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Experimental and Theoretical Studies of the VUV Photoionization of Chloropropylene Oxide

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The photoionization and dissociative photoionization of chloropropylene oxide have been studied both experimentally and theoretically. In experiments, photoionization efficiency spectra for ions $C_3H_5O^+$, CHO^+, $C_2H_4{}^+$, $C_2H_3{}^+$, $C_2H_2{}^+$, $CH_3{}^+$, and CH_2OH^+ were obtained. Theoretically, the energetics of the dissociative photoionizations were examined by ab initio Gaussian-3 calculations. The computational results are useful in our attempt to establish the dissociative photoionization channels of chloropropylene oxide. These proposed channels include six simple bond cleavage reactions as well as a reaction involving intermediates and transition structures. The agreement between experimental and computational dissociation energies or barriers ranges from fair to excellent.

Introduction

Heterocyclic compounds are widely distributed in nature, and many of them have biological activity. In addition, it has been found that the 1,2-epoxy functional group in a large number of natural epoxy products plays a key role in biological growth, heredity, and atrophy.[1,2] The oxirane system is a basic and simple heterocyclic unit with polar covalent bonds in the ring. There is strong ring strain as well. Thus, epoxy compounds undergo ring-opening reactions easily and are highly reactive. It is clearly desirable to obtain quantitative information regarding the photoionization and dissociative photoionizations of various epoxy compounds.

Up to now, studies of ionization and dissociation of chloropropylene oxide (C_3H_5ClO) in the vacuum ultraviolet (VUV) region are not extensive. The ionization energy (IE) of chloropropylene oxide was measured by various groups using photoelectron spectroscopy.[3−5] The appearance energies (AEs) of the principal cations in the mass spectra of chloropropylene oxide were obtained employing electron impact (EI) technique.[6] Moreover, probable dissociation processes were given. However, due to the low energy resolution of the electron beams, the accuracy of the derived thermodynamic properties is not very high. In addition, the AEs determined by electron impact ionization are normally larger than those obtained from photoionization.[7] To our knowledge, the photoionization and photodissociations of chloropropylene oxide with time-of-flight (TOF) mass spectrometry have not been reported in the literature.

The VUV dissociative photoionization technique, especially when performed with the synchrotron radiation source, has been proven to be a powerful tool for studying the energetics and dynamics of ionization and dissociation of organic compounds.[8−10] By using a combination of this technique and TOF mass spectrometry, we have already studied the photoionization and dissociative photoionizations of ethylene oxide and propylene oxide.[11,12] In these previous studies, the AEs of all of the observed ions were measured. The dissociative photoionization channels of ethylene oxide and propylene oxide near the ionization thresholds were established by means of both experiments and high-level computations. In the work described here, we employed similar techniques to investigate and determine the energetics of the photoionization and photodissociation of chloropropylene oxide. Chloropropylene oxide has the same symmetry (C_1) as propylene oxide. But it is noted that chloropropylene oxide has a very strong electronegative chlorine atom in the molecule. Thus its photoionization and dissociative photoionization processes are different from those of other epoxy compounds and other heterocyclic compounds.

In this paper, we report the photoionization efficiency (PIE) curves of all ions resulting from the photoionization of chloropropylene oxide in the photon energy region of 10−40 eV. From these data, we derive the energetics of the dissociation reactions. Combining these results with high-level ab initio calculations, the dissociative photoionization channels of chloropropylene oxide can then be established.

Experimental and Computational Methods

The details of the experimental setup employed in this work were described in some earlier publications.[7,11−19] Hence only a brief account is given below. On the other hand, this is the first time we employ the ab initio Gaussian-3 (G3) method[20] to

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study the energetics of dissociation reactions. Thus, a more detailed description of this model of theory will be given.

Experimental Setup. The apparatus for our experiment has been described in detail elsewhere.[13−16] Briefly, the apparatus consists of a synchrotron radiation source, a 1 m Sega-Namioka VUV monochromator, a molecular beam source, and a TOF mass spectrometor for ion detection.

There are two gratings used in the Sega-Namioka monochromator, 2400 and 1200 lines/mm, covering the wavelength range of 30−300 nm. The gratings have been coated with Au and Al and blazed at 60 and 144 nm, respectively. The wavelength resolution is about 0.1 nm with 150 μm entrance and exit slits. The photon flux of synchrotron radiation from the 800 MeV electron storage ring (National Synchrotron Radiation Laboratory, Hefei, China) is monitored by a sodium salicylate coated glass window with a photomultiplier tube behind the ionization chamber. The PIE curves have been normalized by the photon flux. In the wavelength region longer than the LiF cutoff wavelength (105 nm), a LiF filter (thickness 1 mm) is used to eliminate higher-order radiation of the dispersed light. The absolute wavelength of monochromator is calibrated with the known IEs and atomization peaks of the inert gases He, Ne, and Ar.

