δ_1 and δ_2 gives two activation energies. From Fig. 4 it is further to be seen that the slope of δ_2 is nearly twice that of δ_1. Assuming the activation energies for the breaking reactions zero or at least nearly the same amount, it follows that the temperature dependence of δ_1 and δ_2, respectively, is governed through the reaction heat of the stabilization, *i.e.*, through the K.

Thus it can be seen that the reaction mechanism taken up by us from a unitary viewpoint gives an illustrative interpretation of the course of the reaction in good agreement with experimental data. For the interpretation of the maximum inhibition it is not necessary to suppose the existence of a molecular reaction, which is inevitable when supposing that the effect of nitric oxide appears only in the breaking of the chains, and it is also unnecessary to interpret the catalysis through a direct reaction of nitric oxide with the initial substance, which would not be correct even because the rate does not increase proportionally to the concentration of nitric oxide.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE UNIVERSITY, MANHATTAN, KANSAS]

Electron Impact Spectroscopy of Ethylene Oxide and Propylene Oxide[1]

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Appearance potentials and relative abundances are reported for the principal positive ions in the mass spectra of ethylene oxide and propylene oxide, obtained using a Bendix 12-100 time-of-flight mass spectrometer. Probable ionization and dissociation processes are given consistent with computed energetics and the heats of formation of the various ions derived from the energetics are tabulated. Molecular ionization potentials are calculated using the equivalent orbital method of Hall and are compared to the observed ionization potentials of 10.65 ± 0.1 e.v. for ethylene oxide and 9.80 ± 0.1 e.v. for propylene oxide.

Introduction

Electron impact spectroscopy has been reported for a number of oxygen-containing molecules, including among others, ethers, alcohols, acids, ketones, esters and some inorganic oxygen-containing compounds.[2] However, very little has been done with the cyclic ethers, although the API tables of mass spectra[3] and Beynon[4] list the mass spectral cracking patterns for a number of the cyclic ethers. The present study was initiated to obtain fundamental information concerning the ionization potentials, bond dissociation energies, heats of formation of the various ionic products of the ionization and dissociation processes and the manner in which the mass spectra are produced for these compounds. The measured ionization potential for ethylene oxide is compared with others reported in the literature while that for propylene oxide is newly reported. These results have been used in a theoretical calculation of ionization potentials for other epoxides.

Experimental

The mass spectra and appearance potentials herein reported were obtained using a Bendix time-of-flight (TOF) model 12-100 mass spectrometer with an analog output system consisting of a monitor and a scanner. Wiley[5] and others[6-10] have described the TOF mass spectrometer, and recently Harrington[11] has described in detail the Bendix TOF instrument.

The ions formed were pulsed at a repetition rate of 10 kc. into an electric field of 3000 v., providing ion acceleration. The drift tube has a flight path of one meter. Only analyses for positive ions were made. Ion currents were measured using an electrometer amplifier following the ectron multiplier and the results recorded on a Sanborn model 152 recording system.

Mass spectra were obtained for nominal electron energies of 70 v. The ionizing voltage scale was calibrated by comparing the observed ionization potentials of krypton, xenon and mercury (background from the diffusion pump) with the known spectroscopic values.[12] Appearance potentials were evaluated by the method of extrapolated difference described by Warren.[13] This method has been found to give results in good agreement with reliable kinetic data.[14] The linear portion of the ionization efficiency (i.e.) curves were forced to be parallel in plotting and then the voltage difference, ΔE, between the two i.e. curves at any given current, i, was plotted as a function of i. The resultant curve, upon extrapolation to $i = 0$, gave a value of ΔE which was algebraically added to the ionization potential of the standard to obtain the appearance potential for the ion in question.

Figure 1 shows the calibration of the electron energy scale for this work. The slope of this calibration curve is 1.034. Ionization potentials were also determined using the technique of Lossing, Tickner and Bryce.[15] A typical plot of the i.e. curves for ethylene oxide and propylene oxide is shown in Fig. 2 and is compared to that for the krypton standard.

The samples (white label) of ethylene oxide and propylene oxide were obtained from Eastman Organic Chemicals.

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(2) A compilation of such studies through 1955 is given by F. H. Field and J. L. Franklin in "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

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

(4) J. H. Beynon, in "Advances in Mass Spectrometry," edited by J. D. Waldron, Pergamon Press, London, 1959, pp. 328-354.

