

Ring Opening of the Molecular Ion of 5(4*H*)-Oxazolone

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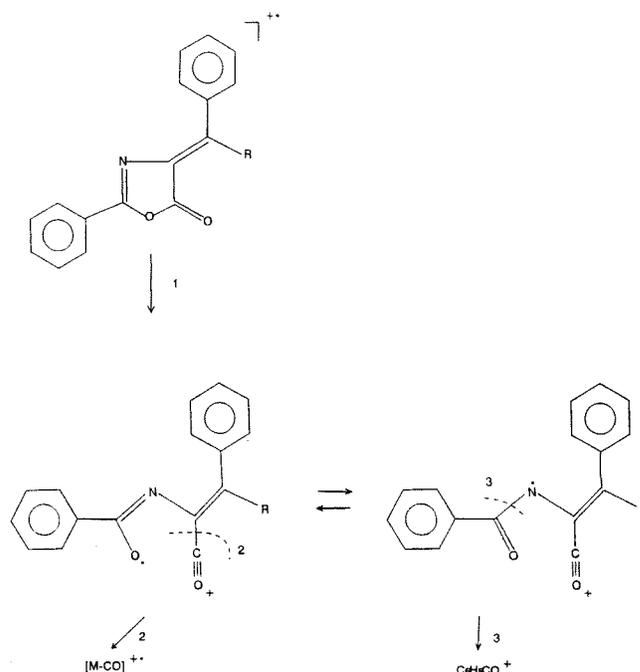
Quantum chemical calculations were carried out at several theoretical levels (semi-empirical, MNDO; *ab initio*, 3–21G SCF, 6–311G** SCF and DZP CISD) to investigate the ring-opening process of and the loss of CO from the molecular ion of 5(4*H*)-oxazolone. The ring-opening process is predicted to be slightly endothermic and the loss of CO from the open-ring molecular ion to be slightly exothermic. Detailed population analysis calculations suggest the weakening of the lactonic C—O bond in the closed-ring molecular ion and weak carbon—carbon and nitrogen—(formyl)—carbon bonds in the open form. Both the open-ring molecular ion and the $[M - CO]^{++}$ ion are suggested to be of distonic type.

INTRODUCTION

In a recent paper, Curcuruto *et al.*¹ discussed the electron impact (EI) mass spectrometric behaviour of a series of 5(4*H*)-oxazolones. Their detailed investigation was based on metastable ion studies and was augmented by bond order calculations applying the semi-empirical method MNDO.² In that study an intermediate, open, distonic-type structure of the molecular ion was proposed (see Scheme 1). This structure allowed a plausible explanation for the observed loss of CO and for the formation of the $C_6H_5CO^+$ ion during electron impact-induced fragmentation processes.

To enhance understanding of the formation and behaviour of the suggested open, distonic ion, detailed quantum chemical calculations have been carried out in the present study on some salient features of the ring-opening process of a simplified model molecular ion M^+ , in which the C_6H_5 groups were replaced by H, and $R = H$ (see Fig. 1). Most so-called small organic molecules and ions, which are of practical interest for organic mass spectrometrists, still prove to be formidable for theoretical treatments of the highest quality, such as the G1 theory.^{3–5} The larger the system under investigation is (both the number of atoms and the number of electrons should be considered), the lower the applicable level of theory becomes. Therefore, a

compromise in the theoretical treatment is usually inevitable. Then the question arises of whether the results obtained from lower level calculations are reliable enough to be able to draw quantitative and definitive conclusions from them. In our opinion, for medium-



Scheme 1

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sized species, which today mean systems containing up to 60 atoms of first-, second- and third-row elements, predictions at semi-empirical levels and at the Hartree-Fock (SCF) level using a moderate basis set (such as 3-21G⁶ or 6-31G*⁷) may be useful, but usually only theoretical treatments which incorporate electron correlation and use significantly larger basis sets than those mentioned can be expected to yield accurate results for the energetic description of mass spectral fragmentation processes. Fortunately, advances in the design and implementation of theoretical methods⁸ combined with the ever-growing power of computer hardware allow quantum-chemical treatments of increasing accuracy on larger and larger systems of chemical interest.

