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UNIMOLECULAR AND BIMOLECULAR REACTIONS OF THE β-DISTONIC ION $^{\cdot}CH_2-CH_2-O-CH_2^+$ AND ITS DEUTERATED DERIVATIVES

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ABSTRACT

The unimolecular and bimolecular reactions of the β-distonic ion $^+CH_2-O-CH_2-CH_2^{\cdot}$ (**a**) and its deuterated analogues **b** and **c** have been studied by tandem mass spectrometry and by Fourier transform ion cyclotron resonance (FT-ICR) spectrometry. The spontaneous reactions of metastable **a** are the loss of $H^{\cdot}$ and CO respectively. $H^{\cdot}$ and $D^{\cdot}$ are eliminated from metastable **b** and **c** irrespective of the position of the D atoms, suggesting an oxetane radical cation **d** as an intermediate for this process. However, a careful examination of the collisional activation (CA) spectra of **a**–**c** reveals that the CH_2 groups of **a** do not scramble by a mutual interconversion of **a** and **d**, in line with previous results.

The reactions of **a** and the isotopomers **b** and **c** with pyridine and acetonitrile respectively have been investigated by FT-ICR spectrometry using an external ion source. Besides the elimination of an H atom which is very probably a collision-induced process, **a** reacts with pyridine by charge exchange, by protonation, and by the formation of an *N*-formyl pyridinium ion but not by the transfer of $C_2H_4^{+\cdot}$. All six H atoms of **a** take part in the protonation. A mechanism involving a rearrangement of **a** into CO and $C_2H_6^{+\cdot}$ in the collision complex with pyridine and subsequent transfer of a proton from $C_2H_6^{+\cdot}$ is suggested. The generation of the *N*-formyl pyridinium ion occurs specifically from the CH_2–O moiety of **a** and corresponds to an electrophilic reaction of the β-distonic ion. In addition to the known transfer of $C_2H_4^{+\cdot}$ from **a** to acetonitrile a proton transfer has been observed. However, the energetically allowed formation of an *N*-formyl nitrilium ion is not detected. The mechanistic origin of this diverse behaviour of the two nucleophiles pyridine and acetonitrile towards the β-distonic ion **a** is discussed.

INTRODUCTION

Distonic ions have attracted considerable interest during the last few years as a new type of ionic species in organic chemistry. For instance, distonic species had been suggested before as reactive intermediates of a McLafferty rearrangement of the radical cations of organic carbonyl compounds [1], of

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the interannular hydrogen exchanges of α,ω-diphenyl alkene radical cations [2], and of other mass spectrometric fragmentations (for a recent study see ref. 3). However, the special properties of distonic ions were realized only after a combined theoretical and experimental study of small distonic "ylide-ions" [4]. Subsequently several reviews concerning the formation and reactivity of distonic ions were published [5]. Of special interest is the rather surprising (thermodynamic) stability of the distonic ions, in particular for small species, which usually surpasses that of the isomer with a conventional structure in spite of the fact that the neutral counterpart of the distonic ion often does not correspond to a stable entity. Furthermore, the charged centre and the radical site reside apart from each other in different parts of the distonic ion and both centres can be expected to exhibit their own reactivity, making a distonic ion a very reactive species for ionic as well as for radical reactions. However, so far only a few studies have dealt with the bimolecular reactions of distonic ions [6].

In contrast with distonic "onium" ions $R-(H^+)X-(CH_2)_n^{\cdot}$ which are known to react mainly by a proton transfer [6], distonic "enium" ions $^+CH_2-X-(CH_2)_n^{\cdot}$ should exhibit electrophilic reactivity besides radical reactions. The α-distonic oxenium ion $^+CH_2-O-CH_2^{\cdot}$ has been reported to transfer $CH_2^{+\cdot}$ to acetonitrile and other bases or unsaturated substrates [7] but it is not known which of the CH_2 groups is transferred and whether this transfer corresponds to an electrophilic or radical attack. The homologous β-distonic enium ion $^+CH_2-O-CH_2CH_2^{\cdot}$ (**a**) transfers $CH_2CH_2^{+\cdot}$ to acetonitrile but no other reaction has been reported [8]. Therefore we studied the formation and reactions of **a** and its deuterated analogues $^+CH_2-O-CD_2-CD_2^{\cdot}$ (**b**) and $^+CD_2-O-CH_2-CH_2^{\cdot}$ (**c**) to obtain more detailed information about the behaviour of these β-distonic ions in unimolecular and bimolecular reactions.

EXPERIMENTAL

Mass spectrometry

The mass spectrometric measurements were performed with a double focusing mass spectrometer VG ZAB 2F [9] and with a Bruker FT-ICR spectrometer CMS 47X [10] equipped with an external ion source. The following conditions were used for the experiments with the VG ZAB 2F: electron energy 70 eV, electron trap current 100 μA, acceleration voltage 6 kV, ion source temperature about 150° C. The sample was introduced into the ion source by a modified heated direct inlet system. The relevant ions were focused magnetically into the second field-free region (2nd FFR) and the product ions of the spontaneous fragmentations were detected by varying the deflection voltage of the electrostatic analyser (mass-analysed ion kinetic

energy (MIKE) spectra). The MIKE spectra were recorded with a pen recorder. The collisional activation (CA) spectra were obtained similarly but by introducing helium as a collision gas into the collision gas cell of the 2nd FFR at such a rate that the main beam was reduced to about 30% of its original intensity. The intensity values given in the tables are the mean values of at least three spectra.

The measurements in the CMS 47X were performed as follows. The sample was ionized in the external EI ion source (electron energy, 20 eV; source temperature, 150° C) and the ions were transferred into the ICR cell. The ion to be studied was isolated by ejecting all other ions using "hard" and "soft" ejection techniques [11]. The neutral reaction component was added by a leak valve starting with a background pressure of about $(0.5–1.0) \times 10^{-9}$ mbar and the total pressure was adjusted to 5.0×10^{-8} mbar. Usually 100 spectra were added, each with 65 k data points. The reaction time of the bimolecular reactions was varied from 1 ms to 10 s. The elemental composition of the ions observed in the ICR experiments was verified by high resolution measurements ($m/\Delta m > 300\,000$).

Compounds

The following compounds were commercially available (pro analysis quality): 1,4-dioxane (**1**), oxetane (**3**), pyridine, acetonitrile, acetonitrile-d_3.

