

# High-energy collisional activation of the molecular ions of thiophene-2-one with different target gases

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Collisional activation of keV thiophene-2-one radical cations  $1^{+\bullet}$  with  $O_2$  or  $NO^\bullet$  as the target gas leads to a desulfuration reaction. This peculiar reaction is insignificant or absent with other targets such as helium, argon, methane or nitrogen. The radical cations produced in this desulfuration reaction are most probably vinylketene ions, as indicated by a triple mass spectrometric (MS/MS/MS) experiment performed on a 'hybrid' tandem mass spectrometer of sector–quadrupole–sector configuration. Tentatively, it is proposed that population of an excited state accounts for the non-ergodic behavior of  $1^{+\bullet}$  upon collision with oxygen or nitric oxide. *Ab initio* molecular orbital calculations using molecular orbital theory (UMP2, UCCSD(T)) and density functional theory (B3LYP) with 6–31G(d,p) and 6–311++G(d,p) basis sets were used to evaluate the relative energy of the excited quartet state of  $1^{+\bullet}$  radical cations. This quartet state is calculated to lie about 3.6 eV above the  $^2A''$  ground state and 0.9 eV above the  $C_4H_4O^{+\bullet} + S$  dissociation products. It is proposed that the quartet ion serves as the precursor for the spontaneous desulfuration. Copyright © 2001 John Wiley & Sons, Ltd.

**KEYWORDS:** thiophene-2-one molecular ions; high-energy collisional activation; target gas; desulfuration

## INTRODUCTION

In recent years, the peculiar role of molecular oxygen as target gas in high-energy (keV range) collisional activation (CA) mass spectrometry (MS) has been reported for several cases.<sup>1–7</sup> A common feature of all the ionic systems studied so far is that oxygen can effectively induce a new reaction channel which is not observed to a significant extent with other common targets such as helium, nitrogen or argon. Nitric oxide resembles the behaviour of  $O_2$  but in most cases the new dissociation reaction is less prominent.<sup>1,4–7</sup>

We have tentatively proposed that triplet oxygen or doublet nitric oxide can populate excited states of the ions by spin-forbidden transitions. Some evidence for this hypothesis was found in a collisional activation study of ONCS<sup>+</sup> cations. These ions fragment preferentially into  $CS^{+\bullet} + NO^\bullet$  upon collision with  $O_2$  or  $NO^\bullet$  despite the fact that the charge is predicted to reside on nitric oxide for ground-state singlet  $O=N^+=C=S$  ions.<sup>4</sup>

In this work, we examined the role of the collision gas on the fragmentation of the molecular ions of thiophene-2-one,  $1^{+\bullet}$ . It will be shown that  $O_2$  and  $NO^\bullet$  induce a unique desulfuration reaction.

## EXPERIMENTAL

The spectra were recorded on a large-scale tandem mass spectrometer of  $E_1B_1\textcircled{E}_2\textcircled{E}_3B_2\textcircled{E}_4$  geometry (E stands for electric sector, B for magnetic sector and  $\textcircled{E}$  for the collision cells installed in various field-free regions) (Micromass AutoSpec 6F).<sup>8,9</sup> Typical conditions were 8 kV accelerating voltage, 200  $\mu\text{A}$  trap current, 70 eV ionizing electron energy and 200 °C ion source temperature. The samples were introduced via a heated (180 °C) septum inlet device.

The high-energy (8 keV) CA spectra were obtained by pressurizing the collision cell located in front of  $E_2$  with helium, nitric oxide, oxygen, nitrogen, argon or methane (~50–70% transmittance) and scanning the field of  $E_2$ ; the fragments were collected with an off-axis photomultiplier detector in the fourth field-free region. In the MS/MS/MS experiment, a beam of mass-selected  $m/z$  100 ions was desulfurated by collision with  $O_2$  in a cell in front of  $E_2$ ; next, the  $m/z$  68 fragment ions produced were collisionally activated (helium) in a cell preceding  $E_3$  and the fragments were collected by scanning the field of  $E_3$ .

