Low-energy Fragmentations of Five Isomeric $[H_3, C, N, O_2]^{+}$ Ions

M. Sirois, J. L. Holmes[†] and C. E. C. A. Hop

Department of Chemistry, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada

The low-energy fragmentation characteristics of the $[H_3, C_1, N, O_2]^{+}$ isomers $[H_3CNO_2]^{+}$ (a), $[H_2C=N(O)OH]^{+}$ (b), $[H_3CONO]^{+}$ (c), $[HC(O)NHOH]^{+}$ (d) and $[HC(OH)=NOH]^{+}$ (e) were studied in detail by metastable ion mass spectrometry. In agreement with most earlier observations, appearance energy measurements established the potential energy surface of the isomers a, b and c, showing the intricate interrelations between them. It was concluded that a isomerizes into b prior to fragmentation by loss of 'OH and H₂O and into c before loss of 'H and H₃CO' moreover, the reverse reactions do not take place on the metastable time-frame. The dominant metastable process for isomers d and e (obtained via HCN loss from glyoxime) was generation of $[H_2NOH]^{+}$. For isomer e this process was proposed to involved a rate-determining isomerization into d. It was concluded that isomers d and e do not intercommunicate with ions a, b and c prior to fragmentation. Neutralization-reionization mass spectrometry indicated that the enol form of formohydroxamic acid as well as the keto counterpart are stable in the gas phase.

INTRODUCTION

The low-energy dissociations of molecular ions in the gas phase often occur only from isomeric ions generated via extensive rearrangement processes. This is especially true for (but by no means limited to) those ions which have lifetimes of $\ge 10^{-6}$ s, i.e. the metastable ions which decompose in the drift regions of a mass spectrometer. This is well illustrated by the metastable fragmentation characteristics of the isomeric nitromethane (a),¹⁻⁷ acinitromethane (b),⁵⁻⁷ and methyl nitrite $(c)^{3-5,7-14}$ radical cations.

 $[H_3CNO_2]^+$ $[H_2C=N(0)OH]^+$ $[H_3CONO]^+$ a b c

Egsgaard et al.⁵ studied the metastable and the collisionally induced decomposition of the isomers a, b and c to investigate the concurrent rearrangements of the nitromethane radical cation into its isomers. For isomer a, they reported five metastable processes: generation of m/z 60 ([H₂CNO₂]⁺), m/z 46 ([NO₂]⁺) (although Lifshitz et al.⁶ have shown that this ion is generated solely by collision), m/z 44 ([H₂CNO]⁺), m/z 43 ([HCNO]⁺ and m/z 30 ([NO]⁺). It was proposed that the signal observed at m/z 44 is due to a $a \rightarrow b$ rearrangement en route to dissociation and the m/z 30 signal was ascribed to O—N bond cleavage in $[H_3CONO]^+$ after a $a \rightarrow c$ rearrangement. Isomer b, obtained via C_2H_4 loss from nitropropane ions, only displayed metastable loss of 'OH and H₂O (generation of m/z 44 and 43), which indicates that a $b \rightarrow a$ isomerization does not take place. With regard to isomer c, it showed only one major fragmentation in the metastable time frame, namely the generation of $[H_2COH]^+ + NO^{.8-10}$ In the metastable ion mass spectrum presented by Egsgaard et al.⁵ signals at m/z 30, [NO]⁺, and 29, [HCO]⁺, were also present,

† Author to whom correspondence should be addressed.

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In addition to the above three species, more $[H_3, C, N, O_2]^{+}$ isomers are known. Formohydroxamic acid was first synthesized by Nef¹⁵ and Schroeter.^{16,17} Two structures were proposed: the keto and enol tautomers. Based on its infrared spectrum, the keto structure has been assigned to formohydroxamic acid.¹⁸ Although formohydroxamic acid has been the source of much biochemical interest, its molecular ion, *d*, has not been investigated mass spectrometrically. Both the molecular ions of the enol tautomer, *e*, and its neutral counterpart have not yet been identified. Recently, carbamic acid and its radical cations, *f*, were identified as stable species in the gas phase.¹⁹

 $[HC(0)NHOH]^{+} [HC(OH)=NOH]^{+} [H_2NC(0)OH]^{+}$ d e f

In this work, the metastable fragmentation characteristics of the isomers a, b and c were reinvestigated in order to establish an unambiguous potential energy surface showing their possible isomerizations. Isomers dand e were identified as stable species in the gas phase and their possible interconversion will be discussed. Lastly, using the relatively new neutralizationreionization technique,^{20–22} the first experimental evidence for the stability of the enol form of formohydroxamic acid will be presented.

