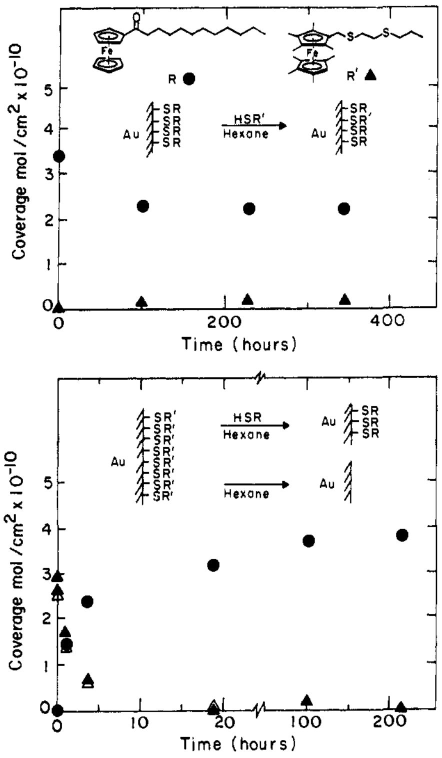

Figure 6. Time dependence of the surface coverage of I (●) and II (▲) for a Au macroelectrode initially derivatized with II and placed in a hexane/1 mM I solution (top) and for a Au macroelectrode initially derivatized with I and exposed to hexane/1 mM II (bottom). The bottom panel also includes data for an independent experiment showing coverage of I on Au upon exposure to hexane only (△). All coverages were measured by cyclic voltammetry in CH_3CN/0.1 M [n-Bu_4N]PF_6 at 500 mV/s.

soaked in hexane only, we find some initial loss of coverage, ~4.5 × 10^{-10} to ~3 × 10^{-10} mol/cm^2, but even after 1300 h, additional loss of redox active material does not occur. Similarly, if an electrode is first derivatized with II and then exposed to 1 mM I in hexane, there is some initial loss of II and a small uptake of I, but thereafter virtually no changes take place over a period of at least 400 h (Figure 6).

The experiments summarized by Figure 5 and 6 show the surfaces derivatized with I to be labile, with a rate of loss of I unaffected by the presence of II in hexane. That Au surfaces derivatized with I are most labile than those derivatized with II (or III) is certain.

Conclusion

Ferrocenyl thiols and disulfides can be used to modify selectively the Au microstructures on a Si_3N_4 surface. Simple immersion of a pretreated Au microelectrode array into a solution of I, II, or III yields Au electrodes functionalized with about one monolayer of the ferrocene reagent; no molecular material is detectable on the Si_3N_4. Auger element mapping can be used to obtain the high lateral resolution necessary to characterize microfabricated structures modified with a molecular monolayer. The octamethylferrocenyl system (I) shows a relatively negative $E_{1/2}$ value consistent with the electron-releasing nature of the CH_3 substituents. With respect to persistence of electrochemical response, all experiments show II or III to yield more durable modified Au surfaces than I. The large size of the "head group" of I and the short tether to the Au are likely factors limiting the durability of Au modified with I, in comparison to Au modified with II or III.

We can draw one mechanistic conclusion regarding the surfaces modified with I: the replacement of I by II appears to proceed by a mechanism involving loss of I followed by uptake of II, a process analogous to an S_N1 substitution mechanism for discrete coordination complexes. This conclusion is based on the observation that the rate of loss of I is unaffected by the presence of II. We caution against generalization of this simple mechanistic hypothesis, because the loss of II, for example, from the surface (Figure 6) appears to be quite different: some material is weakly bound, while the majority is firmly bound. Additional work is needed to establish factors governing rates, mechanisms, and thermodynamics for the coordination and exchange processes of thiols in solution and thiolates on Au surfaces.

Acknowledgment. M.S.W. thanks the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, for support of this research. G.M.W. thanks the Office of Naval Research and the Defense Advanced Projects Agency for partial support of this research. We acknowledge use of XPS and Auger facilities acquired through the joint Harvard/MIT University Research Initiative funded by the Defense Advanced Research Projects Agency.

Reactions of Ionized *n*-Propan-1-ol in the Gas Phase

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Abstract: The reactions of metastable ionized n-propan-1-ol have been reinvestigated by means of extensive ^2H-labeling experiments. The major fragmentation, by loss of water, proceeds by a specific and unidirectional 1,4-hydrogen migration from the methyl group to the oxygen atom. Collision-induced dissociation of the $M^{\bullet+}$ and $[M - H_2O]^{\bullet+}$ ions is consistent with the involvement of the distonic ion $^{\bullet}CH_2CH_2CH_2OH_2^+$ and, probably, the ion–neutral complex $\overline{CH_2CH_2CH_2}{}^{\bullet+}OH_2$ in water elimination. A very minor amount of hydrogen atom expulsion also occurs from metastable $CH_3CH_2CH_2OH^{\bullet+}$ radical cations; this process involves only the α-hydrogen atoms. Both water and hydrogen atom losses manifest extremely large deuterium isotope effects.

