Photoinduced bimolecular cyclization of diarylamines and polyhalogenomethanes into acridines 3.* The study of the intermediate stage of diarylaminoacridine formation in the reaction with tetrabromomethane

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The spectral and kinetic properties of the intermediates in the photoinduced reaction of diarylaminoacridine formation from diarylamine and tetrabromomethane are studied. The data obtained are explained in terms of the following scheme: the recombination of primary radicals to the methyleneiminium salt followed by the alkylation of the second amine molecule at the *ortho*-position and the cyclization into the final product.

Key words: diarylamine, tetrabromomethane, diarylaminoacridine, photoinduced synthesis.

The photochemical reaction of diphenylamine (DPA) with CBr₄ results in the formation of 9-diphenylaminoacridine (DPAA) along with other compounds. The scheme proposed for this reaction includes the stages of cyclization and subsequent nucleophilic substitution.¹ Later results of our studies^{2,3} of a simplified model reaction between substituted DPA molecules and CHBr₃ allowed us to suggest that in reality the substitution precedes the cyclization.³

In the present work, based on studies of the kinetics of the thermal stages and the spectral properties of the intermediates in the photoinduced reaction of DPA derivatives with CBr_4 , the hypothesis given in Ref. 3 is shown to be valid and a more detailed scheme of the reaction is suggested.

Experimental

Prior to use, amines were recrystallized from hexane or ethanol, and CBr₄ was recrystallized from aqueous ethanol. Toluene (spectroscopically pure grade) was used. A thermostated quartz cell was irradiated with the light from a DRSh-1000 lamp using an UFS-5 light filter. The kinetics of dark reactions were followed on a Specord UV-VIS spectrophotometer coupled with a PC 8020 computer. Experiments were carried out at 20 °C. The accuracy of measurements of rate constants was ± 20 %. TLC was performed on Silufol plates in a benzene—ethylacetate (5 : 1) system.

Results and Discussion

The reaction between DPA and CBr_4 results in the formation of triphenylmethane dye $(TPMD)^{1,4}$ along

*	For	report	2,	see	Ref.	3.	
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with DPAA. The spectra of these two products overlap. Since TMPD is formed as the result of attack at the *para*-positions of the benzene rings of the DPA molecule, the use of 4,4'-disubstituted DPA derivatives, di-*p*-tolylamine (DTA), and di-(*p*-cumylphenyl)amine (DCPA), instead of DPA made it possible to rule out this parallel reaction (which is a side reaction in DPAA formation). In this case, diarylaminoacridines (DAAA) are formed instead of DPAA, and they are the sole stable dyes in this system (Scheme 1).

The spectral changes after the irradiation of the reaction mixture are shown in Fig. 1 for the interaction



DPA: R = HDTA: R = MeDCPA: $R = PhCMe_2$



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Fig. 1. Change in the absorption spectra of an evacuated toluene solution containing DCPA (0.01 mol L^{-1}) and CBr₄ (0.025 mol L^{-1}) at 13 °C: before irradiation (*I*); time after irradiation, min: 0 (2), 2 (3), 6 (4), 10 (5), 15 (6), 30 (7).

between DCPA and CBr₄. Spectrum 1 corresponds to the absorption of the DCPA—CBr₄ charge-transfer complex (CTC). As in the model reaction³ with CHBr₃, unstable intermediates (spectra 2-6) are observed immediately after irradiation; the final spectrum 7 corresponds to the DAAAH⁺ salt, which is formed due to the protonation of aminoacridine by the HBr released in the reaction.

Four zones of characteristic changes can be observed in the spectrum: a decrease in the optical density (D) at 340-350 nm and an increase at 370-380 nm in the short-wave spectral range; an increase in D at 500-550 nm and an increase followed by a decrease in D at 600-650 nm in the long-wave range. These changes are similar for both air-saturated and evacuated solutions, *i.e.*, they are not caused by reactions with oxygen.

The kinetic curves measured at four wavelengths are presented in Fig. 2. For convenience the curves are normalized to the maximum change in the optical density at each wavelength. Curve I (see Fig. 2) measured at 345 nm is complicated in shape, with alternating regions of slow and fast drops in the optical density. As in the case of the reaction³ between Am and CHBr₃, the absorption bands of the intermediates and the final products are assumed to overlap in this spectral range,



Fig. 2. Change in the optical density at wavelengths, nm: 345 (1), 375 (2), 515 (3), 610 (4) (for conditions see Fig. 1).

making it impossible to describe the change in D_{345} by a simple kinetic law.

Kinetic curves 2 and 3 characterize the increase in the optical density at 375 and 515 nm, which corresponds to the two main absorption maxima of the DAAAH⁺ salt form. The first maximum is related to the selective absorption of the acridinic ring, while the second maximum is assigned to acridine with the diarylamino group at position 9, *i.e.*, to the absorption of DAAA as a whole. These curves have a distinct exponential shape and almost coincide in semilogarithmic coordinates. Therefore, the formation of the acridinic ring occurs even in the presence of a substituent (the diarylamino group at the C(9) carbon atom) due to a mono- or pseudo-monomolecular reaction (with observed rate constant k_{obs}).

