in that the spectral distortions induced by the quadrupole echo were not considered. In both of these papers it was stated that fast limit spectra are observed when the hopping rate exceeds $\sim 10^5$ s^{-1}. The spectra in Figure 3 above illustrate that because of echo distortions rates $\geq 10^7$ s^{-1} are required to obtain such spectra. It is also clear from Figure 3 that echo distortions lead to intermediate exchange spectra with "pseudo"-rigid-lattice features—e.g., both strong perpendicular edges as well as a fast limit-$D/4$ splitting—and the distorted line shapes appear to be (but are not) a superposition of mobile and immobile rings. It is possible to obtain reasonable simulations of such spectra by superimposing rigid lattice (Figure 2A) and fast limit (Figure 2C) line shapes in varying proportions, implying that both mobile and immobile rings are present. This procedure was recently employed to analyze the ^2H spectra of phenylalanine side chain labeled bacteriorhodopsin[29] and is incorrect. We find that the ^2H spectra for both crystalline phenylalanine-d_5·HCl and phenylalanine-d_5 labeled bacteriorhodopsin can best be simulated by assuming a single jump rate for all rings, and that the "pseudo"-rigid-lattice features result from echo distortions.[22]

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Noncompeting Metastable Losses of Methyl and Ethylene from Gaseous Butanoic Acid Ions due to Isomerization Prior to Methyl Loss

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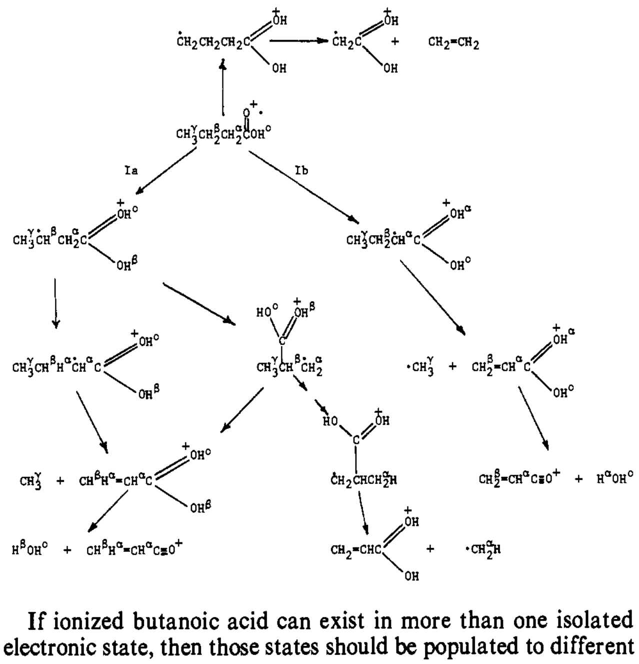
Abstract: Metastable $C_4H_8O^{+\cdot}$ ions obtained from butanoic acid and ethyl butanoate undergo considerable γ-hydrogen exchange prior to losing ethylene, but little exchange prior to losing methyl. Therefore the two fragmentations are not directly competing, contrary to the general assumption that all reactions of an ion in the gas phase are competitive. It is concluded that metastable butanoic acid ions which lose methyl isomerize essentially irreversibly to $CH_3CH_2\dot{C}HC(OH)_2^+$ and/or $CH_3CH(\dot{C}H_2)C(OH)_2^+$ before the γ-methyl becomes exchanged. This accounts for the difference between γ-hydrogen exchange prior to the loss of methyl and ethylene without invoking isolated electronic states, as previously proposed. Butanoic acid ions generated by the McLafferty rearrangement of butanoate esters have a much weaker metastable loss of ethylene than directly ionized butanoic acid. Collisional activation experiments demonstrate that this results from more of the butanoic acid ions derived from ethyl butanoate than from butanoic acid isomerizing prior to collision. Variation in internal energy probably causes this difference in degree of isomerization with the source of the ion.