A homemade TOF mass spectrometer has been used for the VUV photoionization and photodissociation studies. The ion free flight length of TOF tube is 0.4 m long and its mass resolution is larger than 200. Photoions produced by the VUV light are drawn out of the photoionization region by a transistor-transistor logic (TTL) pulse and detected by a microchannel plate detector. The photoion pulse is used to stop a time-to-amplitude converter (TAC) which is started with the TTL pulse. The output of the TAC is sorted in a multichannel analyzer. A mass spectrum is obtained as the photoion number against the flight time of the ions. The ion signal intensity has been controlled so as to avoid the parasitic effect in using the TAC for the TOF measurements. A specific ion can be selected with the TAC combined with a single-channel analyzer. The PIE curve is obtained as the wavelength is scanned.

Chloropropylene oxide (with 99% purity) was obtained from Shanghai Chemical Reagent Plant (No.2) and used without further purification. The vapor of chloropropylene oxide was introduced by supersonic expansion through a continuous beam nozzle (70 μm diameter) from the molecular beam chamber into the ionization chamber through a 1.5 mm skimmer. Helium (with 99.999% purity) was used as the carrier gas, and the stagnation pressure was 0.1 MPa. The pressure of the ionization chamber was about 5×10^{-4} Pa when the molecular beam was introduced. No cluster was observed under this condition, so it was believed that all fragment ions originated from the dissociative photoionization of chloropropylene oxide.

Computational Method. All calculations were carried out on Compaq XP1000, DEC 600au, and DEC 500au workstations and SGI Origin 2000 High Performance Server, using the Gaussian 98 package[21] of programs. In general, the structures of the species involved in this work were optimized at the second-order Mϕller−Plesset theory (MP2) using the 6-31G(d) basis set with all electrons included, i.e., at the MP2(full)/6-31G(d) level. However, according to the experimental result, $C_3H_5O^+$ maintains its ring structure after the parent cation dissociating the Cl atom. This $C_3H_5O^+$ fragment does not have a stable ring structure at the MP2(full)/6-31G(d) level of theory. Instead, the MP2(full)/6-31+G(d) level of theory was chosen to optimize the structure of the cationic species involved in this dissociation reaction, i.e., $C_3H_5O^+$ and $C_3H_5ClO^+$.

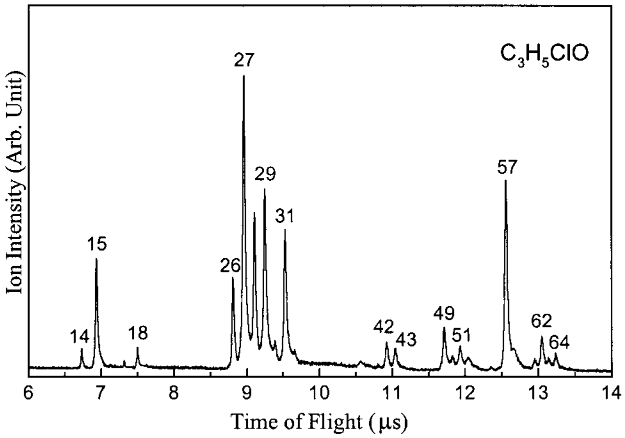

Figure 1. Photoionization TOF mass spectrum of chloropropylene oxide at the wavelength of 30 nm.

TABLE 1: Appearance Energies (eV) Measured in the Photodissociation of Chloropropylene Oxide

m/*e*	ion	relative abundance[a]	this work	EI[b]
92/94	$C_3H_5ClO^{+c}$			
62/64	$C_2H_3Cl^+$	11.1/4.6		
57	$C_3H_5O^+$	64.7	11.45 ± 0.02	11.4
49/51	CH_2Cl^+	15.0/6.2		
43	$C_2H_3O^+$	6.7		
42	$C_2H_2O^+$	8.8		12.1
31	CH_3O^+	47.4	13.33 ± 0.03	13.4
30	CH_2O^+	9.4		
29	CHO^+	61.3	11.54 ± 0.03	12.0
28	$C_2H_4^+$	53.1	13.87 ± 0.03	13.6
27	$C_2H_3^+$	100	12.86 ± 0.03	14.0
26	$C_2H_2^+$	31.0	16.10 ± 0.04	16.6
15	CH_3^+	37.6	13.13 ± 0.03	14.6
14	CH_2^+	6.5		21.6

[a] Relative abundances of the fragmental ions measured at the wavelength of 30 nm. [b] Data obtained using electron impact ionization technique, taken from ref 6. [c] The reported IE values of chloropropylene oxide found in the literature include 10.64 (ref 3), 10.60 (ref 4), and 10.66 eV (ref 5).

