TABLE 1. Effect of the Nature of the Monomer on the Initial Polymerization Rate (v_0) (initiator, ammonium persulfate (APS), 0.005 mole/liter, 60°C, aqueous solutions)

Monomer	v_0, mole/liter·sec for an initial monomer		
	1	2	3
DMDAABF$_4$		1,5·10^{-4}	
DMDAACl	4,8·10^{-5}	1,2·10^{-4}	3,1·10^{-4}
DEDAACl	1,6·10^{-5}	6,1·10^{-5}	2,0·10^{-4}
DMDAACF$_3$COO		6,6·10^{-5}	
DMDAABr*	1,9·10^{-6}	1,3·10^{-5}	
DEDAABr*	1,1·10^{-6}		

*[APS] = 0.009 mole/liter.

evaporated to dryness in vacuo. The residue was dissolved in abs. acetonitrile and precipitated with ether. The yield of the monomeric salt was ~55%.

CONCLUSIONS

In radical polymerization of quaternary N,N-diallyl-N,N-dialkylammonium salts in aqueous solutions, changing the nature of the counterion and N-alkyl substituent in the salt molecule makes it possible to vary the values of the initial polymerization rate within comparatively wide limits.

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DIRECT AND SENSITIZED PHOTOLYSIS OF 1,4-BENZOQUINONE DIAZIDES IN ORGANIC SOLVENTS

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One of the methods for the selective generation of cyclohexadienone carbenes in the triplet or singlet form is the sensitized photolysis of quinone diazides. However, despite the theoretical and practical* prospects for research in this direction, information regarding the sensitized photolysis of quinone diazides is limited [1].

The aim of the present research was the kinetic investigation of the direct and sensitized photolysis of 1,4-benzoquinone diazides in organic solvents.

EXPERIMENTAL

1,4-Benzoquinone diazide (I) and its 2,6-disubstituted analogs, viz., 2,6-dibromo- (II), 2,6-di-tert-butyl- (III), and 2,6-diphenyl-1,4-benzoquinone diazide (IV), were selected as the subjects of this research. The quinone diazides were purified by reprecipitation from solutions in benzene by the addition of hexane, and their purity was monitored by thin-layer chromatography (TLC) on Silufol UV-254. The solvents (methanol, benzene, and dioxane) were purified by the method in [2]. The sensitizer (Acridine Yellow) was crystallized from alcohol.

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*Quinone diazides are widely used as the light-sensitive components of photoresistors.

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TABLE 1. Characteristics of the Direct and Sensitized Photolysis of Substituted 1,4-Benzoquinone Diazides (λ 436 nm, CO_2 atmosphere, ~20°C)

Quinone diazide	Direct photolysis								
	methanol			benzene*			dioxane*		
	$\varepsilon \cdot 10^3$	$k \cdot 10^{-4}$, sec^{-1}	Φ	$\varepsilon \cdot 10^3$	$k \cdot 10^{-4}$, sec^{-1}	Φ	$\varepsilon \cdot 10^3$	$k \cdot 10^{-4}$, sec^{-1}	Φ
(I)	0,13	5,07	0,35	0,09	3,15	0,30	0,15	3,10	0,18
(II)	0,17	8,33	0,44	0,11	6,40	0,52	0,16	5,50	0,30
(III)	0,18	4,05	0,20	0,14	1,94	0,13	0,14	1,76	0,12
(IV)	0,36	15,20	0,38	0,56	18,00	0,29	0,32	13,10	0,36

Quinone diazide	Sensitized photolysis								
	methanol			benzene*			dioxane*		
	$k \cdot 10^{-4}$, sec^{-1}	i_φ	L	$k \cdot 10^{-4}$, sec^{-1}	i_φ	L	$k \cdot 10^{-4}$, sec^{-1}	i_φ	L
(I)	14,34	1,60	4,5†	5,33	1,72	2,9	77,50	2,00	50
(II)	19,18	1,48	3,4	20,07	1,83	5,9	83,15	1,59	24
(III)	5,27	1,23	1,6	9,30	1,27	6,1	18,20	1,53	17
(IV)	15,76	1,45	1,5	17,68	1,83	1,8	44,20	1,48	6

*The solvent contained 4% methanol.

†For a nitrogen atmosphere L ≃ 5 [3].

