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Scission Probabilities of the Skeletal Bond of Aliphatic Ethers by Electron Impact[*1]

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Mass spectra of eight aliphatic mono- and di-ethers have been measured with apparatuses of both ordinary and high resolution type, and scission probability of their skeletal bonds has been determined. By application of the molecular orbital theory on bond-scission by electron impact, the scission probability of the skeletal bonds has been evaluated, using only a few constants peculiar to the C–O bond so as to determine the molecular orbital. Comparison between theory and experiment has been found satisfactory on such ethers, even though they have lone-pair electrons in the inner part of the molecules. Thereby, scission of the skeletal bond has been shown explainable quite well by the primary processes in most ethers, except highly symmetric or large ethers.

Mass spectra of alkyl ethers were extensively studied by McLafferty,1) and several characteristic rules were recognized on the fragmentation by electron impact. Recently, the rules were investigated in more details by Gjerassi and Fenslau.2) Their discussion on the fragmentation processes, however, seems to remain in qualitative explanation and to lack in its molecular-theoretical derivation.

In the present report, probabilities of the skeletal bond-scission of several aliphatic ethers are investigated by determining the ions produced by use of apparatuses of both ordinary and high resolution type, and the molecular orbital (MO) theory is applied to explain the results quantitatively, generalizing the theory if necessary. The ethers to be investigated are methyl ethyl ether (MEE), methyl propyl ether (MPE), methyl butyl ether (MBE), diethyl ether (DEE), di-isopropyl ether (DIPE), methylal, ethyleneglyccl dimethyl ether (EGDME), and ethyleneglycol diethyl ether (EGDEE). Their structures are shown in Table 1, where the numerals attached to the bonds will become necessary in the following paragraphs.

Theory

In the previous reports on chain compounds,3) it was assumed that the scission probability of skeletal bonds of the parent ion produced by electron impact is proportional to the positive charge density of the highest occupied (HO) molecular orbital (MO) localized at the bonds. This assumption on the initial fragmentation, though imcompatible with the widely accepted scheme of competitive and successive fragmentation,4) will be understood, if the parent ion is a kind of super-excited ion of a short life5) which is less than the time of a molecular vibration, so that it dissociates immediately into ion and radical, being followed by secondary fragmentation. A part of the theoretical basis on the above scheme was proposed in details elsewhere, making cycloalkanes as examples. In the present report, theoretical investigation will not be carried out so far, regarding the MO theory just as a semiempirical "tool" of investigating mass spectra of complex organic molecules.

Calculation

In actual calculation, the charge density is assumed to be equal in amount of the electron density of the corresponding neutral molecule, and it will, therefore, be evaluated approximately by the following LCBO*-MO-method. The MO belonging to the skeletal bond, φ, is expressed by **Eq.** (1),6)

$$\Phi = \sum_{i=1}^{n} c_i \varphi_i \tag{1}$$

[*1] The **IX**th report of the molecular orbital theory of mass spectra (VIII: K. Hirota, *J. Phys. Chem.*, **71** sec. (1967).

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

2) C. Gjerassi and C. Fenslau, *J. Am. Chem. Soc.*, **87**, 5747 (1965).

3) K. Fueki and K. Hirota, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **81** 212 (1960).

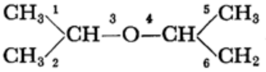
4) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

5) R. L. Platzman, *Radiation Res.*, **17**, 419 (1962).

[*3] Linear Combination of Bond Orbital.

6) R. D. Brown, *J. Chem. Soc.*, **1953**, 2615.