For the transition structures (TSs) identified in this work, the "reactants" and "products" of a given TS were confirmed by intrinsic reaction coordinate calculations.

The energies of all the species involved in this work were calculated using the Gaussian-3 method[20] of theory. This method is an approximation to the ab initio level of QCISD(T,full)/G3large, where G3large is a modified 6-311+G(3df,2p) basis set. The G3 method requires single-point calculations at the QCISD(T)/6-31G(d), MP4/6-31G(d), MP4/6-31G(2df,p), and MP2(full)/G3large levels based on the aforementioned optimized geometry. A small empirical correction is added to include the higher-level correction effect in the calculation of the total electronic energies (E_e). The harmonic frequencies obtained at the level of theory at which geometry optimization is done, scaled by 0.9661, are applied for the zero-point vibrational energy (ZPVE) correction at 0 K ($E_0 = E_e +$ ZPVE). The average absolute deviation from experiment for 148 calculated G3 enthalpies of formation is 3.9 kJ mol^{-1}.[20] For systems such as chloropropylene oxide, the error range for G3 energies should be within ±15 kJ mol^{-1}, or about ±0.15 eV.

Once the G3 energy of a species is obtained, the heat of formation at temperature $T(\Delta H_{fT})$ for this species can be obtained in the following manner. For molecule AB, its ΔH_{fT} is calculated from the G3 heats of reaction ΔH_{fT}(A + B →

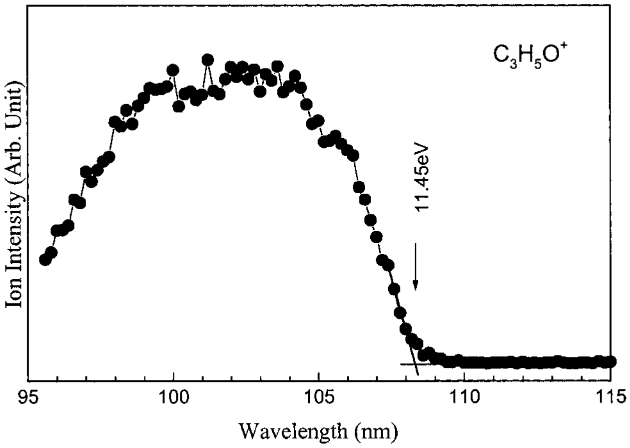

Figure 2. Photoionization efficiency curve of fragmental ion $C_3H_5O^+$ from chloropropylene oxide.

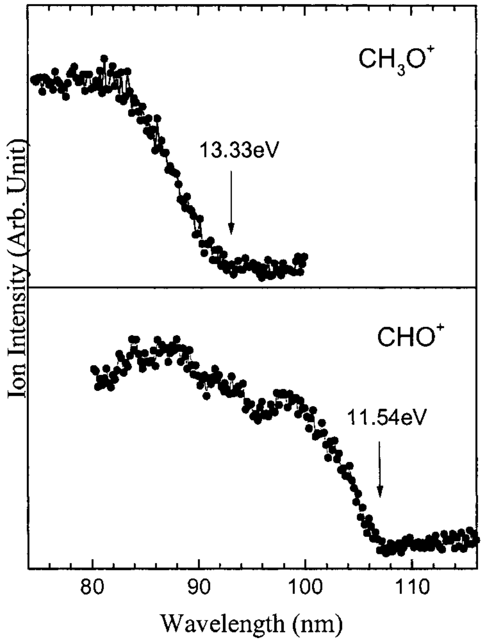

Figure 3. Photoionization efficiency curves of fragmental ions CH_3O^+ and CHO^+ from chloropropylene oxide.

AB) and the respective experimental ΔH_{fT} (A) and ΔH_{fT}(B) for elements A and B.

Results and Discussion

Experimental Measurements. A typical TOF mass spectrum of chloropropylene oxide at the wavelength 30 nm is shown in Figure 1. The fragmental ions at $m/e = 62/64$, 57, 49/51, 43, 42, 31, 30, 29, 28, 27, 26, 15, and 14 are listed in Table 1, along with the relative abundances of these ions measured at the wavelength of 30 nm. The mass peaks at $m/e = 18$ and 17 have been ignored because they arise from the photoionization of background water molecules in the ionization chamber. The mass peak at $m/e = 27$ is the $C_2H_3^+$ ion, corresponding to the highest peak. This indicates that the channel forming the $C_2H_3^+$ ion is the chief dissociative photoionization channel of chloropropylene oxide.

