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Unimolecular Chemistry of Oxazole and Isoxazole Radical Cations in the Gas Phase: Combined Experimental and Molecular Orbital Study

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Molecular radical cations of oxazole (1) and isoxazole (2) dissociate by losing carbon monoxide or a hydrogen atom, respectively. These fragmentations were examined by use of tandem mass spectrometry, flash vacuum pyrolysis and *ab initio* molecular orbital calculations. A multi-step mechanism is proposed which incorporates these new experimental and theoretical data. The case of methylated homologues of 1 and 2 is also considered.

INTRODUCTION

Oxazoles and isoxazoles constitute an important class of heterocyclic compounds whose mass spectrometry, although documented,[1–3] is not yet fully understood. The first detailed investigations of the fragmentation mechanisms of oxazole[2] and isoxazole[3] made in the 1980s used appearance energy determinations and semi-empirical molecular orbital calculations. During the last decade, new techniques have appeared which may bring new insights into the delicate and seemingly complex chemistry of these compounds. Tandem mass spectrometry (MS/MS) and particularly collision-induced dissociations (CID) provide new means to characterize ion structures.[4] Reaction intermediates suspected to intervene during a fragmentation process may be prepared in various ways, in particular by flash vacuum pyrolysis (FVP).[5] Further, molecular orbital (MO) calculations by the *ab initio* method are currently available and may be applied to polyatomic systems of reasonable size.[6]

The purpose of this study was to obtain new information related to the chemistry of the (is)oxazole radical cations by use of MS/MS, FVP and *ab initio* MO calculations. Results are presented by class isomers pertaining to the (is)oxazole group, $[C_3H_3NO]^{+\cdot}$, their methylated homologues, $[C_4H_5NO]^{+\cdot}$ and the fragmentation products $[C_3H_2NO]^+$ and $[C_2H_3N]^{+\cdot}$. The overall isomerization–fragmentation schemes of the (is)oxazole molecular ions and their methylated derivatives are presented.

EXPERIMENTAL

Conventional mass spectra, mass-analysed ion kinetic energy (MIKE) spectra and CID spectra were obtained with a Varian Mat 311 A reversed geometry (B–E) mass spectrometer and a Kratos AEI MS 902 S triple sector (E–B–E) modified instrument.[7] These instruments are equipped with a collision cell in the second and in the third field-free regions, respectively. The ion accelerating potentials were to 3 kV (Varian) or 8 kV (Kratos).

The FVP unit adapted to the triple sector mass spectrometer consists of a heated quartz tube directly connecting the ion source to the all-glass heated inlet system. For the B–E mass spectrometer, the pyrolysis is realized inside an internal oven localized ~20 mm from the ionization region.

Most of the samples used were of commercial origin: oxazole (**1**); isoxazole (**2**); pyruvonitrile (**5**); propiolamide (**6**); 5-methylisoxazole (**15**); 5-methyloxazole (**14**);[8] 4-methyloxazole (**21**);[9] 2-methyloxazole (**22**)[10] and acetylacetonitrile (**23**).[11] Meldrum's acids (**24**, **25** and **26**)[5,12] were synthesized by current methods. For 2,2-dimethyl-5-(N-methylaminomethylene)-1,3-dioxane-4,6-dione (**25**), 7.2 g (50 mmol) of Meldrum's acid was dissolved in 40 ml of triethyl orthoformate (TEOF) and colled to 0 °C. A solution of 1.6 g (2.5 ml; 50 mmol) of methylamine in 5 ml of TEOF, precooled to −10 °C, was slowly added, causing the solution to turn yellow, followed by precipitation of a solid. The mixture was stirred at 0 °C for a further 15 min, the solid filtered, washed with 15 ml portions of TEOF and hexane (twice) and then recrystallized twice from ethanol, giving 4 g (43%) of a colourless solid (RMM from high-resolution mass spectrometry = 185.068 811; calculated for $C_8H_{11}NO_4$, 185.068 802).

For 5-(2-aminoethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**26**), 2 g (9.3 mmol) of 5-(2-ethoxyethylidene)-Meldrum's acid[13] was dissolved in 50 ml of ethanol saturated with ammonia and left at room temperature for 24 h. Evaporation of the solvent gave a slightly yellow solid, which was recrystallized from ethanol–diethyl ether to give 0.8 g (46%) of a colourless solid (RMM from high-resolution mass spectrometry = 185.068 809; calculated for $C_8H_{11}NO_4$, 185.068 802).

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Molecular orbital calculations were carried out by using the set of computer programs MONSTERGAUS,[14] CIPSI[15] and GAUSSIAN 86[16] implemented in the IBM computer of the CIRCE (Centre Inter-Regional de Calcul Electronique, Orsay, France). The geometries of the various $[C_3H_3NO]^{+\cdot}$, $[C_4H_5NO]^{+\cdot}$, $[C_3H_2NO]^+$ and $[C_2H_3N]^{+\cdot}$ ions were optimized with the 3–21G basis set of atomic orbitals. Consideration of the electron correlation effect was systematically made with the 6–31G basis set and using the CIPSI algorithm. In this method a zero-order wavefunction containing the most important configurations (40–70 in the present cases) is first defined. The other configurations resulting from single and double excitations are then generated (i.e. $\sim 10^5$–10^7 configurations) and subjected to a Møller–Plesset perturbational calculation up to the second order. In order to take into account the electron correlation effect at the 6–31G* level the following estimation was made: E(Cl/6–31G* RHF) = E(Cl/6–31G RHF – E(6–31G RHF) + E(6–31G* UHF).[17]

The validity of this additivity rule was checked by comparisons with MP2/6–31G and MP2/6–31G* calculations in the $[C_3H_3NO]^{+\cdot}$ series (data available from the corresponding author on request).

RESULTS AND DISCUSSION

Isomerization–fragmentation of (is)oxazoles

The 70 eV electron impact mass spectra of oxazole and isoxazole show peaks at m/z 69 ($M^{+\cdot}$, base peak), 68 ($[M - H]^+$), 42 ($[M - HCN]^{+\cdot}$), 41 (mixture of $[M - CO]^{+\cdot}$ and $[M - CH_2N]^+$ ions) and 40 ($[M - HCO]^+$) (Fig. 1). The only significant difference between the two spectra is a greater abundance of $M^{+\cdot}$ for oxazole. The situation changes markedly for metastable ions $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$, as demonstrated by the MIKE spectra of both molecular ions (Fig. 1). The dominant fragmentations from ions $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$ of low internal energy are losses of CO and H, respectively:

$$[\mathbf{1}]^{+\cdot} \rightarrow [C_2H_3N]^{+\cdot} + CO$$

$$[\mathbf{2}]^{+\cdot} \rightarrow [C_3H_2NO]^+ + H^\cdot$$

These two fragmentations indeed possess the lowest appearance energies.[2,3]