TABLE 1. ETHERS TO BE STUDIED IN THE PRESENT RESEARCH

(1)	Methyl ethyl ether	MEE	$CH_3\overset{1}{-}O\overset{2}{-}CH_2\overset{3}{-}CH_3$
(2)	Methyl propyl ether	MPE	$CH_3\overset{1}{-}O\overset{2}{-}CH_2\overset{3}{-}CH_2\overset{4}{-}CH_3$
(3)	Methyl butyl ether	MBE	$CH_3\overset{1}{-}O\overset{2}{-}CH_2\overset{3}{-}CH_2\overset{4}{-}CH_2\overset{5}{-}CH_3$
(4)	Diethyl ether	DEE	$CH_3\overset{1}{-}CH_2\overset{2}{-}O\overset{3}{-}CH_2\overset{4}{-}CH_3$
(5)	Di-isopropyl ether	DIPE	
(6)	Methylal		$CH_3\overset{1}{-}O\overset{2}{-}CH_2\overset{3}{-}O\overset{4}{-}CH_3$
(7)	Ethyleneglycol dimethyl ether	EGDME	$CH_3\overset{1}{-}O\overset{2}{-}CH_2\overset{3}{-}CH_2\overset{4}{-}O\overset{5}{-}CH_3$
(8)	Ethyleneglycol diethyl ether	EGDEE	$CH_3\overset{1}{-}CH_2\overset{2}{-}O\overset{3}{-}CH_2\overset{4}{-}CH_2\overset{5}{-}O\overset{6}{-}CH_2\overset{7}{-}CH_3$

where, φ_i is the bond-orbital of the ith skeletal bond, and summation is carried out on all the bonds, adopting united atom approximation.[7] Hence, the electron density in problem may be given by square of the expansion coefficient C_i of the HO molecular orbital. By the calculus variation, the energy levels can be determined by the secular equation (2), as usually done in the LCAO-MO method.

$$|e_{ij} - \delta_{ij}E| = 0 \tag{2}$$

In Eq. (2), e_{ij} denotes the matrix elements given by Eq. (3), and is to be called coulombic or exchange integral, according as $i=j$ or $i=j\pm1$.

$$e_{ij} = \int \varphi_i H \varphi_j \mathrm{d}\tau \tag{3}$$

where H denotes the hamiltonian for an electron in the field of bare nuclei and inner shells of electrons. Both integrals concerning hydrocarbons will be denoted by α and β, respectively, hereafter.

Since the so-called Hückel approximation is adopted, all the e_{ij} in Eq. (2) becomes coulombic integral α_i or exchange integral β_{ij}. However, coulombic integral at the terminal CH_3-C bond α_t is equated to $\alpha+2\beta$. As an exceptional case, $\alpha+1.5\beta$ is used for α_t of MEE, improvement ought to be understood as empirical, but not due to the inductive effect at the terminal methyl group of neutral molecules.[8]

The coulombic and exchange integrals of the C–O bond are equated preliminarily to $\alpha+2\beta$ and β, respectively, but coulombic integrals of the terminal CH_3–O bond are equated to $\alpha+3\beta$. Such a selection of constants for the C–O bond is qualitatively allowable if the effect of lone-pair electrons at the oxygen atom be considered.

Using the α_i and β_{ij} defined above, the energy values of the HO orbital E_h and expansion coefficients at the orbital were calculated. Thereby, it was found sufficient only to determine the value of $\lambda_h=(\alpha-E_h)/\beta$ instead of E_h itself. At the same time, it was found not necessary to know the absolute values of α_i and β_{ij}, but sufficient to know their relative values to α and β.

Experimental

Since the mass spectra obtained with an ordinary apparatus are often difficult to assign each peak to a definite ion, mass spectra were measured on a high

TABLE 2. MASS SPECTAR OF METHYL ETHYL ETHER AND DIETHYL ETHER

A, Hitachi RMU-5; B, Hitachi RMU-7hr; C, API

m/e	MEE $CH_3OCH_2CH_3$			DEE $CH_3CH_2OCH_2CH_3$		
	A	B	C	A	B	C
15	8*	7.2	9	2.5		
16		0.2				
26	3.4	2.5		1.6	1.5	
27	7.9	7.0	7	7.4	2.0	5
28	3.0	4.1	3	2.5	2.0	1.5
29	18.9	15.1	18	15.4	17.3	12
30	1.3	0.9	1	0.6	0.8	0.6
31	7.7	7.3	7	24.3	33.7	30
32	0.8	0.4	1	0.5	0.4	
41	0.3	0.2		1.4	1.3	2
42	0.6	0.4	1	0.3	0.5	0.3
43	2.7	2.0	2	2.3	2.3	2
44	0.3	0.9		0.7	0.7	0.6
45	38.6	35.8	37	10.3	11.0	12
46	0.6	0.7				
59	4.2	3.9	4	15.4	12.0	16
60	10.0	10.8	10	0.5	0.4	
73	—			0.6	0.6	1
74	—			8.9	6.4	11

