The Long-Lived Radical Cations of Simple Carbon Esters Isomerize to the Lowest-Energy Structure

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Abstract: The structures of the low-energy, long-lived radical cations of simple gaseous carbon esters were investigated using bimolecular reactions in a dual-cell FT/ICR mass spectrometer. The molecular ions of dimethyl carbonate, methyl and ethyl formate, methyl and ethyl acetate, and methyl and ethyl propionate were generated by electron impact or thermoneutral charge exchange. Reference ions with the enol and the expected distonic structures (spatially separated odd spin and charge site) were formed by electron impact on suitable neutral precursors or by ion–molecule reactions using distonic reactant ions. Ionized γ-butyrolactone and ionized δ-valerolactone were chosen as models for conventional ester radical cations. The experimental results demonstrate that the lactone ions indeed are stable toward isomerization. The neutral reagents cyclohexanone, triethylamine, and 2-propanol-d_8 proved to be useful when differentiating reference ions with different structures: (1) Cyclohexanone reacts by charge exchange with the conventional ester radical cations while enol and distonic ions react by proton transfer. (2) Triethylamine reacts with the distonic ions by proton transfer while charge exchange dominates for the enol ions and the conventional radical cations. (3) Conventional ester radical cations abstract a deuterium atom from 2-propanol-d_8, while distonic ions and enol ions react by H/D exchange. Some enol ions also abstract a deuterium atom from this reagent. Comparison of the reactions of the reference ions to those of the ester molecular ions demonstrates unambigously that the long-lived ionized carbonates and formates have a distonic structure, while the acetate and propionate radical cations have an enol structure.

Introduction

Identification and characterization of reactive intermediates presents one of the most challenging problems in chemical research. Organic radical cations are an interesting class of intermediates that has recently received significant attention.[1-3] However, some of the most basic questions regarding these reactive species remain unanswered. For example, when a radical cation is generated by removal of an electron from a simple organic compound, does the radical cation retain its connectivity or does it isomerize to another structure? Recent theoretical and experimental results indicate[1-3] that conventional radical cations with the same atoms bound to each other as in their neutral precursors are often thermodynamically as well as kinetically less stable than nonconventional isomeric ions with no stable neutral counterparts. These nonconventional ions include distonic ions[1,4] characterized by a spatially separated charge and radical site. Considering the fact that often only a single intramolecular hydrogen atom transfer is required[1-7] to generate a more stable ion, it seems conceivable that, if the ion lifetime and energy allow, *many organic radical cations may spontaneously isomerize to more stable forms*. This has been demonstrated[1,4-12] to be true for many ions. For example, the molecular ions of trialkyl phosphates and dialkyl-*N*-nitrosamines isomerize by a hydrogen atom transfer to more stable distonic forms.[4]

The determination of the structures of simple carbon ester radical cations has been the pursuit of many scientists for the past ten years.[1,8] Studies of ions in frozen matrices by using electron-spin resonance spectroscopy show that many ester radical cations irreversibly rearrange to their distonic forms upon annealing of the frozen matrix.[9-11] The rearrangement of these ions is thought to occur by an intramolecular hydrogen atom transfer to the carbonyl oxygen (Scheme 1).[9,10]

The structures of various *short-lived* gaseous ester radical cations have been studied using sector tandem mass spectrometers (ion lifetimes in the microsecond time frame).[1,8,12-23]

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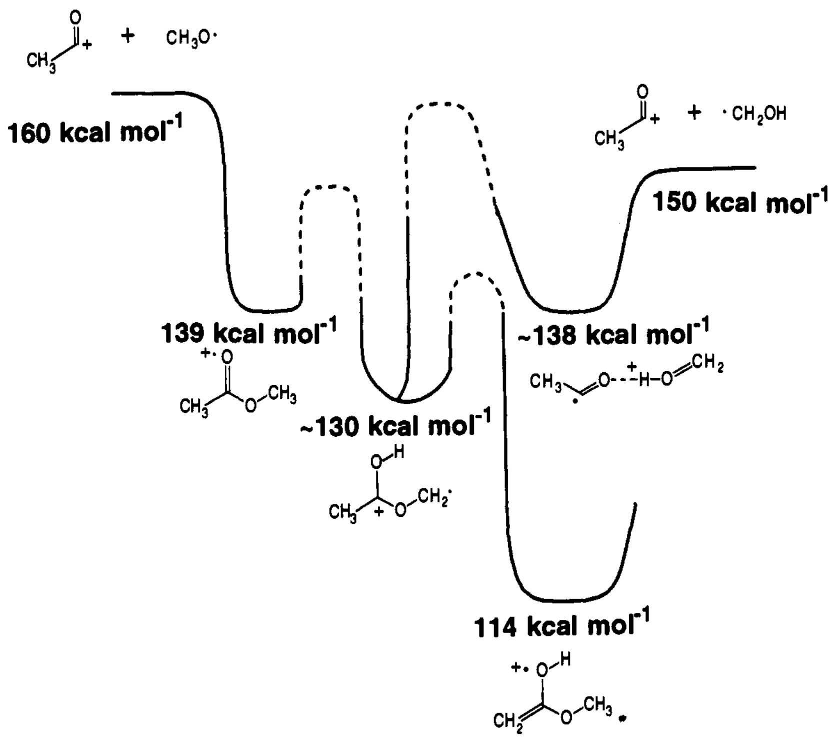

Figure 1. Potential energy surface for the ionized methyl acetate system (data from refs 17, 18, and 20). The heats of formation are experimental values from ref 17, with the exception of the hydrogen-bridged ion (refs 18 and 20). The isomerization barriers are not known (dashed lines).

Scheme 1

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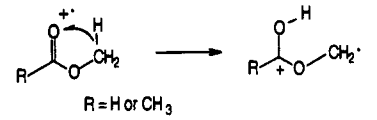

Scheme 2

Experiments[8b,12] carried out on ionized propyl and butyl formates suggest that these internally excited radical cations rearrange to a distonic form during fragmentation. However, isomerization can also occur for nonfragmenting formate ions. Collisional activation and neutralization–reionization studies of ionized methyl formate have shown[13] that this ester radical cation partially isomerizes to its distonic form within the microsecond time frame (prior to collisional activation in a mass spectrometer). This experimental finding is in agreement with ab initio molecular orbital calculations,[14,15] suggesting that the distonic form of ionized methyl formate is more stable than the conventional form by about 15 kcal mol^{-1}. The energy barrier for the rearrangement of the ground state keto form of ionized methyl formate to the distonic isomer has been estimated[14] to be about 10 kcal mol^{-1}. However, only 1.4 kcal mol^{-1} is needed to isomerize ions generated by vertical ionization.[14] Hence, ionized methyl formate generated by electron ionization is not expected to be stable toward isomerization to its distonic form.

For ionized methyl acetate, a distonic isomer as well as the enol form are significantly lower in energy than the keto isomer. The enol structure corresponds to the global miminum on the potential energy surface, according to experimental[16,17] heats of formation as well as ab initio molecular orbital calculations.[18,19] Figure 1 shows a partial potential energy surface for ionized methyl acetate. The calculated[18] energy barriers for the isomerization of the keto isomer to the distonic form and the distonic ion to the enol ion are relatively high: 11 and 15 kcal mol^{-1}, respectively. Indeed, the collision-activated dissociation spectra obtained using sector mass spectrometers for the short-lived keto, enol, and distonic forms of ionized methyl acetate showed certain differences, suggesting that at least some of the ions with internal energies below that required for decomposition are stable toward isomerization.[17,21-23] Examination of internally excited, partially deuterium-labeled isomeric ions revealed extensive H/D-randomization during dissociation, indicating that the internally excited ions undergo partial equilibration.[21,23] According to most recent studies,[17] *nonfragmenting* methyl acetate radical cations partially isomerize to a distonic form (Scheme 1) within the microsecond time frame but the enol ion is not produced to any great extent.

Studies[17] on nonfragmenting, ionized methyl propionate suggest that the keto ion partially isomerizes to a distonic form within the microsecond time frame. This isomerization was expected to occur similarly to the isomerization of ionized methyl acetate: by a [1,4]-hydrogen shift from the alcohol moiety to the carbonyl oxygen (Scheme 1).[23] However, examination of a partially labeled ionized methyl propionate showed[17] that the isomerization occurs via a [1,4]-hydrogen shift from the β-carbon in the acid moiety to the carbonyl oxygen, giving rise to the distonic structure shown in Scheme 2.

