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1-丙醇和 2-丙醇真空紫外光电离质谱研究

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摘要 研究了 9.84 ~ 11.80 eV 光子能量范围内 1-丙醇和 2-丙醇的光电离和离解光电离现象, 测量了 1-丙醇离解光电离产生的碎片离子 $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+$ 、 $\text{CH}_3\text{CH}_2\text{CHOH}^+$ 、 $\text{CH}_2\text{CH}_2\text{OH}^+$ 、 $\text{CH}_3\text{CH}_2\text{CH}_2^+$ 、 $\text{CH}_3\text{CH}=\text{CH}_2^+$ 和 CH_2OH^+ 及 2-丙醇离解光电离产生的碎片离子 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3^+$ 、 $\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+$ 、 CH_3CHOH^+ 、 $\text{CH}_2=\text{CHOH}^+$ 、 $\text{CH}_3\text{CHCH}_3^+$ 和 $\text{CH}_3\text{CH}=\text{CH}_2^+$ 的光电离效率谱, 得到了这些离子的出现势. 结合从头算理论计算, 给出了 1-丙醇的碎片离子 $\text{CH}_3\text{CH}_2\text{CHOH}^+$ 、 $\text{CH}_2\text{CH}_2\text{OH}^+$ 、 $\text{CH}_3\text{CH}_2\text{CH}_2^+$ 、 $\text{CH}_3\text{CH}=\text{CH}_2^+$ 、 CH_2OH^+ 和 2-丙醇的碎片离子 $\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+$ 、 CH_3CHOH^+ 、 $\text{CH}_2=\text{CHOH}^+$ 、 $\text{CH}_3\text{CHCH}_3^+$ 、 $\text{CH}_3\text{CH}=\text{CH}_2^+$ 等的解离通道和解离能. 理论计算结果与实验结果符合得很好.

关键词: 真空紫外光电离, 1-丙醇, 2-丙醇, 解离通道

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A Vacuum Ultraviolet Photoionization Mass Spectrometric Study of 1-Propanol and 2-Propanol

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Abstract The photoionization and dissociative photoionization of 1-propanol and 2-propanols have been studied at the photon energy range of 9.84~11.80 eV. Photoionization efficiency spectra for ions $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+$, $\text{CH}_3\text{CH}_2\text{CHOH}^+$, $\text{CH}_2\text{CH}_2\text{OH}^+$, $\text{CH}_3\text{CH}_2\text{CH}_2^+$, $\text{CH}_3\text{CH}=\text{CH}_2^+$, CH_2OH^+ from 1-propanol, and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3^+$, $\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+$, CH_3CHOH^+ , $\text{CH}_2=\text{CHOH}^+$, $\text{CH}_3\text{CHCH}_3^+$, $\text{CH}_3\text{CH}=\text{CH}_2^+$ from 2-propanol have been measured. In addition, the energetics of the dissociative photoionization has been examined by *ab initio* Gaussian-3(G3) calculations. The computational results are useful in establishing the dissociation channels near the ionization thresholds. With the help of G3 results, the dissociation channels for formation of the fragment ions $\text{CH}_3\text{CH}_2\text{CHOH}^+$, $\text{CH}_2\text{CH}_2\text{OH}^+$, $\text{CH}_3\text{CH}_2\text{CH}_2^+$, $\text{CH}_3\text{CH}=\text{CH}_2^+$, CH_2OH^+ from 1-propanol, and $\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+$, CH_3CHOH^+ , $\text{CH}_2=\text{CHOH}^+$, $\text{CH}_3\text{CHCH}_3^+$, $\text{CH}_3\text{CH}=\text{CH}_2^+$ from 2-propanol have been established. The G3 results are in excellent agreement with the experimental data.

