CONCLUSIONS

1. The reaction of disproportionation of a geminal radical pair formed in photodissociation of desoxybenzoins is magnetic- and isotope-selective to the same degree as the recombination reaction.

2. The efficiency of separation of ¹²C and ¹³C isotopes based on the magnetic isotope effect decreases in the order desoxybenzoin, α -methyldesoxybenzoin, and α,α -dimethyldesoxybenzoin during photolysis, which is due to an increase in the probability of isotope-selective disproportionation of geminal radical pairs.

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HYDROGEN ATOM TRANSFER AND TRIPLET EXCIPLEXES IN PHOTOCHEMICAL

REACTIONS OF ACRIDINE AND 9-CHLOROACRIDINE WITH AROMATIC AMINES

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The reaction of electron acceptors, including aza-aromatic compounds in the triplet state, with aromatic amines (Am) frequently takes place by transfer of an H atom, and short-lived triplet exciplexes (TE) are formed in the intermediate stage [1, 2]. Proton transfer with the formation of neutral radicals, which is due to the elevated basicity of the phenazine radical anion [2], is usually the basic pathway of quenching of TE of phenazine with Am in nonpolar solvents. An even higher proton-acceptor capacity should be expected from the radical anion of acridine, and for this reason, transfer of an H atom to the triplet state should play an important role in photochemical transformations of acridine (A) and its derivatives, for which a photoreduction reaction is characteristic. However, in contrast to phenazine, singlet-excited A is assumed to be the reactive state or it is believed that the reaction takes place according to a molecular mechanism.

In contrast to A, the photochemical properties of 9-chloroacridine (CA) have been comparatively poorly described. Hydrolysis of CA into acridine (I) is accelerated by 100 times in UV irradiation [3]; A is formed photochemically not as a result of substitution of Cl by hydroxyl, but by cleavage of an H atom from the solvent by the excited CA and subsequent reaction with oxygen [4]. This behavior of CA in the excited state is somewhat unusual, since nucleophilic substitution of halogen is the characteristic reaction of aryl halides in the excited state, and in the ground state, both types of compounds exhibit a comparable tendency toward nucleophilic reactions. In this respect, the photoreaction of CA with other nucleophiles, with amines in particular, was studied to compare the first stages of the reactions of excited A and CA. The reaction of CA with aliphatic and primary Am takes place easily in cold and

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for this reason, secondary and tertiary Am, whose solutions with CA are stable (no thermal reaction was observed during photolysis), were used.

EXPERIMENTAL

All of the compounds used: A, CA, diphenylamine (DPA), diethylaniline (DEA), diphenyl-p-phenylenediamine (DPPD), tetramethyl-p-phenylenediamine (TMPD), tetramethylbenzidine (TMB), were purified immediately before the experiments by recrystallization or distillation. The solvents were analytically pure. TLC was conducted on Silufol plates, and the eluent was benzene—ethyl acetate, 5:1. The electron spectra were made on a Specord UV-VIS spectrometer.

The absorption spectra and kinetics of quenching of intermediate products were recorded on a laser photolysis setup based on a dye laser with irradiation at 380 nm, and spectrophotometric recording switched on a signal accumulation system [2]. Averaging was conducted every 16-128 bursts. Oxygen was removed from the solutions by prolonged passage of Ar. The measurements were made at 20°C. Steady-state photolysis was conducted in the presence of the O₂ in the air; irradiation with the light from a DRSh-1000 lamp through a UFS-6 filter, and the power of the light beam was 4-6·10⁻³ J/cm². The concentration of the solutions of A and CA was 10⁻⁵-10⁻² M, and the basic studies were conducted with [CA] = 10^{-4} M.

RESULTS AND DISCUSSION

Photoexcitation of toluene solutions of A and CA ($1\cdot10^{-3}$ M) results in the formation of the triplet states ³A and ³CA characterized by an absorption spectrum with λ_{max} of 430 nm (Fig. 1) [4, 8] and a lifetime of ~10 μ sec. ³A and ³CA are quenched by O₂ with rate constants of 2.5·10⁹ and 1.9·10⁹ (moles/liter)⁻¹·sec⁻¹ (estimated from the concentration of O₂ in air-saturated 1.6·10⁻³ M toluene [9]). Addition of amines (in Ar) to solutions of A and CA is accompanied by acceleration of deactivation of ³A and ³CA (quenching rate constants k_q are reported in Table 1) and symbiotic formation of radicals obtained as a result of cleavage of an H atom from a NH group in DPA (Ph₂N· has an absorption spectrum with λ_{max} at 770 nm [10]) or DPPD (λ_{max} 760 nm, cf. Fig. 1 and [11]), and from the methyl groups in TMPD (λ_{max} 510 nm) or TMB (λ_{max} 650 nm) [2]. Quenching of ³A and ³CA by the DEA donor takes place with low rate constants, and estimation gives a value of 1·10⁷ (moles/liter)⁻¹·sec⁻¹ (CA) and 5·10⁶ (moles/liter)⁻¹·sec⁻¹ (A), but also results in the formation of the corresponding neutral DEA radicals (λ_{max} 440 nm [2]).