1,4-Dioxane-2,3-d_4 (**2**)

This compound was prepared by a condensation of ethylene glycol-d_4 and ethylene glycol ditosylate or ethylene glycol dimesylate catalysed by 2,6-di-*t*-butylpyridine [12]. Diethyl oxalate was reduced to ethylene glycol-d_4 by $LiAlD_4$ in tetrahydrofuran (THF). The labelling degree of **2** was determined mass spectrometrically: d_4, 95%; d_3, 3%; d_2, 2%.

*5,6-Dihydro-4*H*-2-methyl-1,3-oxazine* (**4**)

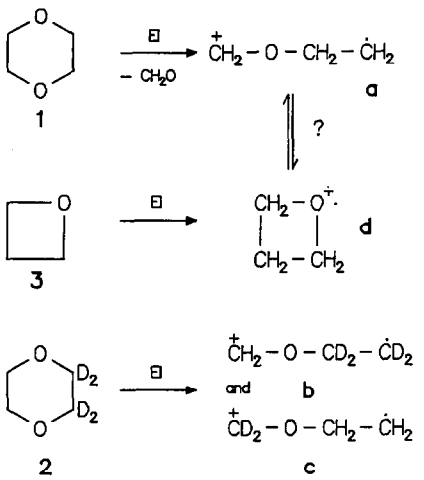
Compound **4** was prepared according to a published method [13].

The purity of the compounds was controlled by GC–MS (Finnigan MAT 1020B); the structures were verified by ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

Unimolecular reactions

The collision-induced decomposition of the distonic ion **a** has been studied before in connection with a study of the structure of isomeric $C_3H_6O^{+\cdot}$ [14]. It had been shown that the spectra obtained by collisional activation (CA) of



Scheme 1.

$C_3H_6O^{+\cdot}$ derived from 1,4-dioxane (**1**) by electron impact induced fragmentation and from oxetane (**3**) by electron impact ionization are identical but different from the other isomers. This is easily explained by an exothermic isomerization of ionized oxetane **d** into the distonic ion **a** [8(a)] without any further isomerization of **a**. In addition, an ICR study of the bimolecular reactions of deuterated analogues of **a** gave no indication for any isomerization of **a** by hydrogen migration [8(b)]. However, an ICR experiment usually samples ions of a much longer lifetime and a lower internal energy than an experiment with ion beam instruments. Hence a degenerate isomerization of excited **a** by a transmutation of CH_2 groups involving **d** as an intermediate (or transition state) cannot be excluded by the ICR experiments, but would easily be detected by comparing the spontaneous fragmentations (MIKE spectrum) and the collisional-induced decompositions (CA spectrum) of the deuterated analogues **b** and **c** of **a** prepared from the deuterated 1,4-dioxane **2** (Scheme 1).

The MIKE spectra of ions **a**–**c** derived from **1** and **2** are shown in Table 1. The main fragmentations of metastable **a** correspond to the loss of $H^{\cdot}$ and a fragment of 28 Da respectively, and in addition a weak signal for the loss of $CH_3^{\cdot}$ is observed. Besides a small contribution from ^{13}C ions the deuterated ions **b** and **c** are formed from the precursor **2** without any interference by isobaric ions of a different elemental composition as shown by high mass resolution. The loss of a fragment of 28 Da is still observed for **b** and **c** in spite of the deuteration. Clearly, this fragmentation corresponds essentially to the loss of CO with only a very small contribution from an elimination of C_2H_4 and cannot give any information about the isomerization of *a* and its

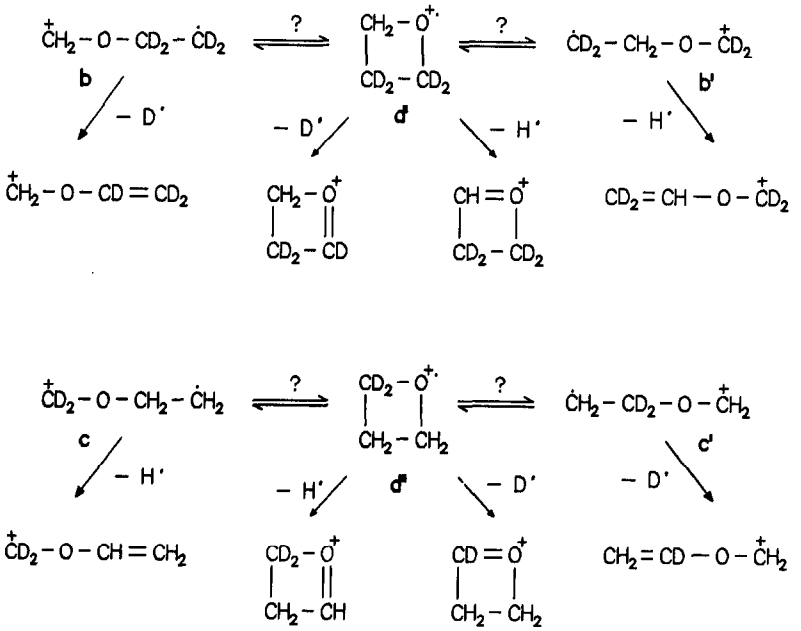
TABLE 1

MIKE spectra and KER of the ions **a**, their isotopomers **b** and **c**, and their isomeric ions **d**

Fragmentation	Relative intensity[a]				T_{50}^{b}			
	a	**b**	**c**	**d**	**a**	**b**	**c**	**d**
– CO	6	6	4	9	130	120	130	115
– CH_3	3							
– CH_2D		< 1	1					
– CHD_2		2	1					
– CD_3		1						
– D		19	5			275	289	
– H	91	70	88	91	254	268	232	270

[a]Percentage total fragment ion current.
[b]In millielectronvolts (± 10 meV), after correction for the width of the main beam.