Keywords: VUV photoionization, 1-propanol, 2-propanol, Dissociation channels

Propanols are used as solvent in paint and cosmetic industry. They are also basic organic reagents in the synthesis of other products, such as medicine, cosmetic. Recently, alcohols are added in gasoline to reduce the formation of soot in combustion. Studying the photoionization of those chemicals will help understanding the degradation of them in the atmosphere. The ioniza-

tion and dissociation properties of 1-propanol and 2-propanol have been studied by many groups using the method of electron impact ionization(EI)^[9-10] as well as photoionization(PI)^[9-10].

Bowen *et al.*^[11] used low energy EI(12.1 eV) to study the ionization and dissociation process of saturated alcohols and ethers. They reported the ionization energies (IEs) of the two

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propanols and appearance energies(AEs) of some fragments. In their 1-propanol results, the fragment ion CH_2OH^+ shares a relatively low intensity at 12.1 eV, which is different from the PI mass spectra of Refaey *et al.*^[9] at 14.0 eV. And the reported AE, featured with its high error bar, of this fragment is outstandingly higher than the values of others^[2, 9-10]. In addition, they did not report the fragment of $\text{C}_2\text{H}_3\text{O}^+$ and $\text{CH}_3\text{CH}_2\text{CH}_2^+$. In the case of 2-propanol, they had no results of $\text{CH}_3\text{CHCH}_3^+$. Holmes *et al.*^[2-4] reported the AEs of fragments CH_2OH^+ and C_3H_6^+ from 2-propanol and C_3H_6^+ from 1-propanol. Friedman *et al.*^[5] studied the ionization and fragmentation of the two propanols with 50 eV EI. They studied the mechanism in detail. But the values of IEs and AEs are usually 0.4 eV higher than others. Lossing^[6] analyzed the fragments CH_3CHOH^+ and $\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+$ from 2-propanol, together with the fragmentation channels. Both of these two fragments are stable and are the products from direct cleavage of the corresponding bonds. McLafferty *et al.*^[7] measured the IE of 1-propanol and the AEs of fragments $\text{CH}_3\text{CH}_2\text{CHOH}^+$ and $\text{CH}_3\text{CH}=\text{CH}_2^+$. But their data seem to be systematically lower than those of others, whether they used EI or PI. Solka *et al.*^[8] studied the $\text{C}_2\text{H}_3\text{O}^+$ ion intensively and argued that this ion is protonated ethylene oxide formed from 1-propanol. In general, the EI results are rather scattered. And some dissociation channels are not included in EI studies.

Refaey *et al.*^[9] studied the ionization of the two propanols using the hydrogen many-line lamp. They reported the IEs of the mother molecules and the AEs of the major fragment ions. They also analyzed the possible formation channels of these ions. But they can not tell the identification of the fragment $\text{C}_2\text{H}_3\text{O}^+$. Besides, they obtained the AEs of fragment C_3H_6^+ , i.e. (10.65±0.03) eV from 1-propanol and ~12.0 eV from 2-propanol. They doubted the latter data but could not tell the reason. Chupka^[10] derived the AEs of fragments $\text{C}_3\text{H}_6\text{OH}^+$, C_3H_6^+ , and CH_2OH^+ from 1-propanol. He interpreted the data in terms of Rosenstock's quasi-equilibrium theory of unimolecular decomposition.

In the present work, we report the photoionization efficiency (PIE) curves of the major ions resulting from the dissociative photoionization of the two propanols in the photon energy region of 9.84~11.80 eV. From these PIE data, the energetics of the dissociations can be derived. Combining these results with high level *ab initio* calculations, the various dissociation channels of 1-propanol and 2-propanol can be established.

1 Experimental and theoretical methods

The experimental and computational techniques employed in this work have been used to study the dissociations of ammonia^[11], vinyl chloride^[12], acetone^[13], epichlorohydrin^[14], bromoethane^[15], 1,2-propylene oxide^[16], and pentafluoroethane^[17]. A brief description of these techniques is given below.

