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The mass spectrometric behaviour of four isomeric oxazolones is rationalized by means of metastable ion studies and bond order calculations *via* semiempirical methods. The data allow the identification of a possible intermediate structure of molecular species that accounts easily for the observed primary decomposition pathways.

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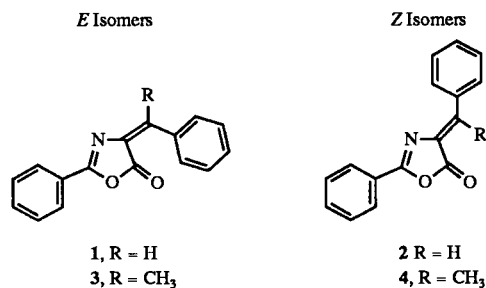
## Introduction.

Unsaturated 5(4*H*)-oxazolones represent an important class of heterocycles and interest in their chemistry continues unabated because of their usefulness as synthons. For example they are useful intermediates in the synthesis of *N*-acyl-2,3-didehydroamino acid derivatives [1] or can afford polyamides by ring-opening polyaddition [2]. These compounds are usually obtained by condensation procedures [3] which in some cases can lead to a mixture of geometric isomers whose stereochemistry can be of great importance on subsequent processes [4], so the unambiguous assignment of both geometric isomers has been the subject of continuous interest [5,6]. Now we wish to report our findings of the structural discrimination of unsaturated 5(4*H*)-oxazolones isomers as obtained by electron impact mass spectrometry and collisional spectroscopy.

While oxazole and its derivatives have been the object of exhaustive mass spectrometric investigation [7], few papers on mass spectrometry of oxazolones have appeared in the literature. The electron impact induced decomposition pattern of some 2-(*p*-bromophenyl)-4,4-disubstituted-5(4*H*)-oxazolones were recently discussed, and the formation of similar, highly stable product ions was emphasized [8]. In particular the mass spectrometry of the title compounds was already discussed by Rai *et al.* [9], but from the analytical point of view only, with the aim to characterize the products arising from a Perkin reaction of azalactone with vanillin Schiff bases. Ballantine and Fenwick [10], discussing the mass spectrometric behaviour of a series of substituted oxazol-5-ones and other related heterocycles, showed the absence of any electron-impact induced isomerization processes and pointed out that

most of the total ion current was due to  $C_6H_5CO^+$  ions, for whose formation a concerted mechanism was proposed.

In the present paper we will discuss the electron impact mass spectrometry of **1-4** with a two-fold aim: i) to describe the intimate mechanism(s) of the fragmentation pathways; ii) to characterize, *via* mass spectrometric techniques, the *Z* and *E* isomers.

