

KINETICS AND MECHANISM OF NITROXYL RADICAL FORMATION DURING SENSITIZED AMINE OXIDATION

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Introduction

A new reaction of secondary and tertiary amine oxidation photosensitized with dyes which results in the formation of stable nitroxyl radicals has recently been discovered [1]. This paper presents the data on the mechanism and kinetics of this reaction. Basically, two possible reaction mechanisms were considered: interaction of amines either with the electronically excited singlet state of oxygen, or with the triplet state of photosensitizer. Preliminary experiments with quenchers of singlet oxygen [1] have shown the validity of the first mechanism. This has been confirmed by the results of this research.

Experimental

All the reagents used were purified by recrystallization or distillation in vacuum. Their boiling and melting points coincided with the values reported in the literature.

High-grade benzene, ethanol, and methyl ethyl ketone were used as solvents.

Commercial polystyrene (PS), poly(methyl methacrylate) (PMMA), and polycarbonate (PC) were used without purification.

The experiments were carried out in air- or oxygen-saturated solutions at atmospheric pressure.

500 or 250 W high-pressure mercury lamps were used as light sources. The 546 nm light was isolated with glass filters. The accuracy of line isolation was 99.1%.

Light intensity was determined using a ferrioxalate actinometer [2].

The polymer films containing amine and dye were obtained by pouring a solution in methyl ethyl ketone onto a glass plate. After evaporation of solvent, the film was delaminated by means of water. The film thickness was 10 - 40 μm .

The electron spin resonance (e.s.r.) method was used to study the kinetics of stable nitroxyl radical formation. The naphthalene photo-oxidation rate was measured from the optical density decrease at 425 nm.

Results and Discussion

Reaction products

Irradiation at 546 nm of the solutions of the amines homotropine, 1,1'- and 1,2'-diadamantylamine, 2,2,6,6-tetramethyl- and 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, 4,4'-dicumyl- and 4,4'-di-*t*-octyldiphenylamine, 2,7-di-*t*-octylphenothiazine, in benzene-ethanol solutions (8:1) and in polymeric matrices (PS, PC, PMMA) containing the Rose Bengal (RB) dye, yielded relevant stable nitroxyl radicals.

The oxidation of 2,2,6,6-tetramethyl-4-hydroxypiperidine (TMHP):



has been studied most thoroughly. When the 10^{-3} - 10^{-2} mol/l amine solutions in a 8:1 benzene-ethanol mixture were irradiated in the presence of a sensitizer (6×10^{-6} mol/l), free radicals were formed. Figure 1 presents the radical e.s.r. spectrum and absorption spectrum in the visible range. The product of photosensitized TMHP oxidation was identified as a stable nitroxyl radical on the basis of coincidence of these spectra with those of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl. Under irradiation of a solution of 150 mg of amine in 20 ml of solvent under experimental conditions, the maximum concentration of radicals was reached within ~ 100 h. A nitroxyl radical was isolated from the reaction mixture in 45% yield by column chromatography on Al_2O_3 (with trichloromethane as solvent). The melting point of the product after recrystallization from heptane was 72°C (lit. [3] m.p. 71.5°C). Since we did not optimize the

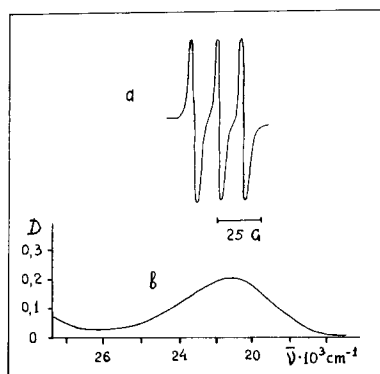


Fig. 1. (a) E.s.r. spectrum and (b) absorption spectra of TMHP oxidation product.

conditions of photochemical synthesis, it seems that the yield of radicals might be greatly increased. We did not study other possible reaction products.

