initio calculations of intensities of uracils are in progress at the University of Florida.[27] The preliminary results confirm the assignment given here.

Acknowledgment. We wish to express our thanks to Professor J. Kolodziejczak for his interest in this work and his help with the initiation of this investigation in the Institute of Physics of the Polish Academy of Sciences. We are grateful to Mr. A. Orlowski for his permanent instrumental and technical assistance. The writers wish to express their thanks to Dr. A. J. Barnes for his critical remarks and suggestions based on the yet unpublished matrix studies of uracils performed at the University of Salford. This investigation was supported by the Polish National Cancer Research Program (Project PR-6) and by Institute of Physics PAN Research Grant (Project C-1). In addition W.B.P. is grateful for partial financial support from NSF Research Grant No. CHE 81-01131.

Registry No. Uracil, 66-22-8; N_1,N_3-dideuteriouracil, 20666-60-8.

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Ionized Oxycarbenes: $[COH]^+$, $[HCOH]^{+\cdot}$, $[C(OH)_2]^{+\cdot}$, $[HCO_2]^+$, and $[COOH]^+$, Their Generation, Identification, Heat of Formation, and Dissociation Characteristics

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Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4. *Received March 2, 1983*

Abstract: The title ions have been generated by appropriate dissociative ionizations and identified by means of their collisional activation mass spectra. Their heats of formation have been measured via appearance energies, ΔH_f for $[COH]^+$, $[HCOH]^{+\cdot}$, $[C(OH)_2]^{+\cdot}$, and $[COOH]^+$ being 220, 238, 175, and 141 kcal mol^{-1}, respectively. The new ions do not readily isomerize to their better known counterparts $[HCO]^+$, $[H_2CO]^{+\cdot}$, $[HCOOH]^{+\cdot}$, there being large energy barriers thereto. For ionized formaldehyde and formic acid the barriers both lie at least 34 kcal mol^{-1} above $[HCOH]^{+\cdot}$ and $[C(OH)_2]^{+\cdot}$. Isotopic labeling experiments permitted the separation of two dissociation pathways for $[HCOH]^{+\cdot}$, one leading to $[HCO]^+$ and the other to $[COH]^+$. Measurement of metastable peak appearance energies showed that the reactions $[HCO]^+ + H\cdot \rightarrow [HCOH]^{+\cdot}$ and $[COOH]^+ + H\cdot \rightarrow [C(OH)_2]^{+\cdot}$ have critical energies of ca. 1 eV, whereas the reactions leading respectively to $[H_2CO]^{+\cdot}$ and $[HCOOH]^{+\cdot}$ have none.

Introduction

Laboratory observations[1,2] of the proposed interstellar species[3] $[COH]^+$ have recently been reported. The ion was generated by dissociative ionization of CD_3OH, and its collisional activation (CA) mass spectrum permitted its ready distinction from the isomeric ion $[HCO]^+$. These experiments were in part prompted by ab initio calculations[4] at a high level of theory, which predicted the heat of formation, $\Delta H_f[COH]^+$, to be 232 kcal mol^{-1} and a high barrier to its exothermic rearrangement to $[HCO]^+$. It should be noted that $[COH]^+$ had been proposed to be generated from CD_3OH by Berkowitz[5] and Momigny et al.,[6] but unequivocal identification of the structure was lacking in these reports. The finding that $[COH]^+$ can readily be identified raised our interest in searching for the related small oxy cations of structure $[HCOH]^{+\cdot}$, $[C(OH)_2]^{+\cdot}$, and $[HCO_2]^+$. $[HCOH]^{+\cdot}$ was recently reported by Wesdemiotis and McLafferty,[7] but its thermochemistry was not determined.

In this paper we describe methods for the production of the above ions, their CA mass spectra, their ΔH_f values, and the magnitude of the energy barriers to their isomerization to $[HCO]^+$, $[H_2CO]^{+\cdot}$, $[HCOOH]^{+\cdot}$, and $[COOH]^+$, respectively. Where appropriate, results will be compared with ab initio calculations.