In a recent paper on theoretical approaches to gas-phase ion chemistry, Radom³ provided several examples where theory successfully complements experiment. The present authors share Radom's assertion that there is a 'useful complementarity between theory and experiment in gas-phase ion chemistry.' Still, there are numerous obstacles for theory to overcome before it becomes an equal partner to high-precision experiments. For closed-shell molecular systems, several *ab initio* methods have been developed which can provide quantitative results at reasonable cost, e.g. the infinite order coupled cluster (CC) methods.^{9,10} For open-shell systems, which are of primary interest to mass spectrometrists, the choice of theoretical methods is, unfortunately, considerably more limited than for closed-shell species. Whereas the spin unrestricted open-shell Hartree-Fock (UHF)¹¹ wave function can be effectively used in perturbative treatments, efficient perturbational improvements over the spin restricted open-shell Hartree-Fock (ROHF)¹² wave function still do not exist (see, however, Ref. 13 and references cited therein). This is a severe limitation since the UHF wave function is not an eigenfunction of the total spin angular momentum, so the UHF method might not result in a reasonable molecular wave function (this is the case if the computed expectation value of the total spin angular momentum $\langle S^2 \rangle$ deviates considerably from its true value). If UHF-based methods cannot be used owing to severe spin contamination (a problem which arises fairly often), then one needs to rely on ROHF-based methods. These include the conceptually simple method of configuration interaction (CI), perhaps including all single and double excitations (CISD).¹⁴

An important drawback of the original CI method (truncated at any excitation level) is that it is not size extensive, i.e. the energy of two non-interacting molecules is not the same as the sum of the energies of the individual molecules (this property is a very important requirement for the accurate calculation of larger molecular systems). On the other hand, CI methods have an advantage over perturbational methods, namely that they are variational, which might become important in determining the quality of the theoretical results obtained. Application of coupled cluster methods to open-shell species has only just started to emerge^{10d} but has a very promising future. An additional difficulty arises from the fact that whereas for most closed-shell systems a single-reference-based *ab initio* method is adequate, for open-shell systems this is usually not the case; use of much more involved multi-

configurational SCF (MCSCF)^{15,16} and related multi-reference correlation methods (such as MR-CI)¹⁷ might be warranted. Although the latter methods usually result in highly accurate wave functions (in simple test cases¹⁸ they approach the accuracy of the full CI method within the given one-particle basis set), they can be applied only for relatively small systems or allow the use of basis sets of lower quality. An additional difficulty is that coupled-cluster or perturbation techniques, as opposed to CI approaches, cannot be readily formulated to handle multi-configurational cases. Finally, in all theoretical methods discussed above, the problem of choosing a basis set which is flexible and large enough to provide an accurate description of the electronic structure under study and small enough to be economical is of principal concern: as the level of theory increases, the requirements on the basis set become more stringent.

In summary, during application of *ab initio* methods to gas-phase ion chemistry one is faced with making intelligent choices on several occasions: (i) choice of the Hartree-Fock method (UHF vs. ROHF); (ii) choice of reference space (single-reference vs. multi-reference); (iii) choice of basis set (core part, polarization and/or diffuse functions, segmented vs. general contraction, etc.); (iv) choice of method to incorporate electron correlation (variational vs. perturbational).

As far as the popular semi-empirical methods are concerned, the ability of the MNDO method to treat open-shell systems has been queried, perhaps justifiably, by several workers. Still, some systematic comparative studies¹⁹⁻²¹ have shown that the mean absolute errors in the calculated heats of formation of open-shell species are not substantially larger than those obtained for well described closed-shell species. For very large systems (with more than 60-70 atoms) it is still the privilege of only a few to carry out detailed *ab initio* SCF calculations with moderately sized basis sets. For these systems, most researchers still need to rely on semi-empirical calculations.

Quantum chemical calculations provide not only total energies (and/or heats of formation) of species under study and, consequently, information about the underlying potential energy surfaces, but also other interesting molecular properties, such as charge densities, bond orders, valences and free valences and spin densities in the case of open-shell systems. (For a compilation of the appropriate definitions of bond orders and valencies and for some special considerations, see Refs 22 and 23.) Recent studies^{1,24,25} provided several examples suggesting the considerable value of Mulliken-Mayer²² bond orders, free valencies and charge densities for the description of ion structures and fragmentation processes. Geometry parameters and charge densities obtained by *ab initio* (4-31G, 3-21G and 6-31G** MP3) and MNDO methods gave sufficiently similar results, indicating the reliability of the latter.²⁶ A detailed comparison of MNDO and *ab initio* (STO-3G SCF and 6-31G** SCF) bond orders led to the conclusion that these indices are in reasonably good agreement.^{25d}

In the course of this study, *ab initio* calculations at the 3-21G⁶ SCF, 6-311G**²⁷ SCF and DZP²⁸⁻³⁰ CISD¹⁴ levels have been carried out for the 5(4H)-oxa-

Table 1. *Ab initio* total energy predictions for 5(4H)-oxazolone and related species^a

