Kinetics and Mechanisms of the Decompositions of the Molecular Ions of Pentanal and its Monomethyl-substituted Homologues in the Picosecond to Microsecond Time Interval following Field Ionization

By **Roger P. Morgan,* Peter J. Derrick,** and **Alexander G. Loudon,*** Department of Chemistry, University College, 20 Gordon Street, London WC1H OAJ

The kinetics of decomposition of pentanal and its monomethyl homologues, including hexanal, have been studied as a function of time following field ionisation (FI). With the aid of these results and other energetic measurements, the McLafferty rearrangement in the case of hexanal is shown to occur by a stepwise mechanism.

FIELD ionisation kinetics[1] (FIK) permits the rates of unimolecular gas-phase decompositions of radical cations to be measured over the time range 10^{-12}—10^{-5} s. Thus a time-resolved view of the fragmentation pathways is provided, which is in contrast to other methods of ionisation such as electron impact (EI), chemical ionisation, and photoionisation. These methods typically afford an integrated view of all events occurring within a lengthy and somewhat ill defined time period of the order of microseconds.

FIK has been shown to be an extremely useful tool for elucidating reaction mechanisms,[1] and in an earlier FIK study of hexanal some fundamental questions were raised concerning the mechanism of the McLafferty rearrangement.[2] The present paper presents the results of an FIK study of pentanal, 2-methylpentanal, 3-methylpentanal, 4-methylpentanal, and hexanal, which was undertaken principally with a view to determining whether the McLafferty rearrangement occurs in a concerted or a step-wise fashion.[3]

Gilpin and McLafferty[4] measured the EI mass spectra of a large number of aliphatic aldehydes *ca.* 20 years ago and identified the rearrangement which has come to be known as the McLafferty rearrangement. Since then, there has been a great deal of discussion concerning the mechanism of this rearrangement and, in particular, the question of whether β-cleavage is concerted with γ-hydrogen transfer.[2,3,5-9] Thorough EI studies of specifically deuterium-labelled hexanals, heptanals, and nonanals have been reported by Liedtke and Djerassi[10] and by Meyerson *et al.*[11] These workers[10,11] confirmed the specific involvement of the γ-hydrogen in the McLafferty rearrangement leading to formation of $[C_2H_4O]^{+\cdot}$, but showed that there were at least two processes leading to formation of the complementary hydrocarbon ion $[C_4H_8]^{+\cdot}$ in the case of hexanal. One of these processes involved γ-hydrogen transfer, and a second major process involved transfer of the δ-hydrogen. Meyerson *et al.*[11] postulated that an ethylcyclobutanol intermediate was involved in the loss of the C(2) and C(3) atoms as ethylene; Harrison[12] has suggested that this process is a concerted four-centred elimination. Cyclobutanol intermediates appear not to be involved in the McLafferty rearrangement.[13]

Field ionization (FI) mass spectra of aldehydes have been measured and found to contain most of the product ions observed under low energy EI.[14,15] The metastable peak for the formation of $[C_4H_8]^{+\cdot}$ from hexanal following FI has been measured and found to be broader than the same peak following EI (energy releases of 3.4 and 2 kJ mol^{-1}, respectively).[16]

TABLE 1

Ionisation energies [I(M)] and appearance energies [A(F)]$^+$ for pentanal and its monomethyl homologues

Ion	Pentanal	2-Methylpentanal	3-Methylpentanal	4-Methylpentanal	Hexanal
$[M]^{+\cdot}$	9.90 (9.72)[a] (9.82)[b]	9.70	9.90	9.80	9.80
$[M - H_2O]^{+\cdot}$	10.00 (9.80)[a]		9.90	10.00	9.80
$[C_2H_4O]^{+\cdot}$	11.40		11.40 (10.88)[c]	11.40	11.60 (10.70)[c]
$[C_4H_8]^{+\cdot}$			11.10 (9.86)[c]	11.10	10.70 (9.89)[c]
$[C_3H_6O]^{+\cdot}$	10.00	10.30	10.10	11.00	10.20
$[C_4H_8O]^{+\cdot}$		10.60	11.00	10.10	10.00
$[C_3H_6]^{+\cdot}$	11.90	11.00			

[a] Value from ref. 18. [b] Value from ref. 20. [c] Value from ref. 19.

RESULTS

Field ionization spectra of the compounds studied are shown in Figure 1. The relative intensities of the peaks in the spectra depend upon, *inter alia*, the sample pressure, temperature of the source, and the method used to condition the emitter.[17] The mass spectrum of hexanal contains all the major peaks observed by Beckey.[15]

The electron impact ionization energies [I(M)] and the appearance energies [A(F)$^+$], measured using the semi-log method, are shown in Table 1. The appearance energies [A(F)$^+$] for the McLafferty rearrangement products $[C_4H_8]^{+\cdot}$ and $[C_2H_4O]^{+\cdot}$ from 3-methylpentanal and hexanal are higher than the values reported by Holmes *et al.*[19] These differences are partly due to different source residence times.[21] The electron impact source residence time of the

MS-9 used in our measurements is of the order of 1 μs, whereas that of the instrument used by Holmes *et al.*[10] is >10 μs. The validity of the use, in this paper, of the semi-log method for determining, semi-quantitatively, appearance potentials differences is discussed in an Appendix. The well known limitations of this method for the exact determination of absolute values are clear from the data in Table 1.