Kinetics and mechanism of the reaction

Figure 2 presents the kinetic curves of the nitroxyl radical accumulation during photo-oxidation of some amines*. It can be seen that the rate of reaction is greatly dependent on the nature of the amine. The number of nitroxyl radicals formed at the initial stage of the reaction is proportional to the exposure dose. The rapidly reached limit for the 4,4'-dimethoxydiphenylamine kinetic curve is probably associated with further conversions of the corresponding nitroxyl radical.

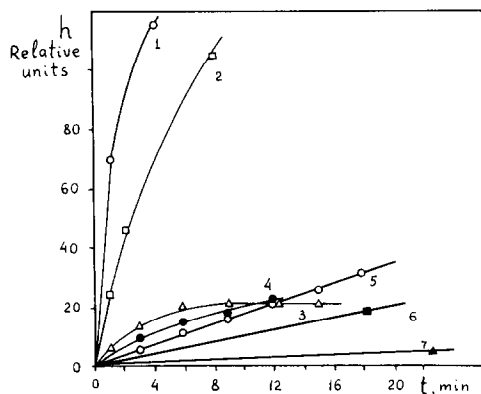


Fig. 2. Kinetic curves for nitroxyl radical formation during photosensitized oxidation of: 1, phenothiazine; 2, 4,4'-di-t-octyldiphenylamine; 3, 4,4'-dimethoxydiphenylamine; 4, 4,4'-dicumyldiphenylamine; 5, 2,2,6,6-tetramethyl-4-hydroxypiperidine; 6, 1,1'-diadamantylamine; 7, homotropine. 8:1 benzene-ethanol solvent, 22 °C, 1×10^{-3} mol/l amine concentration, 6×10^{-6} mol/l RB concentration.

To elucidate the reaction mechanism, the effect of effective quenchers of singlet oxygen (nickel dibutyldithiocarbamate and β -carotene) on the rate of the nitroxyl radical accumulation has been studied.

The quencher effect on photochemical reactions is known to be described by the Stern-Volmer equation:

$$\Phi_0/\Phi = 1 + k_q\tau_0[Q]$$

where Φ_0 and Φ are the quantum yields of the reaction in the absence and presence of a quencher, respectively, k_q is the rate constant of the excited molecule quenching, τ_0 is the lifetime of excited molecule in the absence of a quencher, $[Q]$ is the concentration of a quencher.

Figure 3 presents the quantum yields of the reaction of TMHP sensitized oxidation as a function of quencher concentrations. The values of

* The maximum signal level is used as measure of the amount of radicals. Despite the fact that the amount of radical is strictly proportional to the double integral of a signal, in case of nitroxyl radicals the error associated with the difference in the shape of the radical spectra does not exceed 10%.

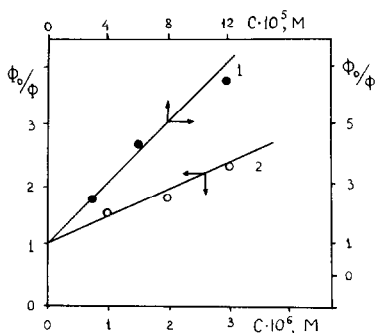


Fig. 3. Effect of quenchers (nickel dibutyldithiocarbamate (●), and β -carotene (○) on quantum yield of the sensitized TMHP oxidation in 8:1 benzene-ethanol mixture.

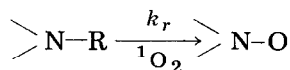
$K = k_q \tau_0$ may be found from the slope of the lines. For singlet oxygen $\tau_0 = 1/k_d$ where k_d is the rate constant of singlet oxygen ($^1\text{O}_2$) deactivation by solvent molecules. For benzene and ethanol $k_d = 3 \times 10^4 \text{ s}^{-1}$ and $6 \times 10^4 \text{ s}^{-1}$, respectively [4]. It may be assumed that the value of k_d for the 8:1 benzene-ethanol mixture is close to $3 \times 10^4 \text{ s}^{-1}$. In this case we obtain from the slope of the lines that k_q for nickel dibutyldithiocarbamate and β -carotene are 1.6×10^9 and 1.3×10^{10} l/mol s, respectively. The literature values of k_q are 4×10^9 l/mol s for the nickel dibutyldithiocarbamate in carbon disulphide [5] and 1.3×10^{10} and 2×10^{10} l/mol s for β -carotene in benzene [6, 7]. Taking into account that the rate constants of $^1\text{O}_2$ quenching are functions of the nature of solvent [8], coincidence of the constants may be considered to be sufficiently good.