isotopomers **b** and **c** prior to the decomposition. However, the loss of CO and not of C_2H_4 from metastable **a** gives additional proof that **a** is a distonic ion and not an electrostatically bound complex of ionized ethylene and formaldehyde. The loss of H$^{\cdot}$ from **a** gives rise to a flat-topped peak in the MIKE spectrum. Similar flat-topped peaks are observed for the losses of H$^{\cdot}$ and D$^{\cdot}$ from **b** and **c**, and the kinetic energy release (KER) measured at 50% peak height (T_{50}) is slightly larger for the D loss (Table 1). The loss of H$^{\cdot}$ dominates the MIKE spectra of all isotopomers in spite of the complementary labelling of the ions **b** and **c**. This eliminates the exclusive formation of an ion $^{+}CH_2$–O–CH=CH_2 from **a** without any accompanying rearrangement (Scheme 2) which would lead to the unique loss of D$^{\cdot}$ and H$^{\cdot}$ from **b** and **c**, respectively. However, it is not possible to uncover completely the mechanism of this H(D) elimination because obviously the relative abundances of the loss of H$^{\cdot}$ and D$^{\cdot}$ from the isotopomers are controlled by isotope effects of unknown magnitude. The heats of formation of $^{+}CH_2$–O–CH=CH_2 (ΔH_f = 751 kJ mol^{-1} [15]) and of the oxetanyl cation (ΔH_f = 759 kJ mol^{-1} [15]) are not very different. Using ΔH_f(H) = 217.95 kJ mol^{-1} [16] the combined heats of formation of the products for both fragmentation routes of 969 kJ mol^{-1} and 977 kJ mol^{-1} respectively are distinctly larger than that of the oxetane radical cation **d** (ΔH_f(**d**) = 852 kJ mol^{-1} [8(a)]). Taking into account also the presence of a reverse activation energy for the H loss indicated by the large KER one concludes that structure **d** as well as some other isomeric structures [8(a)] are definitely accessible by ions **a** with sufficient internal energy to fragment by loss of H$^{\cdot}$. The relative abundances of the eliminations of H$^{\cdot}$ and D$^{\cdot}$ are somewhat different for the isotopomers **b** and **c**, indicating that **d** cannot be the only reactive intermediate for the H loss. Thus it appears that the ions



Scheme 2.

$^{+}CH_2$–O–CH=CH_2 and the oxetanyl ions are formed in competition with each other and that in the latter case the oxetane radical cation **d** may be an intermediate (Scheme 2). But again these results do not allow us to decide whether the ions **a** and **d** mutually interconvert before fragmentation. The remaining fragmentation in the MIKE spectrum of **a** is the loss of $CH_3^{\cdot}$. The isotopomers **b** and **c** lose mainly $CH_2D^{\cdot}$ and $CHD_2^{\cdot}$ (Table 1) but the intensities are too small to infer any conclusion besides the fact that some H migrations precede the fragmentations of **a**.

The CA spectra of **a** and **d** obtained in this study agree well with those published previously [14], and the spectra of the deuterated analogues **b** and **c** give further information about a mutual interconversion of **a** and **d** (Table 2).

The CA spectrum of **a** still contains a prominent peak for the loss of $H^{\cdot}$ which is replaced by peaks for the eliminations of $H^{\cdot}$ and $D^{\cdot}$ in the case of **b** and **c**. The differences between the relative abundances for the losses of $H^{\cdot}$ and $D^{\cdot}$ from the isotopomers are less than in the MIKE spectra (as expected for the operation of isotope effects) but the elimination of $H^{\cdot}$ predominates again in all spectra so that no new information is obtained from the collision-induced process. However, the main new intensity of 71.5% of the total fragment ion current in the CA spectra of **a**–**c** appears at *m/z* 26–34 and is due

TABLE 2

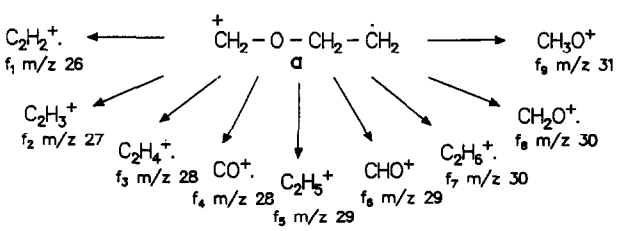
CA spectra of $C_3H_6O^{+\cdot}$ ions **a**, their isotopomers **b** and **c**, and of ions **d**

CA spectra			Partial CA spectra[a]			
m/z	**a**	**d**	*m/z*	**a**	**b**	**c**
13	0.3	0.3	26	7		7
14	0.8	0.5	27	12	1	9
15	0.8	0.3	28	40	7	36
16	0.1		29	14	8	5
			30	23	14	13
26	5.4	4.5	31	4	3	1
27	8.4	6.3	32		41	25
28	28.2	27.7	33		6	4
29	10.3	11.3	34		20	
30	16.1	14.9				
31	3.1	2.5	57	100		
			58			16
42	0.7	0.5	59			84
43	1.4	0.1	60		21	
44	0.5		61		79	
57	23.8	31.2				

[a]The partial CA spectra *m/z* 26–34 and *m/z* 57–61 are normalized to the total fragment ion intensity of the peak group.

to fragment ions $\mathbf{f_1}$–$\mathbf{f_9}$ (Scheme 3) of the elemental composition C_2H_m (m = 2–6) and CH_nO (n = 0–3) or their deuterated analogues. This region of the CA spectra can be used for a detailed analysis of the isomerization reactions. The result of this analysis excludes unequivocally any mutual interconversion between **a** and **d** prior or during the collision-induced fragmentation although some H/D exchange is observed.

For a better analysis of the CA spectra the fragment ion intensities of the region *m/z* 26–34 are given in Table 2, normalized to the intensity of this group of ions, respectively. To start with the decoding of the overlapping peaks of the ions $\mathbf{f_1}$–$\mathbf{f_9}$ (Scheme 3), it is easily seen that the ions $\mathbf{f_1}$, *m/z* 26, in the



Scheme 3.

TABLE 3

Intensity distribution $I(\%)$ between the fragment ions $\mathbf{f_1}$–$\mathbf{f_9}$ in the CA spectra of ions **a**–**c**

Ion	**a**		**b**		**c**	
	m/z	*I*(%)	*m/z*	*I*(%)	*m/z*	*I*(%)
$\mathbf{f_1}$	26	7	28	7	26	7
$\mathbf{f_2}$	27	12	30	12	27	9
					28	3
$\mathbf{f_3}$	28	40	32	37	28	33
			31	3	29	5
$\mathbf{f_4}$	28	0	28	0	28	0
$\mathbf{f_5}$	29	6	33	6	30	6
$\mathbf{f_6}$	29	8	29	8	30	8
$\mathbf{f_7}$	30	20	34	20	32	20
$\mathbf{f_8}$	30	3	30	2	32	3
$\mathbf{f_9}$	31	4	32	4	33	4