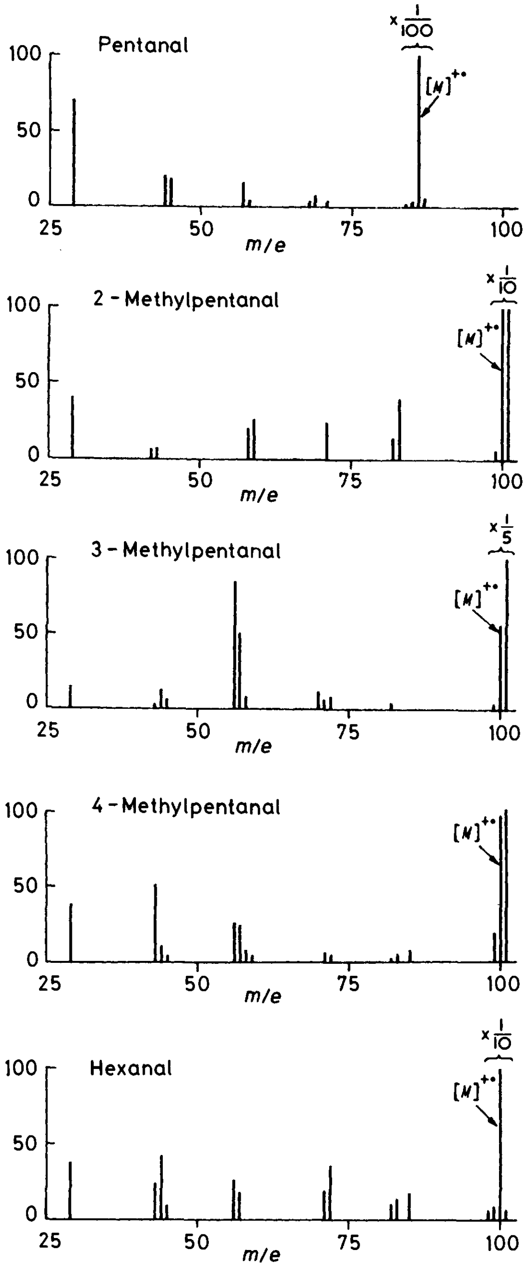


FIGURE 1

The FIK results for pentanal and its monomethylhomologues are shown in Figures 2—6. Certain other ions observed at lower intensities are listed in Table 2. The mass resolution during the FIK measurements was *ca.* 2 000 (10% valley definition). The only doublet observed at times longer than 20 ps was $[CHO]^+/[C_2H_5]^+$ at *m/e* 29 with 4-methylpentanal.

DISCUSSION

McLafferty Rearrangement.—The McLafferty rearrangearrangement involves γ-hydrogen transfer and β-C–C cleavage, and gives rise to $[C_2H_4]^{+\cdot}$ with pentanal, $[C_3H_6O]^{+\cdot}$ with 2-methylpentanal, and both $[C_2H_4O]^{+\cdot}$ and $[C_4H_8]^{+\cdot}$ with each of 3-methylpentanal, 4-methylpentanal, and hexanal (Figures 2—6).

Considering hexanal (Figure 6), the formation of $[C_2H_4O]^{+\cdot}$ is favoured over formation of $[C_4H_8]^{+\cdot}$ at short times, whereas the reverse is the case at longer times. The formation of $[C_2H_4O]^{+\cdot}$ has been shown to be a specific γ-hydrogen rearrangement; however, $[C_4H_8]^{+\cdot}$ contains contributions from both a δ- and a γ-hydrogen process.[1,2]

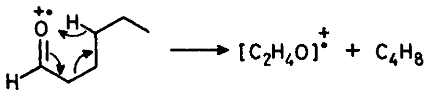
TABLE 2

Other ions formed from pentanal and its monomethyl homologues at times >20 ps after ionisation

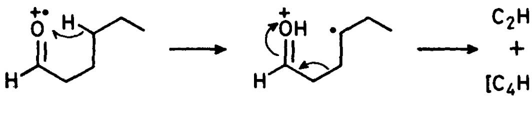
Compound	Ions
Pentanal	$[C_4H_7O]^+$, $[C_4H_9]^+$
2-Methylpentanal	$[C_5H_{11}]^+$, $[C_3H\ ]^{+\cdot}$
3-Methylpentanal	$[C_4H_9]^+$, $[C_2H_5O]^+$
4-Methylpentanal	$[C_nH_{2n+1}]^+$ ($n = 2,4,5$) $[C_5H_9O]^+$, $[CHO]^+$
Hexanal	$[C_5H_9O]^+$, $[C_5H_{11}]^+$, $[C_3H_5O]^+$

