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Abstract

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INVESTIGATION OF THE SENSITIZATION OF THE PHOTOOXIDATION OF ORGANIC COMPOUNDS BY ANTHRAQUINONE DERIVATIVES FROM INFRARED ABSORPTION SPECTRA

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A comparatively small number of works has been devoted to the study of the sensitized oxidation of organic compounds (1), but in recent years their number has been steadily increasing. The sensitized oxidation of those organic compounds that we have studied had previously been the subject of the following works. The photochemical oxidation of benzaldehyde under the action of ultraviolet light has been studied by many investigators, who established that the reaction has a chain character with a quantum yield of 10,000 (2). This reaction was sensitized to visible light with the aid of benzophenone, acetophenone, and other substances (3). At the same time it was established that rhodamine 6G and auramine do not bring about this chain reaction. However, the photooxidation of tetralin can be carried out with the aid of anthraquinone derivatives as sensitizers (4). It should be noted that a sensitized oxidation of ethyl alcohol was carried out with anthraquinone derivatives (5).

In recent years many papers by Schenck have appeared on the photosensitized oxidation of numerous organic compounds, including isopropylbenzene, with the aid of fluorescent dyes (eosin, chlorophyll, methylene blue, and others) in the presence of oxygen (6).

In all the photooxidation reactions of organic substances mentioned above, the manometric method was used to investigate oxygen absorption.

In our laboratory experiments were also carried out on sensitization to visible light of the photooxidation of benzaldehyde and tetralin with the aid of anthraquinone and its derivatives (1). In this case the products of the sensitized photooxidation reaction of benzaldehyde and tetralin were detected from the infrared absorption spectra, as in the case of direct photooxidation of organic substances (7).

The aim of the present work is to investigate the sensitization to visible light of the photooxidation of benzaldehyde, tetralin, and isopropylbenzene (cumene) by molecular oxygen with the aid of anthraquinone and its α- and β-hydroxy- and amino-derivatives. These substances were used by us because oxygen has a sharply different effect on their excited molecules. The fluorescence of anthraquinone and its β-derivatives undergoes strong quenching by oxygen in the vapor and adsorbed states, whereas the fluorescence of the α-derivatives is practically not quenched ([8]). Consequently, by using various anthraquinone derivatives as photosensitizers for the oxidation of organic compounds, it was possible to try to compare the primary stages of the sensitized oxidation reaction with fluorescence quenching.

The sensitized oxidation of organic compounds was carried out in the apparatus described earlier ([7]), and was followed by the appearance of absorption bands at 6800 and 4220 cm^{-1} (OH) in the near infrared region of the spectrum on an automatic recording IR spectrometer with a quartz prism. As the light source we used a super-high-pressure mercury-quartz lamp SVDSh-250-3 and SVDSh-500 in combination with various

glass filters to isolate the corresponding region of the spectrum, which is absorbed only by the sensitizer. For absorption of the infrared radiation of mercury-quartz lamps, a water filter was used (50 mm layer of water).

The concentration of the sensitizer—anthraquinone derivatives—in the organic substances was from 10^{-4} to 10^{-5} mol/l.

A solution of benzaldehyde in CCl_4 (10%) with anthraquinone or with β-aminoanthraquinone, after illumination at $\lambda > 400$ mμ (SVDSh-250 mercury-quartz lamp with ZhS-12 light filter), with continuous bubbling of oxygen (at a rate of 0.2 l/min) for 5 h, causes the following changes in the infrared absorption spectrum (Fig. 1, *I*). An absorption band appears at 4220 cm^{-1}, which corresponds to the absorption band found in the spectrum of a solution of benzoic acid in CCl_4 at approximately the same frequency. At the same time a decrease is observed in the intensity of the absorption bands at 4525 and 4435 cm^{-1}, which are assigned to $\mathrm{C{-\!\!-}H_{al}}$ vibrations. No changes in the infrared absorption spectrum were observed after illumination with the same wavelengths, with simultaneous bubbling of oxygen, of a solution with α-aminoanthraquinone, or of the benzaldehyde solution alone. Consequently, in anthraquinone and β-aminoanthraquinone there is a direct relationship between the ability to sensitize the photooxidation of benzaldehyde and the quenching of their fluorescence by oxygen. A similar conclusion can also be drawn from comparison of the quenching of fluorescence of anthraquinone and six of its derivatives by oxygen with the sensitization of the oxidation of tetralin. In the case of tetralin, it proved possible to use a larger number of anthraquinone derivatives for sensitization, owing to the fact that the intrinsic absorption of tetralin begins only at $\lambda < 320$ mμ. Because of the low rate of the sensitized oxidation reaction of tetralin, and in order to exclude secondary dark reactions, we used a more powerful source of ultraviolet light—a SVDSh-500 mercury-quartz lamp in combination with a BS-7 light filter transmitting $\lambda > 320$ mμ; the duration of the experiment was 8 h. The presence of sensitized oxidation

Fig. 1. *I* —benzaldehyde, *II* —tetralin; *a* —before oxidation, *b* —after oxidation

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of tetralin was established from the appearance in the absorption spectrum, in the near-infrared region, of the first overtone OH band (2ν) at 6800 cm^{-1} (Fig. 1, *II*). The photooxidation of tetralin was sensitized by anthraquinone, β-hydroxy- and β-aminoanthraquinone, anthranol, and α-chloroanthraquinone. Oxidation was not established when α-hydroxy- and α-aminoanthraquinones and 1,4-dioxyanthraquinone were used.

Fig. 1. *I* —benzaldehyde, *II* —tetralin; *a* —before oxidation, *b* —after oxidation.

From the absorption spectra it was established that anthraquinone sensitizes the photoreaction of oxidation approximately twice as effectively as its derivatives, whose sensitizing action is approximately the same.