EXPERIMENTAL

All experiments were performed using a VG Analytical ZAB-2F double-focusing mass spectrometer of reversed geometry²³ modified for neutralization-reionization (NR) mass spectrometry as described earlier.²⁴ Metastable ion (MI) and collision-activated dissociation (CAD)

Received 25 July 1989. Accepted (revised) 9 November 1989 mass spectra were recorded as described previously.²⁵ Helium was used as target gas in the CAD experiments. In the NR experiments the mass-selected ions were neutralized by charge exchange with xenon. After separating the neutrals from the ions by means of a charged electrode, the former were reionized by collision with O_2 . Isotopic contributions from ions of lower mass were negligible, unless stated otherwise.

In the above experiments all slits were fully open to obtain maximum signal strength and to minimize energy resolving effects. The kinetic energy releases $(T_{0.5})$ for the various metastable processes were obtained from the peak widths at half-height measured under high-energy resolution conditions.²⁶ The *n* values, reflecting the overall shapes of the signals present in MI mass spectra, were determined as described.²⁶

The appearance energies (AE) of metastable processes were measured with a Kratos AEI MS 902S mass spectrometer using a comparative method with iodobenzene and diethyl ether as standards.²⁷ As will be seen below (Fig. 2 and Discussion), the metastable peak AE values were uniformly 0.2–0.3 eV above those recorded by photoionization⁶ and present measurements using energy selected electrons. It is therefore possible that these reactions all have a significant kinetic shift; such differences in measured AE values have been discussed earlier.²⁸ Daughter ion appearance energies were obtained with an apparatus consisting of an electrostatic electron monochromator with a quadrupole mass analyser and a minicomputer data system.²⁹

Methyl nitrite was obtained by mixing methanol, sodium nitrite and dilute sulphuric acid. The gaseous methyl nitrite was admitted to the mass spectrometer without further purification. Formohydroxamic acid was synthesized as described by Fishbein *et al.*³⁰ All other compounds were commercially available.

RESULTS AND DISCUSSION

Metastable ion and collisional activation experiments

The metastable ion mass spectra of $[H_3CNO_2]^{++}$, the $[H_2C=N(O)OH]^{++}$ daughter ions from ionized nitropropane, ^{5,6,31} $[H_3CONO]^{++}$, $[HC(O)NHOH]^{++}$ and the $[H_3, C, N, O_2]^{++}$ daughter ions from glyoxime are presented in Table 1. $([H_2C=NO_2H]^{++}$ could also be obtained via CH₂O loss from ionized CH₂OHCH₂NO₂).

Although the m/z 61 signal in the mass spectrum of glyoxime was only 0.1% of m/z 44 (the most intense signal), it was a single peak under high-resolution conditions and an exact mass measurement showed that it indeed corresponded with $[H_3, C, N, O_2]^{++}$; its generation and observation were reproducible. The production of $[H_3, C, N, O_2]^{++}$ from glyoxime molecular ions can be considered an OH shift accompanied by loss of [H, C, N], probably HCN (Eqn (1)).

H H

$$C \rightarrow C \rightarrow [H_3, C, N, O_2]^+ + [H, C, N]$$
 (1)
HON NOH

Table 1	. Mo ion (b) (d) gly	etastable id s [CH ₃ N(, ^a [CH ₃ O and the [oxime (e)	on mass O ₂] ^{+*} , (NO] ^{+*} [H ₃ , C,	spectra a), [CH (c), [H(N, O ₂] ⁺	of the is ₂ =N(O) C(O)NH f from	iomeric OH] ⁺⁺ OH] ⁺⁺ onized
			m/	zb		
lon	30	31	33	43	44	60

1011	30	31	33	43	44	60
а	478	25		47	1000	730
b				152	1000	18
С		1000				148
d			1000			
е			1000	32	245	

^a Obtained via a 1,5-hydrogen shift in the molecular ion of 1-nitropropane as shown in Ref. 31.
 ^b Abundances normalized to the highest peak in the MI mass spectrum = 1000.

