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Kinetics of Bimolecular Oxidation of Anthracene with Singlet Molecular Oxygen ($^1\Delta_g$) in Organic and Aqueous–Organic Media and in Water

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Abstract—The kinetics of photosensitized oxidation of anthracene with singlet molecular oxygen ($^1\Delta_g$) in organic and aqueous–organic media were studied. The bimolecular rate constant of the reaction was determined, and its relation to solvent properties was revealed. On the basis of the obtained data, the empirical reaction rate constant in water was estimated at 2.3×10^6 l mol^{-1} s^{-1}.

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Polycyclic aromatic hydrocarbons and products of their chemical and/or photochemical transformations are classed with the most widespread and hazardous technogenic micropollutants [1–12]. Therefore, photochemistry of polycyclic aromatic hydrocarbons has attracted strong interest in recent time. The mechanism of their photochemical transformations is complicated. It is determined by the whole set of processes such as photoionization, direct and sensitized photooxidation with participation of both molecular oxygen O_2 and other low-molecular compounds, e.g., H_2O_2 and nitrates [1, 2, 4, 5, 7, 8, 11]. The reaction with singlet molecular oxygen ($^1O_2$, $^1\Delta_g$) is among the main processes [1, 2, 4, 5].

Anthracene is the main representative of the above micropollutant series. It is characterized by high specificity for $^1O_2$ [1, 2, 4, 5, 13–16]. The kinetics of anthracene oxidation with $^1O_2$ molecules are solvent-dependent [15–18], and water is the most important activator of this reaction [16]. However, there are no quantitative data on bimolecular rate constant for anthracene oxidation in water due to its very poor solubility in that solvent.

The goal of the present work was to determime the bimolecular rate constant for photosensitized oxidation of anthracene with $^1O_2$ in water on the basis of the kinetic data for analogous reactions in organic and aqueous–organic media.

Anthracene is an efficient photosensitizer for $^1O_2$ [19–21]. The quantum yield of $^1O_2$ in anthracene solution may reach 1.2 due to participation of excited singlet and triplet states of anthracene in activation of O_2. Therefore, the kinetics of photooxidation of anthracene with $^1O_2$ are often studied under direct irradiation of anthracene solution. However, in this case the contribution of photodimerization of anthracene becomes significant [1, 22]. The yield of this reaction depends on the solvent [22] and is eventually determined (assumingly) by the solubility of atmospheric oxygen therein. To avoid competition of these processes, in the present work we examined the kinetics of photosensitized oxidation of anthracene.

As sensitizer we selected tetraphenylporphyrin, taking into account the following factors. First, tetraphenylporphyrin is soluble in all the examined solvents. Second, it ensures high quantum yield of $^1O_2$, which almost does not depend on the solvent [23, 24]. Third, the electronic absorption spectrum of tetraphenylporphyrin only partially overlaps that of anthracene, so that reaction solution may be selectively irradiated at a wavelength corresponding to photosensitizer absorption, and the consumption of anthracene can be followed by spectrophotometry. Fourth, tetraphenylporphyrin is more stable to photooxidation with molecular oxygen [25], as compared to anthracene [14, 15, 18], which ensures constancy of the absorbed light intensity during photochemical experiment.

Figure 1 illustrates variation of anthracene absorbance in benzene solution in the presence of

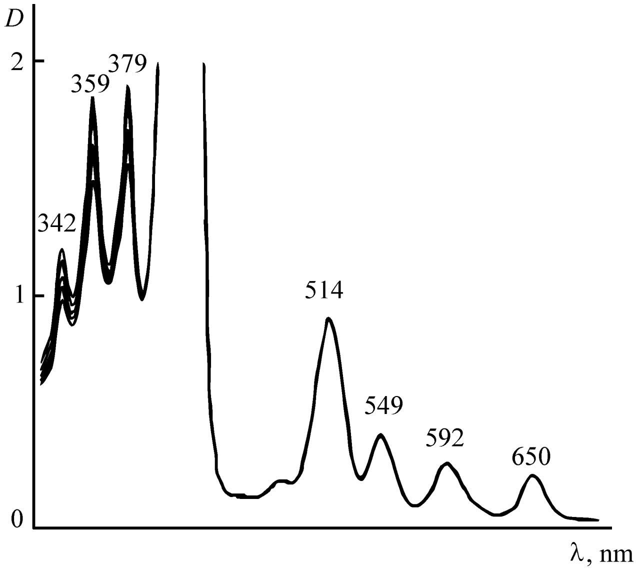

Fig. 1. Variation of the electronic absorption spectrum of a solution of anthracene in benzene in the presence of tetraphenylporphyrin upon irradiation at λ > 400 nm (in 30-min intervals).

tetraphenylporphyrin under irradiation at λ > 400 nm. It seen that the intensity of absorption bands decreases. Analogous pattern is observed in other solvents. In the absence of tetraphenylporphyrin, no consumption of anthracene was observed over the same period of time.