As a summary, while the ESR studies of simple ester radical cations strongly suggest that the keto form of these ester ions rearranges irreversibly to the distonic form, gas-phase studies of the ions in sector tandem mass spectrometers indicate that the molecular ions either retain their original structure or only partially isomerize to the distonic form. A possible explanation for these differences is the different lifetime of the ions:[9-11,15-19,21-23] sector tandem mass spectrometry experiments[17] sample short-lived ions (lifetimes of nonfragmenting ions usually <20 μs) that may not have enough time to isomerize while the matrix isolation experiments involve long-lived ions.[1,9-11]

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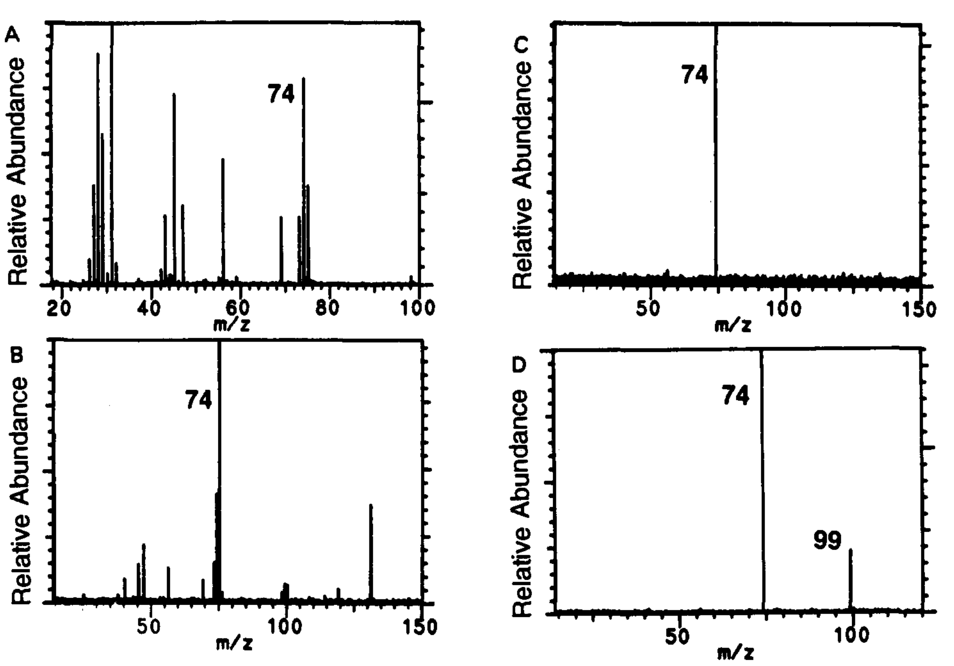

Figure 2. A typical multiple-stage MS experiment: (A) ionization of ethyl formate by 70 eV electron ionization, (B) transfer of the ions into the other cell, (C) isolation of the ion of m/z 74, and (D) reaction of the ion of m/z 74 with cyclohexanone (6×10^{-8} Torr) for 200 ms.

In a preliminary communication[24] we suggested that the gaseous low-energy ethyl acetate radical cation is kinetically unstable toward isomerization to its *enol* form via the distonic structure. A full account of this work is presented here, together with an extension to other ester radical cations. Ion–molecule reactions in an FT/ICR were used to determine the structures of the low-energy, long-lived radical cations of simple formates, acetates, propionates, and lactones, as well as dimethyl carbonate. The results suggest that the long-lived acyclic ester radical cations are unstable toward isomerization in the gas phase.

Experimental Section

All the experiments were performed using a Fourier-transform ion cyclotron resonance (FT/ICR) instrument, an Extrel Model 2001 FT/MS system[25] equipped with a 3 T superconducting magnet operated at 2.5 T. The differentially pumped dual-cell assembly consists of two identical two-inch cubic cells. All the spectra shown are an average of at least 50 spectra acquired at a digitizer rate of 5.3 MHz, and using an excitation sweep with a 2.7-MHz bandwidth, a 3.2-kHz/μs sweep rate, and an amplitude of 107 V_{p-p}. The spectra were recorded as 32K data points and subjected to one zero fill before Fourier transformation.

A baseline pressure of less than 1×10^{-9} Torr in each side of the cell was maintained with two turbomolecular pumps (Balzars TPU 330). Samples were introduced into the FT/ICR by using two Extrel FT/MS heated single batch inlet systems equipped with variable leak valves, or by a pulsed valve inlet system. The nominal reagent pressure in the cell was 1.2×10^{-7} Torr (as measured by an ionization gauge), except for cyclohexanone which was used at a nominal pressure of 6.0×10^{-8} Torr.

The most important stages of a typical MS/MS experiment are shown in Figure 2. Radical cations were generated by electron ionization (EI) or by charge exchange using $CS_2^{\bullet+}$ reagent ions (ionization energy of CS_2 is 10.07 eV[26a]). The latter method results in near thermoneutral ionization (ionization energies of most organic esters are slightly above 10 eV).[26a] Protonated esters were formed by self-chemical ionization in which fragment ions obtained by electron ionization of the sample are used to protonate the neutral sample molecules. The enol and distonic reference ions were formed by dissociation and/or ion–molecule reactions, as described later. Following the generation of the ester ions in one cell, undesired ions formed by the electron beam in the other cell were ejected by applying a negative potential (−9.8 V) to the remote trapping plate of this cell (not the conductance limit plate) for 5–10 ms. After this, the desired ions were transferred into the cleaned cell through a hole in the center of the conductance limit plate by grounding this plate for 100 μs. At all other times, all the three trapping plates were kept at +2 V. The transferred ions were collisionally cooled by pulsing a momentary high pressure of argon into the cell ($\geq 1 \times 10^{-5}$ Torr peak pressure). The pressure of argon was adjusted to be at least two orders of magnitude greater than that of the organic reagent to make sure that collisions of the hot ions occur with argon and not with the organic reagent. In a few experiments, the ions were collisionally cooled by allowing them to collide with neutral reagent molecules other than argon; both procedures gave the same results. Experiments were also carried out *without collisional cooling*. These experiments yielded data which are qualitatively similar to those obtained for the cooled ions. However, hot ions occasionally showed nonlinear kinetics (nonlinear decay of the logarithm of the reactant ion abundance as a function of time) which was not the case for the collisionally cooled ions. Prior to reactions, the reactant ions were isolated by applying a sequence of rf excitation pulses (single frequency pulses and/or frequency sweeps) to the excitation plates of the cell in order to eject unwanted ions from the cell.

The isolated ions were allowed to undergo reactions with the desired neutral reagent for a variable period of time. In order to eliminate all the product ions arising from minor impurity ions still left in the cell after ion isolation, a background subtraction procedure was followed. This procedure involved the removal of the isolated ion from the cell prior to reaction. The product ions obtained during the following reaction time arise from reactions of ions other than the ion of interest and were subtracted from the product distribution obtained for the reaction of the ion of interest.

The rate constants of the ion–molecule reactions were determined on the basis of the decay of the reactant ion abundance (normalized to the total measured ion current) as a function of time, assuming pseudo-first-order kinetics. The largest uncertainty in the rate measurements arises from inaccuracy in the estimated pressure of the neutral reagent.[27] The pressure reading was corrected for the sensitivity of the ion gauge toward each neutral reagent using the method of Bartmess and co-workers.[28b] An instrumental geometry correction factor was calculated for each neutral reagent by using common procedures[6,24,27] based on well-characterized reactions with known rate constants.[28a] The precision

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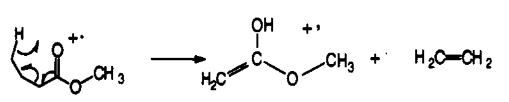
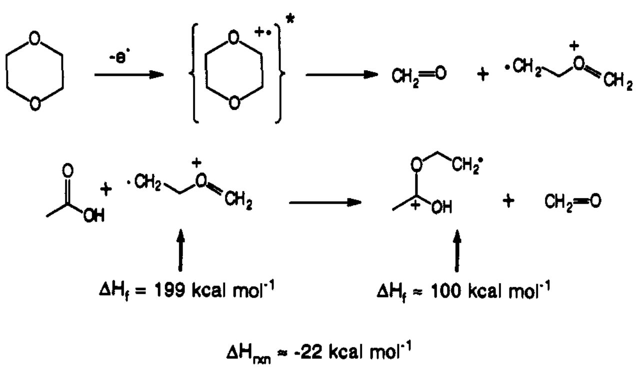
Scheme 3



Scheme 4



of the rate constant measurements is estimated to be ±5% and the accuracy is estimated to be better than ±50%.[6,7]

Partially deuterated methyl acetate, $CH_3C(O)OCD_3$, and methyl propionate, $CH_3CH_2C(O)OCD_3$, were synthesized by mixing an acid chloride with deuterated methanol. All the other reagents were commercially available and were used as received from the manufacturer. The purity of all the reagents were checked by GC and by mass spectrometry.

