Unimolecular Gas-phase Hydrogen Randomization within 2-Methylpropane Radical Cations

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The low and high energy electron impact (EI) mass spectra and the field ionization (FI) mass spectra of 2-methylpropane, 2-methyl[2-^{2}H]propane, and 2-[^{2}H$_3$]methyl[1,1,1,3,3,3-^{2}H$_6$]propane have been measured. Metastable transitions following FI have been measured. There is no hydrogen–deuterium randomization within the molecular ions following FI. There is partial randomization prior to the formation of methyl ions following high energy EI, but not prior to the loss of methane. Hydrogen randomization within the 2-methylpropane ion is seen as having a high activation energy and a high frequency factor.

HYDROGEN randomization within organic ions in the gas phase has been extensively documented over the past few years.[1-9] With aromatic ions and with aliphatic ions containing functional groups it appears to be a low-energy process.[1,2] Such processes can in fact occur at energies which would be too low to induce any decomposition reaction.[10] When hydrogen randomization processes must compete with decomposition, they are often most successful at longer times.[2] In electron impact (EI) studies randomization is typically enhanced relative to decomposition by reducing the kinetic energy of the ionizing electrons.[1,11,12] Such observations have been rationalized [1,2,11] on the basis of the quasi-equilibrium theory,[13] with the assumption that processes responsible for randomization have low activation energy and low frequency factor (low activation entropy). We here report and discuss the fact that randomization processes in the 2-methylpropane radical cation, and hence possibly in all alkane radical cations, do not conform to the foregoing characteristics. The processes in the 2-methylpropane ion appear to demand high energies. This holds mechanistic implication for both the 2-methylpropane ion and other saturated aliphatic molecular ions. That EI mass spectra of partially deuteriated alkanes measured at normal ionizing voltages (50—100 eV) contain evidence of hydrogen–deuterium randomization prior to certain fragmentations of the molecular ion has been known for some time.[14-19] There is, however, much less hydrogen–deuterium randomization prior to the metastable decompositions of the molecular ion [19-22] (corresponding to reaction at *ca.* 10^{-6} s) induced by EI. That there is less evidence of randomization in the metastable peaks than in the mass spectra is in itself of considerable significance (see later).

EXPERIMENTAL

Field ionization (FI) measurements were made with a modified Du Pont (C.E.C.) 21–110B double-focusing mass spectrometer.[23] The standard Du Pont combination FI/EI ion source was employed with the electron collimating magnet removed to avoid mass discrimination. EI mass spectra were measured both on a G.E.C.–A.E.I. MS-902 mass spectrometer on-line to the XDS Sigma 2 LOGOS computer system [24] and on a Varian-Mat 311 mass spectrometer. The deuteriated compounds were supplied by Merck, Sharp, and Dohme. As estimated by FI mass

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spectrometry and by FI kinetics[25] measurements, the percentage composition of the sample supplied as '2-methyl-d_3-propane-1,1,1,3,3,3-d_6' was: $(CD_3)_3CH$, 81; $(CD_3)_3CD$, 11; $(CD_3)_2(CD_2H)CH$, 7. That of the sample supplied as '2-methylpropane-2-d_1' was: $(CH_3)_3CD$, 98; $(CH_3)_3CH$, 2.

RESULTS AND DISCUSSION

The EI mass spectra of 2-methylpropane, 2-methyl-[2-^{2}H]propane (I), and 2-[$^2H_3$]methyl[1,1,1,3,3,3-$^2H_6$]-propane (II) at high (50 eV) and at low (nominally 16 eV) ionizing energies are reproduced in Figure 1.