1.1 Experimental method

The experimental setup has been described elsewhere^[11-12], and it is briefly outlined here. Synchrotron radiation from the 800 MeV electron storage ring of National Synchrotron Radiation Laboratory, China, was monochromized by using a 1 m Seya-Namioka monochromator equipped with two gratings (2400 and 1200 lines·mm⁻¹) covering the wavelength range from 40~200 nm. The wavelength of monochromator was calibrated with the known IEs of inert gases. The calibration is very precise comparing the experimental IE value with the calculated one. The wavelength resolution is about 0.2 nm at the wavelength of 100.0 nm with 120 μm entrance and exit slits. The photon flux was monitored by a silicon photodiode (SXUV-100, International Radiation Detectors Inc., USA). A LiF window (1.0 mm thickness) was used to eliminate higher order radiation of the dispersed light in the wavelength region longer than 105.0 nm. A reflectron time-of-flight mass spectrometer was employed for the study here. Photoions produced by the VUV light were drawn out of the photoionization region by a pulse extraction field triggered with a pulse generator (DG 535, SRS) and detected by a microchannel plate (MCP) detector. The ion signal was recorded by a multiscaler P7888 (FAST Comtec, Germany) after it was amplified with a preamplifier VT120C (EG & G, ORTEC). The total length of the ion flight is 1800 mm. The PIE curve was measured as the wavelength changing with increment of 0.2 nm. The vapor of 1-propanol or 2-propanol (purity 99%) was introduced by supersonic expansion through a continuous beam nozzle with an orifice of 70 μm diameter from the molecular beam chamber into the ionization chamber with a 1.0 mm skimmer. In this experiment, He (purity 99.99 %) was used as carrier gas.

1.2 Computational method

The high level *ab initio* calculations were carried out using the Gaussian-3 (G3) procedure, which is an approximation for the QCISD(T)/G3 large energy. It involves single-point calculations at the MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df, p), and MP2(Full)/G3 large levels, all carried out with the structures optimized at the MP2(Full)/6-31G(d) level. The MP2(Full)/6-31G(d)

Table 1 Experimental appearance energies (eV) of 1-propanol and 2-propanol

	<i>m/e</i>	Ion	Appearance energy (eV)		
			This work	PI ^a	EI ^b
1-propanol	31	CH ₂ OH ⁺	11.11 ± 0.03	~11.3 ^c	12.3 ± 0.9 ^d
	42	CH ₃ CH=CH ₂ ⁺	10.40 ± 0.03	10.65 ± 0.03 ^e	10.65 ± 0.09 ^f
	43	CH ₃ CH ₂ CH ₂ ⁺	11.63 ± 0.03	11.6 ± 0.1	
	45	C ₃ H ₅ O ⁺	10.28 ± 0.03		
			11.29 ± 0.03	11.1 ± 0.1	11.35 ± 0.04 ^g
			10.51 ± 0.03	10.72	10.72 ± 0.09 ^h
2-propanol	60	CH ₃ CH ₂ CHOH ⁺	10.15 ± 0.02	10.22 ± 0.04	10.22 ± 0.07 ⁱ
	42	CH ₃ CH=CH ₂ ⁺	10.26 ± 0.02	~ 12.0	~12.0 ± 0.9
	43	CH ₃ CHCH ₃ ⁺	11.44 ± 0.03	11.6	
	44	CH ₂ =CHOH ⁺	10.16 ± 0.02	10.27 ± 0.03	10.27 ± 0.09 ^j
	45	CH ₃ CHOH ⁺	10.26 ± 0.02	10.40	10.20 ± 0.08
					10.40 ± 0.09 ^k
	59	CH ₃ C(OH)CH ₃ ⁺	10.47 ± 0.03		< 10.48 ± 0.08
				10.6	10.6 ± 0.9 ^l
	60	CH ₃ CH(OH)CH ₃ ⁺	10.05 ± 0.02	10.12 ± 0.03	10.15 ± 0.07