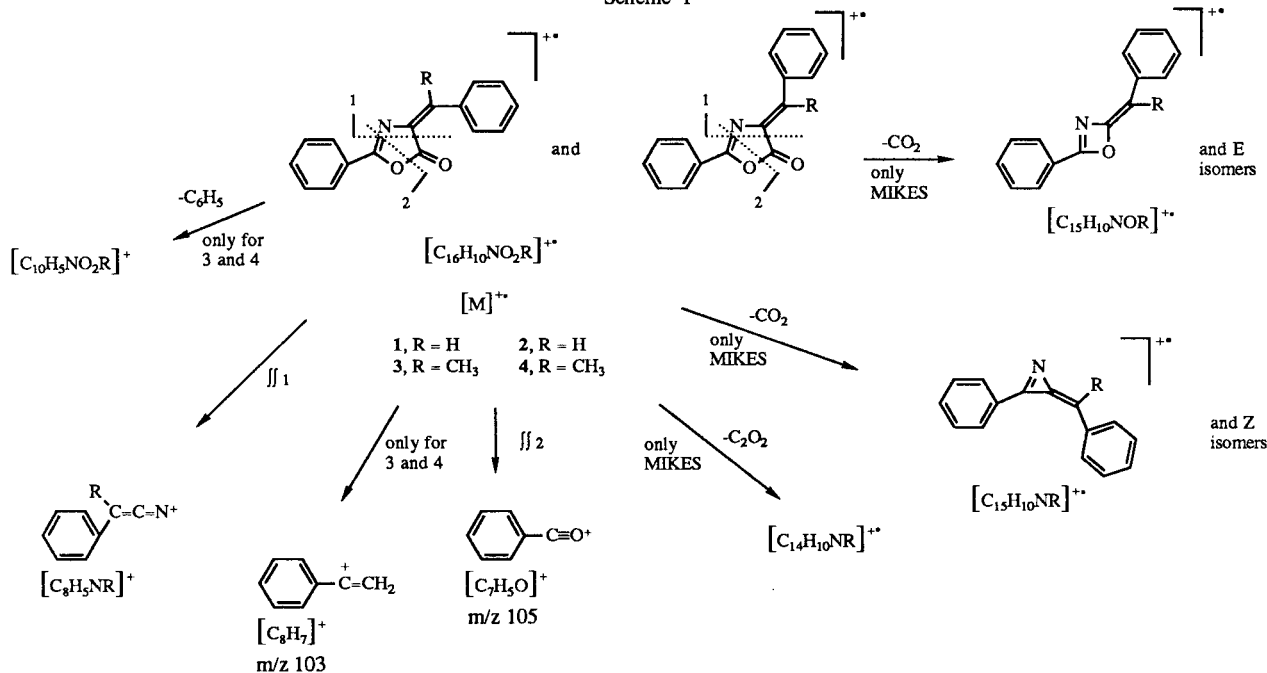


## Results and Discussion.

Pursuing our interest in structural characterization *via* mass spectrometry of stereoisomeric compounds [18] as well as in the EI mass spectrometric behaviour of heterocyclic compounds [19,20] and, in particular of oxazolones [8], we undertook the present study with two different aims, *i.e.* the rationalization of the fragmentation pattern of **1-4**, and the structural identification of the different stereoisomers.

The 70 eV EI induced mass spectrometric behaviour of **1** was already described by Ballantine and Fenwick [10], together with analogous thiazol-5-ones and imidazol-5-ones. It was emphasized that the main fragmentation pathway, due to cleavage of the heterocyclic ring *via* a concerted mechanism, leads to the formation of  $C_6H_5CO^+$

Scheme 1



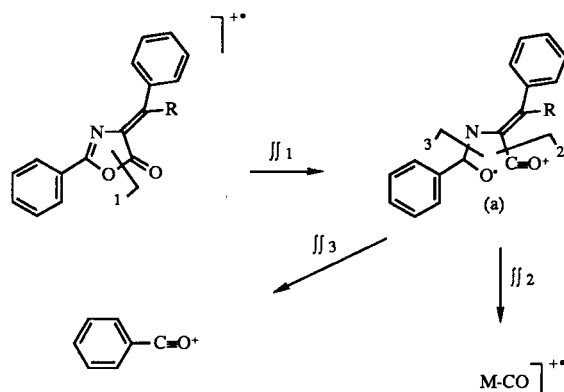
ions.

In our case, such behaviour is observed for all the examined compounds. The EI mass spectra are very similar (see tables 1 and 2); hence a common fragmentation pattern can be proposed for 1-4 (see Scheme 1). The only fragment ions detected in the EI mass spectra are  $C_6H_5CO^+$  ( $m/z$  105),  $C_6H_5-C^+=CH_2$  ( $m/z$  103, only for 3 and 4), those arising from  $C_6H_5\cdot$  loss (only for 3 and 4), and ring cleavage (e.g. 1 of Scheme 1). These fragmentation pathways are detectable also as unimolecular fragmentations detected by MIKE spectra, but together with some other abundant ions due to CO, CO<sub>2</sub> and 2CO losses.

