Oxathiirans. Part 5.[1] Oxathiiran *O*-Oxide, a Possible Intermediate in the Reaction between Singlet Oxygen and Thiocarbonyl Compounds

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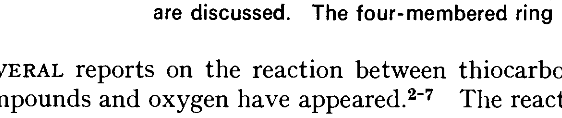
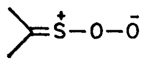
The reaction between thioformaldehyde and singlet oxygen has been investigated theoretically within a CNDO/B framework. Potential energy surface calculations predict a multistep mechanism involving primary formation of an oxathiiran *O*-oxide, which rearranges into a 1,2,3-dioxathietan system. Two possible rearrangement pathways are discussed. The four-membered ring is tentatively suggested to decompose *via* a biradicaloid intermediate.

SEVERAL reports on the reaction between thiocarbonyl compounds and oxygen have appeared.[2-7] The reaction between thiobenzophenone and triplet oxygen, in the dark, has been reported to yield benzophenone and the oxidized product, thiobenzophenone *S*-oxide, in almost equal amounts.[4] In contrast to this the reaction between thiocarbonyls and singlet oxygen affords the corresponding carbonyl compounds in high yield together with elemental sulphur and sulphur dioxide.[5-7] The latter reaction has, by some authors,[2b,5,6] been formulated to proceed *via* a 1,2,3-dioxathietan ring system, analogous to the well known dioxetan formation upon the action of singlet oxygen on alkenes. Recently, Ramamurthy[7] has drawn up a series of possible intermediates; however, no characterization of these, nor a mechanistic evaluation to elucidate the reaction path, was given.

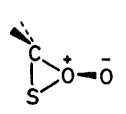
For obvious reasons, as the observed reaction products were carbonyl compounds, sulphur and sulphur dioxide, the reaction path most probably involves the presence of the 1,2,3-dioxathietan ring (1). However, it is, on the other hand, less obvious if the four-membered system (1) is formed directly by a [2 + 2] cycloaddition reaction or, if the primary product possesses the open-chain structure (2) or the three-membered oxathiiran *O*-oxide ring structure (3).



(1)



(2)



(3)

$H_2C{=}S$

(4)

In connection with my interest in the possible intermediates in the oxidative conversion of thiocarbonyl compounds into the corresponding carbonyl compounds, the reaction between thioformaldehyde (4) and singlet oxygen has been studied theoretically within a CNDO/B framework.† This report concerns studies on the $H_2C{=}S + {}^1O_2$ potential energy surface.

The geometry of the three structures (5)—(7), which by analogy are possible intermediates in the reaction between (4) and singlet oxygen, were optimized with respect to energy in an attempt to study their relative stability. The zwitterion (5) was found to be highly energy-rich relative to (4) and $^1O_2$ by 434.6 kJ mol^{-1}, whereas the four-membered 1,2,3-dioxathietan (6) and the three-membered oxathiiran *O*-oxide (7) are each found stabilized relative to (4) and $^1O_2$ by 361.9 and 151.7 kJ mol^{-1}, respectively. Even though a part of the latter energy differences undoubtedly resides in the well known CNDO–INDO underestimate of strain in small rings, a quantity of 40—80 kJ mol^{-1},[8] the predicted relative stability of (6) and (7) *versus* (4) and $^1O_2$ is maintained. The energy–geometry-optimized structures of the intermediates (5)—(7) are shown in Figure 1.

Potential energy surface calculations were carried out for the possible reactions between (4) and singlet oxygen leading to (5)—(7), respectively. The potential energy surfaces under investigation were determined by continuous variation of all geometric parameters between the values of the energy–geometry-optimized structures of the starting materials and the final products, respectively. In general the calculations were carried out for 10 intermediary states.

Ramamurthy estimated the rate constant for the primary interaction of xanthione and thiocamphor with $^1O_2$ to be in the range of 10^6 l mol^{-1} s^{-1}.[7] This is in strong contradiction to a reaction between (4) and singlet oxygen leading to (5), although predicted to be allowed, † as the barrier of activation is predicted to be higher than 434.6 kJ mol^{-1}.