The photolysis of the quinone diazides in organic solvents was carried out in standard quartz cuvettes at room temperature in air, O_2 and CO_2 atmospheres. A DRSh-1000 lamp equipped with a condenser, a heat filter, and a set of light filters (ZhS-11 + interference violet), which made it possible to isolate the mercury line with λ 436 nm, which is weakly absorbed by quinone diazides (Table 1), was used as a source of radiation. The absolute light intensity at λ 436 nm measured by means of a ferrioxalate actinometer was $5.6 \cdot 10^{15}$ quanta/sec. The quinone diazide concentration was $\sim 3 \cdot 10^{-5}$ mole/liter, and the sensitizer concentration was $\sim 1 \cdot 10^{-5}$ mole/liter.

The kinetics of the consumption of the quinone diazides were followed spectrophotometrically (with a Specord UV-VIS spectrophotometer) from the decrease in the optical density at the maximum of the absorption band of the quinone diazides. The quinone diazide was consumed completely in all of the experiments. Isobestic points appeared in the absorption spectra of the reaction mixtures in the case of the formation of reaction products that absorb in the region of the absorption of the quinone diazide or the sensitizer (for example, in the photolysis of IV in dioxane containing 4% MeOH). This indicates the correctness of the determination of the relative concentration of the quinone diazide from the formula $c/c_0 = (D - D_\infty)/(D_0 - D_\infty)$, where D_0, D, and D_∞ are the initial, instantaneous, and limiting values of the optical density at the maximum of the absorption band of the quinone diazide.

Since $D_0 < 0.01$ at λ 436 nm, the quantum yields in the photodecomposition of the quinone diazides were calculated from the formula $\log (D/D_0) = \Phi I_0 \varepsilon t$, where ε is the molar coefficient of absorption of the quinone diazide at λ 436 nm, and the coefficients of shielding (i_φ) of the quinone diazide by the sensitizer were calculated from the formula $i_\varphi = 2.3\ D/(1 - 10^{-D})$, where D is the optical density of the solution at λ 436 nm.

In the case of consumption of the sensitizer during the sensitized photolysis of the quinone diazides, to determine the rate constant of the reaction we used the expression $\ln (D/D_0) = \Phi I_0 \varepsilon \beta \cdot (1 - 10^{D_{sens}})t$, where β is a coefficient that characterizes the probability of energy transfer by the sensitizer, and D_{sens} is the instantaneous optical density of the sensitizer at λ 436 nm.

The efficiency of the sensitized phototransformation of the quinone diazide as compared with its direct photolysis was characterized by the coefficient of sensitization $L = i_\varphi k_s/k_d$, where k_d and k_s, respectively, are the rate constants of the direct and sensitized photolysis of the quinone diazide.

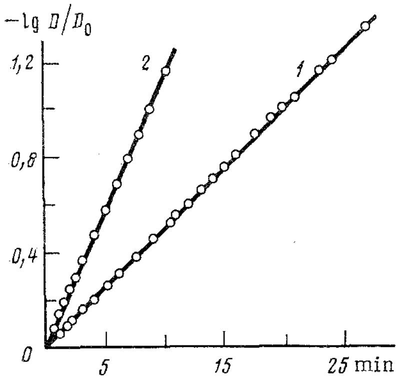

Fig. 1

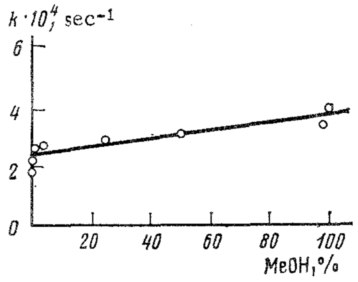

Fig. 2

Fig. 1. Semilogarithmic anamorphoses of the kinetics curves of the phototransformation of quinone diazide II in methanol in the absence (1) and in the presence (2) of a sensitizer in a CO_2 atmosphere.

Fig. 2. Dependence of the rate of phototransformation of quinone diazide III in benzene on the percentage of methanol in the solution (CO_2 atmosphere).

