Consequences of Charge Reversal in Gaseous Alkoxide Ions. Oxenium Ions

Maurice M. Bursey,† J. Ronald Hass,* Donald J. Harvan, and Carol E. Parker

Contribution from the Environmental Chemistry Branch,
National Institute of Environmental Health Sciences, P.O. Box 12233,
Research Triangle Park, North Carolina 27709. *Received July 25, 1978*

Abstract: Positive-ion collision-induced decomposition (CID) mass-analyzed ion kinetic energy (MIKE) spectra of alkoxide anions were compared with the CID MIKE spectra of $CH_2{=}OH^+$, $CH_3CH{=}OH^+$, $CH_3OCH_2^+$, $(CH_3)_2CHOH^+$, $CH_3(CH_2)_2OH^+$, $C_2H_5OCH_2^+$, and $CH_3CH{=}OCH_3^+$, which were previously identified as the major stable forms of CH_3O^+, $C_2H_5O^+$, and $C_3H_7O^+$. The ions formed on charge reversal of methoxide, ethoxide, *n*-propoxide, and isopropoxide are not the same as the previously established stable positive ions. If these CID reactions are fast as previously claimed, there should be minimal rearrangement and the new ions are members of a series with electron-deficient oxygen, oxenium ions, analogous to carbenes and nitrenes.

Formation of gaseous alkoxy ions RO^+ has been of much recent interest. Although attempts to observe such ions for evaluation of their thermochemistry have been made by several workers, results of these experiments have been viewed with suspicion by their authors.[1-4] One test of ion structure, fragmentation induced by collisions with neutral gas molecules, produced data to support this suspicion: $C_2H_5O^+$ generated by fragmentation of $C_2H_5OC_2H_5^+$ is not $CH_3CH_2O^+$ by the time the collision-induced decomposition (CID) is performed, but is $CH_3CH{=}OH^+$.[5] Two successful attempts at generating RO^+ ions from positive ions have been reported. One involved decomposition of the molecular ions of alkyl nitrates:[6]

$$RCH_2ONO_2^{+\cdot} \rightarrow RCH_2O^+ + NO_2\cdot \tag{1}$$

Evidence of methoxy cation structure was the difference in the intensity ratio of the $(M - NO_2)^+$ and $(M - H_2NO_2)^+$ ions for RCH_2O^+ ions and $RCHOH^+$ ions generated by the equation

$$R_2CHOH^{+\cdot} \rightarrow R\cdot + RCH{=}OH^+ \tag{2}$$

Parent and daughter ions were not connected by a metastable peak. This leaves doubt about the origin of the $(M - H_2NO_2)^+$ ion, but it can be argued that a metastable ion is not expected because of a facile 1,1 loss of hydrogen from CH_3O^+ with a low activation barrier. Further support for the mechanism came from the mass spectrum of $CH_3CD_2ONO_2$, in which both $(M - NO_2)^+$ and $(M - D_2NO_2)^+$ were observed.[6]

The second study involved addition of a hydrogen molecule to the formyl ion, as in the equation

$$H_2 + HCO^+ \rightleftarrows CH_3O^+ \tag{3}$$

which has a $\Delta H_f°$ of 3.9 kcal/mol and cannot correspond to an addition across the CO bond to form $CH_2{=}OH^+$; that process would be much more exothermic.[7]

Interest in RO^+ ions as a problem to be studied by theoretical tools has been promoted by these investigations. Both the structure of CH_3O^+ and its intramolecular conversion to $CH_2{=}OH^+$ have been studied. According to MINDO calculations, singlet CH_3O^+ is not a minimum on the potential surface.[8] The ground state of CH_3O^+, from RHF/STO-3G calculations, is a triplet,[9] like that of OH^+.[10] However, formation of CH_3O^+ from H_2 and HCO^+ in a reversible equilibrium suggests a loose complex for the structure,[11] and calculations at the STO-3G and RHF/4-31G levels support a bound structure for $H_2\cdot HCO^+$ (C_{2v}).[9] The relative stability of CH_3O^+ with respect to rearrangement to $CH_2{=}OH^+$ has been ascribed to the forbiddenness of the conversion of triplet CH_3O^+ to singlet $CH_2{=}OH^+$,[9] or a high barrier to conversion of $H_2\cdot HCO^+$ to $CH_2{=}OH^+$.[9] Other arguments based on symmetry have also been advanced.[6]