Note: a) data taken from ref.9, b) data taken from ref.1, c) other reported value for this ion is ~ 11.11 eV (ref.10), d) other reported value for this ion is 11.20 eV (ref.2), e) other reported value for this ion is 10.50 eV (ref.10), f) other reported values for this ion include (10.56 ± 0.05) eV (ref.3), 10.3 (ref.7), g) data taken from ref.8, other reported value for this ion is 11.1 eV (ref.5), h) other reported value for this ion is 10.2 eV (ref.7), i) other reported value for the molecule ion is 10.0 eV (ref.7), j) other reported value for this ion is 10.26 eV (ref.4), k) other reported value for this ion is 10.26 eV (ref.6), l) other reported value for this ion is <10.48 eV (ref.6).

harmonic frequencies, scaled by 0.9661, were used for correction of zero-point vibrational energies (ZPVE). A small semi-empirical correction was also applied to account for the high level correlation effect. The agreement between G3 energetics and experimental results is usually well within 0.15 eV. All the computations involved in this work were carried out using the Gaussian03 suite of programs^[18].

2 Results and discussion

2.1 Ionization of 1-propanol and 2-propanol

The photoionization mass spectra of 1-propanol and 2-propanol at the wavelength of 105.0 nm are shown in Fig.1. As can be seen from the figure, in addition to the molecule ion C₃H₈O⁺, the fragment ions at *m/e*=59 (CH₃CH₂CHOH⁺), 45 (CH₂CH₂OH⁺), 43 (CH₃CH₂CH₂⁺), 42 (CH₃CH=CH₂⁺), and 31 (CH₂OH⁺) from 1-propanol and those at *m/e*=59 (CH₃C(OH)CH₃⁺), 45 (CH₃CHOH⁺), 44 (CH₂=CHOH⁺), 43 (CH₃CHCH₃⁺), and 42 (CH₃CH=CH₂⁺) from 2-propanol can also be observed. Fig.2 shows the PIE curves of the molecule ions (C₃H₈O⁺) of 1-propanol and 2-propanol. The IEs and AEs are determined by the onsets in each PIE curve.

All the AEs obtained from the PIE curves are listed in Table 1, along with the values measured by other researchers.

Generally, the IEs and AEs we reported here are very close to those obtained by using photoionization method, but lower than those obtained by the EI ionization method. This is understandable since the EI ionization method often overestimates the IEs and the AEs. Our experiments were carried out under supersonic cooling conditions, thereby overcoming the hot band effect and other influences on the accurate determination of the AEs. Also,

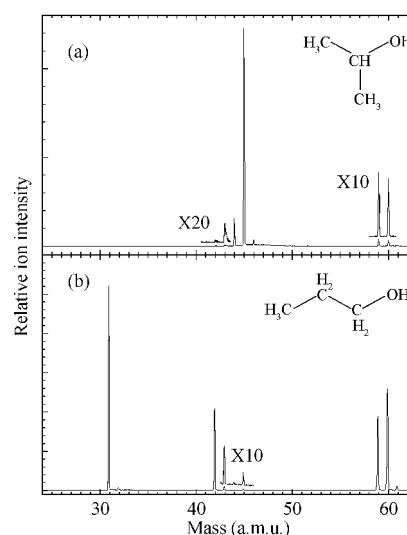


Fig.1 Photoionization mass spectra of 1-propanol and 2-propanol at the wavelength of 105.0 nm (11.81 eV) (a) 1-propanol; (b) 2-propanol

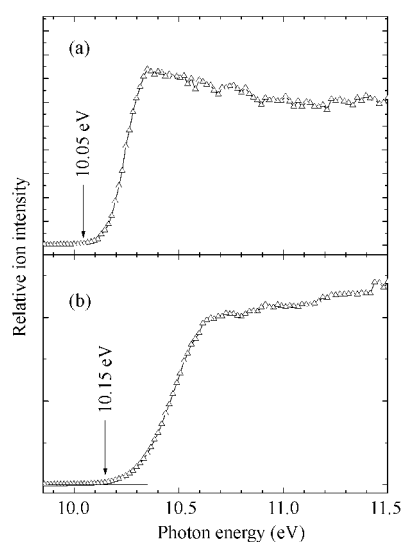


Fig.2 Photoionization efficiency curve of m/e 60 ($C_3H_8O^+$) from photoionization of 1-propanol and 2-propanol
(a) 2-propanol; (b) 1-propanol.