Introduction

Elimination of water is the characteristic reaction of ionized n-alkan-1-ols, especially at low internal energies. Metastable n-$C_3H_7OH^{\bullet+}$ and n-$C_4H_9OH^{\bullet+}$ both undergo water loss in high abundance.[1-7] Higher members of the n-$C_nH_{2n+1}OH$ series do not show appreciable $M^{\bullet+}$ signals in their electron ionization mass spectra, even at low ionizing electron energies and low temperatures (12.1 eV, 75 °C).[8] Instead, these spectra are dominated

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Table I. Unimolecular Reactions of Metastable $C_3H_{7-n}D_nOH^{\bullet+}$ Ions Generated from *n*-Propan-1-ols

	neutral species lost							
	H_2O		HOD		H$^\bullet$		D$^\bullet$	
precursor	RA^a	$T_{1/2}$^{b}	RA^a	$T_{1/2}$^{b}	RA^a	$T_{1/2}$^{b}	RA^a	$T_{1/2}$^{b}
$CH_3CH_2CH_2OH$ (**1**)	98.2	1.25			1.8	3.54		
CH_3CH_2CHDOH (**1**-*1*-$^2H_1$)	98.5	1.36	*c*		1.5	4.42	0.05	
$CH_3CH_2CD_2OH$ (**1**-*1,1*-$^2H_2$)	100	1.41	0		0		0	
$CH_3CD_2CH_2OH$ (**1**-*2,2*-$^2H_2$)	97.4	1.28	*c*		2.6	4.73	0	
$CD_3CH_2CH_2OH$ (**1**-*3,3,3*-$^2H_3$)	*c*		55.5	1.35	44.5	5.69	0	

[a] Relative abundance measured by metastable peak areas for ions decomposing in the second field free and normalized to a total metastable ion current of 100 units. [b] Kinetic energy release (kJ mol^{-1}) computed from the width at half-height of the corresponding metastable peak. [c] Small peaks (RA $\lesssim$1%) were present for these transitions, but these may be attributed to water loss from the ^{13}C satellite of $[M - H]^+$.

by $[M - H_2O]^{\bullet+}$ ions and secondary ions derived by decomposition of the $C_nH_{2n}^{\bullet+}$ species. Elimination of water from ionized *n*-hexan-1-ol has, however, been investigated by means of field-ionization kinetics,[9-11] which permits the study of short-lived ions of extremely low internal energies. ^2H-Labeling experiments showed that water loss from ionized *n*-hexan-1-ol proceeds by both 1,3- and 1,4-eliminations, with the former process occurring more rapidly.[11]

The behavior of ionized *n*-propan-1-ol has been analyzed by a variety of mass spectrometric and theoretical techniques. It has been shown that water expulsion proceeds by a 1,4-elimination and that the reaction gives ionized cyclopropane as the daughter ion.[12] More recently, ab initio calculations have implicated an ion–neutral complex (INC) of ionized cyclopropane attached to water.[13] Compelling evidence has been presented to show that similar INCs comprising ionized cyclopropanes coordinated to an alcohol molecule are involved in the rearrangement and fragmentation of ionized methyl and ethyl *n*-propyl ethers.[14] In view of these developments and the current interest in INCs,[7,13-21] a reinvestigation of the chemistry of ionized *n*-propan-1-ol with the use of more extensive ^2H-labeling experiments is desirable.

Results and Discussion

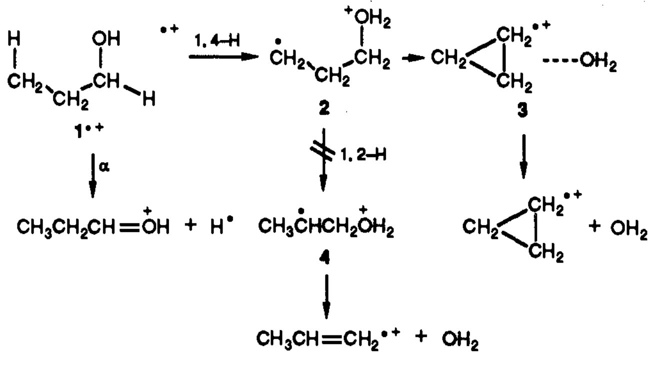
The unimolecular dissociations of metastable $CH_3CH_2CH_2OH^{\bullet+}$ [$(1)^{\bullet+}$] and several ^2H-labeled analogues are given in Table I. Relevant collision-induced dissociation (CID) spectral data for these radical cations are shown in Table II. The results for fragmentation by loss of a hydrogen atom or a water molecule are discussed separately; these processes have, however, several features in common.