The MI mass spectra of a, b and c were in good agreement with reported spectra,⁵ except for the complete absence of m/z 46 and 15 in the MI mass spectrum of nitromethane ions (as has been also reported by Lifshitz *et al.*⁶) and m/z 30 and 29 in that of methyl nitrite ions. These differences can be explained by lower background pressures and therefore less contribution from collisional activation processes in the present experiments (see also Introduction).

CAD mass spectra were also recorded; those of a, b and c were close to those published earlier^{5,7} and those of [HC(O)NHOH]⁺ and the [H₃, C, N, O₂]⁺ ions from ionized glyoxime are shown in Fig. 1.

Potential energy surface of $[H_3CNO_2]^+$, $[H_2C=N(O)OH]^+$ and $[H_3CONO]^+$

The appearance energies and the kinetic energy releases of the metastable decompositions of the isomers a, band c are reported in Table 2. The potential energy surface of the three isomers, derived from the above data, is shown in Fig. 2 and will be discussed in detail below.

First we shall consider the H[•] loss process. In agreement with Lifshitz et al.,6 we find that the CAD mass spectra of the m/z 60 ions from these three precursors are identical within experimental error and assign them the structure $[H_2CONO]^+$. This structure has also been assigned to this ion on the basis of ab initio molecular orbital theory calculations,³² which lead to an energy of 970 kJ mol⁻¹ for the sum of $\Delta H_f \cap [H_2 \text{CONO}]^+ + \Delta H_f \cap [H^-]$. This energy is below that measured from H₃CONO using energy selected electrons, 1014 kJ mol⁻¹ (see Fig. 2), but the latter should be regarded as an upper limit in view of the kinetic energy release. Generation of [H₂CONO]⁺ from nitromethane and its aci form must involve complex rearrangements; these processes will be discussed below. Note, however, that in contrast with an earlier report,⁶ the kinetic energy releases are markedly different, 324 and 37 meV, respectively, indicating that different processes are involved.

Generation of NO⁺, Process (2), for ionized nitromethane takes place via rearrangement⁵ of *a* into *c*. *A* priori this is unexpected, because m/z 31, [H₂COH]⁺, is the dominant process for metastable methyl nitrite ions



Figure 1. CAD mass spectra of (a) $[HC(0)NHOH]^+$ (d) and (b) the $[H_3, C, N, O_2]^+$ daughter ions of ionized glyoxime (e). Helium was used as the target gas. Peaks marked with asterisks are artifacts.

and generation of m/z 30 does not take place on the metastable time scale. However, isomerization of *a* into *c* yields highly excited ions (~150 kJ mol⁻¹ of internal energy, see Fig. 2), which will favour a fragmentation reaction with a high frequency factor, i.e. O—N bond cleavage, instead of a complex rearrangement. This is in good agreement with the breakdown graph, derived from the photoelectron spectrum of methyl nitrite, which shows that at high energy the generation of m/z 30 is favoured over m/z 31.^{3.8}

The occurrence of the $a \rightarrow c$ rearrangement also explains the metastable H^{*} loss, because $[H_3CONO]^{+*}$ loses H^{*} metastably. In addition, the measured transition state energy for H^{*} loss is, within experimental error, equal to that for the $a \rightarrow c$ rearrangement (see Fig. 2). This barrier gives rise to the large kinetic energy release for H^{*} loss.

