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# Loss of Alkanes from Ionized Branched Chain Ethers. Metastable Decomposition from an Electronically Excited State?

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Ethers of the type  $R^1CH(CH_3)OR^2$  show a metastable peak for the loss of  $R^1H$  in their mass spectra. Loss of  $C_2H_5D$  is the principal decomposition of metastable  $C_2H_5CH(CD_3)O^+CH_3$ , demonstrating that vinyl ether ions are formed by the metastable losses of alkanes. Thermochemical and orbital symmetry considerations support the hypothesis that the losses of alkanes occur from an electronically excited state of the ether ions. Other ether ions with the oxygen bonded to a nonterminal carbon also lose alkanes. N,N-Dimethyl-s-butylamine, di-sec-butyl sulfide, sec-butylbenzene, and methyl tert-pentyl ether ions do not lose alkanes.

### Introduction

In a previous mass spectral study of the metastable ion (MI) spectra<sup>1</sup> of labeled *n*-butyl ethyl ether molecular ions, we concluded that the losses of ethyl and methyl follow isomerization to sec-butyl ethyl ether ions. However, the metastable ion spectra of *n*-butyl ethyl and sec-butyl ethyl ethers are quite dissimilar, with the loss of ethane being very weak in the former and dominating the latter (Table I). The loss of an alkane molecule from metastable ether ions had not previously been reported. The present work was undertaken to characterize this novel fragmentation,

### TABLE I: Metastable Decompositions of Ether Ions

ether	$C_2H_5$	$C_2H_6O$	$CH_3$	$C_{2}H_{6}$	
<i>n</i> -butyl ethyl <i>sec</i> -butyl ethyl	$100 \\ < 47^{b}$	13.4 <1	2.4 < 1	0.8 100	

<sup>a</sup> Values are relative peak heights. <sup>b</sup> Not corrected for overlap with  $101 \rightarrow 73$ .

especially to examine the  $proposal^{1b}$  that it occurs from an electronically excited state of the sec-butyl ethyl ether ion.

 TABLE II: Metastable Losses of Ethane from Methyl

 sec-Butyl Ether Ions

species lost						
ether	$C_2H_6$	C <sub>2</sub> H <sub>5</sub> D	$C_2H_4D_2$	$C_2H_3D_3$		
 $2^a$	$2.3^{b}$	100	3.3	<18 <sup>c</sup>		
$3^a$	<1	15	100			

<sup>a</sup> 96%  $d_3$ , 4%  $d_2$ . <sup>b</sup> Corrected for overlap with the <sup>13</sup>C satellite 92  $\rightarrow$  61. <sup>c</sup> Not corrected for overlap with the stronger 90  $\rightarrow$  58. <sup>d</sup> 98%  $d_2$ , 2%  $d_1$ .

Scheme I



CH3OCH=CH2+ C2H6

## **Results and Discussion**

Mechanism of Alkane Loss. We prepared deuterated ethers 2 and 3 for study. The ion formed by the meta-



stable loss of ethane from ionized 2 retains two of its three deuterium atoms, while the daughter ion from ionized 3 contains no deuterium (Table II). The loss of  $C_2H_4D_2$  from 3 and of  $C_2H_5D$  from 2 demonstrates that the neutral contains at least three hydrogen atoms, so losses of C- $(H,D)_2O$  do not contribute appreciably to the results in Table I. The ethane lost from *sec*-butyl ethers contains one of the methyl hydrogens and the ethyl of the *sec*-butyl group. Therefore the reaction is a 1,2 elimination of alkane forming ionized methyl vinyl ether (Scheme I). This ether fragmentation closely parallels metastable decompositions of ionized 3-pentanone and 3-pentanone-2,2,4,4-d\_4.<sup>2</sup>

Transition states such as that depicted in Scheme I are "forbidden" by orbital symmetry<sup>3</sup> if they proceed from the ground electronic state through the transition state of simplest geometry. This difficulty could be resolved in three ways: (1) reaction from an electronically excited state in which it is symmetry allowed, (2) reaction by a more distorted transition state, and (3) reaction by the simplest transition state, despite its forbidden nature.