The samples used were commercially available, except for 2-*tert*-butoxythiophene (4) and thiophene-2-thiol (5a) (thiophene-2-thione (5)), which were prepared according to procedures described in the literature.<sup>10,11</sup>

## RESULTS AND DISCUSSION

### Mass spectrometric results

Thiophene-2-one (1) is a tautomerizable compound<sup>12</sup> which largely exists as a thiolactone rather than an

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hydroxythiophene in both the condensed phase and in the gas phase. In the gas phase, this has been convincingly demonstrated by ionization energy measurements.<sup>13</sup>

Figure 1(a) shows the CA (helium) spectrum of mass-selected molecular ions of thiophenone,  $1^{+\bullet}$ . As expected, this spectrum resembles the conventional electron ionization mass spectrum<sup>14</sup> and features intense peaks at  $m/z$  72 (loss of CO, already observed without the collision gas),<sup>15</sup> 45 (HCS<sup>+</sup>, thioformyl ions) and 39 (C<sub>3</sub>H<sub>3</sub><sup>+</sup> ions). A narrow peak is also detected at  $m/z$  55 ascribed to vinylacylium ions, CH<sub>2</sub>=CH—C<sup>+</sup>=O. When the target gas helium is replaced with nitric oxide (see Fig. 1(b)), or oxygen (see Fig. 1(c)), the CA spectra remain nearly identical with the notable exception of an  $m/z$  68 peak assigned to the generation of vinylketene ions,  $2^{+\bullet}$ , by loss of sulfur (see Scheme 1). By using consecutive CA steps (MS/MS/MS experiment, Fig. 2), we obtained a CA spectrum of the  $m/z$  68 ions which is indeed interpretable in terms of the proposed vinylketene CH<sub>2</sub>=CH—CH=C=O connectivity, by the intense peak at  $m/z$  42 for the loss of ethyne and major peaks at  $m/z$  40–39 resulting from a decarbonylation reaction. The characterization of [C<sub>4</sub>H<sub>4</sub>O]<sup>+</sup> ions has been studied in great detail in previous work.<sup>16</sup>

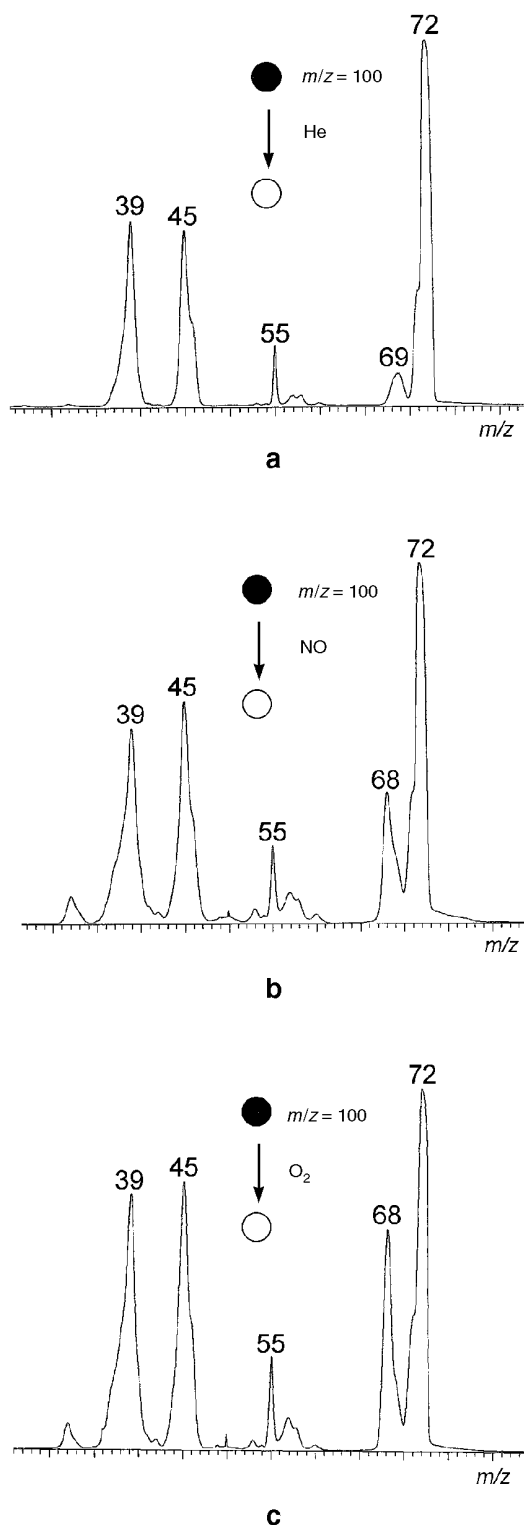
Energy deposition in the center-of-mass of ions in CA is dependent on the mass of the target.<sup>17</sup> However, in the present case, no correlation between the relative intensity of the  $m/z$  68 signal (loss of S) and the mass of the target gas appears (see Table 1). In other words, the strong increase in the intensity of the  $m/z$  68 peak upon collision with O<sub>2</sub> or NO<sup>•</sup> is not related to an effect of the mass of the target gas.