Table I. Partial Collisional Activation Mass Spectra[a] of $[CH_2O]^{+\cdot}$ Ions

precursor	fragment ion *m/z*					
	12	13	14	16	17	18
H_2CO	18	23	43	10	5	1
$\overline{CH_2CH_2C}HOH$	18	45	7	4	18	8
CH_3OH	17	46	9	4	17	7

[a] *m/z* 28 and 29 (unimolecular reaction) omitted. Intensities relative to $\Sigma = 100$, values ±1.

Results and Discussion

The Hydroxymethylidyne Cation $[COH]^+$. Ab initio calculations[4] have explored the potential energy surface for $[COH]^+$ and $[HCO]^+$ and found that the ground state of $[COH]^+$ lies 37.5 kcal mol^{-1} above $[HCO]^+$. The isomerisation barrier was calculated to be 36 kcal mol^{-1} above $[COH]^+$, appreciably below the threshold for the least endothermic reaction to $H^+ + CO$, a further 71 kcal mol^{-1}. These results therefore show that the isomers can interconvert below their dissociation energy. It has been observed[1,2] that the CA mass spectrum of *m/z* 29 from CD_3OH was different from the ion produced by simple bond cleavages, such as *m/z* 29 from CH_3CHO, which has the structure $[HCO]^+$. The spectra are shown in Figure 1 and the ion derived from CD_3OH was assigned the structure $[COH]^+$; the abundance of *m/z* 13 and 16 are clearly structure diagnostic. However, $[COH]^+$ is generated from CD_3OH together with a small amount of its isomer $[HCO]^+$.

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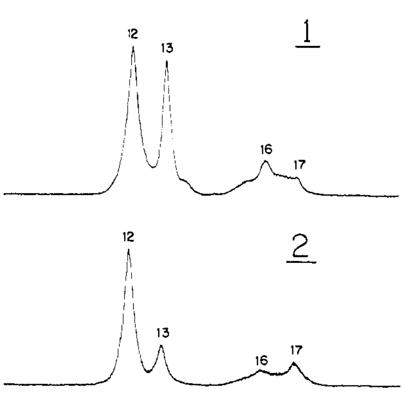

Figure 1. Partial CA mass spectrum of $[CHO]^+$ ions; (1) is for $[HCO]^+$, (2) is for $[COH]^+$. See text for discussion.

The appearance energy (AE) of m/z 29, measured using energy selected electrons (see Experimental Section) showed a long tail, terminating at ca 13.05 ± 0.1 eV, close to the calculated threshold for $[HCO]^+$, 12.8 eV (295 kcal mol^{-1}, from $\Delta H_f[HCO]^+ = 195$ kcal mol^{-1},[8] $\Delta H_f[H\cdot] = 52.1$ kcal mol^{-1},[8] $\Delta H_f[CD_3OH] = -48$ kcal mol^{-1}).[8] That $[HCO]^+$ is indeed formed at low internal energies was shown by the CA mass spectrum of m/z 29, which, at the lowest ionizing electron energy compatible with an acceptable signal to noise ratio (2:1 or better), was clearly that of $[HCO]^+$. As will be described later, the route to $[COH]^+$ is via the ion $[DCOH]^{+\cdot}$ which loses both D· and H· in the metastable time frame. The AE for the D· loss metastable peak, measured by a comparative method,[9] was 13.9 ± 0.2 eV, well above that for $[HCO]^+$ production, and leads to 220 ± 5 kcal mol^{-1} for $\Delta H_f[COH]^+$, somewhat below the calculated value,[4] 232 kcal mol^{-1}.

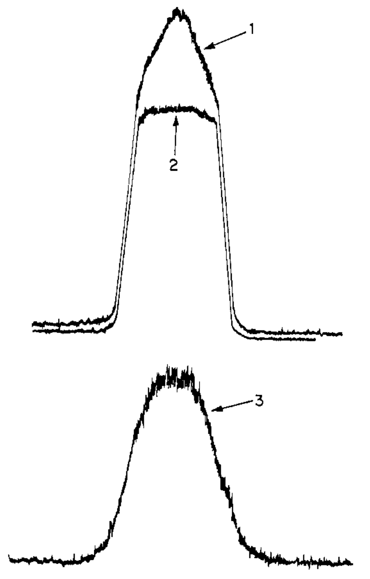

Figure 2. (1) Metastable peak m/z 30 → m/z 29 from $[CH_3OH]^{+\cdot}$; $T_{0.5}$ = 320 meV; (2) metastable peak m/z 31 → m/z 30 from $[CD_3OH]^{+\cdot}$; $T_{0.5}$ = 370 meV; (3) metastable peak m/z 31 → m/z 29 from $[CD_3OH]^{+\cdot}$; $T_{0.5}$ = 160 meV. All peaks have common energy scale.