The primary CO loss, not observed in the EI spectra, must of necessity be a fragmentation competing with  $C_6H_5CO^+$  formation. The kinetic energy release related to the metastable CO loss is about 860 meV for all four examined samples, in agreement with the formation of a very stable product ion. It must be emphasized, however, that the concerted mechanism proposed in the literature for the  $C_6H_5CO^+$  formation cannot account for this CO loss. For the competing loss of CO and the formation of  $C_6H_5CO^+$  two possible mechanisms are proposed; the first considers a possible structure of molecular ions (different from that of neutrals) that explains both the fragmentation pathways, the second considers two completely different fragmentation mechanisms, both starting from molecular ions with the same structure as the neutrals. In the second case, the formation of  $C_6H_5CO^+$  occurs *via* a concerted mechanism (2, Scheme 1) involving the cleavages of the O(4)-C(3) and C(5)-C(4) bonds.

In order to prove the first mechanism, a series of semiempirical calculations were performed on both neutral and ionic molecular species (see Figures 1-4, in which only the bond order values of the bonds of interest are reported). A general trend is observed for all the examined compounds, *i.e.* the bond order of the C(3)-O(4) bond clearly decreases (*i.e.* bond strength weakens) passing from neutral to ionic moieties. Hence it is reasonable to assume that such a bond would be the easiest broken in the fragmentation processes. Such a rupture can lead to molecular ions of an "open" structure (*i.e.* a distonic species), *e.g.* a shown in Scheme 2. Distonic ions are often invoked as intermediate products in EI induced fragmentation mechanisms. A review on this argument has recent-

Scheme 2



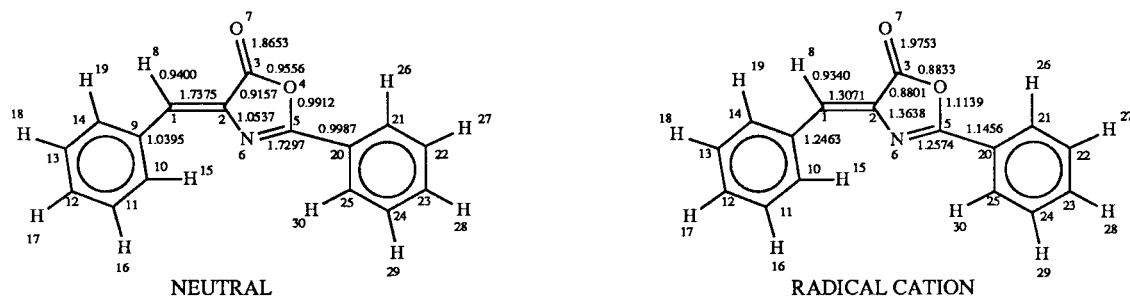


Figure 1 Structures and calculated bond orders for neutral and radical cation of compound 1.

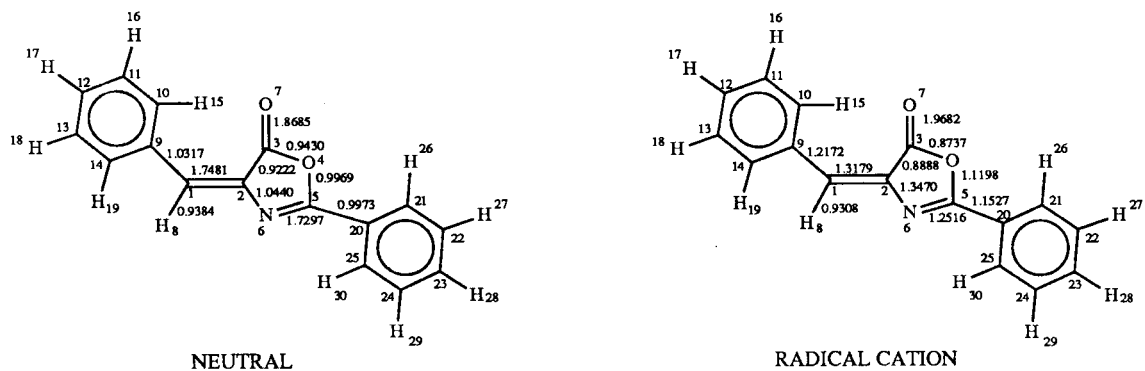


Figure 2 Structures and calculated bond orders for neutral and radical cation of compound 2.