Among the processes which gaseous ions undergo after collisions with neutrals are decompositions (eq 4)[12] and charge stripping (eq 5) [13,14]

$$A\text{-}B^{2+} + N \rightarrow A^+ + B + N \tag{4}$$

$$A\text{-}B^+ + N \rightarrow A - B^{2+} + N^* + e^- \tag{5}$$

Negative ions undergo similar processes. Collision-induced decompositions

$$A\text{-}B^- + N \rightarrow A^- + B + N \tag{6}$$

are observed,[15,16] and the stripping of two electrons on collision with a neutral produces a charge reversal

$$A\text{-}B^- + N \rightarrow A\text{-}B^+ + N + 2e^- \tag{7}$$

or formation of positively charged fragments:[17]

$$A\text{-}B^- + N \rightarrow A^+ + B + N + 2e^- \tag{8}$$

$$A\text{-}B^- + N \rightarrow A^+ + B^- + N + e^- \tag{9}$$

Use of collision-induced decompositions for structural analysis of stable positive ions is well established.[5,12,18,19] Collision with a neutral transforms a sufficient amount of kinetic energy into internal energy so that simple cleavages of the now highly excited ion are usually rapid relative to rearrangement reactions. Decompositions therefore reflect the structure of the stable ion, not a rearrangement product. This principle has also been applied to the structural analysis of negative ions. Negative fragment ions formed on collision give structural information in the same way; because the information on positive fragment ions is more extensive than on negative ions, it has been suggested that cationic collision products will allow structural interpretation for negative ions too.[17,20,21]

It does appear that rearrangements can occur between cation formation from the anion and fragmentation. They have been found to be of low relative intensity (e.g., 15–20% of the major fragmentation) except for examples of ortho effects, where a rearrangement ion may be the most intense collisionally induced product.[21]

Positive fragment ions formed by collision-induced charge reversal of alkoxide ions were examined in this study by mass-analyzed ion kinetic energy spectrometry of the appropriate negative ions. The study was restricted to methoxide ethoxide, *n*-propoxide, and isopropoxide, since only these

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† On leave from the University of North Carolina at Chapel Hill.

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Table I. MIKE Spectra of CH_3O^+ Ions According to Method of Formation

	% of induced dissociations[a]	
m/z	eq 10	eq 11
12	5	2
13	4	3
14	6	6
15	5	
16	2	
17	2	1
28	37	12
29[b]	(177)	(122)
30	39	76
31	main beam	main beam

[a] As percent of total ion current, corrected for contributions from unimolecular decompositions and for multiplier response. [b] Product of low-energy process; therefore excluded from sum of ion currents.

Table II. CID MIKE Spectra of $C_2H_5O^+$ Ions According to Method of Formation

	% of induced dissociations[a]		
m/z	eq 12	eq 13	eq 14
12	4		
13	8	3	3
14	12	12	6
15	21	54	14
16		2	1
19[b]		(1)	(5)
25	2		1
26	6	2	7
27	5	4	12
28	8	2	3
29[b]	(42)	(23)	(13)
30	9	3	8
31			1
41	1		2
42	6	3	9
43	17	6	22
44	1	8	8
45	main beam	main beam	main beam

[a] As percent of total ion current, corrected for contributions from unimolecular decompositions and for multiplier response. [b] Product of low-energy process; therefore excluded from sum of ion currents.

species have the composition of small, extensively studied cations.

Experimental Section

Methanol, ethanol, 1-propanol, 2-propanol, 1,2-dimethoxyethane, 2-butanol, ethyl ether, 3-methoxy-1-butyl acetate, and 2-propyl nitrite were obtained in the highest available purity from commercial sources.

A VG Micromass ZAB/2F mass spectrometer equipped with a collision cell and MIKES scan unit was used to obtain unimolecular and collision-induced MIKE spectra of model ions in the normal MIKE scan mode and to obtain collision-induced charge reversal MIKE spectra of alkoxide ions with appropriate reversals of the draw out and accelerating potentials and magnetic field, but not the electric analyzer. The source was operated at 200 °C with 200-μA trap current and 70-eV electron energy for positive ions, and at 200 °C, 500-μA emission current and 100 eV electron energy (alcohol pressure in the source, 10^{-6} Torr on gage) for negative ions. Methane at 10^{-5} Torr was used as a moderating gas for the formation of negative ions. The accelerating voltage was variously 6 or 8 kV in different experiments; Table I gives data for only 8-kV ions. Samples were introduced through an all-glass heated inlet system. For collision-induced fragmentation the collision cell was operated at a gage pressure of 8×10^{-7} Torr. The true pressure in the cell was then ca. 10^{-3} Torr, and a positive main beam intensity was reduced to roughly half its initial value. Negative main beams were not detected in the experimental setup, and the intensities of RO^+ main beams from charge reversal of the alkoxides were either small or zero.

