Experimental Evidence for the Existence of Neutral and Ionized Thioxoethylenone in the Gas Phase[†]

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Abstract: The elusive thioxoethylenone (ethenonethione, $\mathrm{O{=}C{=}C{=}S}$) can readily be generated in the gas phase via reduction of its cation radical, $\mathrm{OCCS}^{\bullet+}$, with xenon in a neutralization–reionization mass spectrometry (NRMS) experiment. The experimental findings are supported by ab initio MO calculations (at the HF/6-31G* level of theory and including ZPVE contributions), which further indicate that the neutral C_2OS molecule generated corresponds to the triplet state, $^3\Sigma$, of $\mathrm{O{=}C{=}C{=}S}$ (^{3}**2**). Significant energy barriers prevent the cation radical $\mathrm{O{=}C{=}C{=}S}^{\bullet+}$ and its triplet neutral counterpart from spontaneous dissociation.

Linear and/or quasi-linear structured molecules with polycumulated double bonds of the general formula $X(C_n)Y$ (X, Y: lone electron pair, H_2, O, S; $n = 2, 3, 4$, etc.) have recently attracted considerable interest, in part because of their unique spectroscopic and chemical properties. Moreover, some of these species are believed to play a crucial role in the genesis of interstellar organic molecules.

Unfortunately, quite a few of these molecules have such a high reactivity that they cannot even be produced as a transient. This is especially true for cumulenes containing an *even* number of carbon atoms, which are believed to be considerably less stable than their *odd*-numbered analogues.[1b,2] Thus, among the polycarbon dithiones ($\mathrm{S{=}(C_x){=}S}$), propadienedithione ($\mathrm{S{=}(C_3){=}S}$) has been known for nearly a century to be a relatively stable molecule[3] whereas its even-numbered analogue butatrienedithione ($\mathrm{S{=}(C_4){=}S}$), has escaped experimental verification in solution. However, $\mathrm{S{=}(C_4){=}S}$ is accessible in the gas phase[4] where it is readily generated from its radical cation by using the technique of neutralization–reionization mass spectrometry (NRMS).[5] Similarly, confirming Schaefer's theoretical prediction[1b] that ethylenedithione, provided the appropriate conditions are employed, is a "makable" molecule, we were recently able[6] to generate $\mathrm{S{=}C{=}C{=}S}$ from its radical cation in the gas phase. Once more, NRMS[5] turned out to be an extremely versatile tool for studying elusive molecules. The fact that these cumulenes remained undetected in the condensed phase while they appeared to be obervable in the gas phase clearly indicates that their "instability" does not reflect an intrinsic property but rather that they are prone to facile *inter*molecular reactions.

In contrast to $\mathrm{S{=}C{=}C{=}S}$, all efforts, beginning as early as 1913, to prepare a chemically bound $\mathrm{O{=}C{=}C{=}O}$ species have proven unsuccessful,[7] although theory[1b] leaves no doubt that the spin-allowed dissociation of the $^3\Sigma_g^-$ state of C_2O_2 is quite endothermic (74 kcal/mol). This failure[8] is perhaps due to two factors. (i) The C_2O_2 species have not been generated in the bound triplet state but rather in the singlet state $^1\Sigma_g^+$, which is predicted[1b,9] to dissociate spontaneously to two ground-state CO molecules. (ii) The lifetime of the otherwise stable $^3\Sigma_g^-$ C_2O_2 species may be drastically shortened by an efficient spin–orbit coupling if a potential-curve crossing is available not too far from the minimum (e.g., by a $^1\Sigma_g^+$ state that is repulsive with respect to C–C bond stretch[1b]).

To the best of our knowledge, no studies have been reported on the identification of thioxoethylenone (ethenonethione), $\mathrm{O{=}C{=}C{=}S}$.[10] Here we present evidence that this species and its cation radical ($\mathrm{O{=}C{=}C{=}S}^{\bullet+}$) are viable molecules in the gas phase; they are readily generated and characterized in NRMS experiments. The experimental results are supported by the results of ab initio MO studies.

