

STERIC ASPECTS OF THE OXIDATION OF THIOKETONES BY SINGLET OXYGEN

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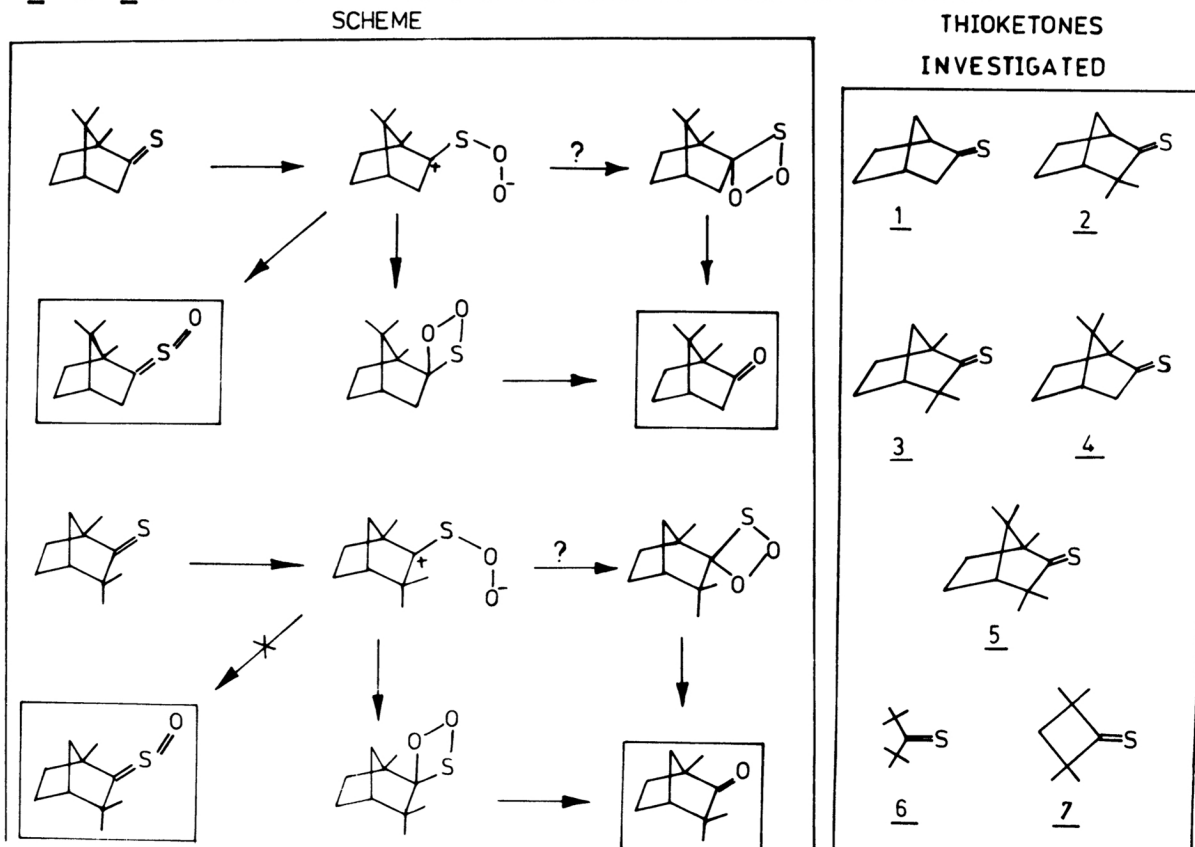
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Singlet oxygen oxidation of dialkyl thioketones yields the corresponding ketones and in some cases sulfoxides in varying amounts. Steric considerations on the reactive zwitterionic/diradical intermediates have been invoked to rationalise the product distribution.

The anomalous behaviour of di-*t*-butylthioketone during the oxidation by singlet oxygen, wherein the major product was the corresponding sulfoxide, suggested the presence of steric influence on the photooxidation process.^{1,2} In order to investigate the nature of steric influence on the thiocarbonyl, oxidations of bicyclo[2.2.1]heptane systems 1-5 together with 6 and 7 were studied and the results are presented below. Oxidation of thioketones 1-7 by singlet oxygen generated by self-sensitisation, by dye sensitisation (methylene blue, rose bengal), and by thermal decomposition of triphenylphosphite ozonide gave the corresponding ketones and/or sulfoxides (Table).³ Formation of ketone and sulfoxide during direct excitation of 1-7 is quenched by singlet oxygen quenchers such as DABCO, dimethyl sulfide, dihydropyran, and tetramethylethylene. Striking observation is that of the thioketones investigated only four (4-7) gave sulfoxide in varying yields.