Measurements [2] on $[4,4\text{-}^2H_2]$hexanal show $[C_2H_3DO]^{+\cdot}$ predominating over $[C_4H_7D]^{+\cdot}$ at short times and the reverse at long times. The formation of $[C_2H_4O]^{+\cdot}$ involving γ-hydrogen transfer and β-cleavage and the formation of $[C_4H_8]^{+\cdot}$ involving γ-hydrogen transfer and β-cleavage would appear to differ only in the location of the charge, so that the markedly differing kinetics are somewhat remarkable.

One suggestion [2] has been that $[C_2H_4O]^{+\cdot}$ is formed by a concerted process (Scheme 1), whereas the complementary $[C_4H_8]^{+\cdot}$ is formed by a step-wise process (Scheme 2). If there were such a concerted process forming $[C_2H_4O]^{+\cdot}$ in hexanal ion, similar concerted processes ought to occur with the other aldehyde ions, and formation of $[C_2H_4O]^{+\cdot}$ ought to be similarly favoured over formation of $[C_4H_8]^{+\cdot}$ at short times with both 3- and 4-methylpentanal. It is evident from Figures 4 and 5 that formation of $[C_2H_4O]^{+\cdot}$ is not as favoured at short times with 3- and 4-methylpentanal as it is with hexanal. The concerted *versus* step-wise explanation is, therefore, not supported by our results.

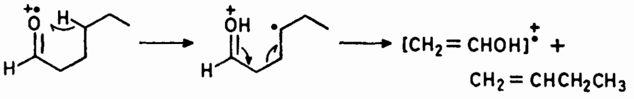


SCHEME 1

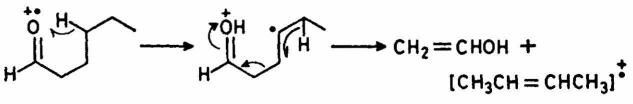


SCHEME 2

If the formation of $[C_2H_4O]^{+\cdot}$ is not a concerted process, then it must involve an intermediate. The results (Figure 6) can be explained on the grounds that both formation of $[C_2H_4O]^{+\cdot}$ and formation of $[C_4H_8]^{+\cdot}$ proceed *via* the same intermediate (Schemes 3 and 4). The difference between the processes is that $[C_2H_4O]^{+\cdot}$ is formed by a direct bond-cleavage *within the intermediate formed by γ-hydrogen transfer*, whereas formation of $[C_4H_8]^{+\cdot}$ necessitates further rearrangement. The direct cleavage might be expected to predominate over the rearrangement at short times because of more favourable frequency factor considerations, while the rearrangement (Scheme 4) predominates at longer times because of a presumed lower activation energy. This argument makes the normal assumption that ions decomposing at short times have more internal energy than those decomposing at long times.[1]



SCHEME 3



SCHEME 4

Having said that ions decomposing at short times (10^{-11}—10^{-9} s) have more internal energy, it is important to emphasise that in general these ions do *not* have so much energy that reactions occur at their limiting rates, *i.e.* reaction probability is *not* determined solely by the frequency factor.[22] Thus, even if two competing reactions have the *same* frequency factor, one can still predominate over the other at 10^{-11}—10^{-9} s given sufficient difference in their activation energies. It should also be borne in mind that the energy imported to a molecule is much less under field ionization than under 70 eV electron impact.[1]

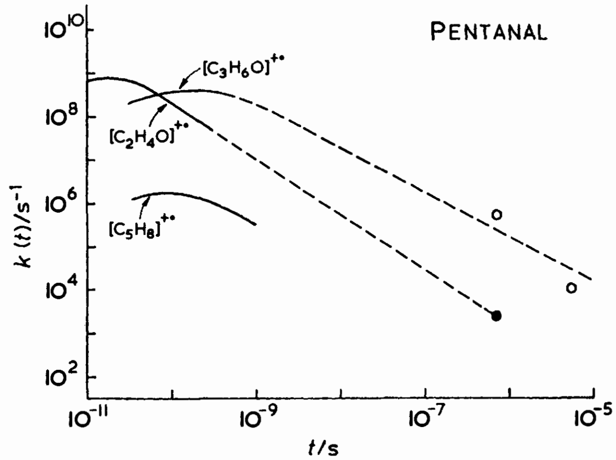


FIGURE 2

Consider the results for the McLafferty rearrangement in pentanal and 2-methylpentanal (Figures 2 and 3). Given that the reactions involve the intermediates shown (Schemes 5 and 6), there are still two possible pairs of products for each compound depending upon the location of the charge. Considering pentanal, formation of $[CH_2{=}CHOH]^{+\cdot}$ and formation of $[CH_3CH{=}CH_2]^{+\cdot}$ (Scheme 5) should have similar frequency factors, however only $[CH_2{=}CHOH]^{+\cdot}$ is observed. That $[CH_2{=}CHOH]^{+\cdot}$ is formed, and $[CH_3CH{=}CH_2]^{+\cdot}$ is not, is attributed to a difference in the activation energies for their formation.