Figure 2 shows the kinetic data for the reaction in some solvents. The kinetic curves became straight lines in the coordinates ln $[(D_0 - D_\infty)/(D_t - D_\infty)]$—$t$, where t is the irradiation time, and D_0, D_t, and D_∞ are, respectively, the initial, current, and final optical densities of the solution at a working wavelength (D_∞ was assumed to be equal to the absorbance of tetraphenylporphyrin at the same wavelength). These findings indicated that the reaction follows pseudofirst-order kinetics. Therefore, its rate is given by Eq. (1) [26].

$$-\partial[\mathrm{A}]/\partial t = k_{\mathrm{obs}}[\mathrm{A}]. \tag{1}$$

Here, $k_{\mathrm{obs}} = k_r[^1\mathrm{O}_2]$ is the observed rate constant; k_r is the bimolecular rate constant; $[^1\mathrm{O}_2]$ is the concentration of $^1\mathrm{O}_2$ which remains constant under continuous irradiation; and [A] is the concentration of anthracene. We used Eq. (2) [27] to calculate k_{obs}.

$$\ln[(D_0 - D_\infty)/(D_t - D_\infty)] = k_{\mathrm{obs}}t. \tag{2}$$

In order to estimate the ratio of k_{obs} and k_r, the obtained data were compared with $k_{\mathrm{obs,b}}$ in benzene, which was determined under analogous conditions. The $k_{\mathrm{obs}}/k_{\mathrm{obs,b}}$ values are given in table. Let us consider quantitative relation between $k_{\mathrm{obs}}/k_{\mathrm{obs,b}}$ and $k_r/k_{r,\mathrm{b}}$.

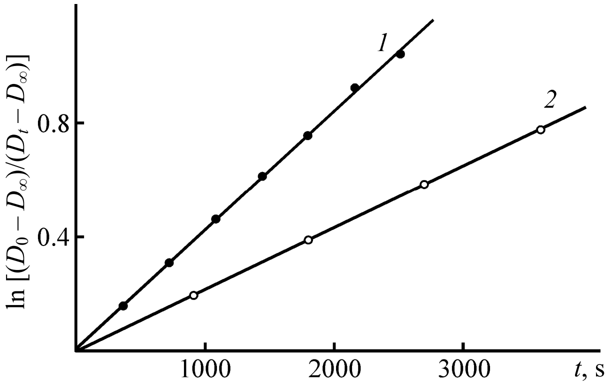

Fig. 2. Kinetic dependences for the photosensitized oxidation of anthracene with $^1\mathrm{O}_2$ in (*2*) 1,4-dioxane and (*1*) 1,4-dioxane containing 11.3 M of water.

The photosensitized oxidation of anthracene may be described by the following scheme [20].

$$\mathrm{S} + h\nu \rightarrow {}^1\mathrm{S}^*,$$

$${}^1\mathrm{S}^* \rightarrow {}^3\mathrm{S}^*,$$

$${}^3\mathrm{S}^* + \mathrm{O}_2\,({}^3\Sigma_g^-) \rightarrow {}^1\mathrm{O}_2 + \mathrm{S},$$

$${}^1\mathrm{O}_2 \xrightarrow{\mathrm{Solv}} \mathrm{O}_2 + h\nu_{\mathrm{lum}}\ (\sim 1270\ \mathrm{nm}),\ k_{\mathrm{d}},$$

$${}^1\mathrm{O}_2 + \mathrm{S} \rightarrow \mathrm{O}_2 + \mathrm{S}\ \text{and its oxidation products},\ k_{\mathrm{Q}},$$

$${}^1\mathrm{O}_2 + \mathrm{A} \rightarrow \mathrm{O}_2 + \mathrm{A},\ k_{\mathrm{q}},$$