Metastable butanoic acid ions in the mass spectrometer lose the γ-methyl with very little hydrogen exchange, while ethylene lost containing the same carbon is highly exchanged.[1] Therefore, the two decompositions must occur from different populations of ions. This is surprising, since both fragmentations take place from ions with the same initial structure, and all metastable decompositions occur in approximately the same time frame. The apparent lack of competition between the losses of methyl and ethylene is of interest because it is generally assumed that the fragmentations of a given ion at a given internal energy are directly competing.[2] For this reason, decomposition from different electronic states has been proposed to account for the difference in the degree of exchange accompanying the two metastable decompositions.[1a]

It has previously been concluded from the decomposition patterns of deuterium-labeled ions that the metastable butanoic acid ion loses ethylene by the McLafferty rearrangement, the γ-methyl following what appeared to be a 1,3-hydrogen shift to form $CH_3CH_2\dot{C}HC(OH)_2^+$, and methyl containing the α-hydrogens (Scheme I).[1,3] Symmetry-forbidden 1,3-hydrogen shifts are generally unfavored processes in gaseous ions,[4] making path Ib unusual. At higher energies, methyl loss occurs following transfer of a β-hydrogen to oxygen and transfer of an α-hydrogen to the β-carbon (Scheme I, path Ia).[1]

Scheme I



If ionized butanoic acid can exist in more than one isolated electronic state, then those states should be populated to different

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Table I. Unimolecular Metastable and Collisionally Activated Decompositions of $C_4(H,D)_8O_2^{+\cdot}$ Ions

			species lost							
ion	source	mode	CH_3	CH_2D	CHD_2	CD_3	C_2H_4	C_2H_3D	$C_2H_3D_2$	C_2HD_3
$CH_3CH_2CH_2CO_2H^{+\cdot}$	$CH_3CH_2CH_2CO_2H$	Uni	100				32 (61)[a]			
		CA	31				100			
$CH_3CH_2CH_2CO_2H^{+\cdot}$	$CH_3CH_2CH_2CO_2CD_2CH_3$	Uni	100				2 (4)[a]			
		CA	100				30			
$CH_3CH_2CD_2CO_2H^{+\cdot}$	$CH_3CH_2CD_2CO_2H$	Uni	100	4	40		60	12	3	
		CA	17		6		100	9	7	
$CH_3CH_2CD_2CO_2H^{+\cdot}$	$CH_3CH_2CD_2CO_2CD_2CH_3$	Uni	100	4	45		2	2	1	
		CA	100	2	38		32	11	4	
$CD_3CH_2CH_2CO_2H^{+\cdot}$	$CD_3CH_2CH_2CO_2H$	Uni	21	6	9	100	3	24	20	2
		CA	8	4	3	27	2	30	100	18
$CD_3CH_2CH_2CO_2H^{+\cdot}$	$CD_3CH_2CH_2CO_2CH_2CH_3$	Uni	19	*b*	*b*	100		1	2	
		CA	12	*b*	<1	100		3	12	
$CH_3CH_2\dot{C}DC(\overset{+}{O}H)_2$	$(CH_3CH_2)_2CDCO_2H$	Uni	100	6			1			
		CA	100	2			1			
$CD_3CH_2\dot{C}HC(\overset{+}{O}H)_2$	$CD_3CH_2CH(CO_2H)C_3H_7$	Uni	5			100			1	
		CA	2			100			1	

[a] C_2H_4 values obtained on a DuPont Model 21-491. [b] ≤5; could not be measured accurately due to interference and noise.

Scheme II

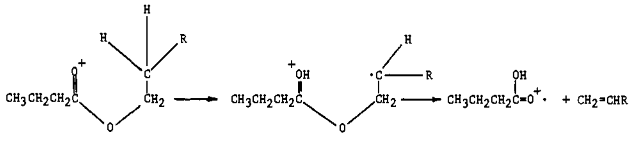

Table II. Metastable Decompositions of $C_2H_4O_2^{+\cdot}$ Ions

source	ion	$-H_2O$	$-OH$	$-CH_3$
$CH_3CD_2CH_2CO_2CH_2CH_3$	$\dot{C}H_2C(OH)_2^+$	100	26	4
$CH_3CH_2CH_2CO_2H$	$\dot{C}H_2C(OH)_2^+$	100	28	5
CH_3CO_2H	$CH_3CO_2H^{+\cdot}$	50	100	41