Table II. Collision-Induced-Dissociation Spectral Data of Ionized *n*-Propan-1-ol

	precursor and relative intensity^a				
m/z	CH_3CH_2-CH_2OH	CH_3CH_2-$CHDOH$	CH_3CH_2-CD_2OH	CH_3CD_2-CH_2OH	CD_3CH_2-CH_2OH
63					M$^{\bullet+}$
62			M$^{\bullet+}$	M$^{\bullet+}$	348^b
61		M$^{\bullet+}$	1.0	184^b	1.9
60	M$^{\bullet+}$	248^b	32.8	1.0	1.3
59	170^b	26.9	0.9	1.3	1.1
58	1.6	1.9			
57	1.8				
45			1.2	1.2	16.2
44		1.9	264^b	209^b	77^b
43	2.4	329^b	5.9	11.0	6.9
42	168^b	9.6	3.4	2.9	2.3
41	7.1	1.9	2.1	1.8	3.0
40	1.1	2.9	3.0	2.9	2.6
39	5.2		1.5	1.5	1.1
38	1.3				
37	0.9				
33		1.0	100	1.9	3.5
32	1.3	100	6.6	8.9	18.1
31	100	5.8	3.9	100	100
30	2.9	3.9	6.5	9.1	8.2
29	16.1	11.5	11.0	14.0	16.3
28	5.5	7.7	7.2	8.6	7.1
27	12.9	9.6	9.4	4.8	4.9
26	4.6	2.9	3.8	1.6	1.6

[a] Intensities measured by peak heights and normalized to a value of 100 units for the most intense signal containing no unimolecular component; values below 1% were not usually included. [b] These peaks contain unimolecular contributions.

Scheme I



(A) Hydrogen Atom Elimination. This reaction usually accounts for only a very minor percentage (1–3) of the metastable ion current for decomposition of ionized *n*-propan-1-ols. It occurs with a very high regioselectivity: Only the hydrogen atoms on the α-carbon atom participate in this process. Moreover, hydrogen atom loss is characterized by an extremely large isotope effect. Thus, $CH_3CH_2CHDOH^{\bullet+}$ [(**1**-*1*-$^2H_1$)$^{\bullet+}$] expels a significant amount of H$^\bullet$, but the signal for D$^\bullet$ loss could not be distinguished from the background noise. A lower limit of ca. 30:1 can be derived for the isotope effect favoring H$^\bullet$ over D$^\bullet$ loss from (**1**-*1*-$^2H_1$)$^{\bullet+}$. In the case of metastable $CH_3CH_2CD_2OH^{\bullet+}$ [(**1**-*1,1*-$^2H_2$)$^{\bullet+}$], H$^\bullet$ and D$^\bullet$ eliminations are suppressed completely and only water loss is observed.

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In contrast, at higher internal energies (dissociations taking place in the ion source, or in CID), expulsion of D$^\bullet$ occurs from both (**1**-*1*-$^2H_1$)$^{\bullet+}$ and (**1**-*1,1*-$^2H_2$)$^{\bullet+}$, in the former case in competition with H$^\bullet$ loss. The CID data are especially informative: (**1**-*1,1*-$^2H_2$)$^{\bullet+}$, $CH_3CD_2CH_2OH^{\bullet+}$ [(**1**-*2,2*-$^2H_2$)$^{\bullet+}$], and $CD_3CH_2CH_2OH^{\bullet+}$ [(**1**-*3,3,3*-$^2H_3$)$^{\bullet+}$] eliminate H$^\bullet$, D$^\bullet$, and H$^\bullet$, respectively, with very high specificities ($\gtrsim$99%, $\gtrsim$97%, and $\gtrsim$99%, respectively). Although some of these CID fragmentations contain a unimolecular component, it is clear that hydrogen atom elimination involves almost exclusive α-cleavage with production of a protonated propionaldehyde as the daughter ion (Scheme I).

The enormous isotope effect that comes into operation for metastable ions possibly represents the result of rotational energy barriers and/or tunneling effects, which can intervene in hydrogen atom losses near the threshold for dissociation. Extremely large isotope effects have been reported in the decomposition of other small organic ions.[22-25] For example, metastable $CH_3D^{\bullet+}$, $CH_2D_2^{\bullet+}$, and $CHD_3^{\bullet+}$ all undergo essentially only H$^\bullet$ loss; $CD_4^{\bullet+}$ is unique in losing D$^\bullet$.[25] The behavior of metastable ionized methane has been explained by invoking rotational energy barriers and tunneling effects.[26-28]

(B) Water Elimination. (i) Regiochemistry of Water Elimination. The data of Table I confirm the earlier finding[12] that water loss from metastable ionized *n*-propan-1-ols proceeds via a specific 1,3-elimination. Thus, (**1**-*3,3,3*-$^2H_3$)$^{\bullet+}$ expels only HOD, whereas ionized *n*-propan-1-ols deuterated at C_1 or C_2 eliminate specifically H_2O.

Very minor amounts (ca. 1%) of HOD, HOD, and H_2O losses apparently occur from metastable (**1**-*1*-$^2H_1$)$^{\bullet+}$, (**1**-*2,2*-$^2H_2$)$^{\bullet+}$, and (**1**-*3,3,3*-$^2H_3$)$^{\bullet+}$, respectively. Some of these signals could be construed to arise by a very small subsidiary channel of 1,2-elimination of water from these ^{2}H-labeled forms of **1**$^{\bullet+}$. It is more likely, however, that these signals actually correspond to expulsion of HOD or H_2O from the ^{13}C-isotope peaks of the $[M - H]^+$ ions, which are present in the normal mass spectra of **1**-*1*-$^2H_1$, **1**-*2,2*-$^2H_2$, and **1**-*3,3,3*-$^2H_3$. Three types of experimental evidence support this explanation.

