

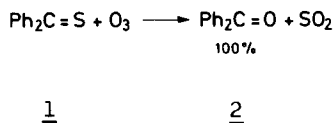
ON THE POSSIBLE INTERMEDIATES IN THE OZONOLYSIS OF THIOCARBONYL COMPOUNDS

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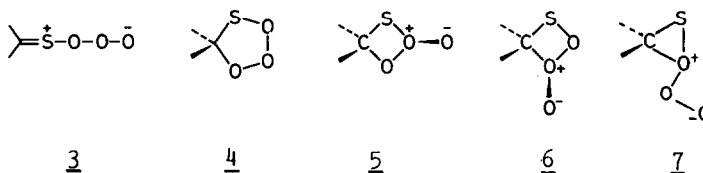
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In contrast to the well known reaction between ozone and alkenes ¹, only a few reports have appeared concerning the ozonolysis of thiocarbonyl compounds. Zwanenburg investigated the reaction between diarylthioketones and ozone in an attempt to synthesize the corresponding sulfines ². However, partial formation of sulfines is only observed with sterically hindered thioketones, unhindered thioketones such as thiobenzophenone (1) giving rise only to the corresponding ketones. A similar reaction has been reported by Senning ³.



One of the present author's current interests is in the intermediates involved in the oxidative conversion of thiocarbonyl compounds into the corresponding carbonyl compounds, and this report concerns the possible intermediates in the ozonolysis of thiocarbonyls.

By analogy with the ozonolysis of alkenes ¹ five intermediary structures (3-7) arising from reaction between the thiocarbonyl double bond and ozone are in principle possible



The fact that formation of elemental sulfur was not observed during the ozonolysis of 1 ² seems to exclude primary extrusion of sulfur monoxide, the latter decomposing to give sulfur and sulfur dioxide. Further evidence for this assumption was obtained from a study of the ozonolysis of 1 in acetone. As found for the reaction in cyclohexane, benzophenone (2) was obtained in quantitative yield, thereby excluding the possibility of an intermediary carbonyl O-oxide (Criegee -

intermediate) formed by primary loss of sulfur monoxide; carbonyl O-oxides have been reported to react with carbonyls present forming ozonides (1,3,4-trioxolanes) containing the new carbonyl moiety ¹. On this basis direct unimolecular formation of benzophenone from intermediates of type 3, 6 and 7 does not seem feasible.

The reaction between 1 and ozone at 130K was monitored by electronic absorption spectroscopy. Benzophenone (2) was detected in 68% yield, together with another product absorbing at λ_{\max} 321nm. Assuming 32% formation of the latter, its extinction coefficient was calculated to be ca. 8000 $\text{mol}^{-1}\cdot\text{cm}^{-1}\cdot\text{l}$. Upon standing (\approx 130K) this absorption slowly decayed following first order kinetics ($t_{1/2}\approx$ 5min), the final product being 2 in 100%yield. On this basis the possibility of a bimolecular reaction leading to 2 can be disregarded, ruling out 3, 6, and 7 as precursors to 2. In an attempt to obtain information concerning the relative stability of the structures 3 - 7 the five structures, 9 - 13, which by analogy are possible intermediates in the model reaction between thioformaldehyde (8) and ozone, were studied theoretically by a CNDO/B procedure ⁴.

The zwitterion 9 was found to be energy-rich relative to 8 and ozone ($\Delta E \approx 20\text{kJ/mole}$). An attempt to optimize the geometry of 9 with respect to energy indicated merely a progressive stretching of the central S-O bond to give the latter fragments. No energy barrier was encountered. The geometry/energy optimized structures of the intermediates 10 - 13 are shown in Fig. 1.

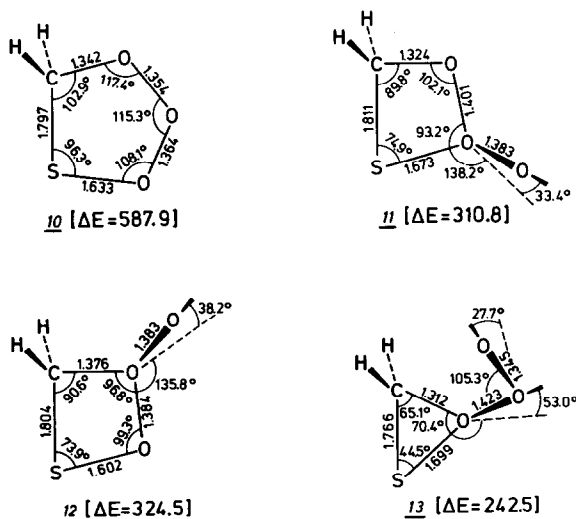


Fig. 1 Energy-optimized geometries of the possible cyclic products of the reaction between thioformaldehyde (8) and ozone. The bonding energies relative to 8 and ozone are given in parentheses (kJ/mole).

The calculations predict both the four- as well as the five membered rings to planar; this probably reflects the inability of this type of calculation to discriminate faultlessly between conformations of vanishingly small energy difference. Thietane ⁵ and oxetane ⁶ both possess folded conformations and interconvert through the planar form with an energy barrier of less than 4 kJ/mole. The interconversion barriers for tetrahydrofuran and 1,3-dioxolane have been estimated to be less than 0.8 kJ/mole ⁷. If capable of existence, 10, 11, and 12 can be expected to exhibit similar equilibrium behaviour.

Potential surface calculations were carried out for the four reaction pathways in the reaction between 8 and ozone leading to the intermediates 10 - 13, respectively.

In agreement with the known 1,3 dipolar nature of ozone ⁸ the 1,3-dipolar addition to 8 forming 10 was found to be symmetry-allowed ⁹. Likewise, the chelotropic addition affording 13 was found to be symmetry-allowed. In contrast, however, the (2 + 2) cycloadditions leading to 11 and 12, respectively, were found to be symmetry-forbidden.

It can be seen (Fig. 1) that the trioxathiolane 10 is predicted to be 345.4 kJ/mole more stable than the three membered intermediate 13, and therefore a facile rearrangement of the latter, if formed, into the far more stable 10 might be expected. No intensive calculations have been carried out on this reaction, however.

The absorption spectrum of 10 was calculated using a CNDO/S procedure ¹⁰, the first absorption band being predicted to be located around 327 nm. Although possibly fortuitous this result is in remarkable accord with the above mentioned experimental observation of absorption at 321 nm.

On the basis of the above it appears likely that formation of carbonyl compounds by ozonolysis of thiocarbonyl compounds takes place via an intermediate of type 4, analogous to the 1,2,3-trioxolanes which are the initial products of the reaction of alkenes with ozone ^{1,11}. The absorption band at 321 nm ($\epsilon = 8000$) observed by low temperature absorption spectroscopy is then assigned to 5,5-diphenyl-1,2,3,4-trioxathiolane (14).

On the basis of the computed lability of intermediates of type 3 we are led to conclude that the formation of sulfines in the reaction between sterically hindered thioketones and ozone ² does not proceed via an open chain intermediate. We suggest that sulfine formation may take place from the above mentioned trioxathiolane intermediate (4) by extrusion of oxygen. The variable course of these reactions may be a consequence of steric and/or electronic effects.

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