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RATES OF OXIDATION OF THIOKETONES BY SINGLET OXYGEN

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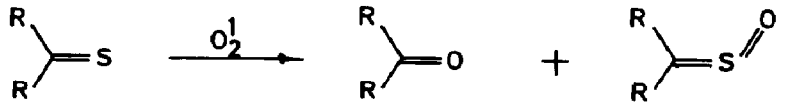
Summary

Rate constants for the quenching of singlet oxygen by a series of thioketones were measured by monitoring the inhibition of the self-sensitized photooxidation of rubrene. A correlation of the quenching rate with the nature of the substituents on the aromatic rings for the diarylthioketones and arylalkylthioketones was found, whereas correlation with the n orbital ionization potential was observed for the dialkylthioketones.

1. Introduction

We have recently shown that thioketones react with singlet oxygen to give the corresponding ketones and in some cases sulphines and that the product distribution is dependent on the nature of the substituents on the aryl rings [1, 2]:



(1)

To investigate the nature of the primary interaction between singlet oxygen and thioketones, the absolute rates of quenching of singlet oxygen by a variety of thioketones were measured by studying the method of inhibition of the self-sensitized rubrene photooxidation in chloroform [3]; the results are discussed below.

2. Results

The rate constants for the quenching of singlet oxygen by thioketones (diaryl, arylalkyl and dialkyl) are given in Tables 1 - 3. These rates are actually the sum of two rate constants: the rate constant of singlet oxygen

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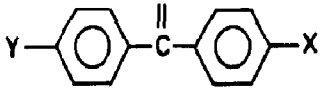
TABLE 1

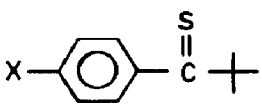
Rate parameters for the quenching of singlet oxygen by diarylthioketones

Substitution number	*Thioketone* 	*Rate of quenching*[a] ($l\ mol^{-1}\ s^{-1}$)	*Quantum yield of oxidation*[b]	*Hammett's parameters*[c]		*Singlet oxygen oxidation products (%)*[d]	
				σ	σ^+	*Ketone*	*Sulphine*
1	X ≡ Y ≡ OCH_3	9.6×10^6	0.54	−0.27	−0.65	60	–
2	X ≡ H; Y ≡ OCH_3	5.4×10^6	0.43	−0.27	−0.65	87	–
3	X ≡ Y ≡ CH_3	3.7×10^6	0.32	−0.14	−0.26	97	–
4	X ≡ H; Y ≡ Ph	3.1×10^6	0.25	−0.01	−0.08	85	–
5	X ≡ H; Y ≡ Cl	1.1×10^6	0.22	+0.23	+0.04	67	2
6	X ≡ Y ≡ Cl	0.2×10^6	0.17	+0.23	+0.04	83	5

[a]The numbers represented are the average of three runs: error, ±10%.
[b]The quantum yields for oxidation of the thioketones (0.006 M) were measured in benzene with the excitation wavelength set at 350 ± 20 nm. A ferrioxalate actinometer was used and the disappearance of thioketone was monitored using their visible absorption.
[c]The values are taken from ref. 4.
[d]Ref. 1.

TABLE 2

Rate parameters for the quenching of singlet oxygen by arylalkylthioketones

Substitution number	*Thioketone*	*Rate of quenching*[a] ($l\ mol^{-1}\ s^{-1}$)	*Hammett's parameters*		*Singlet oxygen oxidation products (%)*[b]	
			σ	σ^+	*Ketone*	*Sulphine*
1	X ≡ OCH_3	9.2×10^5	−0.27	−0.65	80	2
2	X ≡ H	4.3×10^5	0.00	0.00	63	16
3	X ≡ F	3.6×10^5	+0.06	−0.25	43	21
4	X ≡ Cl	2.0×10^5	+0.04	+0.04	52	25

[a] Average of three runs: error, ± 10%.
[b] Ref. 1.

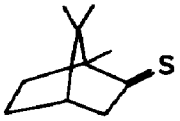
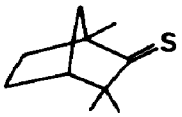
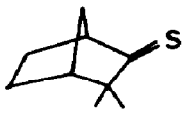
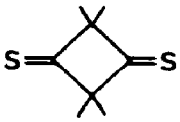
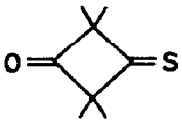
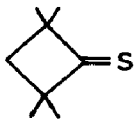
addition and the rate constant of the physical quenching of singlet oxygen. The quantum yields of oxidation of diarylthioketones have been found [6] to reach almost unity at high concentrations (0.01 M), suggesting that physical quenching makes only a small contribution to the measured rate. (At very high concentrations, the quantum yield of oxidation decreases because of the diffusion-controlled self-quenching of thioketones.) Consistent with this is the observation that the quantum yields of oxidation of diarylthioketones at low concentrations (0.005 M) show a linear relationship with the measured rates of quenching (Table 1). Therefore we believe that direct quenching of singlet oxygen by thioketones is not an important process and that the measured rate constants are in fact the rates of chemical interaction which ultimately lead to oxidation.