Only the first hypothesis seems to be fully consistent with the facts, even though it is generally assumed that mass spectral fragmentations occur only from ground electronic states.<sup>4</sup> However, metastable decompositions from isolated electronic states of ionized butanoic acid have recently been proposed.<sup>5</sup> Decomposition from an electronically excited state also seems to be the best explanation for a discrepancy between the actual metastable peak intensities and the intensities that would be predicted from the thermochemical data. The heats of formation at 298 °C of the products of the loss of ethyl are 25.7 kcal/mol for the radical<sup>6</sup> and 121.2 kcal/mol for the ion,<sup>7</sup> totaling  $146.9 \pm 0.3$  kcal/mol. For the loss of ethane, the heat of formation of  $C_2H_6$  is -20.2 kcal/mol,<sup>8</sup> the heat of formation of neutral ethyl vinyl ether is -33.5 kcal/mol,<sup>9</sup> and the adiabatic ionization potential<sup>10</sup> is 8.83 eV (203.5 kcal/mol). The total is  $149.8 \pm 0.3$  kcal/mol. Thus the products of the loss of ethyl are  $2.9 \pm 0.6$  kcal/mol more stable than the products of the loss of ethane. The peak in the normal spectrum of sec-butyl methyl ether formed by loss of ethyl is 20 times as intense as that due to the loss of ethane. This demonstrates that the rate of the

TABLE III:	Losses of	f Neutral	Species	from
Ionized Meth	vl Ethers		_	

		s	ost		
ether	$\overline{\mathrm{CH}_{4}}$	$C_2H_6$	$C_{3}H_{8}$	$C_4 H_{10}$	CH3OH
2-methoxypropane	100	0	0		0
2-methoxybutane <sup>a</sup>	< 0.6	100	< 0.6	< 0.6	<0.6
1-methoxybutane <sup>b</sup>		5			
2-methoxypentane	<1	< 1	19	<1	100
3-methoxypentane	<3	100	<3	<3	< 3
2-methoxyhexane <sup>c</sup>	< 2	<2	< 2	100	38
3-methoxyhexane	<1	100	67	< 1	12
<sup>a</sup> Loss of $C_2H_s = 2$ CH <sub>3</sub> = 52.	9. <sup>b</sup> L	oss of	$C_2H_5 =$	100. <sup>c</sup>	Loss of

simple cleavage reaction increases more rapidly than the rate of the rearrangement with increasing internal energy in the reactant ion.<sup>12</sup> Therefore the loss of ethane should not dominate the loss of ethyl at threshold or higher energies.

Even if there are sufficient errors in the heats of formation such that loss of  $C_2H_6$  is the lowest energy reaction, it is very unlikely that the ethyl sec-butyl ether ions formed by rearrangement could be high enough in internal energy to cause the loss of ethyl to overwhelm the loss of ethane. The sum of the heats of formation of ionized 2-butene and ethanol is 152 kcal/mol,<sup>11</sup> 5 kcal/mol above the combined heats of formation of  $CH_3CH_2O=C^+HCH_3 + \cdot C_2H_5$ . The metastable peak for loss of ethanol from ionized ethyl n-butyl ether is 13% as intense as that for the loss of ethyl, and the peak for loss of ethane is less than 1% as intense as that for the loss of ethyl.<sup>1a</sup> If the 2-butene ion is formed by the loss of ethanol, then the relatively weak intensity of the associated metastable peak indicates that most of the rearranged ethyl sec-butyl ether ions which lose ethyl upon metastable decomposition probably contain 0-5 kcal/mol more energy than they need to decompose. It is highly unlikely that the relative rates of two reactions could change more than 100-fold over such a small energy range, or even 60-fold, as observed for methyl butyl ether (Table III).