Results and Discussion

Generation of the Reference Ions. The use of appropriate reference ions with known structures is very important in mass spectrometry where structural information is obtained indirectly, e.g., through examination of chemical reactivity. Ionized γ-butyrolactone and δ-valerolactone were chosen as reference ions with conventional (keto) structures since these ions are expected to be stable toward isomerization through intramolecular hydrogen transfer. This assumption proved to be correct in the course of the work.

The enol forms of ionized acetates and one of the propionates were formed by the McLafferty rearrangement, as shown in Scheme 3 for the enol form of ionized methyl acetate. The enol form of ionized ethyl acetate was generated from ionized ethyl valerate or from ionized ethyl butyrate[23] and the enol form of ionized methyl propionate was generated from ionized methyl 2-methylbutyrate.[16]

Reference ions expected at least initially to have distonic structures were synthesized by ion–molecule reactions using distonic reactant ions. Reference distonic ions of ionized ethyl acetate and ionized ethyl propionate were formed by transferring ionized ethylene from $^{\bullet}CH_2CH_2OCH_2^+$ (a fragment ion[1,4] of 1,4-dioxane) to acetic acid and to propionic acid, respectively (Scheme 4). Generation of the distonic form $CH_3C(OH)OCH_2^{\bullet+}$ of ionized methyl acetate proved to be difficult. Dissociation of ionized methoxymethyl acetate in the FT/ICR yields an ion which, based on its ion–molecule reactions, does not have the earlier suggested[17,23] distonic structure. Transfer of $CH_2^{\bullet+}$ from $^{\bullet}CH_2OCH_2^+$ ($\Delta H_{rxn} \sim -3$ kcal mol⁻¹) or $CH_2{=}C{=}O^{\bullet+}$ to acetic acid yields an ion which probably initially has the desired distonic structure, but this ion is formed with a low abundance, limiting the quality of the data obtained.

Ion–Molecule Reactions. Collision-activated dissociation (CAD) is the most commonly used tool in the structural characterization of gas-phase ions.[1,4,30-32] However, isomeric ions sometimes produce similar dissociation product distributions. This was found to be the case for the long-lived, isomeric ester ions which produce similar CAD spectra in the FT/ICR. Ion–molecule reactions often provide valuable structural information for gas-phase ions,[4,33] and they were used here to study the structures of the nonfragmenting ester radical cations. FT/ICR mass spectrometers are especially suitable for ion–molecule reaction studies as they allow the isolation of the ion of interest and variation of the reaction time. Only exothermic reactions are observed in the experiments discussed here.[6,7,24,31]

Table 1. The Ionic Products from the Reactions of the Molecular Ions of Various Esters with Cyclohexanone (MW 98)

ester	*m/z*	*m/z* (ionic products)	branching ratio (%)	k^a	k_{Coll}^b	k/k_{Coll}
ethyl formate	74	99	100	3.0	2.7	1.1
methyl acetate	74	99	100	2.0	2.7	0.7
ethyl acetate[d]	88	99[c]	≃100[c]	1.5	2.6	0.6
dimethyl carbonate	90	99	100	*e*	2.6	
methyl propionate	88	99[c]	≃100[c]	0.9	2.6	0.3
ethyl propionate	102	99[c]	≃100[c]	0.4	2.5	≃0.1
γ-butyrolactone	86	98	100	3.2	2.6	1.2
δ-valerolactone	100	98	100	1.7	2.5	0.7

[a] Rate constant in units of 10^{-9} cm³ molecule⁻¹ s⁻¹. [b] Collision rate[29] in units of 10^{-9} cm³ molecule⁻¹ s⁻¹. [c] A small amount of the charge exchange product also appears to be formed. [d] Chemical ionization using CS_2 as the CI reagent yields the same product ion at $k = 1.3 \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹. [e] Rate calculation was not possible because of low signal intensity.

When attempting to determine the structures of gas-phase ions by using ion–molecule reactions, it is important that an exothermic, structurally characteristic reaction occurs *rapidly* with all the isomeric ions. This is needed to ensure that isomerization, followed by reaction of the isomerized form, cannot efficiently compete with the structurally characteristic reaction.[34a] If the desired reaction is exothermic and mechanistically simple, it is likely to occur at or near the collision rate in the gas phase. This is true for example for most proton transfer[34a] and electron transfer reactions[6,7,34b-e] (the more exothermic the reaction, the closer is the rate constant to the collision rate[34b-e]). Indeed, an earlier study[7] successfully utilized exothermic charge exchange and proton transfer reactions to determine whether the long-lived molecular ions of organophosphorus esters have a conventional or a distonic structure: a neutral reagent with a low ionization energy and high basicity (trimethyl phosphite) was found to deprotonate the ions with distonic structures while exclusive electron transfer occurred for the conventional ions. A similar approach was employed here.

Cyclohexanone. Reactions with cyclohexanone were used to study whether the long-lived, nonfragmenting ester molecular ions partially isomerize to their distonic forms, as expected on the basis of the results obtained for ionized methyl formate, methyl acetate, and methyl propionate in sector tandem mass spectrometers.[13,17] Electron transfer between cyclohexanone (ionization

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(36) The enthalpy changes shown in Scheme 5 are based on heats of formation of the neutral radicals estimated as follows: The homolytic C–H bond energy in $H{-}CH_2COOCH_3$ was assumed to be the same as that in acetone, $H{-}CH_2COCH_3$ (93 kcal/mol; ref 38); this yields $\Delta H_f(^{\bullet}CH_2COOCH_3) = -57$ kcal/mol. The homolytic C–H bond energy in $CH_3COOCH_2{-}H$ was assumed to be the same as that in dimethyl ether, $CH_3OCH_2{-}H$ (93 kcal/mol); this yields $\Delta H_f(CH_3COOCH_2^{\bullet}) = -57$ kcal/mol.

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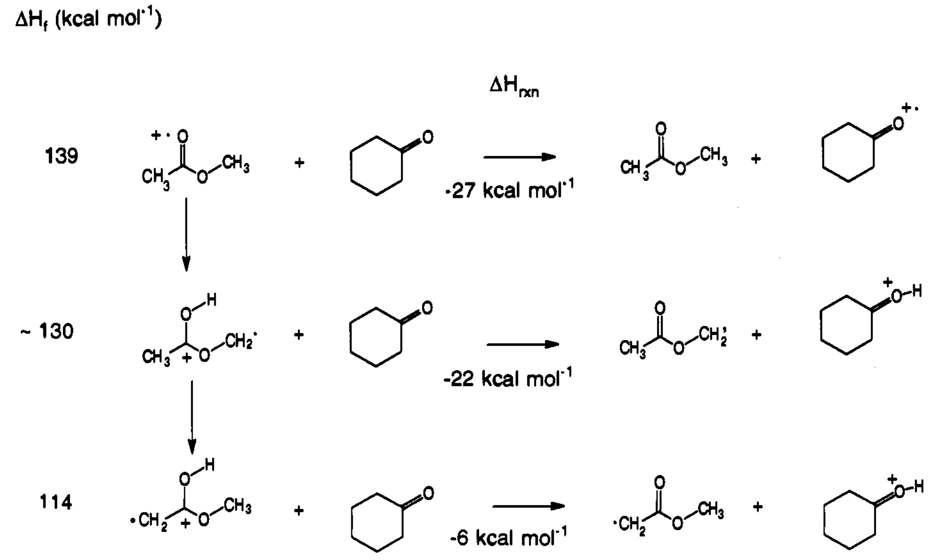
Table 2. Ionic Products from the Reactions of Various Cations with Cyclohexanone (MW 98)