A weaker quencher of singlet oxygen (bismuth dimethyldithiocarbamate [10]) at a 1.8×10^{-5} mol/l concentration practically fails to affect the rate of reaction.

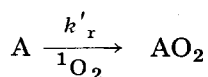
The rate of reaction of TMHP oxidation remains unchanged as the oxygen concentration in solution increases. This fact indicates that the triplet state of dye does not interact directly with the amines. Thus, it follows from the data obtained that the singlet oxygen participates in the formation of nitroxyl radicals.

Rate constants for the reaction between amines and $^1\text{O}_2$ and for quenching of $^1\text{O}_2$ by amines

The rate constants of the reaction of nitroxyl radical formation during singlet oxygen interaction with amines



may be determined by comparing the rate of this reaction with the rate of any reaction (for example that of aromatic hydrocarbon oxidation with formation of transannular peroxides) for which the k_r value is known:



For the competing processes of A and of N-R oxidation the relation

$$k_r = k'_r \frac{[A]}{[N-R]} \frac{w}{w'}$$

holds. Here k'_r is the rate constant of aromatic hydrocarbon oxidation, $[A]$ is the concentration of amine, w is the rate of the nitroxyl radical formation, w' is the rate of the hydrocarbon consumption. The naphthalene oxidation was chosen as standard reaction with a known value of $k'_r = 7 \times 10^7$ l/mol s. We determined k_r for naphthalene from the ratio of oxidation rates of naphthalene and 9, 10-dimethylanthracene and from the data of Wilson [9]. Table 1 lists the values of the reaction rate constants for some amines determined using the method of competing reactions.

TABLE 1

Rate constants of nitroxy radical formation and singlet oxygen quenching

Compound	$k_r \times 10^{-3}$ (l/mol s)	$k_q \times 10^{-5}$ (l/mol s)
2,2,6,6-Tetramethyl-4-hydroxypiperidine	2.9	5
1,2,2,6,6-pentamethyl-4-hydroxypiperidine	2.3	500*
4,4'-di-t-octyldi-phenylamine	26	73

* In methylene chloride [10].

The reaction mechanism was additionally verified using the competing reaction of photo-oxidation of TMHP and naphthalene in the absence of RB under the action of 436 nm light absorbed by naphthalene. In this case, the value of the rate constant of the nitroxyl radical formation virtually coincided with that presented in the Table. Thus, the rate of nitroxyl radical formation is independent of the nature of photosensitizer, which is in agreement with the assumption of singlet oxygen contribution to the reaction.

Another independent kinetic method may be used to determine the rate constants of the amines-singlet oxygen reaction from the dependence of the reaction quantum yield on amine concentration:

$$1/\Phi = 1/\Phi (k_q/k_r + k_d/k_r [>N-R])$$

where φ is the quantum yield of singlet oxygen production by RB excitation.

Figure 4 presents the values of $1/\Phi$ as a function of TMHP concentration. The slope is used to determine the value of $(k_d/\varphi) k_r$. Assuming that

$k_d = 3 \times 10^4 \text{ s}^{-1}$, $\varphi = 0.6$ (estimate made on the basis of the data of Yoshiharu [11]), we get $k_r = 3.3 \times 10^3 \text{ l/mol s}$. The coincidence between the values of k_r for TMHP determined by different methods proves that the limiting step of nitroxyl radical formation is the amine-singlet oxygen interaction.

