oil was extracted with chloroform which was dried and evaporated. Most of the compound was precipitated as an oil on crystallization from dilute ethanol, but a solid, mp ca. 110°, with C=O absorption at 1680 cm⁻¹ and the same nmr as α,α-diphenyl-p-methoxyacetophenone was formed. In a similar experiment the ir of the chloroform-extracted oil showed absorptions at 1605 and 1680 cm⁻¹, and an nmr consistent with a mixture of the ketone and 1-anisyl-2,2-diphenyl 1-ethyl ether. For example, a ketone–ether ratio of 1:1 was obtained from the bromide in refluxing basic 80% ethanol for 140 hr.

Attempts for Uncatalyzed Solvolysis of Triphenylvinyl Bromide. Triphenylvinyl bromide and excess triethylamine in 80% ethanol were kept for 20 hr at 150°, for 10 hr with potassium hydroxide in 50% ethanol, or with sodium or lithium acetate in acetic acid at 150° for 7 hr. The starting material was recovered always unchanged in yields higher than 90%.

Solvolysis of Triphenylvinyl Halides in the Presence of Silver Salts. After reflux for 12 hr of triphenylvinyl chloride in acetic acid containing silver acetate, or in 50% ethanol containing silver oxide, the starting material was recovered unchanged. Reaction of triphenylvinyl bromide (6.7 g, 20 mM) with silver acetate (3.5 g, 21 mM) in acetic acid (50 ml) and acetic anhydride (1 ml), for 10 hr at 118°, followed by filtration and addition of water gave triphenylvinyl acetate: mp 104° (lit.[77] mp 104.5–105.5°) (4.6 g, 74%); ir (Nujol) 1780 cm⁻¹; nmr signals in the ratio 1:5 at 114 cps (CO_2Me) and 426–450 cps (aromatic).

Kinetic Runs. Triarylvinyl halide was weighted individually (90–180 mg) into each of seven to eight glass ampoules, prepared according to Grob.[14] Basic 80% ethanol (7 ml) was added, and the cooled (liquid air) ampoule was sealed. The ampoules were heated for a few minutes to ca. 60–70° in order to facilitate dissolution, and introduced into the oil bath. When thermal equilibrium was achieved (0.5–2 min) the ampoules were shaken vigorously until all the oily substrate was dissolved. If this is not done, much lower steady first-order rate coefficients are obtained. The slow solubility causes apparent lower rate coefficients for the first kinetic point compared to later ones. At appropriate intervals the am-

(77) H. Biltz, *Ann.*, **296**, 219 (1897).

poules were taken out, cooled, and opened, and 5-ml samples were titrated against standard silver nitrate using eosin and dichlorofluorescein indicators for the bromide and the chloride ions, respectively.

Halide analyses in experiments with p-toluenethiolate ion cannot be performed similarly since the sulfur compounds reacted with silver nitrate. In these cases, excess aqueous cupric nitrate was added to the sample to trap all the free p-toluenethiolate ion, the solid obtained was filtered, and the filtrate was titrated as usual. When p-toluenethiolate ion, bromide free, was treated with aqueous cupric nitrate and eosin, a temporary violet color, which disappeared after few minutes, was formed. This was absent in the titrations of the kinetic points, and in control experiments the method gave satisfactory bromide analysis. However, in infinity kinetic points the bromide was less than calculated for 100% reaction. It is not known if this is due to the method, or inherent in the reaction.

Table VI. Kinetic Experiments

(a) 31 × 10⁻³ M trianisylvinyl bromide, 29 × 10⁻² M sodium hydroxide, 109.3°						
Time, min	19	33	44	60	87	137
% reaction	18.1	31.7	39.5	49.6	62.8	79.0
$k_1 \times 10^4$ sec⁻¹	1.75	1.90	1.90	1.90	1.89	1.89
Av k_1 = (1.87 ± 0.04) × 10⁻⁴						

(b) 43 × 10⁻³ M 1-anisyl-2,2-diphenylvinyl bromide, 11 × 10⁻² M sodium p-toluenethiolate, 120.3°							
Time, min	24	30	40	65	92	133	1200
% reaction	20.1	26.1	33.6	49.1	58.4	66.4	88
$k_1 \times 10^4$ sec⁻¹							
a	1.78	1.91	1.93	1.97	1.81	1.76	
b	1.57	1.68	1.70	1.73	1.59	1.40	
Av k_1 = (1.86 ± 0.08) × 10⁻⁴ ᵃ							
Av k_1 = (1.61 ± 0.09) × 10⁻⁴ ᵇ							

ᵃ Based on measured infinity. ᵇ Based on calculated infinity.

Sample Runs. Table VI gives two samples of the kinetic experiments.