(5) W. C. Wiley, *Science*, **124**, 817 (1956).

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

(7) A. E. Cameron and D. F. Eggers, Jr., *ibid.*, **19**, 605 (1948).

(8) M. M. Wolff and W. E. Stephens, *ibid.*, **24**, 616 (1953).

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(10) R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959).

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(13) J. W. Warren, *Nature*, **165**, 811 (1950).

(14) C. A. McDowell and J. W. Warren, *Discussions Faraday Soc.*, **10**, 53 (1951).

(15) F. P. Lossing, A. W. Tickner and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

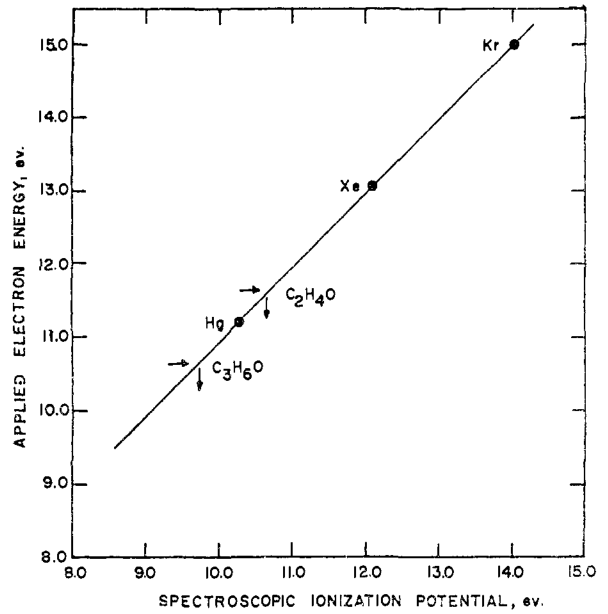

Fig. 1.—Calibration curve relating the applied electron energy and spectroscopic ionization potentials.

No significant impurities were noted either in the mass spectrum or during gas chromatographic analyses using a Fisher-Gulf model 150 Partitioner, and consequently the compounds were used as obtained.

Results

The results of the mass spectral cracking patterns and the appearance potential measurement for these compounds are summarized in Tables I and II. In the first two columns are given the principal ions formed by 70 v. electrons from each compound and their abundances. No isotope correction has been made. In columns 3 and 4 are given the appearance potential for the observed ions from the parent molecule and the probable processes by which they are formed, as calculated from the various appearance potentials and their given processes. ΔH_f^+ indicates the heat of formation of the ion, *eg.*, ΔH_f^+ (C_2H_5), and thereby we distinguish it from the heat of formation of the molecule or radical, *e.g.*, ΔH_f (C_2H_5).

Table I

Mass Spectrum and Appearance Potentials of the Principal Ions of Ethylene Oxide

m/e	Relative abundance at 70 e.v.	A.P. (e.v.)	Process	ΔH_f^+ (kcal./mole)
12	1.88			
13	5.13	22.8 ± 0.4	$C_2H_4O \rightarrow CH^+ + CO + 3H$	384
14	20.9	16.5 ± .4	$\rightarrow CH_2^+ + CHO + H$	344
15	55.0	14.3 ± .2	$\rightarrow CH_3^+ + CO + H$	292
16	7.55	12.3 ± .2	$\rightarrow CH_4^+ + CO$	298
17	0.33			
18	.20			
19	.03			
21	.12			
24	.79			
25	3.65	24.0 ± 0.3	$\rightarrow C_2H^+ + 2H + OH$	427
26	6.70	15.7 ± .3	$\rightarrow C_2H_2^+ + H + OH$	288
27	4.67	14.3 ± .2	$\rightarrow C_2H_3^+ + OH$	308
28	8.55	12.6 ± .4	$\rightarrow CO^+ + CH_4$	296
29	100.0	12.2 ± .1	$\rightarrow CHO^+ + CH_3$	237
30	2.98			
31	1.27			
40	0.42			
41	1.35			
42	16.7	14.0 ± 0.3	$\rightarrow C_2H_2O^+ + 2H$	207
43	23.2	12.1 ± .2	$\rightarrow C_2H_3O^+ + H$	215
44	78.5	10.65 ± 0.1	$\rightarrow C_2H_4O^+$	234
45	2.83			
46	0.51			