Species	Method				
	3-21G SCF// 3-21G SCF	6-311G** SCF// 6-311G** SCF	DZP SCF// 6-311G** SCF	DZP CISD// 6-311G** SCF	DZP CISD+(Q)// 6-311G** SCF
M ¹ A' (ring)	-355.355 084	-357.459 849	-357.411 797	-358.265 448	-358.409 346
M ⁺⁺ ² A' (ring)	-355.009 041	-357.071 922	-357.067 647	-357.873 682	-358.014 651
M ⁺⁺ ² A'' (ring)	-355.023 035	-357.142 505	-357.125 171	-357.927 933	-358.065 599
M ⁺⁺ ² A'' (open)	-355.022 505	-357.125 345	-357.102 043	-357.902 376	-358.042 188
[M-CO] ⁺⁺ ² A''	-242.948 918	-244.378 013	-244.357 705	-244.853 055	-244.967 133
CO ¹ Σ _g	-112.093 299	-112.769 475	-112.758 728	-113.053 237	-113.077 142
[M-CO] ⁺⁺ +CO ^b	-355.042 217	-357.147 488	-357.116 433	-357.906 292	-358.044 275

^a All values in hartrees. The symbol // means 'at the geometry of.' All calculations were based on the spin-restricted Hartree-Fock (RHF) method. In the CI calculations the seven lowest energy 1s core and seven highest energy 1s* virtual orbitals were not correlated.

^b Supermolecule calculation; the separation of the two species is 1000 Å.

azolone molecule and some of its related species, all of which are stationary points on the related potential energy surfaces. The UHF-based methods could not be used for the open-shell species owing to severe spin contamination, so for these the ROHF method was applied. The three different basis sets at the *ab initio* SCF level were used to test the effect of basis set enlargement on the results obtained, although no extensive tests were attempted. The CISD method was used to obtain high-level energy estimates for the species studied and to ascertain the errors introduced by restricting the calculations to only a single reference. MNDO calculations for all species were also performed to provide further data for comparison between semi-empirical and non-empirical methods.

A description of the details of the quantum chemical procedures applied is given later in the section Computational details.

RESULTS AND DISCUSSION

Energies

Ab initio (3-21G SCF, 6-31G** SCF and DZP CISD) total energies for 5(4H)-oxazolone (M), its molecular ions [M⁺⁺ (ring) and M⁺⁺ (open)] and the products [M-CO]⁺⁺ and CO of the CO loss process are collected

in Table 1. The relevant relative energies, together with relative MNDO heats of formation, are given in Table 2.

All the results of this study were obtained from theoretical treatments based on a single reference configuration. It is of extreme importance to ascertain what effect this restriction has on the calculated results. In this study, DZP CISD calculations were performed to achieve this goal: C_0 , the reference configuration coefficient is used as a diagnostic (see Table 3). It is known that, since the CI molecular orbitals are strongly biased toward the SCF reference, this diagnostic might give misleading results in certain cases. Better diagnostics have been developed,³¹ but they have not been available to us. Further, it is our belief that this simplest diagnostic tool is sufficient for the purposes of the present study. Some representative values might be useful to show how C_0 values change in different molecules:^{31b} C_0 is 0.99 for He, 0.97 for HF and CH₄, 0.91 for (NO)₂ and FOOF and 0.88 for Be₅. Thus, as expected, the lower the value of C_0 , the greater is the chance that a single-reference-based electron correlation method might be insufficient and will not yield accurate results. Although this general trend is clear, there are known exceptions. Lee and Taylor^{31b} gave several examples where a relatively low C_0 value (around 0.92) does not mean that a single-reference-based approach is of low quality, whereas a C_0 value of 0.96 for CuH mistakenly suggests that a single-reference-based calculation would be meaningful for this molecule. As far as

Table 2. Relative energies and relative MNDO heats of formation for 5(4H)-oxazolone and related species^a

Method	M	M ⁺⁺ (ring)		M ⁺⁺ (open)	[M-CO] ⁺⁺ +CO ^b
	(¹ A')	(² A')	(² A'')	(² A'')	
3-21G SCF//3-21G SCF	-871.9 (9.04)	0.0	23.4	1.3	-50.2
6-311G** SCF//6-311G** SCF	-833.0 (8.64)	0.0	185.4	45.2	-14.6
DZP SCF//6-311G** SCF	-831.4 (8.62)	0.0	151.0	60.7	23.0
DZP CISD//6-311G** SCF	-886.2 (9.18)	0.0	142.3	68.2	56.9
DZP CISD+(Q)//6-311G** SCF	-902.5 (9.35)	0.0	133.9	61.5	56.1
MNDO ^c	-901.7 (9.43)	0.0	—	70.3	95.8

^a All values in kJ mol⁻¹. All relative energies are compared to the energy of the \bar{X}^2A'' state of the M⁺⁺ (ring) ion. The relative energy of M as compared to \bar{X}^2A'' M⁺⁺ gives the adiabatic ionization energy of 5(4H)-oxazolone; these absolute values in eV are given in parentheses. Zero-point vibrational energies (ZPVE) were neglected in calculations of relative energies.