$${}^1\mathrm{O}_2 + \mathrm{A} \rightarrow \text{Oxidation products},\ k_r.$$

Here, S, $^1\mathrm{S}^*$, and $^3\mathrm{S}^*$ are, respectively, the ground and singlet and triplet excited states of tetraphenylporphyrin; Solv is the solvent; $k_{\mathrm{d}} = 1/\tau$ is the rate constant for $^1\mathrm{O}_2$ decay in the given solvent; τ is the $^1\mathrm{O}_2$ lifetime; k_{Q} is the overall rate constant for $^1\mathrm{O}_2$ quenching with the sensitizer; k_{q} is the physical rate constant for $^1\mathrm{O}_2$ quenching with anthracene. In keeping with the above scheme, Eq. (3) may be written as general for the reaction rate:

$$-\partial[\mathrm{A}]/\partial t = k_r\gamma I[\mathrm{A}]/\{k_{\mathrm{d}} + k_{\mathrm{Q}}[\mathrm{S}] + (k_{\mathrm{q}} + k_r)[\mathrm{A}]\}. \tag{3}$$

Here, γ is the quantum yield of $^1\mathrm{O}_2$; I is the intensity of absorbed light; and [S] is the concentration of tetraphenylporphyrin. The experimental values of τ in the examined solvents (see table) are very similar to published data [19, 28], indicating that inequality (4) is valid for small experimental concentrations [S] and [A]:

$$k_{\mathrm{d}} >> k_{\mathrm{Q}}[\mathrm{S}] + (k_{\mathrm{q}} + k_r)[\mathrm{A}]. \tag{4}$$

Therefore, Eq. (3) may be transformed into a simpler form (5).

$$-\partial[\mathrm{A}]/\partial t = k_r\gamma I[\mathrm{A}]\tau, \tag{5}$$

Lifetimes of $^1O_2$ and rate constants for photosensitized oxidation of anthracene in different solvents

Solvent	$\tau\times10^6$, s	$k_{obs}/k_{obs,b}$	$k_r/k_{r,b}$	$k_r\times10^{-5}$, l mol^{-1} s^{-1}
Diethyl ether	32	0.24	0.23	0.15
Benzene	30	1.00	1.00	0.70
Acetone	50	4.20	2.50	1.80
Pyridine	16	4.20	7.90	5.50
DMF	22	8.50	11.60	8.10
Ethanol	15	0.85	1.70	1.20
1,4-Dioxane	25.8	1.90	2.2	1.50
1,4-Dioxane + 1.7 M H_2O	26.8	2.10	2.4	1.70
1,4-Dioxane + 3.0 M H_2O	20.5	2.70	4.0	2.80
1,4-Dioxane + 4.4 M H_2O	20.1	3.00	4.5	3.20
1,4-Dioxane + 5.8 M H_2O	18.8	3.10	5.0	3.50
1,4-Dioxane + 7.2 M H_2O	18.6	3.30	5.3	3.70
1,4-Dioxane + 8.6 M H_2O	17.6	3.40	5.8	4.10
1,4-Dioxane + 11.3 M H_2O	16.3	4.20	7.7	5.40

Using Eqs. (1) and (5), we obtain Eq. (6) for k_{obs}.

$$k_{obs} = k_r\gamma I\tau. \qquad (6)$$

Insofar as I is constant, k_r may be calculated from the experimental data according to Eq. (7) with the use of the known $k_{r,b}$ value.

$$k_r = k_{r,b}(k_{obs}/k_{obs,b})(\tau_b/\tau). \qquad (7)$$

With a view to determine $k_{r,b}$ we performed comparative study of photosensitized oxidation of anthracene and tetracene in benzene in the presence of phthalocyanine photosensitizer. As follows from Fig. 3, Eqs. (1) and (2) are applicable for both reactions. The $k_{obs,b}$ values found from the kinetic dependences indicate that tetracene is consumed more rapidly than anthracene by a factor of 200. In keeping with Eq. (7), this value may be assigned to the ratio of $k_{r,b}$ for these reactions. Insofar as $^1O_2$ quenchinf with tetracene is a chemical process [14, 15, 25], the $k_{r,b}$ values for the oxidation of tetracene may be assumed to be equal to the rate constant of $^1O_2$ luminescence quenching by tetracene in deuterobenzene, which is equal to 1.4×10^7 l mol^{-1} s^{-1} [29]. The $k_{r,b}$ value for anthracene calculated from the above data by Eq. (7) is 7.0×10^4 l mol^{-1} s^{-1}. This value approaches those reported previously, 1.5×10^5 [14] and 1.0×10^5 l mol^{-1} s^{-1} [18]. The k_r values calculated for other solvents on the basis of $k_{r,b}$ are given in table. It is seen that k_r depends on the solvent properties. For nonaqueous media, k_r is described best by the empirical solvent polarity/polarizability parameter π^* [18]. The relation between ln k_r and π^* may be approximated by a straight line (single-parameter approximation; Fig. 4, $r = 0.962$). Extrapolation of ln k_r to $\pi^* = 1.09$ (water) [30, 31] gives $k_r = 2.3\times10^6$ l mol^{-1} s^{-1}. The data in table show that k_r in aqueous 1,4-dioxane increases in parallel with the concentration of water. This dependence may be linearized (Fig. 5, $r = 0.983$). In this case, extrapolation to $c = 55.6$ M in water gives $k_r = 2.1\times10^6$ l mol^{-1} s^{-1}.