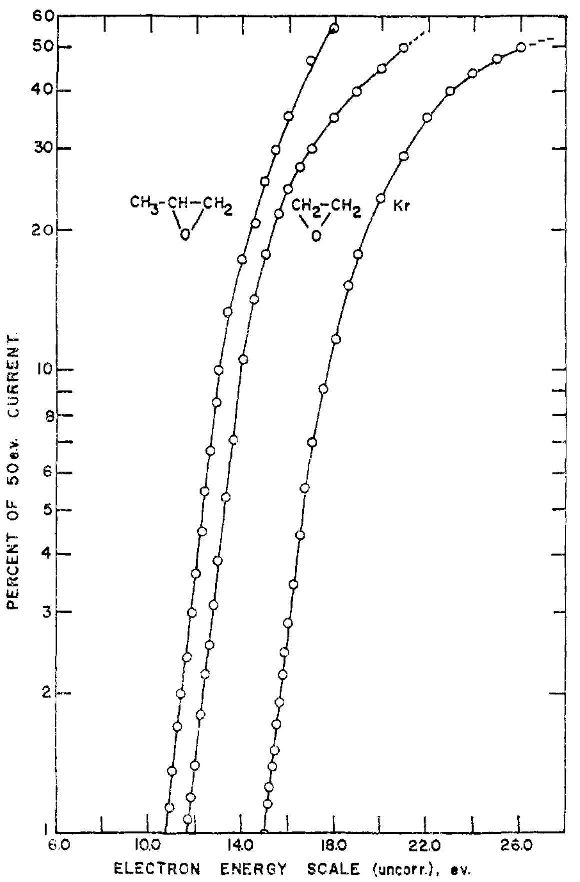

Fig. 2.—Lower energy region of typical ionization efficiency curves for the ethylene and propylene oxides and the krypton standard.

In the thermochemical calculations, NBS values[16] of heats of formation for the various molecules were used, and values of heats of formation for ions were taken from Field and Franklin.[2] The study of the thermochemistry of ethylene and propylene oxides made by Moureu and Dode[17] was also used, and the value of ΔH_f (C_3H_6O) was taken to be −20 kcal./mole.

Discussion

Mass Spectra.—The mass spectra obtained for ethylene oxide and propylene oxide are generally in good agreement with that obtained by high-resolution mass spectrometry[4] and the API tables of mass spectral data, serial Nos. 760 and 768.[3] This is significant in that the TOF instrument has different ion-source geometry and ion draw-out than the other commonly employed instruments. However, we are not able to achieve the resolution obtained by Beynon,[4,18] so that one must be

[16] F. D. Rossini, 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.

[17] H. Moureu and M. Dode, *Bull. soc. chim. France*, (5), **4**, 637 (1937).

TABLE II

MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF PROPYLENE OXIDE

m/e	Relative abundance at 70 e.v.	A.P. (e.v.)	Process	ΔHf^+ (kcal./mole)
12	1.0			
13	2.6			
14	12.6	18.8 ± 0.5	$C_3H_6O \rightarrow CH_2^+ + C_2H_3O + H$ (?)	327
15	28.5	13.9 ± .2	$\rightarrow CH_3^+ + C_2H_3O$	265
16	1.5			
24	0.4			
25	3.6			
26	45.0	13.9 ± .2	$\rightarrow C_2H_2^+ + CH_2O + H_2$ (?)	328
27	64.2	14.3 ± .1	$\rightarrow C_2H_3^+ + CH_2O + H$	285
28	100.0	11.6 ± .2	$\rightarrow C_2H_4^+ + CO + H_2$	274
29	68.7	11.8 ± .2	$\rightarrow CHO^+ + C_2H_5$(?)	230
30	13.3	11.6 ± .3	$\rightarrow CH_2O^+ + C_2H_4$	234
31	33.0	13.4 ± .2	$\rightarrow CH_3O^+ + C_2H_2 + H$	182
32	1.6			
37	2.8			
38	3.7			
39	7.4			
40	0.7			
41	1.8			
42	4.4	12.7 ± .2	$\rightarrow C_2H_2O^+ + CH_3 + H$ (?)	189
43	37.9	10.9 ± .2	$\rightarrow C_2H_3O^+ + CH_3$	199
44	1.7			
45	0.4			
53	0.4			
55	1.2			
56	0.2			
57	4.6	11.5 ± .3	$\rightarrow C_3H_5O^+ + H$	193
58	66.2	9.80 ± .1	$\rightarrow C_3H_6O^+$	204
59	3.3			