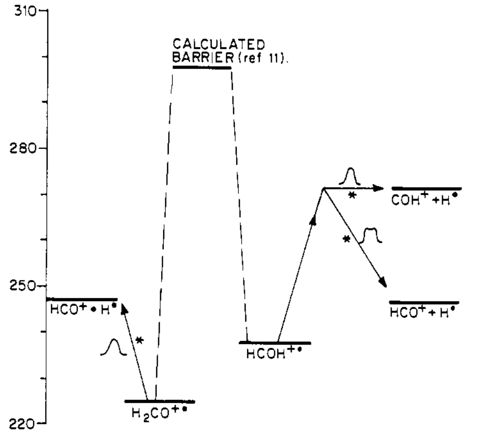

Figure 3. Energy diagram for $[CH_2O]^{+\cdot}$. Metastable peaks shapes as shown.

The Hydroxymethylene Cation $[HCOH]^{+\cdot}$. In 1978, Berkowitz[5] concluded in a photoionization study of methanol that the low energy elimination of H_2 from the molecular ion led to $[HCOH]^{+\cdot}$ rather than $[H_2CO]^{+\cdot}$. More recently, Wesdemiotis and McLafferty[7] produced $[HCOH]^{+\cdot}$, possibly in admixture with $[H_2CO]^{+\cdot}$, by the elimination of C_2H_4 from ionized cyclopropanol. While Hartree–Fock calculations at various levels of sophistication[10] showed $[HCOH]^{+\cdot}$ to lie 22 and 11.5 kcal mol^{-1} above $[H_2CO]^{+\cdot}$, the most recent ab initio calculations of Bouma et al.[11] predict an energy difference of 10 kcal mol^{-1} between the isomers and an interconversion barrier of 59 kcal mol^{-1} above $[HCOH]^{+\cdot}$. Berkowitz[5] avoided drawing any firm conclusion concerning $\Delta H_f[HCOH]^{+\cdot}$ but tentatively concluded that $[HCOH]^{+\cdot}$ was slightly less stable than $[H_2CO]^{+\cdot}$. In Table I, we present our measured CA mass spectra of m/z 30 ions, $[CH_2O]^{+\cdot}$ from formaldehyde, methanol, and cyclopropanol. It should be noted that m/z 30 in the normal mass spectrum of cyclopropanol is a doublet, $[CH_2O]^{+\cdot}$ and $[C_2H_6]^{+\cdot}$, the latter arising from CO loss, a reaction of lower energy requirement than C_2H_4 loss, ($\Delta H_f[H_2CO]^{+\cdot} = 225$ kcal mol^{-1},[8] $\Delta H_f[C_2H_4] = 12.5$ kcal mol^{-1},[8] $\Delta H_f[C_2H_6]^{+\cdot} = 245$ kcal mol^{-1},[8] $\Delta H_f[CO] = -26$ kcal mol^{1} [8]). The CA mass spectra of the $[CH_2O]^{+\cdot}$ ions from methanol and cyclopropanol are identical and different from that of ionized formaldehyde, and our observations are in close agreement with those reported earlier.[7] The differences, as argued by Wesdemiotis and McLafferty, are readily interpreted in terms of the structures $[HCOH]^{+\cdot}$ and $[H_2CO]^{+\cdot}$. The CA mass spectra of the m/z 30 ions from methanol and formaldehyde were unchanged at the lowest ionizing electron energy compatible with an acceptable signal to noise ratio and we conclude that CH_3OH yields essentially ions of structure $[HCOH]^{+\cdot}$, although a small yield of $[H_2CO]^{+\cdot}$ is undoubtedly present (see above).

