Unimolecular Decomposition in the Picosecond Time-frame following Field Ionization of Acyclic C_4H_8 Alkenes

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The kinetics of decomposition of ^2H- and ^{13}C-labelled but-1-ene and 2-methylpropene and ^2H-labelled cis-but-2-ene following field ionization have been determined in the picosecond time-frame. Mechanisms are proposed to account for the major decomposition processes. Carbon randomization in the [but-1-ene]$^{+\cdot}$ ion is a relatively slow process, and it is suggested that this fact could be due to slow vibrational relaxation.

THE gaseous radical-cations formed by ionization of C_4H_8 alkenes undergo extensive intramolecular rearrangement prior to or during unimolecular decomposition.[1] The electron-impact (EI) mass spectra of but-2-ene, but-1-ene, and 2-methylpropene are similar, and isotopic randomization is evident in the spectra of ^2H- and ^{13}C-labelled compounds.[1,2] Photolysis followed by product analysis indicates that isomerizations of the $[C_4H_8]^{+\cdot}$ species also occur below the decomposition threshold.[3] There are, however, probably stable ions, i.e. wells on the $[C_4H_8]^{+\cdot}$ potential energy hypersurface, corresponding to each of the [but-1-ene]$^{+\cdot}$, [but-2-ene]$^{+\cdot}$, and [2-methylpropene]$^{+\cdot}$ structures.[3] Ion-photodissociation provides evidence for the existence of stable [but-1-ene]$^{+\cdot}$ ions.[4] Collisional activation measurements distinguish a [2-methylpropene]$^{+\cdot}$ ion from [but-1-ene]$^{+\cdot}$ and [but-2-ene]$^{+\cdot}$ ions,[5] as has an ion–molecule reaction study.[6] The relative metastable abundances for decomposition of $[C_4H_8]^{+\cdot}$ following EI are the same for all the alkene isomers,[7] and the metastable peak shapes are the same for a number of decompositions.[8] The translational energy released during the formation of $[C_3H_5]^+$ in the EI source (i.e. faster decomposition) is, however, larger with 2-methylpropene than with but-1-ene.[9] The heats of formation of the threshold $[C_3H_5]^+$ ions following EI are the same for all six isomers and indicate an allyl structure.[1,10]

Field ionization kinetics (FIK) shows that these intramolecular rearrangements of $[C_4H_8]^{+\cdot}$ ions can be extremely fast (occurring within 10 ps).[11–13] Indeed, the ions from all the neutral isomers, with the exception of cyclobutane, isomerize to a common structure or mixture of structures prior to decomposition in nanoseconds.[13] FIK results [11,12] for deuterium labelled but-1-ene and 2-methylpropene suggest that 1,3-allylic hydrogen shifts are one type of reaction important in the rearrangement of $[C_4H_8]^{+\cdot}$ species. It is, however, clear that in order to fully elucidate this system, FIK measurements on both ^{13}C- and ^2H-labelled species are necessary. In this paper we report such measurements on [4-^{13}C]but-1-ene, [4,4,4-$^2H_3$]but-1-ene, cis-[2,3-$^2H_2$]but-2-ene, [2-^{13}C]-2-methylpropene, and [1,1-$^2H_2$]-2-methylpropene.
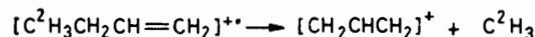
EXPERIMENTAL

The field ionization (FI) source was designed and constructed at University College for a GEC-AEI MS-9 double-focusing mass spectrometer;[14] the emitter is a razor blade
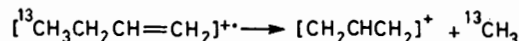
manufactured by the Schick Safety Razor Company. The FIK technique and the procedure for interpreting the results has been described fully.[14–16] The source was at ambient temperature throughout and the sample pressures were in the range 10^{-4}—10^{-3} Pa according to the source ion gauge. The experimental curves of ion current of a particular fragment as a function of the potential on the blade emitter were converted to the distributions of molecular ion lifetimes (from 20 ps to ns) using conformational transformation to obtain the equipotential distribution and numerical integration to obtain the ion trajectory. A fuller description of this method can be found elsewhere.[17]