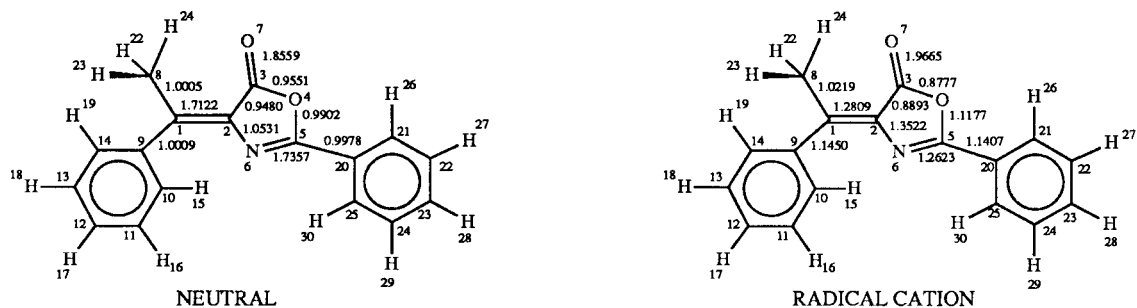


Figure 3 Structures and calculated bond orders for neutral and radical cation of compound 3.

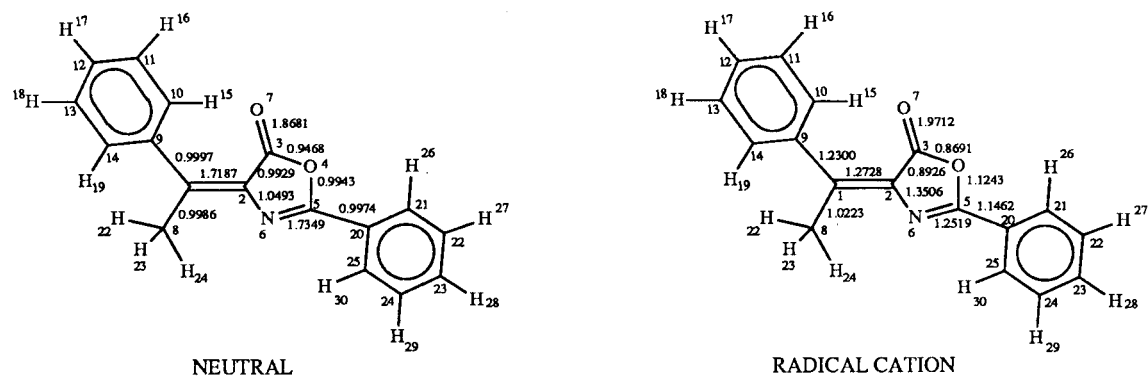


Figure 4 Structures and calculated bond orders for neutral and radical cation of compound 4.

ly been published [21], emphasizing how the knowledge of the properties of these species is important in order to understand the behaviour of radical cations. From structure **a**, the loss of CO would be particularly favoured. With regards to  $C_6H_5CO^+$  formation, it should be noted that there is a general strong decrease of the N(6)-C(5) bond order from neutral to ionic species. So, for example the N(6)-C(5) bond order in neutral **1** is 1.7357, the highest in all the heterocyclic ring, while it becomes 1.2516 in the radical cation **1**, lower even than C(2)-N(6). Thus, a possible cleavage of the C(2)-N(6) bond can be easily envisioned.

In other words, the  $C_6H_5CO^+$  formation can be explained by a two step mechanism, the formation of structurally "open" molecular distonic ion that accounts for both the CO loss and  $C_6H_5CO^+$  formation as competing processes.

The EI mass spectrometry is ineffective in distinguishing *Z* and *E* isomers: the related spectra (see Table 1 and 2) show only very minor differences in relative abundances of product ions.