Accordingly, experimental thresholds for the appearance of $[\mathbf{1} - CO]^{+\cdot}$ and $[\mathbf{1} - H]^+$ ions are 135 and 299 kJ mol^{-1} above the heat of formation of $[\mathbf{1}]^{+\cdot}$; similar measurement for $[\mathbf{2}]^{+\cdot}$ gives 180 and 126 kJ mol^{-1}, respectively. These values may be used to select the best candidates for $[C_2H_3N]^{+\cdot}$ and $[C_3H_2NO]^+$ to be produced from ions $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$ of low internal energy. However, it must be recalled that appearance energies cannot give anything other than an upper limit for the heat of formation of the products of an endothermic fragmentation. Several factors, such as kinetic shift, competitive shift and reverse critical energy, come in addition to the heat of formation of the products. Reverse critical energy may be partly accounted for by considering the kinetic energy T released during the separation of the fragments of metastable ions. In the present case, the $T_{0.5}$ values associated with the CO loss from $[\mathbf{1}]^{+\cdot}$ and with the $H^\cdot$ loss from $[\mathbf{2}]^{+\cdot}$ are 14 and 33 kJ mol^{-1}, respectively. Consequently, for these two lowest energy processes for which no competitive shift is operative and for which only a limited kinetic shift is

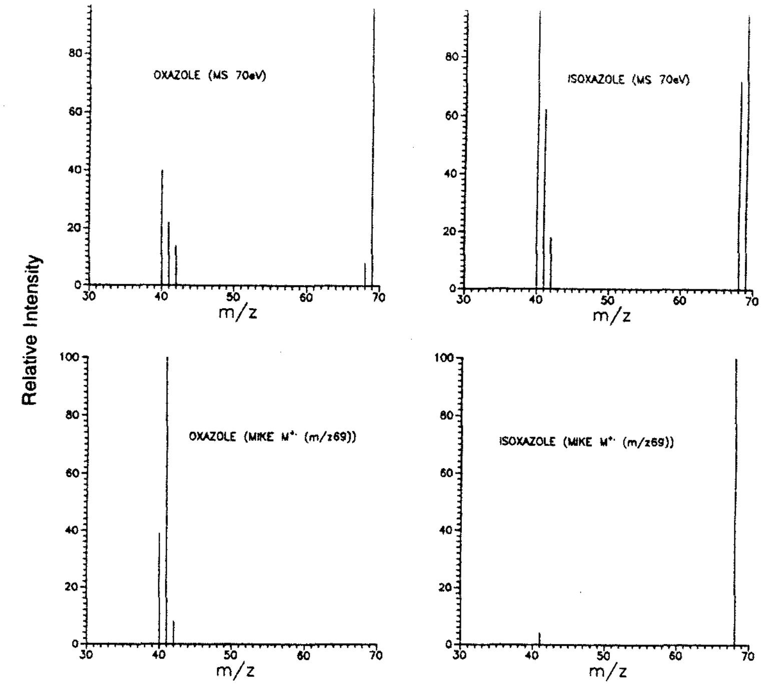


Figure 1. Comparison of the conventional 70 eV mass spectra of oxazole (**1**) and isoxazole (**2**) and the MIKE spectra of the molecular ions.

expected it may be deduced that

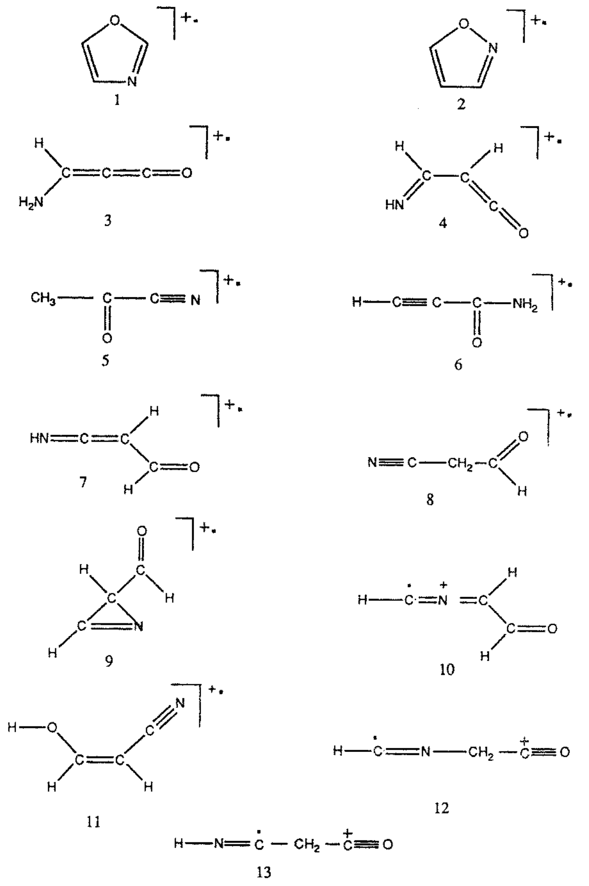
$$\Delta H_f{}^{\circ}([1 - CO]^{\bullet} + CO) \leqslant 1018\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H_f{}^{\circ}([2 - H]^{+} + H^{\bullet}) \leqslant 1130\ \mathrm{kJ\ mol^{-1}}$$

This thermochemical argument is combined below with the theoretical and experimental investigations of possible isomeric structures which may intervene as reaction intermediates or as ionic products during fragmentation of $[\mathbf{1}]^{+\bullet}$ and $[\mathbf{2}]^{+\bullet}$. Several $[C_3H_3NO]^{+\bullet}$ ions and candidate structures for $[M - H^{\bullet}]^{+}$ and $[M - CO]^{+\bullet}$ fragment ions are examined below. Finally, attention is paid to the methyl-substituted (is)oxazole molecular radical cations.

$[C_3H_3NO]^{+\bullet}$. *MO calculations.* Only few thermochemical data of experimental origin are available for $[C_3H_3NO]^{+\bullet}$ ions. The heats of formation of $[\mathbf{1}]^{+\bullet}$ and $[\mathbf{2}]^{+\bullet}$ may be estimated precisely using the experimental heats of formation of the neutral species (−15.5 and +78.6 kJ mol^{-1}, respectively) and their adiabatic ionization energies as determined by 'linear' extrapolation of the first band of the photoelectron spectra (912 ± 5 kJ mol^{-1}) (the oxazole photoelectron spectrum was recorded on the Perkin–Elmer PS 18 spectrometer at the Laboratoire des Mécanismes Réactionnels, Ecole Polytechnique, Palaiseau, France) and 958 ± 5 (Ref. 2) kJ mol^{-1}, respectively). This gives $\Delta H_f{}^{\circ}$ $([\mathbf{1}]^{+\bullet}) = 897$ kJ mol^{-1} and $\Delta H_f{}^{\circ}$ $([\mathbf{2}]^{+\bullet}) = 1037$ kJ mol^{-1}. For the cation $[\mathbf{6}]^{+\bullet}$ a $\Delta H_f{}^{\circ}$ value of 1023 kJ mol^{-1} is tabulated.[18]

In addition to the ionized oxazole $[\mathbf{1}]^{+\bullet}$–isoxazole $[\mathbf{2}]^{+\bullet}$ pair, a set of eleven isomeric open forms $[\mathbf{3}]^{+\bullet}$–$[\mathbf{13}]^{+\bullet}$ (Scheme 1) has been examined by *ab initio* MO calculations. The results obtained at various levels of theory are listed in Table 1. As expected for such (open-shell) unsaturated species presenting various arrangements of the π-electron system, the influence of both polarized basis set and electron correlation on the relative energies is pronounced. However, a general order of stability is preserved from the simple 3–21G// 3–21G calculation to the highest level of theory used here, i.e. CI/6–31G*.