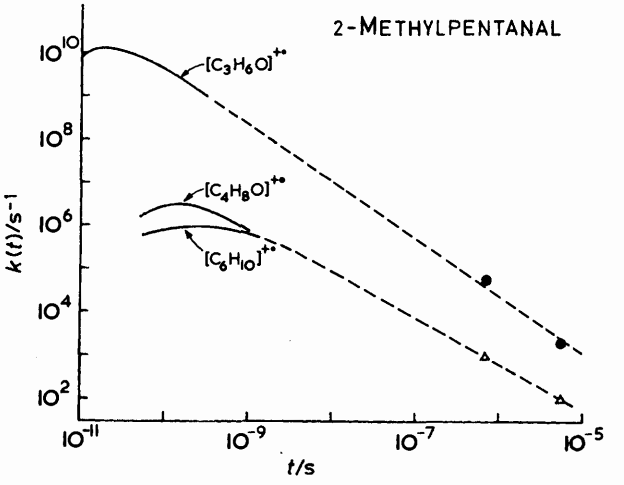
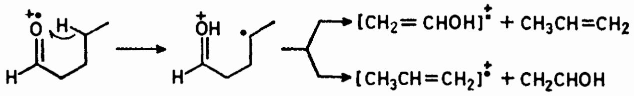
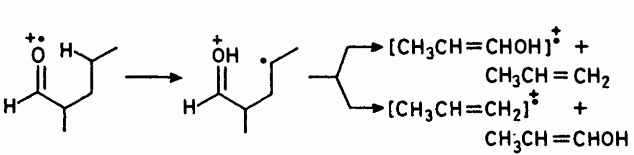


FIGURE 3

If there were no reverse activation energy for either of the second steps (*i.e.* the alternative decompositions of the intermediate) in Scheme 5, the difference in the forward activation energies would be equal to the difference in the enthalpies of reaction (provided that the second steps are endoergic). Using data from standard tables [23] and taking ΔH_f $[CH_2{=}CHOH]^{+\cdot}$ 757 kJ mol^{-1},[19] the enthalpy of reaction at 298 K for formation of $[CH_2{=}CHOH]^{+\cdot}$ and $CH_3CH{=}CH_2$ from $[CH_3CH_2CH_2CH_2CHO]^{+\cdot}$ is *ca.* +60 kJ mol^{-1}, compared with +119 kJ mol^{-1} for the alternative reaction giving $[CH_3CH{=}CH_2]^{+\cdot}$ and $CH_2{=}CHOH$. That $[C_3H_6O]^{+\cdot}$ is formed from 2-methylpentanal, whereas $[C_3H_6]^{+\cdot}$ is not (Figure 3), can be explained in similar terms.



SCHEME 5



SCHEME 6

Returning now to the hexanal results (Figure 6), there would according to Scheme 3 be competition for the charge at short times between $CH_2{=}CHOH$ and $CH_2{=}CHCH_2CH_3$. We explain the retention of the charge at these times by $[CH_2{=}CHOH]^{+\cdot}$, by presuming that formation of $[CH_2{=}CHOH]^{+\cdot} + CH_2{=}CHCH_2CH_3$ requires a lower activation energy than formation of $[CH_2{=}CHCH_2CH_3]^{+\cdot} + (CH_2{=}CHOH)$. At long times, the charge competition is between $CH_2{=}CHOH$ and $CH_3CH{=}CHCH_3$ [instead of $CH_2{=}CHCH_2CH_3$ (Scheme (4)]. The success of the alkene in retaining the charge is explained if the activation energy for formation of $[CH_3CH{=}CHCH_3[^{+\cdot}$ and $CH_2{=}CHOH$ is lower than that for formation of $[CH_2{=}CHOH]^{+\cdot}$ and $CH_3CH{=}CHCH_3$. ΔH_f $[CH_3CH{=}CHCH_3]^{+}$ is *ca.* 54 kJ mol^{-1} lower than ΔH_f $[CH_2{=}CHCH_2CH_3]^{+\cdot}$ at 298 K.[23]