spectrum of **a** stay at *m/z* 26 in the spectrum of **c** and are completely shifted to *m/z* 28 for **b**. At the high mass end of the region considered here the ion $\mathbf{f_9}$ from **a** (CH_3O^+) at *m/z* 31 is completely shifted to *m/z* 33 (CHD_2O^+) for **c**. Hence $\mathbf{f_9}$ from **b** has to be CH_2DO^+ and contributes 4% to the intensity at *m/z* 32. Considering next the ions *m/z* 30, they may correspond to $\mathbf{f_7}$ ($C_2H_6^{+\cdot}$) and $\mathbf{f_8}$ ($CH_2O^{+\cdot}$). The peak intensity of 23% at *m/z* 30 in the spectrum of **a** is completely shifted to m/z 32 (i.e. $C_2H_4D_2^{+\cdot}$ and $CD_2O^{+\cdot}$) in the spectrum of **c** but only 20% relative intensity reappears at *m/z* 34 ($C_2H_2D_4^{+\cdot}$) in the case of **b**. Hence the missing 3% of the original intensity at *m/z* 30 in the spectrum of **a** are due to $CH_2O^{+\cdot}$ ions which are completely transformed into $CD_2O^{+\cdot}$, *m/z* 32, in the case of **c** but remain $CH_2O^{+\cdot}$, *m/z* 30, for **b**. This result already excludes any scrambling of the methylene groups in the distonic ions **a**–**c**. Continuing this type of argument yields the intensity distribution (*I*) of the ions $\mathbf{f_1}$–$\mathbf{f_9}$ shown in Table 3.

The self-consistency of this distribution is excellent regarding the experimental error and leaves no doubt that the terminal CH_2 groups of **a** do not interchange via an intermediate **d**. A clear example for this conclusion is the mass shifts of the ions *m/z* 28 in the CA spectrum of **a**. These correspond exclusively to ions $\mathbf{f_3}$ ($C_2H_4^{+\cdot}$) and remain mostly at *m/z* 28 for **c**, but are shifted to *m/z* 32 for **b**. Thus the ions $\mathbf{f_3}$ are generated from the original ethylene moiety of **a** and only a few H and D exchanges between the individual CH_2 and CD_2 groups accompany the fragmentation.

Bimolecular reactions

The only bimolecular reaction reported for the β-distonic ion **a** is the transfer of $C_2H_4^{+\cdot}$ to acetonitrile, studied by ICR spectrometry [8]. It has been

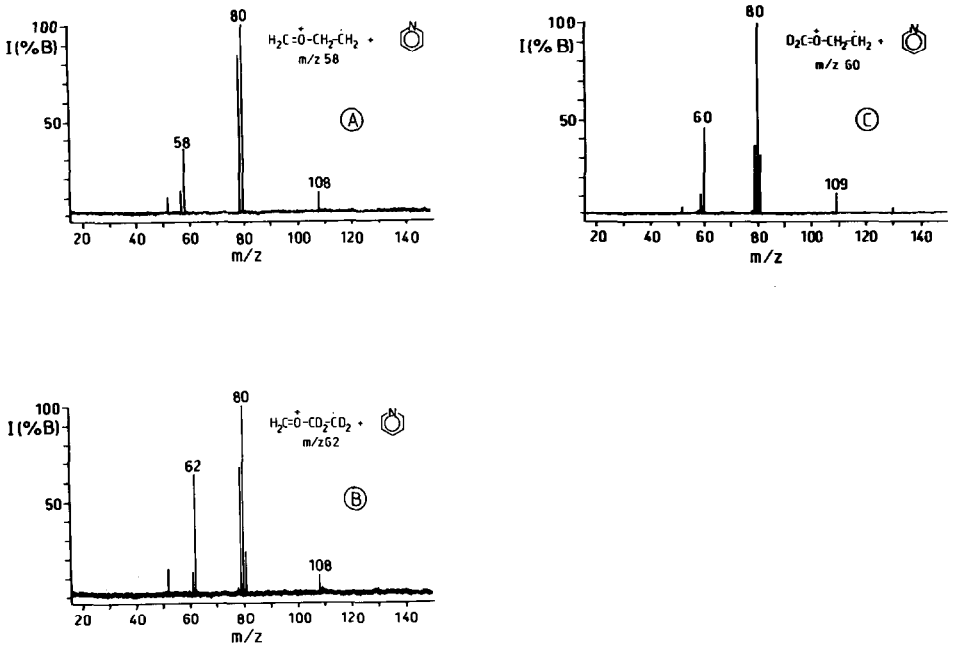
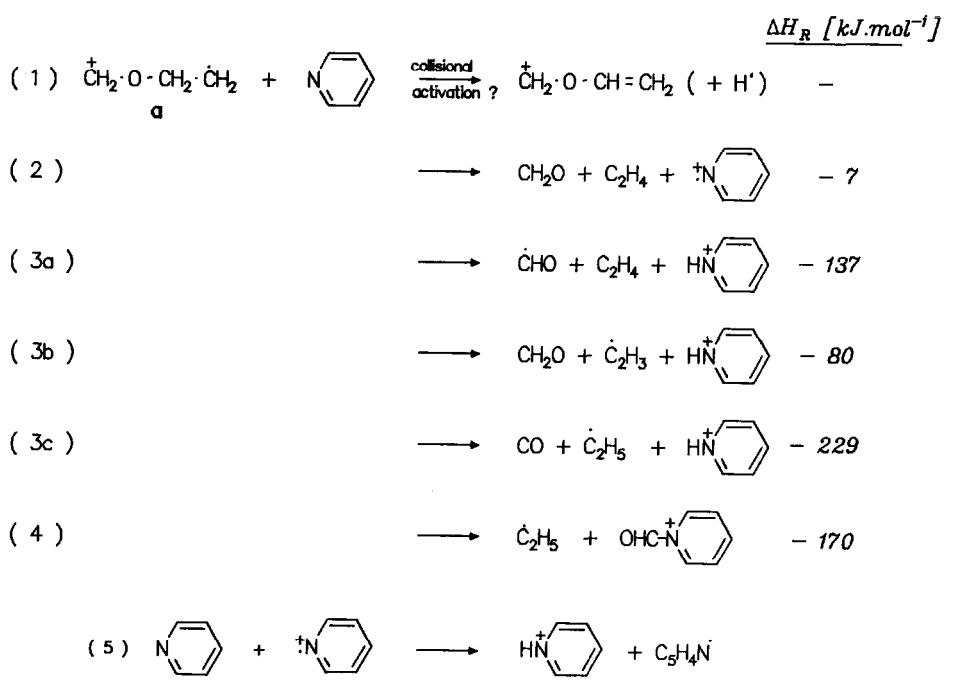