* Estimated value

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[7] J. L. Franklin, *J. Chem. Phys.*, **32**, 1304 (1954). The accuracy of this method was discussed in Part VIII of the present series of research.

[8] *Cf.* L. C. Lorquet, *Molec. Phys.*, **9**, 101 (1965).

resolution apparatus as well as on ordinary one. In order to check the discrimination due to apparatus, the mass spectra obtained on MEE and DEE are compared with those of literature (Table 2), making total sum of the peaks to be 100. Column A is the one run on an apparatus of ordinary type (Hitachi RUM-5A) installed at JARRP, and column B on an apparatus of high resolution type (Hitachi RMU-7hr) installed at Osaka University, its resolution being *ca.* 5000. Both are of a magnetic scanning type, but their normal operating conditions are different as follows:

	Ionizing voltage, V	Accelerating voltage	Electron current, μA
RMU-5A:	90	1500	80
RMU-7hr:	80	2000	100

Column C is the spectra recalculated from the API mass spectral catalog (CEC Model 21-103). In column B, multiplet peaks appearing practically at the same *m/e* are summed up. Discrepancies among these spectra are not large, in spite of the measurement of different apparatuses and operating conditions. Similar tendency was obtained on other six ethers, so that the present data are assumed sufficient to be utilized in discussion.

In order to meet the requirement to be explained, MEE-d$_3$, $CD_3OCH_2CH_3$ was synthesized and its spectrum was measured and used mainly in discussion.

Results

Assignment of Peaks and Allotment of Ions. By combining the results of ordinary and high resolution spectra, multiplet peaks were allotted to each composite ions; *e. g.*, in the case of MPE, ratio of $C_2H_5^+$ to CHO^+ ions was estimated to be 22.5%/77.5% from the doublet peaks at *m/e* 29. Thus, ratio of the doublet peaks was determined and the results are summarized in Table 3, which indicates that some major peaks consist of two ions. Taking this point into consideration, spectral peaks with their assigned ions are shown in Table 4, where sums of the total ions including parents ions are made 100%. Details of the assignment of each peak to corresponding ions are described in the next paragraph as well as number of the ruptured bond to produce the corresponding ions.

Table 3. Allotment of multiplet peaks to ions in MEE, MPE, DEE and methylal

	m/e	MEE	MPE	DEE	Methylal
28	C_2H_4	92	81.5	93	75
	CO	8	18.5	7	25
29	C_2H_5	53.5	22.5	86	
	CHO	46.5	77.5	14	
30	C_2H_6	15		50	
	CH_2O	85		50	
40	C_3H_4		91.5		66.5
	C_2O		8.5		34.5
41	C_3H_5	70		98	
	C_2HO	30		2	
42	C_3H_6		14.5	2.5	80
	C_2H_2O		85.5	97.5	20
43	C_3H_7		29.5	2	85
	C_2H_3O		70.5	98	15
44	C_3H_8	22	14	18.5	22
	C_2H_4O	78	86	81.5	20
	CO_2	—	—	—	58