The semiquinone radical from acridine AH exhibits intense UV absorption (λ_{max} 278 nm, $\varepsilon = 2.4 \cdot 10^4$ (moles/liter)⁻¹ cm⁻¹ [8]. The absorption in the 500-550 nm region is also assigned to radicals AH [12] and CAH [4]. The intense bands observed at 500 (Figs. 1, 3) and 520 nm are due to the absorption of CAH and AH.

A comparison of the absorption of the starting ³A and ³CA and the Ph₂N formed results (assuming 100% yield of radicals from the triplet state) in values of the extinction coefficients of the triplet states of $3\cdot10^4$ and $2\cdot10^4$ (moles/liter)⁻¹·cm⁻¹ (the extinction coefficient of Ph₂N at 770 nm is $3.9\cdot10^3$ (moles/liter)⁻¹·cm⁻¹ [11]), in good agreement with [8]. The use of these extinction coefficients of ³A and ³CA results in the values of the extinction coefficients of the neutral radicals: AH 7·10³, CAH 6·10³, TMB 1·10⁴, and DPPD 1·10⁴ (moles/liter)⁻¹·cm⁻¹. The yield of radicals in quenching of ³A and ³CA by the amines apparently approaches 100%. The CA—TMPD system is an exception, as the yield of neutral radicals is 10 times lower.

The neutral radicals formed as a result of transfer of a H atom from the amines to ³A and ³CA disappear as a result of bimolecular recombination processes.

In the case of TMPD, the dependence of the rate constant of quenching of ³A and ³CA on the concentration of TMPD with a high enough concentration of the amine is nonlinear and goes out to saturation as the concentration of the donor increases. The absorption spectrum of the intermediate products simultaneously changes from the spectrum of ³A or ³CA to superposition of the absorption spectra of the radical cation of TMPD (λ_{max} 570 and 615 nm [1, 2]) and radical anions of the acceptors (λ_{max} 620 nm [13]). This spectral-kinetic behavior indicates a process of reversible formation of TE with complete charge transfer, a contact radical ion pair [1, 2]; ³A + TMPD = ³(A⁻⁷, TMPD⁺⁷).

The kinetics of deactivation of TE obeys a first-order law with rate constants of $1.5 \cdot 10^{-7}$ and $5.0 \cdot 10^{6}$ sec⁻¹ for A and CA, respectively. Proton transfer is the basic pathway of quenching of ³(A⁻⁺, TMPD⁺⁺), and ³(CA⁻⁺, TMPD⁺⁺) is reverse electron transfer; CA⁻⁺ is a weaker proton acceptor than A⁻⁺, and for this reason, the proton transfer rate constant in the corresponding TE is lower. Addition of the oxygen in the air to toluene solutions is accompanied by acceleration of deactivation of TE and a corresponding decrease in the yield of neutral radicals; the quenching rate constants are $7 \cdot 10^9$ (moles/liter)⁻¹·sec⁻¹, which is three times higher than the analogous values of the rate constants of



Fig. 1. Absorption spectra of the triplet state of CA (1); triplet exciplex of CA with TMPD (2), and radicals formed on quenching of ${}^{3}CA$ by DPPD (3) in toluene.

TABLE 1. Rate Constant of Quenching $(k_q \cdot 10^{-7}, (mole/liter)^{-1} \cdot sec^{-1})$ of Triplet States of Acridine and 9-Chloroacridine by Aromatic Amines



Fig. 2. Dependence of the quantum yield (φ) on the concentration of DEA: 1) $\varphi = \varphi_{\text{DMA}}$; 2) $\varphi = \varphi_{\text{DMA}} - \varphi_{\text{tol}}$ (r = 0.9998).

quenching of ³A or ³CA by oxygen. A comparison of the kinetic characteristics of the TE described and TE of phenazine with TMPD [2] shows that in the last case, the rate constants of transfer of H⁺ to TE are more than one order of magnitude lower. This is due to the fact that A^{-} and CA^{-} (especially A^{-}) are significantly stronger bases than the phenazine radical anion.

