ELECTRON IMPACT SPECTROSCOPY OF SOME SUBSTITUTED OXIRANES

by

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INTRODUCTION

Studies of the interaction of electrons with atoms and molecules are of fundamental importance in understanding the mechanisms of unimolecular decompositions of ionic species. Electron impact spectroscopic data have been reported for a large number of molecules containing oxygen; among these are ethers, alcohols, acids, ketones, esters and some inorganic oxygen-containing compounds. Little information of this type is available for cyclic ethers, although the API Tables(26) and Beynon(2) have reported the mass cracking patterns for a few of the cyclic ethers. Gallegos and Kiser(11) in this laboratory conducted electron impact investigations on some oxacycloalkanes of different ring sizes. Investigation of a group of substituted oxiranes, 3,4-epoxy-1-butene, epichlorohydrin(3-chloro-1,2-epoxypropane), epibromohydrin(3-bromo-1,2-epoxypropane) and 1,2-epoxy-3-methoxypropane was initiated in an attempt to further our understanding of the dissociation processes which occur subsequent to the ionization of the substituted three-membered cyclic ethers.

A comparison of the mass spectra, appearance potentials and heats of formation for the ions of related compounds such as these provides useful systematic information about the molecular structure and relative probabilities of bond dissociation processes within the compounds. Too, the fragments formed by electron impact and the energetics of their formation are of general interest in radiation chemistry.

The compounds investigated are low-boiling colorless liquids possessing significant vapor pressure at room temperature. The mass spectral cracking patterns, ionization potentials and appearance

potentials for the principal positive ions reported here are new.

The ionization potentials of 3,4-epoxy-1-butene, epichlorohydrin, epibromohydrin and 1,2-epoxy-3-methoxypropane were calculated from theory to be 9.3, 9.7, 9.4 and 9.2 electron volts, respectively. Ionization potentials were not determined because of the very small parent peak intensities; 3,4-epoxy-1-butene was an exception and it's ionization potential was found to be 9.7 ± 0.3 ev. This latter value is to be comparedd to the theoretical value of 9.3 ev. The probable ionization and dissociation processes have been determined, consistent with computed energetics and heats of formation, for the various ions observed.

THEORETICAL CALCULATIONS

A number of different methods have been utilized to calculate ionization potentials(21,29). G. G. Hall and Sir Lennard-Jones, in their series of papers(13-17, 23 and 24), recognized that a close relation existed between the vertical ionization potential of a molecule and an energy parameter associated with a molecular orbital(16). A vertical ionization potential is defined as the difference in total electronic energy when one electron is removed at constant internuclear distance. Since ionisation removed an electron from a molecular orbital, equations from molecular orbital theory should allow one to calculate ionization potentials. However, equations based on electron pair and molecular orbital theories involve a great amount of computation; therefore a new semi-empirical method was proposed in terms of equivalent orbitals. Equivalent orbitals are defined as having the property of being identical with regard to distribution in space; they differ only in their orientation. According to this

new semi-empirical approach, molecules containing the same atoms or groups of atoms could be described by similar equations that link together a large number of experimental results by means of a small number of empirical parameters and equations(14).

Hall proposed the secular equation

$$\left| e_{ij} - E_{ij} \right| = 0 \qquad (1)$$

in order to calculate ionization potentials from a knowledge of only the equivalent orbital quantity e_{ij}. The parameters are evaluated semi-empirically using a matrix of equivalent orbital parameters whose diagonal elements are the energies and whose non-diagonal elements represent parameters of interaction between the equivalent orbitals or groups treated as one atom. By comparing the matrices and the experimental values for a number of molecules, suitable values for the parameters can be determined and used to predict other ionization potentials. This is illustrated by the following simple application of the theory to the methyl-substituted ethylenes(14). The ionization potential of propene is the lowest root of the equation

$$\begin{vmatrix} d - E & x \\ x & m - E \end{vmatrix} = 0 \qquad (2)$$

where:

d = double bond parameter (taken as equal to the ionization potential of ethylene).

m = methyl group parameter (taken as equal to the ionization potential of methane).

x = methyl-double bond interaction parameter.

It is assumed that the x interaction parameter between groups on two adjacent carbon atoms may be neglected.

Using the ionization potential of propene and knowing the d and m parameters, the x parameter may be calculated. Then, using the calculated x parameter, the ionization potentials of 2-butene can be calculated from the roots of the equation:

$$\begin{vmatrix} m - E & x & 0 \\ x & d - E & x \\ 0 & x & m - E \end{vmatrix} = 0 \qquad (3)$$

The lowest root of equation (3) is then the first ionization potential of 2-butene.

In a similar manner, the y parameter for the interaction between two methyl groups attached to the same carbon atom may then be calculated from 2-methylpropene using the experimentally determined ionization potential of that compound. The ionization potentials for 2-methyl-2-butene and 2,3-dimethyl-2-butene then may be calculated using the previously determined x and y parameters. Results agreeing quite closely with experimental values can be calculated by this method for the methyl-substituted ethylenes(14), and for a large number of other compounds(9,10,13,15,19,22).

A similar theoretical treatment of the ionization potentials based on the Hall equivalent orbital method was applied to the studied ethylene oxide compounds. For this purpose, the $-\underline{CHCH_2}O$ unit was treated as a group and the interaction parameters between the $-\underline{CHCH_2}O$ group and the substituted groups were calculated.

For the molecule $X-\underline{CHCH_2}O$, where X is $-CH{=}CH_2$, $-CH_2Cl$, $-CH_2Br$ and $-CH_2OCH_3$, the general determinental equation is:

$$\begin{vmatrix} f - E & b \\ b & d - E \end{vmatrix} = 0 \qquad (4)$$

where:

b = parameter for interaction of X with -$\underbrace{CHCH_2O}$ group.

f = cyclic ether parameter (taken as equal to the ionization potential of ethylene oxide(25)).

d = X group parameter (taken as equal to the ionization potential of HX).

E = the ionization potential of X-$\underbrace{CHCH_2O}$.

The value of the b parameter of each compound was determined from a knowledge of the ionization potentials of compounds X-$CH(CH_3)_2$, which were assumed to have parameters similar to those of the investigated compounds. The results of these calculations will be discussed in a subsequent section.

EXPERIMENTAL

Mass Spectrometry

The mass spectra and appearance potentials reported here were obtained using a Bendix model 12-100 time-of-flight (TOF) mass spectrometer with an analog output system consisting of a monitor and scanner. This instrument has previously been described in detail by a number of workers(4,11,18-20, 32-34) and therefore it will only be briefly described here. A schematic diagram of the instrument is given in Figure 1.

The Bendix TOF mass spectrometer produces 10,000 mass spectra per second of the gaseous sample introduced into the ion source chamber. The ions initially formed are pulsed at a repetition rate of 10 kc into an electric field and accelerated through a potential drop of 2800 volts to the field-free drift tube which has a flight path of about one meter. All ions gain equal kinetic energy from this potential drop and therefore their

velocities will vary inversely as the square root of their masses (for similarly charged ions). Since all ions leave the ion source at essentially the same time and they are allowed to drift the same distance before striking e the collector, those ions of equal mass will bunch and separate from those of a different mass. As each group of ions strikes the collector cathode, they cause the release of secondary electrons which are in turn amplified by the magnetic electron multiplier. The individual ion currents were recorded on a Sanborn model 152 recording system, as well as displaying the resultant amplified electron pulses with a Tetronix 545A oscilloscope.