It should be pointed out that all observed ions in the photoionization TOF mass spectrum are fragmental ions, and the parent ion $C_3H_5ClO^+$ ($m/e = 92/94$) has not been observed. This result is in agreement with that of Wada and Kiser.[6] This is very different from the photoionization and photodissociations of ethylene oxide[11] and propylene oxide.[12] From the PIE curve of the $C_3H_5O^+$ ion, shown in Figure 2, we can see that the PIE increases very rapidly with the photon energy just exceeding its threshold. Assuming Franck−Condon principle, the $C_3H_5O^+$ cation should retain its ring structure. In addition, Cl atom is also produced in all of the dissociative photoionization channels. This indicates that the parent ion of chloropropylene oxide is very unstable and quickly dissociates a Cl atom to form the $C_3H_5O^+$ ion, which retains the ring structure. This situation is very similar to the dissociative photoionization of the CCl_4 molecule. The parent ion CCl_4^+ from the photoionization of CCl_4 is also very unstable and quickly dissociates a Cl atom to form CCl_3^+ ion.[15,22,23] Such a facile dissociation may be due to the presence of the highly electronegative chlorine atom in the

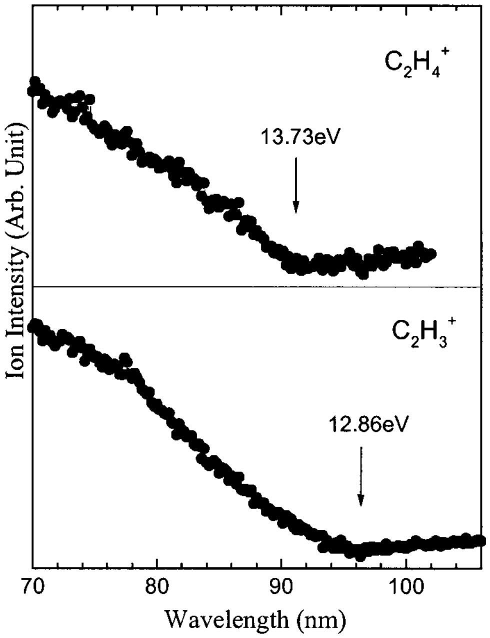

Figure 4. Photoionization efficiency curves of fragmental ion $C_2H_4^+$ and $C_2H_3^+$ from chloropropylene oxide.

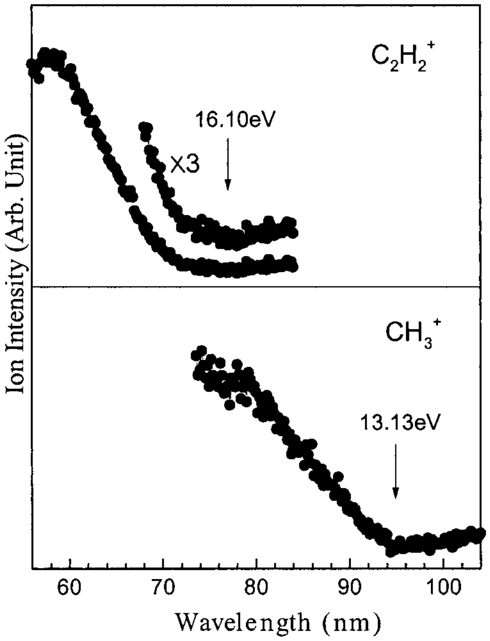

Figure 5. Photoionization efficiency curves of fragmental ions $C_2H_2^+$ and CH_3^+ from chloropropylene oxide. The $C_2H_2^+$ curve has been magnified three times in order to show the position of the threshold more clearly.

TABLE 2: G3 Total Energies (E_0), Enthalpies (H_{298}), and Standard Heats of Formations at 0 and 298 K (ΔH_{f0} and ΔH_{f298})[a] of Various Species Involved in the Dissociation of Chloropropylene Oxide (C_3H_5ClO)