Scheme 1. $[C_3H_3NO]^{+\bullet}$ radical cations.

The most stable ionized species are the enol ion $[\mathbf{11}]^{+\bullet}$, distonic ions $[\mathbf{12}]^{+\bullet}$ and $[\mathbf{13}]^{+\bullet}$ or radical cations containing cumulated double bonds: HN=C=CHCHO $[\mathbf{7}]^{+\bullet}$, 3-aminopropadienone $[\mathbf{3}]^{+\bullet}$, imidoylketene $[\mathbf{4}]^{+\bullet}$ and HC=N=CHCHO $[\mathbf{10}]^{+\bullet}$. All the other triple bond-containing radical cations $[\mathbf{5}]^{+\bullet}$, $[\mathbf{6}]^{+\bullet}$ and $[\mathbf{8}]^{+\bullet}$ and the heterocyclic rings $[\mathbf{2}]^{+\bullet}$ and $[\mathbf{9}]^{+\bullet}$ are found at a higher energy level.

One should note, at this stage, that only structures $[\mathbf{3}]^{+\bullet}$, $[\mathbf{4}]^{+\bullet}$, $[\mathbf{7}]^{+\bullet}$ and $[\mathbf{10}]^{+\bullet}$–$[\mathbf{13}]^{+\bullet}$ are sufficiently stable to intervene before H$^{\bullet}$ loss from oxazole $[\mathbf{1}]^{+\bullet}$.

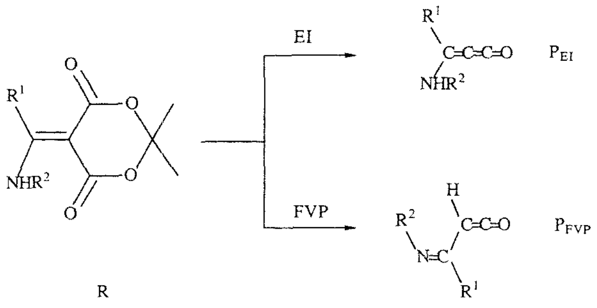
Table 1. Relative energies of $[C_3H_3NO]^{+\bullet}$ ions (kJ mol^{-1}) at different levels of theory on 3–21G optimized geometries[a]

Compound	No.	3–21G	6–31G	6–31G*	CI-6–31G	CI-6–31G*
Oxazole	**1**	0	0	0	0	0
$NH_2CH{=}C{=}C{=}O$	**3**	−102	−99	1	−119	−18
HN=C=CHCHO	**7**	−105	−105	8	−160	−48
HC=NCHCHO	**10**	−52	−61	44	−117	−12
NCCH=CHOH	**11**	−51	−54	29	−70	13
$HN{=}CCH_2C{=}O$	**13**	−40	−24	32	−68	−8
HN=CHCH=C=O	**4**	−35	−41	4	−52	−7
$NC{=}NCH_2C{=}O$	**12**	9	16	68	−34	17
$HC{=}CCONH_2$	**6**	−1	−12	129	8	149
$CH_3COC{=}N$	**5**	54	58	136	63	142
Isoxazole	**2**	203	201	264	164	227
$(HC{=}NCH)_{cy}CHO$	**9**	223	211	245	203	235
$N{=}CCH_2CHO$	**8**	46	52	117	69	134

[a] Reference energies in hartree: 3–21G = −242.93 574; 6–31G = −224.18 797; 6–31G* = −244.33 218; CI-6–31G = −244.66 726; CI-6–31G* = −244.81 134.

Tandem mass spectrometric results. Only six $[C_3H_3NO]^{+\cdot}$ ions were amenable to mass spectrometric investigations: the molecular ions of oxazole $[\mathbf{1}]^{+\cdot}$, isoxazole $[\mathbf{2}]^{+\cdot}$, pyruvonitrile $[\mathbf{5}]^{+\cdot}$, propynamide $[\mathbf{6}]^{+\cdot}$ and ketenes $[\mathbf{3}]^{+\cdot}$ and $[\mathbf{4}]^{+\cdot}$, which may be produced from 5-aminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione $[\mathbf{24}]^{+\cdot}$ by either dissociative ionization or FVP followed by ionization (Scheme 2).

The CID spectra of $[\mathbf{1}]^{+\cdot}$–$[\mathbf{6}]^{+\cdot}$ are presented in Table 2. Ionized oxazole and isoxazole give similar CID spectra and their behaviour under collision conditions is clearly different from that of the four other species $[\mathbf{3}]^{+\cdot}$–$[\mathbf{6}]^{+\cdot}$. The CID spectrum of $[\mathbf{3}]^{+\cdot}$ is characterized by important peaks at *m/z* 53, 42 and 28, which may be interpreted by losses of NH_2, CNH (or HCN) and C_2H_3N (or CHO), respectively. The pyrolysis product $[\mathbf{4}]^{+\cdot}$ presents a CID spectrum dominated by a peak at *m/z* 42 (loss of HCN or HNC). The enhancement of the *m/z* 28 peak is noteworthy because of its origin (loss of C_2HO) in direct relation with the imidoylketene structure $[\mathbf{4}]^{+\cdot}$. Ions $[\mathbf{5}]^{+\cdot}$ and $[\mathbf{6}]^{+\cdot}$ are readily distinguishable from their CID spectra, which are dominated by the α-cleavage products: losses of CH_3 and CN for $[\mathbf{5}]^{+\cdot}$ (*m/z* 54 and 43) and losses of NH_2 and to a lesser extent C_2H for $[\mathbf{6}]^{+\cdot}$ (*m/z* 53 and 44).



R^1	R^2	R	P_{EI}	P_{FVP}
H	H	24	3	4
H	CH_3	25	16	17
CH_3	H	26	18	19

Scheme 2

The obvious conclusion which may be drawn from the present data is that, for ions of low internal energy, there is no structure equilibration between the couple $[\mathbf{1}]^{+\cdot}$–$[\mathbf{2}]^{+\cdot}$ and the four isomers $[\mathbf{3}]^{+\cdot}$–$[\mathbf{6}]^{+\cdot}$.

$[C_3H_2NO]^+$. *MO calculations.* Five $[C_3H_2NO]^+$ ion structures, $[\mathbf{27}]^+$–$[\mathbf{31}]^+$, have been optimized (3–21G basis set) and their energies estimated up to the CI/6–31G* level (Table 3). The ions $[\mathbf{27}]^+$, $[\mathbf{28}]^+$ and $[\mathbf{29}]^+$ are close together in energy and the ion $[\mathbf{31}]^+$ is clearly unstable with respect to the most stable ion $[\mathbf{27}]^{+\cdot}$.