the light source employed was the high-intensity synchrotron radiation. Thus the IEs of the two propanols are more accurate than those of the previous measurements. Field-induced dissociative ionization and kinetic shift cannot have a serious effect (0.002~0.005 eV) here, comparing to the dissociation energies discussed in this article^[19-20].

The formulas of the species involved in this work, along with their symmetry point groups, electronic states, and the calculated G3 energies are summarized in Table 2. With the aid of these results, we have established the dissociation channels of the 1-propanol and 2-propanol cations.

The IE of 1-propanol is calculated to be 10.02 eV with the E_0 (G3) values of $CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2OH^+$. Considering that the error range of G3 results is ± 0.15 eV, this calculation value is in good agreement with the experimental result, (10.15 \pm 0.02) eV. And the calculated IE of 2-propanol is 10.09 eV, which is in excellent agreement with the experimental value of (10.05 \pm 0.02) eV.

2.2 Dissociation channels of 1-propanol cation

Because of the lone pairs of electrons on the hydroxyl oxygen, saturated alcohols are readily ionized at low energies. After being formed, the molecule ion will undergo various dissociation reactions to form the fragments. Dissociations of 1-propanol cation are discussed below.

2.2.1 Formation of the $CH_3CH_2CHOH^+$, $CH_2CH_2OH^+$, $CH_3CH_2CH_2^+$, and CH_2OH^+ ions

1-propanol cation will undergo direct dissociation to form

the fragments $CH_3CH_2CHOH^+$, $CH_2CH_2OH^+$, $CH_3CH_2CH_2^+$, and CH_2OH^+ :



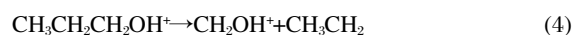
$$\begin{aligned} \Delta E_1 &= AE(CH_3CH_2CHOH^+) - IE(CH_3CH_2CH_2OH) \\ &= (0.36 \pm 0.03) \text{ eV} \end{aligned}$$



$$\begin{aligned} \Delta E_2 &= AE(CH_2CH_2OH^+) - IE(CH_3CH_2CH_2OH) \\ &= (0.13 \pm 0.03) \text{ eV} \end{aligned}$$



$$\begin{aligned} \Delta E_3 &= AE(CH_3CH_2CH_2^+) - IE(CH_3CH_2CH_2OH) \\ &= (1.48 \pm 0.03) \text{ eV} \end{aligned}$$



$$\begin{aligned} \Delta E_4 &= AE(CH_2OH^+) - IE(CH_3CH_2CH_2OH) \\ &= (0.96 \pm 0.03) \text{ eV} \end{aligned}$$

In the above mathematical expressions, we used our experimental IE and AEs. ΔE_i is the dissociation energies of the corresponding reactions. The dissociation energies, along with those calculated by the G3 method (using the results given in Table 2), are tabulated in Table 3 for easy comparison.

Because of the influence of the adjacent hydroxyl group, the $\alpha C-\beta C$ single bond is prone to dissociate. And the product