Mass spectra for each of the compounds were obtained at nominal electron energies of 70 e.v. The resolution of the instrument is quite goodd up to mass 150 and is within $\Delta h/H=0.5$ up to mass 250. Δh is the height of overlap between two adjacent peaks of equal height, H(2). Samples for analysis were introduced into the instrument through a glass inlet system which was connected by copper tubing to the stainless steel inlet system of the ion source. The sample flow was controlled by a stainless steel needle valve.

The determination of mass spectra and appearance potentials were made under pressures between 2×10^{-6} and 5×10^{-6} mm(Hg), obtained with a forepump and a mercury diffusion pump. The cold trap-baffle was always refrigerated with liquid nitrogen coolant. The ion-source filament was operated at 2.5 amperes and the trap current at 0.125 microamperes. As the electron energy was decreased during a determination, some small decrease of the trap current was noted. However, this trap current decrease apparently had no significant effect on the results obtained, since ionization potentials for the rare gases determined in the same way were found to be in fair agreement with literature values(19). The procedure utilized in

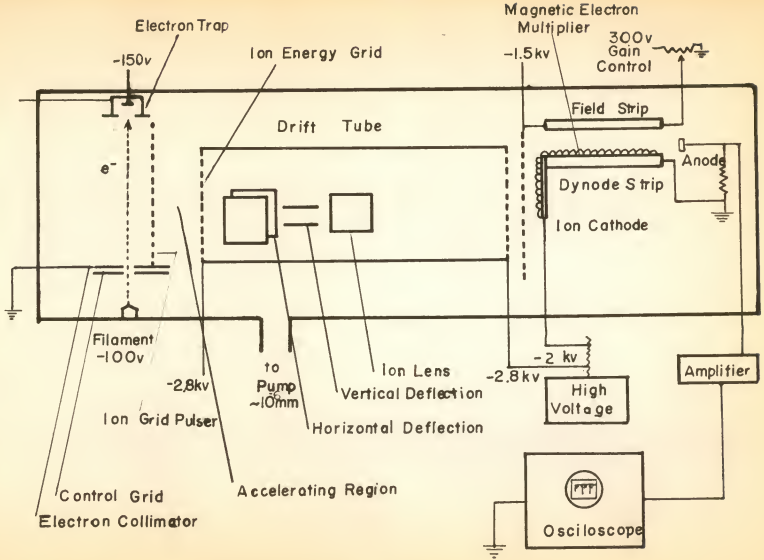

FIGURE 1 TIME—OF—FLIGHT MASS SPECTROMETER

determining appearance potentials involved centering one electronic gate of the electron multiplier on the mass peak on which the determination was being made and a second electronic gate on a major isotope of the calibrating gas which was admixed with the material being investigated. The electron energy was then decreased slowly at recorded intervals. The intensities of the two ions under investigation were subsequently recorded with the Sanborn recording system as a function of the electron energy. Ionization efficiency curves, such as ones shown in Figures 2 and 3, were prepared by plotting ion intensities as a function of the electron energy. Appearance potentials were calculated using the technique of extrapolated voltage difference described by Warren(31). Ionization efficiency curves were plotted for each determination of appearance potential and the linear portion of the curves forced parallel. The electron voltage differences, ΔE, between two curves at a given current were plotted as a function of the current and the value of ΔE obtained upon extrapolation to zero current was added algebrically to the ionization potential of the calibrating gas. Xenon, mixed with the compound being investigated, was used to calibrate the ionizing voltage. The known spectroscopic value for the ionization potentials of xenon were used(27).

Materials Used

3,4-epoxy-1-butene was obtained from Matheson, Coleman and Bell Division, The Matheson Company, Inc. No impurities were noted in the mass spectrum and hence the sample was used as received. Epichlorohydrin and epibromohydrin were obtained from Eastman Organic Chemicals. 1,2-epoxy-3-methoxypropane was received from K and K Laboratories, Inc. No significant impurities were observed in the mass spectra of these

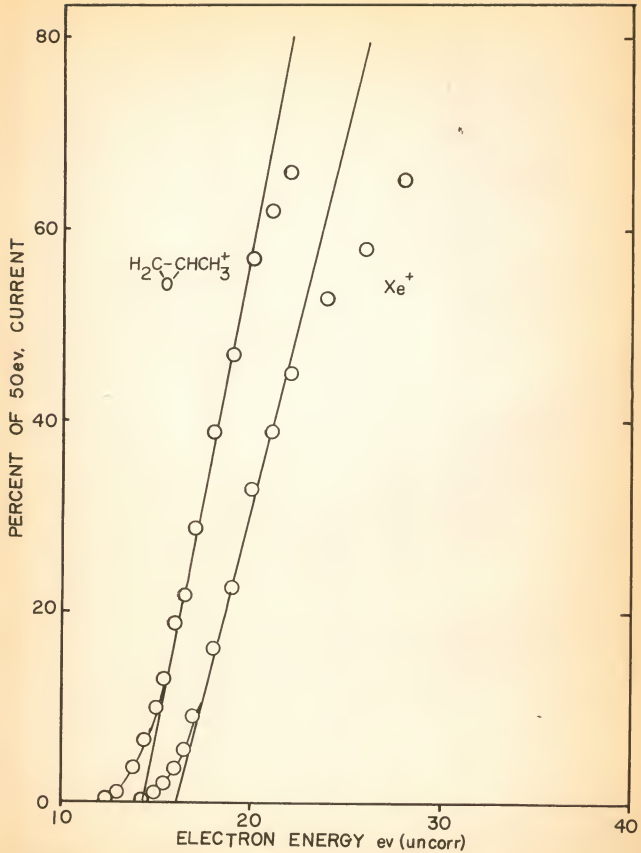

FIGURE 2 TYPICAL IONIZATION EFFICIENCY CURVES

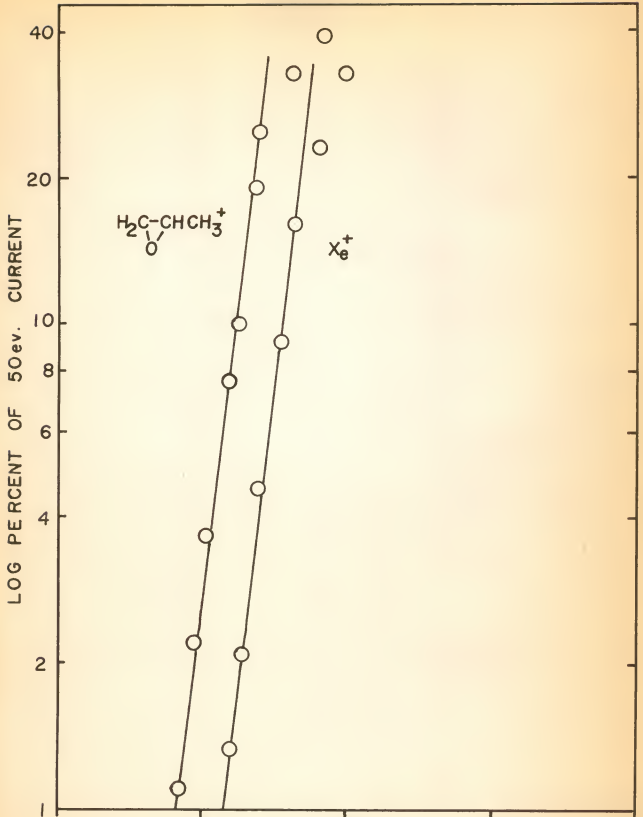

FIGURE 3 TYPICAL IONIZATION EFFICIENCY CURVES

compounds; consequently the samples were used as received for these studies.