RESULTS AND DISCUSSIONS

The normalized rates of decomposition of but-1-ene, cis-but-2-ene, and 2-methylpropene to form $[C_3H_5]^+$, $[C_3H_4]^{+\cdot}$, and $[C_2H_4]^{+\cdot}$ following FI are shown in Figure 1. Figures 2 and 3 show the normalized rates of decomposition of ionized [4-^{13}C]but-1-ene and [4,4,4-$^2H_3$]but-1-ene respectively to form fragments corresponding to $[C_3H_5]^{+\cdot}$ and $[C_3H_4]^{+\cdot}$ with the unlabelled compounds. These results support the view [12,13] that at the shortest times loss of a methyl radical occurs by direct elimination of the allylic methyl (C-4) from the unrearranged molecular ion (Schemes 1 and 2).

$$[C^2H_3CH_2CH{=}CH_2]^{+\cdot} \longrightarrow [CH_2CHCH_2]^+ + C^2H_3$$

SCHEME 1

$$[^{13}CH_3CH_2CH{=}CH_2]^{+\cdot} \longrightarrow [CH_2CHCH_2]^+ + {}^{13}CH_3$$
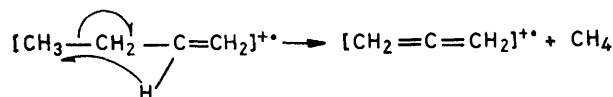
SCHEME 2

At longer times isomerization can occur prior to decomposition, and the ratios of the rates of formation of the various isotopic isomers move towards the statistically random values. The ratios of the rates of formation of m/e 41 (both $[C_3H_5]^+$ and $[C_3H_3{}^2H]^+$), 42 ($[C_3H_4{}^2H]^+$ and $[C_3H_2{}^2H_2]^{+\cdot}$), 43 ($[C_3H_3{}^2H_2]^+$ and $[C_3H{}^2H_3]^{+\cdot}$), and 44 $[C_3H_2{}^2H_3]^+$ are close to random at 500 ps (assuming the relative rates of loss of methyl and methane are the same as in the unlabelled compound). On the other hand, the ratio (1 : 1.5) of the rates of formation of m/e 41 $[C_3H_5]^+$ and $[^{13}CC_2H_4]^{+\cdot}$ and 42 $[^{13}CC_2H_5]^+$ from [4-^{13}C]but-1-ene is far removed from the calculated

random value (1 : 3). The ^{13}C label has probably lost all positional identity however before decomposition at times >1 μs, as the intensity ratio of the metastables for the loss of ^{12}CH$_3$ and ^{13}CH$_3$ from $[M]^{+\cdot}$ is 2.7 ± 0.1 : 1. One immediate conclusion is that the hydrogen rearrangements in [but-1-ene]$^{+\cdot}$ formed by FI are faster than its skeletal rearrangements. It also follows that the skeletal rearrangements in [but-1-ene]$^{+\cdot}$ are slower than in [2-methylpropene]$^{+\cdot}$ (*vide infra*).

The high probability of $[M - CH_3]^+$ formation at

(a)

(b)

(c)

FIGURE 1 The normalized rates of decomposition of (a) but-1-ene, (b) *cis*-but-2-ene, and (c) 2-methylpropene to form [C$_3$H$_5$]$^+$, [C$_3$H$_4$]$^{+\cdot}$, and [C$_2$H$_4$]$^{+\cdot}$ after FI

FIGURE 2 The normalized rates of decomposition of [4-^{13}C]-but-1-ene to give [^{13}CC$_2$H$_5$]$^+$ and [C$_3$H$_5$]$^+$ after FI