Experimental and Theoretical Section

The mass spectrometric experiments were performed by using a VG Instruments ZAB-2F mass spectrometer; this is a two-sector instrument of BE configuration (B stands for magnetic and E for electric sector). Ions are generated by 70-eV electron impact ionization of 4,5,9,10-tetraoxo-2,7-dithiatricyclo[6.2.0.0^{3,6}]deca-1(8),3(6)-diene (**1**), which was prepared and characterized according to Seitz et al.[11] The following conditions were employed in the MS experiments: direct insertion probe, ion source temperature, 200 °C; ion trap current, 100 μA; accelerating voltage, 8 kV. Collision-induced dissociations (CIDs),[12] used to char-

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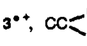
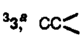
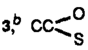
Table I. Total Energies (in Hartrees), Unscaled Zero-Point Vibrational Energies (ZPVEs, in Hartrees), Relative Energies (in Kilocalories/Mole), $\langle S^2 \rangle$ Expectation Values, and Geometry Data of $C_2OS^{\bullet+}$ and C_2OS Isomers

		energies				geometries						
						distance, Å				angle, deg		
species	symmetry	HF/6-31G*	ZPVE	E_{rel}	$\langle S^2 \rangle$	C–O	C–C	C–S	S–O	CCO	CCS	CSO
$2^{\bullet+}$, $OCCS^{\bullet+}$	$C_{\infty v}$	−547.722 70	0.014 98	0	0.79	1.157	1.333	1.498				
$3^{\bullet+}$, 	C_s	−547.625 55	0.011 46	59.0	0.82	1.308	1.490	1.594		55	165	
$4^{\bullet+}$, CCS–O	C_s	−547.574 38	0.010 06	90.3	2.07		1.251	1.623	1.541		180	105
^{3}**2**,[a] OCCS	$C_{\infty v}$	−548.040 34	0.014 48	0	2.07	1.155	1.273	1.563				
^{1}**2**,[b] OCCS	$C_{\infty v}$	−547.998 60	0.014 53	26.2		1.154	1.280	1.563				
^{3}**3**,[a] 	C_s	−547.925 13	0.012 00	70.9	2.46	1.211	1.440	1.781		120	117	
^{1}**3**,[b] 	C_s	−547.945 43	0.012 83	58.6		1.337	1.437	1.584		57	164	
^{3}**4**,[a] CCS–O	C_s	−547.896 67	0.00940	87.6	2.54		1.230	1.701	1.494		180	108
^{1}**4**,[b] CCS–O	C_s	−547.873 70	0.011 95	103.1			1.270	1.574	1.437		180	116

[a] Refers to triplet state. [b] Refers to singlet state.

acterize the primary ions M_1^+, were brought about by mass-selecting a beam of M_1^+ by means of B and colliding it with oxygen in a collision chamber located in the second-field-free region (90% transmittance, T; this transmittance corresponds, on the average, to 1.1–1.2 collisions[13]). Ionic dissociation products were recorded by scanning E. In the NRMS experiments, a beam of mass-selected M_1^+ ions (having 8-keV translational energy) was neutralized in the first cell of a differentially pumped tandem collision cell by colliding it with xenon (90% T). Unreacted ions were deflected away from the beam of neutral species M_1 by putting a voltage on a deflector electrode; subsequent reionization of M_1 occurred in the second collision cell by collision with oxygen (90% T). The mass spectrum of the resulting ions (M_1^+) was recorded by scanning E. The minimal lifetime (t; identical with the transit time from collision cell I to cell II) in the present experiment is ≈0.5 μs.