generation of the reactant ion	assumed initial ion source	m/z	m/z (ionic products)	branching ratio (%)	k^a	$k_{Coll}{}^a$	k/k_{Coll}
transfer of $CH_2^{\bullet +}$ to acetic acid	$CH_3C(OH)OCH_2^{\bullet +}$	74	99	100	c	2.7	
dissociation of methyl butyrate	$CH_2{=}C(OH)OCH_3^{\bullet +}$	74	99	100	2.5	2.7	0.9
proton transfer to methyl acetate	$CH_3C(OH)OCH_3^+$	75	99	100	3.0	2.7	1.1
transfer of $C_2H_4^{\bullet +}$ to acetic acid	$CH_3C(OH)OCH_2CH_2^{\bullet +}$	88	99^d	$\simeq 100^d$	0.7	2.6	0.3
dissociation of ethyl butyrate	$CH_2{=}C(OH)OCH_2CH_3^{\bullet +}$	88	99^d	$\simeq 100^d$	0.8	2.6	0.3
dissociation of ethyl valerate	$CH_2{=}C(OH)OCH_2CH_3^{\bullet +}$	88	99^d	$\simeq 100^d$	0.9	2.6	0.3
dissociation of methyl 2-methylbutyrate	$CH_3CH{=}C(OH)OCH_3^{\bullet +}$	88	99^d	$\simeq 100^d$	0.9	2.6	0.3
transfer of $C_2H_4^{\bullet +}$ to propionic acid	$CH_3CH_2C(OH)OCH_2CH_2^{\bullet +}$	102	e				
proton transfer to γ-butyrolactone	(γ-butyrolactone + H)$^+$	87	99	100	1.2	2.6	0.5
proton transfer to δ-valerolactone	(δ-valerolactone + H)$^+$	101	no reaction				

[a] Rate constant in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Collision rate[29] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] Rate calculation was not possible because of insufficient data. [d] A small amount of the charge exchange product also appears to be formed. [e] Very slow proton transfer and electron transfer seem to occur.

Scheme 5



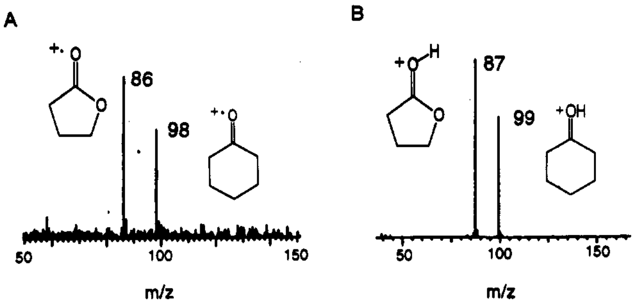


Figure 3. Reaction of (A) ionized γ-butyrolactone (reaction time 500 ms) and (B) protonated γ-butyrolactone (reaction time 1.25 s) with cyclohexanone (1.2 × 10^{-7} Torr).

energy IE = 9.14 eV[26a]) and simple, ionized carbon esters (IE = 10.0–10.8 eV[26a]) is exothermic by 20–38 kcal/mol. Thus, if the ester radical cations have retained their original keto structure, they are expected to rapidly abstract an electron from cyclohexanone.[34b–e] This proposal was supported by the observation of *facile charge exchange for the reference ions with the keto structure* (ionized γ-butyrolactone and ionized δ-valerolactone; Figure 3A; Table 1).

Most protonated esters will react with cyclohexanone by proton transfer (Figure 1; the proton affinity[26a] of cyclohexanone is 201.4 kcal mol^{-1}; that of most simple organic esters is 193–201 kcal mol^{-1}).[26a] Deprotonation of the least acidic ion studied, protonated δ-valerolactone,[38,39] is endothermic by about 13 kcal/mol and does not occur (Table 2). Distonic ester ions are Brönsted acids with the same acidic functional group as the corresponding protonated esters and should therefore react with cyclohexanone by proton transfer if this is exothermic. Most distonic ions do not have known acidities. However, the available data suggest that organic distonic ions are generally stronger acids than the corresponding even-electron ions (ions which would be generated by attaching a hydrogen atom to the radical site of the distonic ion).[26b] For example, protonation of cyclohexanone by the distonic form of ionized methyl acetate is estimated[36,37] to be exothermic by about 22 kcal mol^{-1} (Scheme 5) while proton transfer from protonated methyl acetate is exothermic by only 3.6 kcal mol^{-1} (nevertheless, this reaction occurs at the collision rate: see Table 4). Hence, the distonic ester radical cations should indeed rapidly protonate cyclohexanone, and this expectation proved to be true in the course of the work (see below). Proton transfer to cyclohexanone distinguishes the distonic ions from the keto ions which are not strong Brönsted acids (see Table 1).[4,7]

The results of the reactions of various ester molecular ions with cyclohexanone are given in Table 1. The predominant reaction observed for ionized ethyl formate, dimethyl carbonate, the acetates, and the propionates was proton transfer. The molecular ions generated by charge exchange as well as by electron impact react in the same way. The same applies to collisionally cooled ions and ions which were not collisionally cooled. The observation of dominant proton transfer indicates that the low-energy molecular ions have isomerized to another structure, and that the so-generated ion is a Brönsted acid. The isomerized form of the long-lived formate and carbonate ester ions is likely to be the distonic ion generated by a [1,4]-hydrogen transfer (Scheme 1). While the acetate and propionate ions may have

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(38) Wiberg, K. B.; Waldron, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 7697.

(39) Wiberg, K. B.; Waldron, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 7705.

(40) The ionization energy of the enol form of methyl acetate was estimated from ΔH = 114 kcal/mol (ref 26a) for the enol ion and ΔH_f = −72 kcal/mol for the neutral enol. The latter value was obtained using Benson's Rules.

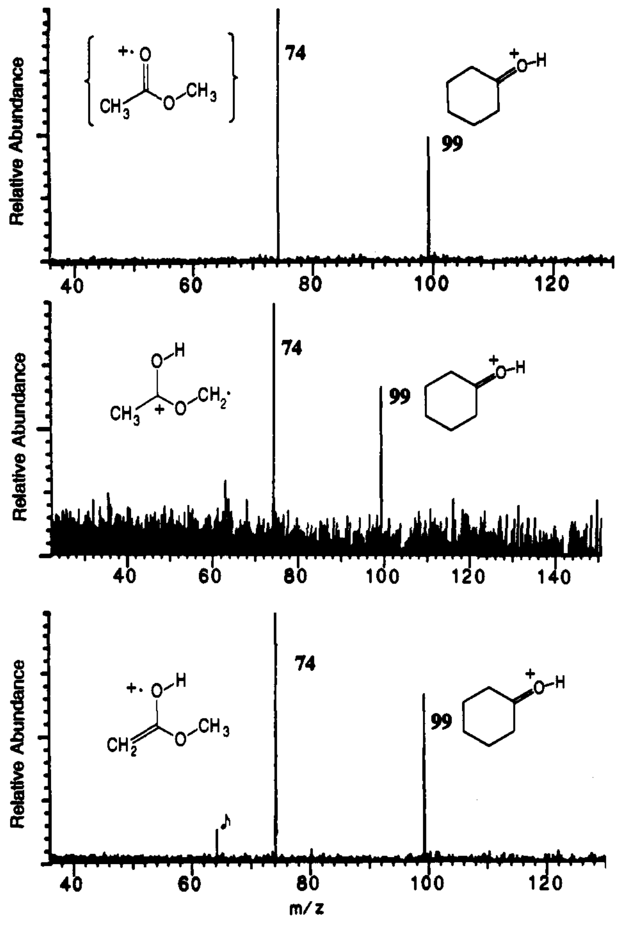


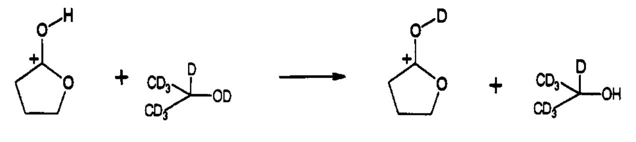
Figure 4. Reaction of (a, top) ionized methyl acetate, (b, middle) the distonic reference ion, and (c, bottom) the enol reference ion with cyclohexanone for 500 ms. For all three reactions, the nominal pressure of cyclohexanone was 6.0 × 10^{-8} Torr. The musical note denotes interference from a local radiostation.

isomerized to a distonic ion, this does not have to be the case: also an enol form may be generated from these ions, and it may be expected to react similarly as the distonic ion. Proton transfer to cyclohexanone is estimated to be exothermic for both the distonic and the enol ions (Scheme 5) while charge exchange is endothermic for both ions.[17,26a,36,40] Indeed, predominant proton transfer occurs for both the distonic and the enol reference ions (Table 2). It should be mentioned here that ionized methyl acetate was earlier found to be an efficient protonating agent in an ICR,[35] and that this observation led to the speculation that an isomerization of the molecular ion via the distonic form to the enol ion might have occurred.[35]

As a conclusion, the ion–molecule reactions with cyclohexanone indicate that the long-lived, nonfragmenting radical cations of simple formates, carbonates, acetates, and propionates undergo complete or nearly complete isomerization to another structure in the gas phase, independent of whether collisional cooling is employed. However, the reaction with cyclohexanone does not allow a conclusive distinction to be made between the distonic and enol isomers of the acetate and propionate ions. Other neutral reagents were used to make this distinction.