3. Discussion

Perusal of Tables 1 - 3 reveals that the diarylthioketones are the most reactive towards singlet oxygen, followed by arylalkyls and dialkyls. Among the diarylthioketones and arylalkylthioketones, it is observed that the electron-donating groups enhance the rate while the electron-withdrawing groups retard it. The rate constants exhibit a linear free-energy relationship (Hammett's plot) and a better correlation is obtained with σ than with σ^+ (Fig. 1). (For diarylthioketones a linear Hammett's plot is obtained only if we assume that the substituent effects are not additive. For a discussion on the question of additivity in the disubstituted diaryl series, see ref. 7.) ρ values of −1.71 for the diaryl series and −1.37 for the arylalkyl series were obtained, consistent with the well-documented characterization of singlet oxygen as an electrophilic reagent [8]. Definitive conclusions regarding the nature of the orbitals involved (n or π) during the quenching of singlet oxygen by thioketones cannot be made owing to the lack of experimental

TABLE 3

Rate parameters for the quenching of singlet oxygen by dialkylthioketones

Substitution number	*Thioketone*	*Rate of quenching*[a] ($l\ mol^{-1}\ s^{-1}$)	*Ionization potential* (eV)		*Singlet oxygen oxidation products* (%)	
			n	π[b]	*Ketone*	*Sulphine*
1		8.1×10^4	—	—	30	15
2		5.1×10^5	8.10	9.60	70	—
3		1×10^5	8.35	9.87	70	—
4		2.2×10^5	8.32	10.2	75	—
5		8.5×10^4	8.48	10.5	75	—
6		3.1×10^5	—	—	—	—
7		1.0×10^4	7.8	9.8	43	57

[a]Average of three runs: error, ±10%.
[b]The values are taken from ref. 5.

data on the ionization potentials of the diarylthioketones and arylalkylthioketones. (Attempts are under way to establish a collaboration to measure these ionization potentials.)

A plot of rate constant against ionization potential for dialkylthioketones indicates that there is a correlation for the n electron ionization potential but not for π electrons (Fig. 2) (UV photoelectron spectroscopy data have been reported for only a few thioketones [5]), suggesting that the quenching of singlet oxygen probably proceeds through the interaction of the n orbital of thioketones with the empty π^* orbital of singlet oxygen.

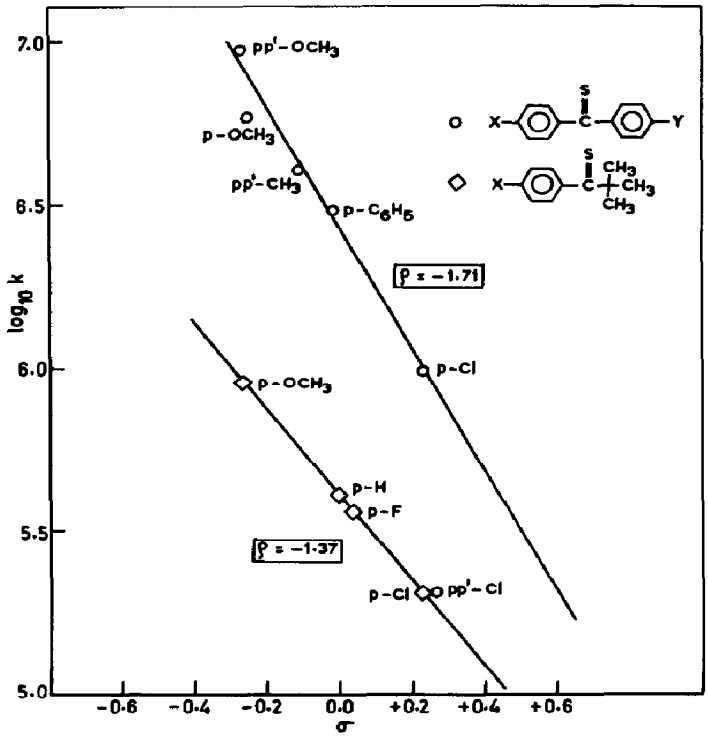


Fig. 1. Linear free-energy relationship for diaryl and arylalkyl ketones: a plot of log k_q (singlet oxygen quenching rate constant) against σ.