FIGURE 3 The normalized rates of decomposition of [4,4,4-^{2}H$_3$]-but-1-ene to give [C$_3$H$_{5-n}$^{2}H$_n$]$^+$ and [C$_3$H$_{4-n}$^{2}H$_n$]$^{+\cdot}$ (*n* ⩽ 3) after-FI

short times from ionized [4,4,4-^{2}H$_3$]but-1-ene is consistent with the facile, successive, 1,3 allylic [11-13] shifts outlined in Schemes 1—3. Since $[M - {}^{13}CH_3]^+$ and $[M - CH_3]^+$ have equal intensities at *ca.* 80 ps for ionized [4-^{13}C]but-1-ene, and $[M - C^2H_3]^+$ and $[M - CH_3]^+$ have equal intensities at *ca.* 100 ps for ionized [4,4,4-^{2}H$_3$]but-1-ene, this suggests that by *ca.* 100 ps about half the

$$[CH_2=CHCHC^2H_3]^{+\cdot} \longrightarrow [CH_3CH=CHC^2H_2]^+$$
$$\underset{H}{\underbrace{\qquad}} \qquad \underset{{}^2H}{\underbrace{\qquad}}$$

$$[CH_3CH^2HCH=C^2H_2]^{+\cdot} \longrightarrow CH_3\cdot + [CH^2HCHC^2H_2]^{+\cdot}$$

SCHEME 3

molecular ions capable of decomposing have gone through two 1,3-hydrogen shifts.

It is significant that while neither *m/e* 40 [$M -$ CH^{2}H$_3$]$^{+\cdot}$ nor [$M - {}^{13}$CH$_4$]$^{+\cdot}$ is observed at short times with [4,4,4-^{2}H$_3$]but-1-ene and [4-^{13}C]but-1-ene respectively; the metastable peaks are observed. We conclude that the 1,3-shift (Scheme 4) to expel methane does *not* occur. The reaction is thermodynamically favoured,
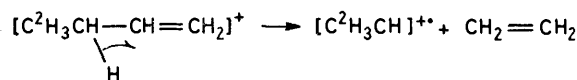
and so presumably its non-occurrence reflects unfavourable kinetics. The vinylic C–H bond rupture may require a large activation energy.

The loss of ethene from [but-1-ene]$^{+\bullet}$ splits the molecule into two halves. Following FI of [4-^{13}C]but-1-ene there is a marked preference for formation of

SCHEME 4

SCHEME 5

[^{13}CCH$_4$]$^{+\bullet}$ over [C$_2$H$_4$]$^{+\bullet}$ at short times (Figure 4); the preferred species [18] at short times following FI of [4,4,4-^{2}H$_3$]but-1-ene are [C$_2$H^{2}H$_3$]$^{+\bullet}$ and [C$_2$H$_3$^{2}H]$^{+\bullet}$ (Figure 5). These observations are explained by the mechanisms shown in Schemes 5 and 6.

The charge localization is attributed to the much lower activation energy for the process giving [CH$_3$CH$^\bullet$]$^{+\bullet}$ and CH$_2$=CH$_2$ as compared with that giving [CH$_2$=CH$_2$]$^{+\bullet}$ and CH$_3$CH$^\bullet$. Assuming that in the transition states the
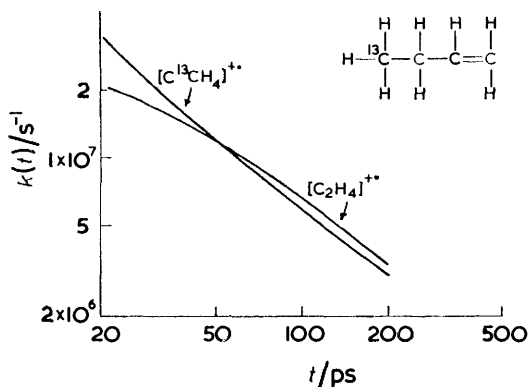
FIGURE 4 The normalized rates of decomposition of [4-^{13}C]-but-1-ene to give [^{13}CCH$_4$]$^{+\bullet}$ and [C$_2$H$_4$]$^{+\bullet}$ after FI
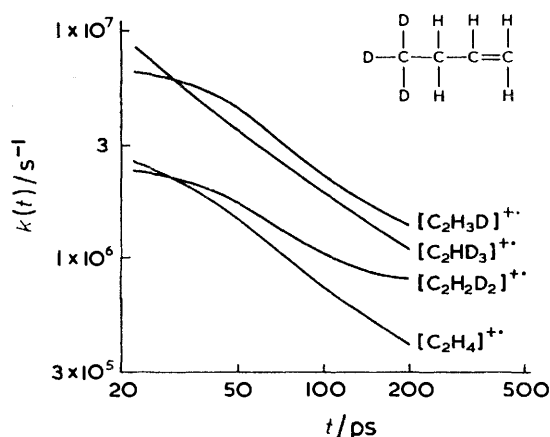
FIGURE 5 The normalized rates of decomposition of [4,4,4-^{2}H$_3$]but-1-ene to give [C$_2$H$_{4-n}$^{2}H$_n$]$^{+\bullet}$ ($n \leqslant 3$) after FI
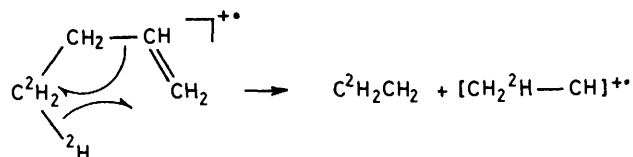
SCHEME 6