degrees when the ion is prepared from different sources. An alternate source of butanoic acid ions is the McLafferty rearrangement of ionized butanoate esters (Scheme II). McLafferty rearrangements normally have activation energies consistent with the heats of formation of the products of the reactions,[5] so such products must generally be in their ground electronic states. We here compare the metastable and collisionally activated (CA) decompositions of $CH_3CH_2CH_2CO_2H^{+\cdot}$ ions generated by McLafferty rearrangement of butanoate esters to those of directly ionized butanoic acid to further explore why the metastable losses of methyl and ethyl from the butanoic acid ion do not directly compete.

Results

Unlabeled and deuterium-labeled butanoic acids and ethyl butanoates (Scheme II) were used to generate the corresponding butanoic acid ions. Ethyl-*1,1-d*$_2$ butanoate was used to generate $CH_3CH_2CH_2CO_2H^{+\cdot}$ to guard against interference from the ca. 6 times more abundant $CH_3CH_2OC(=O^+H)\dot{C}H_2$ ion (based on spectra of labeled esters) in the spectrum of ethyl butanoate. The relative intensities of the metastable and CA losses of methyl and ethylene from a variety of $C_4H_8O_2^{+\cdot}$ ions and some deuterated forms thereof are presented in Table I. As observed previously,[1] there is considerably more exchange of the γ-carbon of butanoic acid prior to the loss of ethylene than of methyl. This is also true of ions generated by the loss of ethylene from the ethoxy group of ethyl butanoate. However, the metastable losses of ethylene from the ions obtained from the esters are much weaker than the same processes from directly ionized butanoic acids.

For comparisons of ions generated from butanoic acid and its ethyl esters to be valid, the butanoic acid ion must be formed by the loss of the ethoxy ethylene from ionized ethyl butanoate. Several pieces of evidence demonstrate that the loss of the ethylene from the ethoxy group of ionized ethyl butanoate gives the butanoic acid ion. The strong $C_2H_4O_2^{+\cdot}$ and $C_3H_5O_2^{+\cdot}$ ions in the spectrum of ethyl butanoate have characteristics which match those of the corresponding ions generated from butanoic acid. Metastable $C_2H_4O_2^{+\cdot}$ undergoes a strong loss of water, a weaker loss of OH, and a still weaker loss of CH_3. This matches the pattern for the enolic $C_2H_4O_2^{+\cdot}$,[6] while the acetic acid ion, which would be formed from $CH_3CH_2OC(=O^+H)\dot{C}H_2$ by a second McLafferty rearrangement, undergoes relatively stronger losses of OH and CH_3 (Table II). The $C_3(H,D)_5O_2^+$ ions formed from the esters lose water predominantly containing the β-hydrogen upon metastable and collision-induced decomposition (Table III), as do the corresponding ions formed from butanoic acid[1] (see Scheme I). The $C_3(H,D)_5O_2^+$ ions formed from each of the ethyl butanoates had predominantly (ca. 80%) the deuterium content expected for formation of that ion via the butanoic acid ion. Thus, both $C_2H_4O_2^{+\cdot}$ and $C_3H_5O^{+\cdot}$ must be formed from ethyl butanoate predominantly via the butanoic acid ion, demonstrating that ion is formed from ethyl butanoate.

$C_3H_3D_2O_2^{+\cdot}$ formed by the metastable loss of methyl from ionized $CH_3CD_2CH_2CO_2H^{+\cdot}$ lost HDO at least 12 times as often as it lost H_2O, contrary to a previous report[1a] that the product of this metastable decomposition lost H_2O 3 ± 1 times as often as it lost HDO. $C_3H_3D_2O^{+\cdot}$ produced by metastable decomposition of the same ion obtained from $CH_3CD_2CH_2CO_2C_2H_5$ lost HDO 2.4 times as often as it lost H_2O.