2-Propanol-d_8. Experiments using 2-propanol-d_8 (or methanol-d_4 for the most acidic ions) were designed to determine the number of acidic hydrogens present in the ester ions. When this neutral reagent was allowed to collide with different ester ions, thermoneutral hydrogen–deuterium exchange was observed for protonated esters (Scheme 6; Table 4), the distonic formate and carbonate ions (the molecular ions of methyl formate and methyl carbonate; Figure 5; Table 3), and the distonic and enol reference ions of the propionates (Table 4), indicating the presence of one exchangeable hydrogen atom in all these ions. In contrast, radical cations with the keto structure (ionized γ-butyrolactone and ionized δ-valerolactone) react with 2-propanol-d_8 by deuterium atom abstraction (Table 3).

Scheme 6



Scheme 7

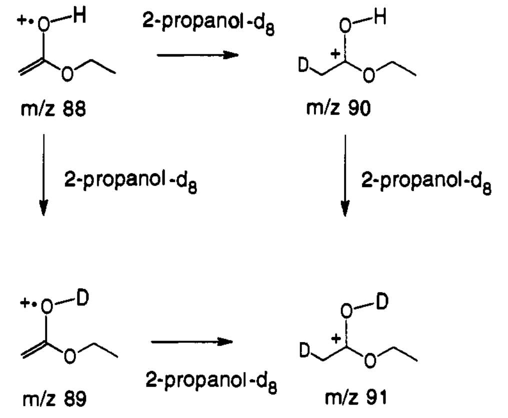


Table 3. Ionic Products from the Reactions of the Molecular Ions of Various Esters with 2-Propanol-d_8

ester ion	m/z	m/z (ionic products)
ethyl formate	74	75[a]
methyl acetate	74	75 76 77[b]
ethyl acetate[c]	88	89 90 91[b]
dimethyl carbonate	90	91
methyl propionate	88	89
ethyl propionate	102	103
γ-butyrolactone	86	88
δ-valerolactone	100	102

[a] This experiment used methanol-d_4 instead of 2-propanol-d_8. [b] Secondary product. [c] Generated by electron impact and chemical ionization using CS_2.

Somewhat surprisingly, the enol reference ions of the acetates were found to yield *three* product ions upon reaction with 2-propanol-d_8 (Figure 6c). The generation of these products is explained on the basis of competitive and consecutive reactions involving deuterium atom abstraction and H/D exchange. For example for the enol form of ionized ethyl acetate (Scheme 7), the primary product ions of m/z 89 from H/D exchange and m/z 90 from a slower deuterium atom abstraction react further to give the secondary product ion of m/z 91 which dominates at long reaction times. This sequence of reactions was verified by allowing the ion to react with undeuterated 2-propanol: only hydrogen atom abstraction was observed. The reference ion assumed to be the distonic form of ionized ethyl acetate reacts with 2-propanol-d_8 producing the same two primary products and the same secondary product as the enol ion (Figure 6). The similarity of these two data sets, together with the fact that the assumed distonic reference ion abstracts a deuterium atom from 2-propanol-d_8 (a reaction which was not observed for other distonic ester ions: the formate and carbonate ions; Table 3), suggests that the distonic acetate ion has largely isomerized to the enol form prior to reaction. However, the enol and distonic reference ions react at a somewhat different rate (Table 4); hence, the isomerization may not be complete.

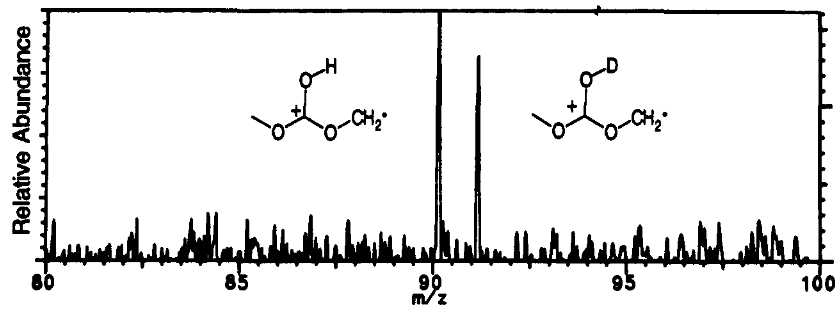


Figure 5. Reaction of the distonic molecular ion of dimethyl carbonate with 2-propanol-d_8 (nominal pressure 1.2 × 10^{-7} Torr) for 1 s.

Table 4. Ionic Products from the Reactions of Various Cations with 2-Propanol-d_8

generation of the reactant ion	assumed initial ion structure	*m/z*	*m/z* (ionic products)
dissociation of methyl butyrate	$CH_2{=}C(OH)OCH_3^{\bullet+}$	74	75 76 77[a]
transfer of $C_2H_4^{\bullet+}$ to acetic acid	$CH_3C(OH)OCH_2CH_2^{\bullet+}$	88	89 90 91[a]
dissociation of ethyl valerate	$CH_2{=}C(OH)OCH_2CH_3^{\bullet+}$	88	89 90 91[a]
proton transfer to ethyl acetate	$CH_3C(OH)OCH_2CH_3^+$	89	90
dissociation of methyl 2-methylbutyrate	$CH_3CH{=}C(OH)OCH_3^{\bullet+}$	88	89
transfer of $C_2H_4^{\bullet+}$ to propionic acid	$CH_3CH_2C(OH)OCH_2CH_2^{\bullet+}$	102	103
proton transfer to γ-butyrolactone	(γ-butyrolactone + H)$^+$	87	88
proton transfer to δ-valerolactone	(δ-valerolactone + H)$^+$	101	102

[a] Secondary product.

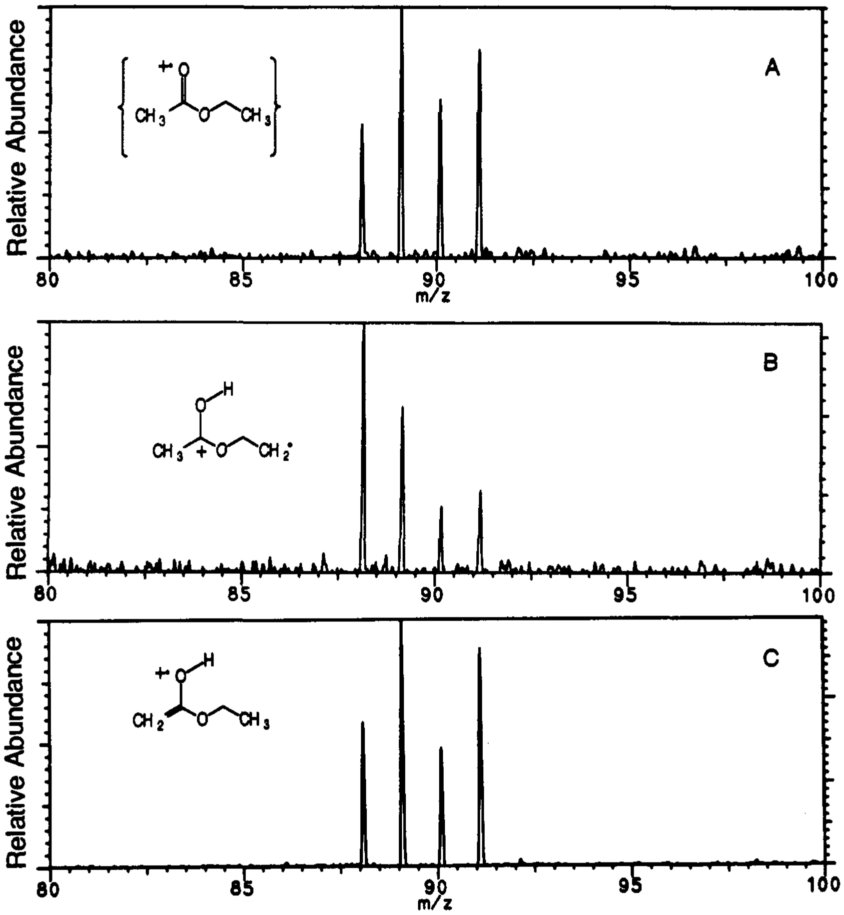


Figure 6. Reaction of (a, top) ionized ethyl acetate, (b, middle) the distonic reference ion, and (c, bottom) the enol reference ion with 2-propanol-d_8. The nominal pressure of 2-propanol-d_8 was 1.2 × 10^{-7} Torr and the reaction time was 2 s.

