Kinetic Energy Release in the Unimolecular Dissociation of 1-Butanol Cation

Joong Chul Choe

Department of Chemistry, Dongguk University, Seoul 100-715, Korea. E-mail: jcchoe@dongguk.edu

Received November 10, 2006

Key Words : 1-Butanol cation, Kinetic energy release, Mass spectrometry

Unimolecular dissociations of ionized aliphatic alcohols have been investigated by several experimental and theoretical methods. It is interesting that loss of H dominates in the dissociations of methanol and ethanol cations while loss of H_2O dominates in 1-propanol and 1-butanol cation reactions.[1-5] Recently, the dissociation mechanisms of ethanol[6] and 1-propanol[5] cations have been proposed. The latter can isomerize to ${}^{\bullet}CH_2CH_2CH_2OH_2^+$ via a five-centered transition state, which is the rate-determining step in the H_2O loss channel.[5] The ${}^{\bullet}CH_2CH_2CH_2OH_2^+$ radical cation can undergo further isomerization reactions to form ion-dipole complexes such as c-$C_3H_6^{+\bullet}\cdots H_2O$ prior to the loss of H_2O. In our recent report,[7] we showed that the kinetic energy release (KER) in the unimolecular (metastable) dissociation of 1-propanol cation, occurring on a microsecond time scale, is determined in the final stage of the dissociation event. Namely, the rate and KER in the dissociation of 1-propanol cation are determined at different elementary steps. Compared to the 1-propanol cation reaction, on the other hand, the detailed mechanism for the loss of H_2O from the 1-butanol cation has not been proposed yet. Shao et al.[2] studied the dissociation using photoelectron photoion coincidence (PEPICO) spectroscopy and suggested that the 2-butene and methylcyclopropane cations are produced by the H_2O loss. McAdoo and Hudson[3] demonstrated that the H_2O loss occurs *via* several ion-dipole complexes. In the present work, the KER distribution (KERD) in the H_2O loss from the metastable 1-butanol cation has been investigated using mass-analyzed ion kinetic energy (MIKE) spectrometry.[8] We compare the experimental result with statistical phase space theory (PST) [9,10] calculations to obtain insight into the dissociation mechanism.

Experimental Section

A double-focusing mass spectrometer with reverse geometry (VG ZAB-E) was used. 1-Butanol was introduced to the ion source via a septum inlet to undergo 70 eV electron ionization. The ion source temperature was maintained at 150 and the generated ions were accelerated to 8 keV. MIKE spectrometry[8,11] was used to observe the unimolecular dissociation of the metastable 1-butanol cation. The molecular ion was mass selected by the magnetic sector and the translational kinetic energy of a product ion generated in the second field-free region (2nd FFR) of the instrument was analyzed by the electric sector. To improve the quality of a MIKE spectrum, signal averaging was carried out over repetitive scans. The best grade of 1-butanol (Aldrich) was used without further purification.

Results and Discussion

The H_2O loss was the only channel in the metastable dissociation of 1-butanol ion. The MIKE spectrum for the H_2O loss is shown in Figure 1a. The method to evaluate KERD from a MIKE profile is well established.[12] Figure 1b shows KERD obtained by analyzing the profile in Figure 1a.

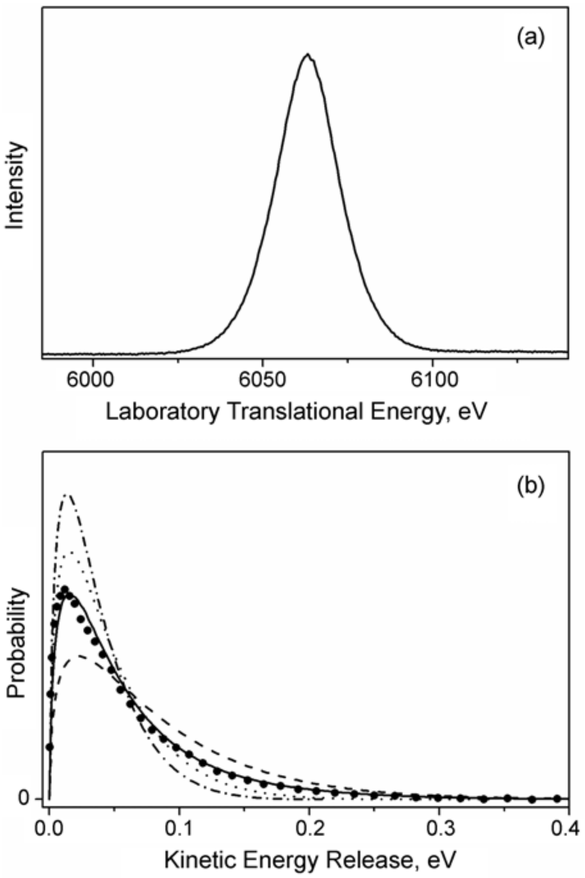
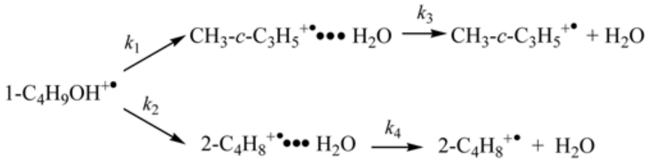