^b Supermolecule calculation, the separation of the two species is 1000 Å.

^c The MNDO heat of formation of M (¹A') is -172.0 kJ mol⁻¹ and that of CO is -25.9 kJ mol⁻¹.

Table 3. Coefficients of the five most important DZP CISD configurations for 5(4*H*)-oxazolone and related species^a

Molecule	No.	Coefficient	Configuration
M ¹ A' (ring) ^b	1	0.908	(21a') ² (1a'') ² (2a'') ² (3a'') ² (4a'') ²
	2	-0.038	(21a') ² (1a'') ² (2a'') ² (3a'') ² (5a'') ²
	3	0.022	(21a') ² (1a'') ² (3a'') ² (4a'') ² (5a'') ¹ (7a'') ¹
	4	-0.021	(21a') ² (1a'') ² (2a'') ² (4a'') ² (6a'') ²
	5	0.021	(21a') ² (1a'') ² (2a'') ² (3a'') ¹ (4a'') ¹ (5a'') ¹ (7a'') ¹
M ² A'' (ring) ^c	1	0.910	(21a') ² (1a'') ² (2a'') ² (3a'') ² (4a'') ¹
	2	-0.028	(21a') ² (1a'') ² (3a'') ² (4a'') ¹ (5a'') ¹ (7a'') ¹
	3	-0.026	(21a') ² (1a'') ² (2a'') ² (4a'') ¹ (6a'') ²
	4	-0.024	(21a') ² (1a'') ² (3a'') ² (4a'') ¹ (7a'') ²
	5	-0.022	(21a') ² (1a'') ² (3a'') ² (4a'') ¹ (5a'') ²
M ² A'' (open) ^d	1	0.908	(21a') ² (1a'') ² (2a'') ² (3a'') ² (4a'') ¹
	2	-0.036	(21a') ² (1a'') ² (3a'') ² (4a'') ¹ (6a'') ²
	3	-0.030	(21a') ² (1a'') ² (2a'') ² (4a'') ¹ (5a'') ²
	4	-0.027	(16a') ⁰ (22a') ² (1a'') ² (2a'') ² (3a'') ² (4a'') ¹
	5	0.025	(21a') ² (2a'') ² (3a'') ² (4a'') ¹ (5a'') ²
[M - CO] ⁺ + CO ^e	1	0.908	(21a') ² (1a'') ² (2a'') ² (3a'') ² (4a'') ¹
	2	-0.038	(21a') ² (1a'') ² (2a'') ² (4a'') ¹ (7a'') ²
	3	-0.038	(20a') ⁰ (28a') ² (1a'') ² (2a'') ² (3a'') ² (4a'') ¹
	4	-0.038	(21a') ² (1a'') ¹ (2a'') ¹ (3a'') ² (4a'') ¹ (5a'') ¹ (6a'') ¹
	5	-0.036	(21a') ² (1a'') ² (3a'') ² (4a'') ¹ (5a'') ²

^a Obtained at the 6-311G** SCF optimized geometries. The seven lowest energy core and the seven highest energy virtual orbitals were kept frozen during the calculations.

^b There are five configurations which have coefficients larger than 0.02.

^c There are six configurations which have coefficients larger than 0.02.

^d There are ten configurations which have coefficients larger than 0.02.

^e There are numerous configurations which have coefficients larger than 0.02.

the present study is concerned, the C_0 coefficients are low in all cases, ranging from 0.908 for the closed-shell $^1A'$ (M) calculation to 0.923 for the $^2A''$ ([M - CO]⁺) calculation. All these values suggest that to achieve quantitative accuracy multi-reference-based methods should be applied. The DZP CISD calculations also reveal that the multi-reference space cannot be meaningfully reduced to only a few configurations, as there are no large second and third (etc.) best coefficients (see Table 3). Since the calculated C_0 values are very similar, it is hoped that neglect of the additional configurations (and excitations from thereof) leads to approximately the same error for the different species. Therefore, the relative energies, which are of basic interest here, should be sufficiently accurate.