The experimental data show a clear relationship between the sensitizing action of anthraquinone and its derivatives and the strong quenching of their fluorescence by molecular oxygen and the presence in them of delayed fluorescence, i.e., the existence of a triplet level.

The same conclusion can be drawn from the sensitized photooxidation of isopropylbenzene by anthraquinone and by α- and β-aminoanthraquinone; moreover, the sensitized reaction proceeds considerably more slowly than in the case of tetralin under otherwise identical conditions.

The quenching of the fluorescence of anthraquinone derivatives was previously explained (8) as a possible transition of the excited molecule, upon collision with O_2, into a metastable (triplet) state, which lies below the singlet state by ~ 0.2 eV for β-aminoanthraquinone. Fluorescence quenching does not occur when the distance between the levels is significantly greater than 0.2 eV, as, for example, in α-aminoanthraquinone (0.8 eV). At the triplet level the molecule, owing to the presence of two unpaired electrons, is capable of adding the valence-unsaturated oxygen molecule, which is a biradical, with formation of an unstable complex—a moloxide (10). Therefore fluorescence quenching is an indication of the addition of oxygen to a light-excited molecule that has a closely situated triplet level.

On the basis of comparing the phenomenon of sensitization with the analogous phenomenon of fluorescence quenching, as well as literature data (2,3,5,6), the following conclusions may be drawn concerning the mechanism of sensitization of oxidation reactions.

On absorbing a quantum of light, the sensitizer passes into an excited state, and then into a metastable (triplet) state as a result of the action of the paramagnetic O_2 molecule.

$$S \xrightarrow{h\nu} S^* \xrightarrow{O_2} \widetilde{\bullet S \bullet} \qquad (1)$$

(the sign $\sim$ denotes an excess of vibrational energy). A biradical, i.e., a molecule in the triplet state, can add oxygen with formation of an unstable complex having the properties of a biradical

$$\bullet S \bullet + O_2 \rightarrow \bullet SO_2 \bullet . \qquad (2)$$

The biradicals $\bullet SO_2 \bullet$, possessing increased chemical activity, are responsible for the sensitization of photooxidation of organic compounds. In this case the following initial stages of the oxidation chain reaction are possible:

a) The biradical $\bullet SO_2 \bullet$ transfers the electronic excitation energy to the molecule being oxidized, converting it into a biradical state; moreover, the transfer of energy should occur with high probability, as is the case in sensitized fluorescence (1,11).

b) The biradical $\bullet SO_2 \bullet$ dehydrogenates the molecule being oxidized with formation of the corresponding radical. Dehydrogenation of organic compounds should occur with lower probability compared with energy transfer, since this process requires a larger amount of energy, necessary for breaking the $C - H$ bond.

Sensitized oxidation of benzaldehyde proceeds mainly by transfer of the excitation energy with conversion of the benzaldehyde molecule into the biradical state*.

$$\bullet SO_2 \bullet + C_6H_5 - C^{=O}_{-H} \rightarrow C_6H_5C^{-O\bullet}_{-H} + S + O_2 \qquad (3)$$

* This conclusion agrees with additional studies of the possibility of sensitized oxidation of benzaldehyde by 2- and 3-aminoderivatives of acridine, one of which ...

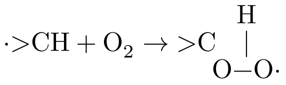
The further development of the chain reaction is effected by the benzaldehyde biradical, as given in (1, 7). Dehydrogenation of the benzaldehyde molecule by $\cdot SO_2 \cdot$ is less probable, but possible

$$\cdot SO_2 \cdot + C_6H_5 - \overset{O}{\underset{H}{C\|}} \rightarrow C_6H_5\overset{O}{\underset{\cdot}{C\|}} + \cdot SO_2H \qquad (4)$$

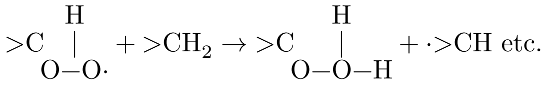
For tetralin and isopropylbenzene, a metastable (triplet) state is unknown; however, by analogy with benzene and its derivatives, it may be assumed that the triplet level lies considerably higher (in the ultraviolet region of the spectrum). Consequently, transfer of excitation energy is unlikely, and therefore it should be considered that the biradical $\cdot SO_2\cdot$ causes dehydrogenation of the hydrocarbon with formation of the corresponding radical, which propagates the chain reaction.

The mechanism of the sensitized oxidation of tetralin and, analogously, isopropylbenzene may be represented in the form of the equations:

$$\cdot SO_2 \cdot + {>}CH_2 \rightarrow \cdot SO_2H + \cdot{>}CH$$



$$\cdot{>}CH + O_2 \rightarrow {>}C\overset{H}{\underset{O-O\cdot}{|}} \tag{5}$$



$$ {>}C\overset{H}{\underset{O-O\cdot}{|}} + {>}CH_2 \rightarrow {>}C\overset{H}{\underset{O-O-H}{|}} + \cdot{>}CH \text{ etc.}$$

Regeneration of the sensitizer may occur by the following mechanism

$$\cdot SO_2H \rightarrow \cdot S + HO_2\cdot \tag{6}$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \tag{7}$$

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has a triplet level corresponding to $\lambda > 500\,\mathrm{m}$ and undergoes quenching of fluorescence by oxygen. Despite this, both substances did not sensitize the photooxidation reaction of benzaldehyde, whereas anthraquinone and its β-derivatives did sensitize it; however, in them the triplet levels lie in the blue region of the spectrum, $\lambda < 500\,\mathrm{m}$.

Note: Figure translations are in progress. See original paper for figures.

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