It is interesting to note that the value for di-*t*-butylthioketone is much lower than that expected on the basis of the above correlation. We believe that this is due to steric hindrance for the singlet oxygen approach by *t*-butyl groups of di-*t*-butylthioketone. This is revealed when di-*t*-butylthioketone is compared with 2,2,4,4-tetramethylcyclobutane-1-thione and related thioketones (Table 3, substitutions 4 - 6) where the methyl groups are held back by the cyclobutane ring, thus reducing the hindrance for approach of the n orbital. Such steric hindrance has been noticed during the quenching of singlet oxygen by amines and sulphides [8].

Thus we have shown that the rates of oxidation of thioketones by singlet oxygen are subject to electronic effects in the diaryl and arylalkyl series and are influenced by steric factors in the dialkylthioketones. Although in the dialkyl series the primary interaction is suggested to occur through the n orbital of thioketone, conclusions for the diarylthioketones and arylalkylthioketones could not be made owing to the lack of experimental data.

4. Experimental details

Rubrene (Aldrich) and doubly distilled chloroform were used. All the thiones were synthesized and purified by procedures reported in the liter-

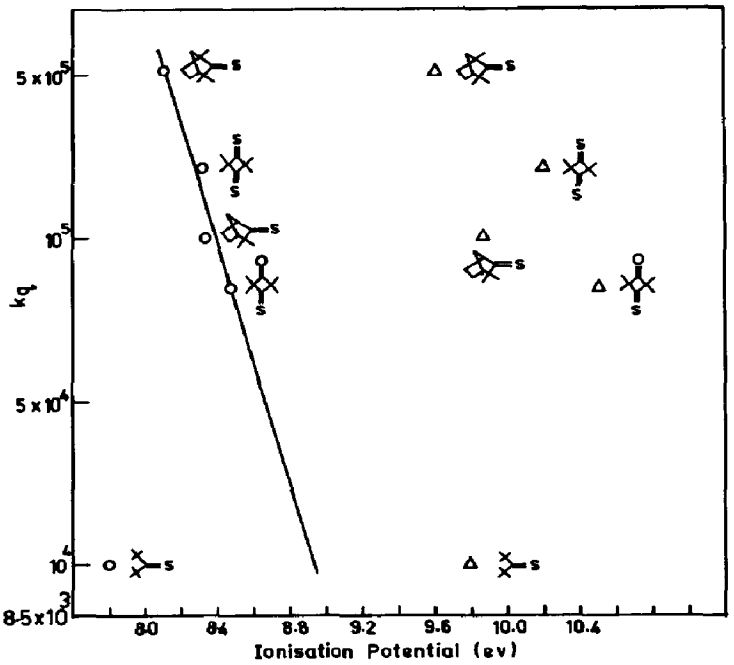


Fig. 2. Correlation of k_q with the n and π electron ionization potentials for dialkylthioketones.

ature. The experimental procedure reported by Monroe [3] was adopted with slight modifications to determine the rate of photooxidation. A Hanovia 450 W medium pressure mercury lamp was used as the source. By a suitable combination of filters the 500 ± 10 nm line was isolated for rubrene excitation in the diarylthioketones and arylalkylthioketones. Excitation of rubrene was effected at 550 ± 10 nm for the dialkylthioketones 1 - 3 and at 440 ± 10 nm for compounds 4 - 7. In all cases the excitation was effected at the wavelength where the absorption by the thione was a minimum at the concentration used. After irradiation, following the reported procedure [2], the disappearance of rubrene was monitored by its electronic absorption. The monitoring wavelength was chosen to be where the thiones did not absorb strongly. The wavelength at which the monitoring was carried out for each of the series was as follows: diarylthioketones, 440 nm; arylalkylthioketones, 445 nm; dialkylthioketones 1 - 3, 545 nm; dialkylthioketones 4 - 7, 440 nm.

The following control experiments were carried out to ensure the reliability of the above method. All thioketones used were found to be stable for more than 5 h in chloroform in the dark. Rubrene endoperoxide, which is formed by the oxidation of rubrene, was found to be stable in the presence of these thioketones. As the triplet energy of rubrene is much lower than that of the thioketones used, quenching of the rubrene triplet is not expected. The emission spectra of rubrene with and without the thione were recorded. Dialkyl thioketones did not quench the fluorescence whereas a

quenching of fluorescence was obtained in the diarylthioketones and arylalkylthioketones. We were able to show that this fluorescence quenching was due not to the quenching of rubrene excited states by the thioketones but to reabsorption of the emitted light by the thioketones. This is expected to introduce some error in our measured rate constants for diarylthioketones and arylalkylthioketones. Hence the rate constants presented in Tables 1 and 2 are lower than the real values. However, the trend among the series and the general conclusions drawn therefrom are not expected to be affected by this minor error.

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