The adiabatic ionization energy of 5(4*H*)-oxazolone is calculated to be in the range 8.6–9.5 eV by the quantum chemical methods applied. All these ionization energy values in Table 2 refer to the $^2A'' \leftarrow ^1A'$ ionization, i.e. when the electron is removed from the highest occupied π -type orbital of the parent molecule. Accidentally, the MNDO value is very close to that predicted by the best DZP CISD + (Q)//6-311G** SCF calculation (9.43 vs. 9.35 eV).

The equilibrium geometry and the total energy of the \tilde{A}^2A' state of the ring-type molecular ion [i.e. when an electron is removed from a σ -type orbital of the parent 5(4*H*)-oxazolone] were also calculated. All *ab initio* calculations predict the energy of the \tilde{A}^2A' state to be higher than that of the \tilde{X}^2A'' state. In contrast to the \tilde{X}^2A'' state, analytical second-derivative calculations at the 3-21G SCF level, performed at the respective opti-

mized geometry, showed the \tilde{A}^2A' state of the ion not to be a minimum, indicating that the constraint of planarity on the structure should be relaxed. Similar second-derivative calculations at the 6-311G** SCF level proved to be computationally prohibitive for us, so it was impossible to check whether a more extended calculation would predict \tilde{A}^2A' to be a minimum. Still, it is reasonable to assume that the energy of the \tilde{A}^2A' state is about 125 kJ mol⁻¹ (i.e. about 1.3 eV) higher than that of \tilde{X}^2A'' . Further, if we take into account energy relaxation and randomization processes, it is certain that the great majority of the molecular ions exist in their \tilde{X}^2A'' state in the ion source. Therefore, in the further discussion we restrict ourselves to the \tilde{X}^2A'' state.

The energy data in Tables 1 and 2 suggest that the ring opening of the molecular ion of 5(4*H*)-oxazolone is possibly not a high-energy process (depending also on the barriers separating the cyclic and ring-opened forms); the DZP CISD + (Q)//6-311G** SCF value is 61.5 kJ mol⁻¹, which is only about 0.64 eV. Further, bond order calculations (see below) predict the weakening of the O(1)–C(5) bond due to ionization, which should facilitate opening of the ring. Consequently, our theoretical data confirm the assumption of Ref. 1 that the ring-opening process is energetically favourable. Since the $^2A''$ open molecular ion was also determined to be a minimum on the potential energy surface, this ion might exist as a stable species (depending on the heights of the associated barriers).

Finally, we note that the process of CO loss from the open molecular ion is calculated to be exothermic by all

ab initio methods. This important result is in disagreement with that of MNDO, showing the limited trust one can have in energy predictions obtained by semi-empirical methods.

Bond orders and valencies

Quantum chemical calculations can produce not only a single number, the energy of the system under investigation, but also additional useful quantities. Unfortunately, these quantities, and the information they bear, are packed in the form of large matrices, which have no direct and easily understandable meaning to chemists and/or spectroscopists. It has been a challenging and particularly interesting task to answer the question of how the results of quantum chemical calculations can be related to 'classical' quantities, such as bond orders between two atoms in a molecule (or ion), atomic valency, atomic charge, etc. As no unique definition can be set forth, various definitions have been proposed for these quantities (for more details see, e.g., Refs 22 and 23 and references cited therein). One possible way to determine the above indices from *ab initio* SCF wave functions has been given by Mayer.^{22b,c} In spite of their recent criticism,^{23,32} these indices (usually called Mulliken–Mayer bond and valency indices or the results of the Mulliken–Mayer population analysis, MMA) have been successfully used, e.g., for the description of chemical reactions³³ and for hypervalent sulphur compounds.³⁴ Although (Mulliken) charge densities have been widely used by mass spectrometrists to characterize ionic structures, surprisingly, bond orders and valencies have been less popular. One reason might be that bond orders cannot be considered as reactivity indices, although it is tempting to assume that the larger the value of the bond order, the stronger the bond becomes, all other things being equal.²³ Nevertheless, recent results on the application of Mulliken–Mayer bond orders and valencies for the description of ion structures and primary fragmentation processes^{1,24,25} suggest that those bonds are preferentially cleaved for which the bond orders are calculated to be significantly lower in the molecular ions than in the corresponding neutral species.

