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LETTERS

Nonrandomization of Energy in Chemically Activated 2-Butanone Ions

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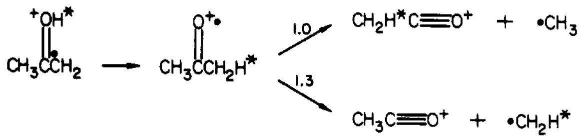
Both $CH_3CH_2C(={}^{+}OH)\dot{C}H_2$ and $CH_3\dot{C}HC(={}^{+}OH)CH_3$ isomerize to the 2-butanone ion and then lose methyl or ethyl in the mass spectrometer. More translational energy is released in the loss of methyl from $CH_3CH_2C(={}^{+}OH)\dot{C}H_2$ than from $CH_3\dot{C}HC(={}^{+}OH)CH_3$, while the energies released in the losses of ethyl are in the opposite order. The opposite order of the energies released is attributed to nonrandomization of energy in the 2-butanone ion formed from at least one of its enol isomers. The nonrandom energy distribution would have to be created in the first of the two steps in the rearrangement to the 2-butanone ion, and so may survive a second isomerization.

The assumption that energy becomes randomly distributed intramolecularly prior to chemical reactions has been widely applied.[1,2] In a recent review, Oref and Rabinovitch[1] concluded that reactive polyatomic molecules behave ergodically at times exceeding 10^{-12} s, and that mode-specific excitation has failed to reveal any substantiated exceptions at longer times. There may be a critical energy below which energy will not become randomized,[3,4] and computational evidence that energy can remain localized to a fraction of the total isoenergetic states of a molecule even at higher energies has been presented.[5] One experimental test for energy randomization is to determine whether the reactions of the same chemical species vary with the method of preparation in ways that cannot be attributed to differing amounts of energy in the reactant.[6,7]

Scheme I



Rabinovitch and co-workers have observed nonrandomization of energy in reactions of symmetric, chemically activated species only at times not greatly exceeding 10^{-12} s.[1,8,9] Isotopic labeling has demonstrated that the symmetric 2-propanone ion loses methyl from opposite sides at unequal rates[10,11] and with unequal translational energy

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(1) I. Oref and B. S. Rabinovitch, *Acc. Chem. Res.*, **12**, 166 (1979).

(2) S. H. Bauer, *Chem. Rev.*, **78**, 147 (1978).

(3) J. S. K. Nordholm and S. A. Rice, *J. Chem. Phys.*, **61**, 203 (1974).

(4) P. Brumer and J. W. Duff, *J. Chem. Phys.*, **65**, 3566 (1976).

(5) S. Nordholm and S. A. Rice, *J. Chem. Phys.*, **62**, 157 (1975).

(6) H. M. Frey, *Trans. Faraday Soc.*, **82**, 759 (1960).

(7) J. N. Butler and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **82**, 759 (1960).

(8) J. D. Rynbrandt and B. S. Rabinovitch, *J. Phys. Chem.* **75**, 2164 (1971).

(9) A. B. Trenwith and B. S. Rabinovitch, *J. Phys. Chem.*, **86**, 3347 (1982).

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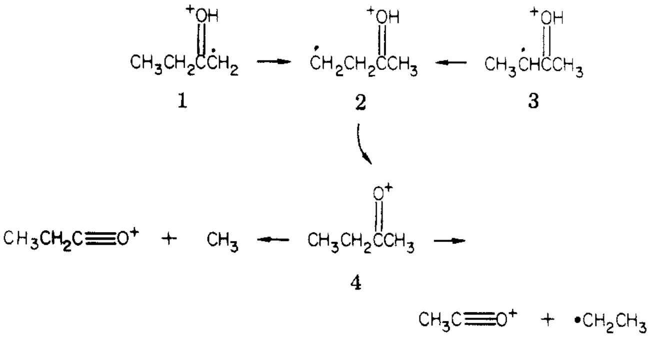
TABLE I: Translational Energy Releases and the Intensities for Metastable Decompositions of $C_4H_8O^{+\cdot}$ Ions[a]