(a) The $M^{\bullet+}$ and $[M - H]^+$ peaks in the ordinary mass spectra of **1**, **1**-*1*-$^2H_1$, **1**-*2,2*-$^2H_2$, and **1**-*3,3,3*-$^2H_3$ are of comparable intensity. Consequently, the "$M^{\bullet+}$" peaks in these spectra contain approximately 3% of the isobaric ^{13}C-isotope peaks of the $[M - H]^+$ peaks. Futhermore, metastable oxonium ions $C_3H_{7-n}D_nO^+$ having the protonated propionaldehyde structure formed by H$^\bullet$ loss from ionized *n*-propan-1-ol are known[39] to expel water. The apparent HOD, HOD, and H_2O losses from metastable (**1**-*1*-$^2H_1$)$^{\bullet+}$, (**1**-*2,2*-$^2H_2$)$^{\bullet+}$, and (**1**-*3,3,3*-$^2H_3$)$^{\bullet+}$ may therefore be ascribed to fragmentation of the ^{13}C satellite signals of ions generated as $CH_3CH_2CD{=}OH^+$, $CH_3CD_2CH{=}OH^+$, and $CD_3CH_2CH{=}OH^+$, respectively, at least in part.

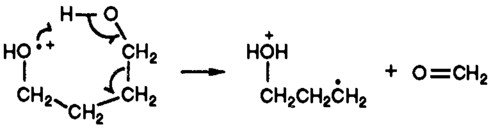
(b) The metastable peaks attributable to water loss from the ^{13}C satellites of $[M - H]^+$ are appreciably broader, corresponding to a greater kinetic energy release, than the much larger peaks arising by genuine water elimination from $M^{\bullet+}$. Moreover, the kinetic energy releases at half-height ($T_{1/2}$ values) associated with water losses from protonated propionaldehydes[29] are similar to those found in this work for reactions attributable to water losses from the ^{13}C-isotope peaks of $C_3H_6DO^+$, $C_3H_5D_2O^+$, and $C_3H_4D_3O^+$.

(c) No minor peak is found for HOD loss from (**1**-*1,1*-$^2H_2$)$^{\bullet+}$. This reflects the absence of a significant $[M - H]^+$ peak in the ordinary spectrum of **1**-*1,1*-$^2H_2$, which contains instead a sizable $[M - D]^+$ peak. As a result, the complications caused by the overlap between the $M^{\bullet+}$ and isobaric ^{13}C-isotope signal of $[M - H]^+$ are unimportant in the case of metastable (**1**-*1,1*-$^2H_2$)$^{\bullet+}$, thus explaining why this ion dissociates purely by 1,3-elimination of H_2O.

(ii) Rearrangement of Ionized *n*-Propan-1-ol Prior to Water Elimination. The specific behavior of metastable ionized ^{2}H-labeled *n*-propan-1-ols indicates that little or no exchange of the hydrogen atoms attached to the various carbon atoms in the original structure takes place before water is lost. Any hydrogen-transfer steps must, therefore, be specific and unidirectional. This view is consistent with photoelectron photoion coincidence (PEPICO) and laser photodissociation experiments, which show that the original ionized *n*-propan-1-ol structure is retained up to the dissociation limit.[13] The CID spectral data of Table II confirm this conclusion. Ethyl radical expulsion, which occurs from low-energy ionized *n*-propan-1-ols energized by collision, involves elimination of the original ethyl group. Similar remarks apply to water and hydrogen and/or deuterium atom losses in CID. Some of these processes contain a unimolecular component; nevertheless, it is clear that water expulsion proceeds mainly via a specific 1,3-elimination, while hydrogen (or deuterium) atom loss involves only those atoms attached to C_1. Thus, there is no evidence that ionized *n*-propan-1-ol species undergo significant hydrogen-exchange processes, prior to dissociation, over a range of internal energies.

One possible unifying mechanism for water loss from **1**$^{\bullet+}$ is depicted in Scheme I. A 1,4-H shift in **1**$^{\bullet+}$ affords the distonic ion $^\bullet CH_2CH_2CH_2OH_2^+$ (**2**). Reorganization of the $-CH_2CH_2CH_2-$ chain in **2** leads to the INC **3**, in which a water molecule is attached to ionized cyclopropane. Separation of the INC then leads to ionized cyclopropane and water. An alternative, but related, mechanism would entail ring closure of the $-CH_2CH_2CH_2-$ chain in **2**, with concomitant H_2O expulsion; according to this modified description, water loss takes place directly from **2**, with production of $\overline{CH_2CH_2CH_2}^{\bullet+}$, without involvement of **3**.

A wide range of experimental and theoretical data may be cited in favor of the mechanism of Scheme I. It is consistent with the ^{2}H-labeling results of Table I; moreover, it also accommodates the observation that metastable $CH_3CH_2CH_2OD^{\bullet+}$ [(**1**-*O*-$^2H_1$)$^{\bullet+}$] expels only HOD in water loss.[12] In addition, neutralization–reionization (NR) studies reveal that **1**$^{\bullet+}$ (generated by ionization of *n*-propan-1-ol) and **2** (formed by ionization and formaldehyde loss from 1,4-butanediol (eq 1)) each contain less than 5% of the other isomer.[30,31] This supports the hypothesis that rearrangement of **1**$^{\bullet+}$ to **2** is unidirectional and that dissociation of **2** is energetically preferable to isomerization to **1**$^{\bullet+}$. Similar, but less quantitative, conclusions stem from CID studies on **1**$^{\bullet+}$ and **2**.