The $[CH_2O]^{+\cdot}$ ion derived from CH_3OH undergoes one reaction in the metastable time frame, loss of H·. The metastable peak is shown in Figure 2 and is clearly composite, the kinetic energy release calculated from the peak width at half height, $T_{0.5}$ = 320 meV. The small Gaussian-type peak on top of the broad component (Figure 2) is characteristic of H· loss from ionized formaldehyde, for which $T_{0.5}$ is 170 meV. The ion $[CDHO]^{+\cdot}$ (generated from CD_3OH), loses H· and D·, metastable peak abundances 5:1; these peaks have significantly different shapes, $T_{0.5}$ = 370 and 160 meV, respectively, and are also shown in Figure 2. The Guassian peak characteristic of $[H_2CO]^{+\cdot}$ is absent; the broad (H· loss) peak is closely similar to that from the unlabeled methanol. Thus this $[CDHO]^{+\cdot}$ ion is *not* $[HDCO]^{+\cdot}$ and is proposed to be $[DCOH]^{+\cdot}$. The AE of m/z 31 was then measured using energy selected electrons (see Experimental Section), AE = 12.40 ± 0.05 eV leading to $\Delta H_f[DCOH]^{+\cdot} = 238$ kcal mol^{-1} in good agreement with the ab initio calculations of Bouma et al.[11] The calculated AE for $[H_2CO]^{+\cdot}$ generation is 11.84 eV.

The AE values for metastable H· and D· loss from $[DCOH]^{+\cdot}$ were measured by a comparative method[9] and were found to be the same, within experimental error, 13.9 ± 0.2 eV. This corresponds to a transition state energy of 274 kcal mmol^{-1}, far above the threshold for $[HCO]^+$ + H· formation, 247 kcal mol^{-1} (see Figure 3). Note that *unlabeled* methanol generated both $[HCO]^+$ and $[COH]^+$ in the ion source, whereas CD_3OH produces $[COH]^+$

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Table II. Metastable Ion Spectra of $[CH_2O_2]^{+\cdot}$ Derived from Formic and Oxalic Acids

	relative abundance[a]				
precursor	*m/z* 46	*m/z* 45	*m/z* 30	*m/z* 29	*m/z* 18
HCOOH	10^5	10^2 (11)	3 (70)	1 (85)	0.2 (16)
$(COOH)_2$	10^5	10^3 (63)		20 (12)	1 (38)[b]

[a] Kinetic energy releases, shown in parentheses, calculated from the peak width at half height ($T_{0.5}$). [b] Flat-topped metastable peak; all others of Gaussian-type.

and $[DCO]^+$ as described above. We propose therefore that the fragmentation of metastable $[DCOH]^{+\cdot}$ ions involves competing bond cleavages requiring closely similar critical energies to yield different daughter ions, i.e.

$$[DCOH]^{+\cdot} \rightarrow [DCO]^+ + H\cdot \qquad (T_{0.5} = 370 \text{ meV})$$

$$[DCOH]^{+\cdot} \rightarrow [COH]^+ + D\cdot \qquad (T_{0.5} = 160 \text{ meV})$$

Thus, the different T values are readily explained in terms of different fragmentation products (having different ΔH_f), rather than by a single reaction product involving a tunnelling mechanism.[12,13] Note that our observations *are* in good agreement with those of Beynon et al.[12] with the caveat that the fragmentation assignments in that work are incorrect (i.e., page 9 in ref 12). Note that we propose that $[H_2CO]^{+\cdot}$ and $[HCOH]^{+\cdot}$ do not interconvert below the H· loss energy, also in agreement with ab initio calculations;[11] thus, the barrier to their interconversion is greater than 34 kcal mol^{-1} above $[HCOH]^{+\cdot}$. This is illustrated in the energy diagram (Figure 3); note that the reaction

$$[HCO]^+ + H\cdot \rightarrow [HCOH]^{+\cdot}$$

has a substantial energy requirement, ca. 25 kcal mol^{-1}, whereas the reaction pathway which yields $[H_2CO]^{+\cdot}$ has no or a very small barrier. Thus attempts to make $[HCOH]^{+\cdot}$ by this reaction are unlikely to succeed, and the ion is unlikely to be observed in the interstellar medium. Charge location may be responsible for the above barrier, i.e., that the ion $[HCO]^+$ has a charge distribution closer to the oxonium ion, $[HC{\equiv}O^+]$, rather than the carbonium ion, $[HC^+{=}O]$.[4]