The direct formation of (6) by a [2 + 2] cycloaddition

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† The calculations were carried out by means of the Boyd–Whitehead SCF-MO-CNDO/B procedure (R. J. Boyd and M. A. Whitehead, *J.C.S. Dalton*, 1972, 73, 78, 81), which is parameterized to give geometries and energies in accord with experimental data. The potential energy minima were found by allowing the internal valence co-ordinates (i.v.c.), *i.e.* bond lengths and bond angles, to vary. Initially a calculation is performed using the geometry corresponding to the input i.v.c. data. The program varies one i.v.c. at a time, the other i.v.c.s remaining constant. The calculation is repeated with two additional values of the i.v.c. being varied and a second-order polynomial is fitted to the three points. This procedure is repeated for each i.v.c. The final results of the energy–geometry optimizations yield the bonding energy as a function of the i.v.c.s: $E_{\text{bond}} = \sum_{i=1}^{k} a_{0i} + a_{1i}q_i + a_{2i}q_i^2$, the summation over k i.v.c.s being denoted by q_i. The first and second partial derivative of E_{bond} with respect to q_i yield the equilibrium values of the co-ordinates and the corresponding quadratic force constant, respectively. (R. J. Boyd, Thesis, McGill University, Montreal, 1970).

was found to be symmetry-forbidden * suprafacially as well as antarafacially. It should be noted that this reaction cannot be rationalized in terms of orbital symmetry conservation principle,[9] frontier orbital theory,[10] or various derivative concepts,[11] as these theories permit only the straightforward rationalization of symmetrical and near symmetrical pericyclic reactions. Strong symmetry introduced specially by heteroatoms seems to be able to alter drastically the conventional conceptions of allowed and forbidden reactions.[12-14], †

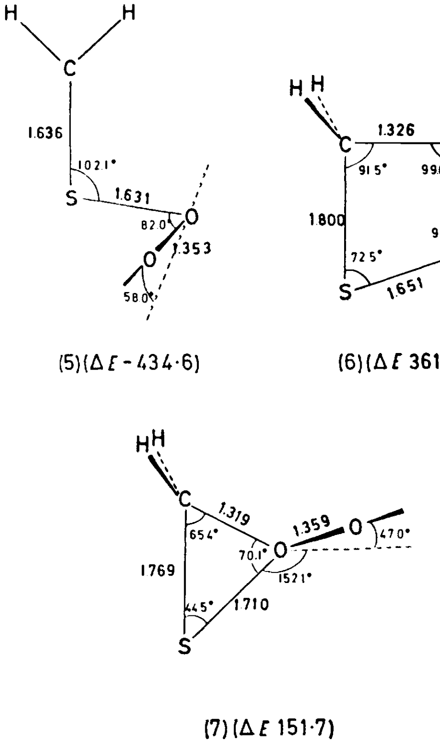
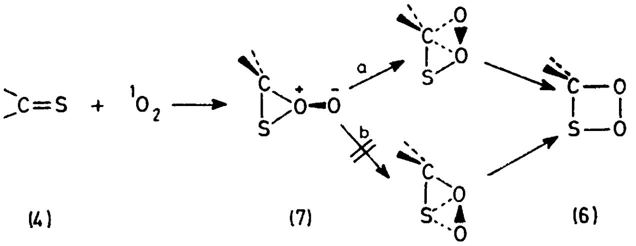


FIGURE 1 Energy-optimized geometries of the possible products of the reaction between thioformaldehyde (4) and singlet oxygen. The bonding energies relative to (4) and singlet oxygen are given in parentheses (kJ mol^{-1})

On the other hand, the chelotropic addition of singlet oxygen to the CS double bond in (4), leading to the oxathiiran *O*-oxide (7) is predicted to be an allowed reaction. In this connection it is noteworthy that recent theoretical and experimental studies strongly support an assumption that the reaction between alkenes and singlet oxygen primarily leads to the formation of oxiran *O*-oxides,[15] which undergo rapid rearrangements into the four-membered, 1,2-dioxetans. As mentioned above, the 1,2,3-dioxathietan (6) most certainly is present on the reaction path from (4) + ${}^1O_2$ to formaldehyde + SO, which, by analogy, suggest a facile rearrangement from (7) to (6). In favour of this it is seen that (7), not unexpectedly, is energy-rich relative to (6) by 210.2 kJ mol^{-1} (Figure 1).