Fig. 1. Bimolecular reaction of the β-distonic ion with pyridine: (A), **a**. (B), **b**; (C), **c**, Mass spectra were obtained after 1 s reaction time. Total pressure, 5.0×10^{-8} mbar; background pressure, $(0.5\text{–}1.0) \times 10^{-9}$ mbar.

shown using the deuterated isotopomers **b** and **c** that the original ethylene moiety of **a** is delivered without any scrambling of the CH_2 groups at both sides of the oxygen atom during this reaction. This structural stability of **a** against a CH_2 group scrambling has been confirmed by the CA experiments discussed in the preceding section. However, the mechanism of the $C_2H_4^{+\cdot}$ transfer is not clear and is in fact difficult to visualize as the reaction of an electrophilic carbenium ion centre with a nucleophile expected for **a**. Therefore, we have repeated the investigation of the reaction of **a**, **b** and **c** using an FT-ICR instrument with an external ion source [17] to avoid any interference by ions co-generated with **a** during an internal ionization in the ICR cell. Furthermore, the study was extended to reactions of **a** and its deuterated isotopomers with other substrates to obtain more information about the dualism "electrophile–radical" expected for a distonic ion [18]. Here only the results obtained for the reactions of **a–c** with pyridine bases besides those with acetonitrile are discussed.

The β-distonic ions **a** prepared from **1** react readily with pyridine after the transfer into the ICR cell. The mass spectra obtained with a reaction time of 1 s after the isolation of the ions are shown in Fig. 1. In the case of **a** (Fig. 1(A))



Scheme 4.

the surviving ions **a** give rise to the signal at *m/z* 58. The adduct ion of $C_2H_4^{+\cdot}$ and pyridine at *m/z* 107 is not observed. Instead, additional signals at *m/z* 57, 79, 80 and 108 are detected which are due to reactions (1)–(4) shown in Scheme 4.*

Reaction (1) looks like the abstraction of an H atom from **a** by a pyridine but the reaction enthalpy of this process is not known. However, the loss of an H atom is the predominant reaction for metastable **a**, thus requiring only a small activation energy, and it is likely that this process occurs also in the ICR cell as a collision-induced fragmentation. In line with this explanation, the three isotopomers **b** and **c** prepared from **2** eliminate H˙ and D˙ (Figs. 1(B) and 1(C)), the former process dominating in all cases in close analogy to the reactions of metastable and collisionally activated ions.

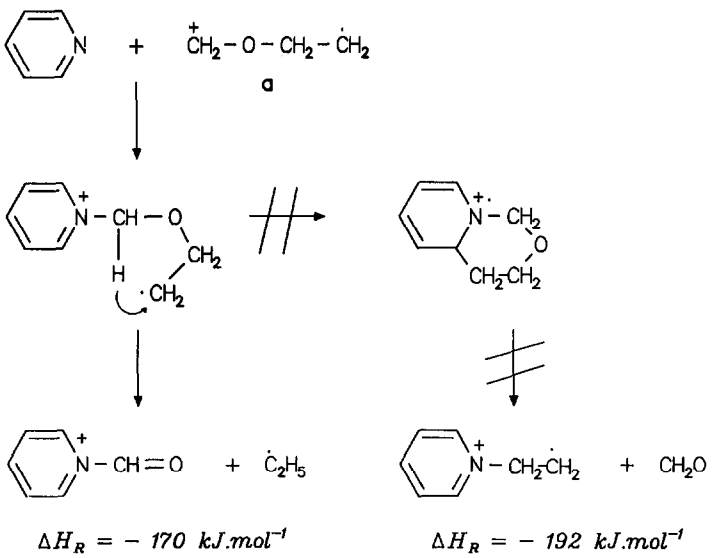
The ΔH_R values of the reactions of **a** with pyridine and acetonitrile respectively have been calculated using the following ΔH_f values (in kJ mol^{-1}): **a**, 842 [7(a)]; C_5H_5N, 140; $C_5H_5N^{+\cdot}$, 1032; $C_5H_5NH^+$, 746; C_5H_5N–CHO^+, 694 (MNDO); C_5H_5N–$C_2H_4^{+\cdot}$, 899 (MNDO); CH_3CN, 74; $CH_3CN^{+\cdot}$, 1251; CH_3CNH^+, 817; CH_3CN–CHO^+, 713 (MNDO); CH_3CN–$C_2H_4^{+\cdot}$, 919 (MNDO); CH_2O, – 109; CHO, 45; CO, – 111; C_2H_4, 54; C_2H_3, 265; C_2H_5, 118. The data were taken from ref. 16 unless stated otherwise.

Reactions (2) and (3) corresponding to a charge transfer and a proton transfer respectively from **a** to pyridine are exothermic by 7 kJ mol^{-1} and 80–229 kJ mol^{-1} (see footnote on p. 554) for the products shown in Scheme 4. Unfortunately, it is not possible to discriminate between the proton transfer reactions (3a)–(3c) using the isotopomers **b** and **c** because of the interfering reaction (5) of the pyridine radical cation (Scheme 4) yielding protonated pyridine [19]. It should be noted, however, that deuterated pyridine, *m/z* 81, is formed from all isotopomers, hence all H atoms of **a** participate in this proton transfer. This result can be explained by assuming either a proton transfer by at least reactions (3a) and (3b) parallel to each other or by assuming only reaction (3c) with a scrambling of the six H atoms of **a** in the collision complex with pyridine. The elimination of CO with formation of $C_2H_6^{+\cdot}$ is the second important fragmentation of metastable **a**, thus representing an energetically favourable process. The same rearrangement of **a** may also be induced by the excess energy released during the formation of the collision complex with a pyridine molecule as a consequence of the electrostatic attraction between the ion and the polar molecule. A transfer of one of the six equivalent H atoms from $C_2H_6^{+\cdot}$ to the pyridine molecule before or during the dissociation of the complex creates the experimental result.

The product ion *m/z* 108 from the reaction between **a** and pyridine is $C_6H_6NO^+$, as established by high mass resolution, and very probably corresponds to an *N*-formyl pyridinium ion. In solution, *N*-acyl pyridinium ions are known as reactive intermediates formed by a nucleophilic attack of the pyridine N on electrophilic acyl derivatives. The reactions of the isotopomers **b** and **c** (Figs. 1(B) and 1(C)) with pyridine prove unequivocally that the formyl group stems specifically from the (CH_2–O) moiety of **a**. The mechanism depicted for the formation of the *N*-formyl pyridinium ion in Scheme 5 consists of a nucleophilic attack of the pyridine N on the electrophilic CH_2 group of **a** followed by an intramolecular hydrogen abstraction of the radical site in a five-membered cyclic transition state. Thus, the formation of the *N*-formyl pyridinium ion corresponds to the expected electrophilic reactivity of the β-distonic ion **a**. An *N*-formyl cation is also the product of a reaction of **a** with 2-picoline as well as charge transfer and proton transfer so this reaction is probably typical of all pyridine bases.