RESULTS

The results of the determinations of the mass spectral cracking patterns and the appearance potentials for the principal ions of 3,4-epoxy-1-butene, epichlorohydrin, epibromohydrin and 1,2-epoxy-3-methoxypropane are summarized in Tables 1-4. In the first two columns are given the principal ions formed at 70 e.v. and their relative abundances. In column 3 are given the appearance potentials of the principal ions. The probable processes by which the various ions are formed, consistent with the measured energetics, are given in the fourth column and the calculated heats of formation of these ions are given in the last column.

The following heats of formation were used in the calculations with the measured appearance potentials: C_4H_6O was estimated thermochemically and taken to be 10 kcal./mole; C_3H_5OCl, -17 kcal./mole was evaluated from the reported heat of combustion, 423 $\pm$ 0.1 kcal./mole(3), and by the method reported by Franklin(9); C_3H_5OBr, -6 kcal./mole; $C_4H_8O_2$, -43 kcal./mole. Standard heats of formation used for the calculations are as follows: CH_3, 32 kcal./mole(28); C_2H_2, 54.2 kcal./mole(28); C_2H_3, 64 kcal./mole(30); C_2H_4, 12.5 kcal./mole(28); C_2H_5, 22 kcal./mole(8); C_3H_4, 45.9(28); C_3H_2, 87 kcal./mole(8); CHO, -2.8 kcal./mole(28); CH_2O, -27.7 kcal./mole(28); CH_3O, 10 kcal./mole(8); C_2H_3O, -11 kcal./mole(12); CO, -27 kcal./mole(28); Cl, 29.0 kcal./mole(28); C_2H_4Cl, 21 kcal./mole(28); Br, 26.7 kcal./mole(28); and C_2H_4Br, -19.3 kcal./mole(28).

Table 1. Appearance Potentials and Heats of Formation of the Principal Ions of 3,4-Epoxy-1-butene.

m/e	Relative Abundance at 70 e.v.	Appearance Potential (e.v.)	Process	ΔH_f^+ kcal./mole
14	2.4			
15	4.8			
26	5.2	13.8±0.3	$C_4H_6O \longrightarrow C_2H_2^+ + C_2H_4O$	340
27	14.1	12.6±0.3	$\longrightarrow C_2H_3^+ + C_2H_3O$	293
28	11.4			
29	12.4	12.9±0.6	$\longrightarrow CHO^+ + C_3H_4 + H$	210
29.7	1.0			
30	1.2			
30.3	0.8			
31	5.8	13.3±0.5	$\longrightarrow CH_3O^+ + C_3H_2 + H$	178
32	2.4			
37	4.4			
38	10.4	15.8±0.5	$\longrightarrow C_3H_2^+ + CH_2O + H_2$	402
			$\longrightarrow C_3H_2^+ + CHO + H_2 + H$	325
39	100.0	13.5±0.3	$\longrightarrow C_3H_3^+ + CO + H_2 + H$	297
			$\longrightarrow C_3H_3^+ + CH_2O + H$	297
40	39.0	11.3±0.3	$\longrightarrow C_3H_4^+ + CO + H_2$	298
			$\longrightarrow C_3H_4^+ + CH_2O$	298
41	32.4	11.1±0.2	$\longrightarrow C_3H_5^+ CO + H$	241
42	74.1	9.8±0.4	$\longrightarrow C_2H_2O^+ + C_2H_4$	224
43	6.2	10.5±0.3	$\longrightarrow C_2H_3O^+ + C_2H_3$	188
44	2.5			
70	19.6	9.7±0.3	$\longrightarrow C_4H_6O^+$	234

Table 2. Appearance Potentials and Heats of Formation of the Principal Ions of 1,2-Epoxy-3-Methoxypropane.

m/e	Relative Abundance at 70 e.v.	Appearance Potential (e.v.)	Process	ΔH_f^+ kcal./mole
14	9.5	21.3±0.5	$C_4H_8O_2 \longrightarrow CH_2 + C_2H_3O + CHO + 2H$	339
15	55.0	16.0±0.3	$\longrightarrow CH_3^+ + C_2H_3O + CHO + H$	269
26	9.3	16.2±0.3	$\longrightarrow C_2H_2^+ + CHO + CH_3O + H$	323
27	34.9	16.3±0.2	$\longrightarrow C_2H_3^+ + 2CHO + H_2 + H$	287
			$\longrightarrow C_2H_3^+ + CH_3O + CHO + H$	274
28	30.7	13.5±0.2	$\longrightarrow C_2H_4^+ + CHO + CH_3O$	261
			$\longrightarrow C_2H_4^+ + 2CHO + H$	274
29	58.2	14.4±0.2	$\longrightarrow CHO^+ + C_2H_2 + CH_2O + H + H_2$	211
30	10.1	10.9±0.2	$\longrightarrow CH_2O^+ + C_2H_4 + CH_2O$	224
31	30.4	13.9±0.4	$\longrightarrow CH_3O^+ + C_2H_2 + CH_2O + H$	199
32	3.0			
33	4.6			
39	7.3	15.9±0.4	$\longrightarrow C_3H_3^+ + CHO + OH + H_2 + H$	264
			$\longrightarrow C_3H_3^+ + CHO + O + 2H_2$	267
40	2.2			
41	6.6	13.0±0.3	$\longrightarrow C_2HO^+ + CH_3 + CH_2O + H_2$ (?)	252
42	8.3	12.3±0.3	$\longrightarrow C_2H_2O + CH_3 + CH_3O$	198
			$\longrightarrow C_2H_2O^+ + CH_3 + CHO + H_2$	211
43	33.4	13.1±0.2	$\longrightarrow C_2H_3O^+ + CH_3 + CHO + H$	177
			$\longrightarrow C_2H_3O^+ + CH_2 + CH_3O$	181
44	5.1			
45	100.0	12.1±0.15	$\longrightarrow C_2H_5O^+ + CHO + CH_2$	170

Table 2. (continued)

m/e	Relative Abundance at 70 e.v.	Appearance Potential (e.v.)	Process	ΔH_f^+ kcal./mole
46	6.6			
57	19.9	11.2±0.2	$\longrightarrow C_3H_5O^+ + CH_3O$	205
58	42.9	10.2±0.2	$\longrightarrow C_3H_6O^+ + CH_2O$	220
59	8.6			
60	2.2			
87	3.6			
88	2.2		$\longrightarrow C_4H_8O_2^+$	

Table 3. Appearance Potentials and Heats of Formation of the Principal Ions of Epichlorohydrin.

m/e	Relative Abundance at 70 e.v.	Appearance Potential (e.v.)	Process	ΔH_f^+ kcal./mole
13	2.9			
14	15.2	21.6±0.5	$C_3H_5OCl \rightarrow CH_2^+ + CO + H_2 + Cl$	360
15	24.9	14.6±0.5	$\rightarrow CH_3^+ + CO + CH_2 + Cl$	251
25	4.5			
26	30.2	16.6±0.1	$\rightarrow C_2H_2^+ + CH_2O + Cl + H$	313
27	100.0	14.0±0.4	$\rightarrow C_2H_3^+ + CH_2O + Cl$	305
28	52.1	13.6±0.4	$\rightarrow C_2H_4^+ + CHO + Cl$	269
29	68.3	12.0±0.5	$\rightarrow CHO^+ + C_2H_4 + Cl$	218
			$\rightarrow CHO^+ + C_2H_4 + Cl$	236
30	7.0			
31	43.0	13.4±0.2	$\rightarrow CH_3O^+ + C_2H_2 + Cl$	209
32	3.9			
35	3.4			
36	2.0			
37	4.9			
38	5.0			
39	9.1			
41	3.9			
42	10.3	12.1±0.1	$\rightarrow C_2H_2O^+ + CH_3 + Cl$	201
43	5.6			