Figure 1. (a) The MIKE profile for the water loss from metastable 1-butanol cation generated by electron ionization. (b) KERDs for the water loss from metastable 1-butanol cation. The experimental result evaluated for the profile in (a) is shown as the closed circles. The PST calculation results for the productions of 1-butene, 2-butene, and methylcyclopropane cations are shown as dotted, dashed, and dash-dotted curves, respectively. The synthesized theoretical KERDs (see text for details) are almost the same as the solid curve

In the PEPICO study by Shao et al.,[2] the TOF spectrum for the H_2O loss was interpreted by invoking the two-component decay scheme of the precursor signal. Namely, two exponential decay functions were needed for analyzing the time decay data. The fast rate constant was too fast to be measured with the instrument (*i.e.*, $> 5 \times 10^6\ s^{-1}$), while the slow rate constant was reported to be varied from 0.33×10^6 to $0.70 \times 10^6\ s^{-1}$ depending on the ion internal energy. This suggests that there are at least two different dissociation channels. The primary isomerization steps are competitive whereas one of the followed steps is the slowest corresponding to the rate-determining step. They proposed the following mechanism.



The experimental result by Shao et al. could be well explained by assuming of $k_3 << k_1$ and $k_4 >> k_2$. They concluded that the fast and slow components are due to the productions of 2-butene and methylcyclopropane cations, respectively. Then, their branching ratio will be determined by k_2 and k_1. There are, however, two other possible products among $C_4H_8^{+\bullet}$ isomers: 1-butene and cyclobutane cations. The methylpropene cation can be ruled out because it is generally accepted that the methyl shift does not occur in the loss of H_2O from 1-butanol cation. The thermochemical data[13,14] of the related species are listed in Table 1. The *cis*-2-butene cation is 5 kJ mol^{-1} less stable than its trans-conformer and only the trans-conformer will be mentioned here. Since the onset for the H_2O loss was determined as 0.19 eV above the ionization energy of 1-butanol by the PEPICO experiment, the production of cyclobutane cation by loss of H_2O can be ruled out considering its endoergicity of 45 kJ mol^{-1} (0.47 eV). Since the 1-butene cation is more stable than the methylcyclopropane cation, its formation is possible by loss of H_2O. The relevant question is whether it is possible to identify which $C_4H_8^{+\bullet}$ isomers are produced by analyzing KERD in the metastable dissociation, as in the case of 1-propanol cation.[7]

Table 1. Enthalpies of formation (kJ mol^{-1}) of 1-butanol cation and its products

	$\Delta_fH^o_{298K}$ [a]	$\Delta_fH^o_{0K}$ [b]
1-butanol$^{+\bullet}$	696	717
1-$C_4H_8^{+\bullet}$	924	942 (−14)
Trans-2-$C_4H_8^{+\bullet}$	866	884 (−72)
CH_3-*c*-$C_3H_5^{+\bullet}$	938	954 (−2)
c-$C_4H_8^{+\bullet}$	985	1001 (45)
H_2O	−241.83	−238.92 [a]

[a]Ref.13. [b]Except for H_2O, the conversions from 298 to 0 K were calculated with the frequencies calculated at the B3LYP/6-31G(d) level of the density functional theory. The calculations were performed with the Gaussian 03 suite of programs (ref. 14). The values in the parentheses are the reaction enthalpies for the H_2O loss.