only difference is the charge location then $E_{[CH_3 = CH_2]^{+\bullet}}$ — $E_{[CH_3CH]^{+\bullet}}$ is given by equation (1) which reduces to (2),

$$E_{[CH_2 = CH_2]^{+\bullet}} - E_{[CH_3CH]^{+\bullet}} =$$
$$\Delta H_f[CH_2=CH_2]^{+\bullet} + \Delta H_f(CH_3CH^\bullet) -$$
$$\Delta H_f[CH_3CH]^{+\bullet} - \Delta H_f(CH_2=CH_2) + \Delta E_{rev} \quad (1)$$
$$= I(CH_2=CH_2) - I(CH_3CH^\bullet) + \Delta E_{rev} \quad (2)$$

$$\Delta E_{rev} = E_{rev}([CH_2=CH_2]^{+\bullet}) - E_{rev}([CH_3CH]^{+\bullet}) \quad (3)$$

where ΔE_{rev} is defined by (3) in which E_{rev} denotes the reverse activation energy for the formation of the ion
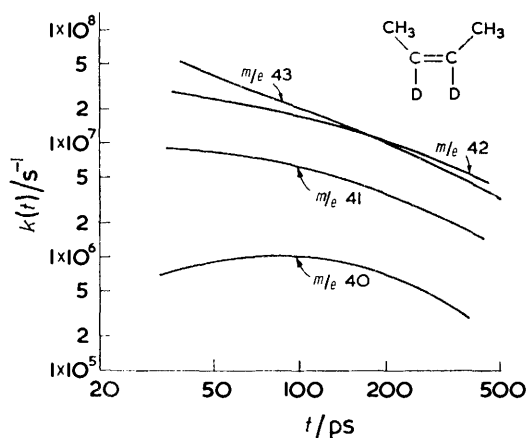
FIGURE 6 The normalized rates of decomposition of cis-[2,3-^{2}H$_2$]but-2-ene to give [C$_3$H$_{5-n}$^{2}H$_n$]$^+$ and [C$_3$H$_{4-n}$^{2}H$_n$]$^{+\bullet}$ ($n < 2$) after FI

indicated in parentheses. If we assume $\Delta E_{rev} = 0$, since we have no method of estimating it, then the calculations of Lorquet and Lorquet [19] show that the right hand side of equation (1) is positive. It should be said that the absolute value calculated by these authors for $\Delta H_f[CH_2=CH_2]^{+\bullet}$ is not in good agreement with the experimental value.[20] If we put $\Delta E_{rev} = 0$ in (2) then the right hand side can be shown to be positive from the following argument. $I(CH_2^\bullet) - I(CH_2=CH_2) = -0.05$ eV [20] and from empirical observations [1,21] the effect of replacing a hydrogen by a methyl group on the charge bearing atom is to lower the ionization potential by between 0.5 and 1 eV. When it is the first hydrogen which is replaced the value is often nearer 1 eV. Thus the right hand side of (2) is likely to be >0.5 eV.