Full MIKE spectra were scanned at 100 ms/eV, where eV refers to the kinetic energy of the energy- and mass-analyzed ion. The tabular data include corrections for contributions due to metastable ions undergoing unimolecular decompositions and for multiplier discrimination due to ion kinetic energy differences.[19] The reproducibility of fractional ion currents reported is ±1.

Results and Conclusions

Table I gives the CID MIKE spectra of the CH_3O^+ ions produced by charge reversal of methoxide (eq 10) and by loss of H from the positive molecular ion of methanol (eq 11).

$$CH_3O^- \rightarrow CH_3O^+ + 2e^- \qquad (10)$$

$$CH_3OH^{+}\cdot \rightarrow CH_2OH^+ + H\cdot \qquad (11)$$

As noted above, the structure of the latter ion is $CH_2{=}OH^+$. The spectra differ in several respects, especially in the presence of *m/z* 15 and 16, and the increased abundance of small fragments (*m/z* 12, 28) in the product from eq 1. It is obvious that the structures differ. The new peaks at *m/z* 15 and 16 can only be due to CH_3^+ and O^+. These new fragments, on applying the rule of fragment formation from ions before rearrangement, suggest the structure CH_3O^+ for this ion. This structure is the one expected if the CH_3O^- ion does not undergo hydrogen rearrangement between charge reversal and fragmentation.[5]

McLafferty and his colleagues proposed[5] that, after a few microseconds, the positive $C_2H_5O^+$ ions they observed had one or both of the two structures: $CH_3O^+{=}CH_2$ and $CH_3CH{=}OH^+$. Positive ions formed from molecules containing the $HOCH_2CH_2Y$ and, in particular, the C_2H_5OY structural units gave the same CID MIKE spectra as $CH_3CH{=}OH^+$ and thus appeared to isomerize to $CH_3CH{=}OH^+$ prior to collision-induced decomposition.

Table II contains the CID MIKE spectra of $C_2H_5O^+$ obtained by charge reversal of ethoxide (eq 12), as well as from two sources shown previously to provide the stable forms: 1,2-dimethoxyethane, which gives $CH_3OCH_2^+$ (eq 13), and 2-propanol, which gives $CH_3CH{=}OH^+$ (eq 14).

$$C_2H_5O^- \rightarrow C_2H_5O^+ + 2e^- \qquad (12)$$

$$CH_3OCH_2CH_2OCH_3^+ \rightarrow CH_3OCH_2^+ + CH_2OCH_3 \qquad (13)$$

$$(CH_3)_2CHOH^{+}\cdot \rightarrow CH_3CH{=}OH^+ + CH_3\cdot \qquad (14)$$

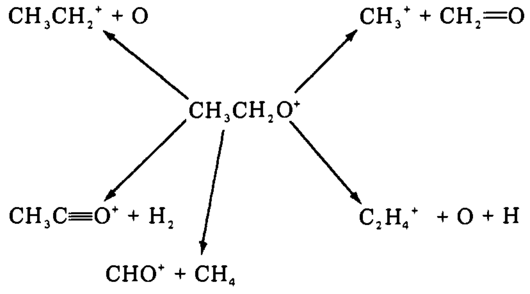
Our spectra for the last two differ somewhat from the published ones; experimental conditions greatly affect MIKE spectra.[19] The ion formed by charge reversal (eq 12) is not the same as that from eq 13 or 14. Comparison of intensities at *m/z* 12, 13, 16, 28, and 44 also indicates that the product of eq 12 cannot be a sum of the products of eq 13 and 14. It must be a third isomer. As a structure choice, the unrearranged ion, expected to be the most likely candidate, is consistent with the observed decomposition (Scheme I). Loss of CH_2O is analogous to loss of CH_2O from $CH_3{}^+O{=}CH_2$, and loss of two hydrogen atoms presumably gives a resonance-stabilized product as found with $CH_3CH{=}OH^+$. The largest peak, unfortunately one whose intensity is variable in other $C_2H_5O^+$ isomers, is the loss of 16 au to give *m/z* 29; comparison with the spectrum of $C_2D_5O^-$ indicates that the 16 au fragment may be either CD_4 or O. The loss of O is analogous to the formation of CH_3^+ from CH_3O^+ noted above. Ethylene may also be formed without rearrangement, in contrast to the other structures. However, loss of one hydrogen atom is less favored than loss of H from $CH_3{}^+O{=}CH_2$ and $CH_3CH{=}OH^+$; the resulting *m/z* 44 ion cannot be stabilized by allylic resonance

