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The Quenching of Singlet Oxygen

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The kinetics and mechanisms of processes involving the quenching of oxygen in the singlet state ($^1\Delta_g$) are examined. The rate constants for the deactivation of singlet oxygen in various solvents, for the reactions of singlet oxygen with unsaturated and aromatic compounds, and for processes involving the quenching of singlet oxygen by amines, metal complexes, and certain other compounds have been compiled. The influence of the polymer matrix on the reactivity of electron acceptors and the efficiency of quenching agents is considered and the role of singlet oxygen in photochemical oxidation reactions of low- and high-molecular-weight organic compounds is discussed.
The bibliography includes 77 references.

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I. INTRODUCTION

It was shown in 1964[1,2] that many photosensitised oxidation reactions proceed with participation of oxygen in an electronically excited singlet state and that "singlet" oxygen can give rise to oxidation products in nearly theoretical yields. These studies aroused much interest and stimulated theoretical and practical investigations of the properties and reactions of singlet oxygen. Among practical problems, the possibility of using singlet oxygen in preparative organic chemistry, the problem of smog and the pollution of the atmosphere, and the problem of protection of biological systems as well as low-molecular-weight and high-molecular-weight compounds from photosensitised oxidation have attracted particular attention.

In connection with the problem of improving the resistance of organic compounds to photochemical oxidation, questions concerning the efficiency of the quenching of singlet oxygen and the mechanism of the action of quenching agents are considered here. A number of recent reviews[3-9] of the properties and reactions of singlet oxygen may be recommended.

II. KINETICS OF PHOTOCHEMICAL OXIDATION BY SINGLET OXYGEN

In photosensitised oxidation reactions the main source of singlet oxygen ($^1O_2$) is believed to be the reaction involving the quenching of the triplet state of the sensitiser ^3S by oxygen in the ground state $^3O_2$:

$$^3S + {}^3O_2 \rightarrow {}^1S_0 + {}^1O_2, \quad (1)$$

where $^1S_0$ is the ground singlet state of the photosensitiser. Other reactions are also known:

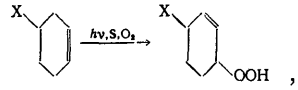
$$^1S_1 + {}^3O_2 \rightarrow {}^1S_0 + {}^1O_2, \quad (2)$$

$$^1S_1 + {}^3O_2 \rightarrow {}^3S + {}^1O_2, \quad (3)$$

where $^1S_1$ is the excited singlet state of the photosensitiser. However, the probability of these reactions is as a rule lower than that of reaction (1).

1. Characteristic Reactions of Singlet Oxygen

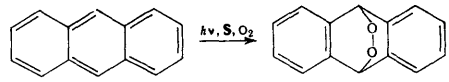
(a) Oxidation of olefins containing an allylic hydrogen atom to hydroperoxides. A characteristic shift of the double bond to the allylic position takes place in the reaction, for example:



(4)

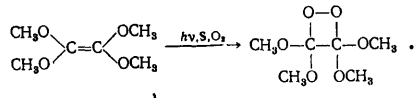
where X is a substituent.

(b) The addition of $^1O_2$ to diene hydrocarbons with formation of cyclic peroxides, for example:



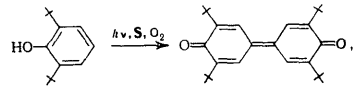
(5)

(c) Addition to olefins having an excess electron density at the double bond with formation of 1,2-dioxetans, for example:

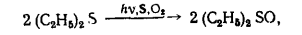


(6)

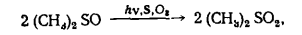
(d) The interaction of $^1O_2$ with reducing agents, for example phenols[10], sulphur-containing compounds[4,11,12], and amines[4,13-15], for example:



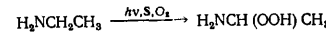
(7)



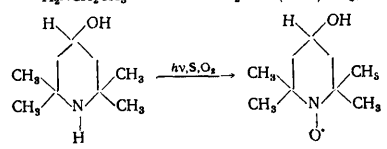
(8)



(9)



(10)



(11)

2. Kinetics of Oxidation in the Absence of Quenching Agents

The oxidation of compounds containing double bonds by singlet oxygen is hardly influenced by effective inhibitors of radical-chain oxidation processes, for example 2,6-di-t-butyl-4-methylphenol. On the other hand, tertiary aliphatic amines, which are typical $^1O_2$ quenching agents, do not inhibit the radical-chain oxidation of tetralin by molecular oxygen[16]. Thus, the oxidation by singlet oxygen of compounds with double bonds does not proceed via a radical-chain mechanism.

The kinetic scheme for the oxidation of an acceptor A can be formulated as follows:

$$^3S \xrightarrow[+O_2]{k_{O_2}} {}^1O_2 \begin{cases} \xrightarrow{k_d} {}^3O_2 \\ \xrightarrow[+A]{k_r} AO_2 \end{cases} \qquad (12)$$

Hence

$$\frac{1}{\Phi_{AO_2}} = \frac{1}{\Phi_{^1O_2}}\left(1 + \frac{k_d}{k_r}\cdot\frac{1}{[A]}\right), \qquad (13)$$

where Φ_{AO_2} and Φ^1O_2 are the quantum yields of the oxidation product AO_2 and of the formation of singlet oxygen respectively. Mechanism (12) can be used not only to describe reactions involving the addition of singlet oxygen to unsaturated compounds [reactions (4)–(6)] but also other reactions of singlet oxygen. Thus, it has been shown recently that the reactions of singlet oxygen with secondary and tertiary amines[15], in which a free valence is produced, are also fully described by scheme (12).

It is clear from Eqn. (13) that the yield of product is determined by the ratio of the rates of deactivation of $^1O_2$ and of the interaction of $^1O_2$ with the acceptor A. The maximum yield $\Phi_{AO_2} = \Phi^1O_2$ is reached under the following condition:

$$k_r[A] \gg k_d.$$

The use of Eqn. (13) makes it possible to determine k_r/k_d—the relative reactivity of the acceptor towards $^1O_2$—from the dependence of the quantum yield on the concentration of the acceptor.

3. Kinetics of Oxidation in the Presence of Quenching Agents

In the presence of a quenching agent Q for singlet oxygen, the kinetic scheme for the oxidation of the acceptor becomes

$$^3S \xrightarrow[+O_2]{k_{O_2}} {}^1O_2 \begin{cases} \xrightarrow{k_d} {}^3O_2 \\ \xrightarrow[+A]{k_r} AO_2 \\ \xrightarrow[+Q]{k_q} {}^3O_2 + Q \end{cases}, \qquad (14)$$

whence

$$\frac{1}{\Phi_{AO_2}} = \frac{1}{\Phi_{^1O_2}}\left[1 + \left(\frac{k_d}{k_r} + \frac{k_q[Q]}{k_r}\right)\cdot\frac{1}{[A]}\right]. \qquad (15)$$

It follows from Eqn. (15) that the variation of Φ_{AO_2} with [A] should be represented by a straight line when $1/\Phi_{AO_2}$ is plotted against 1/[A], and the parameters k_r/k_d and k_r/k_q, characterising the relative reactivities of the acceptor and the quenching agent in relation to $^1O_2$ respectively, may be determined from the dependence of the slope on [Q].