The results for loss of methyl radical and methane from cis-[2,3-^{2}H$_2$]but-2-ene after FI are shown in Figure 6. The predominant process at short times clearly involves loss of one of the original methyl groups. The shape of the curve for methyl loss from the unlabelled compound (Figure 1) would be consistent with concomitant rearrangement such that the product ion had
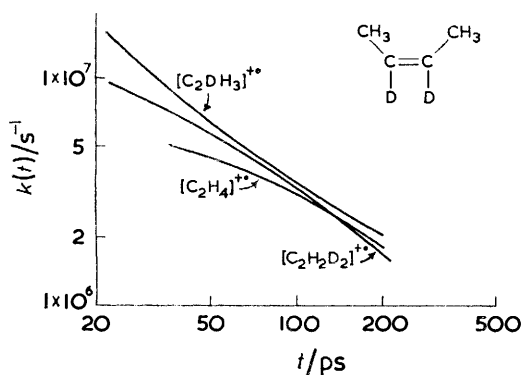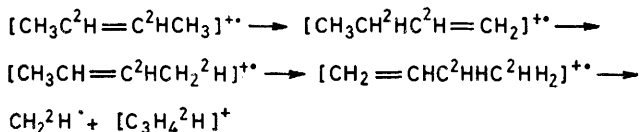
FIGURE 7 The normalized rates of decomposition of cis-[2,3-^{2}H$_2$]-but-2-ene to give [C$_2$H$_{4-n}$^{2}H$_n$]$^+$ ($n \leqslant 2$) after FI

the allyl structure. The intense signal at m/e 42 at short times must be due mainly to $[M - CH_2{}^2H]^+$ rather than $[M - CH_4]^{+\cdot}$, since methyl loss is over an order of magnitude more probable than methane loss at these times (Figure 1). This formation of $[M - CH_2{}^2H]^+$ is as expected (Scheme 7) given that 1,3-allylic hydrogen shifts are facile reactions.[11-13]

$[CH_3C^2H=C^2HCH_3]^{+\cdot} \longrightarrow [CH_3CH^2HC^2H=CH_2]^{+\cdot} \longrightarrow$

$[CH_3CH=C^2HCH_2{}^2H]^{+\cdot} \longrightarrow [CH_2=CHC^2HHC^2HH_2]^{+\cdot} \longrightarrow$

$CH_2{}^2H^{\cdot} + [C_3H_4{}^2H]^+$

SCHEME 7

Results for the loss of ethene from cis-[2,3-^{2}H$_2$]but-2-ene after FI are shown in Figure 7. The curve for this process in the unlabelled compound has the characteristics of a direct bond cleavage, in that probability of reaction increases as time decreases. Direct cleavage of the C(2)–C(3) bond is however unlikely, because the combined heat of formation of the carbene CH_3CH and the carbene ion $[CH_3CH]^{+\cdot}$ is very high.[19] Some rearrangement is therefore likely, perhaps as shown in Scheme 8. This Scheme does not however explain the

$[CH_3C^2H=C^2HCH_2]^{+\cdot} \longrightarrow [CH_3C^2H]^{+\cdot} + CH_2=CH_2$
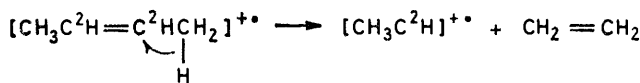
SCHEME 8

high relative intensity of $[C_2H_2{}^2H_2]^{+\cdot}$ at short times. Indeed even at 200 ps this ion has a very high intensity, much higher than that expected for complete loss of positional identity of the hydrogens ($[C_2H_4]^{+\cdot} : [C_2H_3{}^2H]^{+\cdot} : [C_2H_2{}^2H_2]^{+\cdot}$ 3 : 8 : 3).