ion	source	energy release, meV	
		$-CH_3$	$-C_2H_5$
$CH_3CH_2C(=\overset{+}{O}H)\dot{C}H_2$	3-heptanone	23.6 ± 0.2 (11)	23.2 ± 0.2 (10)
$CH_3CH_2C(=\overset{+}{O}H)\dot{C}H_2$	3-hexanone	22.5 ± 0.4 (4)	23.0 ± 0.9 (3)
$CH_3CH_2C(=\overset{+}{O}H)\dot{C}H_2$	3-undecanone	23.7 ± 0.5 (4)	22.6 ± 0.4 (3)
$CH_3CH_2C(=\overset{+}{O}H)\dot{C}H_2$	1-ethylcyclobutanol	23.8 ± 0.3 (3)	24.8 ± 0.3 (3)
$CH_3CH_2C(=\overset{+}{O}H)\dot{C}H_2$	1-ethylcyclopentanol	24.3 ± 1.0 (3)	24.1 ± 0.5 (3)
$CH_3\dot{C}HC(=\overset{+}{O}H)CH_3$	3-methyl-2-heptanone	17.7 ± 0.3 (11)	25.8 ± 0.6 (12)
$CH_3\dot{C}HC(=\overset{+}{O}H)CH_3$	3-methyl-2,4-pentanedione	19.8 ± 0.4 (2)	26.4 ± 0.4 (3)
$CH_3\dot{C}HC(=\overset{+}{O}H)CH_3$	1,3,5-trimethylcyclopentanol	18.1 ± 1.2 (4)	25.6 ± 1.0 (5)

[a] Error limits are standard deviations, the numbers in parentheses are the numbers of measurements. Averages of the values for each process for the ions from the different sources were as follows: $CH_3CH_2C(=\overset{+}{O}H)\dot{C}H_2$: $-CH_3$, 23.6 meV; $-C_2H_5$, 23.5 meV; $CH_3\dot{C}HC(=\overset{+}{O}H)CH_3$: $-CH_3$, 18.5 meV; $-C_2H_5$, 25.9 meV.

Scheme II



releases[12] when those ions are chemically activated on one side by transfer of a hydrogen atom from the oxygen to a carbon (Scheme I). These results have been interpreted[10-13] as evidence that energy is not randomized in the time between the formation and the decomposition of the keto structure. As with the reactions studied by Rabinovitch and co-workers,[8,9] the decompositions of Scheme I occur very rapidly (calculated 0.5 × 10^{-12} s)[12] following the formation of the chemically activated species. $C_5H_{10}O^{+\cdot}$ ions with the oxygen on the middle carbon decompose symmetrically and therefore apparently behave ergodically.[14,15] We here compare the translational energy releases accompanying the losses of methyl and ethyl from chemically activated 2-butanone ions obtained by isomerization from the two enol isomers (Scheme II).[16-18] Differences in energy releases observed are attributed to some energy remaining localized in the decompositions of 2-butanone ions chemically activated according to Scheme II.

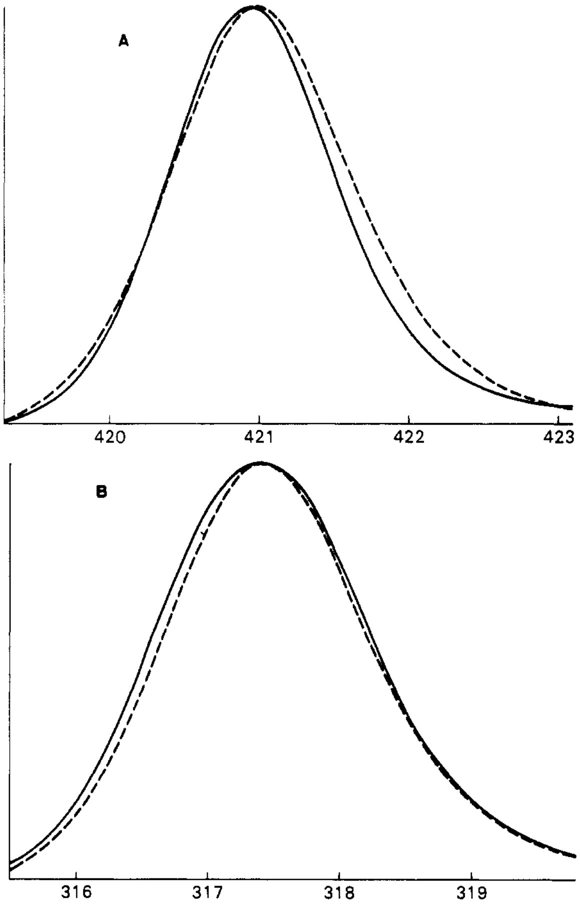


Figure 1. Metastable peaks representing losses of (A) methyl and (B) ethyl from $CH_3CH_2C(=^{+}OH)\dot{C}H_2$ from 3-heptanone, dashed lines, and $CH_3\dot{C}HC(=^{+}OH)CH_3$ from 3-methyl-2-heptanone, solid lines. Figures are traces of original data, which were signal averages of 5-25 scans. Abscissa scale is electric sector voltage.