TABLE 2. Quantum Yields in the Photodecomposition of 1,4-Benzoquinone Diazides in Atmospheres of Various Gases Saturating the Irradiated Solutions

Quinone diazide	Gas	Φ			Quinone diazide	Gas	Φ		
		methanol	benzene	dioxane			methanol	benzene	dioxane
(I)	CO_2	0,35	0,30	0,18	(III)	CO_2	0,20	0,13	0,12
	Air	0,32	–	–		Air	0,21	–	0,21
	O_2	–	–	–		O_2	0,24	–	–
(II)	CO_2	0,44	0,52	0,30	(IV)	CO_2	0,38	0,29	0,36
	Air	–	0,42	0,35		Air	–	0,30	–
	O_2	–	–	–		O_2	0,32	–	–

DISCUSSION OF THE RESULTS

Direct Photolysis of the Quinone Diazides. Under the influence of light with λ 436 nm, quinone diazides I-IV decompose in accordance with a first-order kinetic law, regardless of the nature of the solvent and the gas contained in the irradiated system (Fig. 1). The photodecomposition of II in methanol saturated with air or CO_2 constitutes an exception. The observed retardation of the reaction is associated with the accumulation in the reaction mixture of a product that retards the consumption of II. The addition of a fresh portion of II to a solution containing only products of phototransformation of this quinone diazide led to a sharp decrease in the initial rate of its photolysis.

The rate constants (k) and quantum yields (Φ) of the phototransformation of the quinone diazides are presented in Table 1. It is apparent that the Φ values for quinone diazides in methanol are greater than the analogous values in benzene and dioxane. This is most clearly displayed for quinone diazides I and III. A dependence of the rates of their phototransformation on the amount of methanol in the reaction mixture was observed for the same quinone diazides (Fig. 2). Moreover, the addition of methanol also has an appreciable effect on the character of their absorption spectra: The development of a second maximum in the long-wave part of the spectrum, a change in the ratio of the intensities of these maxima, and a change in the overall intensity of the absorption of the quinone diazides are observed. The noted phenomena are evidently due to the formation of a quinone diazide—CH_3OH hydrogen complex.

It follows from Table 2, in which the Φ values in the photodecomposition of the quinone diazides in various solvents saturated with CO_2, air, and oxygen are presented, that the quantum yield depends only slightly on the nature of the dissolved gas. This is in agreement with data on the photodecomposition of I in methanol saturated with different gases [3].

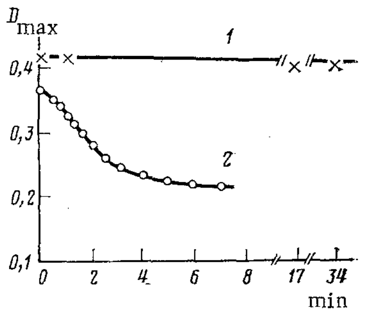

Fig. 3

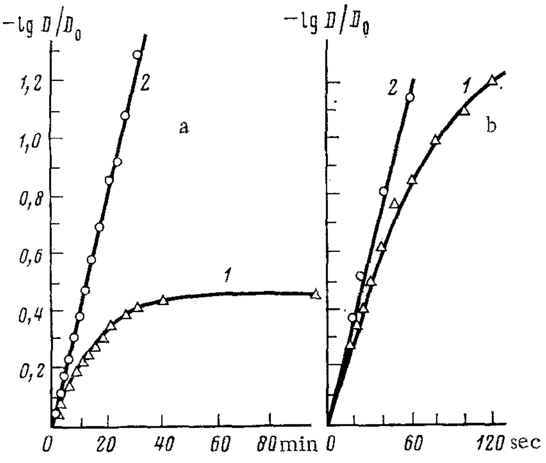

Fig. 4

Fig. 3. Kinetic curves of the consumption of the sensitizer in dioxane + 4% MeOH in the absence (1) and in the presence (2) of quinone diazide IV.

Fig. 4. Semilogarithmic anamorphoses of the kinetic curves of the photosensitized transformation of quinone diazide I in dioxane + 4% MeOH in air (a) and CO_2 (b) atmospheres without (1) and with (2) allowance for consumption of the sensitizer during the reaction.

The introduction of heavy halogen atoms into the quinone diazide ring leads to a certain increase in the Φ values, and this constitutes evidence for participation of the triplet-excited state of the quinone diazide in its photodecomposition [4]. As shown in [5], the photochemically active state of the bulk of the quinone diazide molecules is the singlet-excited state, and ~0.01% of the molecules are in the triplet state.