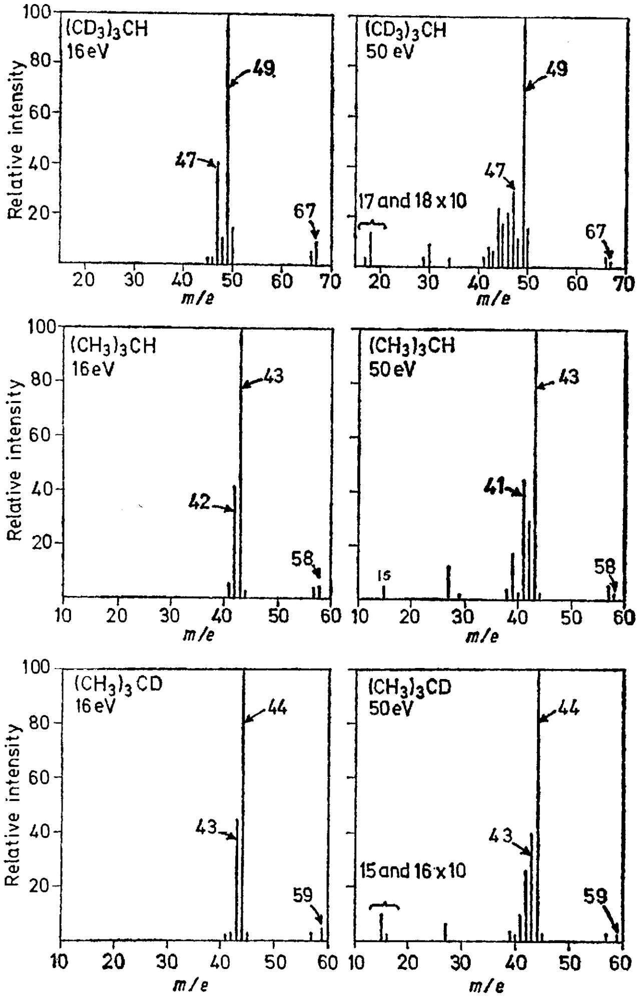

FIGURE 1 The low and high energy EI mass spectra of 2-methylpropane, 2-methyl[2-^{2}H]propane, and 2-[$^2H_3$]methyl-[1,1,1,3,3,3-$^2H_6$]propane

The mass spectra are not corrected either for ^{13}C or for isotopic impurities. Relative intensities of fragment ions after correction for isotopic impurities and ^{13}C are given in Table 1. A search for metastable transitions of the molecular ions following EI proved unsuccessful. The FI mass spectra of 2-methylpropane, (I), and (II) are reproduced in Figure 2. Again the spectra are not corrected for ^{13}C and isotopic impurities. Metastable transitions following FI were measured in the first field-free region by the metastable defocusing technique.[26] Results are shown in Table 2.

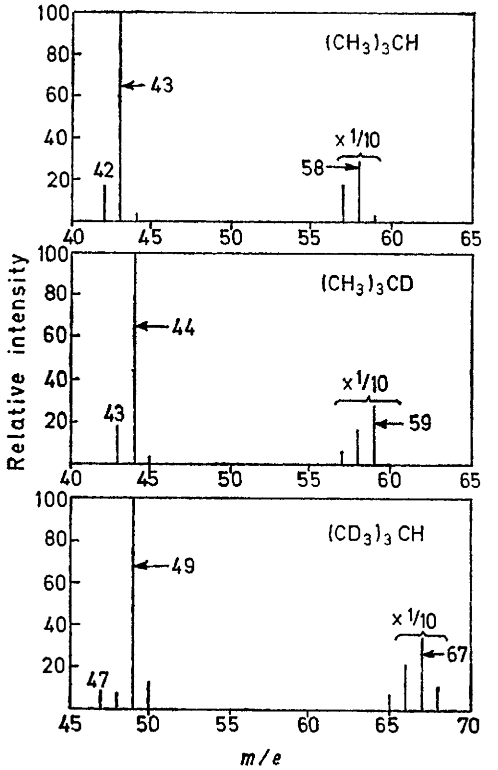

FIGURE 2 The mass FI spectra of 2-methylpropane, 2-methyl [2-^{2}H]propane, and 2-[$^2H_3$]methyl[1,1,1,3,3,3-$^2H_6$]propane

TABLE 1

Relative intensities of selected fragment ions from 2-methyl[2-^{2}H]propane and from 2-[$^2H_3$]methyl-[1,1,1,3,3,3-$^2H_6$]propane following electron impact at high (50 eV) and at low (*ca.* 16 eV) energies[a]

		Intensity	
	m/e	50 eV	16 eV
$(CH_3)_3CD$	15 (CH_3)	77 ± 10	
	16 (CH_2D)	23 ± 10	
	43 ($M - CH_4$)		100
	42 ($M - CH_3D$)		0
$(CD_3)_3CH$	18 (CD_3)	81 ± 10	
	17 (CD_2H)	19 ± 10	
	49 ($M - CD_3$)	97 ± 2	98 ± 2
	50 ($M - CD_2H$)	3 ± 2	2 ± 2
	47 ($M - CD_4$)	100 ± 2	100 ± 2
	48 ($M - CD_3H$)	0 ± 2	0 ± 2

[a] Figures corrected to allow for fragments from isotopic impurities and for ^{13}C.

In the FI mass spectrum of 2-methylpropane (Figure 2a), the important fragments *m/e* 43 and 42 can be identified as $[M - CH_3]^+$ and $[M - CH_4]^{+\cdot}$, respectively. The only other significant peaks are the ions $[M - 1]^+$ and $[M + 1]^+$. Consider now the FI mass

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spectra of the deuteriated species (I) and (II) (Figures 2b and c). It is evident that there is ***no hydrogen–deuterium randomization prior to fragmentation.*** * The *m/e* 48 and 50 fragments in the spectrum of (II) (Figure 2c) must be identified as due to loss of CD_3 from $(CD_3)_2(CD_2H)CH^{+\cdot}$ and from $(CD_3)_3CD^{+\cdot}$, respectively. The fragmentation in the FI mass spectra occurs in the time interval 10^{-14} to 10^{-11} s following FI. We therefore conclude that no hydrogen randomization occurs in the 2-methylpropane ion within 10^{-11} s of FI. Goldenfeld and Korostyshevsky[27] similarly concluded that there is no evidence of either hydrogen or carbon randomization in the FI mass spectra of octane or nonane. Our results support the suggestion[27,28] that FI mass spectrometry can be used to find the location or distribution of isotopes in complex molecules. We stress, however, that the method is not necessarily reliable in all cases, since the FI mass spectra of some compounds, for example alkenes,[2,3,8,29,30] do show evidence of extensive randomization prior to fragmentation.