In the kinetic schemes (12) and (14) it was assumed that $\Phi^1O_2 = \Phi^3S$. However, these quantities are not equal when A or Q interacts with ^3S. If, for example, Q quenches only ^3S (with a rate constant k_Q) and not $^1O_2$, then

$$\frac{1}{\Phi_{AO_2}} = \frac{1}{\Phi_{^3S}}\left(1 + \frac{k_q[Q]}{k_{O_2}[O_2]}\right)\left(1 + \frac{k_d}{k_r[A]}\right). \qquad (16)$$

Like Eqn. (15), Eqn. (16) represents a linear plot of $1/\Phi_{AO_2}$ against 1/[A]. However, in contrast to Eqn. (15), the intercept on the ordinate axis depends on [Q]. Furthermore, the slope of the plot defined by Eqn. (16) depends on $[O_2]$. Quenching of the triplet state of the photosensitiser can be distinguished from the quenching of singlet oxygen by means of these features.

The use of Eqns. (13) and (15) makes it possible to obtain the kinetic parameters k_r/k_d and k_q/k_d from the concentration variation of the quantum yield and k_r/k_q from the concentration variation of the rate of oxidation.

4. The Efficiency of Quenching Agents in Liquid-Phase Systems

In order to obtain absolute values of the kinetic constants characterising the efficiency of quenching agents and the reactivities of singlet oxygen acceptors, the kinetics of the oxidation reactions were investigated and measurements were made of the lifetimes of singlet oxygen in various solutions using flash photolysis[17–25].

Table 1. The constants k_d for various solvents.

Solvent	$10^{-3}k_d$, s^{-1}	Refs.	Solvent	$10^{-3}k_d$, s^{-1}	Refs.
Water	350	21	Cyclohexane	41	21
D_2O	350	21	Isooctane	40	22
Dimethylformamide	140	19	4:1 benzene–methanol	38	23
Methanol	100	21	Pyridine	31	23
	100	11	t-Butyl alcohol	30	23
	(a) 88	23	Dioxan	29	23
	(b) 97	23	Benzene	28	21
	200	19		80	19
1:1 Methanol–t-butyl alcohol	(c) 60	26	Acetonitrile	23	21
			Chloroform	12	21
Ethanol	58	21	Methylene chloride	7,3	22
	180	19	Carbon tetrachloride	1	21
n-Butyl alcohol	52	23			
4:1 Bromobenzene–methanol	43	23			

Note: a) and b) Methylene Blue and Rose Bengal were used respectively as photosensitisers; c) estimated from data in this Table and those of Higgins et al.[26]

It follows from mechanism (12) that there is competition between reactions involving the spontaneous destruction of $^1O_2$ and its interaction with acceptors. Table 1 shows that the values of k_d change very markedly on passing from one solvent to another. These constants are large and correspond to the lifetimes of $^1O_2$ in various solvents ranging from a microsecond to a millisecond. For effective oxidation, the oxygen must be able to react with acceptors during this period; consequently, the rate constant k_r must also be large. It is seen from Eqn. (13) that the fraction η of singlet oxygen interacting with the acceptor is 0.5 when $k_d = k_r[A]$ or

$$[A]_{\eta=0.5} = \frac{k_d}{k_r}. \qquad (17)$$

Eqn. (17) shows clearly at which acceptor concentration or for which values of the kinetic constants the spontaneous destruction of oxygen and the oxidation process proceed at comparable rates.

Table 2. The constants k_r for the reactions of singlet oxygen with olefins in solutions.

Compound	Solvent	k_r, litre mole^{-1} s^{-1}	Refs.
Non-1-ene	Methanol	(a) 7.5×10^2	27
4-Methylcyclohexene	Methanol	(a) 5×10^3	27
Cyclohexene	Methanol	(a) 7.5×10^3	27
2,3-Dimethylbut-1-ene	Methanol	(a) 1.5×10^4	27
Hex-2-ene	Methanol	(a) 6.5×10^4	27
Cyclopentene	Methanol	(a) 1×10^5	27
2,3-Dimethylcyclohexene	Methanol	(a) 3.5×10^5	27
1-Methylcyclohexene	Methanol	(a) 3×10^5	27
2-Methylbut-2-ene	1:1 Methanol–t-butyl alcohol	(b) 5×10^5	26
2-Methylpent-2-ene	Pyridine	(c) 6×10^5	28
p-Chlorotrimethylstyrene	t-Butyl alcohol	(d) 6×10^5	26
1-Methylcyclopentene	Methanol	(e) 8×10^5	29
Cyclohexadiene	1:1 Methanol–t-butyl alcohol	(b) 5×10^5	26
	Methanol	(a) 2.5×10^6	27
Cyclopentadiene	Methanol	(e) 1×10^7	30
1,2-Dimethylcyclohexene	Methanol	(e) 3×10^7	30
2,3-Dimethylbut-2-ene	Methanol	(a) 2×10^7	27
	Methanol	(a) 4×10^7	27
	Methanol	(e) 3×10^7	30
	Methanol	(e) 2×10^7	31
	Methanol–t-butyl alcohol	(b) 2×10^7	26
β-Carotene	Benzene	(f) 1.3×10^{10}	25
	Benzene	(f) 2×10^{10}	21
	4:1 Benzene–methanol	(f) 3×10^{10}	11

Note: a) Recalculated directly from relative values based on $k_r = 4 \times 10^7$ for 2,3-dimethylbut-2-ene; b) recalculated on the basis of $k_d = 6 \times 10^4$; c) recalculated on the basis of $k_q = 1 \times 10^7$ for triethylamine; d) recalculated on the basis of $k_d = 3 \times 10^4$; e) recalculated on the basis of $k_d = 1 \times 10^5$; f) the value of k_q.

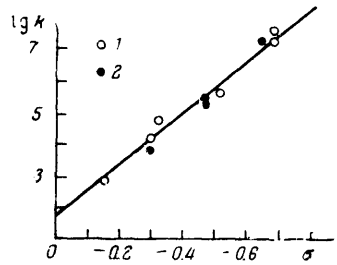


Figure 1. Dependence of the logarithms of the rate constants for the reactions of olefins with singlet oxygen on the σ_n constants of the substituents; 1) acyclic olefins; 2) cyclohexene derivatives.

The values of k_r for certain olefins and aromatic compounds are listed in Tables (2) and (3). It is seen that they depend very markedly on the structure of oxygen acceptors. On the other hand, the dependence of k_r on the nature of the solvent is comparatively slight. Fig. 1 shows that the influence of substituents on k_r can be described by the Hammett equation†.

† In the example quoted, the σ_n constants of the substituents were used to construct the correlation plot.

The rate constants for the quenching of singlet oxygen by amines and their derivatives as well as by organometallic compounds are compiled in Tables 4 and 5. The rate constants for quenching by β-carotene are listed in the last rows of Table 2; the tables show that the rate constants for quenching by β-carotene and certain organometallic compounds are equal or close to diffusional constants. The constants k_q are very large for many amines. They can be described by the Hammett equation (see, for example, Young and coworkers [39,40]).

Table 3. The constants k_r for the reactions of singlet oxygen with aromatic compounds in solutions.