The results for loss of methyl and methane from ionized [2-^{13}C]-2-methylpropene are shown in Figure 8. Assuming the rates of methyl and methane loss are the same in this labelled molecule as in the unlabelled, the ion current at m/e 41 can be resolved into two components. Corresponding results for ionised [1,1-^{2}H$_2$]-2-methylpropene are shown in Figure 9. Clearly at short times the original methyl groups are eliminated, probably accompanied by rearrangement to form the allyl ion,[12] which is more stable than the ion formed by

direct cleavage. The loss of methane can be attributed to a 1,3-shift (Scheme 9). It is interesting to note that complete loss of carbon positional identity does not occur even in the low electron volt spectrum of the 2-^{13}C compound for the loss of methyl, but only in those ions
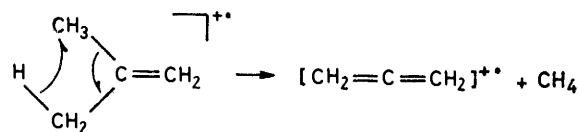
SCHEME 9

decomposing in the first field-free region. This must be due to the average internal of those ions decomposing after electron impact in the source being higher than those ions decomposing after field ionization.

The results for ethylene loss from the labelled 2-methylpropenes are shown in Figure 10, and have been reported in a communication.[22] The mechanism involving a methylcyclopropane intermediate was proposed (Scheme 10) and the charge localization is as shown for reasons discussed earlier. The high intensity of m/e 28 $[C_2H_4]^{+\cdot}$ at short times in the case of [1,1-^{2}H$_2$]-2-methyl-propene is in keeping with this mechanism. The effect is
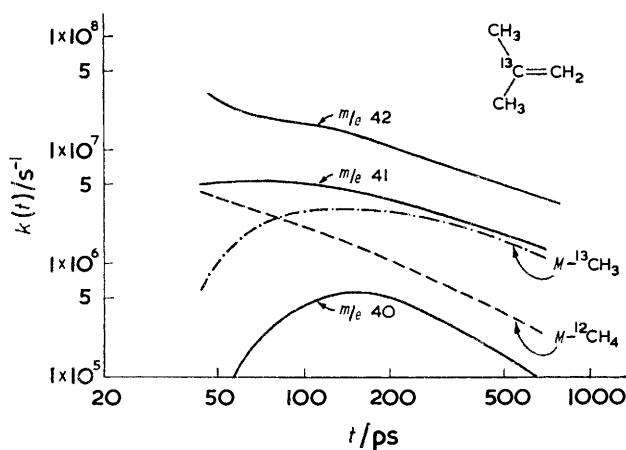

FIGURE 8 The normalized rates of decomposition of [2-^{13}C]-2-methylpropene to give [^{13}CC$_2$H$_5$]$^+$, [C$_3$H$_5$]$^+$, [^{13}CC$_2$H$_4$]$^{+\cdot}$, and [C$_3$H$_4$]$^{+\cdot}$ after FI
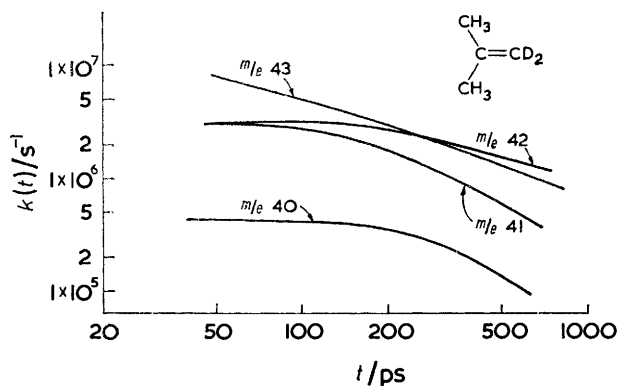
FIGURE 9 The normalized rates of decomposition of [1,1-^{2}H$_2$] 2-methylpropane to give [C$_3$H$_{5-n}$^{2}H$_n$]$^+$ and [C$_3$H$_{4-n}$^{2}H$_n$]$^{+\cdot}$ ($n \leqslant 2$) after FI
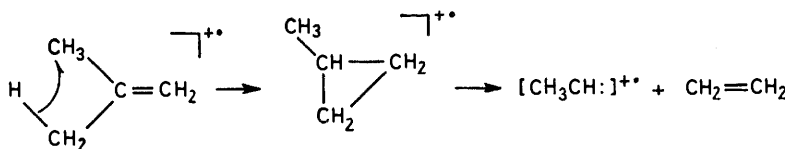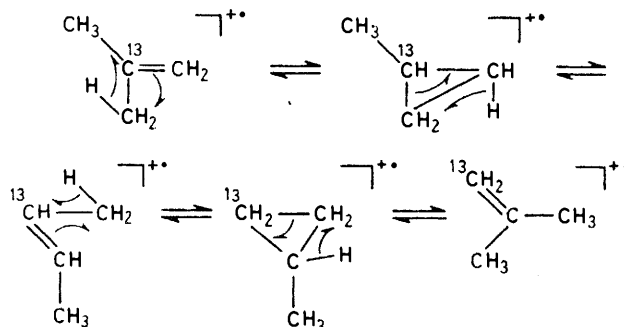
SCHEME 10