TABLE III

MOLECULAR IONIZATION POTENTIALS OF SOME OXACYCLOALKANES

Molecule	Calculated[a]			Measured
	13.31	13.31	13.04	
b	1.55	1.55	1.28	
f	10.52	10.65	10.65	
c	2.08	...	...	
$\underline{\mathrm{CH\ CH_2O}}$	10.71	(10.65)	(10.65)	10.65,[b] 10.57,[c,d] 10.81[e]
$\mathrm{CH_3}\underline{\mathrm{CHCH_2O}}$	10.49	9.94	10.10	9.80,[b] 10.22[f]
$\underline{\mathrm{CH_2CH_2CH_2O}}$	9.48	...	...	...
$\underline{\mathrm{CH_2CH_2OCH_2CH_2O}}$	9.32	...	...	9.52[g]
$\mathrm{CH_3}\underset{\llcorner\mathrm{O}\lrcorner}{\mathrm{CHCH}}\mathrm{CH_3}$	...	9.42	9.50	...

[a] The first column gives the parameters due to Franklin (see ref. 21); the second and third columns assume that the $-\underline{\mathrm{CHCH_2O}}$ unit may be treated as a group and the other parameters are those given by Franklin. [b] Data reported in this work. [c] See ref. 22. [d] See ref. 23. [e] See ref. 24. [f] Dr. J. L. Franklin, Research and Development Division, Humble Oil and Refining Co., Baytown, Texas, has informed us that this value has been reported by K. Watanabe, T. Nakayama and J. Mottl, in "Ionization Potentials of Molecules by a Photoionization Method," Dept. of Army #5B99-01-004, ORD — #TB-2-0001, OOR — #1624, Contract #DA — 04-200-ORD-480 and —737, December, 1959. [g] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

cautious in conclusions drawn only from appearance potential measurements. It is noted that our cracking patterns agree better with those listed in the API tables than with those reported by Beynon.

Appearance Potentials.—The parent molecule-ions are formed by the vertical transition process according to the Franck–Condon principle. Hall[19,20] has used equivalent orbitals for the calculation in a semi-empirical manner of the ionization potentials of similar molecules. Using the parameters given by Franklin,[21] we have calculated the ionization potentials for a number of oxacycloalkanes. The results are given in column 2 of Table III. It is of interest to note that the calculated and experimental values for the ionization potential of propylene oxide do not agree. However, treating the $-\underline{\mathrm{CHCH_2O}}$ unit as a group, in a manner similar to that employed by Franklin,[21] we calculate values of 9.94 and 10.10 e.v. for the ionization potential of propylene oxide. Since the latter calculation tends to give results 0.2 to 0.4 e.v. too great, we conclude that the calculated value of 9.7 to 9.9 e.v. agrees well with our experimental value of 9.80 ± 0.1 e.v. The ionization potential of 10.65 ± 0.1 e.v. reported here for ethylene oxide compares favorably with other literature values: 10.565 ± 0.01[22,23]; 10.81 and 11.2 ± 0.5 e.v.[24] The value of $9.8_0 \pm 0.1$ e.v. reported for the ionization potential of propylene oxide is new.

***m/e* 13.**—This ion could only be CH^+. The other products expected from ethylene oxide are either $H_2CO + H$ or $CO + 3H$. The energetics establish the latter process and in addition rules out $CHO + 2H$ as possible products. The appearance potential was not determined for this ion from propylene oxide.