Ruptured Bond. It is easy for most of the ions to estimate the ruptured bond, if their chemical formula is known, but it is still difficult for several ions. For instance, the *m/e* 15 peak can be assigned to be CH_3^+ ion without ambiguity by high resolution spectra, but the ruptured bond cannot be determined uniquely as shown by the following example:

$$\mathrm{CH_3}\underset{\alpha}{\overset{1}{—}}\mathrm{O}\overset{2}{—}\mathrm{CH_2}\overset{3}{—}\mathrm{CH_2}\underset{\beta}{\overset{4}{—}}\mathrm{CH_3}$$

$$—\begin{cases}\xrightarrow{\alpha} \mathrm{CH_3}^+ + \dot{\mathrm{O}}\mathrm{CH_2CH_2CH_3} \\ \xrightarrow[\beta]{} \mathrm{CH_3OCH_2}\dot{\mathrm{C}}\mathrm{H_2} + \mathrm{CH_3}^+\end{cases} \tag{4}$$

However, both processes could be discriminated in the case of MEE by comparing the spectrum of $CD_3OCH_2CH_3$ with that of $CH_3OCH_2CH_3$, and ratio of α and β bond-scission could be determined, if the isotopic effect be neglected. Such procedure was not taken up in other ethers, because amount of the CH_3^+ ions was always so small that their origin is not important in order to discuss the degree of agreement between theory and experiment entirely.

There are several ions, however, whose ruptured bond is difficult to be determined. Among them, estimation of the origin of the $(CHO)^+$ ion is comparatively easy. In the case of MEE, this ion can be produced from the $(CH_3O)^+$ ion either by successive scission of the second bond with 2H detachment,

$$(\mathrm{CH_3O}\overset{2}{—}\mathrm{CH_2CH_3})^+ \rightarrow (\mathrm{CH_3O})^+ + \dot{\mathrm{C}}\mathrm{H_2CH_3}$$

$$\xrightarrow{-2\mathrm{H}} (\mathrm{CHO})^+ + \dot{\mathrm{C}}\mathrm{H_2CH_3} + 2\mathrm{H} \tag{5}$$

or by double scissions of the first and third bonds with H detachment.

$$(\mathrm{CH_3}\overset{1}{—}\mathrm{O}\overset{2}{—}\mathrm{CH_2}\overset{3}{—}\mathrm{CH_3})^+ \rightarrow$$

$$(\mathrm{OCH_2})^+ + 2\dot{\mathrm{C}}\mathrm{H_3} \rightarrow (\mathrm{OCH})^+ + 2\dot{\mathrm{C}}\mathrm{H_3} + \mathrm{H} \tag{6}$$

However, the process (5) was considered reasonable, because scission probability of the second bond is theoretically large, besides the simpleness of the process. This conclusion is supported by the mass spectrum of MEE-d$_3$, where CH_3O^+ and CH_2O^+ are shown negligible few in Table 4. In the cases of other ethers, (MPE, MBE and EGDME), the same allotment was adopted, because the situation may be the same.

Of all the ethers, DIPE includes the largest number of ambiguous ions, *i. e.,* only 38% of the total ions could be allotted without ambiguity. Of the remaining ions, 51.9% requires at least two bond scissions, and it is difficult to estimate which scission is the first of the two, as explained on the orgin of the CH_3^+ ions. Therefore, determination of scission-probability of DIPE was more difficult than that of other ethers. DEE was also

TABLE 4. ASSIGNED IONS AND THEIR RELATING BOND-SCISSION

1) MEE-d_3

Ion	Peak height %		Ruptured bond
CD_3	9.8	16.5	1
CD_2	1.9		
CD	1.7		
C_2H_3O	0.6		
C_2H_2O	2.5		
C_2H_5	9.9	33.2	2
C_2H_4	3.3		
C_2H_3	6.1		
C_2H_2	3.2		
C_2H	0.3		
CDO	8.9		
CD_2O	1.4		
CD_3O	0.1		
CH_3	3.6	35.1	3
CD_3OCH_3	30.9		
CD_3OCH	0.6		
		84.8	
CD_2H	1.1	5.7	u
CH_3O	0.1		
CD_2HO	3.9		
C_2D_2, CD_4O	0.6		
M-1	2.9	9.6	p
M[a)	6.7		
Total		100.1	