To explain the generation of $[H_2CNO]^+$ (Eqn (3)) by nitromethane molecular ions, a $a \rightarrow b$ rearrangement was proposed.⁵ The AE of metastably generated

Table 2. Appearance energies and kinetic energy releases, $T_{0.5}$, of the metastable processes of the nitromethane, *aci*-nitromethane and methyl nitrite radical cations^a

Metastable process	Equation No.	Appearance energy (eV)	τ _{ο.5} (meV)
$[CH_3NO_2]^+ \rightarrow [NO]^+ + CH_3O^*$	(2)	12.0 ± 0.1 ^b	47 (58°)
		(11.75 ± 0.05)°	
$[CH_3NO_2]^+$ $\rightarrow [CH_2NO]^+ + OH$	(3)	12.0 ≘ 0.1 ^ь	25 (30,° 24 ^d)
		(11.75 ± 0.05) °	
$[CH_3NO_2]^+$ \rightarrow $[HCNO]^+$ $+$ H_2O	(4)	∼12.4 ^b	34
$[CH_3NO_2]^+$ $\rightarrow [CH_2ONO]^+ + H^-$	(5)	12.1 ● 0.1 ^b	324 (320°)
		(11.8±0.1)°	
$[CH_2NO_2H]^+$ \rightarrow $[CH_2NO]^+ + OH^-$	(6)	12.9 ± 0.1 ^b	14 (15 ^d)
$[CH_2NO_2H]^+ \rightarrow [HCNO]^+ + H_2O$	(7)	(Too weak)	33
$[CH_2NO_2H]^+ \rightarrow [CH_2ONO]^+ + H^-$	(8)	(Too weak)	37 (320°)
$[CH_3ONO]^+$ \rightarrow $[CH_2OH]^+ + NO^-$	(9)	11.0 ± 0.2°	(93, ^e 54 ^f)
- - -		$(10.69 \pm 0.03)^{f}$	
$[CH_3ONO]^+ \rightarrow [CH_2ONO]^+ + H^-$	(10)	11.5 ± 0.1 ^b	39 (38°)
	• •	(11 20 ± 0.05) ^b	

^a Appearance energies of source-generated fragment ions and $T_{0.5}$ values obtained from previous studies are given in parentheses.

^b See Experimental.

^c From Ref. 6.

^d From Ref. 5.

° From Ref. 9.

[†]From Ref. 8.

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Figure 2. Potential energy surface of nitromethane, *aci*-nitromethane and methyl nitrite radical cations and their metastable fragmentation routes. All ΔH_{f}° values are from Ref. 33, except $\Delta H_{f}^{\circ}([\text{HCNO}]^{+})$ and $\Delta H_{f}^{\circ}([\text{H}_{2}\text{CNO}]^{+})$, which are from Refs 38 and 35, respectively, and $\Delta H_{f}^{\circ}([\text{H}_{2}\text{C=NO}_{2}\text{H}]^{++})$ and $\Delta H_{f}^{\circ}([\text{H}_{2}\text{CONO}]^{+})$, which were determined in this work. The energies for the transition states are calculated from the data in Table 1; underlined in bold are the transition states for metastable reactions and dots indicate those determined from daughter ion appearance energies (see Experimental).

 $[H_2CNO]^+$ was measured to be 12.0 eV, resulting in a transition-state energy for the rate-determining step of 1083 kJ mol⁻¹ ($\Delta H_1^{\circ}(H_3CNO_2) = -75$ kJ mol⁻¹).³³

No details were given by Egsgaard *et al.*⁵ for the third and fourth metastable processes, generation of [HCNO]⁺ (Eqn (4)) and [H₂CONO]⁺ (Eqn (5)). The *AE* of metastably generated m/z 43 from nitromethane, 12.4 eV, yields a transition-state energy of 1121 kJ mol⁻¹. However, m/z 43 is only a minor peak in the MI mass spectrum of nitromethane ions (see Table 1) and so a competitive shift can be expected, making the measured *AE* too high. Moreover, C—N bond cleavage, which has the same apparent energy requirement $(\Delta H_f^{\circ}([NO_2]^+) + \Delta H_f^{\circ}('CH_3) = 1120 \text{ kJ mol}^{-1})^{33}$ is not an observed metastable process for nitromethane ions.

Note that the above AEs are those of metastable processes, i.e. ions fragmenting after $10^{-6}-10^{-5}$ s. The AEs of some of the daughter ions have also been measured by photoionization⁶ at extended lifetimes and so those AE values are consistently lower than the present results (see Table 2).