***m/e* 14.**—The ion of $m/e = 14$ is CH_2^+. The products in addition to CH_2^+ resulting from ethylene oxide are $CHO + H$, whereas from propylene oxide the products are $C_2H_3O + H$. However, we cannot rule out either $O + C_2H_4$ or vinyl + OH as possible neutral products in the propylene oxide case. $\Delta H_f(C_2H_3O)$ was taken as being approximately 35 kcal./mole, since $\Delta H_f(C_2H_4O)$ is −12.2 kcal./mole, the bond energy of a carbon–hydrogen bond is approximately 100 kcal./mole,[25] and the determined appearance potential of $C_2H_3O^+$ from C_2H_4O is 279 kcal./mole. Using 35 kcal./mole for $\Delta H_f(C_2H_3O)$, $\Delta H_f^+(CH_2)$ is 327 kcal./mole and compares favorably with the literature.[2]

***m/e* 15.**—The heat of formation calculated from the propylene oxide data for m/e 15, assuming this ion to be CH_3^+, is 265 and is in good agreement with the literature,[2] again substantiating the value of $\Delta H_f(C_2H_3O) = 35$ kcal./mole. Since the CH_3^+ group must be formed by rearrangement processes in ethylene oxide, the $\Delta H_f^+(CH_3)$ is expected to be somewhat larger. The value obtained in the ethylene study for the heat of formation of CH_3^+ is 292 kcal./mole.

If, instead of approximating $\Delta H_f(C_2H_3O) = 35$ kcal./mole, we take the values of $\Delta H_f^+(CH_2)$

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(18) J. H. Beynon, R. A. Saunders and A. E. Williams, THIS JOURNAL, **82**, 288 (1960).

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

(20) G. G. Hall, *ibid.*, **50**, 319 (1954).

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

(22) K. Watanabe, *ibid.*, **26**, 542 (1957).

(23) A. Lowrey, III, and K. Watanabe, *ibid.*, **28**, 208 (1958).

(24) T-K. Liu and A. B. F. Duncan, *ibid.*, **17**, 241 (1949).

(25) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1954.

and $\Delta H_f^+(CH_3)$ given by Field and Franklin,[2] we calculate $\Delta H_f(C_2H_3O)$ = 28.5 and 38.6 kcal./mole, respectively, from the *m/e* 14 and 15 data. We have assumed no excess kinetic energy was involved. The average, 33.5 kcal./mole, compares very favorably with the value of 35 kcal./mole, which we estimated above. We conclude then that $\Delta H_f(C_2H_3O) = 33 \pm 5$ kcal./mole.

m/e **16**.—The ion is fairly abundant in the ethylene oxide spectrum and leads to $\Delta H_f^+(CH_4)$ = 298 kcal./mole. This value is slightly larger than that calculated on the basis of the ionization potential of CH_4 and enhances the argument that this ion is the result of rearrangement processes in ethylene oxide. Although observed in the spectrum of propylene oxide, the appearance potential of CH_4^+ was not determined.

m/e **25**.—The ion corresponding to *m/e* 25 is C_2H^+. The appearance potential from C_2H_4O of C_2H^+ was found to be 24.0 ± 0.3 e.v., leading to the result $\Delta H_f^+(C_2H)$ = 427 kcal./mole, in agreement with the literature.[2] Products other than 2H + OH are not favored.

m/e **26**.—The ion corresponding to *m/e* = 26 could only be $C_2H_2^+$. On the basis that either $CH_2O + H_2$ or $CO + 2H_2$ are the neutral products accompanying the ionization of propylene oxide followed by dissociation, $\Delta H_f^+(C_2H_2)$ = 328 kcal./mole. This compares favorably with values of 317–328 kcal./mole.[2] The energetics appear to rule out neutral products other than $CH_2O + H_2$ or $CO + 2H_2$. The study of ethylene oxide results in a value of 288 kcal./mole for $\Delta H_f^+(C_2H_2)$. It appears that H + OH are the most logical neutral products to be expected, but the energetics disagree. We have not yet found a satisfactory explanation for this low value.

m/e **27**.—The ion occurring with *m/e* = 27 in the C_3H_6O spectrum is $C_2H_3^+$. $\Delta H_f^+(C_2H_3)$ is calculated to be 285 kcal./mole, assuming the neutral products to be CH_2O and H. Agreement of this value with the literature[2] supports this process. The formation of $C_2H_3^+$ from C_2H_4O likely requires rearrangement. Thus, the value of ΔH_f^+ = 308 kcal./mole is in fair agreement with the suggested additional product of OH.

