal undergo the same types of decomposition processes following FI, and the measured rates of formation of corresponding fragment ions are in satisfactory agreement. There is, however, one obvious and significant difference between the reaction systems, which is that the formation of $\mathrm{C_2H_4O^{+\cdot}}$, which involves β-cleavage and specific γ-hydrogen transfer,[4,6] is suppressed in 3-methylpentanal as compared to hexanal. The Figure presents rates of formation of $\mathrm{C_2H_4O^{+\cdot}}$ relative to $C_4H_8^{+\cdot}$ for the two systems. $C_2H_4O^{+\cdot}$ is not detected at times longer than 1 ns. The formation of $C_4H_8^{+\cdot}$, which involves β-cleavage and hydrogen transfer predominantly from either the γ- or the δ-position,[4,6] occurs over the whole time-range from 20 ps to μs. The rate of formation of $C_4H_8^{+\cdot}$ at any time tends to be higher in hexanal than in 3-methylpentanal generally by about a factor of 2.



(1)

Our discussion concerns reaction at times longer than *ca.* 20 ps. The suppression of $C_2H_4O^{+\cdot}$ in 3-methylpentanal supports the mechanism[1] in which γ-hydrogen transfer and β-cleavage occur as discrete steps. On β-cleavage the charge is retained by the fragment with the lowest ionisation potential (IP), assuming reverse activation energies to be negligible. This is the situation of charge competition discussed by Meyerson *et al.*[4] With 3-methylpentanal, the enol C_2H_4O (I.P. *ca.* 9·25 eV, *vide infra*) competes with but-2-ene (I.P. 9·1 eV) for the charge. Consequently formation of $C_4H_8^{+\cdot}$ is favoured. The reactants of highest internal energy can be assumed to decompose at the shortest times, and moreover will be the least sensitive to the small difference (*ca.* 0·15 eV) in I.P. between the enol and but-2-ene. This explains the steady rise in the rate of formation of $C_2H_4O^{+\cdot}$ relative to $C_4H_8^{+\cdot}$ as time decreases. With hexanal, the enol competes with but-1-ene (I.P. 9·6 eV), thereby explaining the importance of $C_2H_4O^{+\cdot}$ at short times. The formation of $C_4H_8^{+\cdot}$ at longer times we attribute to β-cleavage being concerted with further rearrangement such that the incipient fragment competing for the charge has the but-2-ene rather than the but-1-ene structure [equation (1)]. Thus the intermediate formed by γ-hydrogen transfer can react either by direct cleavage to form $C_2H_4O^{+\cdot}$ or by rearrangement to form $C_4H_8^{+\cdot}$. The intermediates decomposing at short times having high internal energies follow the direct cleavage pathway, whereas those decomposing at longer times having lower internal energies prefer to rearrange.[9]

The results (Figure) weigh against an alternative mechanism[1] in which the γ-hydrogen transfer and β-cleavage in the formation of $C_2H_4O^{+\cdot}$ are seen as being concerted. This mechanism does not account for the suppression of $C_2H_4O^{+\cdot}$ at times longer than *ca.* 20 ps on substitution of a methyl at C-3.

We make two points in conclusion. Concerning determination of the I.P of vinyl alcohol by the method of Meyerson and McCollum,[10] the figure of 9·25 eV derived by Bentley and Johnstone[11] fits the results[1] with [4,4-$^2H_2$]hexanal better than the original figure of 9·5 eV. We emphasise the role of the intermediate in the hexanal system. It is the characteristics of this species, rather than those of the hexanal molecular ion, which determine the outcome of competition between formation of $C_2H_4O^{+\cdot}$ and formation of $C_4H_8^{+\cdot}$ by γ-hydrogen rearrangement.

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