Let us consider whether the spectral and kinetic regularities obtained correspond to the reaction scheme suggested previously (Scheme 2).¹ According to this scheme, the IC1 intermediate compound formed in the recombination of primary radicals undergoes cyclization into bromoacridine (BA). The latter reacts with the second amine molecule to form DPAA. In fact, the amine radical cation, which disappears in the millisecond time range, has been previously observed by the pulse photolysis technique.⁵ Spectrum 2 observed immediately after irradiation characterizes a more long-





Fig. 3. Dependence of the observed rate constant (k_{obs}) of DAAA formation on the amine concentration for DTA (r = 0.9996) (1) and DCPA (r = 0.9962) (2), [CBr₄] = 0.025 mol L⁻¹, toluene, 20 °C.

living intermediate with a lifetime of an order of tens or hundreds milliseconds. In terms of Scheme 2, spectrum 2 can be assigned only to IC1, and not to BA, because the latter compound has characteristic absorption bands in the 375 nm range,⁶ which are absent in spectrum 2. Therefore, in the sequence of reactions IC1 \rightarrow BA \rightarrow DPAA, the first stage is rate-limiting and, hence, the k_{obs} rate constant characterizes the intramolecular cyclization. The observed first order of the reaction does not contradict this assignment.

However, the study of the effect of the amine concentration on k_{obs} shows that k_{obs} increases proportionally as the concentration increases (Fig. 3), *i.e.*, the amine molecule is involved in the rate-limiting stage.

No DAAA formation is observed when amines substituted at the nitrogen atom, N-methyl-DTA (MDTA) and N-benzyl-DTA, are introduced into the photochemical reaction with CBr₄. This fact can be explained in terms of Scheme 2 by blocking of the latter stage (the nucleophilic substitution at the nitrogen atom is impossible), *i.e.*, the reaction would cease at the cyclization stage to form equimolar amounts of, *e.g.*, N-methyl-9-haloacridinium. However, we failed to observe the latter compound in the reactions of CBr₄ with DTA and MDTA under comparable conditions. Thus, the set of spectral and kinetic data does not fall into the terms of Scheme 2.

Scheme 3 presents the sequence of reactions that can be proposed for the photoinduced formation of DAAA from diarylamine and CBr₄ based on the results of studying³ the model reaction between Am and CHBr₃. The first two reactions (the formation and the photodissociation of CTC) are omitted because they correspond to those reactions in Scheme 2. However, the following reactions are different from those in Scheme 2: the primary radicals recombine to form the In1 intermediate, which produces the In2 intermediate via a reaction with the second amine molecule (rate constant k_1). In2 is shown in Scheme 3 as two tautomeric forms. The reaction (In1 + Am \rightarrow In2) can be considered as nucleophilic substitution with respect to In1 or as electrophilic alkylation with respect to the amine. Then In2 is transformed into DAAA as the result of cyclization (rate constant k_2).

According to Scheme 3, the two latter stages of the photoinduced reaction are described by the following kinetic equations (the preceding stages of the reaction can be neglected because the rate of formation of In1 is several orders of magnitude higher than the rate of its following transformations):

$$d[In1]/dt = -k_1[In1][Am],$$

$$d[In2]/dt = k_1[In1][Am] - k_2[In2]$$

$$d[DAAAH^+]/dt = k_2[In2].$$

It is clear that if $k_2 \gg k_1$ [Am], the observed rate constant k_{obs} , which is equal to k_1 [Am], is proportional to the amine concentration. In this case, the values of the bimolecular rate constants, k_1 (20 °C, toluene/mol⁻¹ L s⁻¹), 0.33 (DTA) and 0.21 (DCPA), found from the dependence of k_{obs} on [Am] characterize the alkylation of amines by the In1 compound. In1 has the structure of a substituted methyleneimine salt. The reaction of Am with CHBr₃ results in the formation of an In1 compound with a similar structure with $k_1 =$ 10.9 mol⁻¹ L s⁻¹. It can be seen from a comparison of the k_1 values that the activity of In1 formed in the reaction with CBr₄ is substantially lower than that of the

Scheme 3



analogous intermediate formed in the reaction with CHBr₃. As a result, the condition $k_2 \gg k_1$ [Am] is achieved, substitution becomes the rate-limiting stage for the whole sequence of thermal stages following the excitation of the Am-CBr₄ CTC, and therefore, the observed rate constant of the formation of DAAA begins to depend on the amine concentration. Recall that in the model reaction with CHBr₃, at [Am] > 0.02 mol L⁻¹ the inverse correlation ($k_2 < k_1$ [Am]) is observed, and the cyclization of In2 is the limiting stage of acridine formation (see Ref. 3).