Table 2 The G3 energies E_0 (in hartrees) along with the corresponding symmetry points and electronic states of various species involved in the dissociation of 1-propanol and 2-propanol

m/e	Formula	Symmetry and electronic state	E_0
60	$CH_3CH_2CH_2OH$	$C_1(^1A)$	-194.175467
60	$CH_3CH_2CH_2OH^+$	$C_1(^2A)$	-193.807409
60	$CH_3CH(OH)CH_3$	$C_1(^1A)$	-194.182466
60	$CH_3CH(OH)CH_3^+$	$C_1(^2A)$	-193.811594
59	$CH_3CH_2CHOH^+$	$C_1(^1A)$	-193.280586
59	$CH_3C(OH)CH_3^+$	$C_1(^1A)$	-193.305238
45	$CH_2CH_2OH^+$	$C_1(^1A)$	-154.006549
45	CH_3CHOH^+	$C_1(^1A)$	-154.006546
44	CH_3CHO^+	$C_1(^2A)$	-153.337328
44	$CH_2=CHOH^+$	$C_3(^2A'')$	-153.358633
43	$CH_3CH_2CH_2^+$	$C_3(^1A')$	-118.050934
43	$CH_3CHCH_3^+$	$C_3(^1A')$	-118.063477
42	$CH_3CH=CH_2^+$	$C_3(^2A'')$	-117.420593
31	CH_2OH^+	$C_1(^1A)$	-114.700257
29	CH_3CH_2	$C_3(^2A')$	-79.063992
18	H_2O	$C_{2v}(^1A_1)$	-76.382044
17	OH	$C_{\infty v}$	-75.694904
16	CH_4	$T_d(^1A_1)$	-40.457626
15	CH_3	$C_{3v}(^2A_1)$	-39.793293
1	H	$O_h(^2A_{1g})$	-0.501003

Table 3 Experimental and calculated (G3) dissociations energies (eV) of the 1-propanol and 2-propanol cations

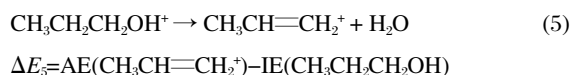
	Dissociation reactions	$\Delta E(\text{exp.})$	$E_b(\text{calc.})$
1-propanol	(1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CHOH}^+ + \text{H}$	0.36±0.03	0.70
	(2) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+ \rightarrow \text{CH}_2\text{CH}_2\text{OH}^+ + \text{CH}_3$	0.13±0.03	0.21
	(3) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^+ + \text{OH}$	1.48±0.03	1.68
	(4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+ \rightarrow \text{CH}_2\text{OH}^+ + \text{CH}_2\text{CH}_3$	0.96±0.03	1.17
	(5) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+ \rightarrow \text{CH}_3\text{CH}=\text{CH}_2^+ + \text{H}_2\text{O}$	0.25±0.03	0.13
2-propanol	(6) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3^+ \rightarrow \text{CH}_3\text{C}(\text{OH})\text{CH}_3^+ + \text{H}$	0.42±0.03	0.14
	(7) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3^+ \rightarrow \text{CH}_3\text{CH}(\text{OH})^+ + \text{CH}_3$	0.21±0.02	0.32
	(8) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3^+ \rightarrow \text{CH}_3\text{CHCH}_3^+ + \text{OH}$	1.39±0.03	1.45
	(9) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3^+ \rightarrow \text{CH}_3\text{CH}=\text{CH}_2^+ + \text{H}_2\text{O}$	0.21±0.02	0.24
	(10) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3^+ \rightarrow \text{CH}_2=\text{CHOH}^+ + \text{CH}_3$	0.11±0.02	-0.13

oxonium is rather stable. As to 1-propanol, its cation can form two different oxoniums. Reaction (1) leads to the formation of protonated propaldehyde ($\text{CH}_3\text{CH}_2\text{CHOH}^+$) by αH elimination, while reaction (4) leads to protonated formaldehyde (CH_2OH^+) by breaking the $\alpha\text{C}-\beta\text{C}$ bond. The calculated dissociation energies are 0.70 and 1.17 eV for channel (1) and (4), respectively. They are a bit higher than the experimental value.