No experimental heat of formation is available for the $[C_3H_2NO]^+$ ions. An estimate may be deduced from the calculation. Tables 1 and 3 contain the data allowing an estimate of the relative energy of each pair of fragments $[C_3H_2NO]^+ + H^\cdot$ with respect to ionized oxazole $[\mathbf{1}]^{+\cdot}$. These values (131, 208, 171, 295 and 494 kJ mol^{-1}, respectively, for $[\mathbf{27}]^+$–$[\mathbf{31}]^+$, CI/6–31G*//3–21G calculations) combined with $\Delta H_f^\circ([\mathbf{1}]^{+\cdot}) = 897$ kJ mol^{-1} and $\Delta H_f^\circ(H^\cdot) = 218$ kJ mol^{-1} lead to heats of formation equal to 810, 887, 850, 974 and 1173 kJ mol^{-1} for $[\mathbf{27}]^+$–$[\mathbf{31}]^+$, respectively.

Tandem mass spectrometric results. CID spectra of $[C_3H_2NO]^+$ cations coming from oxazole $[\mathbf{1}]^{+\cdot}$ and isoxazole $[\mathbf{2}]^{+\cdot}$ are presented in Table 4, where they are compared with that of the $[M - CH_3]^+$ ions coming from 5-methyloxazole $[\mathbf{14}]^{+\cdot}$ and 5-methylisoxazole $[\mathbf{15}]^{+\cdot}$. $[M - OCH_3]^+$ ions originating from $CNCH_2CO_2CH_3$ and $NCCH_2CO_2CH_3$ have also been subjected to CID investigation.

It is apparent that the $[C_3H_2NO]^+$ ions coming from the heterocyclic precursors possess very similar spectral characteristics. The spectra are dominated by the CO loss (*m/z* 40) also observed without collision gas; the structure-significant peaks purely produced by collisions are *m/z* 41 (loss of HCN) and *m/z* 55–50. The former peak remains at *m/z* 41 when the precursor molecule is 5-methyloxazole-2-d_1, **14a** (loss of CDN), and is shifted to *m/z* 42 when the precursor molecule is 5-methylisoxazole-4-d_1, **15a** (loss of CHN).

Table 2. CID–MIKE spectra of $[C_3H_3NO]^{+\cdot}$ ions (*m/z* 69) (relative intensity, %)

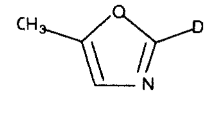
		m/z																	
Compound	Conditions[a]	55	54	53	52	51	50	44	43	42	41	40	39	38	29	28	27	26	25
Oxazole **1**	A	3	1	—	1	3	1	—	—	24	100	86	19	12	19	10	6	5	3
	B	1	—	—	1	—	—	—	—	—	100	—	—	10	12	—	—	—	—
Isoxazole **2**	A	—	1	1	2	4	1	—	2	15	100	91	29	17	22	8	3	8	3
	B	—	—	—	1	—	—	—	—	—	100	100	14	22	—	—	—	5	—
Aminomethyleneketene **3**	A	—	—	61	16	6	2	—	—	80	99	100	28	14	7	29	5	2	8
(**24** → **3**)	B	—	—	46	—	—	—	—	—	58	100	92	—	—	—	29	—	8	—
(**24** → **4**)	B	—	—	7	—	—	—	—	—	100	53	60	—	—	—	42	—	7	—
Pyruvonitrile **5**	A	—	100	1	3	4	1	—	96	14	14	14	14	4	4	—	—	—	—
2-Propynamide **6**	A	—	—	100	4	1	—	8	2	7	12	4	1	—	—	—	—	—	—

[a] (A) Kinetic energy = 8 keV; collision gas, helium; E–B–E mass spectrometer. (B) Kinetic energy = 3 keV; collision gas, argon; B–E mass spectrometer.

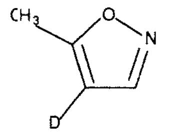
Table 3. Relative energies of $[C_3H_2NO]^+$ $[M - H]^+$ ions (kJ mol^{-1}) at different levels of theory[a]

Structure	Compound	3-21G//3-21G	6-31G//3-21G	6-31G*//3-21G	CI-6-31G//3-21G	CI-6-31G//3-21G
HN=C=CHC=O	**27**	0	0	0	0	0
HC=NCH=C=O	**28**	112	94	86	84	77
$N{=}CCH_2CO$	**29**	92	92	59	73	40
$C{=}NCH_2CO$	**30**	163	153	125	192	164
HC(=N)CH=C=O	**31**	331	298	284	376	363

[a] Total reference energies of $[HN{=}C{=}CHC{=}O]^+$ in hartrees: 3-21G//3-21G = −242.408425; 6-31G//3-21G = −243.644777; 6-31G*//3-21G = −243.765786; CI-6-31G//3-21G = −244142068. Total energies of H' in hartrees: 3-21G = −0.49620; 6-31G = −0.498233; 6-31G* = −0.498233.



14a



15a

Isoxazole precursors **2** and **15** give $[C_3H_2NO]^+$ ions characterized by a small signal at *m/z* 53 (loss of NH), shifted to *m/z* 54 for **15a**. These data suggest that $[C_3H_2NO]^+$ ions produced by H or CH_3 eliminations from isoxazole or 5-methylisoxazole molecular radical cations are rearranged species for which the hydrogen atom originally in position 3 has shifted to the nitrogen atom. No such rearrangement seems to be operative in the case of oxazole and 5-methyloxazole.

The two last lines of Table 4 concern $[C_3H_2NO]^+$ ions expected to have structures $[\mathbf{29}]^+$ and $[\mathbf{30}]^+$:

$$N{\equiv}CCH_2COOCH_3^{+\cdot} \rightarrow \underset{[\mathbf{29}]^+}{N{\equiv}CCH_2CO^+} + {}^\cdot OCH_3$$

$$C{\equiv}NCH_2COOCH_3^{+\cdot} \rightarrow \underset{[\mathbf{30}]^+}{C{\equiv}NCH_2CO^+} + {}^\cdot OCH_3$$

These ions have been prepared by dissociative ionization (loss of $CH_3O^\cdot$) of methyl (iso)cyanoacetates. The two spectra present the two informative peaks of *m/z* 42 (CN loss) and 40 (CO loss), also observed from metastable ions of *m/z* 68. They nevertheless may be differentiated by a careful examination in the *m/z* 56–50 region. It seems clear that these two ions, $[\mathbf{29}]^+$ and $[\mathbf{30}]^+$, are not significantly produced by dissociation of oxazole or isoxazole derivatives.