Table 3. (continued)

m/e	Relative Abundance at 70 e.v.	Appearance Potential (e.v.)	Process	ΔH_f^+ kcal./mole
49	22.8	12.5±0.1	$\longrightarrow CH_2Cl^+ + CO + CH_3$	266
			$\longrightarrow CH_2Cl^+ + C_2H_3O$	236
51	6.7			
55	1.7			
56	2.4			
57	79.7	11.4±0.3	$\longrightarrow C_3H_5O^+ + Cl$	217
61	3.5			
62	11.5			
63	2.6			
64	3.4			
92	0.4		$\longrightarrow C_3H_5OCl^+$	

Table 4. Appearance Potentials and Heats of Formation of the Principal Ions of Epibromohydrin.

m/e	Relative Abundance at 70 e.v.	Appearance Potential (e.v.)	Process	ΔH_f^+ kcal./mole
13	2.2			
14	10.7	21.4±0.5	$C_3H_5OBr \rightarrow CH_2^+ + CO + H + CH_2 + Br$	369
15	13.8	15.6±0.5	$\rightarrow CH_3^+ + CO + CH_2 + Br$	287
25	3.9			
26	26.4	16.7±0.6	$\rightarrow C_2H_2^+ + CH_2O + H + Br$	328
27	100.0	14.4±0.2	$\rightarrow C_2H_3^+ + CH_2O + Br$	327
28	27.5			
29	21.8	11.8±0.2	$\rightarrow CHO^+ + C_2H_4 + Br$	227
			$\rightarrow CHO^+ + C_2H_4 + Br$	230
30	7.1			
31	56.8	12.5±0.2	$\rightarrow CH_3O^+ + C_2H_2 + Br$	201
32	3.4			
37	3.1			
38	4.4			
39	8.1			
42	4.3			
43	2.4			
57	93.0	10.8±0.1	$\rightarrow C_3H_5O^+ + Br$	216
58	3.5			

Table 4. (continued)

m/e	Relative Abundance at 70 e.v.	Appearance Potential (e.v.)	Process	ΔH_f^+ kcal./mole
79	2.9			
81	2.5			
93	2.6			
95	2.8			
136	0.05		$\longrightarrow C_3H_5OBr^+$	
138	0.05			

Mass Spectra

The 70 e.v. mass spectral cracking patterns of these compounds are shown in Figure 4. It is obvious that the mass spectra obtained for these compounds are similar. The mass spectra of 3,4-epoxy-1-butene, epibromohydrin and 1,2-epoxy-3-methoxypropane have not been previously reported.

Variation of Ion Abundances with Electron Energy

The manner in which the relative abundances of the principal ions for each of the compounds varies with the electron beam energy is shown in Figure 5. The curves were prepared by plotting the fraction of the ion current of the total ion current as a function of electron beam energy.

Ionization Potentials

Calculated and observed ionization potentials for 3,4-epoxy-1-butene, epichlorohydrin, epibromohydrin and 1,2-epoxy-3-methoxypropane are tabulated in Table 5. Applying the group orbital treatment due to Franklin (see Theoretical calculations, above), ionization potentials were calculated. These calculations were based on the parameters shown in Table 5; the parameters were evaluated from the experimentally determined ionization potentials: ethylene, ethylene oxide, 3-methyl-1-butene and propane for 3,4-epoxy-1-butene; 2-chloro-2-methylpropane and chloromethane for epichlorohydrin; 2-(bromomethyl)-propane and bromomethane for epibromohydrin; dimethyl ether and an estimated value for ethers isomeric(29)

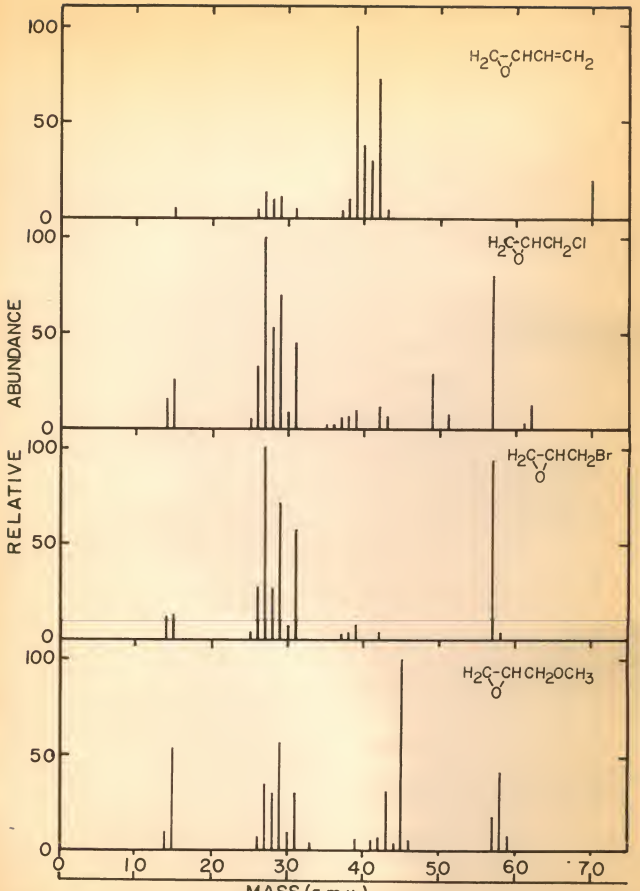

FIGURE 4 MASS SPECTRAL CRACKING PATTERNS OF SOME *SUBSTITUTED OXIRANES*

Table 5. Calculated and Observed Ionization Potentials of $\underbrace{OCH_2CH}$-X

X		$-CH=CH_2$	$-CH_2Cl$	$-CH_2Br$	$-CH_2OCH_3$
Parameters*	f	10.51	11.28	10.52	10.00
	e	10.57	10.57	10.57	10.57
	b	1.23	1.14	1.11	1.02
Obs. I.P.		9.7±0.3	-----	-----	-----
Calc. I.P.		9.3	9.7	9.4	9.2
ΔH_f^+ (Parent)		234	206	218	169

(*) The first row, f, gives the parameters due to Franklin(10); the second and third rows assume that the $-CHCH_2O$ unit may be treated as a group and other parameters are those given by Franklin(10) and in the Tables of Ionization Potentials(22).

with isopropl-methyl ether for 1,2-epoxy-3-methoxypropane.

Ionization potentials were not experimentally determined except for 3,4-epoxy-1-butene. The parent molecule-ion peaks in the mass spectra of the other three compounds were not sufficiently large to allow the determination of the ionization potentials. The calculated value of 9.3 e.v. for the ionization potential of 3,4-epoxy-1-butene compares favorably with the experimental value of 9.7±0.3 e.v.

Considering the qualitative relation between electron withdrawal properties of the substituent groups, $-CH=CH_2$, $-CH_2Cl$ and $-CH_2OCH_3$ and the values of the b parameters calculated for these groups, the $-CH=CH_2$ group is expected to withdraw electrons more strongly than $-CH_2Cl$, and $-CH_2Cl$ more strongly than $-CH_2OCH_3$. The values of the b parameter also decrease in this order. Since the electron withdrawal of $-CH_2Br$ is expected to be intermediate between $-CH_2Cl$ and $-CH_2OCH_3$, and probably closer to the $-CH_2Cl$ value, the b parameter for $-CH_2Br$ was assigned the value of 1.11.