Fragment $\text{CH}_2\text{CH}_2\text{OH}^+$ and $\text{CH}_3\text{CH}_2\text{CH}_2^+$ are also direct dissociation products of the molecule ion. The experimental dissociation energy for the formation of the $\text{CH}_3\text{CH}_2\text{CH}_2^+$ ion is (1.48±0.03) eV, a little lower than the calculated value (1.68 eV). And the experimental dissociation energy of reaction (2) is (0.13±0.03) eV, in good agreement with the calculated 0.21 eV. Refaey *et al.*^[9] reported the AE of the fragment at $m/e=45$ to be (11.1±0.1) eV, which is much higher than that of this work, and they attributed this onset “either to the formation of the less stable ion $\text{CH}_2\text{CH}_2\text{OH}^+$ or to the formation of the more stable ion CH_3CHOH^+ by a rearrangement process which requires excess activation energy”. Other researchers^[5,8] also reported a value near that of Refaey *et al.*^[9]. In fact, we have also obtained a similar AE value of (11.29±0.03) eV. This indicates that there exists an extra path way to the fragment $\text{CH}_2\text{CH}_2\text{OH}^+$. Here we conclude that the AE of (10.28±0.03) eV corresponds to the formation of the less stable ion $\text{C}_2\text{H}_5\text{O}^+$. As to the higher AE, it might correspond to the formation of the more stable ion CH_3CHOH^+ or protonated ethylene oxide.

2.2.2 Formation of the $\text{CH}_3\text{CH}=\text{CH}_2^+$ ion

Cation $\text{CH}_3\text{CH}=\text{CH}_2^+$ may be generated through the following reaction:



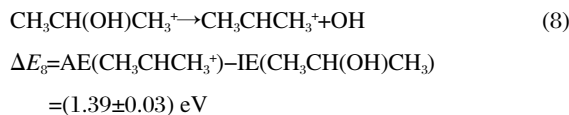
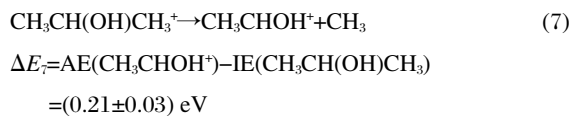
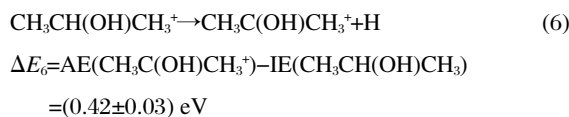
$$= (0.25 \pm 0.03) \text{ eV}$$

We determined the AE of this fragment to be (10.40±0.03) eV, which is in good agreement with the previous value of 10.50 eV^[10] and 10.56 eV^[8]. But the dissociation energy (0.25±0.03 eV) of channel (5) seems somewhat higher than the calculated 0.13 eV. Considering the byproduct of this reaction (H_2O) being a molecule, we are of the opinion that there are transition states in the process. But even so, the maximum energy of the transition states should not be 0.32 eV higher than the products. We have not performed transition states calculation, thus the theoretical dissociation energies listed in Table 3 do not include the reaction barriers.

2.3 Dissociation channels of 2-propanol cation

2.3.1 Formation of the $\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+$, CH_3CHOH^+ , and $\text{CH}_3\text{CHCH}_3^+$ ions

The formation of fragments $\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+$, CH_3CHOH^+ , and $\text{CH}_3\text{CHCH}_3^+$ are shown below:

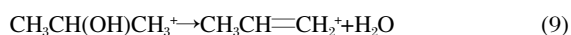


Same as those from 1-propanol cation, they are direct bond cleavage products of 2-propanol cation. We can compare the AEs of the fragments with their counterparts from 1-propanol. The experimental values of AEs of the fragments of (M-1)⁺, (M-15)⁺, and (M-17)⁺ are 10.51, 10.28, and 11.63 eV from 1-propanol and 10.47, 10.26, and 11.44 eV from 2-propanol, respectively. We find that the two sets of AEs are close for each fragment. This is not surprise, since each pair is the results of the same kind of bond cleavage in nature.