Compound	Solvent	k_r, litre mole^{-1} s^{-1}	Refs.
Anthracene	Benzene	(a) 7×10^4	33
	Benzene	(a) 5×10^4	34
	8:1 Benzene–ethanol	(b) 9×10^4	58
9,10-Diphenylanthracene	Benzene	(a) 5×10^5	33
	Benzene	(a) 6×10^5	34
	Pyridine	(c) 8×10^6	35
Naphthacene	Methylene chloride	1.8×10^7	36
	8:1 Benzene–ethanol	(b) 7×10^6	15
9,10-Dimethylanthracene	Pyridine	(c) 4×10^6	35
Rubrene	Pyridine	(c) 9×10^7	35
	—	7×10^7	22
	Benzene	(a) 3×10^7	37
	Benzene	(a) 2×10^7	33
2-Phenylfuran	Methanol	(d) 6×10^7	31
2-Methylfuran	Methanol	(d) 9×10^7	31
2,5-Diphenylfuran	Methanol	(d) 1×10^8	31
	Methanol	4.5×10^7	23
2,5-Dimethylfuran	Methanol	(d) 4×10^8	31
	Methanol	(d) 1×10^8	30
	1:1 Methanol–t-butyl alcohol	(e) 5×10^7	26
	Water	1.5×10^9	38
1,3-Diphenylisobenzofuran	t-Butyl alcohol	0.6×10^9	23
	4:1 Bromobenzene–methanol	0.7×10^9	23
	n-Butyl alcohol	0.8×10^9	23
	4:1 Benzene–methanol	0.9×10^9	23
	4:1 Benzene–methanol	1.5×10^9	25
	Methanol	1.3×10^9	23
	Methanol	0.7×10^9	17
	Pyridine	2.1×10^9	23

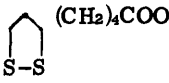
Note: a) Recalculated on the basis of $k_d = 2.8 \times 10^4$; b) recalculated on the basis of $k_r = 4 \times 10^7$ for dimethylanthracene; c) recalculated on the basis of $k_r = 4 \times 10^7$ for 2,3-dimethylbut-2-ene; d) recalculated on the basis of $k_d = 1 \times 10^5$; e) recalculated on the basis of $k_d = 6 \times 10^4$.

In contrast to the constants k_r for olefins and aromatic compounds, the constants k_q for amines can depend markedly on the solvent. However, the nature of the dependence is determined by the structure of the amine. For example, *NN*-dimethylaniline and methylamine quench $^1O_2$ in methanol more effectively than in Freon 113 ($C_2Cl_3F_3$) by three orders of magnitude. On the other hand, the rate constants for quenching by diethylamine and triethylamine differ only by a factor of several units in the same solvents.

Above it was already noted that phenols, azides, and sulphur-containing compounds can behave as quenching agents for singlet oxygen. The kinetic constants for a very small number of compounds of these classes are known. Thus $k_q = 2.2 \times 10^8$ for NaN_3 in methanol[45], $k_q \leq 7 \times 10^7$‡ for hydroquinone in a 4:1 benzene–methanol

‡ Quenches also ^3S.

mixture[11], $k_q = 6 \times 10^6$ for diethyl sulphide in the same solvent[11], and $k_r = 1 \times 10^8$ § for lipoic acid



in benzene[37].

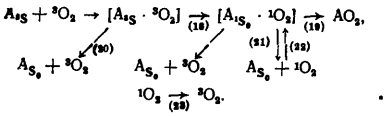
Table 4. The rate constants k_q for the quenching of singlet oxygen by amines and their derivatives in the liquid phase.

Compound	Solvent	k_q, litre mole^{-1} s^{-1}	Refs.
Isopropylamine	Methanol	4.5×10^4	39
Cyclohexylamine	Methanol	8×10^4	39
Pyrrolidine	Methanol	2×10^5	39
Benzylamine	Methanol	2.5×10^5	39
t-Butylamine	Methanol	6.5×10^5	39
Piperidine	Methanol	9×10^5	39
Piperazine	Methanol	1×10^6	39
Nicotine	Methanol	(b) 1.5×10^6	28
Diethylamine	Methanol	2×10^6	39
Diphenylamine	Methanol	6×10^6	39
Diazabicyclo[2,2,2]octane (DABCO)	Methanol	7.5×10^6	39,40
	4:1 Benzene–methanol	1.5×10^7	11
	n-Butyl alcohol	4.5×10^6	40
	Isooctane	3.5×10^7	22
	Methylene chloride	3.5×10^7	22
Triethylamine	Methanol	(c) $1.\times 10^7$	40
4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical	1:1 Benzene–methanol	(b) 1.5×10^7	41
4-Hydroxy-1,2,2,6,6-pentamethylpiperidine	Methylene chloride	(d) 5×10^7	36
1,2,2,6,6-Pentamethylpiperidin-4-yl-nonadecanoate	1:1 Benzene–ethanol	(e) 3×10^7	42
1,2,2,6,6-Pentamethylpiperidin-4-yl-(3,5-di-t-butyl-4-hydroxyphenyl)-β-propionate	1:1 Benzene–ethanol	(e) 7×10^7	42
	Methanol	1×10^8	39
NN-Dimethylaniline	$C_2Cl_3F_3$ (Freon 113)	(a) 7.5×10^7	23
		2×10^5	20
β-Naphthylamine	Ethanol	(a) 8×10^7	43
		3.5×10^8	44
N-Isopropyl-*N'*-phenyl-*p*-phenylenediamine	Isooctane	(f) 6×10^8	43
NNNN'-Tetramethylphenylenediamine	Methanol	6×10^8	39
N-Cyclohexyl-*N*-phenyl-*p*-phenylenediamine	Ethanol	(g) 5×10^8	–
	2-Butoxyethanol	(f) 5×10^9	22
o-Phenylenediamine	Ethanol	(f) 3×10^8	43

Note: a) solvent not indicated; b) obtained on the basis of (k_q)DABCO $= 1 \times 10^7$; c) according to Smith[28], in pyridine (k_q)DABCO $\simeq (k_q)$triethylamine; d) obtained on the basis of $k_d = 7.3 \times 10^3$; e) estimated from Felder and Schumacher's data[42] on the basis of (k_q)DABCO $\simeq 1 \times 10^7$; f) recalculated from the relative rates on the assumption that $k_q = 5 \times 10^8$ for *N*-cyclohexyl-*N*-phenyl-*p*-phenylenediamine; g) the rate constants have been adopted on the basis of data in the preceding two rows; h) obtained on the basis of $k_d = 4 \times 10^5$ for 2-butoxyethanol[22].

5. The Influence of the Polymer Matrix on the Kinetics of the Quenching Processes and Their Rate Constants

In the kinetic schemes for oxidation by singlet oxygen considered above, it was assumed that $^1O_2$ is formed as a result of interaction with the photosensitiser. However, photochemical reactions in which singlet oxygen is formed in a reaction involving the substance being oxidised (excited by light) and then itself interacts with the latter are well known and have been investigated in detail[46]:



(18)-(23)

Table 5. The rate constants k_q for the quenching of singlet oxygen by organometallic compounds in the liquid phase*.