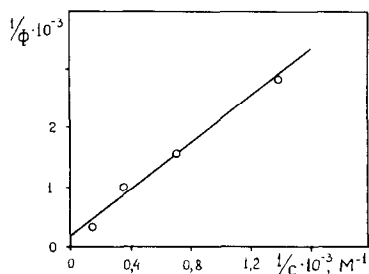


Fig. 4. Quantum yield of the sensitized TMHP oxidation vs. amine concentration. 8:1 benzene-ethanol solvent, 22 °C, [RB] = $6 \times 10^{-6} \text{ mol/l}$.

Table 1 also presents the constants of singlet oxygen quenching by amines. The quenching constants for TMHP and 4,4'-di-*t*-octyldiphenylamine were determined from their effect on naphthalene oxidation. Since, contrary to aliphatic amines, the aromatic amines quench the triplet state of the dye (RB) [8], the rate constant of singlet oxygen quenching by 4,4'-di-*t*-octyldiphenylamine was determined by the amine effect on naphthalene oxidation in the absence and presence of additional quencher (nickel dibutyldithiocarbamate). In the two-quencher system:

$$\frac{[A]'}{[A]''} \frac{w''}{w'} = 1 + \frac{k''_q [Q'']}{k'_q [Q'] + k_d}$$

where w' is the rate of reaction in the presence of amine, w'' is the rate of reaction in the presence of amine and nickel dibutyldithiocarbamate, k_q'

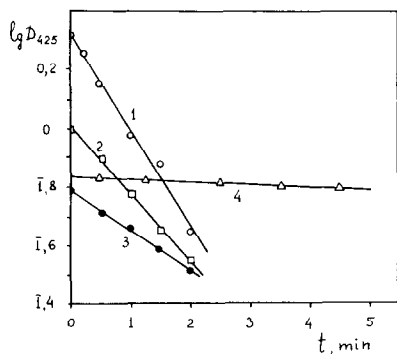


Fig. 5. Effect of quenchers on the kinetics of photosensitized naphthalene oxidation in 8:1 benzene-ethanol mixture; O, without additives; □, $2.5 \times 10^{-2} \text{ mol/l}$ of TMHP; ●, $6.7 \times 10^{-3} \text{ mol/l}$ of 4,4'-di-*t*-octyldiphenylamine; △, $6.7 \times 10^{-3} \text{ mol/l}$ of 4,4'-di-*t*-octyldiphenylamine and $8.4 \times 10^{-5} \text{ mol/l}$ of nickel dibutyldithiocarbamate.

and $[Q']$ are the rate constant of quenching and the amine concentration, k''_q and $[Q'']$ are the rate constant of quenching and the nickel dibutyldithiocarbamate concentration.

Figure 5 presents the linear kinetic relations of naphthalene consumption in the presence of quenchers. It follows from the data obtained that the probability of the reaction of nitroxyl radical formation is much lower than that of singlet oxygen quenching in the interaction with amines.

The limiting quantum yield of the compounds studied is, therefore, of the order of 10^{-4} . 10^{-2} . However, the high total chemical yield of the reaction permits its use for obtaining stable nitroxyl radicals from the corresponding amines. The reaction may be advantageous as compared with the known methods of amine oxidation when, for example, the oxidized amines contain readily hydrolyzed bonds.

It seems that the new reaction may also be used as an indicator when measuring the quencher efficiency both in solutions and in the solid phase. The high sensitivity of the e.s.r. method makes it possible to measure the quencher effect on the rate of radical accumulation under the conditions of practically invariable concentration of indicator when the rate of radical accumulation is constant. Besides, the e.s.r. method makes it possible to avoid using spectrophotometry, which is sometimes connected with difficulties.

Finally, this reaction might be applied as an analytical reaction in measuring the concentration of photochemically generated singlet oxygen. The aliphatic amines seem to be most useful for analytical applications since they do not absorb in the near ultra-violet spectral range.

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