Then the ionization potential of epibromohydrin is calculated to be 9.4 e.v. This value is considered reasonable since the ionization potential of the chloro compound is expected to be a few tenths of a volt higher than that of the bromo compound.

The heat of formation calculated for the parent molecule-ion of 1,2-epoxy-3-methoxypropane from the calculated ionization potential is 169 kcal./mole. This compares favorably with the value of 144 kcal./mole for the heat of formation of the parent molecule-ion of dioxane(11), which

has the same molecular formula. Since dioxane is a stable six-membered cyclic ether, it has less strain than that of 1,2-epoxy-3-methoxypropane, the three-membered ring. According to Franklin(9) the strain energy of the three-membered ring is 24 kcal./mole. Considering this extra energy for 1,2-epoxy-3-methoxypropane, the heat of formation of the molecule-ion agrees quite well with that of the dioxane molecule-ion.

DISCUSSION

Mass Spectra

The mass spectra of the compounds investigated here are qualitatively similar, and for each molecule the abundance of the parent molecule-ion is extremely small, except in the case of 3,4-epoxy-1-butene. However, since both the chlorine and bromine atoms are very readily removed from the parent molecules of epichlorohydrin and epibromohydrin, the removal of halogen from the molecule-ion forms the same type of ion as the propylene oxide molecule-ion with one less hydrogen atom. This then explains the close similarity observed between the mass spectra of propylene oxide(11) and the epihalohydrins. Although the similarity of epichlorohydrin and epibromohydrin is obvious from the mass spectra shown in Figure 4, the similarity of 3,4-epoxy-1-butene to epichlorohydrin and epibromohydrin is seen particularly in the three dominant ionic species of their spectra. Taking into consideration the easy removal of the halogen group from the parent molecule-ion, the three dominant species of 3,4-epoxy-1-butene correspond quite well to those of the latter two compounds. Because the

dominant specie of 3,4-epoxy-1-butene is formed by cleavage of the oxacyclic group rather than the double bond in the molecule, it is suggested that the molecule retains a cyclic structure upon removal of the halogen atom from both epichlorohydrin and epibromohydrin. The mass values are shifted toward higher mass by 12 or 13 atomic mass units, corresponding to the addition of a C or a CH group in the mass spectrum of 3,4-epoxy-1-butene. The higher relative abundance of m/e=57 in the mass spectra of epibromohydrin as compared to that for epichlorohydrin suggests that bromine is dissociated much more readily than chlorine.

In the case of 1,2-epoxy-3-methoxypropane, the similarity to the mass spectra of the other three compounds is still observed. This compound has both the character of a cyclic ether by virtue of the epoxy group and an aliphatic ether due to the oxygen linkage between the methyl group and the $\overset{2}{\underset{1}{OCH_2CHCH_2}}$- group. The 100% abundance of m/e=45 and the large abundance of m/e=59 are evidence of the contribution of oxygen-containing-ions from the aliphatic ether portion of the compound. The three dominant species at m/e=14 and 15, and m/e=30 and m/e=57 qualitatively are similar to the other three compounds mentioned above. This suggests a contribution due to the cyclic ether group. Thus, in the mass spectra of 1,2-epoxy-3-methoxypropane, characteristics of both 3,4-epoxy-1-butene and epichlorohydrin and epibromohydrin are observed.

Variation of Ion Abundances with Electron Energy

The variation of ion abundances as a function of the electron energy

for the compounds investigated are all quite similar. (See Figure 5). In each case there are three categories of shapes of curves. The most readily formed ion, such as m/e=42 for 3,4-epoxy-1-butene, m/e=57 for both epichlorohydrin and epibromohydrin, and m/e=58 for 1,2-epoxy-3-methoxypropane, has a significantly great abundance at lower voltages, and decreases very sharply with an increase of the electron energy. The ion with highest abundance has the general characteristic of passing through a maximum at intermediate voltages. A third category is comprised of those ions which gradually increase in abundance with an increase in the electron energy.

In the case of the 3,4-epoxy-1-butene, it may be noted that the ions of m/e=42 and 70 are more abundant at lower energies, and that the ions m/e=39,40 and 41 decrease markedly at lower voltages. This suggests that the m/e=42 ion is formed by the cleavage of the oxacyclic group from the parent molecule while the m/e=70 ion is formed by ionization of parent molecule, without any further dissociation. These are expected to be relatively easy processes, as evidenced by the appearance potentials.

Curves for epichlorohydrin and epibromohydrin behave quite similarly. m/e=57 is formed from the parent by the rupture of a carbon-halogen bond. The removal of halogen occurs readily, as expected from the appearance potentials.

In the case of 1,2-epoxy-3-methoxypropane, m/e=58 is formed directly by cleavage of the oxacyclic group which, from the appearance potential, is expected to dissociated easily. However, the m/e=45 ion increases

with increasing electron voltages. This ion is likely formed by a C-C bond cleavage β to the oxygen (i.e., between the α and β carbon atoms); this is found in the fragmentation of ordinary aliphatic ethers as well.

3,4-Epoxy-1-butene

The calculation of the heats of formation for the ions produced from 3,4-epoxy-1-butene were made using the approximate value of 10 kcal./mole for the heat of formation of this compound. This value was evaluated thermochemically, as discussed earlier.

m/e 26. The ion corresponding to m/e=26 is $C_2H_2^+$. On the basis that C_2H_4O is the neutral product accompanying the ionization of this compound, followed by dissociation, $\Delta H_f^+(C_2H_2)$ is 340 kcal./mole. This value is considerably higher than other values determined in the present work, 313 kcal./mole from epichlorohydrin and 328 kcal./mole from epibromohydrin, and other values reported in the literature(8,11). 288 kcal./mole for $\Delta H_f^+(C_2H_2)$ from ethylene oxide(II) may be too low. Although the value of $\Delta H_f^+(C_2H_2)$ determined from this molecule is rather high, the assigned process is considered most reasonable.

m/e 27. The ion corresponding to m/e=27 in the C_4H_6O spectrum could only be $C_2H_3^+$. $\Delta H_f^+(C_2H_3)$ is calculated to be 293 kcal./mole, assuming the neutral fragment to be C_2H_3O. This value is a little higher than that reported in the literature(8), but in fair agreement with that for ethylene oxide(11).

m/e 29. This ion is CHO^+, and from the energetics, the neutral products

are C_3H_4 and H. The possibility of $C_2H_5^+$ is ruled out energetically. $\Delta H_f^+(CHO)$, calculated from the appearance potential, is 210 kcal./mole. This value is in fair agreement with the reported value(8), but lower than the value reported for ethylene oxide and propylene oxide(11).

m/e 31. The ion occuring with m/e=31 could only be CH_3O^+. The energetics indicate that the other products are C_3H_2 + H. From this, $\Delta H_f^+(CH_3O)$ = 178 kcal./mole, in good agreement with the value of 173 kcal./mole(8) and 182 kcal./mole for the same ion from propylene oxide(11).

m/e 38. The ion corresponding to m/e=38 must be $C_3H_2^+$. However, the energetics do not distinguish between CH_2O + H and CHO + H_2 + H as the neutral products. $\Delta H_f^+(C_3H_2)$ calculated is 402 kcal./mole and 325 kcal./mole, while 360 kcal./mole has been reported(8); such agreement is not considered very good.

m/e 39. This ion has the greatest abundance. The occurrence also of m/e=38 indicates m/e=39 to be $C_3H_3^+$. However, the energetics appear not to rule out either CO + H_2 or CH_2O + H as neutral products. $\Delta H_f^+(C_3H_3)$ calculated from the appearance potential is 297 kcal./mole both processes. This is a little larger than that reported(8) in the literature.

m/e 40. The ion corresponding to m/e=40 is $C_3H_4^+$. On the basis that either CO + H_2 and CH_2O analogous to the m/e=39 case, are the neutral products, $\Delta H_f^+(C_3H_4)$ is calculated to be 298 kcal./mole. This value is in fair agreement with the value reported(8). This ion is not significant in either the epichlorohydrin or the epibromohydrin spectra.

m/e 41. The corresponding ion formed from this compound is $C_3H_5^+$.