The reactions of **a** and its deuterated derivatives **b** and **c** with acetonitrile produce after a reaction time of 1 s the mass spectra shown in Fig. 2. Additional peaks are observed besides that of the expected ethylene adduct ion, and these are attributed to the reactions (6)–(9) shown in Scheme 6 (see footnote on p. 554).

The losses of $H^{\cdot}$ from **a** and $H^{\cdot}$ and $D^{\cdot}$ from **b** and **c** (reaction (6)) are analogous to reaction (1) and again probably correspond to a fragmentation induced by collisions with acetonitrile in the ICR cell.



Scheme 5.

The acetonitrile radical cation arising from the endothermic charge transfer (reaction (7)) is not observed in the spectra. However, separate ICR experiments show [20] that the acetonitrile radical cation reacts with neutral acetonitrile to yield a protonated acetonitrile (reaction (10)). Conceivably they may not survive under the ICR conditions used to study the reactions if they are formed by collision with **a** still kinetically excited from the transfer into the ICR cell. In fact, the formation of some CD_3CND^+, m/z 46, is observed during the reaction of **a** with CD_3CN (Fig. 2), and these ions must arise via reaction (10). The mechanism(s) of the proton transfer from **a** to acetonitrile (reaction (8)) and to pyridine (reaction (3)) are very probably identical but in the case of acetonitrile only, a protonation according to mechanism (8c) is distinctly exothermic. Since the occurrence of reaction (7) cannot be strictly excluded, reaction (10) may obstruct a quantitative determination of the contributions of the H atoms at the different positions to the proton transfer using the reactions of the deuterated ions **b** and **c**. Nevertheless, the formation of deuterated acetonitrile (CH_3CND^+ m/z 43 and CD_3CND^+ m/z 46; see Fig. 2) is observed for both deuterated analogues **b** and **c** independently of the positions of the D atoms, and the relative abundance of the deuterated acetonitrile increases parallel to the number of D atoms in **b** and **c**. This suggests that all H and D atoms of the β-distonic ions become equivalent prior to the proton transfer as predicted by mechanism (8c). However, the possible interference of reaction (10) and of unknown H/D isotope effects prohibits

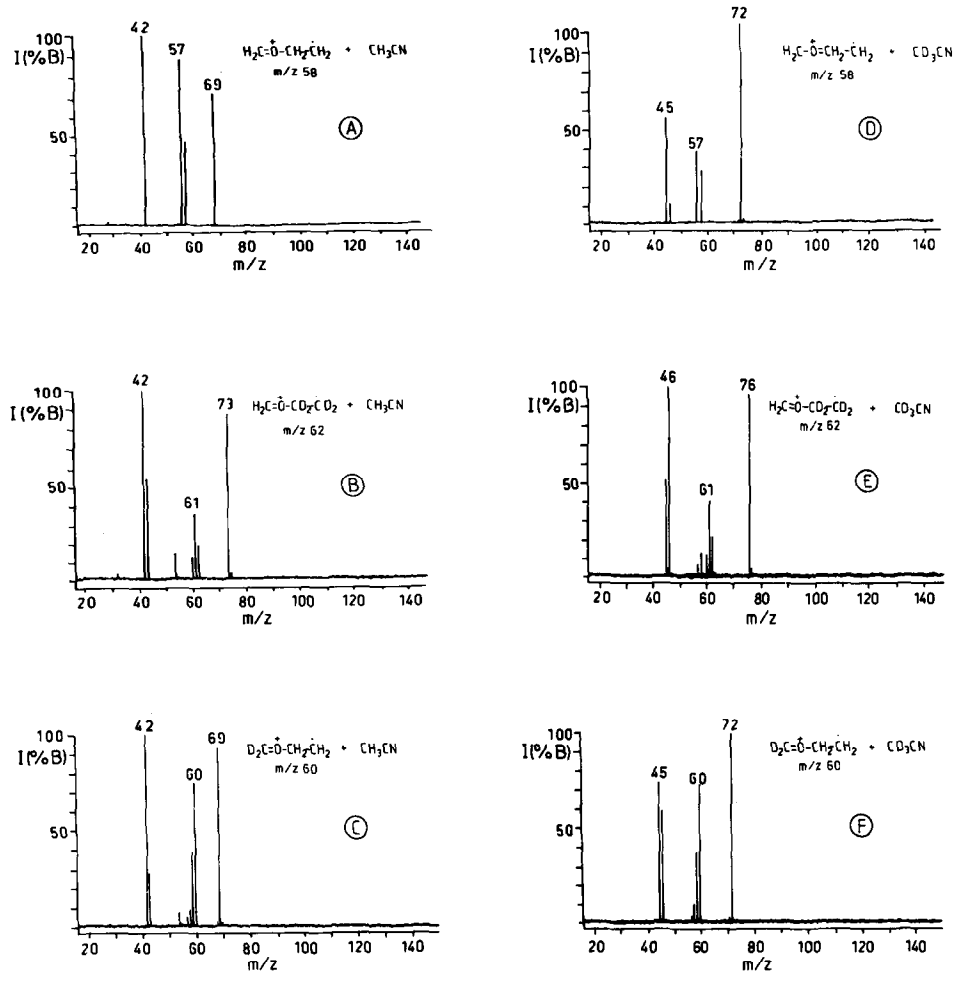
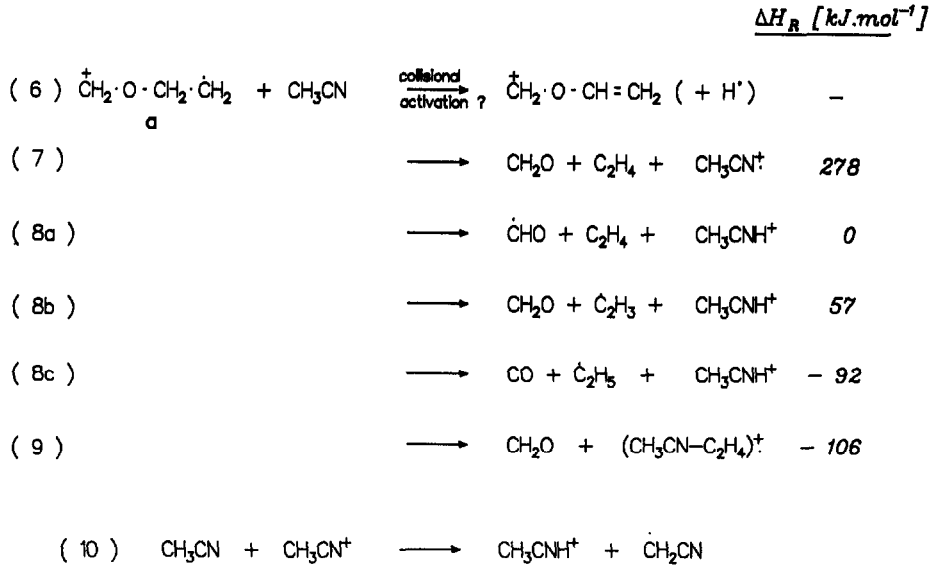