Of course, the bond and valency indices depend on the basis set used in the *ab initio* calculations and on the quantum chemical methods applied. Further, the indices obtained by the MMA are different from those calculated in Löwdin's orthogonalized basis²³ (Table 4). Löwdin bond orders are larger than the corresponding MMA values, which is consistent with the results obtained by Baker.²³ As has been repeatedly shown^{22b-c,25d,35} at the SCF level, the minimal STO-3G basis gives almost the same MMA indices as do medium-sized basis sets, e.g. 6-31G* and 6-31G**, and the 3-21G and 4-31G calculations provide the chemically least meaningful bond orders and valencies. These observations are confirmed in the present study for both the closed- and open-shell species (see Table 4, in which MNDO, STO-3G SCF, 3-21G SCF and DZP SCF bond orders and valencies for the neutral, closed-shell 5(4H)-oxazolone and the $[M - CO]^+$ cation are given). The Mulliken–Mayer definitions have an addi-

tional advantage: in case of an orthogonal basis set, i.e. when the overlap matrix is the unit matrix, they become identical with those used in neglect of differential overlap, NDO (e.g. MNDO) approximations. In a recent paper, Somogyi and Gömörý^{25d} showed that Mulliken–Mayer bond orders calculated by the MNDO method are in good agreement with those obtained from STO-3G SCF and 6-31G** SCF calculations. This observation was also confirmed in the present study (see data in Table 4). Therefore, it seemed reasonable to use the MNDO bond orders and free valencies for the description of the species discussed in this paper (see Figs 1 and 2), especially since this level of theory was used in Ref. 1.

MNDO bond orders in the closed ring neutral molecule and in its molecular ions [see Figs 1(a) and (b)] are close enough to those shown in Fig. 4 in Ref. 1 to assume that the substitution of the C₆H₅ and CH₃ groups by hydrogens has no significant effect on the electronic structure of the 5(4H)-oxazolone ring. The qualitative picture is the same: characteristic delocalization is predicted along the O(1)—C(2)—N(3)—C(4)—C(4') line together with weakening of the C(5)—O(1) and C(4)—C(5) single bonds in the molecular ion. Net charge densities and free valencies show that the closed-ring molecular ion is not a distonic-type ion, i.e. the free valencies are also delocalized and more or less follow the distribution of charge densities. This picture is in accordance with the π -type HOMO in the neutral molecule and that the electron is removed from this π -orbital in the \tilde{X}^2A' state.

In the case of the 'open' molecular ion, the net charges are more pronounced on the C(5)=O(5') carbonyl group while the free valencies remain virtually zero in this part of the molecular ion after the opening process [Fig. 1(c)]. According to the calculations, the free valence cannot be located on the other oxygen atom O(1) but remains to be of a delocalized character. The significant weakening of the C(2)—N(3) and C(4)—C(5) bonds in this 'open' structure is in excellent agreement with the experimentally observed decomposition processes: the easy loss of CO and the formation of C₆H₅CO⁺.¹ Therefore, the MNDO bond indices also suggest that these main fragmentation processes can take place via open-ring molecular ions of 5(4H)-oxazolones.

Assuming the simple cleavage of bond C(4)—C(5) in the open-ring form [Fig. 1(c)], one arrives at the $[M - CO]^+$ ion with a structure shown in Fig. 2. This $[M - CO]^+$ cation is also a distonic ion; about half of the total charge is located on the formyl group connected to the remaining part with a weak N—C bond, and meanwhile a significant (0.701) free valency appears on the methylene carbon (Fig. 2).

CONCLUSIONS

Energy data obtained from 3-21G SCF, 6-31G** SCF and DZP CISD calculations support the suggestion based on mass spectral measurements¹ that the ring-opening process along the lactone O(1)—C(5) bond in the molecular ion of 5(4H)-oxazolone is energetically

Table 4. Bond orders, valencies and free valencies for 5(4H)-oxazolone (M) and the ion [M - CO]⁺⁺ at several theoretical levels^a