Table III. CID MIKE Spectra of $C_3H_7O^+$ Ions According to Methods of Formation

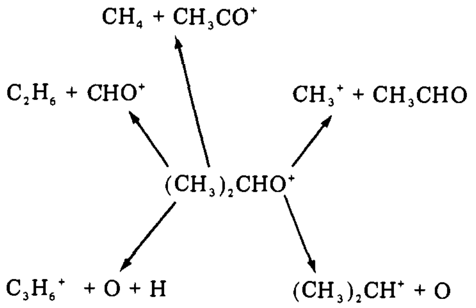
	% of induced dissociation[a]					
m/z	eq 15[c]	eq 16	eq 17	eq 18	eq 19	eq 20
12		2				
13	3	3		1	1	1
14	6	3	4	3	3	3
15	12	6	12	13	4	15
16						
25		1			1	1
26	6	9	3	5	5	5
27	4	15	9	10	13	8
28	6	11	2	13	9	7
29	16	33	12	19	33	25
30		6			7	1
31[b]	(6)	(1)	(47)	(28)	(83)	(25)
33						2
36		1				
38		1	3	1	1	
39	6	3	12	4	2	2
40	2	1	4	1		
41[b]	(3)	(2)	(82)	(8)	(6)	(1)
42	10	1	4	4	2	3
43	22	1	23	12	4	12
44	6		2	1	4	1
55		1	1	1	1	1
57		3	2	5	6	1
58			8	8	4	13
59	main beam	main beam	main beam	main beam	main beam	main beam

[a] As percent of total ion current, corrected for contributions from unimolecular decompositions and for multiplier response. [b] Product of low-energy process; therefore excluded from sum of ion currents. [c] Isopropoxide from 2-propanol; the spectrum using isopropoxide from isopropyl nitrite has the same peaks and relative intensities agree within a ±2 error.

Scheme I



Scheme II



in the case of $CH_3CH_2O^+$. All the interpretable evidence supports $CH_3CH_2O^+$ as the structure of the ion from eq 12.

The conclusion of McLafferty and Sakai concerning the stable forms of $C_3H_7O^+$ generated from positive ions is that the homologues of stable $C_2H_5O^+$, viz., $(CH_3)_2C{=}OH^+$, $CH_3CH_2CH{=}OH^+$, and $C_2H_5O^+{=}CH_2$, are the only stable forms.[22] Attempted generation of many other forms of $C_3H_7O^+$ produced only ions giving the same spectra as these three forms or mixtures of them. Table III lists the CID MIKE spectra of $C_3H_7O^+$ ions formed as follows. The first column is the $C_3H_7O^+$ spectrum from charge reversal of isopropoxide (eq 15), and the second column is the $C_3H_7O^+$ spectrum from *n*-propoxide (eq 16) The other three ions are formed from established precursors: in the third column, $(CH_3)_2C{=}OH^+$ from the positive molecular ion of 2-propanol by loss of H (eq 17); in the fourth, $CH_3CH_2CH{=}OH^+$ from the positive molecular ion of 2-butanol by loss of CH_3 (eq 18); in the fifth, $CH_3CH_2O^+{=}CH_2$ from the positive molecular ion of ethyl ether by loss of CH_3 (eq 19); in the sixth, $CH_3CH{=}O^+CH_3$ from the positive molecular ion of 3-methoxy-1-butyl acetate (eq 20). Our spectra of the last three again differ somewhat from those published previously. Comparison of the spectra of the positive ions formed from the alkoxides (eq 15 and 16) with the model spectra (eq 17–20), especially at *m/z* 12, 13, 55, 57, and 58, indicates that the ions formed by charge reversal differ from any of the models and from each other (e.g., at *m/z* 15, 27, 28, 29, 42, 44, and 57). Assignment of the unrearranged structures to these ions again is supported by the fragmentation observed. The structure of $(CH_3)_2CHO^+$ leads easily to the most intense peaks in the spectrum (Scheme II). Methyl ion can be formed in one step by the loss of acetaldehyde, CHO^+ by loss of two methyl groups, and $(CH_3)_2CH^+$ by loss of O analogous to the losses from CH_3O^+ and $C_2H_5O^+$. These assignments are again confirmed by examination of the spectrum of $(CD_3)_2CDO^-$; as for $C_2D_5O^-$, loss of 16 au can be loss of either O or CH_4. Facile loss of both O and H without rearrangement leads to *m/z* 42. In contrast to all of the model ions, no allylic stabilization of an *m/z* 58 ion formed by loss of H can be expected, and the ion is not seen. Indeed no ions formed by loss of a few hydrogen atoms are seen; because of the structure, loss of methyl fragments is favored. All the evidence from fragmentation supports a structure which has not rearranged, that is, $(CH_3)_2CHO^+$.