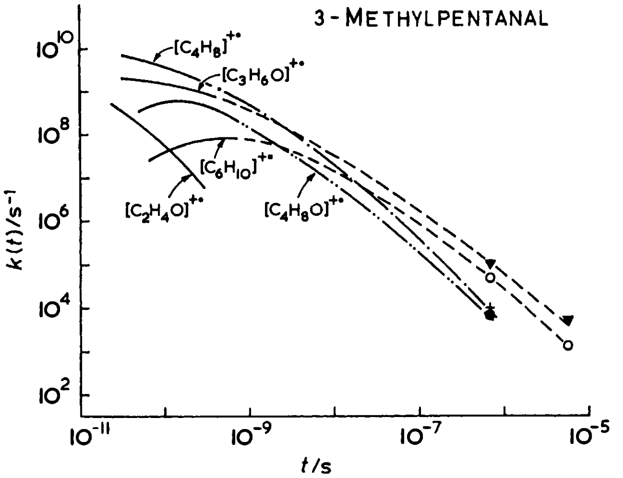


FIGURE 4

The results for 3- and 4-methylpentanal (Figures 4 and 5) are explicable, in the same terms. In the case of 3-methylpentanal (Figure 4), formation of $[C_4H_8]^{+\cdot}$ predominates over formation of $[C_2H_4O]^{+\cdot}$ at all times. γ-Hydrogen transfer forms an intermediate, which can decompose *without further rearrangement* to a but-2-ene ion and vinyl alcohol, *i.e.* even at short times vinyl alcohol must compete for the charge with but-2-ene rather than but-1-ene (Scheme 7). In the case of 4-methylpentanal, γ-hydrogen transfer forms an intermediate which can decompose without further rearrangement to form vinyl alcohol and 2-methylpropene structures (Scheme 8).

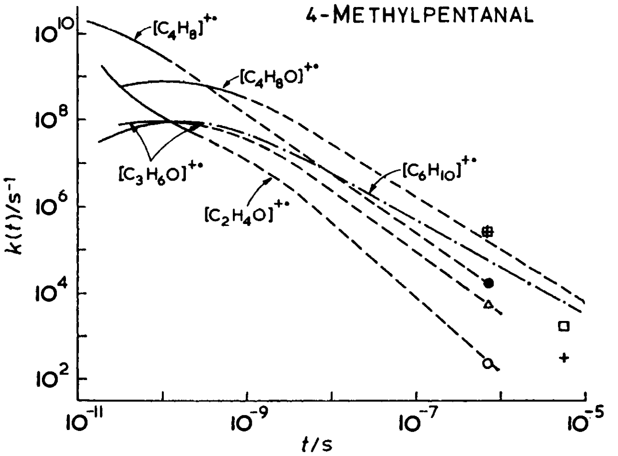
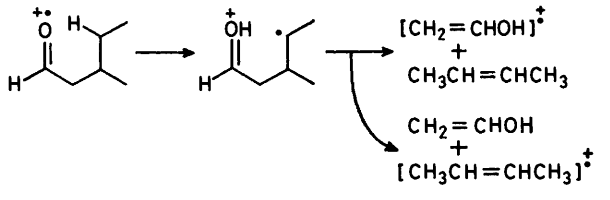


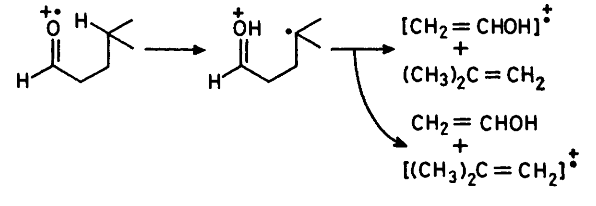
FIGURE 5

The charge is preferentially retained by the alkene, although with 4-methylpentanal (Figure 6) formation of $[C_2H_4O]^{+\cdot}$ is not completely suppressed at long times as it is with hexanal and 3-methylpentanal (Figures 6 and 4, respectively).



SCHEME 7

The mechanisms advanced (Scheme 3—8) constitute a plausible explanation for the kinetic results (Figures 2—6), while remaining consistent with established ideas concerning the mechanism of the McLafferty rearrangement.[4,5,11] That information concerning the activation energies necessary to properly establish the validity of the mechanisms is, however, lacking. Our measured appearance energies (Table 1) are consistent with the mechanisms, in that, with each of 3-methylpentanal, 4-methylpentanal, and hexanal, $A[C_4H_8]^{+\cdot}$ is lower than $A[C_2H_4O]^{+\cdot}$. In the case of pentanal $A[C_2H_4O]^{+\cdot}$ is lower than $A[C_3H_6]^{+\cdot}$, and with 2-methylpentanal $A[C_3H_6O]^{+\cdot}$ is lower than $A[C_3H_6]^{+\cdot}$. The appearance energies (Table 1) obtained by Holmes *et al.*[19] for