Now let us consider the kinetic behavior of an unstable compound (X) with absorption in the range from 600 to 650 nm (see Fig. 1, spectra 2-6). The flattened shapes of the intermediate spectra do not allow us to hold reliably that there is an isobestic point in the 570 nm range in the later stages of the reaction (see Fig. 1, spectra 5-7). The existence of this point could suggest that X is transformed to DAAA, and is an intermediate in DAAA formation. The analysis of the kinetic curve of the change in D_{610} as a whole (see Fig. 2, curve 4) also cannot justify this assumption. In fact, since the kinetic behavior of X is described by a curve with a maximum and the sequence of the reactions ... $\rightarrow X \rightarrow DAAA$ takes place, the curve of the accumulation of DAAA must be S-like in shape, and the rate of DAAA formation should become maximum when the maximum on the D_{610} —time curve is reached. However, as mentioned above, DAAA accumulation within the time range considered follows an exponential law. Therefore, the data available do not suggest that X is an intermediate in DAAA formation.

The change in the D_{515}/D_{375} ratio as the reaction progresses is shown in Fig. 4. This ratio is small at the beginning of the reaction (from seconds to tens seconds) and then tends to the limit equal to the value of this ratio for the pure DAAAH⁺ cation (see Fig. 4, dotted line). The regularities observed agree completely with Scheme 3. Actually, at the moment of the initial observation, which is several seconds after the photoexcitation, the reaction mixture contains the product of the recombination of primary radicals, In1 methyleneimine salt, whose absorption spectrum lies in the near range of the UV spectrum.⁷ This fact explains the small value of D_{515}/D_{375} . For the ratio of the rate constants found, the quasi-equilibrium concentration of the next intermediate (In2) is small, and hence, it is not observed in the spectra. An increase in the D_{515}/D_{375} ratio corresponds to the transformation of In1 to DAAA, which (in the protonated form) is responsible for the final spectrum of the reaction mixture. The other products of the reaction between DCPA and CBr₄, whose existence is indicated by the data of TLC, are likely to absorb in the UV spectral range and their absorption would be obscured by the absorption of the amine and toluene.

The curves of the D_{515}/D_{375} ratio are almost coincident for the air-saturated and evacuated solutions (see Fig. 4, curves *l* and *2*, respectively). Therefore, possible



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Fig. 4. Change in the ratio of the optical densities (D_{515}/D_{375}) at the thermal stages of the reaction (for conditions see Fig. 1): air-saturated solution (*I*), evacuated solution (*2*) (the D_{515}/D_{375} ratio for pure DAAA · HBr is indicated by the dotted line).

oxygen-containing products do not absorb in the spectral range observed.

Unlike the kinetic curves of the change in the D_{525}/D_{370} ratio for DCPA, those for DTA do not reach the value corresponding to the pure DAAAH⁺ cation, *i.e.*, other compounds absorbing in the UV range are formed as final reaction products in addition to DAAAH⁺. At the same time, the curves for the air-saturated and evacuated solutions coincide for both DCPA and DTA, *i.e.*, the additional absorption in the UV spectral range is not related to the formation of oxygen-containing products.

It is likely that the distinction in the photochemical behavior of these amines is associated with the specific features of their structures. One of the channels of the formation of side products can be related to the existence of the methyl group in the *para*-position to the nitrogen atom. For example, *para*-quinone derivatives can be formed in the reaction involving the tribromomethyl radical followed by the formation of side products:



In the DCPA molecule there are no labile hydrogen atoms in the *para*-position to the carbon atom. Therefore, this amine produces fewer side products.

Only key stages and intermediates are shown in Scheme 3. It is clear that σ -complexes are formed first in both the recombination and the substitution reactions according to the general mechanism of aromatic electrophilic substitution,⁸ and then they eliminate HBr and are transformed into In1 and In2, respectively.

A comparison of Scheme 3 with the previously suggested Scheme 2 (see Ref. 1) shows that the difference begins with the recombination of the primary products. According to the quantum chemical calculations, the maximum unpaired electron density in the Ar_2NH^+ and Ar_2N^+ radicals falls on the central nitrogen atom.⁹ Accordingly, the recombination of the halomethyl radical occurs mainly at the nitrogen atom of the radical cation and/or the neutral amine radical. The methyleneimine salt that is formed produces an intermediate compound in the reaction with the second amine molecule. Then this intermediate undergoes cyclization into the final acridine.

At the same time, Scheme 3 as a whole is similar to the set of reactions of the photoinduced formation of acridines from diarylamines and CHBr₃ (see Ref. 3). The only distinction is that an HBr molecule is eliminated from the cyclization product (In2) at the last stage of aromatization in the reaction with CBr₄, while in the reaction with CHBr₃ an amine molecule is eliminated. Therefore, in the reaction with CBr₄ the molecule of the final product includes, in fact, fragments of two molecules of the initial amine, and in the reaction with CHBr₃ it contains fragments of only one amine molecule.

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