It is well known that KERD in a dissociation of polyatomic ions can be well predicted through statistical PST by assuming an orbiting transition state (OTS) when the reverse barrier is negligible. For theoretical evaluation of KERD in the H_2O loss the following formalism was used:[10,11]

$$n(T;J,E) \propto \int_{E_{R,m}}^{E-E_0-T} \rho(E-E_0-T-E_R)P(T,J,E_R)\mathrm{d}E_R\,, \tag{1}$$

where $n(T;J,E)$ is the distribution of KER (T) at the angular momentum J and the internal energy E, ρ and P are the product vibrational and angular momentum state densities, respectively, E_R is the product rotational energy, $E_{R,m}$ is its minimum, and E_0 is the reaction critical energy. The root-mean-square average J (57) evaluated at the ion source temperature (150 °C) was used. It is assumed that OTS is located at the maximum of the effective potential determined by each orbital angular momentum and the Langevin potential.[10] The calculation method had previously been described in detail.[11]

One of the parameters needed in the PST calculation is the internal energy of the 1-butanol cation undergoing the metastable dissociation. Since the dissociation rate constant was faster than $5 \times 10^6\ s^{-1}$ at the appearance energy of $C_4H_8^{+\bullet}$ in the PEPICO experiment, we assume that the onset energy (0.19 eV) is the internal energy undergoing the metastable dissociation. Then, the available energies for the production of 1- and 2-butene, and methylcyclopropane cations by loss of H_2O are 0.34, 0.94, and 0.21 eV, respectively. The PST calculations were carried out using the molecular parameters[15-17] listed in Table 2. As in the case of 1-propanol cation,[7] it is assumed that KER is determined at

Table 2. Molecular parameters used in the PST KERD calculations

	Vibrational frequency (cm^{-1})		
1-$C_4H_8^{+\bullet}$ [a]	80, 194, 249, 295, 420, 624, 783, 834, 904, 969, 995, 1013, 1065, 1190, 1228, 1288, 1304, 1376, 1424, 1447, 1457, 1505, 2651, 2951, 2978, 3024, 3049, 3053, 3056, 3153		
Trans-2-$C_4H_8^{+\bullet}$ [a]	123, 124, 152, 273, 471, 739, 745, 823, 873, 934, 1006, 1109, 1171, 1254, 1276, 1308, 1309, 1372, 1378, 1421, 1452, 1551, 2860, 2868, 2881, 2884, 3048, 3048, 3059, 3068		
CH_3-*c*-$C_3H_5^{+\bullet}$ [a]	172, 231, 359, 402, 586, 696, 748, 841, 924, 934, 943, 994, 1117, 1146, 1166, 1198, 1329, 1353, 1393, 1426, 1447, 1467, 2851, 2970, 2993, 3025, 3032, 3074, 3084, 3154		
H_2O [b]	1595, 3652, 3756		
	Rotational frequency (cm^{-1})		
1-$C_4H_8^{+\bullet}$ [a]	0.931	0.130	0.123
Trans-2-$C_4H_8^{+\bullet}$ [a]	1.13	0.124	0.116
CH_3-*c*-$C_3H_5^{+\bullet}$ [a]	0.523	0.191	0.172
H_2O [b]	27.8	14.5	9.28
	Polarizability (10^{-24} cm^3)		
H_2O [c]	1.45		

[a]Calculated at the B3LYP/6-31G(d) level of the density functional theory. Vibrational frequencies were scaled by 0.9614. (ref. 15). [b]Ref. 16. [c]Ref. 17.