2) MPE

Ion	Peak height %		Ruptured bond
CH_3	4.9	5.1	1 or 4
C_3H_7O	0.2		
CHO	7.0	15.7	2
CH_3O	1.0		
C_3H_7	0.6		
C_3H_6	0.2		
C_3H_5	4.5		
C_3H_3	2.4		
C_2H_5	2.0	77.5	3
C_2H_4	1.7		
C_2H_3	5.3		
C_2H_2	0.8		
C_2H_5O	64.2		
C_2H_6O	1.2		
C_2H_3O	1.4		
C_2H_2O	0.9		
		98.3	
CO	0.5	0.5	u
M-1	0.4	1.4	p
M[a)	1.0		
Total		100.2	

a) M denotes the parent ion.

3) MBE

Ion	Peak height %		Ruptured bond
CH_3	3.3	3.3	1 or 5
CH_3O	0.8	13.2	2
CHO	1.1		
C_4H_9	0.8		
C_4H_8	9.7		
C_4H_7	0.8		
C_3H_8	0.5	66.8	3
C_3H_7	0.5		
C_3H_6	0.1		
C_3H_5	4.8		
C_3H_4	0.3		
C_3H_3	2.4		
C_2H_6O	0.9		
C_2H_5O	56.0		
C_2H_4O	0.3		
C_2H_3O	0.5		
C_2H_2O	0.5		
C_2H_5	6.1	14.7	4
C_2H_4	2.4		
C_2H_3	4.5		
C_2H_2	0.6		
C_2H_7O	1.1		
		98.0	
CO	0.5	0.5	u
M	1.8	1.8	p
Total		100.3	

4) DEE

Ion	Peak height %		Ruptured bond
CH_3	2.5	18.4	1 or 4
C_3H_8O	0.5		
C_3H_7O	15.4		
C_2H_6	0.3	38.6	2 or 3
C_2H_5	13.3		
C_2H_4	2.5		
C_2H_3	7.4		
C_2H_2	1.6		
C_2H_5O	10.3		
C_2H_4O	0.6		
C_2H_3O	2.3		
C_2H_2O	0.3		
		57.0	
CHO	2.4	32.2	
CH_2O	0.3		
CH_3O	29.3		
CH_4O	0.5		
C_3H_8	0.1	1.5	u
C_3H_5	1.4		
M-1	0.6	9.5	p
M	8.9		
Total		100.2	

TABLE 4 (Continued)

5) DIPE

Ion	Peak height %		Ruptured bond
CH_3	2.3	11.1	1, 2, 5 or 6
$C_5H_{11}O$	8.8		
C_3H_8	0.3	26.8	3 or 4
C_3H_7	15.5		
C_3H_6	1.0		
C_3H_5	4.9		
C_3H_7O	4.1		
C_3H_6O	1.0		
		37.9	
C_2H_4	0.4	4.8	i_1 1+3 *etc.*
C_2H_3	4.2		
C_2H_2	0.2		
C_2H_5O	44.1	47.1	i_2 1+4 *etc.*
C_2H_4O	0.3		
C_2H_3O	2.7		
Unknown peaks		8.4	u
M	1.8	1.8	p
Total		100.0	

6) Methylal

Ion	Peak height %		Ruptured bond
CH_3	2.3	2.3	1 or 4
C_2H_6O	0.8	70.2	2 or 3
C_2H_5O	38.1		
C_2H_4O	0.7		
C_2H_3O	0.5		
CH_4O	0.3		
CH_3O	5.1		
CH_2O	2.2		
CHO	22.5		
		72.5	
CO	1.0	3.5	u
m/e 47	1.9		
CO_2	0.4		
C_2H_6	0.2		
M-1	23.3	31.1	p
M	0.8		
Total		100.1	