Deuterium-Labeling Studies of Intramolecular Hydrogen Transfer Reactions and the Problem of Hydrogen–Deuterium Rearrangement in Mass Spectra. The Case of Isopropyl n-Butyl Ether

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Contribution from the University Chemical Laboratory, Cambridge, England. Received February 10, 1969
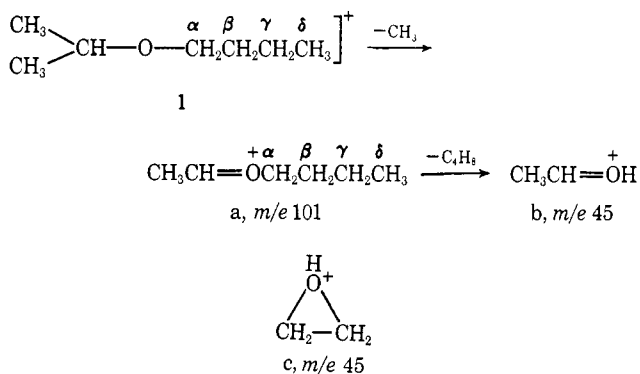
Abstract: In the mass spectrum of isopropyl n-butyl ether, the origin of the hydrogen atom transferred in the loss of C_4H_8 from the M⁺ − CH_3 ion has been studied as a function of the internal energies of the M⁺ − CH_3 ions. Strong evidence in favor of intramolecular H–H rearrangements within the n-butyl chain prior to loss of C_4H_8 (or H_2O) is forthcoming. As a consequence of the internal hydrogen exchange reactions which probably occur, it is concluded that deuterium-labeling studies of hydrogen rearrangement processes do not in the present case allow one to infer the size (assumed) of cyclic transition states where several carbon loci are apparently involved. Competing metastable transitions are utilized to establish that after a few microseconds, the M⁺ − CD_3 ions from $(CD_3)_2CDOCH_2CH_2CH_2CH_3$ and $(CD_3)_2CDOCH(CH_3)CH_2CH_3$ have not undergone, to any large extent, isomerization of the four-carbon atom chain to give common structures.

A s first pointed out by McLafferty,[1] the two most characteristic reactions undergone by simple aliphatic ethers upon electron impact are α cleavage in the molecular ion (e.g., **1** → **a**), followed by elimination of

(1) F. W. McLafferty, *Anal. Chem.* **29**, 1782 (1957).

the remaining alkyl chain as a neutral particle with associated hydrogen migration (e.g., a → b).

Although deuterium labeling clearly establishes which portions of the molecule are eliminated in the above two steps,[2] the structures of the ions a and b are only plau-

$$\left[\begin{array}{c} CH_3 \\ CH_3 \end{array} \hspace{-6pt} >CH-O-\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3 \right]^{+} \xrightarrow{-CH_3}$$

1

$$CH_3\overset{+}{C}H=\overset{\alpha}{O}\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_2CH_3 \xrightarrow{-C_4H_8} CH_3CH=\overset{+}{O}H$$

a, m/e 101   b, m/e 45

$$\overset{\overset{H}{|}}{\underset{CH_2-CH_2}{\overset{O^+}{\diagdown\diagup}}}$$

c, m/e 45

sible representations and are not rigorously established. Indeed, there is a strong possibility that given the appropriate time and internal energy, the m/e 45 ion may isomerize to the protonated oxirane structure c.[3,4]
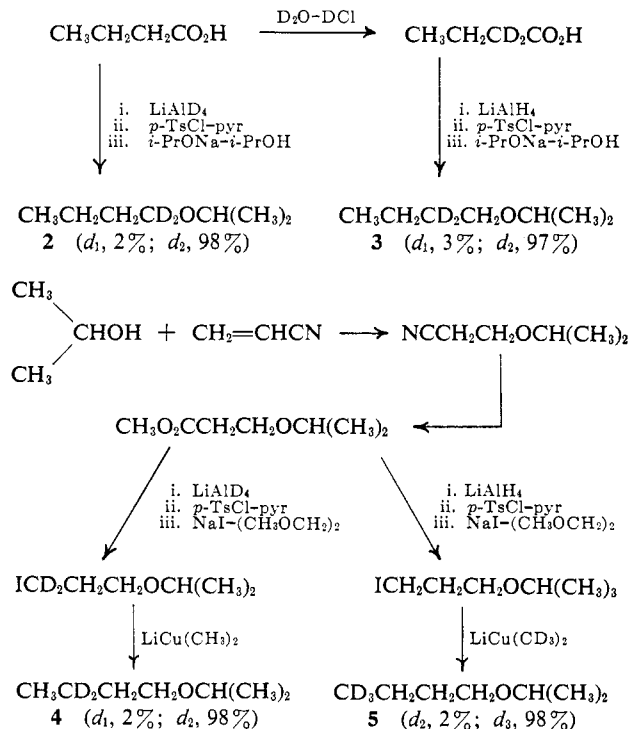
In the case of isopropyl n-butyl ether (1), a definitive deuterium-labeling study by Djerassi and Fenselau[2] established that the hydrogen transferred in the step a → b did not originate from a single carbon atom, but rather originated 15% from the α position, 35% from the β position, 40% from the γ position, and 2–9% from the δ position (see 1). These data, which were appropriate to spectra obtained either at a nominal 15 or 70 eV, were interpreted[2] in terms of competing hydrogen transfer reactions occurring through three-, four-, five-, and six-membered cyclic transition states (transfer to oxygen in each case from the α-, β-, γ-, and δ-carbon atoms, respectively). However, this would not appear to be the only possible interpretation of the data, since it has recently been demonstrated[5] that the hydrogens in aliphatic chains can undergo internal rearrangements between the various carbon atoms in reactions which (in the cases so far investigated) appear to have relatively low activation energies and low frequency factors. Thus the possibility arises that the transferred hydrogen atom could originate even from a single carbon atom, but that extensive (but incomplete) hydrogen randomization could occur within the butyl chain prior to the hydrogen transfer and C_4H_8 elimination. This possibility seemed quite feasible since the step a → b is a rearrangement reaction, and hence, on the average, b ions will be formed from a ions with relatively long lifetimes[6,7] which have ample opportunity to undergo hydrogen randomization.[5] This possible complication in the interpretation of deuterium-labeling results had been recognized earlier,[8] although the relationship of the phenomenon to ion lifetime has only recently become apparent.