The Dihydroxymethylene Cation $[C(OH)_2]^{+\cdot}$. This ion, which could be regarded as the enol of formic acid, has been discussed earlier by one of us, when its possible formation in the mass spectrum of oxalic acid was described.[14] Later work[15] showed that the metastable peaks for the reaction

$$[CH_2O_2]^{+\cdot} \rightarrow H_2O^{+\cdot} + CO$$

in the mass spectra of formic and oxalic acids had markedly different shapes, the former generating a Gaussian-type peak and the latter a flat-topped peak. The latter fragmenting ion was proposed to be $[C(OH)_2]^{+\cdot}$ or $[CO(OH_2)]^{+\cdot}$.

The metastable ion spectra of the *m/z* ions from formic and oxalic acids are given in Table II; both are dominated by H· atom loss (not discussed earlier[15]) and all peaks show greatly different kinetic energy release values ($T_{0.5}$). This is strong confirmatory evidence that the two $[CH_2O_2]^{+\cdot}$ ions have different structures which cannot interconvert even up to the metastable reaction of highest energy requirement, formation of $[H_2O]^{+\cdot}$ + CO, which lies 37 kcal mol^{-1} [8] above $[HCOOH]^{+\cdot}$.

The partial CA mass spectra of these $[CH_2O_2]^{+\cdot}$ ions from *m/z* 12–18 are presented in Table III. The fragment ion abundances *m/z* 28, 29, and 44 were not structure diagnostic and are therefore not recorded here. Distinctive features are the much larger intensities of $[C^+]$ and $[OH^+]$ for the ion derived from oxalic acid, in keeping with a structure $[C(OH)_2]^{+\cdot}$ for this ion. The behavior of the isomeric form $[CO(OH_2)]^{+\cdot}$ would reasonably be expected to be dominated by a high $[H_2O]^{+\cdot}$.

Table III. Partial Collisional Activation Mass Spectra[a] of $[CH_2O_2]^{+\cdot}$ Ions

	fragment ion *m/z*				
precursor	12	13	16	17	18
HCOOH	2	1.5	6.5	18	72
$(COOH)_2$	6.5	1.5	7.2	37	48

[a] *m/z* 14 abundance negligible. Intensities relative to $\Sigma = 100$; *m/z* 18 is partly of unimolecular origin.

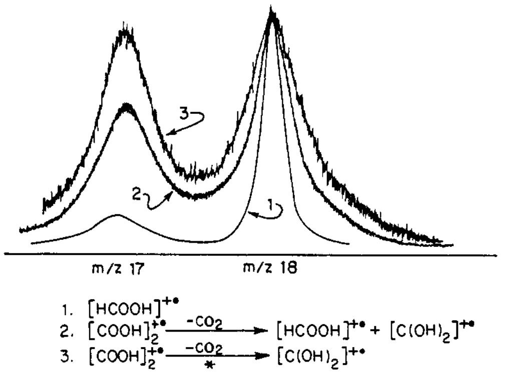

Figure 4. CA mass spectrum of $[CH_2O_2]^{+\cdot}$ ions at *m/z* 17, 18: (1) from $[HCOOH]^{+\cdot}$, *m/z* 46, 4 kV ion acceleration voltage; (2) daughter ions, *m/z* 46 from $[(COOH)_2]^{+\cdot}$; 4 kV ion acceleration voltage; (3) metastable ions, *m/z* 90 → *m/z* 46 from $[(COOH)_2]^{+\cdot}$; ion acceleration voltage 8 kV.