Examination of the reactivity of the molecular ions of the acetates demonstrates that these radical cations have the enol structure: *the reaction rates as well as the product distributions of the molecular ions are identical to those of the enol reference ions* and do not support a distonic structure for these molecular ions (Tables 3 and 4). The molecular ions of ionized propionates show exchange of one hydrogen atom with deuterium, just as was observed for both the distonic and the enol reference ions. While

Table 5. Ionic Products from the Reactions of the Molecular Ions of Various Esters with Dimethyl Sulfide (MW 94)

ester	m/z	m/z (ionic products)	branching ratio (%)	k^a	k_{Coll}^b	k/k_{Coll}
methyl formate	60	95, 97^c	100	1.6	2.0	0.8
ethyl formate	74	94, 96^c	49	1.5	1.9	0.8
		95, 97	51			
methyl acetate	74	94, 96^c	100	1.0	1.9	0.5
ethyl acetate	88	94, 96^c	100	0.8	1.8	0.5
methyl propionate	88	no reaction				
ethyl propionate	102	no reaction				
γ-butyrolactone	86	94, 96^c	100	1.0	1.8	0.6
δ-valerolactone	100	94, 96^c	100	1.0	1.7	0.6

[a] Rate constant in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Collision rate[29] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] One of the ions contains ^{32}S and the other one ^{34}S isotope.

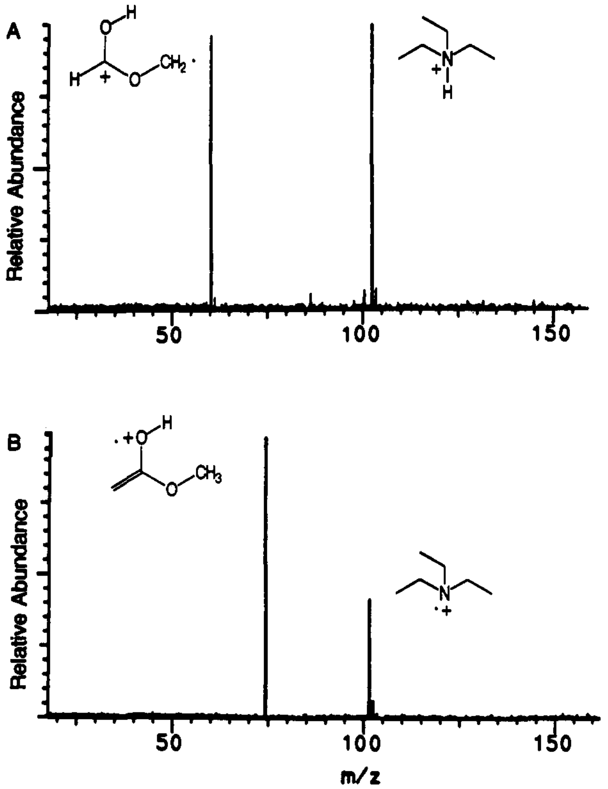


Figure 7. Reaction of (A) the distonic molecular ion of methyl formate and (B) the enol reference ion of ionized methyl acetate with triethylamine for 1 s. For both cases, the nominal pressure of triethylamine was 1.2 × 10^{-7} Torr.

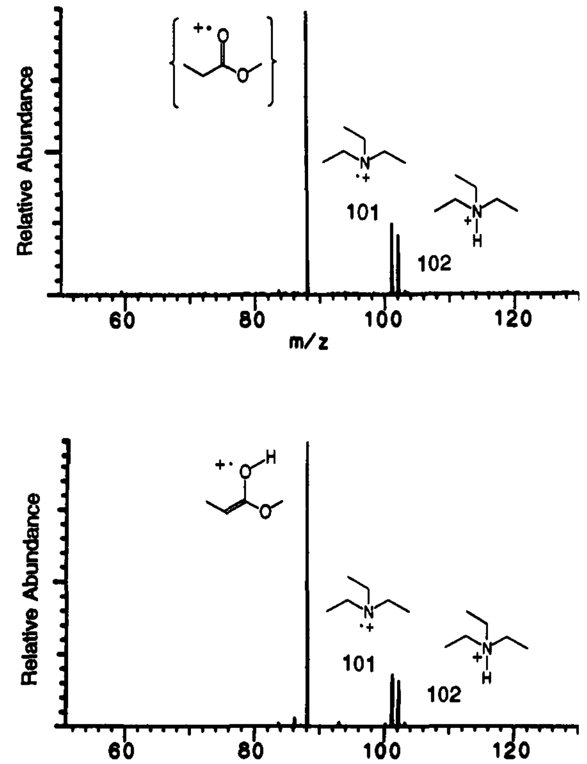


Figure 8. Reaction of (a,top) ionized methyl propionate and (b, bottom) the enol reference ion with triethylamine for 750 ms. For both cases, the nominal pressure of triethylamine was 1.2 × 10^{-7} Torr.

this result rules out the keto structure, it does not allow the distinction between the enol and distonic propionate structures.

Dimethyl Disulfide. Ion–molecule reactions with dimethyl disulfide were of interest because this molecule has a lower ionization energy[26c,d] (about 8 eV[26c,d]) than cyclohexanone[26a] and might be able to transfer an electron to ester ions with either the keto or the enol structure but not to most distonic ions (generation of a biradical is endothermic).[4,41] All the conventional organic radical cations studied[4,6,31a,41] thus far react with dimethyl disulfide by exclusive charge exchange. The same was found to be true for the ester radical cations with the keto structure (Table 5): ionized γ-butyrolactone and ionized δ-valerolactone react by charge exchange with dimethyl disulfide (Table 5).

Charge exchange is not expected for ions with distonic structures unless they can undergo dissociative charge exchange to generate two stable molecules as the neutral products.[4,6,41] Indeed, the molecular ion of methyl formate reacts with dimethyl disulfide by *exclusive and facile proton transfer*. This reactivity confirms the conclusion made above that the long-lived methyl formate molecular ion has the distonic and not the keto structure (electron transfer would be exothermic by ≥57 kcal/mol for the keto ion;[26a,c,d] proton transfer from the keto ion would be less exothermic than electron transfer by about 12 kcal mol^{-1} and is known not to occur[4,6,31a,41] for conventional organic radical cations which can undergo highly exothermic charge exchange with dimethyl disulfide). Ionized ethyl formate, another distonic ion, shows both proton transfer and charge exchange. The latter reaction is likely to be dissociative charge exchange, yielding acetic acid and ethylene as the neutral products.

The acetate molecular ions undergo facile charge exchange with dimethyl disulfide (Tables 5 and 6). This finding provides further evidence against a distonic structure for these ions. The absence of charge exchange for the molecular ions of the propionates (Table 5a) supports the proposal that these ions have rearranged to either the distonic or the enol structure: charge exchange between dimethyl disulfide and the propionate ions with the keto structure would be highly exothermic and should occur readily (e.g., for ionized methyl propionate, $\Delta H \leq -39$ kcal mol^{-1} [26a,c,d]).[34b–e] On the other hand, both the distonic and enol reference ions (Table 6) were found to be unreactive toward dimethyl disulfide, just as is the case for the molecular ion. Hence, the distonic and enol propionate ions (which both must have recombination energies below the ionization energy of dimethyl disulfide) cannot be distinguished using this reaction.

Triethylamine. The most conclusive evidence for the rearrangement of ionized acetates and propionates to their enol isomers was provided by the examination of the reactions of the molecular and reference ions with triethylamine. The ionization energy of this reagent (IE = 7.5 eV) is significantly lower than that of cyclohexanone and dimethyl disulfide.[26a] Hence, charge exchange dominates the reaction of many organic radical cations with triethylamine (e.g., ionized acetone shows predominant and fast charge exchange). Charge exchange is also expected to occur for the enol (but not distonic) forms of ionized esters since they are estimated[16,26a,39] to have recombination energies near 8 eV. For example, electron transfer from the enol isomer of ionized

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[41] (a) Kenttämaa, H. I.; Kiminkinen, L. K. M.; Orlowski, J.; Stirk, K. M. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 734. (b) Stirk, K. M.; Smith, R. L.; Orlowski, J. C.; Kenttämaa, H. I. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 392.