We therefore chose to investigate the apparent origin of the transferred hydrogen in the step a → b for the case of isopropyl n-butyl ether (1) as a function of the energy (lifetime) of the precursor ion a. It was hoped that the interpretation of the deuterium-labeling data

(2) C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87**, 5747 (1965).
(3) D. Van Raalte and A. G. Harrison, *Can. J. Chem.*, **41**, 3118 (1963).
(4) A. G. Harrison and B. G. Keyes, *J. Am. Chem. Soc.*, **90**, 5046 (1968).
(5) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Commun.*, 1269 (1968).
(6) D. H. Williams and R. G. Cooks, *ibid.*, 663 (1968).
(7) F. W. McLafferty and R. B. Fairweather, *J. Am. Chem. Soc.*, **90**, 5915 (1968).
(8) See, for example, W. Benz and K. Biemann, *ibid.*, **86**, 2375 (1964); P. Bommer and K. Biemann, *Ann. Rev. Phys. Chem.*, **16**, 481 (1965).

would be clarified, and that the principles employed would prove generally applicable in deuterium-labeling studies.

Discussion

The observation[2] that the apparent origins of the transferred hydrogen in the step a → b were very similar in 15- and 70-eV spectra suggested that the energy dependence which we were seeking would not be large and therefore it was extremely important to prepare specifically deuterated isopropyl butyl ethers of high purity. The following synthetic sequences were employed.

$$CH_3CH_2CH_2CO_2H \xrightarrow{D_2O-DCl} CH_3CH_2CD_2CO_2H$$

$$\downarrow \begin{array}{l} i. \ LiAlD_4 \\ ii. \ p\text{-}TsCl\text{-}pyr \\ iii. \ i\text{-}PrONa\text{-}i\text{-}PrOH \end{array} \qquad \downarrow \begin{array}{l} i. \ LiAlH_4 \\ ii. \ p\text{-}TsCl\text{-}pyr \\ iii. \ i\text{-}PrONa\text{-}i\text{-}PrOH \end{array}$$

$$CH_3CH_2CH_2CD_2OCH(CH_3)_2 \qquad CH_3CH_2CD_2CH_2OCH(CH_3)_2$$

2 (d_1, 2%; d_2, 98%)   3 (d_1, 3%; d_2, 97%)

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} \hspace{-10pt} CHOH + CH_2=CHCN \longrightarrow NCCH_2CH_2OCH(CH_3)_2$$

$$CH_3O_2CCH_2CH_2OCH(CH_3)_2 \longleftarrow \rule{10pt}{0pt}$$

$$\swarrow \begin{array}{l} i. \ LiAlD_4 \\ ii. \ p\text{-}TsCl\text{-}pyr \\ iii. \ NaI\text{-}(CH_3OCH_2)_2 \end{array} \qquad \searrow \begin{array}{l} i. \ LiAlH_4 \\ ii. \ p\text{-}TsCl\text{-}pyr \\ iii. \ NaI\text{-}(CH_3OCH_2)_2 \end{array}$$

$$ICD_2CH_2CH_2OCH(CH_3)_2 \qquad ICH_2CH_2CH_2OCH(CH_3)_2$$

$$\downarrow LiCu(CH_3)_2 \qquad\qquad \downarrow LiCu(CD_3)_2$$

$$CH_3CD_2CH_2CH_2OCH(CH_3)_2 \qquad CD_3CH_2CH_2CH_2OCH(CH_3)_2$$

4 (d_1, 2%; d_2, 98%)   5 (d_2, 2%; d_3, 98%)

The amounts of deuterium originating from each carbon atom in the transitions $M^+ - CH_3 \rightarrow CH_3CH=O^+H$ (m/e 45) or $M^+ - CH_3 \rightarrow CH_3CH=O^+D$ (see a → b) were then determined for each labeled ether. The widest possible energy spread for the formation of daughter ions was studied by making quantitative measurements on the relative m/e 45 and 46 intensities in 70, 20, 18, 16, and 14 eV spectra. Most important, competing metastable transitions for the $M^+ - CH_3 \rightarrow CH_3CH=O^+H$ and $M^+ - CH_3 \rightarrow CH_3CH=O^+D$ reactions were carefully investigated in the first and second field-free regions in the AEI MS 9 mass spectrometer. The metastable transitions occurring in the second field-free regions were examined by operating the mass spectrometer in the normal mode at 8 kV and high multiplier gain. Under such circumstances, the lifetime of the ion prior to decomposition is of the order of 10 μsec.[9,10] Those occurring in the first field-free region were examined using the technique of Barber and Elliott[11] and, specifically, the modification described by Jennings.[12] The first field-free region metastable transitions

(9) I. Howe and D. H. Williams, *Chem. Commun.*, 220 (1968).
(10) J. H. Beynon, J. A. Hopkinson, and G. R. Lester, *J. Mass. Spectrosc. Ion Phys.*, **1**, 343 (1968).
(11) M. Barber and R. M. Elliott, ASTM E-14 Conference on Mass Spectrometry, Montreal, June 1964.
(12) K. Jennings in "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davies, Ed., United Trade Press, London, 1967, p 105.
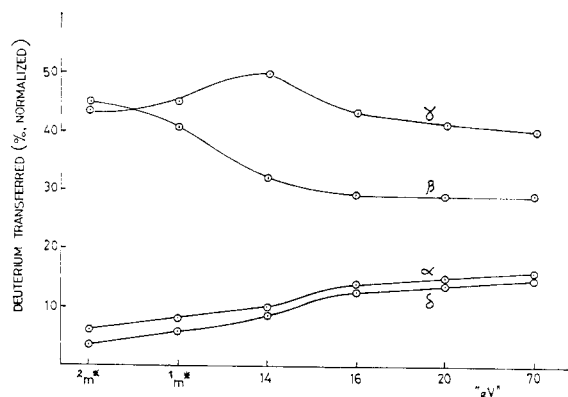
Figure 1. Normalized percentages of deuterium transfer from the α-, β-, γ-, and δ-carbon atoms as a function of beam energy (ion lifetime).