m/e **28**.—The appearance potential of *m/e* = 28 from propylene oxide suggests that this ion is $C_2H_4^+$. $\Delta H_f^+(C_2H_4)$ calculated is larger than that reported by Field and Franklin[2]; however, it does eliminate the possibility of *m/e* = 28 being CO^+. The energetics here will not distinguish between $C_2H_4^+ + CO + H_2$ and $C_2H_4^+ + H_2CO$ as the products of this ionization and dissociation. On the other hand, the appearance potential of *m/e* 28 from C_2H_4O rules out the possibility of this ion being $C_2H_4^+$, and in fact the energetics give good evidence that the ion is CO^+. Taking the products to be $CO^+ + CH_4$, $\Delta H_f^+(CO)$ is found to be 296, in good agreement with the literature.[2] These facts then explain the large *m/e* 28 peak in the C_3H_6O spectrum, and the small peak at *m/e* 28 in the C_2H_4O spectrum. These results are also in good agreement with Beynon's results[4] using high resolution mass spectroscopy.

m/e **29**.—The large abundance of this ion in both spectra indicates that it is the same for both C_2H_4O and C_3H_6O and may be CHO^+. However, this ion might also be $C_2H_5^+$ in the propylene oxide case. The $\Delta H_f^+(CHO)$ calculated from the appearance potentials and the suggested processes for both C_2H_4O and C_3H_6O is 230–237 kcal./mole. This value agrees with that reported by Cummings and Bleakney[26] in their study of CH_3OH but disagrees with the value given by Mariner and Bleakney[27] from studies of formic acid. Beynon[4] noted that *m/e* 29 is CHO^+ for C_2H_4O but is composed of both CHO^+ and $C_2H_5^+$ for C_3H_6O, a point which the energetics does not bring out, as noted above.

m/e **30**.—The appearance potential of 11.6 e.v. for *m/e* 30, CH_2O^+, from propylene oxide leads to the value of $\Delta H_f^+(CH_2O)$ = 234 kcal./mole, using the suggested process. This value is in fair agreement with the literature.[2] The appearance potential of *m/e* 30 from C_2H_4O was not obtained because of the small abundance of this ion in its mass spectrum.

m/e **31**.—The relative abundance of this ion from propylene oxide at 70 e.v. rules out any significant contribution from $C^{13}H_2O$, as does also the appearance potential. Thus the ion is considered to be CH_3O^+. This suggests that the other products are C_2H_2 + H, and from this $\Delta H_f^+(CH_3O)$ is calculated to be 182 kcal./mole, is fair agreement with the value of 173 kcal./mole.[2] Energetic considerations eliminate C_2H_3 as a product. The small abundance of this ion from C_2H_4O did not allow measurements of its appearance potential.

m/e **39**.—This ion occurs only in the mass spectrum of propylene oxide. The occurrence also of *m/e* 38 and *m/e* 37 indicate *m/e* 39 to be $C_3H_3^+$. The process is similar to the formation of *m/e* 26 from C_2H_4O except that with *m/e* 39, H_2 rather than 2H, is formed. $\Delta H_f^+(C_3H_3)$ = 288 kcal./mole agrees with the literature[2] and suggests that the structure of this ion is $CH_2{=}C{=}CH^+$.[28]

m/e **42**.—This ion formed from propylene oxide might be $C_2H_2O^+$ or $C_3H_6^+$. Beynon[4] indicates both ions are present at 50 e.v. However, since it would require an appearance potential of nearly 13.5 e.v. for the formation of $C_3H_6^+ + O$, and the observed value is 12.7 ± 0.2, it is concluded that the appearance potential is for the $C_2H_2O^+$ ion. Energetics rule out the CH_4 as the accompanying product. Thus, the neutral products are considered to be CH_3 + H, although $CH_2 + H_2$ is also possible, and $\Delta H_f^+(C_2H_2O)$ is calculated to be 189 kcal./mole. This value is lower than that given in the literature.[2] It is plausible that this ion still has a cyclic structure. The *m/e* 42 ion from ethylene oxide also is $C_2H_2O^+$. From the energetics this ion is CH_2CO^+.

m/e **43**.—The peak at *m/e* = 43 from propylene oxide could only result from the removal of CH_3 from the parent molecule. Then, $\Delta H_f^+(C_2H_3O)$ is 199 kcal./mole. It is reasonable to expect this ion to still be cyclic following ionization and

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(26) C. S. Cummings and W. Bleakney, *Phys. Rev.*, **58**, 787 (1940).

(27) T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 807 (1947).