Discussion

Isomerization of Butanoic Acid Ions and the Loss of Methyl. The similarity of the terminal (CD_3 from *4,4,4-d*$_3$ ions, CH_3 from *2,2-d*$_2$ ions) and interior (CH_3 from *4,4,4-d*$_3$ ions, CHD_2 from *2,2-d*$_2$ ions) methyl loss patterns between labeled butanoic acid ions from the two sources (Table I) indicates that the pathways to methyl loss (Scheme I) are the same from butanoic acid ions from both sources. This is confirmed by the dominant loss of $H^{\beta}OH^{0}$ decompositions of $C_3H_3D_2O_2^{+\cdot}$ ions formed in the ion source from both labeled butanoic acid[1] and ethyl butanoates

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Table III. Decompositions of $C_3H_3D_2O_2^{+\cdot}$ Ions Generated from Ethyl Butanoates

source	butanoic acid ion	CA		metastable	
		$-H_2O$	$-HDO$	$-H_2O$	$-HDO$
$CH_3CD_2CH_2CO_2CH_2CH_3$	$CH_3CD_2CH_2CO_2H^{+\cdot}$	29	100	35	100
$CH_3CH_2CD_2CO_2CH_2CH_3$	$CH_3CH_2CD_2CO_2H^{+\cdot}$	100	15	100	5

(Table III). However, the ratio –ethylene/–methyl differs 16-fold between the metastable spectra of ionized butanoic acid and $C_4H_8O_2^{+\cdot}$ from ethyl-*1,1-d_2* butanoate. The corresponding ratio in the CA spectra decreases from 3.22 to 0.30. The drastic differences between the CA spectra demonstrate that the $C_4H_8O_2^{+\cdot}$ ions from the two sources have structural differences by the time they reach the field free region where the decompositions take place.[7] Since these ions are formed with the same initial structure (see Results), a much larger fraction of the ions from one source than of the ions from the other must isomerize prior to collision.

Loss of the terminal methyl from ionized butanoic acid follows enolization and probably some $CH_3CH(\dot{C}H_2)C(OH)_2^+$ formation (Scheme I).[1,3] The weak losses of ethylene from the butanoic acid ion obtained from ethyl butanoate are consistent with the conclusion that the major fraction of these ions rapidly isomerize to the enol ion, and/or $CH_3CH(\dot{C}H_2)C(OH)_2^+$,[1,3] since the enol ion loses very little ethylene upon unimolecular or CA decomposition (Table I), and ionized α-methyl propanoic acid, which decomposes predominantly via $CH_3CH(\dot{C}H_2)C(OH)_2^+$, loses methyl 100 times as often as it loses ethylene.[8]

Assuming that the CA losses of methyl take place from isomerized ions which do not return to the butanoic acid structure, that ethylene losses occur from ions which have not so isomerized, and that the cross sections for the CA methyl and ethyl losses from the respective structures are identical leads to the conclusion that directly ionized butanoic acid was 24% isomerized to the intermediates from which methyl was lost prior to collision. Similar calculations indicate that 77% of the ions obtained from ethyl butanoate were so isomerized. Applying the same assumptions to the metastable decompositions gives 76% and 98% isomerization, respectively, for ions containing enough energy to undergo metastable decomposition.

The isomerization of some butanoic acid ions to enol and/or other ions which subsequently lose methyl but very little ethylene provides an explanation other than an isolated electronic state for the difference in hydrogen exchange prior to the loss of methyl and ethyl from those ions. Ions which lose methyl isomerize essentially irreversibly before appreciable exchange has taken place. Ions which ultimately lose ethylene exchange hydrogens between the γ-carbon and the oxygen, but few of them isomerize to the enol ion. Very few enol or $\dot{C}H_2CH(CH_3)C(OH)_2^+$ ions return to the butanoic acid structure after being formed from it (see above). Other cases of partial isomerization leading to hydrogen exchange prior to some slow decompositions of an ion but not others have been reported. Ionized cyclohexanol[9a] and 1-methylcyclopentene[9b] decompose partially with and partially without prior ring opening. Substantial hydrogen interchange occurs only in the ring-opened ions.