Figure 2. Competing metastable transitions for the loss of $C_4H_6D_2$ (to m/e 45) and C_4H_7D (to m/e 46) from the $M^+ - CH_3$ ion in the 70-eV mass spectrum of $(CH_3)_2CHOCH_2CD_2CH_2CH_3$.

(using the modification for $m_1 > 2m_2$[12]) can be probed at the collector at accelerating voltages of approximately 5 kV and the ion lifetime prior to decomposition in these cases is around 3 μsec.[9,10] The quasi-equilibrium theory of mass spectrometry predicts an initial rapid rise of the rate constant (k) with internal energy in excess of the activation energy for reaction.[13] Hence, since the difference between appearance potentials of daughter ions and metastable ions is usually of the order of 1 eV or less[14] (in representative C-, H-, N-, and O-containing ions of mass $ca.$ 100 or less), we may conclude that (i) the internal energy necessary to raise the rate constant by an order of magnitude in the range 10^4-10^6 sec^{-1} is of the order of 1 eV (23 kcal) or less and (ii) metastable transitions occurring in the second field-free region will usually, in these relatively small ions, correspond to internal energies of only around 0–50 kcal or so in excess of the activation energy. While such a generalization is obviously very crude, we think it worthwhile to emphasize that the internal energies appropriate to metastable transitions are not very different from the energies appropriate to thermal or photochemical reactions. It follows that the spread of internal energies of $M^+ - 15$ ions, which undergo decomposition to m/e 45 or 46 and which we are able to examine, is relatively wide (probably several electron volts).

The experimental data are summarized in Table I. In the absence of an isotope effect, a total corresponding to exactly one deuterium atom would be transferred in the spectra of the α-, β-, and γ-d_2 and δ-d_3 derivatives. The operation of an isotope effect is established by a systematic energy dependence of the total amount of deuterium transferred (column 3 of Table I). The results normalized to 100% for each range of energies examined are summarized in Table II and plotted graphically in Figure 1; the energy scale in Figure 1 is, of course, arbitrary. In Figure 2, the competing metastable transitions for the steps $M^+ - CH_3 \rightarrow m/e$ 45 (loss of $C_4H_6D_2$) and $M^+ - CH_3 \rightarrow m/e$ 46 (loss of C_4H_7D) in the 70-eV mass spectrum of $(CH_3)_2CHOCH_2CD_2$-CH_2CH_3 (3) are reproduced.

There are several noteworthy points with regard to the data summarized in Figure 1. First, in the spectra

of all the deuterated derivatives (2–5) there are competing metastable transitions in both field-free regions for the reactions $M^+ - 15 \rightarrow CH_3CH=O^+H$ and $M^+ - 15 \rightarrow CH_3CH=O^+D$ (see, for example, Figure 2). This necessitates that in compounds originally con-

Table I. Percentage Transfers of Deuterium in the Mass Spectra of 2–5 in Competition between the Transitions $M^+ - 15 \rightarrow CH_3CH=O^+H$ and $M^+ - 15 \rightarrow CH_3CH=O^+D$[a,b]

eV or field-free region	Position of deuteration				Total D transferred, %
	α	β	γ	δ	
	Deuterium transferred, %				
70	15	27	37	14	93
20	14.5	28	40	14	96.5
16	14	29	43	12.5	98.5
14	10	32	50	9	101
$^1m^*$	9	47	51.5	7	114.5
$^2m^*$	6	54	52	4	116

[a] The m/e 45 and 46 daughter ions were examined under high resolution, so that no spurious contributions could arise from deuterium-containing hydrocarbon peaks. [b] The individual figures in the table correspond to $100[CH_3CH=O^+D]/[CH_3CH=O^+D] + [CH_3CH=O^+H]$; the figures represent the averages of a large number of scans.

Table II. Normalized Percentage Transfers of Deuterium in the Mass Spectra of 2–5

eV or field-free region	Position of deuteration			
	α	β	γ	δ
	Deuterium transferred, %			
70	16	29	40	15
20	15	29	41.5	14.5
16	14	29.5	43.5	13
14	10	32	50	9
$^1m^*$	8	41	45	6
$^2m^*$	5	46.5	45	3.5

taining deuterium specifically in the α, β, γ, or δ positions, the activation energies for transfer of H or D must be similar (for example, it has been suggested[15] that if activation energies differ by more than, say, 50%, competing metastable transitions will not be observed).