Quenching agent	Solvent	k_q, litre mole^{-1} s^{-1}	Refs.
Nickel(II) 3,5-di-t-butyl-4-hydroxybenzoate	1:1 Benzene–ethanol	8×10^6**	42
Ferrocene	Benzene	9×10^6	25
Bismuth(III) dimethyldithiocarbamate	Methylene chloride	1×10^7	36
Nickel(II) bis(butyl-3,5-di-t-butyl-4-hydroxybenzylphosphonate)	Methylene chloride	1.4×10^7	22
	1:1 Benzene–ethanol	8×10^6**	42
	Methylene chloride	6×10^6	36
Zinc(II) bis(n-butyldithiocarbamate)	Carbon disulphide	2×10^7	24
Nickel(II) acetylacetonate	Methylene chloride	7.5×10^7	44
Nickel(II) bis[2,2'-thiobis(4-t-octylphenoxide)]	Isooctane	1.3×10^8	22
(n-Butylamine)nickel(II) bis[2,2'-thiobis(4-t-octylphenoxide)]	Carbon disulphide	1.5×10^8	24
	Isooctane	1.8×10^8	22
Nickel(II) bis[2,2'-thiobis-(4-t-octylphenoxide)]	Carbon disulphide	5×10^8	24
Cobalt(II) diisopropyldithiocarbamate	Methylene chloride	1.9×10^9	44
Nickel(II) bis-(2-hydroxy-5-methoxyphenyl-*N*-n-butylaldimine)	Isooctane	2.4×10^9	44
Bis-(2-hydroxy-4-methylphenyl undecyl ketone oximato)nickel(II) (Negopex B)	Benzene	2.7×10^9	25
Bis-(2-hydroxy-4-methylacetophenone oximato)nickel(II) (Negopex A)	Benzene	3×10^9	25
Palladium(II) N-hydroxyformheptadecylimidoyl-4-t-butylphenoxide	Benzene	6×10^9	25
Nickel(II) diisopropyldithiocarbamate	Methylene chloride	3.4×10^9	44
Iron(III) diisopropyldithiocarbamate	Methylene chloride	3.8×10^9	44
Nickel(II) diisopropyl phosphorodithioate	Methylene chloride	5.4×10^9	44
Nickel(II) di-n-butyldithiocarbamate	Carbon disulphide	4×10^9	24
	Isooctane	7×10^9	22
	Methylene chloride	3.5×10^9	36

Note: * Several new studies, in which the values of k_q were determined for a large number of transitional metal complexes, have been published recently[75-77]; the most effective of these quench singlet oxygen with nearly diffusional rate constants[77].
** Estimated from Felder and Schumacher's data[42] on the basis of (k_q)DABCO $= 1 \times 10^7$.

Here singlet oxygen is formed in a reaction with the acceptor A_{3_S} in the excited triplet state. A characteristic feature of this scheme is that the complex $A_{S_0}.^1O_2$, the precursor of the product AO_2, is formed in two different reactions: in reaction (18) within a cage, designated by brackets (at the point of encounter of A^3_S and $^3O_2$), and in reaction (22) between an unexcited acceptor molecule and singlet oxygen which has emerged from the cage into the bulk phase.

It is readily seen that, for the specified values of the kinetic constants, the kinetic law governing the reaction is determined by the concentration of A. In the region of very low values of [A] the complex $A_{S_0}.^1O_2$ is formed exclusively via reaction (18) and the reaction involving the formation of AO_2 is of first order with respect to the substance oxidised.

§ It has not yet been established whether lipoic acid reacts with $^1O_2$ or whether it behaves as a quenching agent[37].

The $^1O_2$ species which have emerged from the cage [reaction (21)] are destroyed in reaction (23) without having sufficient time to react with A [reaction (19)], since the distances between the species A are very small. In the region of very high concentrations [A], the complex $AS_0.^1O_2$ is formed via reactions (18) and (22). Having emerged from the cage each species $^1O_2$ reacts with A, and therefore the quantum yield is independent of [A]. In the region of moderate concentrations the complex $AS_0.^1O_2$ is also formed via reactions (18) and (22), but the quantum yield increases with increase of [A]; the order of the reaction with respect to the substance oxidised is intermediate between first and second.

It has recently been shown[47-49] that, when the photochemical reaction is carried out in a polymer matrix, the kinetics are different: the order of the reaction with respect to the substance oxidised is much higher than the second and the reaction is rapidly retarded. As an example, Fig. 2 presents kinetic curves for the variation of the concentration of anthracene dissolved in a polystyrene film, in photochemical oxidation under the influence of light at a wavelength of 365 nm in air at room temperature. If irradiation is stopped at some instant, the specimen is heated at 95–100°C for 15–20 min in the dark, cooled to room temperature, and then irradiation is continued, the reaction starts again (curve *2*) and is again retarded under the conditions of continuous irradiation. With periodic and fairly frequent heating after irradiation (thermal activation), the reaction is faster (curve *3*) and follows liquid-phase kinetics.

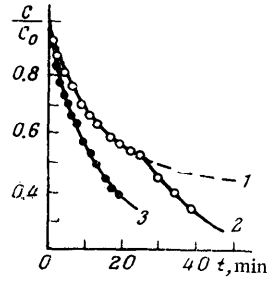


Figure 2. Variation of the concentration of anthracene C (initial concentration $C_0 = 2.8 \times 10^{-3}$ M) in a polystyrene film during irradiation in air with light at a wavelength of 365 nm: 1) continuous irradiation; 2) repeated irradiation after 10-min heat treatment at 100°C; 3) periodic conditions: after the determination of each experimental point indicated on the curve, the system was heated at 100°C for 10 min.

In general terms, the effect involving the rapid inhibition and arrest of the reaction can be accounted for by the fact that the polymer is an inhomogeneous system and therefore the probabilities of photochemical oxidation are not the same at various points within it. Species located at the points where the quantum yield is highest react initially, the quantum yield decreasing gradually in the course of the reactions. In order to describe the inhomogeneity of the polymer and the influence of the polymer matrix on the oxidation kinetics, a model has been proposed[48,49] according to which the substrate molecules in the polymer are located together with oxygen molecules in cages which differ in their permeability to oxygen. Within the framework of this model, the probability of the photochemical reaction is higher at low substrate concentrations for low permeability of the cage, since an increase of the lifetime of the $A-^1O_2$ pair corresponds to a decrease of permeability. On the other hand, at high concentrations of the acceptor A in the region corresponding to the preferential occurrence of the bimolecular reaction, species in cages with a high permeability react first. In this model the inhibition of the reaction is attributed to the gradual consumption of the species located in the regions of the polymer matrix more favourable for the reaction and thermal activation is accounted for by the restoration of the initial distribution of the substrate among the cages with different permeabilities as a result of the increase of the intensity of molecular motion at elevated temperatures. On the basis of the concepts described above, a quantitative theory of such self-inhibiting processes, involving oxidation by singlet oxygen, has been devised[49] for various selected laws governing the distribution of the cages with respect to permeability.

Table 6. Comparison of the kinetic constants for a solution (in methylene chloride) and a polymer (polystyrene) at room temperature[36].

Compound	Methylene chloride		Polystyrene		$\frac{(k_q/k_d)L}{(k_q/k_d)S}$	$\frac{(k_r/k_d)L}{(k_r/k_d)S}$
	$k_q \cdot k_d$, litre mole^{-1}	k_r/k_d, litre mole^{-1}	k_q/k_d, litre mole^{-1}	k_r/k_d, litre mole^{-1}		
β-Carotene	$3.6 \cdot 10^6$	—	$8 \cdot 10^3$	—	450	—
Nickel dibutyldithiocarbamate	$4.7 \cdot 10^5$	—	$1.1 \cdot 10^3$	—	420	—
Rubrene	—	$9 \cdot 10^3$	—	70	—	140
4-Hydroxy-1,2,2,6,6-pentamethylpiperidine	$7.3 \cdot 10^3$	—	$4.2 \cdot 10^2$	—	17	—
Tetracene	—	$2.5 \cdot 10^3$	—	50	—	50
Bismuth dimethyldithiocarbamate	$1.5 \cdot 10^3$	—	$2.4 \cdot 10^2$	—	6	—
Nickel(II) bis-(3,5-di-t-butyl-4-hydroxybenzylphosphate)	$5.1 \cdot 10^2$	—	$1.7 \cdot 10^2$	—	3	—
Anthracene	—	1.8	—	0.25	—	7

Note: The subscripts L and S denote the liquid and solid phases respectively (Ed. of Translation).