species	E_0(G3) (hartree)	H_{298}(G3) (hartree)	$\Delta H°_{f0}$ (kJ mol^{-1})	$\Delta H°_{f298}$ (kJ mol^{-1})
equilibrium structures				
C_3H_5ClO (**1**)	−652.40939	−652.40321	−93.6	−108.4 (−108 ± 4)
$C_3H_5ClO^{+}$[b](**2**)	−652.02188	−652.01549	923.8	909.6
	−652.02186	*−652.01547*	*923.8*	*909.7*
$C_3H_5O^{+}$[b](**3**)	*−191.99676*	*−191.99138*	*893.9*	*881.5*
CH_2OH^{+} (**4**)	−114.69938	−114.69552	719.6 (718 ± 1.7)[c]	713.1
CHO^{+} (**5**)	−113.49199	−113.48854	826.7	827.7 (825.6)
$C_2H_4^{+}$ (**6**)	−78.11545	−78.11123	1089.3 (1074)	1082.0 (1066)
$C_2H_3^{+}$ (**7**)	−77.51838	−77.51406	1125.5 (1120)	1122.7 (1112)
$C_2H_2^{+}$ (**8**)	−76.85688	−76.85305	1330.8 (1328.5)	1331.0 (1327.9)
CH_3^{+} (**9**)	−39.42928	−39.42548	1100.5 (1098)	1097.1 (1093.3±0.4)
Cl	−459.99096	−459.98860		
C_2H_2 (**10**)	−77.27727	−77.27311	227.1 (228.6)	228.2 (228 ± 1)
C_2H_4 (**11**)	−78.50601	−78.50200	63.9 (60.7)	56.1 (52.2 ± 1)
CHO (**12**)	−113.79139	−113.78758	40.7	42.5 (44.8)
CH_2O (**13**)	−114.43077	−114.42695	−106.6 (−104.7)	−108.9 (−108.7±0.7)
CH_2OH (**14**)	−114.97585	−114.97165	−6.3	−11.9 (−9.0 ± 4)[d]
CH_2CO (**15**)	−152.50641	−152.50189	−46.3 (−44.6)	−47.5 (−47.7 ± 2.5)
Trans-c−$C(CH_2)OHCH_2^{+}$ (**16**)	−192.00902	−192.00376	861.7	849.0
$CH_2CCH_2OH^{+}$ (**17**)	−191.99572	−191.98940	896.6	886.7
$C_2H_2{\cdot}CH_2OH^{+}$ (**18**)	−191.99459	−191.98747	899.6	891.8
transition structures				
TSa	−191.93152	−191.92625	1065.1	1052.5
TSb	−191.99210	−191.98623	906.1	895.1
TSc	−191.97913	−191.97266	940.1	930.7

[a] Experimental values, where available, are given in brackets. Unless specified, all experimental ΔH_f values are taken from ref 28. [b] Calculated energies based on the structures optimized at the MP2(full)/6-31+G(d) level of theory are given in italic. [c] Reference 29. [d] Reference 30.

molecule. Additionally, it is noted that, while our TOF mass spectrometric experiments failed to detect the parent cation of chloropropylene oxide, the IE of this molecule was successfully measured by PES.[3−5] This is due to the fact that, in the PES experiments, we need only to detect the photoelectron corresponding to the formation of the parent cation, and no measurement is made on the parent cation itself.

The PIE curves of the other fragmental ions, including CH_3O^+, CHO^+, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, and CH_3^+ from the dissociative photoionization of chloropropylene oxide, are presented in Figures 3−5. The AE in each PIE curve has been determined by the linear extrapolation method.[14,15,24] In arriving at our AE values, we ignored the temperature effect in our data analysis. Under the nozzle expansion condition described above, a certain extent of cooling is expected (below 200 K). The thermal energy has the effect of lowering the observed AEs. In addition, no correction has been made for possible kinetic shifts in determining the AE values. As these factors tend to shift the observed onset to higher energies, the AEs we estimated give only upper limits. This kind of data analysis method has also been carried out by other researchers and proved to be useful in studying dissociative photoionization processes in general.[25−27]

All of the AEs for various fragmental ions derived from the PIE curves are tabulated in Table 1, along with the error ranges that reflect either the bandwidth of our monochromator or the wavelength interval of the data points for performing the measurements. Also listed in Table 1 are the AEs obtained using the EI technique.[6] The present work represents the first time where the AEs of the fragmental ions $C_3H_5O^+$, CH_3O^+, CHO^+, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, and CH_3^+ from the photodissociation of chloropropylene oxide have been obtained using synchrotron radiation. Comparing the two sets of results listed in Table 1, it can be seen that the AEs obtained in this work are in general agreement with those derived from the EI experiments, but the EI results are sometimes a bit higher than ours. It is known that the EI ionization method often overestimates the AEs of both the parent and fragmental ions. It should be mentioned that in measuring the PIE curve of $C_3H_5O^+$, a LiF filter was used to eliminate the effect of higher-order radiation from the grating of 1200 lines/mm. For the AE measurements of CH_3O^+, CHO^+, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, and CH_3^+, the grating of 2400 lines/mm was used without filter. According to our experience, the effect of the second-order radiation from the grating of 2400 lines/mm is negligible.[7,11−19] In addition, our experiments were carried out under supersonic cooling conditions, thereby the influences of hot band effect on the accurate determinations of the AEs could be overcome to a large extent. We therefore believe that the AEs from chloropropylene oxide we have measured are reasonably accurate. The experimental IEs of chloropropylene oxide measured by various groups are 10.64,[3]