(13) See, for example, M. Vestal, *J. Chem. Phys.*, **43**, 1356 (1965), and references cited therein.
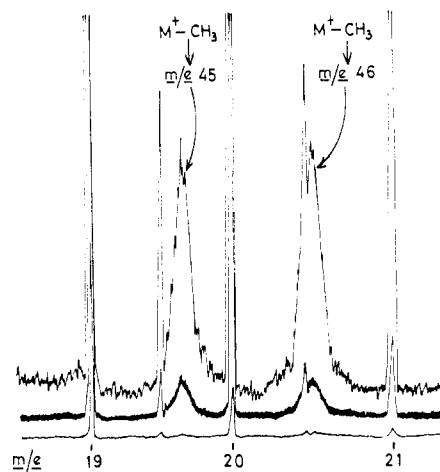(14) I. Hertel and Ch. Ottinger, *Z. Naturforsch.*, **22a**, 40 (1967).
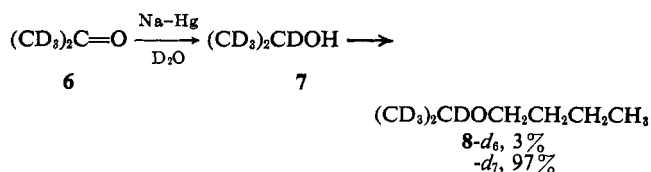(15) H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 36.

It does not seem at all plausible that the activation energy for transfer from the α position in a three-membered cyclic transition state, with the breaking of two bonds to the same carbon atom, should have an activation energy within 50% of that for transfer from the β, γ, or δ positions. Hence, on this reasoning alone we conclude that transfer *directly* from the α position to the $C_2H_5O^+$ ion in the decomposition of the $M^+ - 15$ ion from 1 is unlikely.

Second, the energy dependence of the apparent origin of the deuterium transferred is very low when 16-, 18-, 20-, and 70-eV spectra are compared (see also ref 2), but in 14-eV, $^1m^*$ and $^2m^*$ spectra there is a gradual and marked decrease in the amount of deuterium originating from the α and δ positions. Two interpretations of the data can be proposed with equal weight on the basis of the actual evidence presented. First, in ions of low internal energy (decomposition in the $^2m^*$ region), the data are consistent with a relatively rapid 1,2 exchange between hydrogens attached to the β and γ carbons, with exchange reactions involving the hydrogens on α and δ carbons being relatively slow. On the basis of this plausible interpretation, the actual hydrogen transfer to oxygen could occur specifically from the β or γ positions, or from both. Second and alternatively, there could be no $\beta-\gamma$ randomization but direct transfer from both the β and γ positions with very similar activation energies for processes involving four- and five-membered transitions states (1-butene and, perhaps, 1-methylcyclopropane, respectively, being the ejected neutral particles). The former possibility, involving $\beta-\gamma$ randomization, seems moreattr active than the latter, involving no $\beta-\gamma$ randomization, since we have already indicated that there is a strong case for relatively slow hydrogen scrambling involving the α-methylene group and hence there is reason to suppose that exchange between the other methylene groups may also be involved. However, it is emphasized that both mechanisms may operate. We reiterate that the case of four competing metastable transitions involving four different ring sizes of transition states seems extremely improbable.

Third, it is apparent from the data accumulated in Table I that an energy-dependent isotope effect operates. Thus, when high energy ions are most heavily weighted (in 70-eV spectra), there is over-all discrimination against deuterium transfer (only 93%), while at the lowest energies (near threshold) there is an over-all preference for deuterium transfer (apparent deuterium transfer of 116%). Before this was interpreted as a true energy-dependent isotope effect (or combination of isotope effects), it was necessary to check that in ions of low internal energy ($^2m^*$ region) there was no H–D randomization between the alkyl chains on opposite sides of the ether oxygen.[16] If such scrambling occurred, then deuterium could be incorporated in the isopropyl group from the labeled butyl chain and a "metastable peak" for the $M^+ - 15 \rightarrow m/e$ 46 transfer would then be observed for a *hydrogen* transfer in the reaction which results in the elimination of the butyl chain. However, a further consequence of such internal H–D rearrangement between alkyl chains is that

(16) This type of scrambling has in fact been observed in the mass spectrum of isopropyl *n*-perdeuteriobutyl sulfide: S. Sample and C. Djerassi, *J. Am. Chem. Soc.*, **88**, 1937 (1966).

$M^+ - 15 \rightarrow m/e$ 47 (*e.g.*, $CH_2DCH=O^+D$) transitions should be observable, but could not in fact be detected even using the sensitive metastable defocussing technique. This type of between-chain scrambling was further precluded in the present case from the mass spectrum of isopropyl-d_7 *n*-butyl ether (prepared by the sequence $6 \rightarrow 7 \rightarrow 8$). Thus, in the mass spectrum of 8 no metastable transitions due to the decomposition $M^+ - CD_3 \rightarrow m/e$ 48 (*e.g.*, $CD_2HCD=O^+H$) could be detected.

$$(CD_3)_2C=O \xrightarrow[D_2O]{Na-Hg} (CD_3)_2CDOH \longrightarrow$$
$$\quad \text{6} \qquad\qquad\qquad \text{7}$$

$$(CD_3)_2CDOCH_2CH_2CH_2CH_3$$
$$8\text{-}d_6, 3\%$$
$$\text{-}d_7, 97\%$$

We do not feel that any secure interpretation of the "isotope effect" can be offered, since the observed figures may be due to more than one isotope effect operating in two or more competing unimolecular reactions.

The $M^+ - CH_3$ ion from isopropyl *n*-butyl ether (1) undergoes a second decomposition, loss of water, giving rise to a "metastable peak." The origins of the deuteriums lost (as HDO or D_2O) in the mass spectra of the specifically labeled derivatives are summarized in Table III.