In a collisional activation study of butyl cations, Aubry and Holmes also reported a peculiar effect of oxygen and attributed this to its polarizability.<sup>3</sup> Such an effect does not account, however, for the oxygen effect in the present system as indicated by the polarizability values given in Table 1, which do not correlate with the relative intensity of the  $m/z$  68 peak (quantified with the  $m/z$  45 :  $m/z$  68 branching ratio).

A reviewer has suggested a radical mechanism for the abstraction of S in which the sulfur atom is expelled in the form of SO<sub>2</sub> (or NOS when NO<sup>•</sup> is used as the target gas). However, such an abstraction process is highly improbable given the translational energy regime used (8 keV). In line with this, the signal for the C<sub>4</sub>H<sub>4</sub>O<sup>+</sup> ionic fragment in the kinetic energy spectrum appears at the energy value expected for a unimolecular decay.

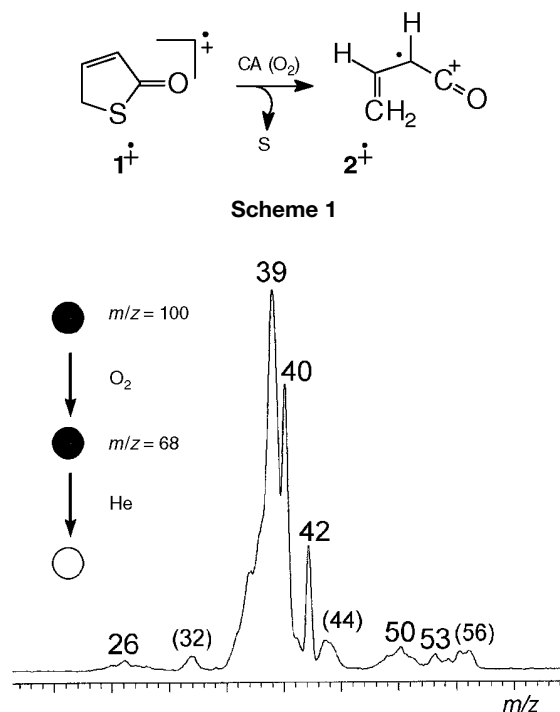
To determine if certain structural features are required to observe this peculiar behavior, some model compounds were investigated. The molecular ions of thiobutyrolactone,  $3^{+\bullet}$  (Scheme 2), lose predominantly C<sub>2</sub>H<sub>4</sub>S in the CA (O<sub>2</sub>) spectrum with the production of ketene ions ( $m/z$  42); the loss of sulfur is not detected, indicating that the cyclic C=C double bond is required for the detection of the effect of the nature of the collision gas.