$$(CH_3)_2CHO^- \rightarrow (CH_3)_2CHO^+ + 2e^- \qquad (15)$$

$$CH_3CH_2CH_2O^- \rightarrow CH_3CH_2CH_2O^+ + 2e^- \qquad (16)$$

$$(CH_3)_2CHOH^{+\cdot} \rightarrow (CH_3)_2C{=}OH^+ + H\cdot \qquad (17)$$

$$CH_3CH_2CHOHCH_3^{+\cdot} \rightarrow CH_3CH_2CH{=}OH^+ + CH_3\cdot \quad (18)$$

$$CH_3CH_2OCH_2CH_3^{+\cdot} \rightarrow CH_3CH_2O^+{=}CH_2 + CH_3\cdot \quad (19)$$

$$CH_3CH(OCH_3)CH_2CH_2OCOCH_3^{+\cdot} \rightarrow CH_3CH{=}^+OCH_3 + CH_3COOCH_2CH_2\cdot \quad (20)$$

For the ion formed from *n*-propoxide, most of the fragment ion current is carried by two-carbon fragments. The largest peak, $C_2H_5^+$ at *m/z* 29, is formed by loss of formaldehyde:

$$CH_3CH_2CH_2O^+ \rightarrow CH_3CH_2^+ + CH_2O \quad (21)$$

The formation of large amounts of $C_2H_2^+$, $C_2H_3^+$, and $C_2H_4^{+\cdot}$ support this assignment rather than CHO^+, as in the case of $(CH_3)_2CHO^+$, where yields of these ions are much less. Again, loss of H from $CH_3CH_2CH_2O^+$ is not observed, because there is no allylically stabilized product. It is interesting that loss of O is no longer important here, probably because of the more favorable competition by formation of $C_2H_5^+$ and CH_2O.

We have considered the question of whether the model cations of stable structure would have the same CID spectrum if they had been formed by charge stripping from anions of the same structure instead of by the literature routes using cleavage of positive molecular ions. One major expected difference would be a lower internal energy content for the ions formed by charge reversal, since it would cost energy to remove two electrons. A direct experimental answer to this question has eluded us for the following reasons. Our experience is that one cannot generate the precursors by known routes. The formation of R_2COH^- ions, from which one would make the stable R_2COH^+ ions, from alcohols R_3COH is precluded by the diversion of the alcohols to R_3CO^-; likewise, the formation of $R_2COR'^-$ ions, from which one would make the stable $R_2COR'^+$ ions, from ethers R_3COR' is precluded by the diversion of the ethers to R_3CO^- and/or $R'O^-$. However, there is indirect evidence that our ions are not excited to low internal energies. First, after collision they produce at least as much C^+ and CH^+ ion current as the model ions, giving evidence of a significant population with internal energies in excess of the sum of the energies of four bonds to C (14 eV). Second, the ion currents due to low energy processes (in parentheses in the tables) are not disproportionately large, giving evidence of only a small population with low internal energies. (The *m/z* 29 ion from $C_2H_5O^+$ has an interference, as noted.) In addition to the internal evidence, the literature yields examples of large molecules whose negative molecular ions, on charge reversal, give spectra similar to their positive electron impact spectra, and therefore to the CID spectra of their positive molecular ions,[17,20] but it is possible to choose molecules where this is not the case.[21] We have confirmed the similarity of the CID spectra of $C_6H_5O^+$ from anisole positive molecular ion and from phenoxide.[23] Not much literature speaks to this point yet, but what is available and what we glean internally from our spectra indicate that our model cations are good models.