Table III. Percentages of Loss of H_2O, HDO, and D_2O from the $M^+ - 15$ Ions in the 70- and 16-eV Spectra of 2–5

eV	Position of Deuteration	Obsd %			Calcd, %[a]		
		$-H_2O$	$-HDO$	$-D_2O$	$-H_2O$	$-HDO$	$-D_2O$
70	α	57	26	16.5			
	β	56	41	3.2	58.3	39.0	2.8
	γ	56	41	3.4			
	δ	53	44	3.3	41.6	50.0	8.3
16	α	56	33	11			
	β	53	43	3	58.3	39.0	2.8
	γ	54	43	3			
	δ	48	49	3	41.6	50.0	8.3

[a] Calculated on the basis of H/D randomization within the butyl chain.

The data in Table II, in conjunction with data from the spectrum of the isopropyl-d_7 *n*-butyl ether (8), establish that both hydrogen atoms eliminated as water originate from the butyl chain and not from the isopropyl chain which has undergone α cleavage. The observed values for loss of H_2O, HDO, and D_2O in the β- and γ-d_2 and δ-d_3 derivatives agree moderately well with a statistical loss from the butyl chain in either 70- or 16-eV spectra, assuming that no large isotope effects operate; it is, however, noteworthy that the loss of D_2O from the 1,1-d_2 derivative is significantly greater than the random value. The loss of D_2O from the CD_2 derivatives 2–4 and from the CD_3 derivative 5 strongly supports the case for internal H–D exchange in the butyl chain prior to D_2O loss, since otherwise the breaking of two bonds to one carbon atom would be necessary.

Although we feel that a good case has been made in favor of some measure of internal hydrogen rearrangement within the butyl chain, the possibility that the carbon skeleton of the butyl chain might rearrange in M^+

— 15 ions of at least some internal energies has not yet been discussed. For example, the possibility that the M^+ — CD_3 ions from isopropyl-d_7 n-butyl ether (**8**) and isopropyl-d_7 sec-butyl ether (**9**) might isomerize to a common structure after several microseconds was investigated by comparing the relative abundances of the competing metastable transitions

$$M^+ - CD_3 \xrightarrow{m_a^*} M^+ - CD_3 - C_4H_8 \qquad (a)$$

and

$$M^+ - CD_3 \xrightarrow{m_b^*} M^+ - CD_3 - H_2O \qquad (b)$$
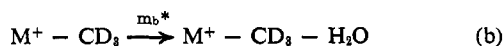
in the spectra of **8** and **9**. If the ratio $[m_a^*]/[m_b^*]$ were the same in both spectra, then assuming that the transitions occur from the same, or "communicating,"[17] electronic states there is strong evidence for common structures of the M^+ — CD_3 ions after several microseconds. Alternatively, if the ratios of $[m_a^*]/[m_b^*]$ are very different, then complete or predominant isomerization to a common structure is excluded.[18] The data are summarized in Table IV; the ratios $[M^+ - CD_3 - C_4H_8]/[M^+ - CD_3 - H_2O]$ of daughter ion intensities in the spectra of **8** and **9** at various electron volts are also given.

$$\overset{\overset{\textstyle CH_3}{\textstyle |}}{(CD_3)_2CDOCHCH_2CH_3}$$

9
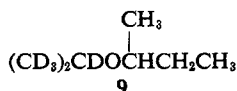
Table IV. Relative Abundances $[M^+ - CD_3 - C_4H_8]/[M^+ - CD_3 - H_2O]$ in the Spectra of $(CD_3)_2CDOCH_2CH_2CH_2CH_3$ (**8**) and $(CD_3)_2CDOCH(CH_3)CH_2CH_3$ (**9**) at Various Electron Volts and for Transitions in the First Field-free Region

eV or field-free region	I [M^+ − CD_3 − C_4H_8]_{n-butyl} / [M^+ − CD_3 − H_2O]_{n-butyl}	II [M^+ − CD_3 − C_4H_8]_{sec-butyl} / [M^+ − CD_3 − H_2O]_{sec-butyl}	I/II
70	22	27	0.8
20	16	14	1.1
18	14	11	1.3
16	10	6.3	1.6
15	6.6	3.8	1.7
14	5.2	1.6	3.2
$^1m^*$	2.4	0.18	13

The relative abundances of the competing metastable transitions for loss of C_4H_8 and H_2O from the M^+ — CD_3 ions are very different (bottom row, Table IV), establishing that after several microseconds the M^+ — CD_3 ions derived from the n-butyl and sec-butyl structures have not completely or predominantly isomerized to a common intermediate.[19] Water loss competes far more effectively with C_4H_8 loss from the sec-butyl structure. In both **8** and **9**, the reaction involving loss of C_4H_8 becomes much more important than loss of water when ions of high internal energy are weighted

(17) The term "communicating" is used to imply electronic states whose potential surfaces cross. Such electronic states are not isolated from one another and it is possible to pass from one to the other in times comparable to vibrational frequencies.

(18) (a) H. M. Rosenstock, V. H. Dibeler, and F. N. Harlee, *J. Chem. Phys.*, **40**, 591, (1964); (b) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966); (c) F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951, 5953 (1967); (d) W. T. Pike and F. W. McLafferty, *ibid.*, **89**, 5954 (1967).