The CA mass spectrum of the *m/z* 46 daughter ion from oxalic acid (Table III) is not that of pure $[C(OH)_2]^{+\cdot}$ ions. This is illustrated by Figure 4 in which the CA mass spectrum of *m/z* 46 ions formed by metastable decomposition of ionized oxalic acid in the first field-free region of the ZAB-2F mass spectrometer is compared with that of the ion-source generated species and with the molecular ion of formic acid all ions having the *same* translational energy. We propose that the ions generated in the metastable time frame are solely $[C(OH)_2]^{+\cdot}$ and that in the ion source, oxalic acid also yields $[HCOOH]^{+\cdot}$. Note also the different shapes of the *m/z* 18 peak in the CA spectra, Figure 4, narrow for $[HCOOH]^{+\cdot}$, broad for $[C(OH)_2]^{+\cdot}$, and intermediate for the mixture. From the relative sensitivities of the *m/z* 17 and *m/z* 18 peaks (intensity ratios *m/z* 17:*m/z* 46 and *m/z* 18:*m/z* 46) for items 1, 2, and 3 in Figure 4, it was calculated that ca. 10% of the source generated ions in oxalic acid are $[HCOOH]^{+\cdot}$.

ΔH_f for $[C(OH)_2]^{+\cdot}$ was obtained from the AE[9] of the metastable peak, *m/z* 90 → *m/z* 46 (Gaussian-type peak, $T_{0.5}$ = 33 meV), 11.1 ± 0.1 eV. This leads to ΔH_f $[C(OH)_2]^{+\cdot}$ = 175 kcal mol^{-1}, (ΔH_f $[COOH]_2$ = −175 kcal mol^{-1},[16] $\Delta H_f[CO_2]$ = −94.1 kcal mol^{-1} [8]), slightly above ΔH_f $[HCOOH]^{+\cdot}$, 170 kcal mol^{-1}.[8] The former result is in keeping with a predicted value of 167 ± 5 kcal mol^{-1}, based on a consideration of the multiple OH substitution effect[17] in the ion $[CH_2]^{+\cdot}$.[18] We have also measured AE values for the metastable peaks *m/z* 46 → *m/z* 45 in oxalic and formic acids. For the latter, AE = 12.4 ± 0.1 eV, in good agreement with photoionization measurements, 12.3 ± 0.1 eV.[19] For oxalic acid, AE = 12.6 ± 0.1 eV, corresponding to a transition state energy of 209 kcal mol^{-1}, significantly above that for $[COOH]^+$ + H·, 193 kcal mol^{-1} (using AE *m/z* 45 from formic acid,[19] ΔH_f = −90.5 kcal mol^{-1},[8] as a measure of ΔH_f $[COOH]^+$ = 141 kcal mol^{-1}). Note that this oxalic acid AE is not interfered with by the 10% of $[HCOOH]^{+\cdot}$ ions referred to above. This is

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Table IV. Partial Collision Activation Mass Spectra[a] of $[CHO_2]^+$ and $[CDO_2]^+$ Ions

precursor	neutral fragment	relative abundance $[O^+]:[OH^+]$	relative abundance $[O^+]:[OD^+]$
HCOOH	$H\cdot$	0.90	
DCOOH	$D\cdot$	0.89	
	$H\cdot$		0.51
$(COOH)_2$	$CO_2H\cdot$	0.90	
CH_3COOH	$CH_3\cdot$	0.88	
CH_3COOD	$CH_3\cdot$		0.54
$HCOOCH_3$	$CH_3\cdot$	0.97	
$HCOOCD_3$	$CD_3\cdot$	1.02	
	$CD_2H\cdot$		0.4–0.55[b]
$DCOOCH_3$	$CH_2D\cdot$	0.89	
	$CH_3\cdot$		0.71
CO_2/CH_4[c]	-	0.89	
CO_2/CD_4[c]	-		0.55

[a] Average of many measurements. Estimated uncertainty ±0.02. When necessary, $[O^+]$ abundances were corrected for contributions from $[^{13}CO_2]^{+\cdot}$. [b] Interference from $[C_2D_3O]^+$, $[M-OH]^+$. [c] Chemical ionization with $[CH_5]^+$ and $[CD_5]^+$.