SCHEME 8

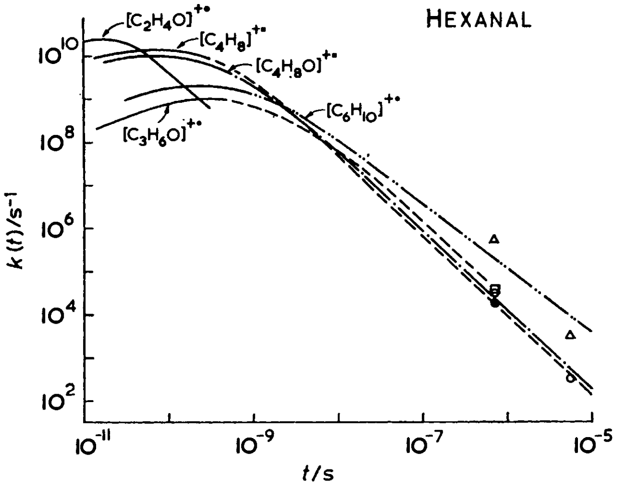


FIGURE 6

$[C_4H_8]^{+\cdot}$ from 3-methylpentanal and hexanal, however, demand a fuller discussion.

The figure of 9.89 eV for formation of $[C_4H_8]^{+\cdot}$ from hexanal (Table 1) corresponds to products ($[C_4H_8]^{+\cdot}$ + neutral) with a combined enthalpy of formation of <706 kJ mol^{-1} [19] {*cf.* ΔH_f ($[CH_3CH{=}CHCH_3]^{+\cdot}$) + ΔH_f ($CH_2{=}CHOH$) *ca.* 747 kJ mol^{-1} (see below and Table 3)}. It is not possible to form the but-2-ene ion and vinyl alcohol from hexanal at this energy (9.89 eV), hence Scheme 4 cannot apply in this situation. Holmes *et al.*[19] have suggested that this appearance energy corresponds to formation of the but-2-ene ion and acetaldehyde (combined enthalpy of formation 704 kJ mol^{-1}). The figure of 9.86 eV with 3-methylpentanal (Table 1) corresponds to products with a combined enthalpy of formation of <696 kJ mol^{-1},[19] and again Holmes *et al.*[19] suggest formation of the but-2-ene ion and acetaldehyde. That the appearance energy still appears too low (696 kJ mol^{-1} is observed and 704 kJ mol^{-1} is required) has been attributed to inaccuracies in enthalpies of formation in particular that of 3-methylpentanal.[19] The significance of these very low appearance energies as regards interpretation of the field ionization kinetics results is not completely clear. It is obviously not easy to write a mechanism for the formation of but-2-ene ion and acetaldehyde from the hexanal ion. Appearance energy measurements on isotopically labelled aldehydes might help in this regard. The formation of acetaldehyde and the but-2-ene ion would of necessity involve extensive intramolecular rearrangement, so that it would not be surprising if the process were characterised by a very low frequency factor ($<10^5$ s^{-1}). Such a process might be observed at threshold despite its unfavourable frequency factor, given a sensitive instrument with an energy resolved ionizing beam, but would be unlikely to make any significant contribution to the total decomposition at microseconds and shorter times either following FI or under 70 eV EI. This point has been emphasised in a recent paper; [24] McMaster has recently reviewed the whole question of the significance of appearance energies.[25]

The combined enthalpies of formation of various possible pairs of products from the McLafferty rearrangement in hexanal, 3-methylpentanal, and 4-methylpentanal are shown in Table 3. Enthalpies of formation of products are given, rather than enthalpies of reaction, since accurate thermodynamic data is not available for the branched aldehydes. The enthalpy of formation of $CH_2{=}CHOH$ has been estimated by the additive procedure (1). The enthalpy of formation of ethyl vinyl

$$\Delta H_f(CH_2{=}CHOH) = \Delta H_f(CH_2{=}CHOCH_2CH_3) - \Delta H_f(CH_3CH_2OCH_2CH_3) + \Delta H_f(CH_3CH_2OH) \quad (1)$$

ether has been determined by two different methods, and the agreement between the results is good.[26,27] This additive procedure leads to $\Delta H_f(CH_2{=}CHOH)$ -124 kJ mol^{-1}. Holmes *et al.*[19] estimate $\Delta H_f(CH_2{=}CHOH)$ to be -111 kJ mol^{-1}, using additive procedures which neglect interaction between the double bond and the oxygen lone pairs. Pilcher *et al.*[27] have discussed this form of interaction in some detail, and estimate its magnitude as 12 kJ mol^{-1} in ethyl vinyl ether. Taking $\Delta H_f(CH_2{=}CHOH)$ -124 kJ mol^{-1} and combining this with $\Delta H_f([CH_2{=}CHOH]^{+\cdot})$ 757 kJ mol^{-1},[19] the ionization energy of vinyl alcohol is obtained as 9.13 eV. This compares reasonably well with Bentley and Johnston's estimate of 9.25 eV.[28]

The enthalpies in Table 3 are presented as 298 K values, although strictly speaking this is not correct. The appearance energies, upon which the enthalpies of formation of the ions are based, correspond most closely to enthalpy differences at 0 K, and ought to be corrected if they are to be used with 298 K values for neutrals.[23] Since it has not been possible to make these corrections there could be errors of tens of kJ mol^{-1} in the values in Table 3.