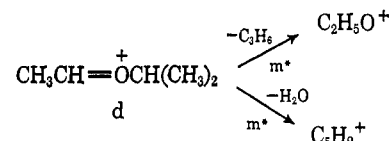(19) The generation of a very small fraction of common ions cannot be rigorously excluded.
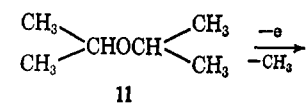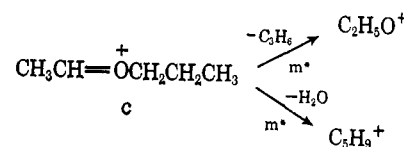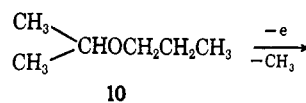
more. It is noteworthy that in 20- or 70-eV spectra, the relative abundances of the (M^+ — CD_3 — C_4H_8) and (M^+ — CD_3 — H_2O) daughter ions are almost the same in both spectra (values close to 1 in the last column of Table IV). Although no secure conclusions can be based on these data, it would seem to be a possibility that M^+ — CD_3 ions of high internal energies from **8** and **9** do isomerize to a common structure.

Very similar conclusions have been reached (Table V) in the cases of isopropyl n-propyl ether (**10**) and diisopropyl ether (**11**). The M^+ — CH_3 ions from **10** and

Table V. Relative Abundances $[M^+ - CH_3 - C_3H_6]/[M^+ - CH_3 - H_2O]$ in the Spectra of Isopropyl n-propyl Ether (**10**) and Diisopropyl Ether (**11**) at Various Electron Volts and for Transitions in the First Field-free Region

eV or field-free region	I [M^+ − CH_3 − C_3H_6]_{n-propyl} / [M^+ − CH_3 − H_2O]_{n-propyl}	II [M^+ − CH_3 − C_3H_6]_{isopropyl} / [M^+ − CH_3 − H_2O]_{isopropyl}	I/II
70	65	32	2.0
16	37	8.4	4.4
14	10	1.9	5.1
$^1m^*$	1	0.034	29

11 which are most simply represented as c and d, respectively, both undergo competing metastable transitions for the loss of C_3H_6 and water. Once more (i) the M^+ — CH_3 ions do not have a common structure after several microseconds, (ii) water loss is more facile at the threshold from the iso structure (see d) or from a rearranged form of d.

$$\underset{\textstyle CH_3}{\overset{\textstyle CH_3}{>}}CHOCH_2CH_2CH_3 \xrightarrow[-CH_3]{-e}$$

10

$$CH_3CH\overset{+}{=}OCH_2CH_2CH_3 \begin{array}{c} \xrightarrow{-C_3H_6}{}^{m^*} C_2H_5O^+ \\ \xrightarrow{-H_2O}{}^{m^*} C_5H_9^+ \end{array}$$

c

$$\underset{\textstyle CH_3}{\overset{\textstyle CH_3}{>}}CHOCH\underset{\textstyle CH_3}{\overset{\textstyle CH_3}{<}} \xrightarrow[-CH_3]{-e}$$

11

$$CH_3CH\overset{+}{=}OCH(CH_3)_2 \begin{array}{c} \xrightarrow{-C_3H_6}{}^{m^*} C_2H_5O^+ \\ \xrightarrow{-H_2O}{}^{m^*} C_5H_9^+ \end{array}$$

d

Conclusions

It seems worthwhile to summarize the conclusions reached in this study, which are as follows.

1. Strong evidence has been presented in favor of intramolecular H–H rearrangements in the butyl chain of isopropyl n-butyl ether prior to loss of C_4H_8 or H_2O from the M^+ — CH_3 ion.

2. As a consequence of 1 above, it will in many cases not be possible to infer securely the size (assumed) of cyclic transition states for hydrogen rearrangement processes as a result of deuterium-labeling experiments.

3. In the case of isopropyl *n*-butyl ether, $M^+ -$ CH₃ ions undergoing C_4H_8 loss after approximately 10 μsec (metastable transitions in the second field-free region) rearrange the hydrogen atom predominantly (*ca.* 90%) from the β and/or γ position of the butyl chain. If $\beta-\gamma$ H–H exchange is rapid relative to fragmentation at internal energies appropriate to C_4H_8 elimination after approximately 10 μsec, then hydrogen transfer in the reaction resulting in C_4H_8 loss could occur virtually exclusively from one of these positions.

4. The carbon skeleton of the *n*-butyl chain in $M^+ - CH_3$ ions which lose C_4H_8 and H_2O in metastable transitions may well be retained, since evidence is presented to suggest that $M^+ - CH_3$ ions incorporating a *sec*-butyl chain retain very perdominantly, or totally, a different structure. However, we cannot preclude the possibility that the two $M^+ - CH_3$ ions isomerize to a common structure in ions of high internal energy.

The mechanism of the hydrogen scrambling reactions remains a point of considerable interest but one which we feel, in the absence of experimental evidence, it would be pointless to speculate upon further at present. Eminently reasonable suggestions for the activated complexes which may account for H–D exchange in deuterated butanes have previously been made by McFadden and Wahrhaftig.[20] Since such exchanges are rearrangement reactions, they can occur with partial bond formation in the transition state. It is therefore reasonable that the H–D exchange reactions should have activation energies which are comparable to, or even lower than, the activation energies for rearrangement reactions which result in fragmentation, *e.g.*, C_4H_8 loss in the present instance.

