

Ultraviolet Photodissociation Dynamics of 1-Propanol and 2-Propanol by High- n Rydberg-Atom Time-of-flight(HRTOF) Technique^{*}

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Abstract 193.3 nm photodissociation dynamics of jet-cooled 1-propanol and 2-propanol has been examined by using high- n Rydberg-atom time-of-flight(HRTOF) technique. Isotope labeling study indicates that O – H bond fission is the primary H-atom production channel. Center-of-mass(CM) product translational energy release of this channel is large , with $f_T = 0.76$ for H + 1-propoxy and 0.78 for H + 2-propoxy. Maximum CM translational energy release yields an upper limit of the O – H bond dissociation energy : (432 ± 2) kJ/mol in 1-propanol and (433 ± 2) kJ/mol in 2-propanol. H-atom product angular distribution is anisotropic (with $\beta \approx -0.79$ for 1-propanol and -0.77 for 2-propanol) , indicating a short excited-state lifetime. The 193.3 nm H-atom dissociation of both 1-propanol and 2-propanol is prompt and occurs on a repulsive excited-state potential energy surface.

Key words Photodissociation dynamics , 1-propanol , 2-propanol

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1 Introduction

Ultraviolet(UV) photochemistry of small saturated alcohols via the first UV absorption bands($S_1 \leftarrow S_0$) has been studied before^[1-10]. These UV absorption bands are centered at 185 nm ; they are broad , featureless , and nearly identical. The transition is due to promotion of an electron from the non-bonding $2p\pi$ orbital on the oxygen atom to an excited orbital which has been described as either an antibonding σ^* (O – H) orbital , a $3s$ Rydberg orbital or a combination of both($n_o \rightarrow \sigma^*/3s$)^[11,12].

It is well known that $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}$ is the dominant fragmentation channel in the UV photodissociation of methanol via its first absorption band between 165200 nm^[1-3,5,6]. Translational energy release and angular distribution of this channel have

been measured by Doppler broadened fluorescence line shape of the nascent H-atoms^[5] and the HRTOF technique^[6], indicating that the first electronic excited state of CH_3OH (via $n_o \rightarrow \sigma^*/3s$) is repulsive in the O – H coordinate and dissociates rapidly. The conclusion is consistent with the theoretical studies of methanol photochemistry^[8-10].

Similarly , the O – H bond cleavage is the main dissociation channel in the UV photolysis of ethanol via its first absorption band^[1-3,6,7]. A large fraction of the available energy is channeled into translation of the H + ethoxy fragments , with $E_T = 0.84 E_{\text{avail}}$ at 193.3 nm photolysis^[7]. A perpendicular electronic transition with an anisotropic parameter ($\beta = -0.9$) has been observed at 193.3 nm , similar to that of methanol. The similar behaviors observed in the UV

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photolysis of small alcohols are consistent with their similar and localized electronic excitations, in which a lone-pair $p\pi$ electron on the oxygen atom is promoted to the antibonding $\sigma^*(O-H)$ orbital or 3s Rydberg orbital that undergoes rapid dissociation.

Compared to methanol and ethanol, photochemistry of propanol is little studied^[2-4]. H-atom elimination has been reported to be important in the photolysis of 1- and 2-propanol, which competes with other dissociation pathways involving C-C and C-O bond fission^[2-4]. However, the fragmentation mechanism is still unclear. In this work, the high- n Rydberg-atom time-of-flight (HRTOF) technique is applied to study the H-atom elimination channel in the UV photolysis of 1- and 2-propanol. Product center-of-mass (CM) translational energy and angular distributions are obtained, revealing the detailed photodissociation dynamics of the propanols.

2 Experiment

The HRTOF setup has been described previously^{7,13-16}. A pulsed molecular beam was produced by expanding a mixture of 2%5% propanol in He (at a total pressure of 120 kPa) into the source chamber, and was collimated by a 1 mm diameter skimmer at 2.5 cm downstream. Both 1- and 2-propanol samples were commercial products (Fisher, 99.7% purity) and were used without further purification. At 5 cm downstream the skimmer, a 193.3 nm photolysis radiation (typically 3 mJ from an ArF excimer laser, focused with a 70 cm $f.l.$ lens) crossed with the molecular beam. For angular distribution measurements, the 193.3 nm radiation was polarized with a ten-plate stack of UV fused silica slides placed at the Brewster's angle, with a degree of polarization of $\sim 90\%$. The H-atom photoproducts resulting from the 193.3 nm photolysis of propanols were first excited to the 2^2P state by the Lyman- α radiation at 121.6 nm, and were further excited to a high- n Rydberg state ($n = 4090$) by a UV radiation at 366 nm. The Lyman- α radiation was generated by tripling the 364.7 nm output of a dye laser in a Kr cell. The high- n Rydberg H-atom fragments are radiatively metastable and drifted with their nascent velocities toward a mi-

crosphere plate detector, and were detected after being field-ionized in front of the detector. The nominal flight length was 37.1 cm. The TOF spectra were recorded and averaged by using a multichannel scaler. The H-atom TOF spectra presented here represent the results of 50 thousands laser shots.