Introduction of 5 vol. % MeOH in the toluene solutions results in a decrease in the values of k_q for DPA and DPPD, while the yield and nature of the radicals do not change. This effect of small amounts of a solvating solvent is characteristic if a hydrogen bond plays an important role in the reaction of the triplet state with the H atom donor [1].

Amine	Solvent	Φυ	kτ*, M-1	$k_q \tau_T, M^{-1}$
DEA	Toluene	0,024	1,0	3
DPA	Toluene Benzene	0,033 0,028	1,1 5,7	19 -

TABLE 2. Photoreduction and Photosubstitution in 9-Chloroacridine by Aromatic Amines

The presence of an H bond between ${}^{3}A$ or ${}^{3}CA$ and DPPD or DPA results significant acceleration of the reaction of H atom transfer and high values of k_{g} (Table 1) in comparison to TMPD and TMB.

By analogy with quinoid compounds, it is possible to hypothesize that cleavage of an H atom from secondary aromatic amines by the molecules of acridine and its derivatives in the triplet state takes place as a result of ultrafast proton transfer in the unrelaxed state of a primary radical ion pair with a H bond [1]. It is also possible that the reaction takes place in one stage in a complex with an H bond between the triplet state of the acceptor and donor, and the process is characterized by a polar transition state [1].

Small amounts of MeOH have a totally different effect in quenching of ³A or ³CA by tertiary aromatic amines. A significant increase in k_q is observed (Table 1) due to a decrease in the energy of the state with complete charge transfer (radical ion pair). The radical cations TMPD⁺ and TMB⁺ are formed as a result of quenching (λ_{max} 440, 470, 890, and 1000 nm [2]), and their lifetime does not change on addition of O₂ to the solutions. During the reaction with TMPD, neutral TMPD radicals are virtually not formed: the stable radical cation TMPD⁺ accumulates with a low yield. In the case of TMB, formation of neutral radicals from TMB symbatic to the disappearance of TMB⁺ with a characteristic time of 200 nsec is observed.

Fast protonation of A^{-'} and CA^{-'} apparently takes place in the presence of MeOH with the formation of AH and CAH radicals and an ion pair which contains the radical cation of the amine and MeO⁻ (protonation of A^{-'} formed on capture of an electron by acridine by alcohol was previously observed in [12]). The newly formed ion pair (Am^{+'}, MeO⁻) is stable in the case of Am-TMPD (accumulation of TMPD^{+'}). Transfer of a proton from TMB^{+'} to MeO⁻ and the formation of TMB (Me₂NPhPhN(Me)CH₂) effectively takes place in the ion pair containing TMB^{+'} (a stronger H⁺ donor than TMPD^{+'}).

A more detailed study of the effect of addition of MeOH on the behavior of TE in the CA-TMPD system shows that an increase in the contribution of the relatively long-lived TMPD^{+'} is observed with a successive increase in the concentration of MeOH in toluene, and on the other hand, the disappearance of TE is accelerated due to protonation of A^{-'} in TE. It should be noted that absorption of A^{-'} apparently makes the basic contribution to absorption of TE with $\lambda > 652$ nm, where TMPD^{+'} only exhibits very weak absorption. The rate constant of proton transfer from MeOH to A^{-'} in the TE, ~1.10⁷ (moles/liter)⁻¹·sec⁻¹, was estimated from the dependence of the rate constant of quenching of the TE on the concentration of MeOH.

On irradiation of solutions of CA in toluene in air, formation of acridone (I) and diacridyl (II) was observed (cf. [4]). The quantum yield of disappearance of CA, measured with the decrease in the absorption of CA in the 365 nm region, $\varphi_{tol} = 0.0018$, is close to the value estimated in [4] ($\varphi \approx 0.0022$). On addition of DEA to the reaction mixture, photolysis of CA is accelerated, and (I) and (II) are still the basic products of the reaction, and 9-(p-diethylaminophenyl)acridine (III), which is formed in a thermal reaction in melting of CA with DEA (Scheme 1), is not a possible product of nucleophilic substitution. By analogy with the kinetic scheme for DPA (Scheme 2), the experimental results should be linearized in coordinates of φ_{DEA}^{-1} -[DEA]⁻¹. Actually, if the background reaction with toluene is considered, we obtained a linear dependence of ($\varphi_{DEA} - \varphi_{tol}$)⁻¹ vs. [DEA]⁻¹ (Fig. 2), from which the corresponding constants are calculated (Table 2). Solutions of CA in benzene are photochemically stable, since there is no active hydrogen donor. Addition of DEA initiated photolysis, but (I) and (II) were the basic products of the reaction, as in toluene. In the photoreaction with CA, DEA thus reacts as an H atom donor.