Contrary to a previous report,[1a] $C_3H_3D_2O_2^{+\cdot}$ formed from metastable $CH_3CD[_2CH_2CO_2H^+$ loses predominantly HDO rather than H_2O upon collision. This demonstrates that metastable methyl loss from ionized butanoic acid occurs following the shift of a β-hydrogen to oxygen, as is true for higher energy methyl losses (Scheme I, path Ia).[1b] This revision leaves no evidence that an isolated electronic state is involved in the metastable decompositions of the butanoic acid ion. As is generally observed,[4a] 1,4-hydrogen shift involving the carbonyl oxygen occurs to the exclusion of a potential 1,3 shift.

Ion Internal Energy and the Metastable Decompositions of the Butanoic Acid Ion. The 50-fold dominance of the loss of methyl in the metastable decompositions of butanoic acid ions formed from ethyl butanoate is surprising, since the activation energy for ethylene loss is 60 meV lower than that for methyl loss,[10] and ethylene is lost about five times as often as methyl from high-energy butanoic acid ions.[1b] Therefore loss of ethylene should be favored over loss of methyl from butanoic acid ions at all energies. The 16-fold difference between the relative rates of methyl and ethylene loss from the mestastable butanoic acid ions from the two sources is also much larger than is generally observed under identical instrumental conditions for ions with the same initial structure.[11] Variations in such rates have previously been attributed to differences between the internal energy distributions of the populations of ions undergoing metastable decomposition.[12] The conclusion that the losses of methyl and ethylene are not directly competing by the time the metastable decompositions occur provides an explanation for both the dominance of the methyl losses and the differences in the ratios of the rates of the metastable decompositions as a function of the sources of the butanoic acid ions.

The lower activation energy for ethylene loss suggests that most metastable butanoic acid ions which undergo exchange at the γ-carbon and lose ethylene contain too little energy to lose methyl in the time of metastable decomposition. Butanoic acid ions with enough energy to lose methyl either isomerize or decompose by loss of ethylene too rapidly to contribute substantially to the metastable loss of ethylene. This picture is consistent with the lack of hydrogen exchange in ethylene lost from ionized butanoic acid in the ion source.[13] More isomerized ions which lose methyl exist than ions which lose ethylene by the time ions reach the field free region where metastable decomposition takes place.

The preceding explanation implies that more metastable butanoic acid ions containing sufficient energy to isomerize are obtained from ethyl butanoate than from butanoic acid, since directly ionized butanoic acid has the much more intense ethylene loss. The higher energy content of butanoic acid ions obtained from the esters could be caused by competition from lower energy processes with butanoic acid ion formation from ionized ethyl butanoate. The heat of formation of the butanoic acid ion is about 18 kcal mol^{-1} above that of $CH_3CH_2OC(=O^+H)\dot{C}H_2$,[5] so formation of the latter ion should be strongly favored over that of the butanoic acid ion near the threshold for butanoic acid ion formation. This would raise the average internal energy of the butanoic acid ions formed from ethyl butanoate,[14] causing more of those ions to either rearrange to the enol isomer, or to decompose prior to reaching the field free region where metastable decomposition takes place.

Experimental Section

Results were obtained on a Kratos MS 50 TA mass spectrometer. Metastable and CA decompositions were recorded between the magnet and second electric sector. All results are reported based on peak heights.

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CA spectra of the products of metastable decomposition were obtained by lowering the voltage of the first electric sector and the magnetic field to pass the products of metastable decompositions in the first field free region, colliding those ions in the third field free region and scanning the voltage of the second electric sector. Helium was used as the CA gas at a pressure of $1 \pm 0.1 \times 10^{-6}$ torr at the vacuum wall outside the collision chamber. Experiments were carried out at an electron energy of 70 eV and an ion source temperature of 200 °C.

Ethyl-*1,1*-d_2 butanoate was prepared by reaction of ethanol-*1,1*-d_2 with butanoyl chloride. The former compound was prepared by reducing acetic anhydride with $LiAlD_4$. Butanol-*4,4,4*-d_3, available from an earlier study,[15] was oxidized to butanoic-*4,4,4*-d_3 acid with $Na_2Cr_2O_7/H_2SO_4$ and converted to the acid chloride with excess $SOCl_2$ and to the ethyl ester with ethanol. Butanoic-*2-2*-d_2 acid was prepared by reduction of propanoic acid with $LiAlD_4$, conversion to the bromide with HBr/H_2SO_4, and carbonation of the Grignard reagent. Butanoic-*3,3*-d_2 acid was prepared by treatment of ethanol-*1,1*-d_2 with HBr/H_2SO_4, followed by Grignard homologation with ethylene oxide. The resulting butanol-*3,3*-d_2 was oxidized with $Na_2Cr_2O_7/H_2SO_4$. The acids were converted to the esters as described above.