The second model compound, 2-*tert*-butoxythiophene, **4**, has been reported to eliminate butene upon electron ionization,<sup>18</sup> if the migrating hydrogen is transferred to oxygen in this rearrangement reaction,  $4^{+\bullet}$  should produce the tautomeric 2-hydroxythiophene molecular ions  $1a^{+\bullet}$  and this seems indicated by the intense peak at  $m/z$  61 in the



**Figure 1.** CA spectra of the molecular ions of thiophene-2-one ( $m/z$  100) using different collision gases: (a) helium, (b) nitric oxide and (c) oxygen. The terminology introduced by Schwartz *et al.*<sup>20</sup> is used to schematize the sequence of reactions: a filled circle represents a fixed (or selected) mass and an open circle a variable (or scanned) mass, and the neutral reagent or collision gas that causes the mass transitions is shown between the circles.

CA (O<sub>2</sub>) spectrum for protonated carbon oxysulfide ions, S=C=OH<sup>+</sup> (Fig. 3(a)). Loss of atomic sulfur is again not



**Figure 2.** MS/MS/MS experiment: CA (He) spectrum of the  $m/z$  68 ions produced by collisional desulfuration ( $O_2$  collision gas) of the mass-selected molecular ions of thiophene-2-one ( $m/z$  100). The masses in parentheses correspond to a minor contribution of  $C_3S^+$  isobaric ions.

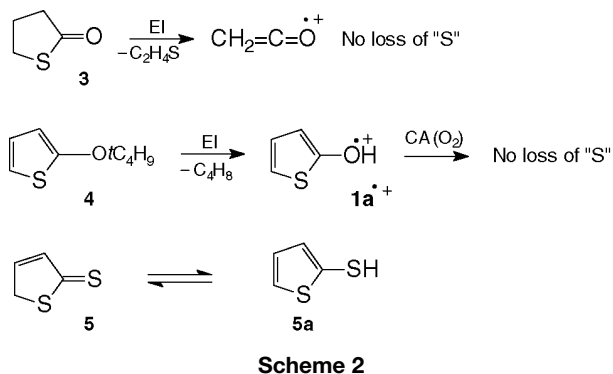
**Table 1.** Polarizabilities and ionization energies of various target gases and  $m/z$  45 : 68 branching ratios

Collision gas <sup>a</sup>	Branching ratio <sup>b</sup>		Ionization energy (eV)
	$m/z$ 45 : $m/z$ 68	Polarizability <sup>c</sup>	
Oxygen	1.2	1.6	12.1
Nitric oxide	1.7	3.0	9.3
Nitrogen	3.9	1.9	15.5
Methane	4.8	2.6	12.5
Argon	5.2	1.7	15.8
Helium	5.6	0.2	24.6

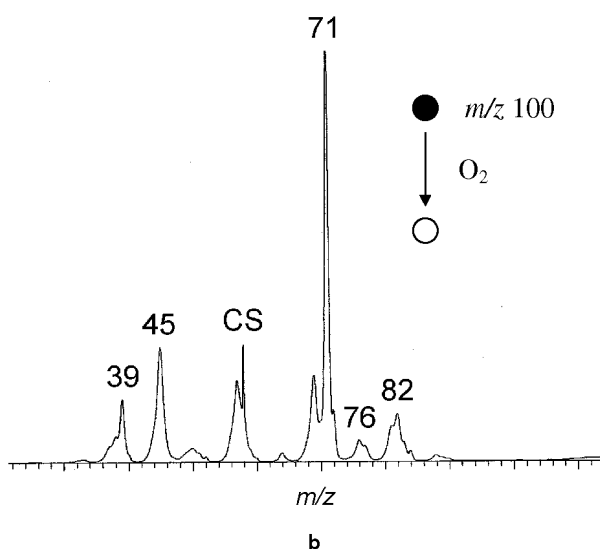
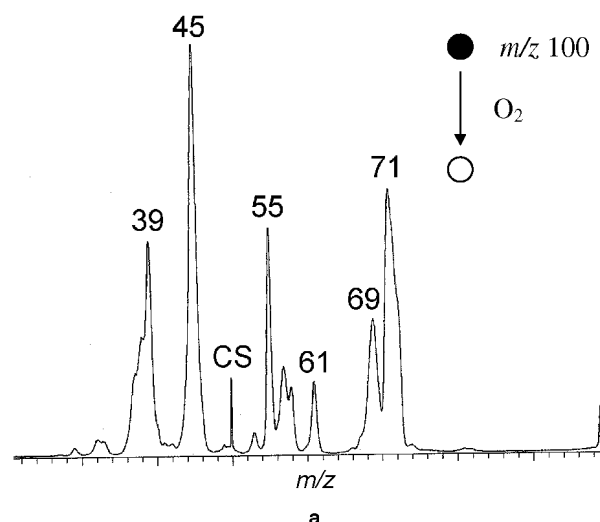
<sup>a</sup> Transmittance: 50–70%.