All computations have been performed by using the CRAY-XMP versions of the GAUSSIAN 82 and 86 series of programs.[14] Open-shell species were treated in the unrestricted and closed-shell species in the restricted Hartree–Fock formalisms. The geometries (bond length in angstroms, bond angle in degrees) were fully optimized with the polarized 6-31G* basis set,[15] using analytical gradient techniques. All stationary points have been characterized to correspond either to local minima or to transition structures by having zero or one negative eigenvalue in the analytically evaluated force constant matrix, respectively. Zero-point vibrational energies (ZPVEs) have been calculated from the 6-31G* harmonic normal frequencies. For their inclusion in the calculations of relative energies, E_{rel}, they were scaled by a factor of 0.89 in order to account for the errors due to the harmonic approximation used.[16] In order to estimate the degree of spin contamination, we have calculated the $\langle S^2 \rangle$ values. The total energies, calculated at HF6-31G*, are given in hartrees, and the relative energies, including the ZPVEs, are given in kilocalories/mole.

Results and Discussion

The $C_2OS^{\bullet+}$ radical cation (m/z 72) is easily accessible by dissociative ionization of **1**; its CA mass spectrum, given in Figure 1, is compatible with the connectivity of $O{=}C{=}C{=}S^{\bullet+}$ ($2^{\bullet+}$). The energetically most favored reaction of $2^{\bullet+}$ corresponds to the generation of $CS^{\bullet+}$ (m/z 44) by loss of CO. This is also born out by the ab initio Mo results: at the HF/6-31G* + ZPVE level of theory, this reaction is continuously endothermic, with an endothermicity, $\Delta H_r°$, of 23.6 kcal/mol (relative to $2^{\bullet+}$). All other reactions giving rise to the products shown in Figure 1 are significantly higher in energy. For example, dissociation of $2^{\bullet+}$ to $CO^{\bullet+}$ and CS has a calculated $\Delta H_r°$ of 95.5 kcal/mol. The theoretically calculated difference of >70 kcal/mol for these two reactions (i.e., generation of $CO^{\bullet+}$ versus $CS^{\bullet+}$) corresponds quite well with the estimates based on the well-known heats of formation, $\Delta H_f°$, of the respective species.[17] By use of these data, the combined heats of formation of $CS^{\bullet+}$/CO are 60 kcal/mol lower than those for $CO^{\bullet+}$/CS. The energetic requirements of the other reactions, leading eventually to $C_2S^{\bullet+}$, $C_2O^{\bullet+}$, and $S^{\bullet+}$, respectively,

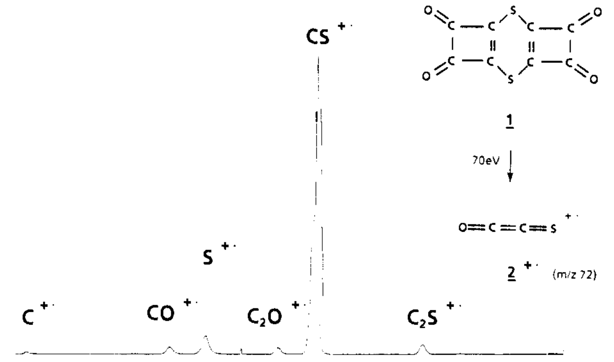


Figure 1. Collisional activation mass spectrum of $C_2OS^{\bullet+}$ (m/z 72) (collision gas: oxygen (90% T)).

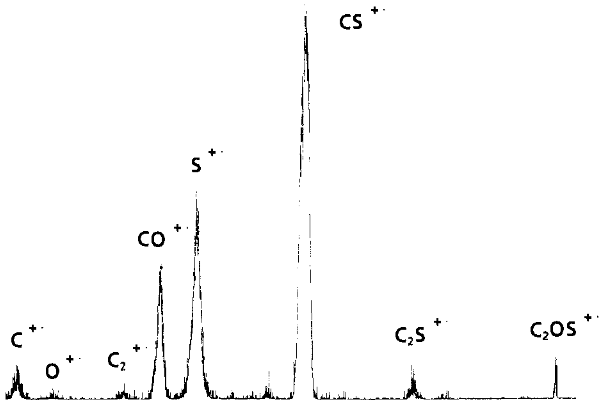


Figure 2. Neutralization–reionization mass spectrum of $C_2OS^{\bullet+}$ (m/z 72) (xenon 90% T/oxygen 90% T).