Experimental Section

All mass spectra were determined on an AEI MS 9 double focussing mass spectrometer of Nier–Johnson geometry. Samples were introduced through a heated inlet system. Metastable transitions were observed in 70-eV spectra, those occurring in the second field-free region being examined in normal 8-kV spectra at high multiplier gain, and those occurring in the first field-free region being examined by use of the modifications described by Jennings.[12]

Butyric-2,2-d_2 Acid. The acid (1 g), deuterium oxide (1 g), and concentrated DCl (1–2 drops) were heated in a sealed tube at 200° for 3 days. Four such exchanges were carried out, the partially deuterated acid being isolated after each exchange by continuous extraction with ether. After the final extraction, the deuterium of the carboxylic acid group was back-exchanged by shaking with water (4 g to 1 g of acid) at room temperature for a few minutes followed by continuous extraction with ether. The isotopic purity of the acid so obtained was d_1 3, d_2 97% as determined from the $M^+ - OCH_3$ peak in the mass spectrum of the derived methyl ester (prepared by reaction of the acid with diazomethane).

n-Butyl p-Toluenesulfonate (d_0 and d_2). *n*-Butyric acid (0.9 g) in ether (10 ml) was added to a cooled slurry of lithium aluminium hydride (or deuteride) (0.5 g) in ether (10 ml) and heated under reflux for 2 hr. The excess of hydride was destroyed with water and the ethereal layer washed with dilute hydrochloric acid, dried, and evaporated. The residual *n*-butyl alcohol was dissolved in

pyridine (2 ml) and treated with *p*-toluenesulfonyl chloride (1.9 g) at 0° for 12 hr. The reaction mixture after pouring onto ice was extracted with ether, and the ethereal layer washed with excess dilute hydrochloric acid, neutralized with sodium bicarbonate, dried, and evaporated under reduced pressure to give butyl *p*-toluenesulfonate (2.2 g, 96%).

Isopropyl *n*-Butyl Ether. The butyl tosylate was added to a solution of excess sodium in isopropyl alcohol, and heated under reflux for 2 hr. The product was partitioned between pentane and water and the petrol phase evaporated to give crude isopropyl *n*-butyl ether, which was purified by preparative vapor phase chromatography.

Methyl 3-Isopropoxypropionate. Acrylonitrile (50 ml) was added with stirring over 15 min to a suspension of sodium hydroxide (3 g) in isopropyl alcohol (150 ml). The nitrile absorption changed from 2240 to 2260 cm⁻¹. The product was partitioned between ether and dilute hydrochloric acid to give, after evaporation of the ether phase, crude 3-isopropoxypropionitrile (120 ml). The nitrile was heated under reflux in dry methanol (360 ml) containing concentrated sulfuric acid (72 ml) and water (20 ml) for 24 hr. Neutralization, ether extraction, and distillation of the product at 64° (18 mm) gave methyl 3-isopropoxypropionate (59 g, 39%).

3-Isopropoxypropan-1-ol (d_0 and d_2). The ester (15.0 g) was heated under reflux with lithium aluminium hydride (5.0 g) in ether (100 ml) for 2 hr. The excess reagent was destroyed by addition of water (10 ml), the ethereal layer decanted, and the product distilled at 70° (15 mm) to give 3-isopropoxypropan-1-ol (9.25 g, 76%). The *p*-toluenesulfonate was prepared as above.

1-Iodo-3-isopropoxypropane (d_0 and d_2). 3-Isopropoxypropyl tosylate (9.0 g) was heated at 50° in glyme (90 ml) with sodium iodide (18 g) and worked up by ether extraction to give 1-iodo-3-isopropoxypropane (7.5 g, 99%).

Alkylation Procedure.[21] In a typical experiment, methyl iodide (0.7 g) was added slowly at 0° under nitrogen to a stirred suspension of lithium metal (0.15 g) in ether (5 ml). The resulting mixture was filtered into a stirred suspension of cuprous iodide (0.4 g) in ether (5 ml) under nitrogen and left at 0° for 30 min. 1-Iodo-3-isopropoxypropane-2,2-d_1 (1.5 g) was added to the clear colorless solution and the mixture stirred overnight. The yellow precipitate formed on addition of water was removed by filtration, the ether layer separated, and isopropyl *n*-butyl-2,2-d_2 ether (**4**) isolated *via* preparative gas–liquid partition chromatography. Based on 1-iodo-3-isopropoxypropane, the yields were typically 50–70%.

Isopropyl-d_8 Alcohol. Mercury amalgam was prepared from sodium (4.0 g) and mercury (200 g) and covered with a solution of sodium deuterioxide (from 1.5 g of sodium) in deuterium oxide (75 ml) under nitrogen. Acetone-d_8 (5.0 g) was added and the mixture stirred overnight under dry nitrogen. The phases were separated and the aqueous layer was twice distilled at atmospheric pressure through a 25-cm helix-packed column to give isopropyl-d_8 alcohol (40 g, 80%) and pure recovered deuterium oxide (60 ml). This procedure is thus much cheaper than the use of lithium aluminum deuteride for the reduction of relatively large amounts of low molecular weight ketones.

All the ethers were purified *via* preparative gas–liquid partition chromatography prior to determination of the mass spectra.

The integrity of deuterium labeling in the ethers in all cases was checked by the lack of both particular absorption and coupling in their nuclear magnetic resonance spectra.

(20) W. H. McFadden and A. L. Wahrhaftig, *J. Am. Chem., Soc.*, **78**, 1572 (1956); see also ref 5.

(21) E. J. Carey and G. H. Posner, *ibid.*, **89**, 3911 (1967).