<sup>b</sup>  $m/z$  45 is the base peak in the CA spectra.

<sup>c</sup> Taken from Ref. 21.



observed. Finally, a sulfur analogue of thiophene-2-one (1), thiophene-2-thione (5), has also been considered. In this



**Figure 3.** CA ( $O_2$ ) spectra of the  $[M - C_4H_8]^+$  ions ( $m/z$  100) generated by dissociative ionization of (a) 2-*tert*-butoxythiophene (4) and (b) ionized thiophene-2-thiol (5) ( $m/z$  116). CS refers to charge stripping.

case, the loss of sulfur is also absent in the CA ( $O_2$ ) spectrum of the  $5^+$  molecular ions (see Fig. 3(b)); this result is not too unexpected as replacement of the exocyclic oxygen by sulfur could displace the tautomeric equilibrium towards the thiophene-2-thiol isomer 5a.<sup>18</sup>

Experimentally, it is therefore concluded that the use of oxygen or nitric oxide in the CA of ionized thiophene-2-one induces a new reaction channel (the loss of S) which is insignificant with other targets. A possible mass or polarizability effect of the target gas plays no role in the present experiments. All the structural modifications examined resulted in the suppression of this peculiar effect.

### Quantum chemical calculations

In recent studies<sup>4–7</sup> on the unusual behavior of oxygen as a target gas, we suggested that upon collision an excited state of the molecular ions is formed with a certain population large enough to undergo an observable *specific* fragmentation

reaction. In an attempt to probe this mechanism further, we performed quantum chemical calculations on a selection of structures for thiophene-2-one and its radical cation. For the purpose of comparison, the analogous system **5**–**5a** was also considered.

It is obvious that a molecule possesses a large number of excited states, and a few of these are expected to have excitation energies (relative to the ground state) comparable to the dissociation threshold of a given set of fragments. Our main interest here was to identify at least one such electronic state which in view of the results obtained with the ONCS cations (see Introduction) could be considered as potentially responsible for the specific dissociation channel opened up by collision with oxygen or nitric oxide.

The Gaussian 94 set of programs<sup>19</sup> was used for both the *ab initio* molecular orbital (MO) and the density functional theory (DFT) calculations. For the MO calculations we used second-order perturbation (MP2) and coupled-cluster (CCSD(T)) theory, whereas the DFT calculations involved the popular DFT/B3LYP method with hybrid functionals. The basis sets ranged from the 6–31G(d,p) to the 6–311++G(3df,2p), depending on the system and property considered. Within the framework of the unrestricted Hartree–Fock (UHF) theory, the lowest lying state of each multiplicity and irreducible representation can be calculated. The energy differences allow the ground electronic state to be identified.

For the neutral species, the calculations confirm that thiophene-2-one (**1**) is more stable than its enol tautomer **1a**, by 47 kJ mol<sup>-1</sup>. At the same level of theory, the thiol tautomer **5a** is found to be 8 kJ mol<sup>-1</sup> more stable than the corresponding thione **5**. It thus appears that upon replacement of oxygen by sulfur the enol form is significantly stabilized. In this context, we note that the predominant existence of **1** is in agreement with an earlier photoelectron spectrometric (PES) study.<sup>13</sup>