Bond or atom	MNDO	STO-3G SCF		3-21G SCF		DZP SCF	
	MMA	MMA	Löwdin	MMA	Löwdin	MMA	Löwdin
<i>Bond orders</i>							
O(1)-C(2)	1.024	1.025	1.064	0.861	1.075	1.118	1.303
C(2)=N(3)	1.790	1.821	1.841	1.700	1.982	1.958	2.054
N(3)-C(4)	1.033	1.031	1.049	0.944	1.083	1.113	1.187
C(4)-C(5)	0.918	0.946	0.967	0.937	0.987	0.983	1.005
O(1)-C(5)	0.939	0.944	0.981	0.765	1.025	1.064	1.270
C(2)-H(2')	0.927	0.947	0.961	0.875	0.937	0.981	0.896
C(4)=C(4')	1.827	1.859	1.865	1.764	1.905	1.786	1.924
C(5)=O(5')	1.900	1.944	1.954	1.841	2.146	2.200	2.417
C(4')-H(a)	0.963	0.971	0.981	0.921	0.940	0.985	0.896
C(4')-H(b)	0.962	0.971	0.981	0.917	0.941	0.978	0.903
<i>Valencies</i>							
O(1)	2.236	2.267	2.348	1.794	2.474	2.209	2.920
C(2)	3.839	3.914	3.964	3.468	4.199	4.074	4.626
N(3)	2.981	3.027	3.067	2.719	3.353	3.080	3.608
C(4)	3.918	3.960	3.986	3.605	4.254	3.810	4.622
C(5)	3.826	3.902	3.956	3.530	4.349	4.223	5.052
C(4')	3.896	3.963	3.989	3.706	4.041	3.858	4.095
O(5')	2.121	2.212	2.233	1.990	2.461	2.256	2.687
H(2')	0.976	0.988	0.996	0.881	1.005	0.984	1.022
H(a)	0.997	0.991	0.997	0.902	1.004	0.980	1.026
H(b)	0.995	0.991	0.997	0.900	1.003	0.976	1.035
[M - CO] ⁺⁺ (² A')							
<i>Bond orders</i>							
C(1)=O(1')	2.154	2.149	2.172	2.009	2.340	2.342	2.621
C(1)-N(2)	0.617	0.725	0.780	0.523	0.780	0.738	0.952
N(2)-C(3)	2.461	2.648	2.682	2.368	2.708	2.757	2.684
C(3)-C(4)	1.193	1.108	1.134	1.000	1.208	0.984	1.239
C(1)-H(1')	0.887	0.899	0.932	0.794	0.790	0.935	0.875
C(4)-H(a)	0.943	0.942	0.963	0.846	0.919	0.944	0.888
C(4)-H(b)	0.943	0.942	0.963	0.848	0.920	0.944	0.892
<i>Valencies [Free valencies]^b</i>							
C(1)	3.693	3.783	3.891	3.331	4.108	4.007	4.581
	[0.004]	[0.000]		[0.000]		[0.002]	
N(2)	3.452	3.602	3.613	2.932	3.727	3.639	3.942
	[0.196]	[0.089]		[0.100]		[0.078]	
C(3)	3.841	3.860	3.873	3.445	4.098	3.821	4.214
	[0.077]	[0.033]		[0.049]		[0.081]	
C(4)	3.822	3.877	3.081	3.435	3.122	3.761	3.175
	[0.701]	[0.870]		[0.842]		[0.823]	
O(1')	2.344	2.310	2.337	2.096	2.544	2.378	2.822
	[0.021]	[0.008]		[0.009]		[0.006]	
H(1')	0.967	0.967	0.988	0.824	0.997	0.945	0.998
	[0.000]	[0.000]		[0.000]		[0.000]	
H(a)	0.982	0.967	0.984	0.840	0.982	0.951	0.992
	[0.000]	[0.000]		[0.000]		[0.005]	
H(b)	0.982	0.967	0.984	0.842	0.982	0.951	0.997
	[0.000]	[0.000]		[0.000]		[0.005]	

^a The MNDO and 3-21G SCF values were obtained at the respective optimized geometries, while all other *ab initio* values were obtained at the 6-311G** SCF geometries. MMA: the values are calculated according to the definitions of the Mulliken-Mayer population analysis;²² Löwdin: the values are calculated according to the definitions based on the Löwdin density matrix.²³ The numberings of atoms are shown in Fig. 1 (a) (M) and Fig. 2 ([M - CO]⁺⁺).

^b Free valencies calculated for the open-shell [M - CO]⁺⁺ ²A' cation are given in square brackets. For 'Löwdin' the 'valencies' do not include 'free valencies'.

favoured. The calculations also reveal that the opening molecular ion might exist as a stable species. The loss of CO from this ion is found to be exothermic by all *ab initio* methods.

All the present calculations show that net charges and free valencies are significantly separated in the

open-ring molecular ion of 5(4H)-oxazolone (M) and in the [M - CO]⁺⁺ cation, proving their distonic-type character suggested earlier intuitively.¹ Although bond orders alone cannot be regarded as reactivity indices, in accordance with earlier observations^{1,24,25} the present results suggest that significantly reduced bond order