the final dissociation step, which is probably the H_2O departure from an ion-dipole complex, $C_4H_8^{+\bullet}\cdots H_2O$. The resultant KERDs are compared with the experimental equivalent in Figure 1b. No theoretical distribution can fit the experimental one, indicating that the observed KERD is due to more than one dissociation channels. Without considering the production of 2-butene cation, the large KER portion (>0.2 eV) of the experimental KERD cannot be fitted, which strongly suggests that the 2-butene cation is one of the product ions in the metastable dissociation. One or both of the 1-butene and methylcyclopropane cations can be the other candidate(s) contributing to the metastable dissociation. To fit the experimental KERD, we synthesized the theoretical KERD by the following formula:

$$n(T) = \Sigma f_i n_i(T) \qquad (2)$$

where $n_i(T)$ is KERD for the production of 1-butene, 2-butene-, or methylcyclopropane cations, and f_i is its fraction. The best-fit synthesized KERDs are almost the same as the solid curve shown in Figure 1b. Ignoring the production of methylcyclopropane cation, the best ratio of the production of 1- and 2-butene cations is 3.0 : 2.0. Ignoring the production of 1-butene cation, the best ratio of the production of methylcyclopropane and 2-butene cations is 2.0 : 3.0. Considering all three products, the best ratio of the productions of 1-butene, methylcyclopropane, and 2-butene cations is 1.0 : 1.0 : 2.0. Since the production of 2-butene cation is energetically most favorable, it occurs much faster than that of the others, which agrees with the conclusion of the aforementioned PEPICO study. The 1-butene cation, however, as well as the methylcyclopropane cation, may be the product corresponding to the slow dissociation observed by the PEPICO experiment. However, the KERD analysis presented here cannot resolve the identity of the second product ion. Determination of the theoretical potential energy surface for the H_2O loss will be helpful to identify the dissociation products detected in the present study and the previous experiments. Such determination is currently being investigated in this laboratory. It is to be noted that the present estimation of the branching ratios is based on the assumption that the KERDs are well described by PST. In addition, the internal energy undergoing the metastable dissociation was estimated from the PEPICO and literature thermochemical data. Therefore, the branching ratios obtained here can be erroneous quantitatively.

In conclusion, the present results show that the loss of H_2O from metastable 1-butanol cation is due to the production of 2-butene cation and one or both of 1-butene and methylcyclopropane cations. Despite the rate constant of the production of 2-butene cation being larger than 5×10^6 s^{-1} near the threshold, it is noteworthy that some of the reactions can occur in the 2nd FFR where the metastable dissociation is detected at tens of microseconds after the generation of the molecular ions. Such reactions can be detected only when the fraction of the slow dissociation channel (the production of 1-butene and/or methylcyclopropane cations) is very small in the primary competitive isomerization steps. To ensure good agreement of theoretical and experimental KERDs, we suggest that the final exit channels, probably simple H_2O departures from ion-dipole complexes, occur statistically without considerable reverse barriers.

References

1. Refaey, K. M. A.; Chupka, W. A. *J. Chem. Phys.* **1968**, *48*, 5205.
2. Shao, J. D.; Baer, T.; Lewis, D. K. *J. Phys. Chem*. **1988**, *92*, 5123.
3. McAdoo, D.; Hudson, C. E. *Org. Mass Spectrom*. **1987**, *22*, 615.
4. Bowen, R. D.; Mandeville, S. J.; Trikoupis, M. A.; Terlouw, J. K. *Chem. Commun.* **1999**, 2111.
5. Choe, J. C. *Int. J. Mass Spectrom.* **2005**, *245*, 53.
6. Lu, H.-F.; Li, F.-Y.; Nagaya, K.; Hayashi, M.; Mishima, K.; Lin, S. H. *J. Mol. Struct.: THEOCHEM*. **2006**, *791*, 159.
7. Choe, J. C. *Bull. Korean Chem. Soc.* **2006**, *27*, 596.
8. Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.
9. Light, J. C. *J. Chem. Phys.* **1964**, *40*, 3221.
10. Chesnavich, W. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 8301; *J. Chem. Phys.* **1977**, *66*, 2306.
11. Choe, J. C.; Kim, B. J.; Kim, M. S. *Bull. Korean Chem. Soc.* **1989**, *10*, 167.
12. Yeh, I. C.; Kim, M. S. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 115; 293.
13. Lias, S. G.; Bartmass, J. E.; Liebman, J. F.; Holmes, J. L.; Levine, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **17** (1988) Suppl. 1.
14. Frisch, M. J. et al. *Gaussian 03* (Revision B.04); Gaussian, Inc.: Pittsburgh, PA, 2003.
15. Scott, A. P.; Radom, L. *J. Phys. Chem*. **1996**, *100*, 16502.
16. Herzberg, G. *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1945.
17. *Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC: Cleveland, 1995.