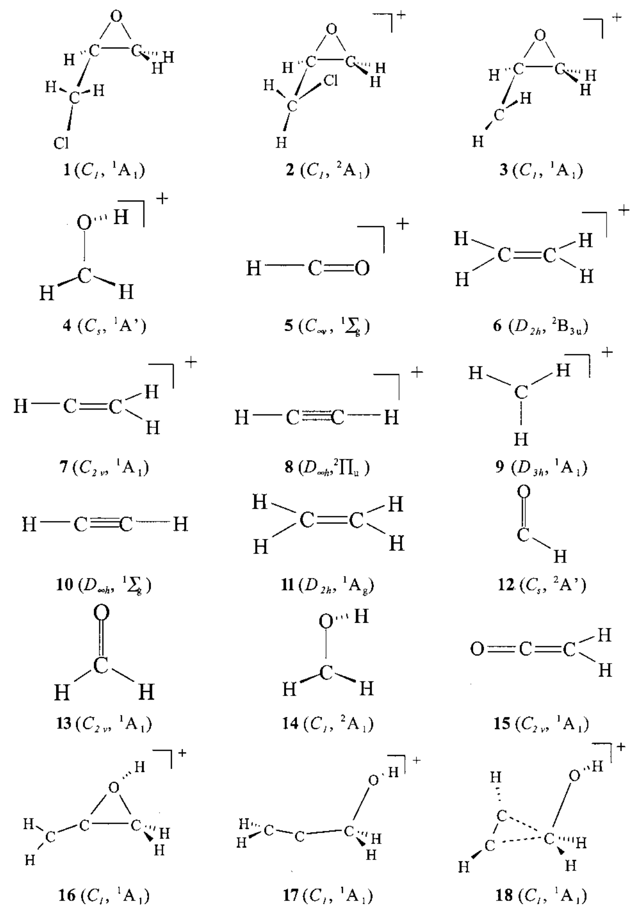

Figure 6. The structural formulas of the various polyatomic species with three or more atoms involved in this work, along with their symmetry point groups and electronic states.

10.60,[4] and 10.66 eV,[5] all using photoelectron spectroscopy, which are in good agreement with the G3 result of 10.54 eV.

From the mass spectrum of chloropropylene oxide (Figure 1), other smaller fragmental ions at m/e = 62/64, 49/51, 43, 42, 30, and 14 can be identified. The mass peaks at m/e = 62/64, 43, and 42 are the fragmental ions $C_2H_3Cl^+$, $C_2H_3O^+$, and $C_2H_2O^+$, respectively. They all may come from the directly transannular cleavages of the three-membered ring. The mass peak at m/e = 49/51 is the fragmental ion CH_2Cl^+, which may come directly from the cleavage of the bond linking the methyl group and the three-membered ring. The mass peak at m/e = 14 is the fragmental ion CH_2^+, which may come from the further dissociation of $C_3H_5O^+$. Therefore, the photodissociation of chloropropylene oxide may also proceed through the channels of directly transannular cleavage and the cleavage of the aforementioned C−C bond. But the abundances of these fragmental ions are relatively small, and hence the dissociative photoionization channels involved are comparatively unimportant.

Computational Results

The G3 total energies and enthalpies, as well as the standard heats of formations at 0 and 298 K, for the species involved in this work are given in Table 2. The structures of the stable polyatomic species with three or more atoms involved in this work, along with their electronic states, are shown in Figure 6. The calculated G3 IE of chloropropylene oxide, energies of six dissociation reactions, and reaction barrier of one dissociation reaction are tabulated in Table 3. The corresponding experimental reaction energies (ΔE, where ΔE = AE − IE) measured in this work are also given in this table. For the dissociation reaction leading to the formation of CH_2OH^+, three TSs have been located, and the potential energy surface for this reaction is displayed in Figure 7.

Because, according to experiment, $C_3H_5ClO^+$ is very unstable, C_3H_5ClO will dissociate into the $C_3H_5O^+$ and Cl immediately and directly upon ionization. Thus, we were unable to obtain the adiabatic IE for C_3H_5ClO experimentally. However, three experimental IEs of C_3H_5ClO, 10.64,[3] 10.60,[4] and 10.66 eV,[5] are found in the literature. According to our G3 calculations, the adiabatic IE(G3) of C_3H_5ClO is 10.54 eV, and this value is in fair accord with the aforementioned experimental IEs. In the following, we use the G3 IE to calculate the experimental reaction energies (ΔE). The choice of the G3 IE over the experimental data is admittedly somewhat arbitrary, but in any event we have no reason to choose one experimental value over the other two. Also, as we shall see, the G3 IE does lead to a set of ΔE values which are in good to excellent agreement with the experimental energies of dissociation.

Dissociative Photonization Channels. Seven dissociative photoionization channels are proposed in this work. Out of these seven channels, only one involves TSs, whereas the remaining six are regarded as "simple bond cleavage reactions."