Table 1  
70 eV EI Mass Spectra and CAD MIKE Spectra of  $M^+$  of  
Compounds **1** and **2**

m/z values	Origin	Relative abundances			
		EI Mass Spectra		CAD MIKES	
		1	2	1	2
249	$[M]^{++}$	25	22	---	---
221	$[M-CO]^{++}$	---	---	100	30
205	$[M-CO_2]^{++}$	---	---	5	---
193	$[M-2CO]^{++}$	---	---	10	10
117	$C_6H_5-CH=C=NH]^{++}$	3	---	---	---
116	$C_6H_5-CH=C=N^+$	4	3	---	---
105	$C_6H_5-C\equiv O^+$	100	100	60	100
77	$C_6H_5]^+$	41	41	---	---
124.5	$[M]^{++}$	1.5	0.5	---	---

Table 2  
70 eV EI Mass Spectra and CAD MIKE Spectra of  $M^+$  of  
Compounds **3** and **4**

m/z values	Origin	Relative abundances			
		EI Mass Spectra		CAD MIKES	
		3	4	3	4
263	$[M]^{++}$	15	17	---	---
235	$[M-CO]^{++}$	---	---	100	65
219	$[M-CO_2]^{++}$	---	---	25	7
207	$[M-2CO]^{++}$	---	---	3	5
186	$[M-C_6H_5]^+$	---	---	12	5
130	$C_9H_8N]^{++}$	---	5	---	1
115	$C_8H_5N]^{++}$	---	3	---	1
105	$C_6H_5-C\equiv O^+$	100	100	83	100
103	$C_6H_5-C^+=CH_2$	5	12	---	---
77	$C_6H_5]^+$	44	62	---	---
131.5	$[M]^{++}$	4	2	---	---

The capabilities of collisional spectroscopy in isomer differentiation are well known, and it has been successfully applied by us in many different systems [18-20]. For this reason we undertook a series of collisional mass spectra on the molecular ions of **1-4**. The spectra (see Tables 1 and 2), show clear differences in the relative abundances of the ions arising from the competing processes described above. Specifically, for the *E* isomers, the  $[M-CO]^+$  ions represent the base peak of the CAD-MIKE spectra, while for the *Z* isomers the  $C_6H_5CO^+$  ionic species represent the base peak.

These experimental results are in accord with the bond order values shown in Figures 1-4; *viz* for compounds **1** and **2** the C(2)-C(3) bond order is lowest for the *E* isomers, whereas the reverse is true for the N(6)-C(5) bond orders, thus giving rise to easier loss of the CO for the *E*-isomers.

### Conclusions.

The comparison of electron impact and metastable data with the calculated bond orders of the four examined compounds, allowed us to propose a common intermediate that can easily explain the mechanism of the main competing decomposition processes. Collisional spectroscopy led to a clear characterization of the *Z* and *E* isomers and the bond order calculations also fit with the collisional data.

## EXPERIMENTAL

### Mass Spectrometry.

All mass spectrometric measurements were performed on a double focusing, reverse geometry VG ZAB2F instrument [11], operating in electron impact (EI) conditions (70 eV, 200  $\mu$ A). Samples **1-4** were introduced *via* a direct inlet system without any probe heating, and with a source temperature of 180°. Metastable transitions were detected by either B/E = const linked scans [12] or mass analyzed ion kinetic energy (MIKE) spectrometry [13]. Collisional experiments were performed by 8 keV ions colliding with air in the second field free region [14]. The pressure in the collision cell was such to reduce the main beam intensity to 40% of its initial value.

### Synthesis.

Compounds **1-4** were analytically pure samples synthesized and purified according to literature [5,15].

### Theoretical Calculations.

Semiempirical MO-SCF calculations were performed using the AM1 method [16] included in the AMPAC program [17].

Closed-shell systems were calculated within the RHF formalism, using the standard options of the AM1 method. Open-shell systems were calculated using the UHF option included in the program. No relevant spin contamination was noticed in applying the UHF formalism to this type of structures.

Molecular geometries were partially optimised in order to save computer time. Standard values of bond lengths, valence angles

and dihedral angles were used for phenyl group geometries. Structures were kept planar, except for the phenyl group when linked to the exocyclic double bond, and the methyl group in tetrasubstituted 5(4H)-oxazolones **3** and **4**. Dihedral angles of these groups with respect to the double bond-oxazolone ring plane were optimized. The remaining bond lengths and valence angles were also optimized in all structures.

Bond orders were calculated from density matrices using the standard option included in the AMPAC program.

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