7) EGDME

Ions	Peak height %		Ruptured bond
CH_3	0.3	1.5	1 or 5
CH_2	1.2		
C_2H_6	0.1	32.5	2 or 4
C_2H_5	3.1		
C_2H_4	1.9		
C_2H_3	1.9		
C_2H_2	0.7		
CH_3O	3.2		
CH_2O	0.9		
CHO	9.9		
C_3H_8O	5.8		
C_3H_7O	1.5		
C_3H_6O	3.5		
C_2H_6O	1.2	59.1	3
C_2H_5O	53.6		
C_2H_4O	0.3		
C_2H_3O	3.2		
C_2H_2O	0.7		
		93.1	
CO	0.6	1.0	u
CO_2	0.4		
M	5.8	5.8	
Total		99.9	

8) EGDEE

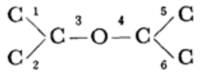
Ions	Peak height %		Ruptured bond
CH_3	2.1	2.4	1 or 7
$C_5H_{10}O_2$	0.3		
C_2H_6	0.2	16.1	2 or 6
C_2H_5	7.8		
C_2H_4	2.0		
C_2H_3	5.2		
C_2H_2	0.9		
C_2H_6O	0.4	34.8	3 or 5
C_2H_5O	17.8		
C_2H_4O	1.5		
C_2H_3O	6.2		
C_2H_2O	0.6		
$C_4H_{11}O$	0.3		
$C_4H_{10}O$	6.4		
C_4H_9O	1.1		
C_4H_8O	0.5		
C_3H_9O	0.3	17.4	4
C_3H_8O	0.5		
C_3H_7O	16.6		
		70.7	
CH_4O	0.3	20.2	i
CH_3O	18.1		
CH_2O	0.2		
CHO	1.6		
Unknown peaks		7.7	u
M		0.6	p
Total		99.2	

difficult, though of lesser degree in allotment of ions, because 57% of the total ions would be allotted without ambiguity. Similar difficulty exists in the largest ethers (EGDEE). The reason of bringing about such results will be explained afterwards.

After the above procedure, scission probability of each bond can mostly be evaluated on all the ethers. For instance, the probability at the second bond of DEE is given by the sum of $C_2H_5^+$ and $(C_2H_5O)^+$ ions. Summarized result on eight ethers is shown in Table 4, where u and p in the column of the ruptured bonds denote undeterminable ions and parent ions (M and M-1), respectively, and i in the same column denotes the ions produced by multiple scissions.

Table 5. Observed and calculated scission probability of ethers

MEE			MPE			MBE			DEE		
Bond	Obs.	Calcd.	Bond	Obs.	Calcd.	Bond	Obs.	Calcd.	Bond	Obs.	Calcd.
1	19.4	7	1, 4	5.2	10	1, 5	3.4	4	1, 4	32.3	$27._5$
2	39.2	44	2	16.0	12	2	13.5	5		(38.9)	
3	41.2	48	3	78.8	77	3	68.2	48	2, 3	67.4	$72._5$
						4	15.0	45		(61.3)	
$C\overset{1}{-}O\overset{2}{-}C\overset{3}{-}C$			$C\overset{1}{-}O\overset{2}{-}C\overset{3}{-}C\overset{4}{-}C$			$C\overset{1}{-}O\overset{2}{-}C\overset{3}{-}C\overset{4}{-}C\overset{5}{-}C$			$C\overset{1}{-}C\overset{2}{-}O\overset{3}{-}C\overset{4}{-}C$		
$x=3\ \ 2\ \ 1.5$			$x=3\ \ 2\ \ 0\ \ 2$			$x=3\ \ 2\ \ 0\ \ 0\ \ 2$			$x=2\ \ 2\ \ 2\ \ 2$		
$\lambda_h=-0.54$			$\lambda_h=0.76$			$\lambda_h=1.32$			$\lambda_h=-0.38$		