The RO^+ ions formed by charge reversal thus appear to have adequate internal energy such that high-energy cleavage fragmentations are favored over low-energy rearrangements to stable isomers, as would be expected on the basis of the quasi-equilibrium theory for ions of high energy content. Most of the ions sampled have the structure RO^+. From the data given in the tables this structure may be contaminated as follows: CH_3O^+, by 0 ± 20% of CH_2OH^+; $CH_3CH_2O^+$, by 0 ± 25% of both of its stable isomers; $(CH_3)_2CHO^+$, by 0 ± 15% of $(CH_3)CHOH^+$; $CH_3CH_2CH_2O^+$, by 0 ± 15% of $CH_3CH_2CHOH^+$. The actual spectra compared contain either a substantial peak at the mass used for discrimination or no peak detectable in our instrument, and so the limit of the error given above is extremely conservative; from the appearance of the spectra, we would estimate no more than 5% contamination based upon comparison of the same peaks used for the estimates from the tables given above.

The ions formed by charge reversal therefore have the structure RO^+ The analysis of their decompositions by MIKE spectroscopy is free of the ambiguity of the previous analysis of CH_3O^+ and $CH_3CH_2O^+$ ions formed in the ion source.[6] Further, all of the collision-induced decompositions may be used to compare the ions (with the exception of the low-energy processes, which in fact were used in the previous study),[6] not merely a single decomposition channel. Charge reversal, then, provides a general method for the study of these ions. Alkoxy ions belong to the class of electron-deficient oxenium ions, which have six valence electrons like carbenium ions. Rearrangements acknowledged to pass through positive oxygen intermediates are well-known—the Baeyer–Villiger reaction, the Criegee rearrangement, acid-catalyzed rearrangement of hydroperoxides, and ionic decompositions of peresters, for example—though the list may be extended to include most acid-catalyzed reactions of hydrogen peroxide and the NIH shift. Detection and spectral analysis of an oxenium ion in solution is, however, unknown to us.

A few observations of oxenium ions in the gas phase are scattered throughout earlier mass spectrometric literature. The simplest oxenium ion, HO^+, was observed by Aston.[23] Another well-known example is the ion corresponding to loss of methyl from anisole,[24-26] because the atoms are lost as the *O*-methyl group,[25] and the difference between the ionization potential of phenoxy radical (8.84 eV[27]) and the appearance potential of $C_6H_5O^+$ from anisole (11.89 eV[27,28]) is 70 kcal/mol. This corresponds to a O–CH_3 bond strength in anisole which compares favorably with the average O–CH_3 bond strength of methyl ethers,[29] 80 kcal/mol. Thermodynamic data therefore indicate that only the O–CH_3 bond is broken in making $C_6H_5O^+$ from anisole. This ion has also been generated by charge reversal from the phenoxide anion.[30]

MIKE data, therefore, confirm the theoretical conclusion that methoxy ion has a high barrier to isomerization to $CH_2{=}OH^+$ and the inference that this holds for homologues. Why did $C_2H_5O^+$ ions presumably generated as $CH_3CH_2O^+$ and $C_3H_7O^+$ ions which are presumably generated as $CH_3CH_2CH_2O^+$ or $(CH_3)_2CHO^+$ from positive molecular ions of ethers or carbonate esters isomerize to the structures of protonated carbonyl compounds in earlier MIKES studies?[5,22] Since we have shown that the alkoxy structures generated by charge reversal have high enough internal energy to fragment rapidly without rearranging, clearly the presumption about the original structure was not correct. The possibility of this was discussed in the original paper.[22] These ions arise, then, as a result of rearrangements or multistep fragmentations, and apparently are generated not as RO^+ but as structures observed or some other structures from which isomerization to the final structures is facile.