not so marked as in the ^{13}C-labelled compound, as 1,3-hydrogen shifts, which are rapid but do not result in skeletal scrambling, will result in a quicker drop off in the intensity of the $[C_2H_4]^{+\cdot}$ ion.

Considering Figure 8, it can be seen that C(2) is lost as methyl from ionized 2-methylpropene in statistical proportion at times as short as 200 ps. This contrasts sharply with ionized but-1-ene where random loss of carbon as methyl has not been arrived at by 500 ps. The explanation for this differing behaviour is not simple. It is clear that loss of the central C(2) from [2-methylpropene]$^{+\cdot}$ as methyl demands extensive rearrangement, and this apparently occurs relatively rapidly. It has been suggested [14] that the [but-2-ene]$^{+\cdot}$ and [methylcyclopropane]$^{+\cdot}$ ions can interconvert within very short times (10 ps), and that [2-methylpropene]$^{+\cdot}$ ions rearrange to a [methylcyclopropane]$^{+\cdot}$ structure during the rapid loss of ethylene.[22] The loss of positional identity of carbon atoms following ionization of 2-

methylpropane might therefore be reasonably attributed to isomerizations to and from [but-2-ene]$^{+\cdot}$ via [methylcyclopropane]$^{+\cdot}$ (Scheme 11). There is also strong evidence (Scheme 3) that [but-1-ene]$^{+\cdot}$ and [but-2-

SCHEME 11

ene]$^{+\cdot}$ ions can interconvert. (It should be noted that isomerization of [{4-[13]C}but-1-ene]$^{+\cdot}$ to [cis-{1-[13]C}but-2-ene]$^{+\cdot}$ followed by Scheme 8 would result in an apparent loss of positional identity of the ^{13}C atom for the loss of ethylene).

If this theory is correct, the outstanding question is why does the [but-1-ene]$^{+\cdot}$ ion not rearrange at short times to [but-2-ene]$^{+\cdot}$ and thence to [2-methylpropene]$^{+\cdot}$, thereby entering a reaction sequence which would destroy the positional identities of the carbon atoms? It appears that at short times the [but-2-ene]$^{+\cdot}$ ion formed from [but-1-ene]$^{+\cdot}$ would prefer to isomerize back or forwards to [but-1-ene]$^{+\cdot}$, rather than rearrange to [2-methylpropene]$^{+\cdot}$ {despite the fact that the [2-methylpropene]$^{+\cdot}$ ion has a lower (by 55 kJ mol^{-1}) heat of formation than the [but-1-ene]$^{+\cdot}$ ion}. In contrast a significant proportion of [but-2-ene]$^{+\cdot}$ formed from [2-methylpropene]$^{+\cdot}$ must isomerize back to [2-methylpropene]$^{+\cdot}$ otherwise the carbons could not be randomized. There is no reason to suppose that the internal energy content of the [but-2-ene]$^{+\cdot}$ ions formed from [but-1-ene]$^{+\cdot}$ would differ significantly from that of but-2-ene ions formed from 2-methylpropene. The supposed differences in behaviour might, however, be due to differing distributions of that energy among the internal degrees of freedom.[2,*] This would necessitate that rate