The second and third possibilities above imply losses of ethane with reverse activation energy because of angle strain or the violation of orbital symmetry.<sup>13,14</sup> A substantial fraction of the reverse activation energy associated with a mass spectral fragmentation is often released as kinetic energy.<sup>15</sup> The kinetic energy of  $0.14 \pm 0.02$  kcal/ mol calculated at the peak half height is small. It is considerably smaller than the  $0.62 \pm 0.14$  kcal/mol released in the loss of ethyl. Therefore the energy release does not support decomposition by a symmetry forbidden arrangement, though it may not exclude this possibility. Orbital symmetry does not apply rigorously to the fragmentations since the requisite molecular symmetry is lacking, and reasoning by analogy may not be adequate, as it must be assumed that the RO<sup>+</sup> group does not materially affect the nature of the reaction. In addition, orbital symmetry imposes weaker constraints on reactions of odd than of even electron species.<sup>16</sup>

In summary, the most probable interpretation of the differences in the metastable decompositions of n-butyl and *sec*-butyl ether molecular ions is that those ions decompose predominantly from different electronic states of the same structure. However, this conclusion is based only on indirect evidence.

Ålkane Losses from Other Ethers. Alkanes are lost in the metastable decompositions of the ionized ethers of other secondary alcohols (Table III). The loss of  $CH_4$  was observed only from ethers which could not eliminate another alkane. Methyl ether ions in which a six-membered Loss of Alkanes from Jonized Branched Chain Ethers

ring hydrogen transfer to oxygen is possible also lose methanol.

Alkane Losses from Non-Ether Ions. Aliphatic ketones lose alkanes by 1,2 eliminations similar to those reported here for secondary ethers. The losses of methane from ionized butane and isobutane have been studied by Wolkoff and Holmes.<sup>17</sup> Their results do not lend themselves to ready interpretation, and the mechanism involved may not be similar to the loss of alkanes from ionized ethers.

Di-sec-butyl sulfide, N,N-dimethyl-sec-butylamine and sec-butylbenzene exhibited metastable peaks for loss of ethyl but not ethane. No molecular ion or any metastable peaks resulting from its decomposition were detected for methyl tert-pentyl ether.

#### **Experimental Section**

A Du Pont 21-491B mass spectrometer modified to allow control of the voltage across the electric sector was used for intensity measurements. The source was operated at 250 °C with the inlet of 120 °C. Metastable ion spectra were recorded by repeated scans of the magnetic field at 0.5 V increments of the electric sector voltage. Energy release data were recorded on an Hitachi RMU-6D of reversed geometry. The magnet was adjusted to pass m/z88 and the electric sector scanned. Energy release values were corrected for the width of the main beam.<sup>18</sup>

All ethers were prepared by the following Williamson procedure: an excess of NaH was washed free of mineral oil with CH<sub>3</sub>I and filtered. It was then covered with 25 mL of diglyme in a round-bottomed flask. The precursor alcohol (2 mL) was added dropwise with stirring. When hydrogen evolution had ceased, the mixture was warmed for 1 h and then cooled. A 20% excess of CH<sub>3</sub>I was added and the product distilled out. It was redistilled from  $LiAlH_4$  and purified by gas chromotography.

sec-Butyl-1,1,1- $d_3$  alcohol was prepared from CD<sub>3</sub>I and propanal via the Grignard reagent. Ethanol- $1, 1, 1-d_2$  was prepared by LiAlD<sub>4</sub> reduction of acetic anhydride<sup>19</sup> and converted to bromoethane- $1, 1-d_2$  with HBr-H<sub>2</sub>SO<sub>4</sub>. The bromoethane- $1,1-d_2$  was converted to the Grignard reagent and reacted with acetaldehyde to produce sec-butyl-3,3- $d_2$  alcohol. Deuterium contents were assayed by comparing the m/z 62 and 61 peaks for 2 and the m/z 75 and 74 peaks for 3.

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