The energetics suggest that the neutral products are CO + H, rather than CHO. Then the $\Delta H_f^+(C_3H_5)$ calculated from the appearance potential is 241 kcal./mole. This value is only slightly higher than other reported values(8).

m/e 42. The ion corresponding to m/e=42 might be either $C_2H_2O^+$ or $C_3H_6^+$. However, since the ion has a large abundance in the mass spectrum and the appearance potential is only 9.8 e.v., it is concluded that the ion is $C_2H_2O^+$ and that the neutral product is C_2H_4. Then $\Delta H_f^+(C_2H_2O)$ is 224 kcal./mole, which is rather high; however, the energetics indicate that this process is the most logical one.

m/e 43. The ion of m/e 43 is $C_2H_3O^+$, which is formed by the removal of the vinyl group, $-CH=CH_2$, from the parent molecule-ion. $\Delta H_f^+(C_2H_3O)$=188 kcal./mole. It is not unreasonable to expect that this ion may retain its cyclic structure following the ionization and dissociation processes, although $\Delta H_f^+(C_2H_3O)$ for a non-cyclic is reported to be 174 kcal./mole(8).

m/e 70. This ion could only result from ionization without further dissociation of the molecule. Therefore, $\Delta H_f^+(C_4H_6O)$ calculated from the ionization potential is 234 kcal./mole. The ionization potential evaluated by the equivalent orbital method gives 203 kcal./mole as $\Delta H_f^+(C_4H_6O)$. $\Delta H_f^+(C_4H_6O)$=234 kcal./mole is somewhat higher than other reported values(8).

1,2-Epoxy-3-Methoxypropane

The heat of formation of this molecule was calculated thermochemically and by using Franklin's method(9); it was taken to be approximately -43 kcal./mole.

m/e 14. The ion corresponding to m/e=14 is CH_2^+, assuming the neutral products to be C_2H_3O + CHO + 2H. From this $\Delta H_f^+(CH_2)$ is calculated to be 339 kcal./mole, in good agreement with the values in the literature(8,11). However, the value does not agree with the values determined from epichlorohydrin and epibromohydrin. It is not understood why the values from epichlorohydrin and epibromohydrin are found to be considerably higher.

m/e 15. This ion must be CH_3^+. Assuming the neutral products to be C_2H_3O + CHO + H, which is a process analogous to the formation of the m/e=14 ion, $\Delta H_f^+(CH_3)$ is calculated to be 269 kcal./mole. This value is in good agreement with the value of propylene oxide(11) and that in the literature(8).

m/e 26. The ion corresponding to m/e=26 is $C_2H_2^+$. The neutral products assumed to be formed in the dissociation process are CH_3O + CHO + H_2. $\Delta H_f^+(C_2H_2)$ calculated from the appearance potential is 323 kcal./mole. This value is in fair agreement with the values determined here and also that in the literature(8,11).

m/e 27. The ion corresponding to m/e=27 is $C_2H_3^+$. Assuming the neutral products to be either 2CHO + H_2 + H or CH_3O + CHO + H, $\Delta H_f^+(C_2H_3)$ calculated from the above processes are 287 kcal./mole and 274 kcal./mole, respectively. The value of 287 kcal./mole is numerically in good agreement

with the reported value. However, the process of $CH_3O + CHO + H$ is also in good agreement with the other dissociation processes for this compound.

m/e 28. From the energetics this ion must be $C_2H_4^+$ rather than CO^+. However, the energetics here will not distinguish between $CH_3O + CHO$ and $2CHO + H_2$ as the neutral products. $\Delta H_f^+(C_2H_4)$ is calculated to be 261 kcal./mole and 274 kcal./mole, respectively.

m/e 29. The ion may be either CHO^+ or $C_2H_5^+$, but appears to be CHO^+. The neutral products are assumed to be $C_2H_2 + CH_2O + H + H_2$. $\Delta H_f^+(CHO)$=211 kcal./mole is in fair agreement with the value determined from other compounds in this study and with values in the literature(8).

m/e 30. Assuming the neutral products to be $C_2H_4 + CH_2O$, the appearance potential of 10.6 e.v. for m/e=30, CH_2O^+, leads to the value of $\Delta H_f^+(CH_2O)$= 224 kcal./mole. The energetics rule out other processes. The value calculated here is in good agreement with the literature(8), and in fair agreement with the propylene oxide study(11).

m/e 31. This ion is considered to be CH_3O^+, by analogy with m/e=29 and 30. The neutral products are assumed to be $C_2H_2 + CH_2O + H$. $\Delta H_f^+(CH_3O)$ is calculated to be 199 kcal./mole.

m/e 39. The ion corresponding to m/e=39 is $C_3H_3^+$. Other products could be either $CHO + OH + H_2 + H$ or $CHO + O + 2H_2$. The energetics will not distinguish between these processes. $\Delta H_f^+(C_3H_3)$ is calculated to be 264 kcal./mole or 267 kcal./mole. This is in good agreement with the value 274 kcal./mole for the $CH{\equiv}C\text{-}CH_2^+$ ion(8).

m/e 41. This ion may be C_2HO^+, assuming $CH_3 + CH_2O + H_2$ to be the neutral fragments. This ion may also possibly be $C_3H_5^+$, but by analogy with the m/e=42 ion, C_2H_2O, it is believed that C_2HO is the more reasonable assignment for the m/e=41 ion. The energetics then give $\Delta H_f^+(C_2HO) = 252$ kcal./mole.

m/e 42. This is $C_2H_2O^+$. Beynon(1) indicates both ions of $C_2H_2O^+$ and $C_3H_6^+$ are present at 50 e.v. for propylene oxide. The appearance potential observed suggests that this ion is $C_2H_2O^+$. However, the energetics will not distinguish between the processes $CH_3 + CH_3O$ and $CH_3O + H_2$. $\Delta H_f^+(C_2H_2O)$ calculated is 198 kcal./mole or 211 kcal./mole. These values are in fair agreement with the literature(8).

m/e 43. This ion with m/e=43 is $C_2H_3O^+$. The neutral products are either $CH_3 + CHO + H$ or $CH_2 + CH_3O$. From these $\Delta H_f^+(C_2H_3O)$ is calculated to be either 177 kcal./mole or 181 kcal./mole. These values are in fair agreement with the value for the non-cyclic $C_2H_3O^+$ ion listed in the literature(8).

m/e 45. This ion is almost surely $C_2H_5O^+$ since this ion has the greatest abundance in the mass spectrum. $\Delta H_f^+(C_2H_5O)$ is calculated to be 170 kcal./mole, assuming the neutral products to be $CHO + CH_2$. This value is in good agreement with other values in the literature(8).

m/e 57. The ion corresponding to m/e=57 is $C_3H_5O^+$ formed by the removal of a CH_3O group from the parent molecule-ion. The energetics rule out other groups than CH_3O as the neutral product. $\Delta H_f^+(C_3H_5O)$ is calculated to be 205 kcal./mole, in fair agreement with the values determined from epichlorohydrin, epibromohydrin, and propylene oxide(11).

m/e 58. This ion is $C_3H_6O^+$. The $\Delta H_f^+(C_3H_6O)$ calculated is 220

kcal./mole, in fair agreement with propylene oxide(11), if the neutral fragment is CH_2O.