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The Role of Ligand π-Donation in Electron-Deficient Organometallic Group 6 Complexes

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Abstract: Molecular orbital descriptions for six monomeric molybdenum complexes are presented as derived from extended Hückel calculations. The six model compounds were chosen to reflect the electronic features of both molybdenum and tungsten compounds of the types $M(CO)(RC{\equiv}CR)(S_2CNR'_2)_2$, $M(CO)(RC{\equiv}CR)(\pi\text{-}C_5H_5)(R')$, $M(O)(RC{\equiv}CR)(S_2CNR'_2)_2$, $M(RC{\equiv}CR)_2(S_2CNR'_2)_2$, $M(CO)_2(OR)_2L_2$, and $M(CO)_2(S_2CNR_2)_2$. Each of these compounds is formally electron deficient with respect to the effective atomic number rule based on common electron bookkeeping procedures. The role of ligand π-donation in destabilizing the LUMO, which would be filled for analogous compounds obeying the inert gas formalism, is identified as a common phenomena which links each of these compounds to this single concept and accounts for their seemingly anomalous stability when compared to other coordinatively unsaturated group 6 carbonyl monomers.

Introduction

The majority of the numerous molybdenum(II) and tungsten(II) carbonyl complexes reported in the literature to date adhere to the effective atomic number (EAN) rule. Coordination of seven two-electron donor ligands to the central d^4 metal ion is typical and produces a total of 18 metal valence electrons in accord with expectations based on the inert gas formalism. Drew's comprehensive review of seven coordination, published in 1977, lists more than 100 seven-coordinate molybdenum(II) and tungsten(II) carbonyl derivatives.[1]

Recently several six-coordinate molybdenum(II) and tungsten(II) carbonyl derivatives have been reported, and in cases where six two-electron donor ligands constitute the complete coordination sphere of a d^4 ion this produces a total of only 16 electrons in the metal valence shell. Such complexes would be expected to be highly electrophilic and display reactivity patterns typical of coordinatively unsaturated metal compounds. Experimental results are inconsistent with this simple scheme when an alkyne is one of the six ligands coordinated to Mo(II) or W(II).[2] The concept of four-electron donation from an alkyne ligand to a single metal center has been set forth by McDonald and coworkers based on EAN considerations and the observed reactivity, or lack thereof, of $M(CO)(RC{\equiv}CR)(S_2CNR'_2)_2$ (M = Mo or W) compounds.[3] An empirical correlation between C-13 NMR chemical shifts for metal-bound alkyne carbons and the extent of electron donation to molybdenum or tungsten has been published.[4]

This article describes bonding interactions accessible to metal–alkyne moieties based on extended Hückel molecular orbital (EHMO) calculations, and as a consequence places the two-electron vs. four-electron question in perspective on a continuum molecular orbital basis. The resultant bonding picture provides information about the geometrical preferences exhibited by nonlinearly ligating (or single-faced π) alkyne ligands and predicts surprisingly accurate quantitative barriers for alkyne rotation processes.

Two additional six-coordinate molybdenum(II) carbonyl derivatives are considered in detail in the second part of this study. The trigonal prismatic structure reported for the coordinatively unsaturated $Mo(CO)_2(S_2CNPr^i_2)_2$ compound[5] suggested that electronic factors were dictating the geometry of this six-coordinate d^4 complex, and indeed the octahedral structure of the 18-electron nitrosyl analogue, $Mo(NO)_2(S_2CNEt_2)_2$,[6] confirms this hypothesis. A molecular orbital description of this carbonyl complex has been generated from EHMO calculations and guided us to the conclusion that, as was the case for the metal–alkyne complexes, the role of ligand π-donation is crucial to the stability of this formally electron deficient molybdenum(II) carbonyl complex and is also

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