The dissociation reactions involving only cleavage of bond(s) are summarized below:

$$C_3H_5ClO^+\ (\mathbf{2}) \xrightarrow{\Delta E_1} C_3H_5O^+\ (\mathbf{3}) + Cl \qquad (1)$$

$$\Delta E_1 = AE(C_3H_5O^+) - IE(C_3H_5ClO) = 0.91 \pm 0.02\ eV$$

$$C_3H_5ClO^+\ (\mathbf{2}) \xrightarrow{\Delta E_2} CHO^+\ (\mathbf{5}) + C_2H_4\ (\mathbf{11}) + Cl \qquad (2)$$

$$\Delta E_2 = AE(CHO^+) - IE(C_3H_5ClO) = 1.00 \pm 0.03\ eV$$

$$C_3H_5ClO^+\ (\mathbf{2}) \xrightarrow{\Delta E_3} C_2H_4^+\ (\mathbf{6}) + CHO\ (\mathbf{12}) + Cl \qquad (3)$$

$$\Delta E_3 = AE(C_2H_4^+) - IE(C_3H_5ClO) = 3.33 \pm 0.03\ eV$$

$$C_3H_5ClO^+\ (\mathbf{2}) \xrightarrow{\Delta E_4} C_2H_3^+\ (\mathbf{7}) + CH_2O\ (\mathbf{13}) + Cl \qquad (4)$$

$$\Delta E_4 = AE(C_2H_3^+) - IE(C_3H_5ClO) = 2.32 \pm 0.03\ eV$$

$$C_3H_5ClO^+\ (\mathbf{2}) \xrightarrow{\Delta E_5} C_2H_2^+\ (\mathbf{8}) + CH_2OH\ (\mathbf{14}) + Cl \qquad (5)$$

$$\Delta E_5 = AE(C_2H_2^+) - IE(C_3H_5ClO) = 5.56 \pm 0.04\ eV$$

$$C_3H_5ClO^+\ (\mathbf{2}) \xrightarrow{\Delta E_6} CH_3^+\ (\mathbf{9}) + CH_2CO\ (\mathbf{15}) + Cl \qquad (6)$$

$$\Delta E_6 = AE(CH_3^+) - IE(C_3H_5ClO) = 2.59 \pm 0.03\ eV.$$

From Table 3, it is seen that, except for reaction 5, our G3 dissociation energies are in good to excellent agreement with the experiment. For reaction 5, only fair agreement was obtained (the experimental reaction energy ΔE_5 is 0.17 eV higher than the G3 result). In view of this relatively poor result, we attempted to locate plausible TS(s) for this reaction, but none was found. Also, for this reaction, if we take CH_3O instead of its isomer CH_2OH (**14**) as one of the products, ΔE_5 would become 5.75 eV. Hence, CH_2OH is the more likely product.

TABLE 3: Experimental and Calculated Ionization Energies (IE) and Energies of Dissociations of Chloropropylene Oxide (C_3H_5ClO)

	reaction	Δ*E*(exp) (eV)	Δ*E*(G3) (eV)
ionization			
	C_3H_5ClO (**1**) → $C_3H_5ClO^+$ (**2**) + e^-	10.64,[a]10.60,[b]10.66[c]	10.54
simple bond cleavage reactions			
(1)	$C_3H_5ClO^+$ (**2**) → $C_3H_5O^+$ (**3**) + Cl	0.91 ± 0.02	0.93
(2)	$C_3H_5ClO^+$ (**2**) → CHO^+(**5**) + C_2H_4 (**11**) + Cl	1.00 ± 0.03	0.90
(3)	$C_3H_5ClO^+$ (**2**) → $C_2H_4^+$(**6**) + CHO (**12**) + Cl	3.33 ± 0.03	3.38
(4)	$C_3H_5ClO^+$ (**2**) → $C_2H_3^+$(**7**) + CH_2O (**13**) + Cl	2.32 ± 0.03	2.23
(5)	$C_3H_5ClO^+$ (**2**) → $C_2H_2^+$(**8**) + CH_2OH (**14**) + Cl	5.56 ± 0.04	5.39
(6)	$C_3H_5ClO^+$ (**2**) → CH_3^+ (**9**) + CH_2CO (**15**) + Cl	2.59 ± 0.03	2.59
reaction involving reaction barrier			
(7)	$C_3H_5ClO^+$ (**2**) →CH_2OH^+ (**4**) + C_2H_2 (**10**) + Cl	2.79 ± 0.03	2.71

[a] Reference 3. [b] Reference 4. [c] Reference 5.