TABLE 2

Relative intensities of metastable transitions in the first field-free region following field ionization of 2-methylpropane, 2-methyl[2-^2H]propane, and 2-[$^2H_3$]methyl-[1,1,1,3,3,3-$^2H_6$]propane

Transition	Relative intensity
2-Methylpropane	
$58^+ \longrightarrow 42^+$	100 ± 5
2-Methyl[^2H]propane	
$59^+ \longrightarrow 43^+$	102 ± 5
$58^+ \longrightarrow 42^+$	2 ± 1
$59^+ \longrightarrow 42^+$	Undetected (*i.e.* <1)
2-{$^2H_3$]Methyl[1,1,1,3,3,3-$^2H_6$]propane	
$67^+ \longrightarrow 47^+$	167 ± 10
$68^+ \longrightarrow 48^+$	16 ± 2
$66^+ \longrightarrow 47^+$	5 ± 1
$66^+ \longrightarrow 46^+$	5 ± 1
$67^+ \longrightarrow 48^+$	Undetected (*i.e.* <1)

The only metastable transition observed following FI of 2-methylpropane (Table 2) is identified as loss of methane from the molecular ion. All metastable transitions observed within the deuteriated samples similarly represent loss of methanes from molecular ions. The *only* reactions of the deuteriated species in the metastable region are: $(CH_3)_3CD^{+\cdot} \longrightarrow CH_4 + C_3H_5D^{+\cdot}$, and $(CD_3)_3CH^{+\cdot} \longrightarrow CD_4 + C_3D_5H^{+\cdot}$. A specific 1,3-hydrogen (deuterium) transfer is therefore implicated.[25] More pertinent to the present discussion is the fact that there is no significant hydrogen–deuterium randomization prior to loss of methane in the metastable region. We conclude that there is no hydrogen randomization within the 2-methylpropane ion in times less than 10^{-6} s following FI. This behaviour contrasts sharply with that of other aliphatic molecular ions investigated to date.[2] Within times of 10^{-6} s following FI, there appears to be complete hydrogen randomization within 2-methylpropene,[30] but-1-ene,[8] and cyclohexene,[3,29] and extensive hydrogen randomization within ketones,[31,32] aldehydes,[29,33,34] and possibly alcohols.[35]

Consider now the EI mass spectra (Figure 1) and in particular Table 1. There is considerable hydrogen–deuterium randomization prior to the formation of *methyl ions* in the high energy EI mass spectra of the deuteriated analogues (I) and (II), and there appears to be a very small amount of randomization prior to loss of methyl radicals from the molecular ions. There is no randomization prior to loss of methanes. The appearance potential (13·6 eV) of CH_3^+ from 2-methylpropane is at least 2 eV higher than those (11·2 and 10·9 eV, respectively) of $[M - CH_3]^+$ and $[M - CH_4]^{+\cdot}$ (refs. 36 and 37). The formation of $[M - CH_4]^{+\cdot}$ necessitates rearrangement, whereas CH_3^+ and $[M - CH_3]^+$ can be formed by direct bond cleavages. The formation of $[M - CH_4]^{+\cdot}$ would be expected to have a lower frequency factor (if we employ the concepts of the simplified quasi-equilibrium theory[13]) than either of the other reactions. We can assume that the loss of methane competes with loss of methyl and formation of methyl ions only at low energies. A detailed field ionization kinetics (FIK) study[2,25,38] of these reactions of the 2-methylpropane molecular ion strongly supports this assumption. We can say that molecular ions reacting to eliminate methane generally have lower internal energies than those reacting to lose methyl or to form methyl ions. Randomization occurs in the latter molecular ions but not in the former. We conclude, therefore, that randomization in the 2-methylpropane ion demands high internal energies to be able to compete with decomposition. This conclusion is corroborated by the failure to observe any randomization prior to fragmentation *at any time* from 10^{-14} to 10^{-6} s

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* However, no accurate mass measurements were performed to indicate the compositions of the ions. A referee has pointed out that rearrangement among the H(D) atoms of the methyl groups would pass unnoticed with the particular isotopic isomers studied.

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following the low energy FI process.[39] That there is less randomization in the metastable region than in the mass spectrum [19-22] with alkane molecular ions following EI provides additional support. Further, that randomization competes effectively with formation of methyl ions presumably at very high energies suggests that randomization has a high frequency factor (comparable to that for the formation of methyl ions).† A process in which two atoms move simultaneously so that each takes up the position previously occupied by the other [5,16,40] might have such characteristics. The results suggest that hydrogen randomization in the 2-methylpropane ion differs fundamentally from the major randomization processes in functionalized aliphatic ions (*e.g.* alkenes and ketones).

The financial support of the National Aeronautics and Space Administration and the National Science Foundation is acknowledged.

[4/1374 *Received*, 8*th July*, 1974]

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