The *aci* form of nitromethane was obtained via a 1,5hydrogen shift in the molecular ion of 1-nitropropane.³¹ The *AE* of the $[H_2C=N(O)OH]^{+\cdot}$ daughter ion, measured using energy selected electrons, 11.75 eV, gave $\Delta H_f^{\circ}(b) = 958 \text{ kJ mol}^{-1} (\Delta H_f^{\circ}(C_3H_7NO_2) = -124 \text{ kJ} \text{ mol}^{-1} \text{ and } \Delta H_f^{\circ}(C_2H_4) = 52 \text{ kJ mol}^{-1}$,³³ assuming that there is no excess energy involved in the reaction. Thus, *b* is more stable than *a* ($\Delta H_f^{\circ}(a) = 987 \text{ kJ} \text{ mol}^{-1}$),³³ by 29 kJ mol⁻¹, which is considerably less than the difference obtained by Egsgaard *et al.*,⁵ 80 kJ mol⁻¹, from the same *AE* measurement.

With regard to metastable processes, *aci*nitromethane ions yield $[H_2CNO]^+$ + 'OH (Eqn (6)), $[HCNO]^+$ + H_2O (Eqn (7)) and $[H_2CONO]^+$ + H'

(Eqn (8)). Note that the metastable peaks for these three reactions arise from an ion of low abundance in the normal mass spectrum of nitropropane (only $\sim 1.5\%$ of the base peak). Only the metastable peak for reaction (6) was sufficiently intense for a reasonably accurate AEdetermination. The transition-state energy for the reaction $[H_2C=N(O)OH]^{+} \rightarrow [HCNO]^{+} + H_2O$ (Eqn (7)) could only be roughly estimated as lower than ~1121 kJ mol⁻¹ and certainly no less than that for reaction (6). The H loss metastable peak was the weakest. The AE of metastable reaction (6), 12.9 eV, gave a transition state energy of 1069 kJ mol⁻¹ for 'OH loss from b. The latter is lower than the transition state energy for 'OH loss from a via b (Eqn (3)), 1083 kJ mol^{-1} (see above). Thus, the rate-determining step for dissociation of $[H_3CNO_2]^+$ into $[H_2CNO]^+$ + OH is proposed to be the isomerization into the aci form, $[H_2C=N(O)OH]^+$; this is supported by the $T_{0.5}$ value for reaction (3) being larger than the $T_{0.5}$ value for reaction (6), 25 versus 14 meV (see Table 2). In addition, the metastable peak shapes for the two processes are different; the n values are 1.60 and 1.75, respectively (see Table 3). It now remains to explain the metastable gen-

Table 3. Peak [H ₂ CN by the Ref. 20	Peak shapes of metastably generated $[H_2CNO]^+$ and $[HCNO]^{+\cdot}$ ions as reflected by the <i>n</i> values, determined as described in Ref. 26.				
		Equation			
Metasta	able process	No.	n		
$[CH_3NO_2]^{+} \rightarrow$	[CH2NO]+ + OH.	(3)	1.60		

Metastable process	No.	n
$[CH_3NO_2]^+$ $\rightarrow [CH_2NO]^+ + OH^-$	(3)	1.60
$[CH_3NO_2]^+ \rightarrow [HCNO]^+ + H_2O$	(4)	1.75
$[CH_2NO_2H]^+ \rightarrow [CH_2NO]^+ + OH^-$	(6)	1.75
$[CH_2NO_2H]^+ \rightarrow [HCNO]^+ + H_2O$	(7)	1.75

eration of $[\text{HCNO}]^{+}$ from isomers *a* and *b*. Since the $T_{0.5}$ values as well as the *n* values of both metastable peaks are the same (see Tables 2 and 3), we propose that for nitromethane ions a $a \rightarrow b$ isomerization takes place prior to dissociation of $[\text{H}_2\text{C}=\text{N}(\text{O})\text{OH}]^{+}$ into $[\text{HCNO}]^{+} + \text{H}_2\text{O}$, with the latter step being rate determining.

Note that the inverse process, $b \rightarrow a$, does not take place because m/z 30 is not produced metastably by the aci form. Since the transition state energy for the $b \rightarrow a \rightarrow [NO]^+ + H_3CO^\circ$ process is only 1083 kJ mol⁻¹ (see Fig. 2), the barrier for H₂O loss from $[H_2C=N(O)OH]^+$, a metastable process, is probably significantly lower than the value given in Fig. 2, 1121 kJ mol⁻¹. Additionally, H₂O loss could be kinetically favoured over the $b \rightarrow a \rightarrow [NO]^+ + H_3CO^\circ$ process because it involves a less complex mechanism, i.e. one instead of two rearrangement reactions (see Fig. 2).