$[C_2H_3N]^{+\cdot}$. *MO calculations.* Five $[C_2H_3N]^{+\cdot}$ ion structures were investigated by MO calculations; their total and relative energies are given in Table 5. The following order of decreasing stability is predicted: $CH_2{=}C{=}NH^{+\cdot}$, $[\mathbf{32}]^{+\cdot}$; $CH_2{=}N{=}CH^{+\cdot}$, $[\mathbf{33}]^{+\cdot}$; $HC{\equiv}CNH_2^{+\cdot}$, $[\mathbf{34}]^{+\cdot}$; $CH_3NC^{+\cdot}$, $[\mathbf{35}]^{+\cdot}$; and $CH_3CN^{+\cdot}$, $[\mathbf{36}]^{+\cdot}$. The high stability of $[\mathbf{32}]^{+\cdot}$ with respect to $[\mathbf{33}]^{+\cdot}$–$[\mathbf{36}]^{+\cdot}$ has also been observed by several other workers.[19–21]

Absolute heats of formation of ions $[\mathbf{32}]^{+\cdot}$–$[\mathbf{36}]^{+\cdot}$ may be deduced after calculation of the energy of the fragments $[C_2H_3N]^{+\cdot}$ + CO relative to ionized oxazole $[\mathbf{1}]^{+\cdot}$. The values (−39, −7, +51, +222 kJ mol^{-1} for $[\mathbf{32}]^{+\cdot}$–$[\mathbf{36}]^{+\cdot}$, respectively, CI/6-31G//3-21G calculation) combined with ΔH_f° ($[\mathbf{1}]^{+\cdot}$) = 897 kJ mol^{-1} and ΔH_f° (CO) = −111 kJ mol^{-1} lead to ΔH_f° values of 969, 1001, 1059, 1152 and 1230 kJ mol^{-1}, respectively. A reasonable agreement is found with experimental[19] values in the case of $[\mathbf{32}]^{+\cdot}$ (ΔH_f°(exp) = 1004 kJ mol^{-1}) and $[\mathbf{36}]^{+\cdot}$ (ΔH_f°(exp) = 1251 kJ mol^{-1}). The calculation overestimates the stability of the methyl isocyanide molecular ions $[\mathbf{35}]^{+\cdot}$ (ΔH_f°(exp) = 1257 kJ mol^{-1}).

Tandem mass spectrometric results. The CID spectra may be used to differentiate the various $[C_2H_3N]^{+\cdot}$ isomers $[\mathbf{32}]^{+\cdot}$–$[\mathbf{36}]^{+\cdot}$.[21,22] The signal at *m/z* 41 in the mass spectra of oxazole and isoxazole consists of a mixture containing $[C_2H_3N]^{+\cdot}$ as a major component in addition to a small amount of $[C_2HO]^{+\cdot}$. The CID spectra of these mixtures thus present undesirable peaks at *m/z* 29, 28, 25, 24, 13 and 12, as evidenced by the CID spectrum of $[HC{=}C{=}O]^+$ generated by dissociative ionization of ketene. A comparison of peak intensities

Table 4. CID–MIKE spectra (8 keV, helium) of $[C_3H_2NO]^+$ (*m/z* 68) and $[C_3HDNO]^+$ (*m/z* 69) ions (relative intensity, %)

	m/z																	
Compound	56	55	54	53	52	51	50	43	42	41	40	39	38	29	28	27	26	25
Oxazole **1**	—	2	1	—	1	3	1	—	—	11	100	19	11	1	4	4	1	1
5-Methyloxazole **14**	—	2	2	—	1	3	1	—	2	20	100	26	14	2	6	5	2	1
5-Methyloxazole-2*d*$_1$ **14a**	3	2	2	2	2	2	—	—	100	13	9	11	3	5	2	1	—	—
Isoxazole **2**	—	—	—	4	3	4	2	—	—	12	100	24	15	1	5	4	1	2
5-Methylisoxazole **15**[a]	—	1	—	3	3	4	2	—	—	12	100	24	15	2	6	5	1	2
5-Methylisoxazole-4*d*$_1$ **15a**	1	—	3	2	3	2	2	1	14	100	14	9	13	4	4	4	3	—
$N{=}CCH_2COOCH_3$	—	—	1	2	2	3	2	—	14	6	100	16	12	2	5	1	3	2
$C{=}NCH_2COOCH_3$	2	—	1	—	—	2	1	—	10	2	100	9	7	1	3	1	1	—

[a] No change is observed in the CID–MIKE spectra when *m/z* ions are sampled from the metastable transition *m/z* 83 → *m/z* 68 occurring in the 1st FFR of the triple-sector mass spectrometer.

Table 5. Relative energies of $[C_2H_3N]^{+\cdot}$ $[M - CO]^{+\cdot}$ ions (kJ mol^{-1}) at different levels of theory[a]

Structure	Compound	3-21G//3-21G	6-31G//3-21G	6-31G*//3-21G	CI-6-31G//3-21G	CI-6-31G*//3-21G
$CH_2{=}C{=}NH$	**32**	0	0	0	0	0
$CH_2{=}N{=}CH$	**33**	50	59	51	39	31
$HC{=}CNH_2$	**34**	76	78	92	75	89
$CH_3N{=}C$	**35**	208	241	220	204	183
$CH_3C{=}N$	**36**	289	317	294	284	261

[a] Total reference energies of $[CH_2{=}C{=}NH]^{+\cdot}$ (**32**) in hartrees: 3-21G//3-21G = −130.880713; 6-31G//3-21G = −131.545281; 6-31G*//3-21G = −131.597553; CI-6-31G//3-21G = −131.82389. Total energies of CO in hartrees: 3-21G//3-21G = −112.09330; 6-31G = −113.667215; 6-31G* = −112.73788; CI-6-31G = −112.879176.

being significant only for the assignment of the $[C_2H_3N]^{+\cdot}$ structure in Table 6.

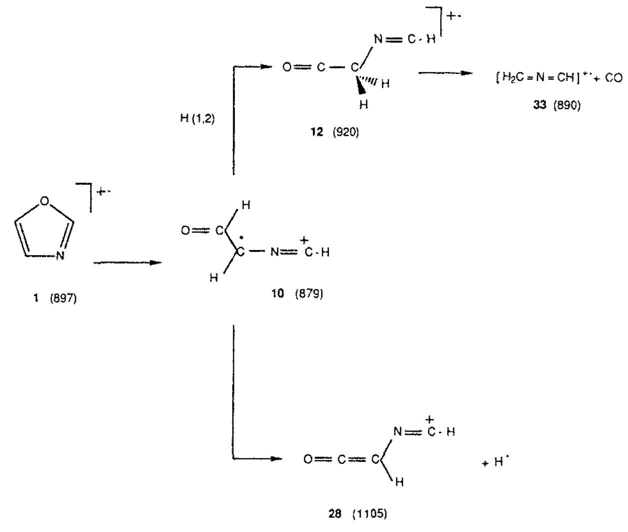
Structures $[\mathbf{35}]^{+\cdot}$ and $[\mathbf{36}]^{+\cdot}$ are clearly distinguishable from $[\mathbf{32}]^{+\cdot}$–$[\mathbf{34}]^{+\cdot}$ and it appears that neither $[\mathbf{1}]^{+\cdot}$ nor $[\mathbf{2}]^{+\cdot}$ eliminates CO to give $[\mathbf{35}]^{+\cdot}$ or $[\mathbf{36}]^{+\cdot}$ (based on examination of the peak at m/z 15, specific for $[\mathbf{35}]^{+\cdot}$, and the peak at m/z 26, significantly more important for both $[\mathbf{35}]^{+\cdot}$ and $[\mathbf{36}]^{+\cdot}$).