FIGURE 10   The normalized rates of decomposition of [2-^{13}C]-2-methylpropene to give [[13]CCH$_4$]$^+$ and$\cdot$ [C$_2$H$_4$]$^{+\cdot}$ and of [1,1-[2]H$_2$]-2-methylpropene to give [C$_2$H$_{4-n}$[2]H$_n$]$^{+\cdot}$ ($n \leqslant 2$) after FI

* It has been suggested that internal energy is not randomized prior to loss of CH$_3$$\cdot$ from [CH$_3$COCH$_3$]$^{+\cdot}$ species formed by rearrangement of the enol [CH$_3$COHCH$_2$]$^{+\cdot}$ (F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfeld, J. Amer. Chem. Soc., 1971, 93, 3720. Vibrational relaxation in stilbene seems to be slower than cis–trans isomerization (50 ns) (M. H. Hui and S. A. Rice, J. Amer. Chem. Phys., 1974, 61, 833). Chemical activation studies on bicyclopropyl species find rate constants of 10^{12} s^{-1} for intramolecular energy randomization (J. D. Rynbrandt and B. S. Rabinovitch, J. Chem. Phys., 1971, 54, 2275). For a current view of vibrational relaxation see P. J. Robinson in ' Reaction Kinetics ', ed. P. G. Ashmore, Specialist Periodical Report, The Chemical Society, 1975, vol 1, p. 96.
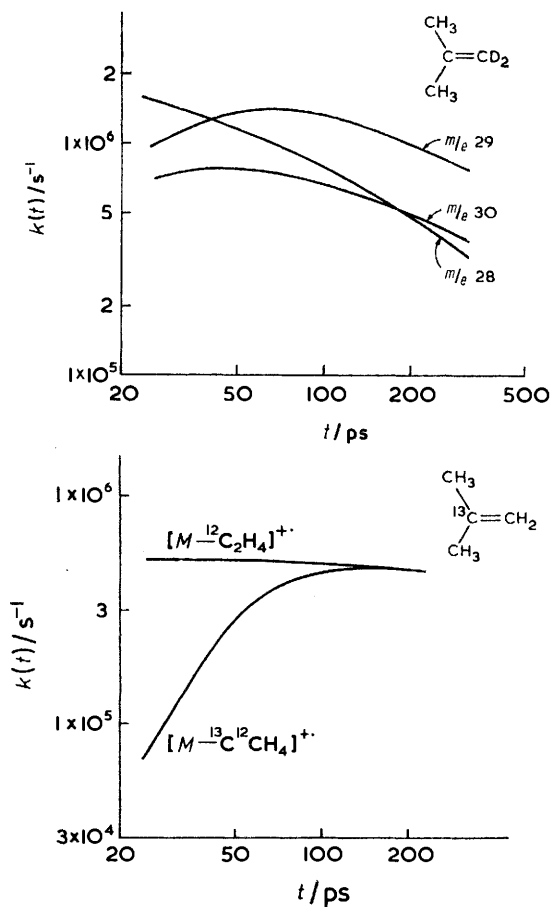
at which energy flows among certain normal modes be comparable to or slower than reaction rates. It would be reasonable to suppose that the hydrogen shift converting the [but-1-ene]$^{+\cdot}$ ion to the [but-2-ene]$^{+\cdot}$ would be associated with excitation of C–H modes (it should be borne in mind that there could be as few as four vibrational quanta). The conversion of the [2-methylpropene]$^{+\cdot}$ ion to [but-2-ene]$^{+\cdot}$ via [methylcyclopropane]$^{+\cdot}$ might reasonably be expected to demand excitation of C–C torsions and bends. If the flow of energy between these two types of modes were to occur relatively slowly ($>$ ps) a [but-2-ene]$^{+\cdot}$ ion formed from [but-1-ene]$^{+\cdot}$ in the picosecond time-frame might be energized in such a way that it would prefer to undergo hydrogen rather than carbon rearrangements. In this way, the slow randomization of carbon atoms in the but-1-ene ion would be explained. This difference in behaviour is consistent with the difference in translational energy released in the EI source [9] on formation of C_3H_5 from 2-methylpropene and but-1-ene.

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