Initial interaction between thioketone and singlet oxygen is expected to involve the filled "n" orbital of thioketone and the empty π^* orbital of singlet oxygen and this would lead to bonding with the sulfur atom to give either a zwitterionic or a diradical intermediate.⁵ This intermediate could give the sulfoxide or close to give a 1,2,3-dioxathietane type intermediate which would lead to a ketone (scheme). The ease of closure of the intermediate, however, will depend on the substituents at the C₇ carbon atom (1-5) and the gem dimethyl groups at C₇ hinders the closure. The absence of C₇-dimethyl groups in 1-3 favors the

closure of the intermediate to 1,2,3-dioxathietane and consequently only the ketone is obtained. On the other hand, in the case of 4 and 5 the C₇-methyl groups hinder the closure. As a result sulfoxide formation competes. The steric effect is all the more evident when one considers 6 and 7. The bulky t-butyl groups in 6 sufficiently hinder the intermediate closure resulting in the corresponding sulfoxide as the major product. This large decrease in the sulfoxide yield is appreciable in 7, where one can visualise the t-butyl groups being drawn back to form a cyclobutane ring, thereby releasing the steric crowding which eases the zwitterionic/diradical closure. A decrease in the sulfoxide yield is therefore expected and is indeed observed. However, it is interesting to note that 7 yields a small percentage of the corresponding sulfoxide whereas 3 fails to do so. This may be attributed to the difference in steric hindrance offered by α -methyl groups of 3 and 7 for the closure of zwitterionic/diradical intermediate.



The rate of quenching of singlet oxygen by the thiones (1-7) as determined by the inhibition of the self-sensitised photooxidation of rubrene in chloroform⁶ is presented in table 1. A plot of the rate constants against the ionisation potentials (I.P.) in the case of a few dialkyl thioketones (2,3,6, tetramethyl-1,3-cyclobutanedithione, and tetramethyl-3-thio-1,3-cyclobutanedithione) showed a

correlation for n electron ionisation potential but not for π electron indicating that initial interaction occurs along the n -orbital of the thioketone as suggested above.⁸ This is consistent with the large energy difference (>40 Kcal/mole) between the n and π levels as measured by the electronic spectra. Observed rate constants do suggest that the attack of singlet oxygen on the thiocarbonyl chromophore is sensitive to the steric environment. However, the trend in the rates suggests that steric factors alone are not operative. Electronic factors arising out of the inductive effects of the α -methyl groups may also be involved.

Presently, we have no direct evidence for zwitterionic/diradical and 1,2,3-dioxathietane intermediates. However, the yield of ketones based on sulfur dioxide evolved agrees fairly well with the ketone isolated (Table) supporting the involvement of 1,2,3-dioxathietane type intermediates. Identifying these intermediates and understanding the mechanism of the photooxidation form part of our further investigation.⁹

Table 1. Oxidation of Thioketones by Singlet Oxygen

Thioketone	Products		Expected yield of K(%) based on SO ₂ evolution	Rate of ¹ O ₂ quenching by Thioketone M ⁻¹ sec ⁻¹ x 10 ⁵	Ionisation Potential (eV)	
	K %	S %			n	π
<u>1</u>	62	-	68	1.8	8.32	9.94
<u>2</u>	82	-	86	1.0	8.15	-
<u>3</u>	74	-	80	5.1	8.1	9.6
<u>4</u>	30	15	29	0.8	8.17	-
<u>5</u>	60	20	58	0.6	8.01	-
<u>6</u>	25	75	28	0.1	7.8	9.8
<u>7</u>	32	7	35	3.1	8.17	-
<u>8</u> ^a	-	-	-	2.2	8.32 8.76	10.2 10.7
<u>9</u> ^b	-	-	-	0.85	8.48 9.18	10.5 11.80

(a) 8 : tetramethyl-1,3-cyclobutanedithione

(b) 9 : tetramethyl-3-thio-1,3-cyclobutanedione

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3. A typical oxidation experiment is as follows: A chloroform solution (200 ml) of thioketone (500 mg) and dye (methylene blue or rose bengal; 10 mg) was taken in a pyrex immersion well consisting of a gas inlet and an outlet. The outlet was connected to a trap containing aqueous sodium hydroxide (0.3 M) solution. The immersion well was irradiated (500-W tungsten lamp) while oxygen was continuously bubbled through the inlet. Sulfur dioxide evolved ($2SO \rightarrow SO_2 + S$) was collected as sodium sulfite in the trap and was oxidised to the sulfate by the addition of bromine. The sulfate was gravimetrically estimated by following the reported procedure.⁴ Ketones and sulfoxides were isolated from the irradiation mixture by column chromatography (silica gel - hexane/benzene). Yields represented in Table 1 are the average of three independent runs.
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6. The experimental procedure reported by Monroe⁷ was adopted with slight modifications to determine the rates of 1O_2 quenching by thioketones. A Hanovia 450 W medium pressure mercury lamp was used as the source. By a suitable combination of filters 440±10 nm line was isolated for rubrene excitation. After irradiation, following the reported procedure,⁷ the disappearance of rubrene was monitored by its electronic absorption at 440 and 545 nm.
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9. We thank the Department of Science and Technology, Government of India for financial support and Prof. R.Gleiter for ionisation potential data. V.J.Rao and V.Ramesh thank the Atomic Energy Commission and the University Grants Commission respectively for Junior Research Fellowships.

(Received August 31, 1981)