Conclusion. The above theoretical data lead to the conclusion that $[\mathbf{1}]^{+\cdot}$ cannot give $[C_2H_3N]^{+\cdot}$ cations other than $[\mathbf{32}]^{+\cdot}$, $[\mathbf{33}]^{+\cdot}$ or $[\mathbf{34}]^{+\cdot}$ and that $[\mathbf{2}]^{+\cdot}$ cannot give $[C_3H_2NO]^{+}$ cations other than $[\mathbf{27}]^{+}$, $[\mathbf{28}]^{+}$ or $[\mathbf{29}]^{+}$. These suggestions from theory are clearly in agreement with the CID spectra, from which it has been concluded that $[\mathbf{1}]^{+\cdot}$ may only give $[\mathbf{32}]^{+\cdot}$, $[\mathbf{33}]^{+\cdot}$ or $[\mathbf{34}]^{+\cdot}$ (+CO) and that **2** may only give $[\mathbf{27}]^{+}$, $[\mathbf{28}]^{+}$ or $[\mathbf{31}]^{+}$ (+H$^{\cdot}$). The fragmentation mechanisms for $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$ proposed to account for these observations are presented in Schemes 3 and 4.

The ring opening of $[\mathbf{1}]^{+\cdot}$ along the C(2)—O bond leads to structure $[\mathbf{10}]^{+\cdot}$, which may give rise to $[\mathbf{28}]^{+}$ + H$^{\cdot}$ by direct C(5)—H bond cleavage or, after a 1,2-H(5) migration, to the distonic ion $[\mathbf{12}]^{+\cdot}$. The latter is a direct precursor for ion $[\mathbf{33}]^{+\cdot}$, i.e. a $[C_2H_3N]^{+\cdot}$ structure having retained the original CNC arrangement.

In the case of isoxazole, a two step mechanism, $[\mathbf{2}]^{+\cdot} \rightarrow N{=}CHCHCHO \rightarrow [\mathbf{7}]^{+\cdot}$ seems to be too endothermic (CI/6-31G*/3-21G calculation gives for the intermediate structure N=CHCHCHO an energy of 425 kJ mol^{-1} relative of $[\mathbf{1}]^{+\cdot}$); it is therefore proposed that the O—N bond cleavage is assisted by a concomitant 1,2-hydrogen shift. Again, either direct C(5)—H bond cleavage or 1,2-H(5) migration may occur from the intermediate ion $[\mathbf{7}]^{+\cdot}$. The latter process produces distonic ion $[\mathbf{13}]^{+\cdot}$, which, in turn, may generate ion $[\mathbf{32}]^{+\cdot}$, i.e. the most stable $[C_2H_3N]^{+\cdot}$ structure bearing the original CCN arrangement.

The main difference between the behaviour of $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$ at low internal energy is due to the energetic of the first steps $[\mathbf{1}]^{+\cdot} \rightarrow [\mathbf{10}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot} \rightarrow [\mathbf{7}]^{+\cdot}$. In the first case, for ions $[\mathbf{10}]^{+\cdot}$ originating from metastable $[\mathbf{1}]^{+\cdot}$ the competition favours the rearrangement



Scheme 3

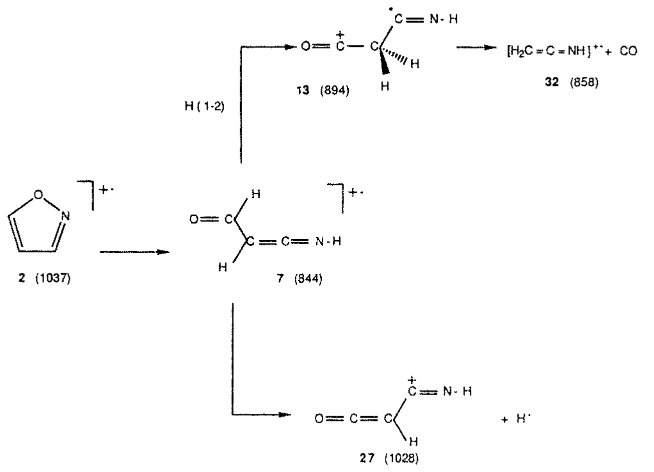
Table 6. CID–MIKE spectra (8 keV, air) of $[C_2H_3N]^{+}$ (m/z 41) (relative intensity, %)

		m/z														
Precursor	Compound	29	28	27	26	25	24	20	19.5	19	17	16	15	14	13	12
$CH_3C{=}N$	**36**	1	100	49	42	15	5	3	—	—	—	—	11	39	12	10
$CH_3N{=}C$	**35**	2	100	47	40	3	1	3	3	—	—	—	38	33	9	15
$HC{=}CNH_2$	**34**	3	100	23	12	19	8	1	—	—	1	4	2	33	12	6
$CH_2{=}C{=}NH$	**32**	2	100	43	31	15	5	3	—	—	—	—	5	55	13	8
$CH_2{=}N{=}CH$[a]	**33**					Not given							5	100	24	14
Oxazole, 94% C_2H_3N–6% C_2HO	**1**	6	100	44	25	8	3	7	—	—	—	—	3	41	13	6
Isoxazole, 84% C_2H_3N–16% C_2HO	**2**	15	100	32	20	14	5	2	2	—	—	—	4	64	22	8
$CH_2{=}C{=}O$ [M − H]		100	88	—	—	30	14	—	—	—	—	—	—	—	75	19

[a] From Ref. 21.

Table 7. 70 eV electron impact mass spectra of methylated oxazoles 14, 21, 22 and 15 (relative intensity, %)

		m/z																	
Compound	No.	84	83	82	68	56	55	54	53	52	51	50	44	43	42	41	40	39	38
B-Methyloxazole	**14**	6	100	3	40	6	23	30	5	7	5	1	7	40	5	47	26	5	4
4-Methyloxazole	**21**	4	82	1	1	11	100	49	6	6	5	1	7	1	2	2	2	3	3
2-Methyloxazole	**22**	6	100	8	—	1	38	56	2	8	6	1	1	6	23	5	4	2	3
5-Methylisoxazole	**15**	4	64	1	41	1	5	9	4	5	7	7	—	100	12	25	29	12	11



Scheme 4

$[10]^{+\cdot} \rightarrow [12]^{+\cdot}$ over the more energy-demanding dissociation $[10]^{+\cdot} \rightarrow [28]^{+} + H^{\cdot}$. In the isoxazole case, ions $[7]^{+\cdot}$ originating from metastable ions $[2]^{+\cdot}$ possess a large amount of internal energy above the dissociation limits, in such a situation the most favoured pathway is that of the highest frequency factor, i.e. the direct dissociation $[7]^{+\cdot} \rightarrow [27]^{+} + H^{\cdot}$.

Methyl-substituted (is)oxazoles 14, 15, 21 and 22

The 70 eV electron impact and MIKE spectra of the methylated oxazoles **14**, **21** and **22** and of 5-methylisoxazole **15** are listed in Tables 7 and 8.

For $[21]^{+\cdot}$ and $[22]^{+\cdot}$ the elimination of carbon monoxide dominates the MIKE spectra, a result reminiscent of the bare oxazole case. Isomers bearing the methyl group in position 5, such as $[14]^{+\cdot}$ and $[15]^{+\cdot}$, show in their conventional mass spectra a peak at *m/z* 68 $[M - CH_3]^{+}$. This methyl loss is also observed for metastable ions $[15]^{+\cdot}$ ($T_{0.5} = 12$ kJ mol^{-1}) but is not apparent for $[14]^{+\cdot}$. A simple cleavage of an alkylaryl C—C bond is generally not a low-energy process and, at least for $[15]^{+\cdot}$, it is highly probable that the methyl elimination follows an opening of the heterocyclic ring.