Fig. 2. Bimolecular reaction of the β-distonic ion with acetonitrile and acetonitrile-d_3: (A) and (D), **a**; (B) and (E), **b**; (C) and (F), **c**. Mass spectra were obtained after 1 s reaction time. Total pressure, 5.0×10^{-8} mbar; background pressure, $(0.5\text{–}1.0) \times 10^{-9}$ mbar.

confirmation of this interesting mechanism involving a complex between three components.

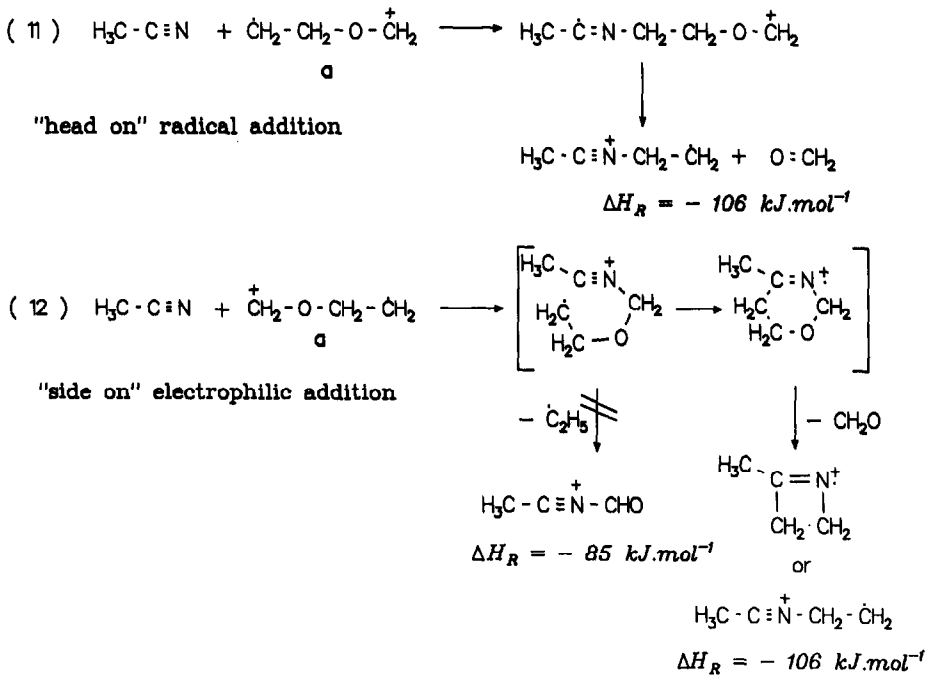
Reaction (9) is the known $C_2H_4^{+\cdot}$ transfer reaction studied previously [8] and our results are in good agreement with the published data. Mass shifts are observed for the product ion m/z 69 from **a** and CH_3CN in the case of a reaction of **b** and **c** as well as of CD_3CN. These shifts agree with a transfer of the original ethylene unit of **a** without any scrambling of the CH_2 groups or of any of the H atoms between both reaction components. Analogous reactions were observed between **a** and other aliphatic nitriles [18] but in no case



Scheme 6.

does the transfer of a formyl group take place as in the case of the pyridines. This diverse behaviour of the β-distonic ion **a** in its reaction with the two types of nucleophiles is rather puzzling. An MNDO calculation of the heats of formation of the product ions arising from the addition of CHO^+ and $C_2H_4^{+\cdot}$ respectively to acetonitrile and pyridine shows that the CHO^+ adduct would be more stable for both neutrals. Hence it must be the reaction mechanism which determines the different outcome of the reaction of **a** with pyridine and acetonitrile. One explanation could be that the reaction between **a** and a nitrile is initiated by a "head on" radical addition to the nitrile group followed by the loss of CH_2O (Scheme 7, reaction (11)). In the case of pyridine a corresponding radical addition would destroy the aromatic system, thus being energetically unfavourable compared with the electrophilic addition of **a** to the N atom.

Another explanation could be a reaction involving an electrophilic addition to the N atom for both types of nucleophiles but different mechanisms for the stabilization of the resulting intermediate (Scheme 7, reaction (12)). While an intramolecular H-abstraction occurs in the pyridine adduct ion as depicted in Scheme 5, the acetonitrile adduct eventually cyclizes "side on" to a dihydrooxazine derivative which subsequently decomposes by elimination of CH_2O. This cyclization step corresponds to an intramolecular radical addition to an activated unsaturated C–N group needing probably not much activation energy in the case of the nitrile but again being unfavourable in the case of pyridine because of the loss of aromaticity.



Scheme 7.

The structures of the product ions of the two mechanisms (11) and (12) of the reaction between **a** and acetonitrile are very probably identical. However, in the case of the "head on" radical attack (11) the terminal CH_2 group of the ethylene unit of **a** is attached to the N atom in the product ion while in the "side on" cyclization mechanism (12) by an initial electrophilic attack the internal CH_2 group is eventually bonded to the N atom. Furthermore, some hydrogen migrations may accompany the loss of CH_2O from the intermediate dihydro-oxazine ion. The structures of $C_2H_4^{+\cdot}$ adduct ions from the reactions of **a** and the deuterated analogues **b** and **c** with acetonitrile have been studied by CA mass spectrometry using the VG ZAB 2F instrument, and the CA spectra are compared with the CA spectrum of a $C_4H_7N^{+\cdot}$ ion generated from the dihydro-oxazine **4**.