Epichlorohydrin

The heat of formation for this molecule has not been reported in the literature. The heat of formation was calculated from the reported value for the heat of combustion, 423±0.1 kcal./mole(3). The value of -17 kcal./mole was taken as the heat of formation.

m/e 14. The ion of m/e=14 is CH_2^+, and we assume the neutral fragments are CO + H + CH_2 + Cl. From this, $\Delta H_f^+(CH_2)$ is calculated to be 360 kcal./mole. This value is considerably higher than that reported in the literature(8,11). However, from the energetics, this process is most logical.

m/e 15. The ion corresponding to m/e=15 must be CH_3^+. Assuming the neutral products to be CO + CH_2 + Cl, $\Delta H_f^+(CH_3)$ calculated for the compound is 251 kcal./mole. This value is considerably lower than that of propylene oxide reported(11) and the value listed by Field and Franklin(8).

m/e 26. The ion corresponding to m/e=26 is apparently $C_2H_2^+$. Neutral products are assumed to be CH_2O + H + Cl. From this, $\Delta H_f^+(C_2H_2)$ is calculated to be 313 kcal./mole. This value is in good agreement with results of the propylene oxide study(11) and values in the literature(8).

m/e 27. The ion corresponding to m/e=27 is $C_2H_3^+$, and the neutral products are assumed to be CH_2O + Cl. $\Delta H_f^+(C_2H_3)$is calculated to be 305 kcal./mole. This is somewhat higher than the values in the literature(8),

but in good agreement with the results from the ethylene oxide study(11).

m/e 28. This ion is $C_2H_4^+$. The neutral products are believed to be CHO + Cl. From this, $\Delta H_f^+(C_2H_4)$ is calculated to be 269 kcal./mole. This value is larger than that reported in the literature(8). However, energetic considerations eliminate the possibility of m/e=28 being due to CO^+.

m/e 29. This ion must be CHO^+, and the neutral products are either C_2H_4 + Cl or C_2H_4Cl. The possibility of the ion being $C_2H_5^+$ was eliminated by energetic considerations. However, the energetics will not distinguish between C_2H_4 + Cl and C_2H_4Cl as the neutral products. The heat of formation for C_2H_4Cl was taken to be approximately 24 kcal./mole, and the bond energy of a carbon-hydrogen bond is approximately 100 kcal./mole(5). $\Delta H_f^+(CHO)$ is calculated to be 218 kcal./mole or 236 kcal./mole, depending upon the nature of the neutral fragments.

m/e 31. This ion is CH_3O^+. The neutral products accompanying its formation are C_2H_2+ Cl. $\Delta H_f^+(CH_3O)$, calculated from the appearance potential, is 209 kcal./mole. This is considerably higher than the value of 173 kcal./mole given in the literature(8).

m/e 42. $C_2H_2O^+$. The energetics indicate that the neutral products are CH_3 + Cl. $\Delta H_f^+(C_2H_2O)$= 201 kcal./mole is in good agreement with the literature(8).

m/e 49. The only possible ion for m/e=49 is $CH_2{}^{35}Cl^+$. However, the energetics here will not distinguish between neutral products of CO + CH_3 and C_2H_3O. $\Delta H_f^+(CH_2Cl)$ calculated is 266 kcal./mole and 236 kcal./mole, respectively. The corresponding ion from epibromohydrin was not observed.

m/e 57. This ion is $C_3H_5O^+$, which is formed by removal of chlorine

from the parent molecule-ion. $\Delta H_f^+(C_3H_5O)$ is calculated to be 217 kcal./mole. This value is a little higher than that reported from the propylene oxide study(11). Since removal of chlorine is apparently readily accomplished, it is reasonable to assume that a cyclic structure is retained for this ion.

Epibromohydrin

The heat of formation for this molecule has not to the author's knowledge been reported in the literature. The heat of formation was estimated from thermochemical data and by the method of Franklin(9). These calculations agreed quite well. The value of -6 kcal./mole was taken as the heat of formation for this compound.

m/e 14. The ion of m/e=14 is CH_2^+; analogous to the epichlorohydrin study, the neutral fragments were assumed to be CO + H + CH_2 + Br. $\Delta H_f^+(CH_2)$ is calculated to be 369 kcal./mole. This value is in fair agreement with that determined from epichlorohydrin. However, both results are somewhat higher than the data given in the literature(8,11).

m/e 15. The ion corresponding to m/e=15 is CH_3^+. Assuming the neutral products to be CO + CH_2 + Br, $\Delta H_f^+(CH_3)$ is calculated to be 287 kcal./mole. This is in fair agreement with that of the ethylene oxide study(11), but higher than that reported of Franklin(8). However, the energetics indicate that the process assigned is the most logical one.

m/e 26. The ion corresponding to m/e=26 could only be $C_2H_2^+$. The neutral products are assumed to be CH_2O + H + Br. From this, $\Delta H_f^+(C_2H_2)$ is calculated to be 328 kcal./mole, a little higher than the values reported

in the literature(8,11). The energetics rule out neutral products other than CH_2O + H + Br; we not that this process agrees with that for epichlorohydrin.

m/e 27. The ion corresponding to m/e=27 is $C_2H_3^+$. The neutral products are CH_2O + Br. $\Delta H_f^+(C_2H_3)$ is calculated to be 327 kcal./mole. This value is much higher than reported values, but the process is quite similar to the formation of the corresponding ion from epichlorohydrin. We do not have an explanation for this apparent discrepancy.

m/e 29. This ion is CHO^+. The neutral products are either C_2H_4 + Br or C_2H_4Br. The possibility of this ion being $C_2H_5^+$ was eliminated from energetic considerations. However, the energetics do not distinguish between C_2H_4 + Br and C_2H_4Br as the neutral products. The heat of formation of C_2H_4Br was taken as being approximately -19 kcal./mole; $\Delta H_f^+(CHO)$ is then calculated to be 227 kcal./mole and 230 kcal./mole, which agree with the results of the propylene oxide study(11).

m/e 31. This ion is CH_3O^+. Assuming the neutral products to be C_2H_2 + Cl, the $\Delta H_f^+(CH_3O)$ calculated from the appearance potential is 201 kcal./mole. This is in fair agreement with the epichlorohydrin study, but still is higher than the values in the literature(8,11).

m/e 57. This ion must be $C_3H_5O^+$, formed by removal of a bromine atom from the parent molecule-ion. $\Delta H_f^+(C_3H_5O)$= 216 kcal./mole is in excellent agreement with the epichlorohydrin data, but higher than 182 kcal./mole(11). Since removal of bromine is noted to be easier than that of chlorine, it is again reasonable to assume a cyclic structure for this ion.

SUMMARY

Qualitative similarities have been shown to exist between the mass spectra of this group of substituted oxiranes, and a number of interesting relationships were noted.

The ionization potentials of 3,4-epoxy-1-butene, epichlorohydrin, epibromohydrin and 1,2-epoxy-3-methoxypropane were calculated using Franklin's group orbital treatment; they are 9.3, 9.7, 9.4 and 9.2 ev., respectively. The interaction parameters were calculated from the experimental ionization potentials of related compounds.

