

$[Cd(^3P_0)]/[Cd(^3P_1)] = K = k_1/k_2 = 1.35$ at $265^\circ C$ at equilibrium by Boltzmann statistics. The measured value of k_3 is $1.95 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ if the radiative lifetime of $Cd(^3P_1)$ is $2.0 \times 10^{-6} \text{ s}$ and the quenching cross section (σ_3^2) is 0.015 \AA^2 per ethane molecule. The estimated value of k_3/k_4 at $265^\circ C$ is 4, if $E_4 = E_3 + 1.50 \text{ kcal}$ and $A_4 = A_3$; σ_4^2 is about 0.004 \AA^2 . It has been shown that the auto-acceleration is due to the $Cd(^3P_1)-H_2$ reaction, while ethylene inhibits the $Cd(^3H_1)-C_2H_6$ reaction. The quenching rate constant of the reaction $Cd(^3P_{1,0}) + H_2 \rightarrow CdH + H$ was found to be $2.09 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$, which gives 4.60 \AA^2 for the quenching cross section.

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ON THE REACTIVITY OF SINGLET OXYGEN IN AQUEOUS MICELLAR SYSTEMS

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Singlet oxygen (1O_2) in aerated aqueous solutions can be conveniently produced by a process of energy transfer between certain sensitizers (S) in their triplet state (3S) and molecular oxygen (3O_2 or simply O_2):



Many fluorescent dyes can be used as sensitizers in photooxidation of different substrates (A, acceptor) in which besides the singlet oxygen mechanism, reaction (3), the so-called free radical mechanism may also play an important role, reactions (4) and (5):



The transient formation of 1O_2 in aqueous systems is usually checked by some tests based on interception or quenching of 1O_2 by a more or less selective reagent. Recently, a general method for identification of the mechanism of dye sensitized photooxidations has been developed [1]. Using this method one can "calculate" the mechanism of any chemical change observed in sensitized photooxidation provided that the corresponding rate constants for 3S and 1O_2 reactions are known. Since in many sensitized photooxidations the free radical mechanism may take place, the determination of 1O_2 rate constants in aqueous solutions can be a rather difficult problem. Accordingly, only a limited number of its rate constants have been determined thus far. Owing to a lack of specific 1O_2 reagents, its reactivity can be studied in systems with no or negligible participation of free radical mechanism. The use of sensitizers showing a rather low reactivity in their triplet state is one possibility, at least for some substrates [2, 3]. Prevention of reactions between a 1O_2 producing triplet sensitizer and a substrate by their "separation" would be another possibility. Such a rather "clean" system for the study of singlet oxygen reactions can be constructed in micellar systems since 1O_2 can diffuse through thin membranes. Thus, by the choice of a water insoluble sensitizer, which would be dissolved inside the micelle with a substrate outside it, only the 1O_2 mechanism would lead to the

photooxidation of A. The influence of an appropriate $^1\text{O}_2$ quencher on such a reaction can then serve as a check on the participation of $^1\text{O}_2$ and for the determination of its rate constant.

In this work the reactivity of $^1\text{O}_2$ in micellar solutions containing Triton X-100 as a surfactant with chlorophyll a (insoluble in water) and hematoporphyrin (sparingly soluble in water) as sensitizers has been examined and compared with results obtained without a micelle building agent. In micellar solutions of chlorophyll a, the photooxidation of the singlet oxygen acceptors imidazole, 2-methylfuran and N-allylthiourea (ATU) has been followed simply by measuring the oxygen consumption during irradiation with visible monochromatic light in a closed system. The dependence of oxygen consumption on substrate concentration in these systems shows a sigmoidal curve as expected for a capture of $^1\text{O}_2$ by these substrates, a process which is in competition with the deactivation of $^1\text{O}_2$ by the solvent etc.

Rate constants of $^1\text{O}_2 + \text{A}$ reactions in these micellar systems have been determined from competition experiments using N_3^- ion as an efficient quencher of $^1\text{O}_2$ which can suppress the consumption of oxygen:



The influence of concentration of N_3^- on oxygen consumption by these substrates gives typical simple competition curves from which rate constants of $^1\text{O}_2$ reactions can be calculated assuming that $k(\text{N}_3^- + ^1\text{O}_2) = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [4]. With hematoporphyrin as sensitizer we have also determined $^1\text{O}_2$ rate constants of reactions with imidazole and 2-methylfuran in micellar solutions with Triton X-100 as well as in pure aqueous solutions. The results obtained in these systems are shown in Table 1 in which some published results are included for comparison. These results will be discussed.

TABLE 1

Rate constants ($\text{M}^{-1} \text{ s}^{-1}$) of singlet oxygen reactions with imidazole (Im), N-allylthiourea (ATU) and 2-methylfuran (MF) in micellar and aqueous solutions at pH 7.0

Sensitizer	Concentration of Triton X-100	$k(\text{Im} + ^1\text{O}_2)$	$k(\text{ATU} + ^1\text{O}_2)$	$k(\text{MF} + ^1\text{O}_2)$
Chlorophyll a	1.0%	2.0×10^7	4.5×10^6	1.0×10^8
	2.0%	2.9×10^7		1.1×10^8
	5.0%	3.9×10^7		1.0×10^8
Hematoporphyrin	1.0%	3.6×10^7		0.7×10^8
	0.0	3.4×10^7		0.6×10^8
Phenosafranine	0.0	4.0×10^7 ^a	4.0×10^6 ^b	

^aRef. 3; ^bref. 2.

Results obtained in this work indicate that well-chosen micellar systems can be used in determination of $^1\text{O}_2$ rate constants for different substrates. This may be of interest especially for some "difficult" substrates which react more rapidly or more efficiently with triplet sensitizers than with singlet oxygen.

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