(1)

(iii) Energetics of Water Elimination. The energetics of this system, which are relatively well-defined,[32-34] are also in accord with Scheme I. The enthalpies of formation of **1**$^{\bullet+}$ and each of the plausible combinations of products are known. Futhermore,

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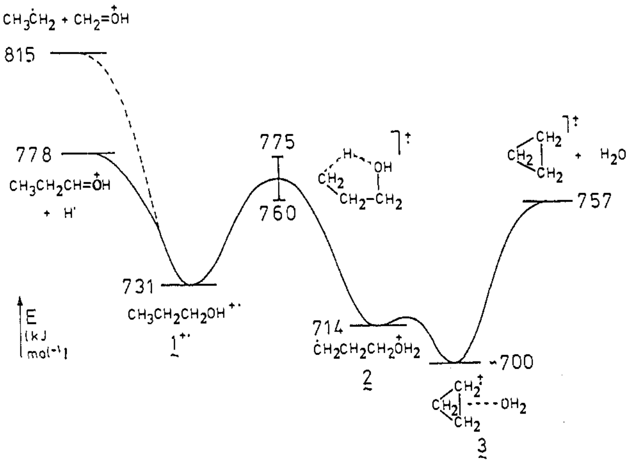


Figure 1. Potential energy profile for isomerization and dissociation of $CH_3CH_2CH_2OH^{\bullet+}$.

the enthalpy of formation of **2**, generated as shown in eq 1, has also been measured and found to lie below that of $1^{\bullet+}$. Finally, the appearance energy for water loss from $1^{\bullet+}$ has been determined as 10.65 eV,[2] 10.56 ± 0.05 eV,[12] and 10.67 eV,[13] respectively, with photoionization, energy-resolved electron ionization, and PEPICO techniques. By analogy with the stabilizations found in related systems,[35-38] the INC **3** ought to be stabilized by 30–70 kJ mol^{-1}, relative to the total energy of the separated components. Ab initio molecular orbital calculations give a value of 60–70 kJ mol^{-1},[13] depending on whether or not a correction is made to allow for the zero-point energy, for the stabilization energy of **3**. These energy data are conveniently summarized by the potential energy profile (PEP) shown in Figure 1. Several significant deductions may be made from Figure 1.

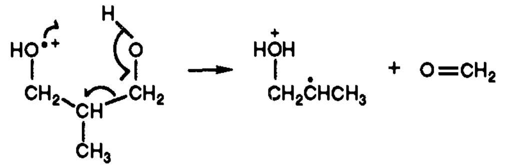
Firstly, the transition state for isomerization of $1^{\bullet+}$ to **2** is higher in energy (760–775 kJ mol^{-1}) than the total enthalpy of formation of the products of water loss. This is in agreement with the view that the 1,4-hydrogen shift leading from $1^{\bullet+}$ to **2** is unidirectional and that it is the rate-determining step in expulsion of water from $1^{\bullet+}$. Moreover, the earlier finding[12] that **2**, generated via eq 1, is metastable with respect to decomposition via water loss is consistent with Figure 1, since elimination of water from **2** requires less energy than rearrangement of **2** to $1^{\bullet+}$.

Secondly, the transition state for rearrangement of $1^{\bullet+}$ to **2** lies only slightly lower in energy than the total enthalpy of formation of the products of hydrogen atom elimination. This is in accord with the poor competition of H$^\bullet$ loss with H_2O expulsion from metastable $1^{\bullet+}$. The usual discrimination[39-42] against formation of higher energy species is evidently very pronounced in this system. Thus, elimination of an ethyl radical, which yields products ca. 35 kJ mol^{-1} higher in energy than those produced by hydrogen atom expulsion, does not occur in metastable transitions. Ethyl radical loss does, however, figure prominently in the CID of $1^{\bullet+}$.

Thirdly, **2** and probably **3** lie in substantial potential energy wells. Dissociation via water loss is energetically preferable to rearrangement to $1^{\bullet+}$. This explains the contrasting behavior of $1^{\bullet+}$ and **2** when subjected to investigation by CID or NR. There remains some uncertainty surrounding the relative energies of **2** and **3** and the size of the barrier toward their interconversion. It is possible to estimate the enthalpy of formation of **2** by means of known data for the proton affinity of **1** (790[43] kJ mol^{-1}) and the hydrogen radical abstraction energy (418[44] kJ mol^{-1}) for homolytic fission of the H–CH_2R bond. Combined with the value (−260[33,34] kJ mol^{-1}) for the enthalpy of formation of **1**, these data give values of 485 and 685 kJ mol^{-1}, respectively, for the enthalpies of formation of $CH_3CH_2CH_2OH_2^+$ and $^\bullet CH_2CH_2CH_2OH_2^+$. The value for the enthalpy of formation of **2**, obtained in this fashion, is somewhat lower than the experimental figure. This discrepancy may merely represent inaccuracies in the estimation procedure, which makes no allowance for interaction between the notional charge and radical sites in **2**. On the other hand, it is possible that the experimental value is slightly too high, perhaps owing either to an error in estimating the enthalpy of formation of 1,4-butanediol or to an additional critical energy associated with the formation of **2** by eq 1.