The first values of the rate constants for the quenching and oxidation processes[36] showed that the polymer matrix has a significant influence on these processes (Table 6). The correlation between the constants in the liquid and solid phases and the levelling of the kinetic constants for the solid phase are the most striking features. For example, the highest value of k_q/k_d for polystyrene is 50 times higher than the lowest value, whereas the corresponding values for methylene chloride differ by a factor of 5000. In other words, the efficiencies of various quenching agents differ much less in the solid phase than in the liquid phase. A similar levelling phenomenon was observed previously for the reactivities of various antioxidants in relation to peroxy-radicals in solid polystyrene[50]. In this case the levelling was accounted for by the dependence of the rate of the chemical reaction both on the reactivity of the antioxidants and on the mobility of the reactants in the polymer matrix. It is at present difficult to say whether this mechanism can be extended also to the $^1O_2$ quenching reactions, since there are few experimental data.

The data in Table 6 create the impression that the efficiency of the most powerful quenching agent is disproportionately reduced in the polymer matrix. Experiments with rubrene, tetracene, and anthracene also revealed that, on passing from the liquid to the solid phase, the values of k_q decrease less than those of k_r.

In polystyrene the quenching of $^1O_2$ by nickel(II) dibutyldithiocarbamate, bismuth(III) dimethyldithiocarbamate, and the nickel(II) salt of 3,5-di-t-butyl-4-hydroxybenzylphosphonic acid in polystyrene is not accompanied by a change in the absorption spectra of these substances. Their concentrations hardly change, which means that in both the solid polymer and in solutions the compounds quench $^1O_2$ via a physical mechanism.

III. THE QUENCHING MECHANISM

1. Quenching via Charge Transfer

Ideas about the quenching mechanism have been developed [51] on the basis of the observed correlation between the values of k_q for the gas phase and the ionisation potentials I_p of the quenching agents (amines). Later similar correlations were found for quenching by sulphur-containing compounds in the gas phase (Table 7) and by amines in the liquid phase (Table 8).

Table 7. The ionisation potentials of sulphur-containing compounds and the rate constants for the gas-phase quenching of $^1O_2$ by these compounds [12].

Quenching agent	I_p, eV	k_q, litre mole^{-1} s^{-1}
Methanethiol	9.44	$2.3\cdot10^8$
Dimethyl disulphide	9.05	$1.0\cdot10^8$
Thiophen	8.86	$3.6\cdot10^7$
Dimethyl sulphide	8.69	$1.6\cdot10^8$
Diethyl sulphide	8.42	$4.1\cdot10^8$

These correlations led to the conclusion that quenching takes place via the formation of a charge-transfer complex in which $^1O_2$ behaves as the electron acceptor [51]. This complex is formed only at the instant of collision and is not in equilibrium with the reactants. This is evident from the fact that the rate constant for the quenching of $^1O_2$ by amines (A) in the gas phase increases with temperature [51]. For an "equilibrium" complex, one might have expected the opposite relation, since an increase of temperature leads to a decrease of its equilibrium concentration.

The overall equation for the quenching process

$$^1O_2 + {}^1A_0 \rightarrow {}^3O_2 + {}^1A_0 \qquad (24)$$

shows that it takes place with a change in the overall spin and therefore its probability should be reduced, according to Wigner's rule, particularly since the system considered here does not contain either heavy atoms or paramagnetic quenching agents or catalysts, which reduce the degree of prohibition as a result of spin–orbit interaction. However, it is believed [51] that, in a $^1O_2$–quenching agent system in the singlet state, even weak spin–orbit interactions are sufficient to reverse the spin.

The initial state of the $^1O_2$–$^1A_0$ system can be regarded as a superposition of the unperturbed singlet state of the complex $^1O_2.{}^1A_0$ and the singlet state of the charge-transfer complex $\lambda(^1CT)$, where λ indicates to what extent the compound $^1O_2.{}^1A_0$ has the properties of a charge-transfer complex. Accordingly, the final state may be represented as a superposition of the triplet state of the complex $^3O_2.{}^1A_0$ and the charge-transfer triplet state $\mu(^3CT)$. Since the singlet and triplet states of the charge-transfer complex differ little in energy, even a weak spin–orbit interaction between the singlet and triplet charge-transfer states (involving, for example, nitrogen or sulphur atoms) can convert the initial and final states into states with "mixed" multiplicity and thus allow at least partially the transition

$$^1[^1O_2 \cdot {}^1A + \lambda\,(^1CT)] \rightarrow {}^3[^3O_2 \cdot {}^1A + \mu\,(^3CT)]. \qquad (25)$$

From this point of view, the observed correlation between the quenching rate constants and the ionisation potentials can be accounted for by the increase of the contribution of the charge-transfer states in the initial and final systems and by the corresponding increase of the mixing of states with different multiplicities [51].

Table 8. The rate constants for the quenching of $^1O_2$ by amines in methanol solution [39].

Quenching agent	I_p, eV	$k_q\cdot10^{-8}$, litre mole^{-1} s^{-1}	Quenching agent	I_p, eV	$k_q\cdot10^{-8}$, litre mole^{-1} s^{-1}
Cyclohexylamine	8.86	0.08	1,4-Piperazine	8.21	1.2
t-Butylamine	8.83	0.66	Diethylamine	8.01	1.9
Isopropylamine	8.72	0.05	Piperidine	7.85	0.92
Benzylamine	8.64	0.26	DABCO	7.52	7.3
Pyrrolidine	8.30	2.1	Triethylamine	7.50	9.3
Hexamethylenetetramine	8.26	0.20	*N*-Methylaniline	7.30	27
			NN-Dimethylaniline	7.10	120

The hypothesis that the $^1O_2$ quenching processes proceed via charge-transfer states was confirmed further in a study [40] of the quenching of $^1O_2$ and of the fluorescence of aromatic hydrocarbons by different amines, which takes place in an electronically excited charge-transfer complex formed by the aromatic compound and the amine. A linear correlation between the logarithm of the quenching rate constant and a quantity characterising the affinity of the excited singlet molecule for oxygen was demonstrated [40] for each amine investigated. It is of interest that the point characterising the rate constant for the quenching of singlet oxygen also fits on the straight line plotted for data on the quenching of the fluorescence of the singlet states of aromatic compounds.

2. Quenching via Energy Transfer

The quenching of $^1O_2$ via energy transfer proceeds in accordance with the equation

$$^1O_2 + {}^1Q_0 \rightarrow {}^3O_2 + {}^3Q_0, \qquad (26)$$

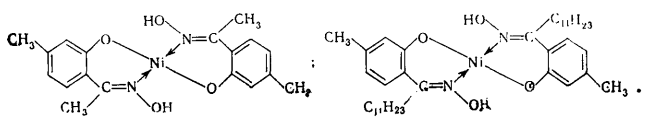
where $^1Q_0$ and $^3Q_0$ are the ground singlet and triplet states of the quenching agent. This process does not require a change in the overall spin and is therefore allowed. The change in the multiplicity of the energy levels of oxygen alone is forbidden by Wigner's rule and its probability is

therefore low. In order that reaction (26) should have a high rate constant, it is necessary that the condition $E^1O_2 \geqslant E^3Q_0$ holds for the energies of the corresponding states of oxygen and the quenching agent. Since E^1O_2 is only 22.6 kcal mole^{-1}, the energy of the triplet level of the effective quenching agent for $^1O_2$ must be very low.