The photoreaction of CA with DPA took place differently. The formation of the product of nucleophilic substitution, 9-diphenylaminoacridine (IV) (Scheme 1), was observed in both toluene and in benzene in addition to (II) and (III), and the quantum yield was measured with the increase in the absorption of (IV) in the 500 nm region. A possible pathway of formation of (IV) is recombination of CAH and Ph_2N radicals with subsequent ejection of HCl and aromatization of the products of recombination, i.e., photosubstitution takes place like photoaddition—splitting, in contrast to the thermal reaction, which takes place as a result of nucleophilic attack by Am at the C⁹ carbon atom of the CA molecule.

With a high concentration of DPA (0.5 M), the quantum yields φ for (IV) are similar in toluene and benzene (~1-2·10⁻²). However, in dilution of the solutions, φ in toluene decreases sharply in comparison to benzene; for example, with [DPA] = 0.05 M, $\varphi = 1.7 \cdot 10^{-3}$ and 6·10⁻³, respectively.





In toluene, the excited CA is apparently partially consumed for the reaction with the matrix, and with [DPA] < 0.05 M, this background reaction begins to predominate, since $\varphi_{tol} = 1.8 \cdot 10^{-3}$.

The photoreaction of CA with DPA can be described by simplified scheme 2, where the second reaction includes all processes of deactivation of CA^{*} and its reactions, except for the reaction with DPA. We obtain the following expression for the quantum yield of compound (IV) from this scheme:

$$\frac{1}{\varphi} = \frac{k_1 + k_2 + k_3}{\varphi^* k_1} + \frac{1}{\varphi^* k_1 \tau^*} \frac{1}{[DPA]}$$
(1)

where τ^* is the lifetime of the reaction state of CA^{*} in the absence of DPA; φ^* is the quantum yield of this state (in the case of the singlet state, $\varphi^* = 1$); $k_1 + k_2 + k_3 = k$ is the constant of quenching of CA^{*} by the amine (if the reaction takes place in the triplet state, $k = k_a$ measured in laser photolysis).

Scheme 2

$$CA \xrightarrow{hv} CA^{*}$$

$$CA^{*} \rightarrow CA, hv', \text{ products}$$

$$CA^{*} + DPA \longrightarrow \left| \begin{array}{c} \frac{k_{1}}{k_{2}} & (IV) \\ \frac{k_{2}}{k_{3}} & (I) + (II) \\ \frac{k_{3}}{k_{3}} & CA + DPA \end{array} \right|$$

The free term in Eq. (1) gives the value of the limit quantum yield $1/\varphi_0$, and dividing this term by the coefficient with 1/[DPA] is the product $k\tau^*$. These values for DPA, calculated from linearization of the experimental results in the coordinates of Eq. (1) (Fig. 3), are reported in Table 2. The data for photoreduction of CA by diethylaniline, obtained on the assumption that $k_1 = 0$ for the reaction of formation of (III), are also reported here. As follows from a comparison of the values of φ_0 , DEA is slightly less active in the reaction with CA^{*} than DPA. This is apparently due to the high ionization potential of DEA (7.51 eV) in comparison to DPA (7.2 eV [14]), and consequently its lower donor activity in this reaction. A similar relation of the activities of DEA and DPA was observed in quenching of the triplet state of CA (see above), and for this reason, it is possible to hypothesize that the reactions in Scheme 1 take place in the triplet-excited state of CA. The products of $k_q(r_t)$ calculated using $r_t = 3 \cdot 10^{-7}$ sec (in an air-saturated solution) are reported in Table 2. These values differ, especially significantly in the case of DPA, from



Fig. 3. Dependence of the quantum yield (φ) on the concentration of DPA: 1) toluene (r = 0.9999); 2) benzene (r = 0.9898).

the measured kr^* for photoreactions of formation of products of reduction and substitution. The singlet excited state is probably the most reactive state of CA in reactions of photoreduction and photosubstitution with aromatic amines. By analogy with reactions of singlet-excited A [15], it is possible to hypothesize that an alternative pathway of formation of (IV) (beside recombination of CAH and Ph₂N) is the reaction of CA with DPA according to a molecular mechanism (without radicals) with intermediate formation of 9-chloro-9-diphenylamino-9,10-dihydroacridine, which is transformed into the final product (IV) in splitting with HCl.