The major fragmentations of the alkoxy ions given in the schemes may contain information on their structures. Thus, the loss of 2 H from CH_3O^+ is accommodated conveniently by its preferred formulation as a hydrogen molecule embedded in a formyl ion.[9,11] The structures of other alkoxy cations must be able to accommodate not only a facile loss of H_2 but the facile formation of other major fragments in the tables too,[31] with the reservation that most of these must be simple cleavages. The correlation of structure with fragmentation by the CID technique assumes mostly simple cleavages The generation of $(M - 1)^-$ negative ions from compounds with active hydrogen is generally a favored process, and frequently such $(M - 1)^-$ negative ions carry most of the negative ion current.[31] Charge reversal produces an ion which generally has a high heat of formation relative to isomeric ions formed in positive ion electron impact. The combination of generating ions with structures both unstable toward fragmentation and close to the structure of the original compound and using a technique which favors simple cleavages seems of special interest: it may provide more useful structural information about many compounds than conventional positive ion mass spectrometry in its several forms. The example at hand certainly supports this hypothesis, and we intend to explore it further.

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Consequences of Charge Reversal of Gaseous Formate and Acetate Ions. Acyloxy Ions

Maurice M. Bursey,[1a] Donald J. Harvan,[1b] Carol E. Parker,[1b] Lee G. Pedersen,[1a] and J. Ronald Hass*[1b]

Contribution from the William R. Kenan, Jr., Laboratories of Chemistry,
University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514,
and the Environmental Biology and Chemistry Branch,
National Institute of Environmental Health Sciences, P.O. Box 12233,
Research Triangle Park, North Carolina 27709.

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Abstract: Positive-ion collision-induced decomposition (CID) mass-analyzed ion kinetic energy (MIKE) spectra of formate and acetate anions were compared with the CID MIKE spectra of $COOH^+$, CH_2COOH^+, and $COOCH_3^+$, the likely simple rearrangement products of the formyloxy and acetyloxy cations. The spectra of the charge-reversed ions formed from the carboxylate anions differed from the spectra of the models, and gave fragment ions consistent with no structural rearrangement. The initially formed ion was found to rearrange with no energy barrier to $COOR^+$ using MINDO/3; for $HCOO^+$ this was duplicated by STO-3G and 4-31G calculations.

The acyloxy or acyloxoniumylidene cations $RCOO^+$ are examples of electron-deficient species which have not previously been detected or isolated. They are a subset of the class of oxenium ions of which alkoxy ions RO^+ form another subset. There has been much interest recently in alkoxy ions, both from an experimental[1-3] and theoretical[4,5] viewpoint. On the other hand, not so much has appeared on acyloxy ions.

Evidence for the simplest member of the series, the formyloxy cation $HCOO^+$, does not appear to have been clearly established experimentally. Long ago it was noted that, in the mass spectrometer, formic acid molecules specifically labeled with deuterium attached to either carbon or oxygen may lose either hydrogen on electron impact:[6]

$$DCOOH^{+\cdot} \rightarrow D + COOH^+ \quad 37\% \qquad (1)$$

$$HCOOD^{+\cdot} \rightarrow H + COOD^+ \quad 61\% \qquad (2)$$

$$DCOOH^{+\cdot} \rightarrow H + DCOO^+ \quad 40\% \qquad (3)$$

$$HCOOD^{+\cdot} \rightarrow D + HCOO^+ \quad 18\% \qquad (4)$$

The percentage values given in eq 1–4 refer to the percent intensities of these ions in the electron-impact mass spectra of the labeled formic acids. The further reactivity of these molecules has been studied by analysis of the ion–molecule reactions in formic-*d* acid.[7] The two ions react with neutral formic-*d* acid at different rates:

$$DCOO^+ + DCOOH \rightarrow DCOOHD^+ + CO_2$$
$$K = 1.7_2 \times 10^{-9}\ \mathrm{cm^3/molecules \cdot s} \qquad (5)$$

$$COOH^+ + DCOOH \rightarrow DCOOH_2^+ + CO_2$$
$$k = 1.9_3 \times 10^{-9}\ \mathrm{cm^3/molecule \cdot s} \qquad (6)$$

but the difference in reactivity is not large. If $DCOO^+$ has time to rearrange to $COOD^+$ before reactive collision occurs

$$DCOO^+ \rightarrow COOD^+ \qquad (7)$$

then the difference in reactivity could be explained as an isotope effect upon the reactivities of $COOH^+$ and $COOD^+$ as well as by the difference in structure between $DCOO^+$ and

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