The first investigation of a quenching agent operating via an energy transfer mechanism was carried out by Foote et al.,[11] who observed a very marked (20-fold) decrease of the rate of photosensitised oxidation of 2-methylpent-2-ene (0.1 M) in the presence of a β-carotene concentration smaller by a factor of 1000. The efficiency of this quenching agent surpasses all others which have been investigated. The quenching process results in the *cis–trans* isomerisation of β-carotene. It was known that β-carotene quenches the low-energy (29 kcal mole^{-1}) triplet state of chlorophyll with a diffusional rate constant, i.e. $E^3Q_0 \leqslant 29$ kcal mole^{-1}.[52] The efficiency of the quenching of $^1O_2$ decreases when β-carotene, which contains a system of 11 conjugated bonds, is replaced by other quenching agents of this class but with shorter conjugated chains. The compound with five conjugated bonds altogether failed to inhibit the oxidation reaction.

Although the energy of the triplet level of β-carotene was unknown, Foote et al.[11] concluded on the basis of these findings that the quenching of $^1O_2$ by β-carotene proceeds via an energy transfer mechanism with a diffusional rate constant. The value of k_q which they adopted is listed in Table 2. The constant k_d calculated from it for methanol proved to be 1×10^5 s^{-1}, which agrees very well with subsequent direct measurements (Table 1).

The quenching of $^1O_2$ by the transfer of the electronic excitation energy to β-carotene was demonstrated by a direct method in a study[25] where singlet oxygen, obtained by laser flash photolysis induced the formation of the triplet state of β-carotene, and the kinetics of its accumulation and destruction were investigated. The constant k_q was found to be close to the value obtained[11] on the hypothesis that the quenching proceeds in each encounter between $^1O_2$ and β-carotene. Other quenching agents with low triplet levels were discovered by Farmilo and Wilkinson[25], for example:



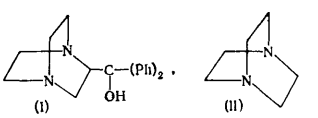
These quench $^1O_2$ with near diffusional rate constants—3.0×10^9 and 2.7×10^9 respectively. The quenching by these compounds apparently proceeds via the energy transfer mechanism. This can also be confirmed by the fact that, for example, the palladium complex having the same structure but with a higher triplet level quenches with a significantly lower rate constant (6×10^7).[25] Carlsson et al.[44] obtained $k_q > 10^9$ litre mole^{-1} s^{-1} (Table 5) for a number of organometallic compounds and at least some of them presumably function as energy acceptors. For less effective organometallic compounds, it has not so far been possible to establish any correlation between their geometry, properties, and ability to quench $^1O_2$.[22] However, in later investigations it was stated that diamagnetic nickel chelates quench $^1O_2$ and also the triplet state of ketones more effectively than the paramagnetic chelates[54]. It has been suggested[22] that the quenching mechanism may involve the formation of complexes of different kinds between the organometallic compounds and $^1O_2$.

IV. CHEMICAL REACTIONS OF QUENCHING AGENTS

The data presented above show that substances with low ionisation potentials, which are typically reducing agents, and substances with a low triplet level are able to quench singlet oxygen. Presumably the reducing agents react with singlet oxygen, since it is an oxidising agent and the excited states formed after energy transfer to the triplet levels of the quenching agents react with both $^1O_2$ and $^3O_2$. The literature data[12,16] showing that certain quenching agents, for example diazabicyclo[2,2,2]octane (DABCO), ethyldiisopropylamine, *NNNN'*-tetramethylethylenediamine, and allylamine in bromobenzene and thiophen and methanethiol in the gas phase do not react at all with $^1O_2$ should probably be understood as merely an indication that the rate constants for the chemical interactions of these compounds with $^1O_2$ are low in absolute magnitude and are much smaller than the quenching rate constants.

Apart from the reaction with $^1O_2$, in photosensitised oxidation processes the quenching agent may interact with the triplet state of the photosensitiser. The reaction of the quenching agent (with $^1O_2$ or ^3S) which becomes dominant under the given conditions depends on the nature of the photosensitiser, the quenching agent, the medium, and the concentrations of the quenching agent and oxygen.

The possible involvement of the triplet states of sensitisers in the photochemical oxidation reactions of quenching agents belonging to the class of amines has been examined most fully and proved by Batholomew and Davidson[55,56]. In the first of these investigations, a study was made of the composition of the product and the quantum yields of the absorption of oxygen and the formation of products in the oxidation of primary, secondary, and tertiary amines as well as *N*-alkylanilines photosensitised by benzophenone were measured. Aliphatic amines reacted with formation of carbonyl compounds (after the rupture of the C–N bond) and imines. *N*-Alkylanilines formed products resulting from the rupture of the C–N bond. The involvement of amines in the direct reaction with ^3S was demonstrated by measurements of the quantum yields Φ_{O_2} of the absorption of oxygen. The values of Φ_{O_2} for tertiary amines, for example triethylamine (0.1 M in benzene) and tribenzylamine (0.1 M in benzene), exceed unity, although these compounds are known to be powerful quenching agents for $^1O_2$. Additional confirmation was obtained by investigating the composition of the products. *In vacuo* and in the presence of oxygen, the dealkylation reaction characteristic of *N*-alkylanilines takes place and the same product (I) of the reaction of DABCO (II) is formed:



In the second study[56], where the same reactions were investigated but dyes were employed as photosensitisers, the formation of the same products was observed, i.e. the dyes behave like benzophenone, which acts typically as a dehydrogenating agent. It was shown that the most readily oxidisable tertiary amines effectively decolorise the dye in the absence of oxygen and that the rate of photochemical oxidation increases with decrease of the concentration of oxygen. Both these findings support the involvement of amines in the direct reaction with ^3S.

Another mechanism, involving the direct interaction of amines with $^1O_2$, was examined and its validity was proved

in other investigations[14,15]. The authors observed a new reaction of $^1O_2$—the formation of stable nitroxy-radicals in the sensitised oxidation of secondary and tertiary amines: homotropine, 1,1′- and 1,2′-diadamantylamines, 2,2,6,6-tetramethyl- and 1,2,2,6,6-pentamethyl-4-hydroxypiperidines, 4,4′-dimethoxy-, 4,4′-dicumenyl, and 4,4′-di-t-octyl-diphenylamine, and 2,7-di-t-octylphenothiazine. The oxidation was observed in liquid (8 : 1 benzene–ethanol mixture, concentration 10^{-3}–10^{-2} M) and solid [polystyrene, poly(methyl methacrylate), and polycarbonate] solutions irradiated with light corresponding to the absorption bands of the photosensitisers—Bengal Rose or Methylene Blue. The degree of conversion of amines in this process depends on the structure of the amine and the stability of the nitroxy-radicals and can reach several tenths. The involvement of $^1O_2$ in this reaction is confirmed by the lack of dependence of the measured rate constant for the formation of nitroxy-radicals on the oxygen concentration and the nature of the photosensitiser and also by the inhibition of the oxidation reaction by $^1O_2$ quenching agents, the efficiency of which may be calculated beforehand from the literature values of k_q.

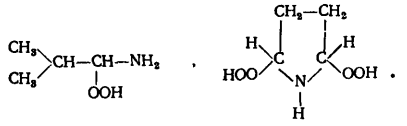
In most studies on the photosensitised oxidation of amines, the composition of the products and the rates and stoichiometries of the reactions are considered, but not the mechanisms of the primary photochemical processes. Below we shall therefore speak of the reactions of quenching agents in photosensitised oxidation processes without discussing specific mechanisms.