3 Results and discussion

The H-atom TOF spectra from photodissociation of 1- and 2-propanol at 193.3 nm are shown in Fig. 1 a and b, respectively. The arrival times in both spectra are in the range of 2030 μ s. The corresponding CM product translational energy distributions $P(E_T)$ s, which are converted from the H-atom TOF spectra^[16], are shown in Fig. 2 a and b. Preliminary results from isotope labeling studies indicate that O-H

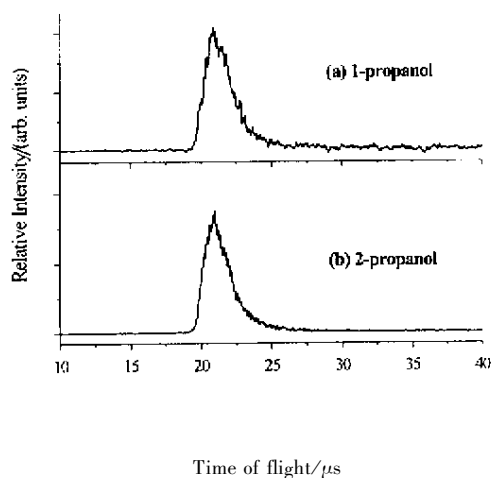


Fig. 1 H-atom TOF spectra from photodissociation of propanols at 193.3 nm (laser power was 3 mJ/pulse)

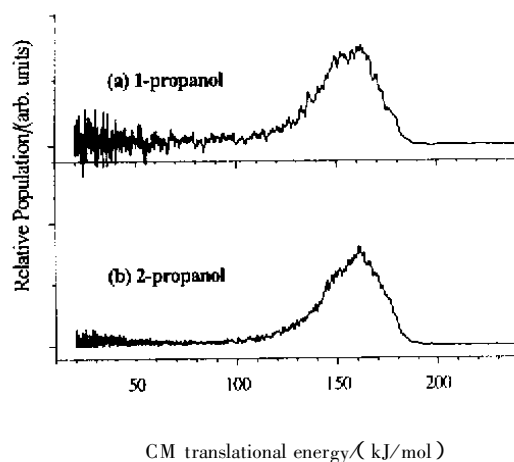


Fig. 2 CM product translational energy distributions $P(E_T)$ s derived from the TOF spectra in Fig. 1

bond fission is the primary H-atom production channel in propanols. The photolysis power dependence of the H-atom TOF spectra and the maximum translational energy release in the $P(E_T)$ s are consistent with one-photon photodissociation processes in both 1- and 2-propanol in this experiment.

The $P(E_T)$ s of both $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ and $\text{C}_2\text{H}_5\text{CH}_2\text{OH}$ photodissociation are quite large. The fraction of the total available energy into fragments' translation is $f_T = 0.76$ for 1-propanol and 0.78 for 2-propanol. These results are similar to that of 193.3 nm photolysis of methanol^[6] with $f_T = 0.82$ and ethanol^[7] with $f_T = 0.8$. Such a large product translational energy release suggests a rapid dissociation taking place on a repulsive potential energy surface (PES) before internal conversion. In addition, both propanols have nearly identical $P(E_T)$ s in the H-atom elimination processes, indicating very similar dissociation mechanisms.

From the measured maximum translational energy release and the principle of energy conservation, an upper limit of the bond dissociation energy, $D_0(\text{C}_2\text{H}_5\text{CH}_2\text{O}-\text{H})$ and $D_0((\text{CH}_3)_2\text{CHO}-\text{H})$, can be estimated^[16]. With a maximum translational energy release 187 kJ/mol for 1-propanol, a value $D_0(\text{C}_2\text{H}_5\text{CH}_2\text{O}-\text{H}) \leq (432 \pm 2)$ kJ/mol is derived. The uncertainty in determining the bond energy is 2 kJ/mol, including the photolysis laser linewidth and the uncertainty in identifying the maximum energy release. This result of $D_0(\text{C}_2\text{H}_5\text{CH}_2\text{O}-\text{H})$ is in good agreement with the 430 kJ/mol value by Ross *et al.*^[4]. Similarly, an O-H bond energy in 2-propanol is derived to be (433 ± 2) kJ/mol.