Table 6. Ionic Products from the Reactions of Various Cations with Dimethyl Disulfide (MW 94)

generation of the reactant ion	assumed initial ion structure	*m/z*	*m/z* (ionic products)	branching ratio (%)	k^a	$k_{\text{Coll}}{}^b$	k/k_{Coll}
dissociation of hexanoic acid	$CH_2{=}C(OH)OH^{\bullet+}$	60	94, 96^c	74	1.8	2.0	0.9
			95, 97^c	26			
dissociation of methyl butyrate	$CH_2{=}C(OH)OCH_3{}^{\bullet+}$	74	94, 96^c	100	0.8	1.9	0.4
proton transfer to methyl acetate	$CH_3C(OH)OCH_3{}^+$	75	NR				
dissociation of ethyl butyrate	$CH_2{=}C(OH)OCH_2CH_3{}^{\bullet+}$	88	94, 96^c	100	0.9	1.8	0.5
dissociation of methyl 2-methylbutyrate	$CH_3CH{=}C(OH)OCH_3{}^{\bullet+}$	88	NR				
proton transfer to dimethyl carbonate	$CH_3OC(OH)OCH_3{}^+$	91	NR				
transfer of $C_2H_4{}^{\bullet+}$ to propionic acid	$CH_3CH_2C(OH)OCH_2CH_2{}^{\bullet+}$	102	NR				

[a] Rate constants in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Collision rate[29] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] One of the ions contains ^{32}S and the other one ^{34}S isotope.

Table 7. Ionic Products from the Reactions of the Molecular Ions of Various Esters with Triethylamine (MW 101)

ester	*m/z*	*m/z* (ionic products)	branching ratio (%)	k^a	$k_{\text{Coll}}{}^b$	k/k_{Coll}
methyl formate	60	102	100	1.6	1.6	1.0
methyl acetate	74	101	100	0.4	1.5	0.3
methyl propionate	88	101	58	1.3	1.4	0.9
		102	42			
δ-valerolactone	100	101	100	1.0	1.3	0.8

[a] Rate constant in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Collision rate[29] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.

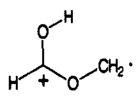
methyl acetate to triethylamine is exothermic[40] by about 10 kcal mol^{-1}. In support of this expectation, charge exchange was observed for all the keto and enol reference ions studied (Tables 7 and 8).

On the other hand, triethylamine is a strong base (proton affinity = 232 kcal mol^{-1})[26a] and should be able to abstract the acidic hydroxyl hydrogen from the distonic and enol ester ions. Facile and exclusive proton transfer indeed occurs upon reaction of triethylamine with the distonic methyl formate radical cation (to yield *m/z* 102: Figure 7A; Table 7) as well as with the enol reference ion of ionized methyl propionate (accompanied by charge exchange; Table 8).

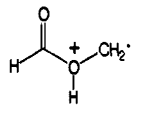
The enol reference ions of the acetates do not transfer a proton to triethylamine: electron transfer is the only reaction observed here. The difference in the reactivity between the enol forms of ionized acetates and propionates may be explained on the basis of the lower recombination energy of the larger propionate ions (see discussion on dimethyl disulfide reactions: the acetate ions undergo electron transfer but the propionate ions do not). Exothermic electron transfer is usually very facile upon low-energy ion–molecule collisions in the gas phase,[34b–e] and the reaction rate constant may even exceed the classical collision rate constant.[34e] On the other hand, proton transfer is limited to collision rate and may not be able to compete with very facile electron transfer. However, the lower recombination energy of the enol propionate ions makes electron transfer to these ions less exothermic than to the acetate ions. Indeed, if electron transfer between triethylamine and the enol form of methyl propionate is actually slightly endothermic, the reaction may still occur (if the endothermicity is less than a few kilocalories per mole) but proton transfer is likely to be able to compete with this reaction.

The results obtained for the reactions of triethylamine with the acetate and propionate molecular ions (Table 7) demonstrate that these molecular ions have the enol and not the distonic structure. The methyl acetate molecular ion shows no proton transfer (a reaction characteristic of a distonic structure) but undergoes exclusive charge exchange with triethylamine, and this reaction occurs at the same rate as for the enol reference ion. The propionate molecular ion shows both charge exchange as well as proton transfer, and the product distribution as well as the reaction rate are identical to those measured for the corresponding enol reference ion (Tables 5 and 6).

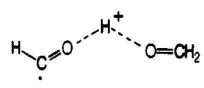
Alternative Ion Structures. In the earlier[13] mass spectrometry studies on ionized methyl formate, three alternative structures to the keto form were considered: the distonic form (A; see below; ΔH_f = 164 kcal mol^{-1}), the ylide ion $HC(O)(OH^+)CH_2{}^{\bullet}$ (**B**; ΔH_f = 173 kcal mol^{-1}), and the hydrogen-bridged radical cation $^{\bullet}CH{=}O{\cdot\cdot}H^+{\cdot\cdot}O{=}CH_2$ (**C**; ΔH_f = 163 kcal mol^{-1}).[14] The experimental results discussed here do not support a hydrogen-bridged structure $^{\bullet}CH{=}O{\cdot\cdot}H^+{\cdot\cdot}O{=}CH_2$: this ion should show facile replacement of $CHO^{\bullet}$ by neutral reagents such as cyclohexanone, in accordance with the reactivity observed[20] for the higher homolog $CH_3C^{\bullet}{=}O{\cdot\cdot}H^+{\cdot\cdot}O{=}CH_2$ and for other loosely bonded ions.[4] However, such replacement reactions were not observed. The possible formation of the ylide ion (**B**) cannot be ruled out on the basis of the results discussed here. However, generation of this ion is highly unlikely due to its relatively high heat of formation. The ylide ion has been calculated to lie 22 kcal mol^{-1} higher in energy than the distonic ion $HC(OH)OCH_2{}^{\bullet+}$, and its formation from the molecular ion has been estimated to require 38–44 kcal mol^{-1}.[15]



A

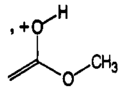


B

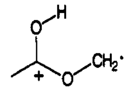


C

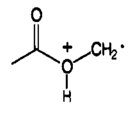
While the enol form of ionized methyl acetate (**D**) was ruled out by the earlier investigators, three nonconventional structures (see below) have been considered[18] as possible intermediates during fragmentation of ionized methyl acetate. Besides the distonic ion (**E**), these include the ylide ion $CH_3C(O)(OH^+)CH_2{}^{\bullet}$ (**F**) and the hydrogen-bridged complex $CH_3C^{\bullet}{=}O{\cdot\cdot}H^+{\cdot\cdot}OCH_2$ (**G**). Again, formation of the ylide ion from the low-energy, long-lived methyl acetate radical cation is highly unlikely: the isomerization of ionized methyl acetate to the ylide ion (higher in energy by about 3 kcal mol^{-1}) has an estimated barrier of 30–45 kcal mol^{-1}.[18] Moreover, the reactivity observed for ionized methyl acetate for example with 2-propanol-d_8, rules out a distonic structure for this ion (distonic ions were not found to abstract a deuterium atom from this neutral reagent). While the hydrogen-bridged ion, $CH_3C^{\bullet}{=}O{\cdot\cdot}H^+{\cdot\cdot}OCH_2$, may be generated from the internally activated, fragmenting methyl acetate molecular ions, this ion is not formed from the long-lived, low-energy molecular ions, as evidenced by the absence of replacement reactions. This hydrogen-bridged ion was recently



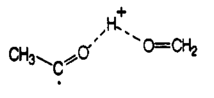
D



E



F



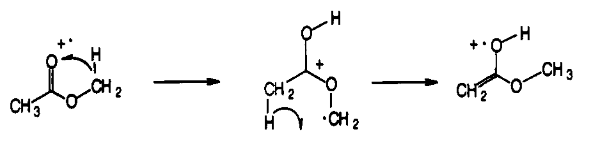
G

Table 8. Ionic Products from the Reactions of Various Cations with Triethylamine (MW 101)

generation of the reactant ion	assumed initial ion structure	m/z	m/z (ionic products)	branching ratio (%)	k^a	$k_{\mathrm{Coll}}{}^b$	k/k_{Coll}
dissociation of methyl butyrate	$CH_2{=}C(OH)OCH_3{}^{\bullet+}$	74	101	100	0.5	1.5	0.3
dissociation of ethyl butyrate	$CH_2{=}C(OH)OCH_2CH_3{}^{\bullet+}$	88	101	100	0.4	1.4	0.3
dissociation of methyl 2-methylbutyrate	$CH_3CH{=}C(OH)OCH_3{}^{\bullet+}$	88	101	58	1.1	1.4	0.8
			102	42			

[a] Rate constant in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Collision rate[29] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.