The calculated dissociation energy for reaction (6) is 0.14 eV, a little lower than the experimental one, (0.42±0.03) eV. However, the calculated results and experimental ones of the other two fragments are in good agreement, with 0.32 eV and (0.21±0.03) eV for fragment CH_3CHOH^+ and 1.45 eV and (1.39±0.03) eV for fragment $\text{CH}_3\text{CHCH}_3^+$, respectively.

2.3.2 Formation of the $\text{CH}_3\text{CH}=\text{CH}_2^+$ and $\text{CH}_2=\text{CHOH}^+$ ions

Fragment $\text{CH}_3\text{CH}=\text{CH}_2^+$ and $\text{CH}_2=\text{CHOH}^+$ can be generated through the following reactions:



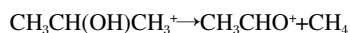
$$\begin{aligned} \Delta E_9 &= \text{AE}(\text{CH}_3\text{CH}=\text{CH}_2^+) - \text{IE}(\text{CH}_3\text{CH}(\text{OH})\text{CH}_3) \\ &= (0.21 \pm 0.03) \text{ eV} \end{aligned}$$



$$\begin{aligned} \Delta E_{10} &= \text{AE}(\text{CH}_2=\text{CHOH}^+) - \text{IE}(\text{CH}_3\text{CH}(\text{OH})\text{CH}_3) \\ &= (0.11 \pm 0.03) \text{ eV} \end{aligned}$$

The experimental dissociation energy of channel (9) is (0.21 ± 0.03) eV, which is in good agreement with the calculated value of 0.24 eV. Refaey *et al.*^[9] reported an “unreliable” AE of this fragment to be ~ 12.0 eV. They said so partly because of the AE of the same fragment from 1-propanol, which they measured to be (10.65 ± 0.03) eV. It is reliable that this same fragment should have an AE value from 2-propanol close to that from 1-propanol. Basing on the theoretical calculation, the calculated AE of fragment $\text{CH}_3\text{CH}=\text{CH}_2^+$ from 2-propanol is 10.34 eV, in good agreement with our experimental result, (10.26 ± 0.03) eV.

Channel(10) leads to the formation of the fragment of $\text{CH}_2=\text{CHOH}^+$. At first, we designated this fragment as the acetaldehyde cation(CH_3CHO^+), and supposed such a reaction



But the calculation result shows that the dissociation energy of this channel is 0.45 eV, much higher than the experimental one, (0.11 ± 0.03) eV. So this reaction cannot be a possible channel and acetaldehyde cation cannot be the corresponding species for mass 45. Then we tried another isomer, i.e. $\text{CH}_2=\text{CHOH}^+$, and considered the reaction again, *via* reaction (10). The calculated dissociation energy of this channel is -0.13 eV. This time the value is lower than the experimental one. It is understandable since enols have low IEs than its aldehyde tautomers. The low dissociation energy reminds us of the existence of transition states. But even so, the maximum energy of the transition states should not be 0.44 eV higher than the products.

3 Conclusion

We have measured the IEs of 1-propanol and 2-propanol as well as the AEs of the fragment ions $\text{CH}_3\text{CH}_2\text{CHOH}^+$, $\text{CH}_2\text{CH}_2\text{OH}^+$, $\text{CH}_3\text{CH}_2\text{CH}_2^+$, $\text{CH}_3\text{CH}=\text{CH}_2^+$, CH_2OH^+ from 1-propanol and $\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+$, CH_3CHOH^+ , $\text{CH}_2=\text{CHOH}^+$, $\text{CH}_3\text{CHCH}_3^+$, $\text{CH}_3\text{CH}=\text{CH}_2^+$ from 2-propanol in the dissociative photoionizations of the two propanols by the combined techniques of synchrotron radiation and molecular beam mass spectrometry. Both of the mass spectra show that at the wavelength of 105.0 nm, the predominant signals come from the oxoniums. With the aid of *ab initio* G3 results, we have established the dissociation

channels for the formation of these oxoniums as well as other fragments.

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