Probable formation processes for the principal ions observed have been determined, consistent with the computed energetics and the heats of formation obtained. Table 6 summarizes the determined heats of formation of the various ions.

Table 6. A Summary of the Heats of Formation for the Ions Studied.

$\underbrace{OCHCH_2}-X$

Ion \ X	This Work -CH=CH$_2$	-CH$_2$Cl	-CH$_2$Br	-CH$_2$OCH$_3$	-CH$_3$(a)	Literature -----(a)	F & F (b)
CH_2^+	----	360	369	339	327	344	333
CH_3^+	---	251	287	269	265	292	262
CH_4^+	---	---	---	---	---	298	285
$C_2H_2^+$	340	313	328	323	328	288	317
$C_2H_3^+$	293	305	327	(287, 274)	285	308	280
$C_2H_4^+$	---	269	---	(261, 274)	274	296	255
CHO^+	210	(218, 236)	(227, 230)	211	230	237	203
CH_2O^+	---	---	---	224	204	---	222
CH_3O^+	178	209	201	199	182	---	173
$C_3H_2^+$	(402, 325)	---	---	---	---	---	360
$C_3H_3^+$	297	---	---	(264, 267)	---	---	(274, 283)
$C_3H_4^+$	298	---	---	---	---	---	(279, 284)
$C_3H_5^+$	241	---	---	---	---	---	(220, 230)
C_2HO^+	---	---	---	252	---	---	---
$C_2H_2O^+$	224	201	---	(198, 211)	189	207	205
$C_2H_3O^+$	188	---	---	(177, 181)	199	215	174
$C_2H_5O^+$	---	---	---	170	---	---	165
CH_2Cl^+	---	(266, 236)	---	---	---	---	---
$C_3H_5O^+$	---	217	216	205	193	---	---
$C_3H_6O^+$	---	---	---	220	204	---	---
$C_4H_6O^+$	234	---	---	---	---	---	199

(a) reference 11; (b) See reference 8.

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REFERENCES

1. Beynon, J. H., in "Advances in Mass Spectrometry", edited by J. D. Waldron, Pergamon Press, Inc., New York, 1959. p. 328-354.

2. Beynon, J. H., "Mass Spectrometry and Its Applications to Organic Chemistry", Elsevier Publishing Co., Amsterdam, 1960.

3. Bjellerup, L. and L. Smith, Kgl. Fysiograf. Sallskap. Lund. Froh., 24, 21 (1954).

4. Cameron, A. E., and D. F. Eggers, Jr., Rev. Sci. Instr., 19, 605 (1948).

5. Cottrell, T. L., "The Strength of Chemical Bonds", Second edition, Butterworth Scientific Publications, London, 1958.

6. Dibeler, V. H., J. Research Natl. Bur. Standards, 49, 235 (1952).

7. Dibeler, V. H., and R. L. Mohler, J. Research Natl. Bur. Standards, 47, 337 (1951).

8. Field, F. H. and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions", Academic Press, Inc., New York, 1957.

9. Franklin, J. L., Ind. Eng. Chem., 41, 1070 (1949).

10. Franklin, J. L., J. Chem. Phys., 22, 1304 (1954).

11. Gallegos, E. J. and R. W. Kiser, J. Am. Chem. Soc., 83, 773 (1961).

12. Gray, P. and A. Williams, Chem. Revs., 59, 239 (1959).

13. Hall, G. G., Proc. Roy. Soc. (London), A 205, 541 (1951).

14. Hall, G. G., Trans. Faraday Soc., 49, 113 (1953).

15. Hall, G. G., Trans. Faraday Soc., 50, 319 (1954).

16. Hall, G. G. and J. Lennard-Jones, Proc. Roy. Soc. (London), A202, 155 (1950).

17. Hall, G. G. and J. Lennard-Jones, Proc. Roy. Soc. (London), A205, 357 (1951).

18. Harrington, D. B., in "Advances in Mass Spectrometry", edited by J. D. Waldron, Pergmon Press, London, 1959. p. 249-265.

19. Hobrock, B. G., Master's Thesis, "Electron Spectroscopy of Tetramethyl-Silicon,-Germanium,-Tin and -Lead, Trimethyl-Silane and Dimethyl Mercury", Kansas State University (1961).

20. Katzenstein, H. S. and S. S. Friedland, Rev. Sci. Instr., 26, 324 (1955).

21. Kaufman, J. J. and W. S. Koski, J. Am. Chem. Soc., 82, 3262 (1960).

22. Kiser, R. W., "Tables of Ionization Potentials", U. S. Atomic Energy Commission, TID-6142, June 20, 1960.

23. Lennard-Jones, J., Proc. Roy. Soc. (London), A198, 1 (1949).

24. Lennard-Jones, J., and J. A. Pople, Proc. Roy. Soc. (London), A202, 166 (1950).

25. Lowrey, A., III, and K. Watanabe, J. Chem. Phys., 28, 208 (1958).

26. "Mass Spectral Data", American Petroleum Institute Research Project 44, National Bureau of Standards, Washington, D.C.

27. Moore, C. E., "Atomic Energy Levels", National Bureau of Standards Circular 467, Vol. III, U.S. Government Printing Office, Washington, D.C., 1958.

28. Rossini, F. D., D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

29. Streitwieser, A., Jr., J. Am. Chem. Soc., 82, 4123 (1960).

30. Szwarc, M., Chem. Revs., 47, 75 (1950).

31. Warren, J. W., Nature, 165, 811 (1950).

32. Wiley, W. C., Science, 124, 817 (1956).

33. Wiley, W. C. and I. H. McLaren, Rev. Sci. Instr., 26, 1150 (1955).

34. Wolff, M. M. and W. E. Stephens, Rev. Sci. Instr., 24, 616 (1953).

ELECTRON IMPACT SPECTROSCOPY OF SOME SUBSTITUTED OXIRANES

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An examination of the literature reveals that electron impact data has been reported for a large number of molecules containing oxygen; among these are ethers, alcohols, acids, ketones, esters and some inorganic oxygen-containing compounds. However, relatively little information of this type is available for cyclic ethers. The present investigation of a group of substituted oxiranes, namely, 3,4-epoxy-1-butene, 1,2-epoxy-3-methoxypropane, epichlorohydrin and epibromohydrin, has provided specific data for many of the gaseous ions formed from these compounds upon electron impact.

The mass spectra and appearance potentials reported herein were obtained using a time-of-flight mass spectrometer. Mass spectra were obtained at nominal electron energies of 70 ev. Appearance potentials were determined using the method of extrapolated voltage differences as described by Warren. Rare gases, mixed with the compound being investigated, were used to calibrate the ionizing voltage.

Mass spectral cracking patterns of these substituted oxiranes were qualitatively similar, with the dominant ion currents in the m/e=30 range. The parent molecule-ions were of low intensity.

Molecular ionization potentials were calculated using Franklin's group orbital method and were compared to the observed ionization potentials determined experimentally. The ionization potentials calculated in this work are 9.3 ev. for 3,4 epoxy-1-butene, 9.7 ev. for epichlorohydrin, 9.4 ev. for epibromohydrin and 9.2 ev. for 1,2-epoxy-3-methoxypropane. The experimentally observed value of 9.7 ev. for 3,4-epoxy-1-butene is to be compared to the theoretical value of 9.3 ev.

The probable ionization and dissociation processes for the formation of the principal ions in the mass spectrum of the substituted oxiranes, consistent with the observed energetics, are tabulated and discussed.