In any event, it is clear that **2** and **3** have comparable energies, lying well below that of the products of water loss. It seems intuitively improbable that there is a sizable barrier toward interconversion of **2** and **3**. Indeed, it is conceivable that at sufficiently high internal energies reorganization of **2** to **3** takes place smoothly as the C–O bond in **2** is progressively elongated en route to water loss. According to this modified mechanism, the distinction between **2** and **3** becomes blurred at energies appropriate to water loss from $1^{\bullet+}$ via **2** and **3**. It is, in fact, possible to explain most of the experimental data on this basis, or by assuming that water loss takes place directly from **2**, without participation of **3**, provided that a ring-closed form of $CH_2CH_2CH_2^{\bullet+}$ is formed.

Fourthly, the formation of ionized cyclopropane rather than the energetically more favorable isomer, ionized propene, indicates that **2** does not readily undergo a 1,2-hydrogen shift to yield **4**. It is known that **4** is a stable distonic ion, which may be generated by ionization and formaldehyde loss from 2-methyl-1,3-butanediol, eq 2.[12] Furthermore, **4** has been shown to expel mainly H_2O over a range of internal energies and to produce ionized propene as the daughter ion.[12]



(2)

Consequently, there must be an energy barrier of at least ca. 757 − 714 = 43 kJ mol^{-1} toward a 1,2-hydrogen shift in **2**. This is compatible with the behavior of other distonic ions containing a radical site on carbon. 1,2-Hydrogen shifts in such systems are much less facile than those in the corresponding carbocations.[45-47] A parallel argument shows that there must be a significant barrier toward isomerization of **3** to an INC containing ionized propene and water. This barrier is probably at least of comparable size to the stabilization energy of **3**.

Fifthly, the energy barrier toward the 1,4-hydrogen transfer in 1^+ lies in the range 29–44 kJ mol^{-1}. This reflects the slight strain involved in this five-membered-ring transition state. Similar barriers toward 1,4-hydrogen shifts from carbon to oxygen atoms have been reported in other ionic systems.[29,47,48]

(iv) Isotope Effects in Water Elimination. The variation of the ratio of the relative abundance of water loss to hydrogen atom

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Table III. Charge-Stripping Spectral Data of $C_3H_6^{\bullet+}$ Ions

	precursor and relative intensity[a]		
m/z	$[M - H_2O]^{\bullet+}$ in $CH_3CH_2CH_2OH^{\bullet+}$	$\overline{CH_2CH_2CH_2}^{\bullet+\,b}$	$\overline{CH_2CH_2CH_2}^{\bullet+\,c}$
21	1	1 ± 1	1
20.5	9	8 ± 2	7
20	36	34 ± 4	38
19.5	20	21 ± 5	19
19	34	36 ± 2	35
19/20.5	3.7	4.5 ± 1.1	5.0

[a] Values normalized to a total of 100 units. [b] Reference 49. [c] Reference 50.

elimination with deuteration of the methyl group of $1^{\bullet+}$ reveals that water loss is subject to a substantial isotope effect. Thus, whereas $1^{\bullet+}$ expels H_2O and $H^{\bullet}$ in the ratio 98.2:1.8, $(1\text{-}3,3,3\text{-}^2H_3)^{\bullet+}$ eliminates HOD and $H^{\bullet}$ in comparable quantities (55.5:44.5). This powerful discrimination against HOD loss from $(1\text{-}3,3,3\text{-}^2H_3)^{\bullet+}$ corresponds to an isotope effect of ca. 44:1 favoring hydrogen over deuterium atom transfer in the elimination of water from ionized *n*-propan-1-ols. The intervention of an isotope effect is consistent with the deduction that $1 \rightarrow 2$ is the rate-determining step in water elimination.

(v) CID Studies on the $[M - H_2O]^{\bullet+}$ Species. The normal CID spectra, in which singly charged daughter ions are considered, of $CH_3CH{=}CH_2^{\bullet+}$ and $\overline{CH_2CH_2CH_2}^{\bullet+}$ are practically indistinguishable. Fortunately, however, the charge-stripping (CS) spectra corresponding to production of doubly charged daughter ions contain diagnostic differences.[49,50] This distinction allowed the structure of the $C_3H_6^{\bullet+}$ ions formed by water expulsion from $1^{\bullet+}$ to be assigned as $\overline{CH_2CH_2CH_2}^{\bullet+}$.[12] The CS spectrum of $[M - H_2O]^{\bullet+}$ generated from $1^{\bullet+}$ in this work is in excellent agreement with the spectra previously reported for $\overline{CH_2CH_2CH_2}^{\bullet+}$ (Table III). This confirms that water loss from $1^{\bullet+}$ affords ionized cyclopropane.