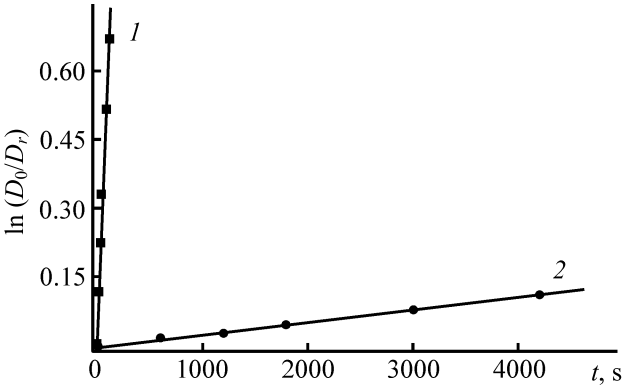

Fig. 3. Kinetic dependences for the photosensitized oxidation of (*1*) tetracene and (*2*) anthracene with $^1O_2$ in benzene.

It should be noted that k_r in aqueous–organic media may be related to properties of water molecules as hydrogen bond network [32]. According to [33–35], the presence of such water in aqueous solution is indicated by absorption in the region ~3200 cm^{-1} (Fig. 6). Figure 7 shows that the dependence between k_r and D_{3200} in aqueous 1,4-dioxane may be approximated by a straight line ($r = 0.971$), starting from a water concentration of about 3.0 M. By extrapolation to $D_{3200} = 1.6$ in water we obtain $k_r = 2.5\times10^6$ l mol^{-1} s^{-1}.

Thus all estimates of k_r for the oxidation of anthracene with $^1O_2$ molecules in water are approximately similar, $k_r = (2.3\pm0.2)\times10^6$ l mol^{-1} s^{-1}.

EXPERIMENTAL

Anthracene of analytical grade was additionally recrystallized from acetone and was dried under reduced pressure. Tetraphenylporphyrin was synthesized accord-

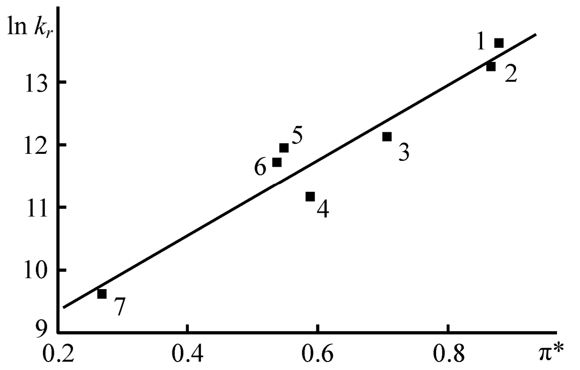

Fig. 4. Semilog plot of the bimolecular rate constant k_r for the photosensitized oxidation of anthracene with $^1O_2$ vs empirical solvent polarity/polarizability parameter π*: (*1*) DMF, (*2*) pyridine, (*3*) acetone, (*4*) benzene, (*5*) 1,4-dioxane, (*6*) ethanol, (*7*) diethyl ether.

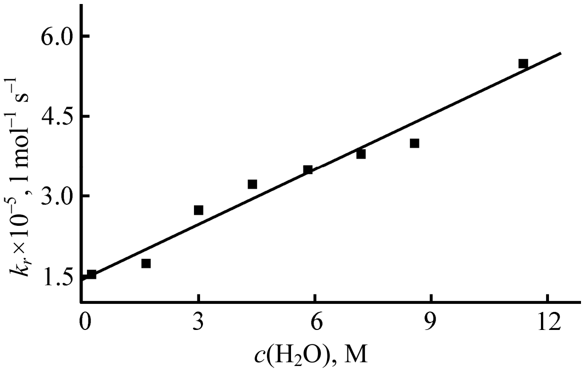

Fig. 5. Plot of the bimolecular rate constant k_r for the photosensitized oxidation of anthracene with $^1O_2$ in mixed binary solvent 1,4-dioxane–water versus water concentration.