In order to elucidate this question, theoretical calculations and CID experiments were undertaken.

MO calculations. Some $[C_4H_5NO]^{+\cdot}$ ions have been examined theoretically: 5-methyloxazole $[14]^{+\cdot}$, 5-methylisoxazole $[15]^{+\cdot}$ and methyl-substituted aminomethyleneketenes $[16]^{+\cdot}$ and $[17]^{+\cdot}$ and imidoylketenes $[18]^{+\cdot}$ and $[19]^{+\cdot}$. Finally, structure $[20]^{+\cdot}$, $CH_3COCH{=}C{=}NH^{+\cdot}$, was also considered in view of the high stability of $[7]^{+\cdot}$, $HCOCH{=}C{=}NH^{+\cdot}$, among the $[C_3H_3NO]^{+\cdot}$ isomers.

Table 8. MIKE spectra (8 keV) of $[C_4H_5ON]^{+\cdot}$ ions (*m/z* 83) (relative intensity, %)

		m/z					
Precursor	No.	68	56	55	54	43	41
5-Methyloxazole	**14**	—	56	86	100	—	—
4-Methyloxazole	**21**	—	36	100	72	—	—
2-Methyloxazole	**22**	—	—	100	11	—	—
5-Methylisoxazole	**15**	100	4	5	25	13	7
Acetylacetonitrile	**23**	100	6	24	22	7	5

Calculations were performed at the 3–21G//3–21G level; results are summarized in Table 9.

Good agreement is found with the conclusions drawn previously during the study of the $[C_3H_3NO]^{+\cdot}$ homologues. The excellent stability of imidoylketene and azaallene-type structures $[16]^{+\cdot}$, $[17]^{+\cdot}$ and $[20]^{+\cdot}$ is confirmed. Methyl-substituted oxazole $[14]^{+\cdot}$ and methyleneketene molecular cations $[18]^{+\cdot}$ and $[19]^{+\cdot}$ are predicted to have comparable stability, well below that of the 5-methylisoxazole ion $[15]^{+\cdot}$.

Tandem mass spectrometric results. Ten radical cations of general formula C_4H_5NO were examined by mass spectrometry. The molecular ions of the three positional isomers of methyloxazole **14**, **21** and **22**, of 5-methylisoxazole **15** and of acetylacetonitrile **23** were produced by direct ionization of the neutral molecules. The other $[C_4H_5NO]^{+\cdot}$ isomers were obtained from the Meldrum's acids **25** and **26** either by dissociative ionization or by ionization of the flash pyrolysis product. The conventional 70 eV electron impact mass spectra of **25** and **26** obtained at low temperature exhibit a base peak afforded by ions of *m/z* 83. On the basis of CID spectra and by analogy with the behaviour of their lower homologues,[5] it is proposed that **25** and **26** dissociate on electron impact ionization by simple

Table 9. Relative energies of the $[C_4H_5NO]^{+\cdot}$ ions at the 3–21G//3–21G level (kJ mol^{-1})[a]

Compound	No.	3-21G//3-21G
5-Methyloxazole	**14**	0
5-Methylisoxazole	**15**	230
$CH_3NHCH{=}C{=}C{=}O$	**16**	−26
$NH_2(CH_3)C{=}C{=}C{=}O$	**17**	−69
$CH_3N{=}CHCH{=}C{=}O$	**18**	30
$HN{=}C(CH_3)CH{=}C{=}O$	**19**	10
$CH_3COCH{=}C{=}NH$	**20**	−66

[a] Reference energy in hartree: −281.78594.

Table 10. CID–MIKE spectra of $[C_4H_5NO]^{+\cdot}$ ions (relative intensity, %)

Compound	Conditions[a]	68	67	66	56	55	54	53	52	51	50	43	42	41	40	39	38
5-Methyloxazole **14**	A	47	—	—	34	58	100	2	4	2	—	17	1	16	11	2	1
	B	52	—	—	38	54	100	—	—	—	—	22	—	25	18	—	—
4-Methyloxazole **21**	A	4	—	—	27	100	71	6	5	3	2	—	3	5	4	3	2
	B	7	—	—	—	100	—	9	6	—	—	—	1	—	9	—	—
2-Methyloxazole **22**	A	1	—	2	—	100	37	8	10	5	2	4	12	6	7	4	2
	B	1	—	—	—	100	—	12	11	—	—	—	13	—	10	—	—
5-Methylisoxazole **15**	A	100	2	—	3	3	14	—	2	3	2	52	—	8	3	2	—
	B	100	3	—	—	4	—	4	6	—	—	—	8	—	11	—	—
Acetylacetonitrile **23**	A	100	2	—	5	18	20	—	3	4	3	35	—	10	5	4	2
N-Methylaminomethyleneketene **16**	A	5	5	—	—	100	14	15	4	2	—	—	5	3	5	3	2
(**25** → **16**)	B	2	5	—	—	100	27	—	—	—	—	—	2	—	6	—	—
Aminomethylmethyleneketene **17**	A	55	17	5	—	100	20	—	8	4	1	2	13	3	13	7	5
(**26** → **17**)	B	84	—	—	—	100	—	—	12	—	—	—	17	—	22	—	—
(**25** → **18**)	B	—	—	—	—	100	8	—	—	—	—	—	34	—	6	—	—
(**26** → **19**)	B	48	—	—	—	9	—	—	3	—	—	—	100	—	10	—	—

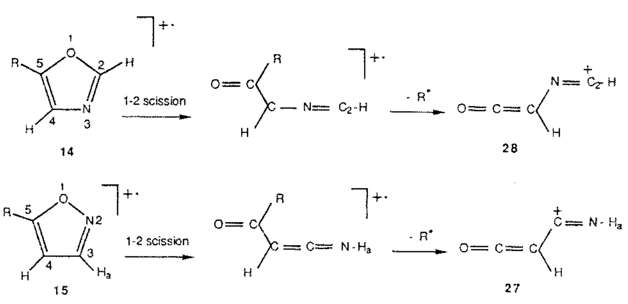
[a] (A) Kinetic energy = 8 keV; collision gas, helium; E–B–E mass spectrometer. (B) Kinetic energy = 3 keV; collision gas, argon; B–E mass spectrometer.

bond cleavage, leading to N-methylaminomethyleneketene $[\mathbf{16}]^{+\cdot}$ and amino(methyl)methyleneketene $[\mathbf{17}]^{+\cdot}$, respectively (Scheme 2). Pyrolysis of **25** and **26** is essentially complete at 650 °C, as demonstrated by the disappearance of the molecular ion at *m/z* 185 and the rise of the signals associated with acetone and carbon dioxide (*m/z* 58, 44 and 43). However, a peak at *m/z* 83 remains, which must be attributed to structures different from $[\mathbf{16}]^{+\cdot}$ or $[\mathbf{17}]^{+\cdot}$, as will be shown below. Again, by analogy with the $[C_3H_3NO]^{+\cdot}$ case, it is suggested that the pyrolysis products are ionized *N*-methylimidoylketene $[\mathbf{18}]^{+\cdot}$ and imidoyl(methyl)ketene $[\mathbf{19}]^{+\cdot}$ (Scheme 2).