The ionization energy of **1** has been measured,<sup>13</sup> but the identity of its ground state has not yet been established. As this molecule has a planar framework with C<sub>s</sub> symmetry and an orbital configuration of ... (21a')<sup>2</sup>(5a'')<sup>2</sup>, two distinct electronic states, namely <sup>2</sup>A' and <sup>2</sup>A'', could be envisaged for its radical cation (1<sup>+•</sup>). Calculations at either the CCSD(T) or the B3LYP level of theory in conjunction with the 6–311++G(d,p) basis set reveal that both vertical <sup>2</sup>A' and

<sup>2</sup>A'' states lie fairly close to each other, at 9.57 eV (<sup>2</sup>A'') and 9.78 eV (<sup>2</sup>A') above the neutral state (coupled-cluster values). These values are of the same order of magnitude as the reported PES value of 9.78 eV.<sup>13</sup>

Examination of the singly occupied orbital (SOMO) indicates that, in the <sup>2</sup>A'' state, ionization occurs essentially at the S atom (atomic spin density 0.9). Because one electron of the pπ(S) lone pair is actually removed, this state could be qualified as a <sup>2</sup>Π state. Concerning the <sup>2</sup>A' state, as electron removal mainly involves the in-plane lone pair orbital of the exocyclic oxygen atom (atomic spin density 0.75 (O) and 0.15 (C of C=O)), it corresponds to a <sup>2</sup>Σ state. Thus, in the vertical ion 1<sup>+•</sup> (vert), the <sup>2</sup>Π state is marginally favored over the <sup>2</sup>Σ state.

Of special interest is the energy gap between the <sup>2</sup>A' and <sup>2</sup>A'' states. The calculated results in Table 2 indicate that the adiabatic <sup>2</sup>A'' state lies consistently below the <sup>2</sup>A' counterpart, even though the separation gap is small, amounting to about 0.3 eV. Hence it can be concluded that the thiophene-2-one radical cation 1<sup>+•</sup> possesses a <sup>2</sup>A'' ground state. Use of CCSD(T)/6–311++G(3df,2p) + ZPE calculations leads to the corresponding ionization energy that is calculated to be 9.6 ± 0.2 eV (IE<sub>a</sub>). As mentioned above, the experimental vertical IE is reported to be 9.78 eV.<sup>13</sup>

We also considered the lowest lying quartet state (<sup>4</sup>A') of ion 1<sup>+•</sup> and its optimized geometry is shown in Fig. 4. At the B3LYP level of theory, this quartet structure of 1<sup>+•</sup> (<sup>4</sup>A') tends to be slightly distorted from C<sub>s</sub> symmetry, but the energy gain from such distortion is marginal. The lowest lying quartet state (<sup>4</sup>A') is calculated to lie 3.6 eV above the doublet ground state (<sup>2</sup>A''). Even more interesting, this <sup>4</sup>A' state lies about 0.9 eV above the desulfuration products C<sub>4</sub>H<sub>4</sub>O<sup>+•</sup> + S. As previously mentioned, the C<sub>4</sub>H<sub>4</sub>O<sup>+•</sup> ion has been identified as ionized vinylketene, CH<sub>2</sub>=CH–CH=C=O<sup>+•</sup>, 2<sup>+•</sup>; its cyclic counterpart, the cyclobutenone ion, is not a local minimum on the C<sub>4</sub>H<sub>4</sub>O<sup>+•</sup> potential energy surface.

The fact that the excited quartet state 1<sup>+•</sup> (<sup>4</sup>A') of the thiophene-2-one radical cation lies about 1 eV above the desulfuration products suggests its possible involvement in this reaction. In view of such a significant exothermicity, a desulfuration reaction starting from the quartet (<sup>4</sup>A') becomes a virtually spontaneous process. Owing to the limitation of the computational methods based on UHF wavefunctions, excited doublet states could not be calculated. Therefore,