CONCLUSIONS

1. Molecules of acridine and chloroacridine in the triplet state form triplet exciplexes of the radical ion pair type with tertiary aromatic amines. Proton transfer from the radical cation to the radical anion with formation of neutral radicals is the basic pathway of quenching of these exciplexes in a nonsolvating medium. In the presence of an alcohol, the triplet exciplexes disappear due to protonation of the radical anion in the exciplex.

2. Quenching of triplet states of acridine and chloroacridine by secondary aromatic amines take place by transfer of an H atom from the amine regardless of the nature of the solvent.

3. The singlet excited state is the most probable reactive state of 9-chloroacridine in photoreduction and photosubstitution reactions with aromatic amines.

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COMPLEXING OF ZINC AND EOSIN PORPHYRINS WITH

VIOLOGENS IN AQUEOUS SOLUTIONS

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The reactions of excited molecules of organic dyes (Dy) and metalloporphyrins (photosensitizers) with electron acceptors of the viologen (N,N'-dialkyl dipyridyl derivatives) type (Vg) are widely used for photogeneration of strong reducing agents (radicals capable of separating H_2 from water in the presence of catalysts [1, 2]. Complexing of a photosensitizer with Vg can significantly affect the efficiency of photogeneration of radicals [3-5]. The effect of electrostatic and donor—acceptor reactions on complexing of a photosensitizer with an electron acceptor in aqueous solutions was investigated in detail in the present study.

EXPERIMENTAL

The following Vg were used: 1,1'-bis(2-sulfonatoethyl)-4,4'-dipyridyl (I), 1-methyl-1'-(2-sulfonatoethyl)-4,4'dipyridyl chloride (II), 1,1'-dimethyl-4,4'-dipyridyl dichloride (III), 1-methyl-1'-(3-methylammoniumpropyl)-4,4'dipyridyl trichloride (IV), 1,1'-bis(3-methylammoniumpropyl)-4,4'-dipyridyl tetrachloride (V); the following Dy were used: eosin disodium salt (VI), zinc meso-tetrakis(1-methyl-4-pyridyl)porphine tetrachoride (VII), zinc meso-tetrakis(4sulfonatophenyl)porphine tetrasodium salt (VIII), which permitted varying the value and sign of the electrostatic interactions within broad limits. The spectra of the solutions were recorded on a Specord M-40 spectrophotometer, and the fluorescence spectra were recorded on an Aminco Bowman spectrofluorimeter.

Serva eosin was used without additional purification. The porphyrins were prepared by the method in [6], and the Vg were prepared according to [7]. All measurements were made in water, and the pH of the solution was 6.3. (VII) and (VIII) dissociated in these conditions, while (VI) is a dianion ($pK_2 = 4.3$) at this pH according to [3].

RESULTS AND DISCUSSION

Addition of Vg ($10^{-6}-4\cdot10^{-2}$) to a solution of (VIII) ($3\cdot10^{-7}-2\cdot10^{-5}$) is accompanied by the disappearance of the 421 nm Soret band of porphyrin and the appearance of an absorption band at 427 nm (Fig. 1). Since Vg do not absorb in this region, the new absorption band can be assigned to the photosensitizer—Vg complex formed in the solution (with $\varepsilon_{427} = 4.8\cdot10^5$ M⁻¹·sec⁻¹). The number of molecules of Vg in the complex (n) was determined from the dependence

$$\log (X_0 - X)/X = \log K + n \log C$$

where K is the complexing constant; X_0 , X are the concentrations of porphyrin with a concentration of Vg equal to zero and C. In all cases, n = 1 (the corresponding values of K are reported in Table 1), which corresponds to the formation of complexes of 1:1 composition. Similar values of K are obtained from the dependence of the intensity of fluorescence on the concentration of Vg on the assumption that the complex formed does not fluorescence

$$K = (I_0/I_C - I)/C$$

where I_o , I_C are the intensity of fluorescence with a concentration of Vg equal to zero and C. We note that the

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