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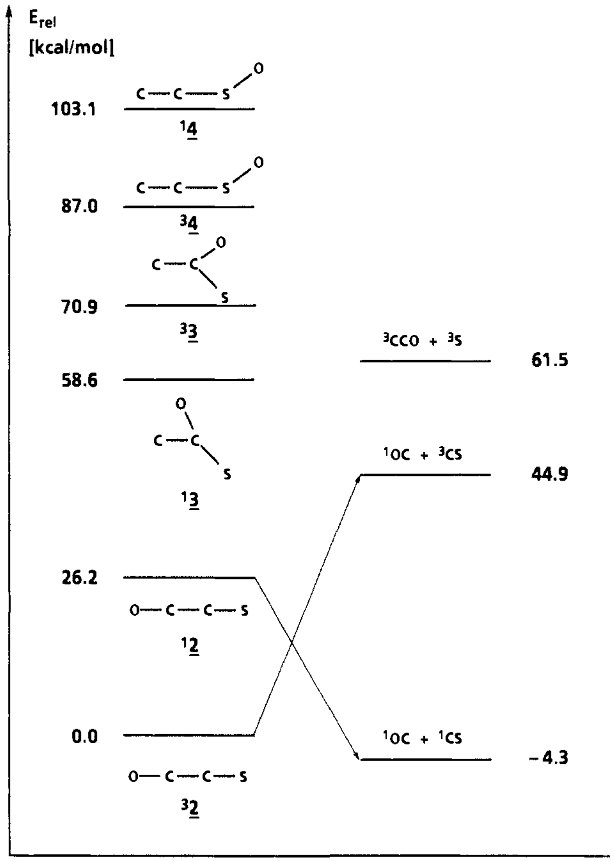
(17) $\Delta H_f°$ (in kcal/mol) for $CS^{\bullet+}$ (327), CO (−26.4), $CO^{\bullet+}$ (297), and CS (64). Data are taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*, supplement 1.

Chart I. Relative Energies (HF/6-31G* + ZPVE) of C_2OS Isomers and Some Dissociation Products



are comparable to (if not higher than) the dissociation $2^{\bullet+} \rightarrow CO^{\bullet+} + CS$.

In the MO analysis, we have also included $3^{\bullet+}$ and $4^{\bullet+}$ as conceivable $C_2OS^{\bullet+}$ isomers, although their generation from $1^{\bullet+}$ would require substantial skeletal reorganization. In addition, loss of CO from $3^{\bullet+}$ to generate $CS^{\bullet+}$ would either involve an isomerization (oxygen migration from C(1) to C(2)) or, alternatively, consecutive losses of oxygen and carbon atoms. The latter is, no doubt, energetically extremely unfavorable. Similar arguments would apply for $4^{\bullet+}$. In addition, at the HF/6-31G* + ZPVE level of theory, species $3^{\bullet+}$ is 59.0 kcal/mol and $4^{\bullet+}$ is 90.3 kcal/mol higher in energy than $2^{\bullet+}$. Thus, we conclude that the $C_2OS^{\bullet+}$ cation radical fromed in the dissociative ionization of **1** is ionized thioxoethylenone (ethenonethione), $O{=}C{=}C{=}S^{\bullet+}$ ($2^{\bullet+}$), which according to the MO calculations corresponds to the global minimum of the $C_2OS^{\bullet+}$ potential surface.