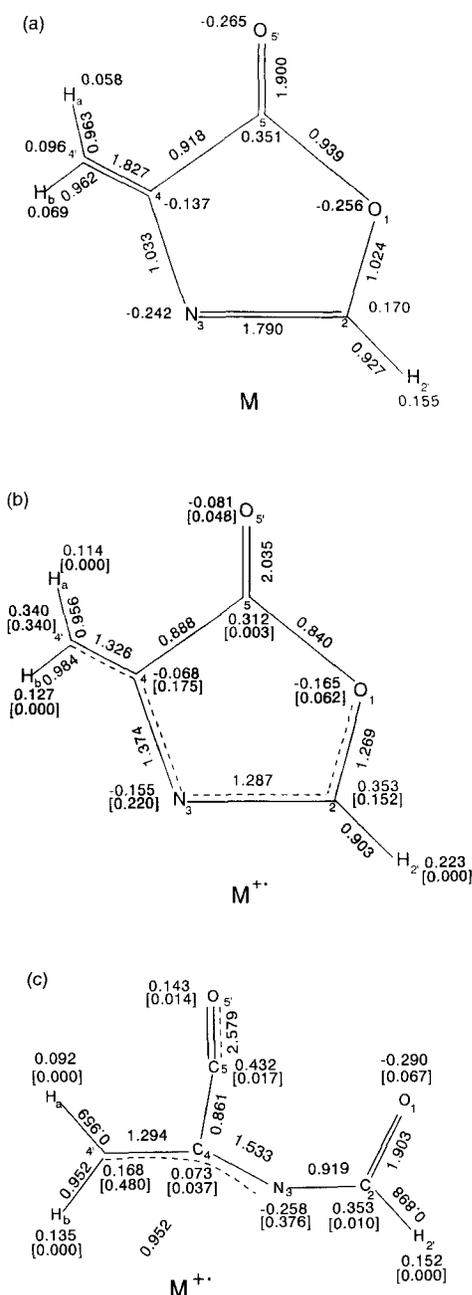


Figure 1. MNDO bond orders, net charges and free valencies (in square brackets) of the (a) neutral molecule, (b) ring molecular ion and (c) open molecular ion.

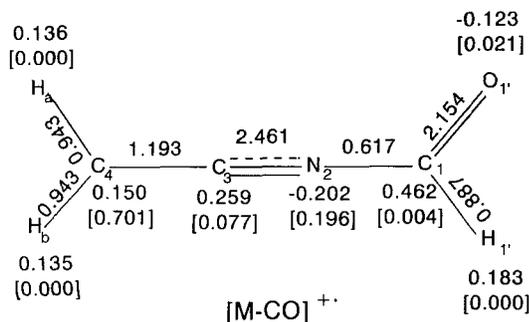


Figure 2. MNDO bond orders, net charges and free valencies (in square brackets) in the [M-CO]⁺ fragment ion.

values in ions indicate bonds susceptible to energetically preferred cleavages.

The *ab initio* and MNDO results presented in this paper also serve as additional examples for the usefulness of quantum chemical methods in the description of ion structures and primary fragmentation processes. Although, as pointed out several times in this study, caution should be exercised in selecting the appropriate theoretical procedures and in interpreting the results obtained by their employment, we have every reason to share the opinion of Radom³ and believe in a long-living, happy association of theory and experiment.

Computational details

Three basis sets were selected for this study: the standard 3-21G⁶ and 6-311G(d, p)²⁷ basis sets and a DZ(d, p)²⁸⁻³⁰ basis set. The DZ basis set is that of Huzinaga²⁸ and Dunning,²⁹ exponents of the single set of polarization functions were obtained from Dunning.³⁰ All d sets included only the true spherical harmonics. As usual, the 6-311G(d, p) and DZ(d, p) basis sets are denoted in this paper as 6-311G** and DZP, respectively.

Electronic wave functions were determined in this study by the single-configuration, self-consistent-field, restricted Hartree-Fock (SCF) method,¹³ and by the single- and double-excitation configuration interaction (CID) method.¹⁴ The spin-unrestricted Hartree-Fock (UHF) wave functions¹¹ suffered from large spin contaminations for all open-shell species; typically the $\langle S^2 \rangle$ values were higher than 1.0. Therefore, the UHF method and correlation treatments based on the UHF wave function could not be applied in the present study.

The geometrical structures of the different forms of 5(4H)-oxazolone were fully optimized at the 3-21G SCF and 6-311G** SCF levels of theory. The residual Cartesian gradients were in all cases less than 5×10^{-4} hartree bohr⁻¹. Analytical second-derivative calculations³⁶ were carried out at the 3-21G SCF level to determine whether the optimized stationary points were minima.

In the DZP CISD single-point energy calculations the 6-311G** SCF optimized geometries were used as references, and the seven lowest energy 1s core and seven highest energy 1s* virtual orbitals were kept frozen.

Ab initio electronic structure computations were performed with the program packages GAMESS,³⁶ Gaussian 86,³⁷ Gaussian 90³⁸ and PSI.³⁹ The program package AMPAC⁴⁰ was used for MNDO calculations and in this case the half-electron method⁴¹ was applied for open-shell species.

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