All these $[C_4H_5NO]^{+\cdot}$ ions were characterized by collisional activation; the relevant spectra are presented in Table 10.

Methyl-substituted oxazole and isoxazole are clearly distinguishable by CID: 4- and 5-methyloxazoles eliminate HCN (*m/z* 56) whereas for 2-methyloxazole the neutral species lost is CH_3CN (*m/z* 42); a methyl loss is also observed for 5-methyloxazole (*m/z* 68). This latter reaction is associated with a large kinetic energy release ($T_{0.5} = 138$ meV). The CID spectrum of 5-methylisoxazole $[\mathbf{15}]^{+\cdot}$ is close to that of acetylacetonitrile $[\mathbf{23}]^{+\cdot}$; they are dominated by the methyl loss which is also observed in the unimolecular (MIKE) spectra. There are also, however, significant differences which allow identification of structures $[\mathbf{15}]^{+\cdot}$ and $[\mathbf{23}]^{+\cdot}$, viz. the *m/z* 55/54 ratio and the *m/z* 29–26 region (absent from Table 10). Structures $[\mathbf{16}]^{+\cdot}$ and $[\mathbf{17}]^{+\cdot}$ are characterized by the elimination of CH_3NH (*m/z* 53), CH_3 (*m/z* 68) and NH_2 (*m/z* 67) (a peak at *m/z* 28 not shown confirms the presence of the carbonyl moiety).

The two pyrolysis products $[\mathbf{18}]^{+\cdot}$ and $[\mathbf{19}]^{+\cdot}$ give under collisional activation a strong *m/z* peak. The *m/z* 42 ions result from the two collision-induced fragmentations evidenced for $HN{=}CHCH{=}C{=}O^{+\cdot}$, $[\mathbf{4}]^{+\cdot}$. In the present situation the loss of HCN is replaced by a CH_3NC (CH_3CN) loss giving $CH_2CO^{+\cdot}$ (*m/z* 42) and the loss of C_2HO leads to CH_3NCH^+ (CH_3CNH^+) (*m/z* 42), in agreement with the postulated structures $[\mathbf{18}]^{+\cdot}$ and $[\mathbf{19}]^{+\cdot}$.



Scheme 5

The main conclusion related to the (is)oxazole chemistry is that no facile isomerization seems to occur between $[\mathbf{14}]^{+\cdot}$–$[\mathbf{23}]^{+\cdot}$ in spite of the high stability of compounds such as $[\mathbf{16}]^{+\cdot}$ and $[\mathbf{17}]^{+\cdot}$. On this basis, it has to be concluded that no isomerization occurs between these various undecomposed species. This rules out, for example, the possibility of $[\mathbf{14}]^{+\cdot} \rightleftharpoons [\mathbf{15}]^{+\cdot}$ isomerization in the low internal energy range (lifetime greater than 10^{-5} s: stable and metastable ions) and consequently a rearrangement of $[\mathbf{14}]^{+\cdot}$ or $[\mathbf{15}]^{+\cdot}$ into an acylaziridine ion $[\mathbf{37}]^{+\cdot}$ as observed during gas-phase thermal isomerization of neutral (is)oxazole.[23] The structure of the $[M - CH_3]^+$ fragment ions may be inferred from the corresponding CID spectra. As mentioned previously, data are compatible with the formation of a cation bearing an NH group containing the H atom originally in position 3. In the case of $[\mathbf{14}]^{+\cdot}$ the original C(2)H group is not modified during the methyl loss. It consequently appears that the isomerization–fragmentation mechanisms of (is)oxazoles presented in Schemes 3 and 4 may be extended to the methyl-substituted derivatives, as summarized in Scheme 5.

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REFERENCES

1. Q. N. Porter, *Mass Spectrometry of Heterocyclic Compounds*. Wiley-Interscience, New York (1981).
2. H. E. Audier, M. Fetizon, Y. Henry and T. Prange, *Org. Mass Spectrom.* **11**, 1047 (1976).
3. G. Bouchoux and Y. Hoppilliard, *Org. Mass Spectrom.* **16**, 459 (1981).
4. F. W. McLafferty (Ed.), *Tandem Mass Spectrometry*. Wiley, New York (1983).
5. C. Wentrup, H. Briehl, P. Lorencak, U. V. Vogelbacher, H. W. Winter, A. Maquestiau and R. Flammang, *J. Am. Chem. Soc.* **110**, 1337 (1988).
6. W. J. Heyre, L. Radom, P. von R. Schleyer and J. A. Pople, *Ab initio Molecular Orbital Theory*. Wiley, New York (1986).
7. A. Maquestiau, Y. Van Haverbeke, R. Flammang, R. Abrassart and D. Finet, *Bull. Soc. Chim. Belg.* **87**, 765 (1978).
8. A. Maquestiau, E. Puk and R. Flammang, *Tetrahedron Lett.* **27**, 4023 (1986).
9. J. W. Cornforth and R. H. Cornforth, *J. Org. Chem.* **18**, 93 (1953).
10. J. W. Cornforth and R. H. Cornforth, *J. Org. Chem.* **12**, 96 (1947).
11. J. D. Perez, G. I. Yranzo and D. A. Wunderlin, *J. Org. Chem.* **47**, 982 (1982).
12. J. P. Celerier, E. Deloisy, P. Kapron, G. Lhommet and P. Maitte, *Synthesis*, 130 (1981).
13. G. A. Bihlmayer, G. Derflinger, J. Derkosch and O. E. Polansky, *Monatsh. Chem.* **98**, 564 (1967).
14. M. Peterson and R. Poirier, *Program MONSTERGAUS 80*. Chemistry Department, University of Toronto (1981).
15. B. Huron, J. P. Malrieu and P. J. Rancurel, *J. Chem. Phys.* **32**, 5945 (1973).
16. M. J. Fisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder and J. A. Pople, *GAUSSIAN 86*. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh (1984).
17. R. Nobes, W. J. Bouma and E. L. Radom, *Chem. Phys. Lett.* **89**, 497 (1982).
18. S. G. Lias, J. E. Bartmess, J. F. Liebmann, J. L. Holmes, R. D. Levine and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).
19. G. D. Willett and T. Baer, *J. Am. Chem. Soc.* **102**, 6774 (1980).
20. E. K. Chess, R. L. Lapp and M. L. Gross, *Org. Mass Spectrom.* **10**, 475 (1982).
21. B. Van Baar, W. Koch, C. Lebrilla, J. K. Terlouw, T. Weiske and H. Schwarz, *Angew. Chem., Int. Ed. Engl.* **25**, 827 (1986).
22. J. Van Thuijl, J. J. Van Houte, A. Maquestiau, R. Flammang and C. De Meyer, *Org. Mass Spectrom.* **12**, 197 (1977).
23. G. E. Davico and J. D. Perez, *J. Phys. Org. Chem.* **3**, 611 (1990).