The ethylene adduct ion $C_4H_7N^{+\cdot}$, *m/z* 69, from the reaction of **a** and acetonitrile can be prepared in the ion source of the ZAB 2F mass spectrometer by electron impact ionization of a mixture of **1** with acetonitrile under the conditions of a CI experiment. However, an interfering ion *m/z* 69 is formed from **1** alone under these conditions. Hence, the $C_4H_7N^{+\cdot}$ adduct ion was prepared from **c** by using a mixture of the tetradeuterated dioxane **2** and acetonitrile. The CA spectrum of this ion obtained by the usual technique

(Table 4) exhibits prominent peaks for the loss of CH_3CN and $C_2H_3^{\cdot}$ to yield $C_2H_4^{+\cdot}$, *m/z* 28, and CH_3CNH^+, *m/z* 42, respectively, in accord with a *β*-distonic nitrilium ion structure. The formation of protonated acetonitrile is also observed as a spontaneous process of metastable ions. An identical CA spectrum is obtained for the fragment ion $C_4H_7N^{+\cdot}$ arising from ionized 5,6-dihydro-4*H*-2-methyl-1,3-oxazine **4**. This is an isomer of the 4,5-dihydro-2*H*-6-methyl-1,3-oxazine ion proposed as an intermediate for the formation of the ethylene adduct ion (see Scheme 7). Therefore, it is of significance that ionized **4** indeed fragments by elimination of CH_2O and that the CA spectrum of the resulting fragment ion is identical with that of the ethylene adduct ion.

The CA spectra of the adduct ions from **c** with CH_3CN and CD_3CN respectively agree well, taking into account the mass shifts due to the CD_3 group. Thus the methyl group and the ethylene moiety remain basically intact in the adduct ion. The agreement of the CA spectrum of the adduct ion of the tetradeuterated **b** with the other spectra is not as good but is still reasonable. It reveals that the ions originally at *m/z* 28 are not only $C_2H_4^{+\cdot}$ shifted to *m/z* 32 in the case of **b** but also CH_2N^+ (very probably protonated HCN) shifted to *m/z* 30. However, the formation of a protonated HCN, a protonated acetonitrile, and an ethylene radical cation in the CA spectra of the adduct ions does not allow us to distinguish straightforwardly between the "head on" and the "side on" mechanism (Scheme 7) even if the adduct ion is generated from $^+CH_2$–O–CD_2–$CH_2^{\cdot}$, an isotopomer transferring an asymmetrically labelled CD_2–$CH_2^{+\cdot}$. This is confirmed by preliminary experiments with this isotopomer.

CONCLUSION

The investigation of the spontaneous fragmentations and of the collision-induced reactions of the *β*-distonic ion **a** and its deuterated analogues shows again that this distonic ion is surprisingly stable against an isomerization by an exchange of the individual methylene groups via an intermediate oxetane radical cation. The MIKE spectra of the isotopomers show that the loss of a fragment of 28 Da from metastable **a** is due to the loss of CO and not of C_2H_4, as one might have expected from a distonic structure. The elimination of CO to form an ethane radical cation requires a migration of two H atoms in **a**, and for a stepwise rearrangement the ethoxymethylene radical cation [8(a)] must be an intermediate. This latter ion as well as the cyclic isomer of **a**, the oxetane radical cation **d**, are probably also intermediates during the loss of an H atom from **a** which is shown to be an unspecific process both for metastable and collisionally activated ions.

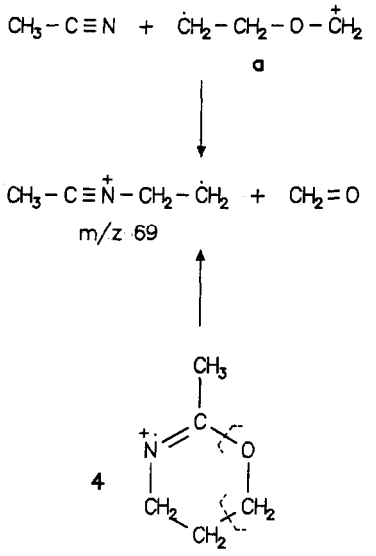
Besides the known $C_2H_4^{+\cdot}$ transfer from **a** to acetonitrile [8] a protonation of acetonitrile has been observed by an ICR study of the bimolecular reactions

TABLE 4

CA spectra of $C_4H_7N^{+\cdot}$ and deuterated analogues

	Ion from			
m/z	**5**	**c** + CH_3CN	**c** + CD_3CN	**b** + CH_3CN
14	1.9	2.1	0.8	0.9
15	5.2	6.2	0.9	2.0
16			0.9	0.7
17			1.3	
18			4.2	1.9
26	11.5	10.7	11.5	2.1
27	17.9	18.9	17.4	7.4
28	31.4	28.5	27.2	6.1
29			3.9	5.8
30			4.0	11.7
31				2.0
32				10.1
39	3.5	4.1	0.9	1.9
40	4.8	5.3	1.8	3.0
41	8.9	11.9	2.1	2.4
42	(90)	(87)	3.9	5.0
43			5.6	(33)
44			3.4	5.9
45			(71)	14.1
46				2.8
47				2.3
52	2.2	2.1		
53	0.4	0.4		
54	2.0	2.1		0.4
55	1.3	2.8		4.6
56				0.2
57			1.4	1.1
58			2.8	0.7
67	0.8			
68	8.0	4.9		
69			0.3	
70			0.8	0.4
71			4.9	1.6
72				2.9
(Parent ion)	(*m/z* 69)	(*m/z* 69)	(*m/z* 72)	(*m/z* 73)

of **a**. Proton transfer as well as charge exchange is also observed in the reaction of **a** with pyridine and 2-picoline. All six H atoms of **a** participate in these protonation reactions exhibiting an H/D isotope effect. This lack of specificity can be explained by isomerization of **a** into CO and $C_2H_6^{+\cdot}$ in the collision



Scheme 8.

complex with the neutral bases prior to the proton transfer. The ion **a** reacts with the pyridines by a formylation and not by a transfer of $C_2H_4^{+\cdot}$. The formyl group arises specifically from the terminal (CH_2–O) group of **a**, and this reaction exemplifies the long-sought electrophilic reactivity of **a**. In view of these results it is also likely that the $C_2H_4^{+\cdot}$ transfer to acetonitrile and other aliphatic nitriles is initiated by an electrophilic attack of **a**, and the mechanism suggested in Schemes 5 and 7 respectively rationalizes the different outcomes of the reaction of **a** with pyridine and acetonitrile. However, the present results do not provide definite evidence for this mechanism, and further investigations are needed for a better understanding of the "electrophile–radical" dualism in the reactivity of distonic ions.

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