Moreover, the CS spectra of $[M - H_2O]^{\bullet+}$ formed from $1\text{-}1,1\text{-}^2H_2$ and $1\text{-}2,2\text{-}^2H_2$ are almost identical (Figure 2). This phenomenon is naturally accommodated on the basis of rearrangement of both $(1\text{-}1,1\text{-}^2H_2)^{\bullet+}$ and $(1\text{-}2,2\text{-}^2H_2)^{\bullet+}$ to an INC comprising $\overline{CH_2CH_2CD_2}^{\bullet+}$ attached to H_2O. At the very least, the close similarity in the CS spectra establishes that a ring-closed form of $\overline{CH_2CH_2CD_2}^{\bullet+}$ must be involved[51] at some stage in the development of the product ion as water is lost.

(vi) Kinetic Energy Release Accompanying Water Elimination. The metastable peaks associated with water loss from the ionized *n*-propan-1-ols are of a simple Gaussian shape. The corresponding kinetic energy releases at half-height ($T_{1/2}$ values) are relatively small (1.25–1.41 kJ mol^{-1}). These values are typical of those that pertain when an INC is formed by irreversible rearrangement of a precursor structure. When the fragmenting INC is formed on a reversible basis from an isomeric precursor, much smaller $T_{1/2}$ values are found.[18,19] The magnitude of these $T_{1/2}$ values, therefore, offers some additional circumstantial evidence that water elimination from ionized *n*-propan-1-ols involves irreversible formation of an INC.

Conclusion

Dissociation of ionized *n*-propan-1-ol occurs with a very high regioselectivity. Expulsion of a hydrogen atom involves only the α-hydrogens, while water loss proceeds essentially exclusively via a 1,3-elimination. Both processes are governed by extremely large isotope effects. Loss of water is logically interpreted as occurring via a specific and unidirectional 1,4-hydrogen transfer, followed probably by reorganization of the resultant distonic ion to give an INC consisting of ionized cyclopropane and water. These results do not, however, exclude an interpretation of this reaction based on direct elimination of water from **2**, without postulating the intermediacy of **3**, provided it is assumed that a cyclic isomer of $C_3H_6^{\bullet+}$ is produced. Thus, the experimental evidence that $\overline{CH_2CH_2CH_2}^{\bullet+}OH_2$ is involved in water loss from ionized *n*-propan-1-ol is less compelling than that[14] implicating $\overline{CH_2CH_2CH_2}^{\bullet+}HOR$ ($R = CH_3, C_2H_5$) in the fragmentation of ionized *n*-propyl methyl and ethyl ethers.

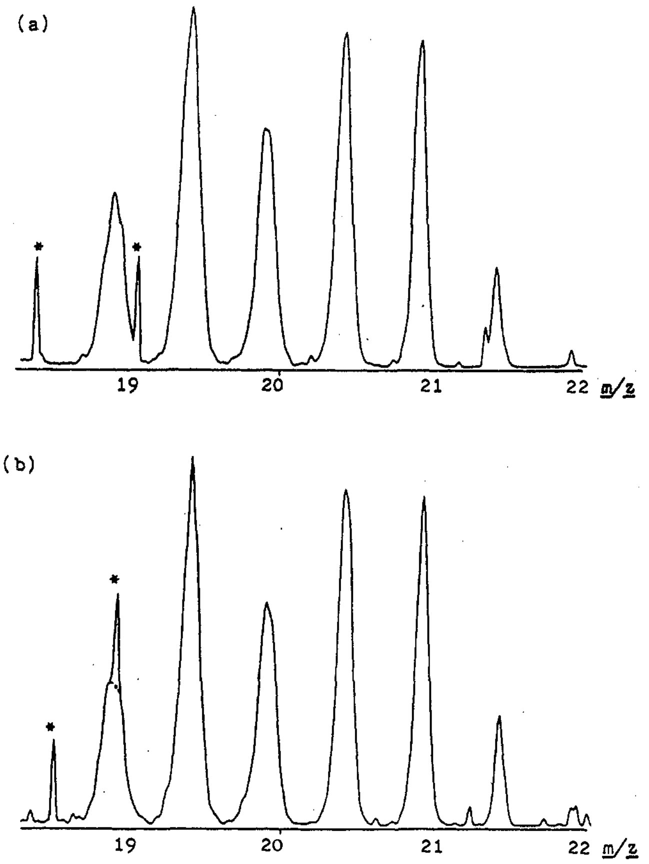

Figure 2. Charge-stripping spectra of $[M - H_2O]^{\bullet+}$ formed from (a) $CH_3CH_2CD_2OH$ and (b) $CH_3CD_2CH_2OH$. "Spike" peaks, arising from causes other than formation of doubly charged ions, are marked with asterisks.