Table 9. The stoichiometry of the photosensitised oxidation of amines.

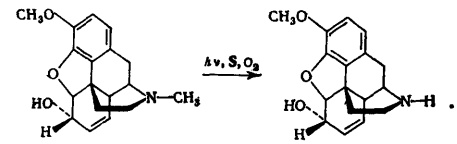
Amine	Absorption of O_2, moles per mole of substrate	References
Nicotine	1*	57
Methyl-, n-propyl-, isopropyl-, isobutyl-, and isopentyl-amines	1	13
Diethylamine, piperidine, pyrrolidine	2	13
Triethylamine	2.6	13
	3.06	28
t-Butylamine	No reaction	13

* Reaction in aqueous solution. The pyrrolidine component of the molecule is oxidised. In methanol three moles of O_2 are absorbed[32] instead of one.

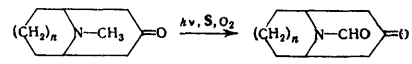
The data on the stoichiometry of the photosensitised amine oxidation reactions are presented in Table 9. According to Schenck[13], the formation of α-aminohydroperoxides corresponds to this stoichiometry, for example:



Accordingly, t-butylamine, which does not contain hydrogen atoms in the α-position, does not undergo photosensitised oxidation. However, as stated above, the photosensitised reactions can lead to other products—imines, carbonyl compounds, and products of the dealkylation of N-alkylamines[55,56]. Products of this type have been detected together with the formation of hydroperoxides in photosensitised oxidation reactions of primary, secondary, and tertiary n-butylamines.[57] Demethylation reactions have been observed in the photosensitised oxidation of steroid derivatives of the type $R-N(CH_3)_2$ (R = steroid residue)[58] and codeine[59]:



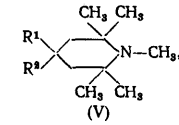
In the reactions of the alkaloids[60] pseudopelletierine (III) and tropinone (IV) and the steroid derivatives $R-N(CH_3)_2$,[58] the N-methyl groups were found to be oxidised to N-formyl groups, for example:



(III) $n = 1$;
(IV) $n = 0$

There are as yet no literature data concerning the ability of these compounds to quench $^1O_2$; they should probably behave as strong quenching agents, like other tertiary amines.

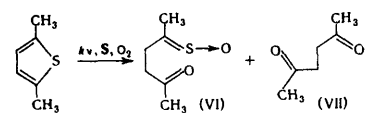
The absorption of oxygen by piperidine derivatives,



(V)

where $R^1 = R^2 = H$ or $R^1 = H$ and $R^2 = OH$, has been observed[41]. These compounds are probably oxidised fairly rapidly, since the rate of absorption of oxygen in the photochemical oxidation of 2-methylpent-2-ene (8×10^{-3} M), or 9,10-dimethoxyanthracene (8×10^{-3} M), or 9,10-dimethoxyanthracene (8×10^{-3} M) after the addition of compound (V) at a concentration of 5×10^{-2} M actually increases somewhat, although compounds (V) are known as quenching agents for $^1O_2$ (Table 4).

The absorption of oxygen and the formation of oxidation products were also observed in the presence of quenching agents of another class—sulphur-containing compounds. For example, analysis of the products of the oxidation of dimethyl and diethyl sulphides by singlet oxygen in the gas phase revealed the formation of sulphoxides[12]. The absorption of oxygen was observed in the photosensitised oxidation in methanol of disulphides related to cystine[61]. In the oxidation of 2,5-dimethylthiophen (0.01 M) photosensitised by Methylene Blue two main products were detected—the *cis*-sulphene (VI) and the *trans*-diketone (VII):



The ratio of the concentrations of (VI) and (VII) depends significantly on the solvent. In chloroform the yield of (VI) is 56% and that of (VII) 28%, while in Methanol the yields are 70% and 2% respectively.[62] The medium can have a significant influence not only on the composition of the product but also on the rate of oxidation. In this respect the influence of the medium is clearly manifested in the photochemical oxidation of β-carotene, which is

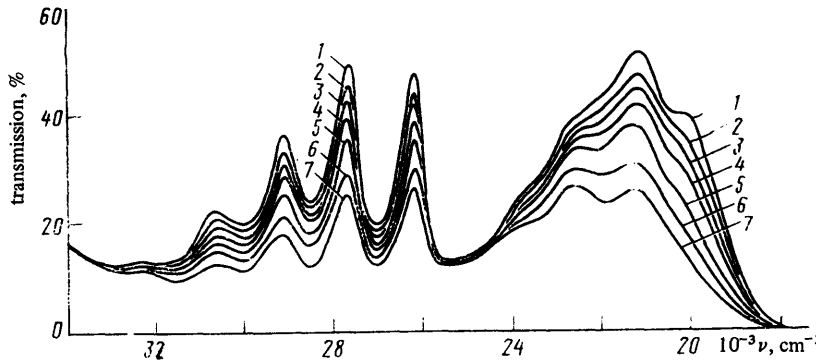


Figure 3. Changes in the absorption spectrum during the joint oxidation of anthracene (concentration 2.8×10^{-2} M) and β-carotene (concentration 0.67×10^{-2} M) in polystyrene; duration of irradiation (min): 1) 0; 2) 15; 3) 30; 4) 45; 5) 75; 6) 135; 7) 180.

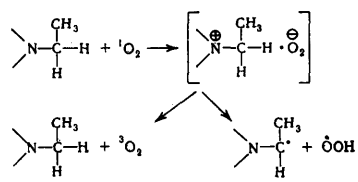
stable towards $^1O_2$ in solution but interacts readily with $^1O_2$ in a polymer matrix (polystyrene) with formation of an oxidation product, whose spectrum is illustrated in Fig. 3.[63]

Table 10. The ratios of the rates of physical and chemical quenching of singlet oxygen.

Quenching agent	Solvent	No. of $^1O_2$ quenching steps per reaction step	Refs.
β-Carotene	4:1 Benzene-methanol	>1000	11
β-Carotene	4:1 Benzene-methanol	< 250	64
Diethyl sulphide	4:1 Benzene-methanol	20	11
NNN'N'-Tetramethyl-*p*-phenylene-diamine	Methanol	>100	39
Diethyl sulphide	Gas phase	>40	12
Dimethyl sulphide	Gas phase	>16	12
Dimethyl disulphide	Gas phase	>1	12
Triethylene	Pyridine	9	28
Triethylamine	Gas phase	>100	28
Nicotine	Methanol	6	32
Mono-, di-, and tri-methylamines and mono-, di-, and tri-ethylamines	Gas phase	>100	51

The ratios of the rates for "physical" and "chemical" quenching presented in Table 10 show that the number of quenching steps per reaction step depends both on the properties of the quenching agent and on the medium in which the interaction takes place.

The mechanism of the effect of the solvent has not in essence yet been investigated. The hypothesis put forward by Smith[28] explains the tenfold increase of the rate constant for the chemical interaction of $^1O_2$ with triethylamine on passing from the gas phase to a pyridine solution by the increase of the lifetime of the triethylamine radical-cation in the polar solvent:



Very few rate constants for the chemical interaction of $^1O_2$ with quenching agents are as yet available. They are listed in Table 11.

Table 11. The rate constants for the chemical interaction of quenching agents with singlet oxygen.