Scheme 8



demonstrated[20] to undergo replacement of the acetyl radical for example with cyclohexanone.

Isomerization Mechanisms. Isomerization of the ester radical cations does not occur via *intermolecular* hydrogen transfer within the collision complex with the neutral reagent molecules. The lactone molecular ions can only isomerize via an intermolecular hydrogen transfer since the ring structure prohibits intramolecular hydrogen transfer. These ions are stable toward isomerization. It is concluded that isomerization of the acyclic ester radical cations must occur by intramolecular hydrogen transfer. This isomerization is likely to occur *prior to* the formation of the collision complex with neutral reagent molecules because facile proton transfer rather than charge exchange occurs with reagents such as cyclohexanone and triethylamine. Most exothermic electron transfer reactions involving a long-lived collision complex of an organic radical cation proceed at or near the collision rate in the gas phase.[7,34b-e] This is true, for example, for collisions of ionized phosphorus esters[7] and various other organic radical cations with different neutral molecules,[4,6,31a,41] and was demonstrated here to apply to collisions of the molecular ions of cyclic carbon esters and to the enol forms of ionized carbon esters with the neutral molecules used as ion structural probes. Hence, it is highly unlikely that a complete isomerization could occur for the entire molecular ion population of the acyclic esters within the ion–molecule complex before any electron transfer takes place.

In most of the experiments discussed here, the ester ions were collisionally cooled prior to examining their ion–molecule reactions (see the Experimental Section). This cooling process does not cause the isomerization, as demonstrated by the observation of the same product ions for cooled ions and for ions which were not collisionally cooled. The ion lifetimes in the experiments discussed here are probably long enough (from 100 ms to several seconds) to allow substantial cooling to occur through emission of light[42] even in the absence of collisional cooling. Because of these two cooling processes, ions which can undergo isomerization are likely to relax to the lowest-energy structure. This is an important difference between the present study and those carried out earlier in sector tandem mass spectrometers: ions in these devices cannot lose energy through these two mechanisms.

In order to examine which hydrogen atom is transferred to the carbonyl oxygen upon isomerization of ionized acetates and propionates, the partially labeled molecular ions of methyl acetate, $CH_3C(O)OCD_3$, and methyl propionate, $CH_3CH_2C(O)OCD_3$, were studied. The ionized, partially labeled methyl acetate reacts with cyclohexanone mostly by deuterium transfer. This result suggests that a major part of the isomerization does not occur by a [1,3]-hydrogen shift but by two consecutive [1,4]-hydrogen shifts via a distonic intermediate (Scheme 8), a mechanism in agreement with that proposed[23] earlier for the equilibration of the highly excited, short-lived ions prior to dissociation.

The ionized, partially labeled methyl propionate ($CH_3CH_2COOCD_3$) predominantly transfers a proton to cyclohexanone. This finding suggests that a different isomerization mechanism predominates for this ion. Indeed, it was proposed[17] earlier that the partial rearrangement of the short-lived methyl propionate molecular ions to a distonic form occurs via transfer of a hydrogen from the acid and not the alcohol moiety. Accordingly, the isomerization of the long-lived propionate ester ions to the enol form is most likely initiated by a [1,4]-hydrogen shift from the β-carbon of the acid moiety to generate the distonic ion A (Scheme 9). This transfer is followed by a [1,5]-hydrogen shift to form another distonic ion intermediate B which is unstable toward a final [1,4]-hydrogen shift from the α-carbon to the radical site on the alcohol moiety to generate the enol structure (Scheme 9). It should be noted that the experimental results discussed here do not unambiguously exclude a direct [1,3]-hydrogen shift. However, [1,3]-hydrogen shifts in radical cations are unfavorable and are usually associated with high energy barriers (see discussion above).

Conclusions

Most mass spectrometric studies on gaseous radical cations deal with short-lived species. However, the examination of the long-lived ions is necessary in order to know whether the structure of organic molecular ions is maintained over time. This study shows that the structures of the low-energy, long-lived gaseous ester radical cations are different from those of the short-lived ions, independent of whether or not the ions are collisionally cooled. Further, the long-lived acetate radical cations have different structures in the gas phase and in frozen matrices.

Ion–molecule reactions can be used to distinquish between isomeric ester radical cations. The reagents found to be most useful include cyclohexanone, which allows the distinction between the keto forms of ester radical cations (charge exchange) from the enol and distonic forms (proton transfer), and triethylamine, which can be used to distinguish the distonic isomers (proton transfer) from the enol and keto forms (predominant charge exchange). The use of 2-propanol-d_8 is another way to carry out this distinction (only ions with hydroxyl groups were found to react by H/D exchange). The enol forms of ionized methyl and ethyl acetates can be conclusively identified by using this reagent alone since these ions, as the only ions studied, showed both H/D exchange as well as deuterium atom abstraction upon reaction with 2-propanol-d_8.

Examination of ester ions with the reagents discussed above shows that the long-lived, low-energy molecular ions of unsubstituted lactones are stable toward isomerization in the gas phase. However, all the acyclic ester ions studied were found to isomerize to the lowest energy isomer (a distonic ion or an enol form if one exists), including those ester ions which were generated by near-thermoneutral chemical ionization. The isomerization is likely to occur unimolecularly (not within a collision complex with the neutral reagents used to collisionally relax the ions or to examine their structures), and it seems to be complete under the experimental conditions used here. Partial isomerization to distonic ions has been reported to occur for some of these gaseous molecular ions in sector mass spectrometers.[13,17] The differences between the results presented earlier using sector mass spectrometers and those obtained in this work using FT/ICR may be explained on the basis of the different experimental conditions used in these studies. Under conditions wherein collisional cooling was not allowed to occur in the FT/ICR, the most significant

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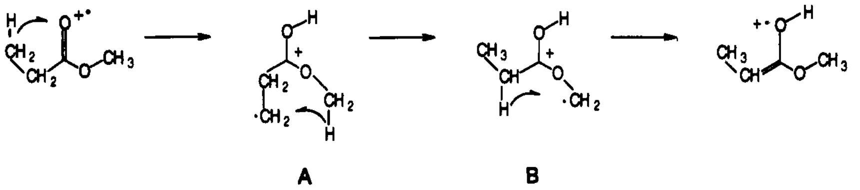
[42] See, for example: Huang, F.-S., Dunbar, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 6497.

Scheme 9



difference in the experimental conditions is the different time scale. If the isomerization reactions are slow relative to the microsecond time frame, only partial isomerization is expected to be observed in sector mass spectrometers. In the FT/ICR, the ions have a longer lifetime which allows a more complete isomerization. Furthermore, even in the absence of collisional cooling, the isomerizing ions can lose energy through emission of light. This process, just like collisional cooling, is likely to relax any isomerizing ions into the lowest energy structure. This is not the case for the ions studied in sector mass spectrometers.

In agreement with the conclusions made earlier concerning the mechanism of the isomerization of the long-lived ions in frozen matrices,[9] the radical cations of dimethyl carbonate and the formates were found to rearrange via a [1,4]-hydrogen shift to the carbonyl oxygen. However, the gaseous acetate and propionate radical cations isomerize via one or several distonic intermediates to their *enol* forms. This finding contrasts the conclusions made on the basis of ESR studies[10] that the acetate radical cations isomerize to a distonic form in frozen matrices. The enol isomer may not be accessed in frozen matrices because of rapid collisional cooling of the internally excited distonic intermediate with the surrounding matrix molecules before further rearrangement occurs (the collision rate in FT/ICR is significantly lower). However, it must be noted that the interpretation of the ESR spectra of ester radical cations is not always straightforward,[9-11] and also that the results obtained may be affected by the solvent used since strong radical–matrix interactions have been reported for ester radical cations.[10a]

The spontaneous rearrangement reactions observed for ester radical cations generated by near-thermoneutral charge exchange suggest that the barriers for isomerization of the keto form to the distonic intermediate and especially the further isomerization of the distonic ion to the enol form are likely to be significantly lower than previously proposed.[18,21] In support of this conclusion, the distonic isomers of the ionized acetates and propionates were found to partially isomerize to the enol structure.

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