because the metastable peak *m/z* 46 → *m/z* 45 in formic acid is one-tenth as intense as that for oxalic acid (see Table II); thus, the net contribution is only ca. 1%. The method of measuring these AE values[9] also precludes its interference. The kinetic energy release, $T_{0.5}$, for the formic acid fragmentation (= 12 meV) is substantially less than that for oxalic acid, 65 meV, in keeping with the higher transition state energy. Note, therefore, that the reaction

$$[COOH]^+ + H\cdot \cdot [C(OH)_2]^{+\cdot}$$

has a large energy barrier, ca. 16 kcal mol^{-1}, as was the case for the analogous reaction of $[HCO]^+$, and moreover, that $[HCOOH]^{+\cdot}$ formation has no barrier, compare again $[HCO]^+$ behavior described above. The isomerisation barrier for $[C(OH)_2]^{+\cdot} \rightarrow [HCOOH]^{+\cdot}$ is at least 34 kcal mol^{-1}.

The Dioxamethylium ion $[HCOO]^+$. Finally, we present some preliminary evidence that this isomer of the carboxyl cation $[COOH]^+$ exists as a stable species in the gas phase. Table IV shows that partial CA mass spectra of $[CHO_2]^+$ and $[CDO_2]^+$ ions generated from a variety of precursor molecules; only *m/z* 16 17, and 18 intensities are listed because the remaining peaks, *m/z* 12, 28, 29, and 44 showed no structure characteristic differences in relative abundance. Although the differences in relative abundance are not large, they are well outside the experimental error; the reproducibility of the observations over a period of months proved to be excellent. We propose that the *m/z* 45 and 46 ions generated from formic, acetic, and oxalic acids and from the reaction of $[CH_5]^+$ and $[CD_5]^+$ with CO_2 have the carboxyl cation structure and that the $[O^+]:[O^+H]$ ratio of 0.89 is characteristic of this structure. The CA mass spectra of these labelled ions display an isotope effect on the $[O^+]:[O^+D]$ ratios. We further propose that the ions produced by loss of $CH_3\cdot$ and $CD_3\cdot$ from methyl formate consist, at least in part, of $[HCOO]^+$. The significantly enhanced $[O^+]:[O^+H]$ ratio and $[O^+]:[O^+D]$ ratio is in keeping with this proposal. However, it could be argued that internal energy effects, rather than structural isomers, are responsible for the observations. This we doubt; note the loss of $CD_2H\cdot$ from $[HCOOCD_3]^{+\cdot}$, which clearly generates $[COOD]^+$ and is the major fragmentation (loss $[CD_2H]\cdot$: loss $[CD_3]\cdot$ = 10:1) in the CA mass spectrum. The rearrangement $[HCOOCD_3]^{+\cdot} \rightarrow HC^+(OD)O\dot{C}D_2$, followed by a 1,3 H shift readily permits the formation of $[COOD]^+$. This constitutes yet another example of a hidden hydrogen migration.[20] The isotope effects described above and related observations will be discussed in detail elsewhere.[21] Finally, the ion $[HCOO]^+$ can be generated by charge reversal and also will be described in a future publication.

Experimental Section

The collisional activation mass spectra were obtained with a Vacuum Generators ZAB-2F mass spectrometer as described elsewhere.[22] CA mass spectra were obtained under the following conditions: main beam reduction of ca. 25% with He as a collision gas; ion source temperature, 200 °C; ionizing electron energy, 70 eV unless stated otherwise. All Y and Z collimating slits were wide open to minimize effects of energy resolution on peak intensities. The CA mass spectra of ions originating from metastable fragmentations in the first field free region were obtained by selecting the appropriate *m/z* value with the magnet; all other conditions were as above. Metastable peak shapes were measured using both a ZAB-2F and a Kratos-AEI MS 902S mass spectrometer. Appearance Energies were measured with an apparatus comprised of an electrostatic electron monochromator together with a quadrupole mass analyzer and minicomputer data system.[23] Metastable peak AE values were measured with a MS902 instrument as described elsewhere.[9]

All compounds were commercially available or synthesized by unexceptional methods. Cyclopropanol was prepared as described in ref 24 and 25.

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Registry No. $[COH]^{+\cdot}$, 60528-75-8; $[HCOH]^{+\cdot}$, 86549-47-5; $[C(OH)_2]^{+\cdot}$, 71946-83-3; $[HCOO]^+$, 54375-27-8; $[COOH]^+$, 638-71-1.

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