Results

Table I gives the translational energies (T) associated with the metastable decompositions of both enol isomers of the 2-butanone ion, each ion being obtained from several precursors. Translational energy releases in the decompositions of $CH_3CH_2C(=^{+}OH)\dot{C}H_2$ were nearly equal, while those for losses of methyl from $CH_3\dot{C}HC(=^{+}OH)CH_3$ were an average of 7.4 meV lower than those for loss of ethyl from that ion. The translational energy released in the loss of methyl from $CH_3CH_2C(=^{+}OH)\dot{C}H_2$ exceeded that for the corresponding process from $CH_3\dot{C}HC$-

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(10) D. J. McAdoo, F. W. McLaffery, and J. S. Smith, *J. Am. Chem. Soc.*, **92**, 6343 (1970).

(11) F. W. McLafferty, D. J. McAdoo, J. S., Smith, and R. Kornfeld, *J. Am. Chem. Soc.*, **93**, 3720 (1971).

(12) C. Lifshitz and E. Tzidony, *Int. J. Mass Spectrom. Ion Phys.*, **39**, 181 (1981).

(13) D. J. McAdoo and D. Witiak, *J. Chem. Soc., Perkin Trans. 2*, 770 (1981).

(14) G. Depke and H. Schwartz, *Org. Mass Spectrom.*, **16**, 421 (1981).

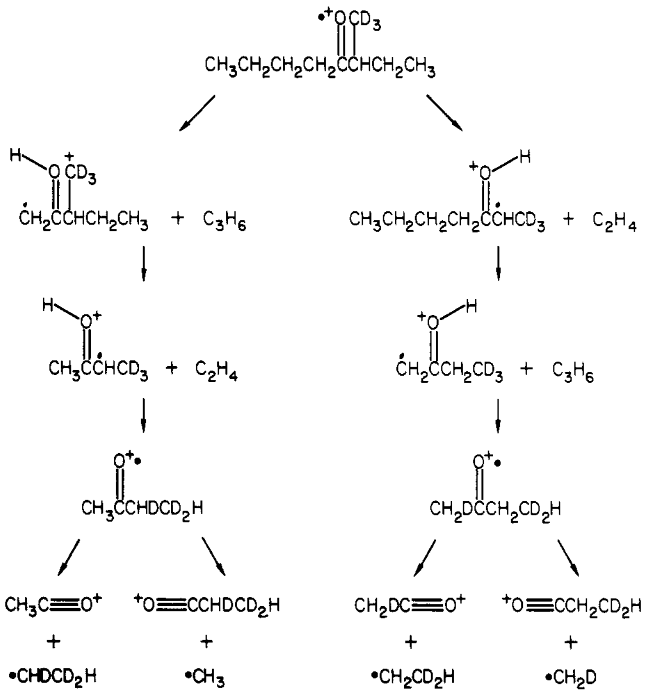
(15) D. J. McAdoo and C. E. Hudson, *Org. Mass Spectrom.*, in press.

(16) $CD_3CH_2C(=^{+}OH)\dot{C}H_2$ loses CH_2D in 97% of its methyl losses and $C_2H_3D_2$ in 98% of its ethyl losses. $CH_3CH_2C(=^{+}OD)\dot{C}H_2$ loses CH_3 in 99% of its methyl losses and C_2H_5D in 98% of its ethyl losses. Metastable $CH_3\dot{C}HC(=^{+}OD)CH_3$ loses C_2H_4D in more than 99% of its ethyl losses. D. J. McAdoo, F. W. McLafferty, and T. E. Parks, *J. Am. Chem. Soc.*, **94**, 1601 (1972). These results, together with the collisional activation spectra of the products of methyl loss,[18] demonstrate that ketonization fully precedes both ethyl losses. Scheme II provides the only possible rationalization of the dominant reactions.