DIPE			Methylal			EGDME			EGDEE		
Bond	Obs.[a]	Calcd.	Bond	Obs.	Calcd.	Bond	Obs.	Calcd.	Bond	Obs.	Calcd.
1+2	29	9	1, 4	3.2	16	1, 5	1.6	2	1, 7	3.4	1
5+6	(41)		2, 3	96.8	84	2, 4	34.9	24	2, 6	22.6	4
3, 4	71	91				3	63.5	75	3, 5	49.3	24
	(59)								4	24.6	71
			$C\overset{1}{-}O\overset{2}{-}C\overset{3}{-}O\overset{4}{-}C$			$C\overset{1}{-}O\overset{2}{-}C\overset{3}{-}C\overset{4}{-}O\overset{5}{-}C\cdots$			$C\overset{1}{-}C\overset{2}{-}O\overset{3}{-}C\overset{4}{-}C\overset{5}{-}O\cdots$		
$x=2\ \ 2\ \ 2\ \ 2$			$x=3\ \ 2\ \ 2\ \ 3$			$x=3\ \ 2\ \ 0$			$x=2\ \ 2\ \ 2\ \ 0$		
$\lambda_h=1.45$			$\lambda_h=-0.69$			$\lambda_h=0.79$			$\lambda_h=0.83$		

a) Values in parenthesis are calculated by allotting u peaks equally to both kinds of scissions.

Scission Probability. Scission probability thus determined from the data of Table 4 is summarized in Table 5. Thereby, only the ions whose ruptured bonds were determinable are considered and the probability is expressed in %. In Table 5, calculated probability is compared with the observed and the HO energy level in λ_h unit on each ether is shown, in addition to the $x_i=(\alpha-\alpha_i)/\beta$ used in the calculation.

Among the eight ethers, DIPE is the worst in coincidence between theory and experiment, because of the particular situation of this ether, whose determinable ions were less than 40% of the total. Similar tendency, though of less degree, is shown in the case of DEE. Other ethers especially, if MBE and EGDEE are excluded, show a good coincidence between theory and experiment.

Before entering into the paragraphs of discussion, it might be noted that the above probability obtained is the one at normal operating condition of the mass spectrometer.

Discussion

First, the peculiarity of ethers might be noted in comparison with the compounds hitherto investigated in the present series of study; *i. e.*, an atom containing lone-pair electrons exists in the inner skeletal bond of each ether. Considering this situation, such a degree of agreement of the theory with the experiment is quite good. Taking it into account, several points will be discussed.

Table 6. Main peaks in the spectra of DEE and MBE *vs.* ionizing potential

A. DEE $C\overset{15}{\underset{59}{-}}C\overset{29}{\underset{45}{-}}O\overset{45}{\underset{29}{-}}C\overset{59}{\underset{15}{-}}C$

m/e		Ionizing pot. volt[a]				
		90	50	25	20	15
15	CH_3	0.4	0.3	—	—	—
29	C_2H_5	15	14	11	5	1
31	CH_3O	30	30	34	33	17
45	C_2H_5O	10	10	11	10	4
59	C_3H_7O	11	15	21	27	34
74	Parent ion	10	9	13	19	40
Sensitivity		5.5	1.0	0.41	0.34	0.13

B. MBE $C\overset{15}{-}O\overset{31}{\underset{57}{-}}C\overset{45}{-}C\overset{59}{\underset{29}{-}}C\overset{73}{\underset{15}{-}}C$

m/e		Ionizing pot. volt[a]				
		90	50	25	20	15
15	CH_3	2	3	—	—	—
29	C_2H_5	6	8	—	4	0.6
31	CH_3O	0.7	0.9	—	—	—
41	C_3H_5	5	5	4	3	2
45	C_2H_5O	56	53	65	68	67
56	C_4H_8	11	10	14	17	20
57	C_4H_9	1	1	1	1	1
59	C_3H_7O	1	1	2	1	2
Sensitivity		—	1.0	0.1	0.1	0.07

a) Absolute values are not so exact.

Secondary Scissions. Among the three unsymmetric ethers, MPE is the best in coincidence, followed by MEE-d_3 and MBE. Concerning MBE, the result may be partly due to improper selection of integral values. Another important cause would be occurrence of multiple scissions which ought to be expected. Even though this process cannot be recognized in the procedure of determining the ruptured bond, this possibility exists, as will be discussed again. Comparatively large disagreement in MEE-d_3 may be due to the same reason rather than the isotopic effect of bond scission.