TABLE 3

Enthalpies of formation (kJ mol^{-1}) at 298 K of alternative pairs of products from the McLafferty rearrangement in hexanal, 3-methylpentanal, and 4-methylpentanal

Identity of C_4H_8	$\Delta H_f([CH_2{=}CHOH]^{+\cdot})$ $+\Delta H_f(C_4H_8)$	$\Delta H_f(CH_2{=}CHOH)$ $+\Delta H_f([C_4H_8]^{+\cdot})$
But-1-ene	757	801
trans-But-2-ene	746	747
cis-but-2-ene	750	747
2-Methylpropene	740	747
	$\Delta H_f(CH_3CHO)$ $+\Delta H_f([C_4H_8]^{+\cdot})$	
But-1-ene	759	
trans-But-2-ene	705	
cis-But-2-ene	705	
2-Methylpropene	705	

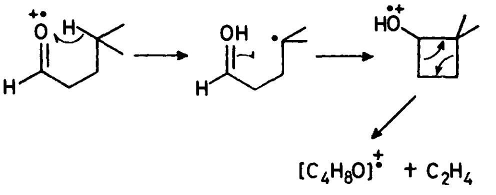
If the McLafferty rearrangements in hexanal, 3-methylpentanal, and 4-methylpentanal did not have reverse activation energies, the figures in Table 3 would indicate the relative magnitudes of forward activation energies. It would then follow that the activation energies for formation of $[CH_2{=}CHOH]^{+\cdot}$ + $CH_3CH{=}CHCH_3$ and $CH_2{=}CHOH$ + $[CH_3CH{=}CHCH_3]^{+\cdot}$ (from anyone of the precursors) were similar, while that for $[CH_2{=}CHOH]^{+\cdot}$ + $(CH_3)C{=}CH_2$ was lower than that for $CH_2{=}CHOH$ and $[(CH_3)_2C{=}CH_2]^{+\cdot}$. If these were the facts, the mechanistic explanation (Schemes 3, 4, 7, and 8) of the kinetics for hexanal, 3-methylpentanal, and 4-methylpentanal would be undermined. Two points concerning the enthalpies in Table 3 and their significance to the kinetics need, however, to be considered. The first is the obvious fact that the McLafferty rearrangements may have reverse activation energies. Contrary to what has been suggested,[19] the observation of a narrow metastable peak for formation of $[C_4H_8]^{+\cdot}$ from hexanal does not necessarily indicate the absence of a reverse activation energy. A process such as this involving hydrogen transfer and separation into two relatively massive entities could well partition much of any reverse activation energy into products' vibrations.[29] Secondly, the enthalpies in Table 3 may be significantly in error, due to the temperature effect already discussed and due to the lack of a measured value for $\Delta H_f(CH_2{=}CHOH)$.

In conclusion it is probable that the enthalpies in Table 3 do not provide a sufficiently accurate guide to the relative magnitudes of the forward activation energies of the various possible decompositions. It is, perhaps, worth noting that if the formation of $[C_2H_4O]^{+\cdot}$ from these six-carbon aldehydes were to have a reverse activation of say 20 kJ mol^{-1} greater than that of the $[C_4H_8]^{+\cdot}$ process, the figures in Table 3 would lead to relative values for forward activation energies which would be consistent with the mechanistic rationale proposed (Schemes 3, 4, 7, and 8).

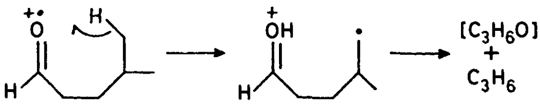
Elimination of Neutral Alkenes.—The product ions $[C_3H_6O]^{+\cdot}$ with pentanal (Figure 2), $[C_3H_6O]^{+\cdot}$ and $[C_4H_8O]^{+\cdot}$ with each of 2-methylpentanal (Figure 3), 3-methylpentanal (Figure 4), 4-methylpentanal (Figure 5), and hexanal (Figure 6) correspond to loss of either ethylene or propene from the molecular ions.

With hexanal there are two processes effecting loss of ethylene following FI.[1,10,11] In one, C-2 and -3 are contained in the eliminated alkene, and in the other C-5 and -6. Assuming both processes are operative in the isomers, $[C_3H_6O]^{+\cdot}$ is formed by loss of C-2 and -3 (and associated methyl) from 3-methylpentanal and $[C_4H_8O]^{+\cdot}$ by loss of C-4 and -5. With 4-methylpentanal, $[C_3H_6O]^{+\cdot}$ is due to loss of C-4 (plus associated methyl) and C-5 and $[C_4H_8O]^{+\cdot}$ to C-2 and -3 loss. With 2-methylpentanal, $[C_4H_8O]^{+\cdot}$ is formed by loss of C-4 and -5.