(17) D. J. McAdoo, C. E. Hudson, and D. Witiak, *Org. Mass Spectrom.*, **14**, 350 (1979).

(18) D. J. McAdoo and C. E. Hudson, *Org. Mass Spectrom.*, submitted for publication.

Scheme III



(=$^+$OH)CH_3 by about 5 meV; differences for the associated ethyl losses averaged 2.4 meV in the opposite direction. Figure 1 compares actual peaks for the metastable decompositions of the two enol isomers of $C_4H_8O^{+\cdot}$.

$CH_3CH_2C(=^+OH)\dot{C}H_2$ would be formed from 3-heptanone with its hydroxyl hydrogen oriented away from the ethyl, while $CH_3\dot{C}HC(=^+OH)CH_3$ formed from 3-methyl-2-heptanone would have the opposite orientation. Therefore, decompositions of $C_4H_5D_3O^{+\cdot}$ generated from 5-methyl-d_3-4-octanone were examined to determine the effects of the orientation of the hydroxyl hydrogen on translational energy release (Scheme III). The results attributed to **1**-*4,4,4*-d_3 were as follows: $-C_2H_3D_2$, 26.5 meV; $-CH_2D$, 24.0 meV; and for **3**-*4,4,4*-d_3: $-C_2H_2D_3$, 27.1 meV; $-CH_3$, 19.3 meV. These patterns are similar to those for the corresponding unlabeled ions in Table I, indicating that the orientation of the hydroxyl hydrogen is not the cause of the differing patterns of energy release.

$T_{1/2}$ values in MeV for collision-induced dissociations were for $CH_3CH_2C(=^+OD)\dot{C}H_2$: $-CH_3$, 42 ± 1; $-C_2H_4D$, 40 ± 1; for $CH_3\dot{C}HC(=^+OD)CH_3$: $-CH_3$, 41 ± 2.0; $-C_2H_4D$, 60 ± 2. Deuterium labeled ions were used to eliminate the possibility of contributions from **1** → **4**, even though the direct reactions of **1** → **4** and **3** → **4** do not occur in metastable ions.[18] $T_{1/2}$ values for the CA decompositions of ionized 2-butanone were as follows: $-CH_3$, 13.8 ± 0.5; $-C_2H_5$, 37.2 ± 1.2.

About 7% $CH_2{=}CHCH{=}^+OH$ is formed in the methyl loss from $CH_3CH_2C(=^+OH)\dot{C}H_2$.[18] In order to determine the effect of this on $T_{1/2}$ for methyl loss, a synthetic peak was generated consisting of 20% of the peak for methyl loss from $CH_3\dot{C}HCH_2CH{=}^+OH$ (an ion in which $CH_2{=}CHCH{=}^+OH$ is formed in 35% of its methyl losses),[18] which has a $T_{1/2}$ of 27.0 meV and 80% of the peak for methyl loss from $CH_3\dot{C}HC(=^+OH)CH_3$ generated from 3-methyl-2-heptanone. This raised $T_{1/2}$ from 17.7 meV for $CH_3\dot{C}HC(=^+OH)CH_3$ to 18.7 meV. Therefore the different $T_{1/2}$ values for the methyl losses examined here cannot be due to the minor formation of $CH_2{=}CHCH{=}^+OH$.

All of the widths at 10% height of the metastable peaks were 1.8–1.9 times the widths at half-height, while the ratio for a Gaussian distribution is 1.8.

Discussion

The greater energy release accompanying the loss of methyl and the smaller energy release in the ethyl loss from $CH_3CH_2C(=^+OH)\dot{C}H_2$ relative to $CH_3\dot{C}HC(=^+OH)CH_3$ cannot be consistent with energy randomization in both ions if all of the values are for decompositions via 2-butanone ions in their ground electronic state. Formation of higher energy 2-butanone ions from $CH_3CH_2C(=^+OH)CH_2$ than from $CH_3\dot{C}HC(=^+OH)CH_3$ could cause the enhanced energy release in the loss of methyl from the former ion. However, this should also result in there being more energy on the ethyl side of the ion if energy were randomized, leading to enhanced energy release in the associated ethyl losses, contrary to what was observed. The similar energy releases in collision-induced dissociations of **1**-*O*-d_1 and 50% greater energy release in the loss of ethyl than methyl from **2**-*O*-d_1 demonstrates that parallel energy release patterns are present at higher ion internal energies than those involved in metastable decompositions. This provides evidence that the difference in the energy released in the unimolecular reactions is not simply a function of the amounts of energy in the ions. The much greater energy release in the loss of ethyl than methyl from the 2-butanone ion upon collision indicates that this may be the "normal" pattern for energetic 2-butanone ions.