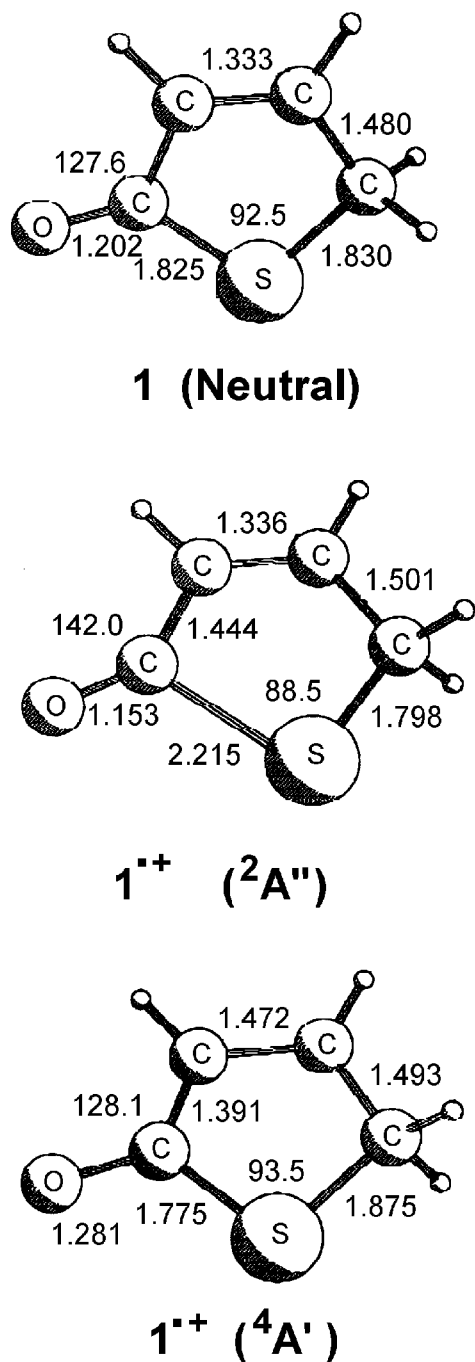
**Table 2.** Energy differences (eV) of some electronic states of ionized thiophene-2-one, 1<sup>+•</sup>, calculated at various levels of theory

Property <sup>a</sup>	B3LYP/ 6–311++G(d,p)	CCSD(T)/ 6–31G(d,p)	CCSD(T)/ 6–311++G(d,p)	CCSD(T)/ 6–311++G(3df,2p)
IE <sub>a</sub> = [ΔE(1 <sup>+•</sup> ( <sup>2</sup> A'') – 1)] <sup>b</sup>	9.21	8.87	9.32	9.57
[ΔE( <sup>2</sup> A' – <sup>2</sup> A'')]	0.32	0.28	0.37	—
[ΔE( <sup>4</sup> A' – <sup>2</sup> A'')]	3.33	3.56	3.60	—
[ΔE((S + C <sub>4</sub> H <sub>4</sub> O <sup>+•</sup> ) – <sup>2</sup> A'')] <sup>c</sup>	2.35	2.40	2.74	—

<sup>a</sup> Based on B3LYP/6–311++G(d,p) optimized geometries. All values are corrected for zero-point energy contributions obtained at the B3LYP/6–31G(d,p) level of theory without scaling.

<sup>b</sup> Adiabatic ionization energy in eV.

<sup>c</sup> C<sub>4</sub>H<sub>4</sub>O<sup>+•</sup> ions represent ionized vinylketene; see text.



**Figure 4.** Selected geometric parameters of thiophene-2-one in different electronic states [(U)B3LYP/6-311++G(d,p)]. Bond lengths are given in Å and bond angles in degrees.

we cannot rule out their eventual participation. However, considering that the main difference between  $O_2$  and  $NO^\bullet$  and other common gases such as He lies in the spin multiplicity of their ground states, a quartet state seems a more likely precursor for the desulfuration process.

## CONCLUSION

Desulfuration of thiophene-2-one molecular ions is an efficient process in the high-energy (8 keV) CA regime if the target gas employed is oxygen or nitric oxide.

This desulfuration is insignificant with other commonly employed collision gases such as helium, argon, nitrogen or methane.

Quantum chemical calculations provide a further probe into this peculiar behavior of  $O_2$  and  $NO^\bullet$ . The calculations indicate that if collisions with  $O_2$  or  $NO^\bullet$  populate the first low-lying quartet state of the ion, the so-excited ions may spontaneously undergo desulfuration.

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