Quenching agent	Solvent	k_r, litre mole^{-1} s^{-1}	Refs.
Dimethyl sulphide	Gas phase	1×10^4	12
Diethyl sulphide	Gas phase	1×10^4	12
Dimethyl disulphide	Gas phase	1×10^4	12
Diethyl sulphide	4:1 Benzene-methanol	3×10^5	11
Nicotine	Methanol	2×10^5	32
Triethylamine	Pyridine	1×10^6	28
4-Hydroxy-2,2,6,6-tetramethyl-piperidine	8:1 Benzene-methanol	2.9×10^3*	15
4-Hydroxy-1,2,2,6,6-pentamethyl-piperidine	8:1 Benzene-ethanol	2.3×10^3*	15
Di-(4-t-octylphenyl)-amine	8:1 Benzene-ethanol	2.6×10^4*	15

* The rate constant for the formation of the nitroxy-radical.

V. TRENDS IN FUTURE RESEARCH

1. Quenching Agents Acting via a Charge-Transfer Mechanism

The most effective of the quenching agents investigated, acting via a charge-transfer mechanism, have reaction rate constants of about 5×10^8 litre mole^{-1} s^{-1}. There is no doubt that compounds with maximum possible efficiency, quenching $^1O_2$ in each encounter, can be obtained within the framework of this mechanism by introducing more powerful electron-donating substituents. However, it is so far difficult to answer the question whether such quenching agents would be suitable for practical use. Unduly strong reducing agents may prove to be unstable towards oxidation by oxygen in the ground state. Furthermore, the interaction of $^1O_2$ with an unduly strong reducing agent may lead to the formation of free radicals and hence to a radical-chain reaction of the substrate. Effects of this kind have been observed, for example, in a study[65] where, in an oxidation reaction photosensitised

by thionine, a transition was observed to a radical mechanism after a change of substrate—from 9,10-dimethylanthracene and tetramethylethylene, which are weak reducing agents, to thiourea, which is a much stronger reducing agent. Finally, in order to be able to predict the suitability of quenching agents with maximum efficiency for practical employment, it is necessary to know the resulting ratio k_r/k_q, i.e. whether or not such quenching agents would react too rapidly with $^1O_2$. In order to be able to answer this question, one must investigate the dependence of k_r/k_q on the ionisation potentials or σ constants of the substituents in the quenching agents.

2. Quenching Agents Acting via the Energy Transfer Mechanism

It is evident from the foregoing that several very effective quenching agents, acting via the energy transfer mechanisms and deactivating $^1O_2$ in each encounter, are now known. The energy transfer from $^1O_2$ to an electronic level of the quenching agent probably takes place only on direct contact between the electron shells of $^1O_2$ and the energy acceptor. Transfer over large distances, for example via an inductive-resonance mechanism, is hardly possible, since the probability of a radiative transition of $^1O_2$ to the ground state is very low. One must therefore assume that the practical limit of the efficiency of the quenching agent has already been reached. Of the two types of quenching agents—compounds with a system of conjugated bonds and complexes—the latter are preferable, since the class of complexes is much larger and within its limits there is a much greater scope for obtaining stable quenching agents with the required properties. β-Carotene and compounds having similar structures are very reactive in relation to free radicals and are readily oxidised by molecular oxygen ($^3O_2$). There is therefore little prospect for their employment as quenching agents, although in plant organisms one of the functions of carotenoids is the quenching of $^1O_2$.[64]

One cannot rule out the possibility that carbon black, which contains structures with fairly long chains of conjugated bonds, can act similarly to β-carotene.

3. Quenching in Polymer Matrices and the Role of Singlet Oxygen in the Photochemical Oxidation Reactions of Polymers

It follows from the only investigation[36] which has so far been carried out that the efficiencies of quenching agents in a solid matrix (polystyrene) are to a large extent equalised. On the basis of general considerations, this effect is presumably related to the limitation of the diffusional mobility of oxygen and of molecular motion in the matrix, which hinders the formation of the activated complex. This is confirmed by data[36] showing that sharp changes in the kinetic constants occur in the region of the glass temperature (T_g). In order to elucidate the mechanism of this phenomenon, systematic studies on various polymers above and below T_g, combined with measurements of the diffusion coefficients of oxygen and of the characteristics of molecular mobility, are now required.

As far as one can judge from the available data[36], the efficiencies of quenching agents in polymers at $T < T_g$ differ comparatively little and therefore in selecting quenching agents one should be guided more by their stability during processing and under the conditions obtaining in the employment of polymers, their solubility in and compatibility with the polymer, their low volatility, etc. rather than by their efficiency in the liquid phase.

In the measurements of the efficiencies of quenching agents both in solution and in the solid phase, it is desirable to employ the formation of nitroxy-radicals during the oxidation of secondary or tertiary amines by singlet oxygen as the indicator reaction[15]. The ESR method is highly sensitive. It is therefore possible to measure the influence of quenching agents on the rate of accumulation of radicals under the conditions of an almost constant concentration of the indicator substance. Furthermore, measurement of the rate by ESR obviates the need to determine the rate from absorption spectra, which is sometimes difficult.

The possible involvement of $^1O_2$ in the photochemical oxidations of polymers began to be discussed in the literature in recent years[43,44,66-74]. Depending on the type of polymer, two mechanisms are considered. The first mechanism, which obtains in polymers containing double bonds, involves the direct interaction of $^1O_2$ with the macromolecule. The second mechanism, which applies to polymers without double bonds, presupposes the interaction of $^1O_2$ with the unsaturated compounds formed as a result of the photochemical process. In both mechanisms, the effect of $^1O_2$ reduces to the acceleration of the accumulation of hydroperoxides giving rise to photochemical branching. Processes involving the quenching by oxygen of the triplet states of carbonyl or aromatic compounds, which may be present as impurities or can form part of the composition of the macromolecules, are considered as sources of $^1O_2$.

Neither the first nor the second mechanisms has yet been proved. Very convincing experiments on certain polymers (for example polymers containing double bonds) established the possibility of their oxidation by the singlet oxygen generated chemically, or photochemically, or in an electric discharge. However the possibility, in principle, of the involvement of $^1O_2$ in the oxidation process does not by itself imply that the $^1O_2$ reactions really make any considerable contribution to the photochemical oxidation of polymers with double bonds in the absence of artificially created sources of $^1O_2$.

The difficulty of proving this mechanism consists in the fact that $^1O_2$ does not oxidise directly polymers without electron-accepting groups (unsaturated, condensed aromatic, etc.). The effect of $^1O_2$ must therefore be investigated not by itself but against the background of the photochemical reaction of the polymer, which generates groups capable of accepting $^1O_2$.

We believe that the problem of the involvement of $^1O_2$ in photochemical oxidation reactions of polymers can be usefully solved in two stages. The first stage involves the study of the possibility, in principle, of the acceleration of the photochemical oxidation of the given polymer with the aid of an artificial source of $^1O_2$. When a photosensitiser dye is used as the source of $^1O_2$, one can suggest for the elucidation of the possible involvement of $^1O_2$ experiments with two light sources—a short-wavelength source whose light is absorbed by the polymer or the photosensitising mixture and a long-wavelength source whose light is absorbed only by the dye. After appropriate control experiments with both sources, the acceleration of the photochemical reaction of the polymer with periodic or permanent inclusion of the additional long-wavelength source could probably be regarded as proof of the involvement of singlet oxygen.

In the second stage of the investigation it is necessary to measure the power of the internal source of singlet oxygen. A conclusion concerning the role of oxidation by singlet oxygen can probably be arrived at by comparing the power of the internal source with that of an external source sufficient for an appreciable acceleration of the photochemical process.

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