The results are not strongly influenced by fragmentations in addition to those in Scheme II (see Results). Isolated electronic states are thought to seldom play a role in mass spectral fragmentations. If such a state were influencing our observations, it would have to survive at least one isomerization, which seems unlikely. The first excited state of the 2-butanone ion detected by photoelectron spectroscopy is at 857 ± 4 kJ mol^{-1}.[20] Lifshitz and coworkers place the highest energy transition state along the pathway between **1** and **4** at 816 ± 4 kJ mol^{-1},[19] while we have placed it at about 790 ± 13 kJ mol^{-1}.[18] Thus the first electronically excited state of the 2-butanone ion is probably too high for it to be influencing our observations.

It has been stated that observation of a given metastable transition with a variety of peak shapes would be strong evidence for nonrandomization of energy.[21] Since neither additional reactions nor a high activation energy associated with an isomerization prior to decomposition appear able to account for the opposite order of the energies released in the two decompositions of metastable $CH_3CH_2C(=^+OH)\dot{C}H_2$ and $CH_3\dot{C}HC(=^+OH)CH_3$, *we attribute those differences to nonrandomization of internal energy in at least one of those ions*, probably to retention of energy in the methyl formed by **1** → **3**. Lifshitz and coworkers[19] have recently concluded that a component of the translational energy release associated with the metastable loss of ethyl from **1** formed from 1-ethylcyclobutanol is larger than statistically predicted. Energy localization might be more likely in an asymmetric ion, where the components of the normal vibrational modes on opposite sides of the ion differ, than in a symmetric one, where such motions are identical.

If energy localization following **1** → **3** is the cause of the different patterns of energy release reported here, that localization would have to persist through **3** ⇄ **2** as well the ketonization reaction, since **3** and **2** appear to interconvert a number of times following **1** → **3**.[18] Lifshitz and

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[19] C. Lifshitz, P. Berger, and E. Tzidony, *Chem. Phys. Lett.*, **95**, 109 (1983).

[20] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

[21] G. Khodadai, R. Botter, and H. M. Rosenstock, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 397 (1969).

co-workers have calculated an RRKM rate coefficient of 4×10^9 s for the decomposition of the metastable 2-butanone ion formed by isomerization from 1.[19] Therefore, more than 10^{-10} s probably elapses between $1 \rightarrow 3$ and subsequent ketonization and decomposition. Thus energy appears to be localized for much longer than 10^{-12} s in at least one of the ions examined, and apparently through a rearrangement of the intermediate ion.

Experimental Section

All results are for decompositions that occurred between the magnet (second sector) and second electric sector of a Kratos MS-50 TA mass spectrometer.[22] Peaks were recorded by scanning the second electric sector voltage. Data were taken at 70-eV electron energy, 8000-V accelerating potential, a source temperature of 200 °C, and an electric sector resolution of 1/1600. Collision-induced dissociations were caused by introducing helium into a collision cell in the third field-free region until the precursor signal intensity was reduced by 50%. Translational energy releases were calculated according to standard methods.[23] Corrections for the width of the normal beam were made by the procedure of Baldwin et al.[24] The sources of most of the compounds are given elsewhere.[16-18] 3-Undecanone was prepared by the addition of octylmagnesium bromide to propanal followed by chromic acid oxidation. 3-Methyl-2,4-pentanedione was synthesized according to published procedures.[25] 1,2,5-Trimethylcyclopentanol was prepared by addition of methyl magnesium iodide to 2,5-dimethylcyclopentanone. 5-Methyl-d_3-4-octanone was prepared by the addition of CD_3MgI to 1-butanal, preparation of the bromide by addition of triphenyl phosphine/CBr_4, preparation of the Grignard, reaction with 1-butanal, followed by Jones oxidation of the resulting alcohol.

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