Considering the results for 3-methylpentanal (Figure 4), the rate of formation of $[C_3H_6O]^{+\cdot}$ is greater than that of $[C_4H_8O)^{+\cdot}$ at all times, *i.e.* the internal elimination is always faster than the terminal. Similarly, formation of $[C_4H_8O]^{+\cdot}$ is always faster than formation of $[C_3H_6O]^{+\cdot}$ with 4-methylpentanal (Figure 5), *i.e.* internal elimination is faster than terminal. The appearance energies for the ions formed from 3- and 4-methylpentanal by internal ethylene loss are lower than those of the ions formed by terminal loss (Table 1). A mechanism (Scheme 9) involving γ-hydrogen transfer has been proposed[11] to account for the internal loss of ethylene from aldehyde ions; the terminal loss is probably initiated by transfer of a hydrogen from the terminal carbon (Scheme 10).



Scheme 9



Scheme 10

If these mechanisms (Schemes 7 and 8) are correct, the two processes effecting alkene loss are only competitive at their initial steps. The terminal hydrogen transfer competes with the γ-hydrogen transfer, but the decomposition of the intermediates so formed will proceed independently. The internal elimination initiated by γ-hydrogen transfer must in fact compete with the McLafferty rearrangements, which it does most successfully at long times (Figures 4—6). This is in agreement with the measured appearance energies.

Elimination of Water.—The ions $[C_5H_8]^{+\cdot}$ with pentanal and $[C_6H_{10}]^{+\cdot}$ with hexanal and its isomers correspond to elimination of water from the molecular ions. The rates of water loss vary very considerably from molecule to molecule. Water loss is least important with 2-methylpentanal and most important with hexanal (Figures 2—6). The appearance potential of $[M - H_2O]^{+\cdot}$ with 2-methylpentanal is not reported (Table 1), because the ion intensity was too weak to obtain reproducible results. That of the $[M - H_2O]^{+\cdot}$ from hexanal is lower than that of any of the other $[M - H_2O]^{+\cdot}$ ions (Table 1).

Conclusions.—Evidence is provided for the existence of an intermediate in the McLafferty rearrangement. The electron impact results[10,11] which suggested that expulsion of C-2 and -3 is preferred over the expulsion of the terminal carbons are supported.

EXPERIMENTAL

The FIK measurements were made with a home-built FI source on a G.E.C.–A.E.I. MS9, and the results analysed using standard methods.[17,30] The appearance potential measurements were obtained by Lossing's semi-log plot method[31] using iodomethane as a standard [I(M) 9.61 eV] and were measured on a standard G.E.C.–A.E.I. MS9 electron bombardment source using 8 kV accelerating potential. Pentanal, 2-methylpentanal, and hexanal were used after being freshly distilled from commercially obtained samples. 3-Methylpentanal was prepared from 2-methylbutanol, and 4-methylpentanal from 3-methyl-1-bromobutane by standard methods.[32]

APPENDIX

Justification of Our Method of determining Semi-quantitative Appearance Potential Differences.—This discussion concerns only this paper. For 3-methylpentanal and hexanal the appearance potential differences for the pairs of ions produced by the McLafferty rearrangement agree semiquantitatively with those of Holmes *et al.*[19] Their values were determined using a monoenergetic electron source. Some ions, derived from simple alkyl ketones have had their appearance potentials determined both by using a monoenergetic source and the semi-log method on data obtained on our MS9. As long as the semi-log plot for an ion was parallel to that of the standard then the appearance potentials determined by both methods agreed within 0.20 eV.[21] Thus if the semi-log plots for two ions are parallel it is likely that their appearance potential difference, derived from these plots, is semiquantitatively correct. These plots are parallel for the pairs of ions produced by the McLafferty rearrangement both in the cases of pentanal, 2- and 4-methylpentanal, as well as for 3-methylpentanal and hexanal. This is also the case for the semi-log plots from which the appearance potential differences, discussed under the heading ' Elimination of Neutral Alkenes ', were obtained. The only case discussed, for which the plots are not parallel is for the pair of ions produced by the McLafferty rearrangement in the case of 2-methylpentanal. However our experimental assignment is consistent with the fact that $I(C_3H_6) > I(CH_2{=}CHOH)$, the latter in turn being likely to be greater than $I(CH_3CH{=}CHOH)$, judging by the normal effect of methylation on ionisation potentials.[23]

We are grateful to the Ramsay Memorial Fellowships Trust for the award of General Fellowship (to P. J. D.) and to the S.R.C. for a maintenance grant (to R. P. M.). The setting up of the apparatus was made possible by two separate grants from the Central Research Fund, University of London. We are indebted to Schick Safety Razor Company for generous gifts of razor blades. We acknowledge valuable technical help from Dr. M. A. Baldwin, J. T. Hill, and C. Cooksey. We are also pleased to acknowledge valuable advice from Professor A. Maccoll.

[8/350 *Received, 27th February*, 1978]

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