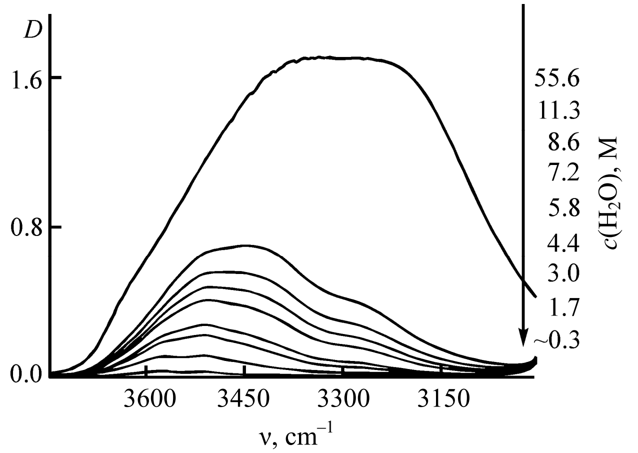

Fig. 6. IR spectra of mixed binary solvent 1,4-dioxane–water in the region of OH stretching vibrations at different concentrations of water.

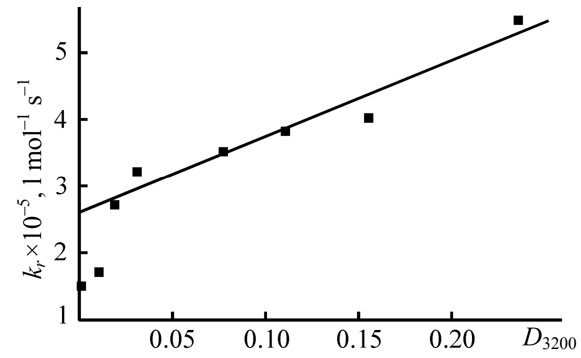

Fig. 7. Plot of the bimolecular rate constant k_r for the photosensitized oxidation of anthracene with $^1O_2$ in mixed binary solvent 1,4-dioxane–water with variable composition vs optical density at ν 3200 cm^{-1}.

ing to [36]. Benzene of analytical grade was used without additional purification. The other solvents (analytical grade) were prepared as described in [37]. Singly distilled water was used for the preparation of mixed solvents.

Photosensitized oxidation of anthracene ($c = 1 \times 10^{-4}$ M) with $^1O_2$ molecules was performed on exposure to air in the presence of tetraphenylporphyrin ($c = 4 \times 10^{-5}$ M). The source of exciting light was an OVS-1 lighter equipped with a KGM-9-70 halogen lamp (70 W). Experiments were performed in such a way that the exciting light be absorbed only by tetraphenylporphyrin. For this purpose, reaction solutions were placed into 1 × 1-cm quartz cells and were irradiated through a ZhS-11 glass light filter with a short-wave transmission boundary at λ 400 nm. The consumption of anthracene was monitored by spectrophotometry at its second absorption maximum. Palladium tetra(4-*tert*-butyl)phthalocyanine was used as photosensitizer in experiments with tetracene, and reaction solutions were irradiated through a KS-15 light filter (shortwave boundary at λ 640 nm). The consumption of tetracene was monitored by spectrophotometry at λ 476 nm (in benzene). The error in the determination of k_{obs} did not exceed 2%.

The $^1O_2$ luminescence lifetime (τ) was measured with the aid of an LIF-200 laser pulse fluorimeter additionally equipped with an FD-10 GA IR photoreceiver and an operation amplifier with a time resolution of about 2 μs. The excitation source was an IGT-50 nitrogen laser (λ 337 nm, pulse frequency 30 Hz, pulse power 20 μJ). The scheme of the setup was described in detail in [38]. The error in the measurement of τ did not exceed 5%.

The electronic absorption spectra were recorded on a Specord M40 spectrophotometer using 1-cm quartz cells. The IR spectra were measured on a Bruker Vertex 80 spectrometer equipped with an ATR adapter (Zn, Se cell, cell volume 0.1 ml, layer thickness 0.01 mm).

The concentration of water in initial 1,4-dioxane was determined according to Fisher with the aid of a UKT-5 colorimetric titration instrument. All solutions were kept for 20 h at room temperature (~295 K) after preparation prior to use. The kinetic data were processed by the least-squares procedure.

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