Sensitized Photolysis of the Quinone Diazides. As compared with direct photolysis, acceleration of the phototransformation is observed in the sensitized photolysis of quinone diazides I-IV in methanol, benzene, and dioxane solutions saturated with CO_2 (see Fig. 1 and Table 1). The data in Table 1 show that the coefficient of sensitization (L) varies over a wide range (1.5-50) and depends on the nature of the solvent and the substituents in the quinone diazide ring. As a rule, L for the investigated quinone diazides increases on passing from methanol to benzene and then to dioxane, whereas it decreases for methanol and dioxane in the order I > II > III > IV.

The observed regularities are evidently due to a change in the fraction of the triplet-excited molecules in the overall number of excited molecules of the decomposed quinone diazide. There are different reasons for these changes. Thus if it is assumed that the photochemical parameters of the sensitizer do not depend on the nature of the solvent, the increase in L in the investigated series of solvents can be explained by an increase in the lifetime of the triplet-excited state of the quinone diazide in dioxane as compared with methanol and benzene and the higher probability of transfer of the energy of the triplet state from the sensitizer.*

The reasons for the change in the coefficient of sensitization in the series of quinone diazides in the case of their photolysis in the same solvent are less obvious. However, it is most likely that the observed regularity in the decrease in L in the order I > II > III > IV is due to the nature and steric effects of the substituents in the quinone diazide ring. The nature of the substituent evidently affects primarily the energies of the triplet state and the constants of intercombination conversion of the quinone diazides, whereas the steric effects of the substituents determine the probability of drawing together of the sensitizer and quinone diazide molecules at distances sufficient for effective energy transfer. Thus, in

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The participation of the T-excited state of Acridine Yellow in the photosensitized transformation of quinone diazides was proved in [3] by a change in the composition of the products of the photodecomposition of I. In addition, it is known [5] that O_2 does not quench the fluorescence of Acridine Yellow and should not hinder sensitization in the case of participation of the S state of the sensitizer in the reaction. However, L = 1 in the presence of O_2.

the case of the sensitized photolysis of the quinone diazides in dioxane the coefficient of sensitization decreases in the order I > II > III > IV. Proceeding from the magnitude of the steric effects of the substituents one might have expected the following order of the change in L: I > II > IV > III. However, 2,6-diphenyl-1,4-benzoquinone diazide (IV) has the lowest L value; this is evidently associated with a decrease in the triplet level of quinone diazide IV owing to the presence in its molecule of a large conjugation system.

The introduction of bromine atoms into the quinone diazide molecule (quinone diazide II) should, on the one hand, decrease the L value because of the steric effects of the bromine atoms and, on the other hand, increase the L value owing to the "heavy-atom effect." However, judging from the magnitude of the coefficient of sensitization, the steric effects prevail.

Some peculiarities are observed in the photosensitized transformation of the quinone diazides. Thus the sensitizer concentration does not change during the reaction in the photolysis of solutions of the quinone diazides in methanol and benzene, whereas it decreases in the case of dioxane (Fig. 3). Violation of the first-order law for the consumption of the quinone diazides in dioxane is also observed (Fig. 4) (the reaction is retarded). Since the sensitizer is consumed during the photoreaction to give products that do not absorb appreciably at λ 436 nm, the change in its concentration can be taken into account. This made it possible to correct the kinetic curves of the photosensitized transformation of the quinone diazides in dioxane and to obtain a linear dependence in semilogarithmic coordinates (see Fig. 4).

Under the conditions of the experiments described the Acridine Yellow concentration remains virtually unchanged in the absence of a quinone diazide (see Fig. 3). Consequently, it may be concluded that intermediates (for example, a cyclohexadienone carbene) formed during the photolysis of the quinone diazide are responsible for the consumption of the sensitizer. In conclusion, let us note that the kinetics of the consumption of the sensitizer and the composition of the products of its transformation during the photolysis of the quinone diazide depend substantially on the presence of oxygen in the irradiated solution.

CONCLUSIONS

1. The quantum yields in the phototransformation of 1,4-benzoquinone diazides in organic solvents range from 0.1 to 0.5; the yields are determined by the structure of the quinone diazide and the nature of the solvent.

2. Acceleration of the phototransformation of 1,4-benzoquinone diazides is observed in the presence of a sensitizer, viz., Acridine Yellow; the coefficient of sensitization varies over a wide range (1.5-50) and depends on the nature of the solvent and the substituents in the quinone diazide molecule.

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