Reduction of $O{=}C{=}C{=}S^{\bullet+}$ in a NRMS experiment yields a recovery signal at *m/z* 72 as shown in Figure 2. The fragmentation pattern in the NR spectrum is virtually that observed in the CA mass spectrum of the original radical cations (compare Figures 1 and 2). The enhanced relative intensity of the *m/z* 28 [$CO^{\bullet+}$] signal in the NR spectrum results from reionization of neutral CO molecules generated by collision-induced dissociation (in the neutralization cell) of $O{=}C{=}C{=}S^{\bullet+}$ ions, whose major dissociation pathway involves loss of CO. A second contribution may come from the neutralization process, which yields neutral species with a broad range of internal energies. As a result, the energy-rich fraction of $O{=}C{=}C{=}S$ molecules will decompose, preferably into CO and CS molecules.[18] This process may also account for the enhanced relative intensity of the *m/z* 32 [$S^{\bullet+}$] signal, which we ascribe to the dissociation of reionized energy-rich CS molecules.

The MO studies, though being more qualitative than quantitative as far as numerical accuracy is concerned, support the experimental findings. Noteworthy are the following results. (i) The triplet $^3\Sigma$ of $O{=}C{=}C{=}S$ (^{3}2) is 26.2 kcal/mol more stable than the singlet electromer $^1\Sigma$ (^{1}2) (Chart I). The singlet ($^1A'$) and triplet ($^3A''$) forms of the branched isomers, **3** and **4**, are significantly higher in energy (58.6 for ^{1}3, 70.9 kcal/mol for ^{3}3, 103.1 kcal/mol for ^{1}4, and 87.6 kcal/mol for ^{3}4). (ii) In analogy with the well-understood C_2S_2 and C_2O_2 systems,[1b] the spin-allowed dissociation of ^{3}2 is quite endothermic (44.9 kcal/mol), while dissociation of ^{1}2 is exothermic. (iii) The generation of other neutral product combinations, like C_2O/S, are high-energy processes.

Thus, the MO data suggest that the neutral C_2OS formed in the neutralization of $C_2OS^{\bullet+}$ (presumably $2^{\bullet+}$) corresponds to the yet unknown monothio analogue of the long-sought-after ethylenedione $O{=}C{=}C{=}O$.[1b,5c,7] The observed neutral very likely is the triplet species ^{3}2. Comparison of the geometries of $O{=}C{=}C{=}S^{\bullet+}$, $2^{\bullet+}$, with those of the singlet/triplet states ^{1}2 and ^{3}2, respectively (Table I), shows that the C—O, C—C, and C—S bond lengths differ only marginally. The neutralization step involves a vertical transition, and it is thus reasonable to assume that both ^{3}2 and ^{1}2 are generated. While neutrals of structure ^{3}2 survive transit from collision cell I to II (thus giving rise to the observed recovery signal), the isomeric species ^{1}2 will dissociate to CO and CS. In addition, spin–orbit coupling in ^{3}2 may facilitate a potential-curve crossing and thus further deplete the concentration of nondissociating $O{=}C{=}C{=}S$ molecules. This may explain why, in spite of the minor geometry changes between ion and neutral, the flux of nondissociating neutrals in the $O{=}C{=}C{=}S^{\bullet+}$ system is weak and much smaller than that observed in the related $S{=}C{=}C{=}S^{\bullet+}$ system.[6]

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Registry No. 1, 70597-76-1; $S{=}C{=}C{=}S$, 83917-77-5; $S{=}C{=}C{=}S$ radical cation, 116952-95-5; $:C^+CO\dot{S}$, 124153-28-2; $\dot{C}{\equiv}CS^+{=}O$, 124125-63-9; $:\dot{C}CO\dot{S}$, 124125-64-0; $\dot{C}{\equiv}CS\dot{O}$, 124125-65-1.

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[18] As rightly noted by a reviewer, the relative intensities of $CO^{\bullet+}$ and $CS^{\bullet+}$ in the NR spectrum of **2** also depend on the reionization efficiences of the corresponding molecules, which have not been determined in the present experiment.