(28) V. Čermák (private communication) of the Institute of Physical Chemistry, Czechoslovak Academy of Sciences, believes that a cyclic structure of $C_3H_3^+$ is also possible, analogous to the cyclopentadienyl and tropylium ions.

dissociation. $\Delta H_f^+(C_2H_3O)$ for a non-cyclic is 174 kcal./mole,[2] supporting this conclusion. The value of $\Delta H_f^+(C_2H_3O)$ obtained from the appearance potential study of ethylene oxide is 215 kcal./mole, only in fair agreement with that determined from propylene oxide. Although the agreement is within approximately the accumulative quoted errors, it is possible that this ion is cyclic and also that this ion be CH_2CHO^+. It is fairly certain the ion is not CH_3CO^+.

m/e **44.**—Ionization of ethylene oxide requires 10.65 ± 0.10 e.v., giving $\Delta H_f^+(C_2H_4O) = 234$ kcal./mole. This indicates the cyclic nature of this ion. The *m/e* 44 ion abundance in the spectrum of C_3H_6O was too small to allow a determination of its appearance potential.

m/e **57.**—Ionization and dissociation of C_3H_6O to $C_3H_5O^+$ and H is responsible for the observed ion at *m/e* = 57. From the experimental appearance potential, $\Delta H_f^+(C_3H_5O)$ is found to be 193 kcal./mole. We suggest that this ion retains its cyclic structure.

m/e **58.**—This ion could only result from ionization without further dissociation of propylene oxide. Thus, $\Delta H_f^+(C_3H_6O)$ is 204 kcal./mole, and for this ion it is reasonable to assume a cyclic structure. $\Delta H_f^+(C_3H_6O)$ for non-cyclics, although depending on the structure, is about 180 kcal./mole.[2]

From the above data, we concluded that $\Delta H_f(C_2H_3O) = 33 \pm 5$ kcal./mole. Assuming the C–H bond energy to be about 100 kcal./mole, and taking the appearance potentials of the ions from their respective molecules, the ionization potentials of the radicals C_3H_5O and C_2H_3O are calculated to be approximately 7.2 and 7.8 e.v., respectively.

The low values for the appearance potentials of *m/e* 43 and 29 and their large abundances suggests these ions are formed directly from the parent molecule ion. The less abundant *m/e* 42, 28, 16 and 14 ions indicates these are likely due to secondary dissociation. *m/e* 15 is likely the result of a secondary process and involves rearrangement, as does *m/e* 16. Further theoretical considerations of the construction of the mass spectrum will be treated in more detail in a future publication.

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Free Radicals by Mass Spectrometry. XXI. The Ionization Potentials of Some *meta* and *para* Substituted Benzyl Radicals

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The ionization potentials of a number of *meta* and *para* substituted benzyl radicals have been determined by electron impact. The substituents, in order of decreasing ionization potential of the radical, were *m*-CN, *m*-NO_2, *p*-CN, *m*-F, *p*-Cl, *p*-F, *p*-*i*-Pr and *p*-CH_3O. The results are in agreement with the known electron-releasing or electron-attracting powers of the substituents. Since the effect of the substituents on the stability of the radicals themselves is very small, the results permit a consideration of the stabilization of ions in the gas phase where solvation plays no role.

Introduction

Since the ionization potentials of hydrocarbon free radicals reflect the effects of structural factors on the stabilities of radicals and ions, a knowledge of the ionization potentials of a wide variety of radicals is of importance both in the development of theoretical methods in molecular structure and in the understanding of the reactivities of radicals and carbonium ions. The ionization potentials of a number of conjugated hydrocarbon radicals, measured directly by electron impact,[3,4] are in excellent agreement with values calculated by a semi-empirical molecular orbital method.[5] Recently the simple molecular orbital theory has been modified[6] to permit the examination of the hyperconjugative effect of a methyl group on ionization potentials. Ionization potentials of a number of methyl substituted allyl, benzyl and alkyl radicals calculated by this method[6] are in reasonable agreement with experimental values obtained by electron impact.[7-9]

Such theoretical calculations have not been made as yet for radicals containing hetero-atoms, presumably because of the mathematical complexity of the calculations and the lack of experimental data for comparison. Some experimental data on the effect of halogen hetero-atoms on the ionization potential of the methyl radical has been published recently,[10] and it appears desirable to examine further the effect of such hetero substituents on radicals of various types. The present paper is

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