The highest energy fragmentation for the metastable $[H_2CN(O)OH]^+$ ions is H[•] loss. The reaction sequence $b \rightarrow a \rightarrow c$ can be ruled out because the *aci* form does not isomerize to nitromethane (see above). Although the kinetic energy releases for H[•] loss from $[H_2CN(O)OH]^+$ and $[H_3CONO]^+$ are similar, the MI mass spectra (Table 1) do not provide support for a direct $b \rightarrow c$ isomerization.

Finally, for the methyl nitrite radical cation, thermodynamically the most stable of the three isomers $(\Delta H_f^{\circ}(c) = 935 \text{ kJ mol}^{-1})$,³³ the absence of m/z 44 and 43 in its MI and CAD mass spectra indicates that it does not communicate with isomers *a* and *b*. The potential energy surface, Fig. 2, shows that dissociation into $[H_2COH]^+ + NO^{\circ}$ is thermochemically much more favourable than the $c \rightarrow a$ isomerization. The metastable generation of $[H_2COH]^+$ has been the subject of numerous investigations⁸⁻¹⁴ and will not be discussed further.

Characterization of [HC(O)NHOH]⁺ and its tautomer [HC(OH)=NOH]⁺

The MI mass spectra of $[HC(O)NHOH]^{+}$ and the $[H_3, C, N, O_2]^{+}$ daughter ions from glyoxime are both dominated by m/z 33, but the latter spectrum also contains peaks at m/z 44 and 43 (see Table 1). In addition, the $T_{0.5}$ values of the m/z 33 signals are different, 21 and 113 meV, respectively (the $T_{0.5}$ value for m/z 44 in the MI mass spectrum of the m/z 61 daughter ions from glyoxime is 49 meV). This shows that we are dealing with two different $[H_3, C, N, O_2]^{+}$ isomers, and this is confirmed by their having different CAD mass spectra (see Fig. 1). The ions of m/z 32 and 29 are relatively more abundant in the CA mass spectrum of $[HC(O)NHOH]^{+}$. In contrast, the CAD mass spectrum of the m/z 61 ions from ionized glyoxime has relatively more intense signals at m/z 44, 43 and 30.

The CAD mass spectrum of the $[H_3, N, O]^{+}$ ions generated metastably in the first field-free region from ionized formohydroxamic acid is identical with that of the source-generated $[H_3, N, O]^{+}$ daughter ions and that of ionized hydroxylamine (hydroxylamine was obtained via thermolysis of hydroxylamine hydrochloride on a heated ion source probe). The high-mass regions of these spectra are dominated by m/z 32, 30 and 31 and the low-mass regions by m/z 16 and 17, in decreasing order of intensity. Hence the $[H_3, N, O]^{+}$ ions generated metastably from ionized formohydroxamic acid have the $[H_2NOH]^{+}$ structure. It is worth noting that the NR mass spectrum of $[H_2NOH]^{+}$ has m/z 33 as the base peak and closely resembles the CAD mass spectrum, which is in keeping with the stability of $H_2NOH.^{34}$

Generation of $[H_2NOH]^{+}$ via a 1,2-hydrogen shift in $[HC(O)NHOH]^{+}$ can be ruled out, because the ion thus obtained, $[OCNH_2OH]^{+}$, would be expected to dissociate into $[H_2NCO]^{+}$ + 'OH, the bond cleavage of lower energy requirement. $(\Sigma \Delta H_f^{\circ}([H_2NOG]^{+}$ + 'OH) = 711 kJ mol^{-1 33,35} and $\Sigma \Delta H_f^{\circ}([H_2NOH]^{+}$ + CO) = 773 kJ mol^{-1 33} (the ionization energy of H_2NOH mentioned in Ref. 33, 10.0 eV, is the vertical ionization energy. The adiabatic ionization energy, 9.6 eV,³⁶ yields $\Delta H_f^{\circ}(H_2NOH) = 884$ kJ mol⁻¹). By analogy with the mechanism proposed for the generation of CH₃OH₂⁺ from ionized ethylene glycol,³⁷ oddelectron hydrogen-bridged species are suggested to be intermediates:



Two mechanisms can be proposed for the generation of the ion of m/z 61 from glyoxime: an OH shift to the carbon atom yielding [HC(OH)=NOH]⁺⁺, e (Eqn (12a)) or an OH shift to the nitrogen atom yielding [HCN(OH)₂]⁺⁺, g (Eqn (12b)). Ab initio molecular orbital theory calculations¹⁰ predicted the heat of formation of e to be 117 kJ mol⁻¹ lower than that of a, i.e. ΔH_f° ([HC(OH)=NOH]⁺⁺) = 870 kJ mol⁻¹. No experimental or theoretical results were available for ion g.



Considering structures e and g, the metastably generated m/z 44 and 43 ions are most likely [HCNOH]⁺ and [HCNO]⁺ and the calculated difference between the sum of the heats of formation of the fragmentation products $(\Delta H_f^{\circ}([\text{HCNOH}]^+) + \Delta H_f^{\circ}(^{\circ}\text{OH}) = 998 \text{ kJ}$ mol⁻¹ ^{33,35} and $\Delta H_f^{\circ}([\text{HCNO}]^+) + \Delta H_f^{\circ}(\text{H}_2\text{O}) =$ 1031 kJ mol⁻¹ ^{33,38}) is in keeping with the ratio of the two signals in the MI mass spectrum, $\sim 8:1$. Generation of [H₃, N, O]^{+•} is the most intense metastable process and consequently the energy of the transition state for this process is expected to be lower than 998 kJ mol⁻¹. The $\overline{T}_{0.5}$ value for the m/z 33 ion, 113 meV, indicates that this is not a threshold process and so a considerable barrier for the reverse reaction is expected. Note that generation of $[H_3, N, O]^{+}$ involves a complex rearrangement. Assuming that the [H₃, C, N, O₂]^{+•} daughter ions from ionized glyoxime have structure e, two hydrogen atoms have to be transferred. If the m/z 61 ions have structure q, an OH transfer has to take place in addition to the transfer of two hydrogen atoms. At this point the former argument seems more feasible than the latter.

To aid structure assignment of the m/z 61 daughter ions of ionized glyoxime, the NR mass spectrum of these ions was recorded (see Fig. 3b). The spectrum is clearly different from that of ionized formohydroxamic acid (see Fig. 3a). Since the contributions from metastable fragmentation of ions are reduced in NR mass spectra compared with those in CA mass spectra,³⁹ it can be safely stated that the NR and CAD mass spectra of the m/z 61 daughter ions of ionized glyoxime are in good agreement (the signal at m/z 28 is due to ionization of metastably generated CO). An important feature of the NR mass spectrum is the presence of a recovery signal at m/z 61, indicating that the neutral counterpart of the mass-selected m/z 61 ions is a stable species in the gas phase. The stability of the [H₃, C, N, O₂] neutrals is best explained by assigning structure *e* to the m/z 61 ions, rather than the (neutral) carbene shown in reaction (12b).

Hence we propose that the $[H_3, C, N, O_2]^{+\cdot}$ ions from ionized glyoxime have structure *e*, the enol form of formohydroxamic acid. The m/z 33 peak in the MI mass spectrum is then explained by a rate-determining isomerization of the enol form into the keto form (a 1,3hydrogen shift) followed by the mechanism depicted in Eqn (11). The rate-determining character of the $e \rightarrow d$ isomerization explains the $T_{0.5}$ value of m/z 33 for isomer *e* being larger than that for isomer *d*, 113 versus 21 meV. None of the above results lead us to suggest that ions *a*, *b* and *c* communicate with ions *d* and *e* prior to their dissociation.

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Figure 3. Neutralization-reionization mass spectra of (a) $[HC(O)NHOH]^{++}$ (d) and (b) the $[H_3, C, N, O_2]^{++}$ daughter ions of ionized glyoxime (e). Xenon was the charge exchange neutralization agent and oxygen the reionization target gas.

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