Similar cause of disagreement may occur in the cases of symmetric ethers, and EGDEE is the typical example, because many ions (about 20%) cannot be explained without assuming multiple scissions, besides the unassignable ions reaching *ca.* 8%. Concerning other symmetric ethers, secondary scissions also seem to occur with high probability, as already mentioned, though the assignment to definite ions was easy.

For the sake of confirmation of the secondary scission, the effect of ionizing potential on bond-scission was investigated on several ethers. The result on DEE is shown in Table 6A.

Though the *m/e* 59 peaks may be produced from DEE by the primary scission of bond 1 or 4, the highest *m/e* 31 peaks can be ascribed to a secondary scission from the *m/e* 59 ion.

$$CH_3\overset{1}{—}CH_2\overset{2}{—}O\overset{3}{—}CH_2\overset{4}{—}CH_3$$

$$\rightarrow \underset{m/e\ 59}{CH_3CH_2\text{-}O^+\text{-}CH_2}$$

$$\rightarrow CH_2{=}CH_2 + \underset{m/e\ 31}{HO^+{=}CH_2} \qquad (7a)$$

$$\rightarrow \underset{m/e\ 29}{CH_3\text{-}CH_2^+} + O{=}CH_2 \qquad (7b)$$

If the above mechanism be true, the *m/e* 31 ion will be smaller at lower ionizing voltage, because excess energy which is necessary for the secondary processes would decrease. At the same time, the *m/e* 59 ion would increase on the contrary. This expectation is supported by comparing the ratio of the *m/e* 31 ion to the *m/e* 59 ion in Table 6A. The effect of ionizing potential on the *m/e* 29 peak can be explained similarly. *Cf.* Eq. (7b).

Another example of the effect of ionizing potential on the bond-scission is shown on MBE. Table 6B indicates that the *m/e* 56 ion increases and *m/e* 29 ion decreases with the decrease of ionizing potential. This finding denotes apparently increase of scission at bond 4 and decrease of scission at bond 2, suggesting that the observed scission probability has to increase at bond 4 and to decrease at bond 2, as compared with the data in Table 5. Thus the agreement of the calculated result of MBE with the observed would be improved.

It was found also that the discrepancy in MEE-d_3 decreased markedly by lowering the ionizing potentil; *i. e.*, scission probability at bond 2 becomes apparently larger than the theoretical due to secondary scission. The worst result of DIPE may be explained similarly, if the effect of ionization potential be studied.

Lone-pair Electrons and Fragmentation. In connection to the above discussion, the behavior of the lone-pair electrons at oxygen atom against the electron bombardment will be discussed, taking DEE as an example. The HO level of this ether is calculated to be -14.43 V from $\lambda_h=-0.38$ (*cf.* Table 5), assuming α and β of C-C bond to be -13.75 V and -1.80 V, respectively. The value is lower by four volts than its ionization energy (10.2 V).[9] This result indicates that at lower ionizing potential the lone-pair electrons would be expelled out, producing parent ions. However, as the ionizing potential is increased, electrons at the skeletal bonds are also expelled out, because the difference of the energy level of both electrons is so small that the ionizing potential of normal operating condition of mass spectrometers is sufficiently large. This reasoning can be explained by the fact that relative amount of the parent ion decreases according to the increase of the ionizing potential, as Table 6 indicates.

Concerning the role of lone-pair electrons, the difference of the C-C bond and C-O bond might be mentioned. In the present treatment, the MO of the skeletal bond was constructed from both kinds of bond, putting aside the presence of lone-pair electrons. However, some interaction may exist between the positive hole at the C-O bond and lone-pair electrons. The effect would appear to decrease the positive hole formed at the C-O bond. The reason why proper coulombic integral at the C-O bond may be $\alpha+2\beta$ can be explained.

Conclusion

It has been shown possible to apply the MO method of mass spectra to alkyl ethers which include lone-pair electrons in the inner part of the molecules.

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[9] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952). Unpublished result measured by J. Takezaki.