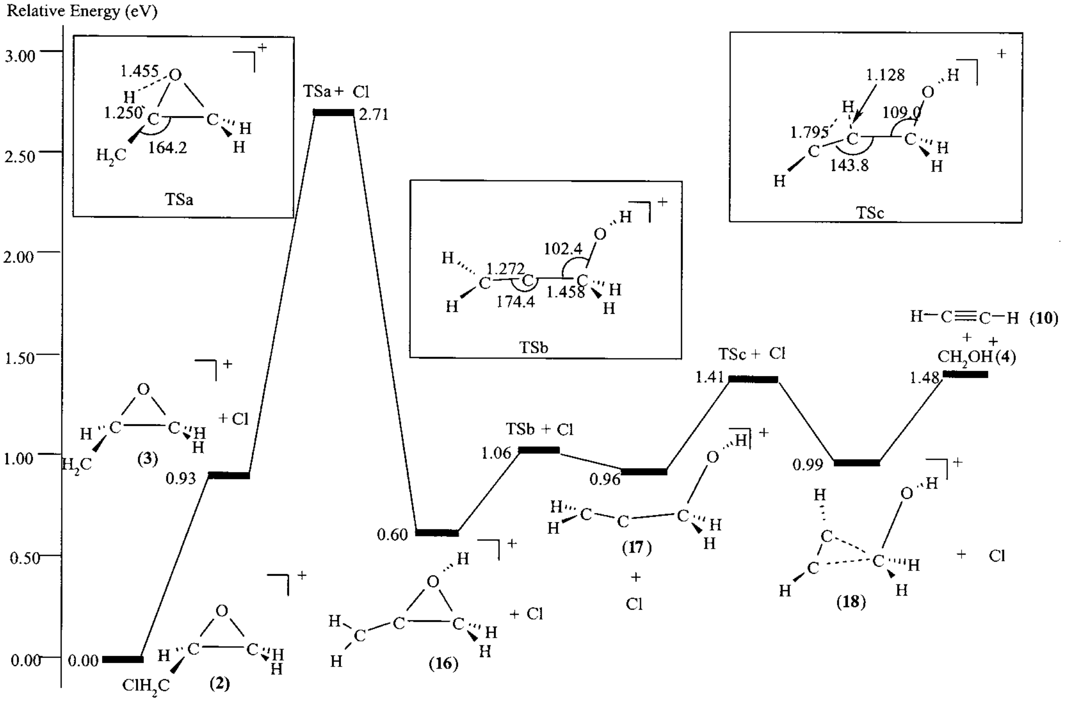

Figure 7. Potential energy surface showing the possible mechanism for dissociation $C_3H_5ClO^+ \rightarrow CH_2OH^+ + C_2H_2 + Cl$.

Finally, we consider the dissociative photoionization channel (7):

$$C_3H_5ClO^+\ (\mathbf{2}) \xrightarrow{\Delta E_7} CH_2OH^+\ (\mathbf{4}) + C_2H_2\ (\mathbf{10}) + Cl \quad (7)$$

$$\Delta E_7 = AE(CH_2OH^+) - IE(C_3H_5ClO) = 2.79 \pm 0.03\ eV$$

The energy profile of this reaction is shown in Figure 7. To yield CH_2OH^+ (**4**), C_2H_2 (**10**), and Cl, $C_3H_5ClO^+$ (**2**) first dissociates the chlorine atom to yield $C_3H_5O^+$ (**3**). Cation **3** then undergoes a hydrogen transfer, through TSa, to form **16**. Ring opening of **16**, and through TSb, leads to the formation of **17**. Upon 1,2-hydrogen shift and through TSc, cation **17** forms **18**. Cation **18** may be considered as a complex between C_2H_2 and CH_2OH^+, the distances between the carbon atom on the CH_2OH^+ moiety and the two carbon atoms on the C_2H_2 moiety are 2.478 and 2.406 Å. This complex then dissociates to form CH_2OH^+ (**4**) and C_2H_2 (**10**) directly, at a relatively low energy cost of 0.49 eV. The overall reaction barrier is calculated to be 2.71 eV, in very good agreement with the experimental dissociation energy, 2.79 ± 0.04 eV. Finally, if we take CH_3O^+ instead of its isomer CH_2OH^+ (**4**) as the cationic product, ΔE_7 would become 6.25 eV. Hence, CH_2OH^+ is the more likely product.

Conclusion

By combining the techniques of synchrotron radiation, molecular beam spectrometry, and mass spectrometry, we have measured the AEs of $C_3H_5O^+$, CHO^+, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, CH_3^+, and CH_2OH^+ in the dissociation of chloropropylene oxide. With the aid of ab initio Gaussian-3 results, we have established the dissociative photoionization channels for the formation of these fragments. These proposed channels include six simple bond cleavage reactions and a reaction involving intermediates and transition structures. The agreements between the experimental and computational dissociation energies of the barrier are well within ±0.15 eV. The only exception is the dissociation reaction involving $C_2H_2^+$, for which the discrepancy between experiment and calculation is 0.17 eV.

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