Scheme II[a]

$$CH_3CH_2CH{=}O \xrightarrow{i,\ ii} CH_3CH_2CHDOH$$

$$(CH_3CH_2CO)_2O \xrightarrow{i,\ ii} CH_3CH_2CD_2OH$$

$$CH_3CH_2CH{=}O \xrightarrow{iii} CH_3CD_2CH{=}O \xrightarrow{iv,\ ii} CH_3CD_2CH_2OH$$

$$CD_3I \xrightarrow{v,\ vi} CD_3CH_2CH_2OH$$

[a] Reagents: (i) $LiAlD_4$, triglyme [triethylene glycol dimethyl ether, $CH_3(OCH_2CH_2)_3OCH_3$]; (ii) tetragol [tetraethylene glycol, $H(OCH_2CH_2)_4OH$]; (iii) D_2O/pyridine reflux overnight (repeat twice); (iv) $LiAlH_4$, triglyme; (v) Mg, $(C_4H_9)_2O$; (vi) $\overline{CH_2CH_2O}$ (0 °C).

Experimental Section

The ^2H-labeled propanols required in this work were synthesized according to the routes shown in Scheme II; further particulars of these procedures are available on request.

All mass spectra were recorded with a double-focusing research mass spectrometer (MMM) of unusually large dimensions.[52] The typical source pressure was 2×10^{-6} Torr, and the usual accelerating voltage was

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8065–8078 V. The relative abundances of the reactions corresponding to water and hydrogen atom losses were measured from the areas of the associated metastable peaks in the MIKES[40] spectra of the $M^{\bullet+}$ ions of the appropriate *n*-propan-1-ol. Kinetic energy release data were computed by means of a one-line formula,[41] from the width at half-height ($w_{1/2}$) of the relevant metastable peak; the usual correction (eq 3) was applied for the width at half-height ($W_{1/2}$) of the main beam.[53] The quoted results were obtained from data accummulated over 50–200 scans.

$$w_{1/2}(\mathrm{corr}) = (w_{1/2}{}^2 - W_{1/2}{}^2)^{1/2} \qquad (3)$$

The CID and CS measurements were made with the MIKES[40] technique, after helium had been admitted as the collision gas so as to give 60% attenuation of the original signal due to $M^{\bullet+}$. The CID spectra were accumulated over 5–15 scans, and the CS spectra were accumulated over 50–150 scans.

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Thermal Decomposition of Alkyl Halides on Aluminum. 1. Carbon–Halogen Bond Cleavage and Surface β-Hydride Elimination Reactions

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Abstract: The themal decomposition of alkyl iodides adsorbed on Al(100) and Al(111) surfaces has been studied by using temperature-programmed desorption, integrated desorption mass spectrometry, and high-resolution electron energy loss spectroscopy. We find that alkyl iodides with three or more carbons adsorb dissociatively on aluminum at temperatures $\gtrsim$130 K. The adsorbed alkyl ligands generated by C–I bond scission are stable on the surface up to ~450 K and are not significantly affected by the presence of the coadsorbed halogen atom. The dominant mechanism for thermal decomposition of the alkyl fragment is β-hydride elimination, and the kinetics of this surface reaction are similar to those for β-hydride elimination by aluminum alkyls in both the gas phase and solution.

1. Introduction

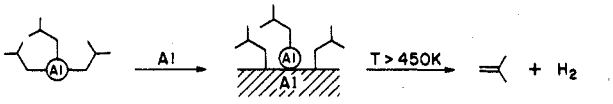
Recent studies have established that adsorbate bonding on metal surfaces is often analogous to the bonding of ligands in metal complexes.[1] An understanding of the extent to which reactivity patterns of discrete molecular complexes are predictive of reaction pathways on surfaces has yet to emerge, however. This failing arises, in part, because many adsorbates decompose on *transition-metal* surfaces rather than desorb intact. Consequently, extensive spectroscopic studies are often required to identify the products of even the simplest surface reactions.

We have recently found that both saturated and unsaturated hydrocarbons bind only weakly to aluminum surfaces.[2] As a result, mass spectrometry can be applied readily to determine both the products[3] and kinetics[2] of hydrocarbon-producing reactions. In the present work, we have exploited this fact and determined the thermal surface reaction pathways followed by a variety of alkyls and metallacycles on aluminum surfaces generated by the dissociative adsorption of alkyl halides. We discuss our results in the context of the extensive literature for the reactivity patterns exhibited in the gas phase and in solution by aluminum–alkyl complexes.

It should be noted that in all of the studies described below, the coadsorbed halogen atom remains on the surface throughout the temperature range where the adsorbed alkyl moiety decomposes (and the products subsequently desorb). This is a particularly striking observation given that the reaction of aluminum with alkyl halides is an industrially important process for the synthesis of aluminum sesquihalides in bulk (eq 1). Although

$$3RX + 2Al \rightarrow R_2AlX + RAlX_2 \qquad (1)$$

this metal-consuming reaction is extremely facile in solution, under ultrahigh vacuum (UHV) conditions alkyl decomposition predominates. Thus, for example, previous studies of the decomposition of adsorbed isobutyl groups formed on aluminum by the adsorption of either triisobutylaluminum (TIBA, eq 2) or 1-iodo-2-methylpropane (eq 3) have shown that the adsorbed alkyl ligands (with or without coadsorbed iodine atoms present) decompose thermally by β-hydride elimination to evolve isobutene and hydrogen at ~500 K.[2,4,5]



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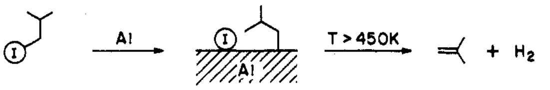

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