A priori, three possible pathways for the (7) ⟶ (6) interconversion have to be considered, *i.e.* formation of a CO (path a) or an SO bond (path b), or rearrangement involving the high-energy open-chain structure (5), respectively. However, the latter was rejected as a possibility, owing to an extremely high energy barrier for the (7) ⟶ (5) conversion ($E_a > 586.3$ kJ mol^{-1}). Potential surface calculations on the former two rearrangements predict that path a, and formally also path b are each allowed reactions. However, based on the discussion below, path a is suggested to be more favourable.



In contrast to path a, where the MO correlation diagram shows a gradual correlation between ground state levels only, and excited levels only, respectively, it appears by studying the MO correlation diagram corresponding to path b that the frontier orbitals (HOMO–LUMO) in the transition state are almost degenerate, which causes strong mixing of these orbitals. This, complementary with the total lack of symmetry of the molecules involved, means that it is rather complicated to assure the correct orbital correlation near the transition state. However, as all the MOs exhibit the same symmetry, *i.e.* the identity *E*, HOMO–LUMO crossing is

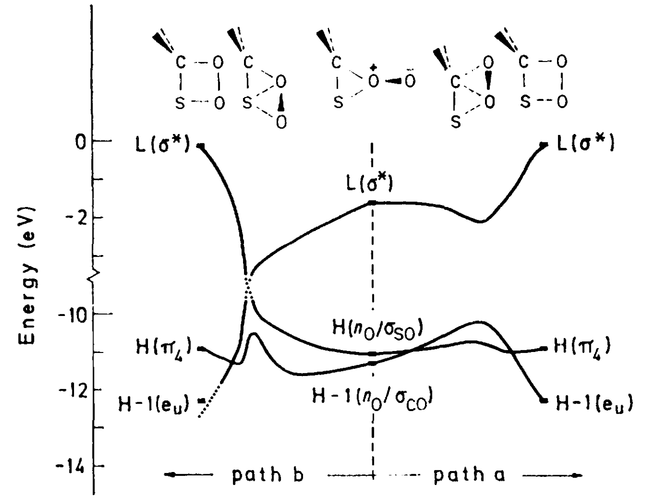


FIGURE 2 Orbital correlation for the two possible rearrangements of oxathiiran *O*-oxide (7) to 1,2,3-dioxathietan (6). a, Formation of CO bond; b, formation of SO bond. H and H−1 refer to the highest and next highest occupied MOs and L to the lowest unoccupied MO, respectively

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* In the discussion of allowed and forbidden reactions, these terms mean the presence or absence of a HOMO–LUMO orbital crossing, respectively, at the single-determinant level as defined by Woodward and Hoffmann.[9]

† Further work on the nature of pericyclic reactions involving components with an ' excess ' of non-bonding electron pairs is in progress, J. P. Snyder and L. Carlsen, to be published.

not possible. Thus, the correlation has to be formulated as the so-called avoided-crossing.[9] This means that although the reaction (path b) is formally predicted to be allowed, the ground-state levels, corresponding to the transition state, will be of high energy, disfavouring path b. The MO correlation diagrams for paths a and b are depicted in Figure 2.

The paramount difference between the two rearrangements is probably to be sought in the number of lone-pair bearing atoms involved. Path a involves two heteroatoms (the two oxygen atoms) together with the carbon atom, whereas all three heteroatoms play a role in the bond-breaking and -formation process along path b.

Finally the decomposition of (6) into formaldehyde and sulphur monoxide should be mentioned, although no intensive calculations have been carried out on this reaction. However, direct loss of ^{1}SO by a [2 + 2] retrocycloaddition was found to be a forbidden reaction. Furthermore rearrangement into oxathiiran *S*-oxide, prior to SO loss, seems not to be feasible, as this rearrangement would involve all three heteroatoms. The arrangement has previously been rejected[13] for this reason. Thus, and by analogy with the dioxetan system,[16] a biradicaloid intermediate in the formation of formaldehyde and singlet sulphur monoxide from (6) is tentatively suggested.

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