The H-atom product angular distributions in the 1- and 2-propanol dissociation have been investigated by using linearly polarized laser radiation. Fig. 3 shows the H-atom TOF spectra from photodissociation of 1-propanol by polarized 193.3 nm laser with its polarization direction parallel or perpendicular to the TOF axis. Linearly polarized light preferentially excites those sample molecules with their electronic transition dipole moment parallel to the electric vector \mathbf{E} of the polarized laser radiation. The photofragment

angular distribution is given by^[17]

$$I(\theta) = (1/4)\pi[1 + \beta P_2(\cos\theta)]$$

where β is the anisotropy parameter ($-1 \leq \beta \leq 1$), θ is the angle between the electric vector of the polarized laser radiation \mathbf{E} and the recoiling velocity vector of the H-atom product (the direction of detection), and $P_2(\cos\theta)$ is the second Legendre polynomial. From the measured H-atom TOF spectra with the polarized photolysis radiation, a significant anisotropy in the angular distribution is observed. After the correction for imperfect polarization of the photolysis light, a spatial anisotropy parameter $\beta \approx -0.79$ is obtained for 1-propanol and -0.77 for 2-propanol. This negative β value indicates that the transition dipole moment is perpendicular to the O-H bond from where the H-atom recoils, and that the propanol molecule dissociates in a time scale that is shorter than its rotational period. Thus it is concluded that the dissociation of O-H bond in the propanols at 193.3 nm is a prompt process, which likely occurs on a repulsive excited-state PES. The β values for the propanols are similar to the reported values for methanol ($\beta = -0.60$ or -0.70)^[6] and for ethanol ($\beta = -0.90$)^[7].

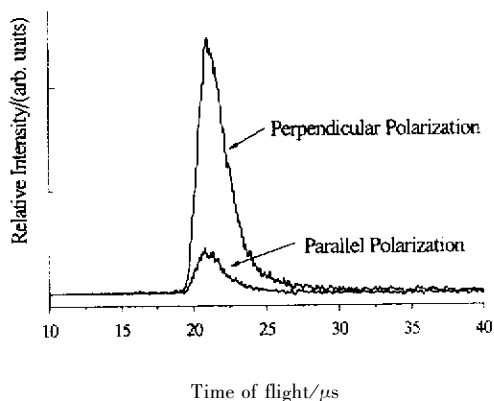


Fig. 3 H-atom TOF spectra of 193.3 nm photodissociation of 1-propanol, with the polarization \mathbf{E} vector of the photolysis radiation perpendicular and parallel to the TOF axis. The signals have been normalized to the same laser power and laser shots.

In the UV photolysis of methanol and ethanol, the O-H bond fission has been shown to be the main source of H-atom products and also the major dissociation channel^[6,7]. In the early photochemistry study of 2-propanol, the H-atom product channel has also

been identified as the predominant pathway^[3]. In addition, the dynamic information of the photodissociation of both propanols (such as $P(E_T)$ s and angular distributions) is essentially identical, and is also very similar to that of methanol and ethanol. This is consistent with the common nature of the first electronic excited states of these small saturated alcohols. The first absorption bands of methanol, ethanol and propanols have identical shape and location, and the corresponding electronic excitation via the $n_o \rightarrow \sigma^*/3s$ transition is largely localized on the H-O-C moiety and is essentially the same for these small alcohols. With the localized excitation in H-O-C and the repulsive nature of the first electronic excited state (along the O-H coordinate), the UV photodissociation of 1- and 2-propanol is similar to that of methanol and ethanol, and the H-atom dissociation channel in propanols is prompt and occurs on a repulsive excited-state PES.

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正丙醇和异丙醇的紫外光解动力学*

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摘要: 利用高里德堡态氢原子飞行时间(HRTOF)探测技术,研究了正丙醇和异丙醇的紫外光解动力学过程.在193.3 nm光辐射下,O-H键快速断裂过程构成主要的氢原子生成通道.伴随O-H键的碎裂,相当大的一部分能量转换成氢原子及其相应碎片的平动能(正丙醇 $f_v = 0.76$; 异丙醇 $f_v = 0.78$).氢原子碎片具有各向异性的角度分布,其角分布异向因子 β 分别为-0.79(正丙醇)和-0.77(异丙醇).研究结果表明,吸收1个193.3 nm光子后,丙醇分子跃迁到一个寿命很短的电子激发态,沿着O-H反应坐标,该激发态势能面是排斥的,因而O-H键快速断裂.此外,还得到了丙醇的O-H键离解能:(432±2)kJ/mol(正丙醇)和(433±2)kJ/mol(异丙醇).

关键词: 光解动力学;正丙醇;异丙醇

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