Photoinduced formation of 9-diarylaminoacridines from diarylamines and tetrabromomethane: reaction mechanism

M.F. Budyka

Photochemistry Department, Institute of Chemical Physics, Russian Academy of Sciences, 142432, Chernogolovka, Moscow Region, Russia

Abstract

The UV irradiation of di-para-substituted diphenylamines and CBr_4 results in the formation of 2,7-disubstituted 9-diarylaminoacridines (DAAAs) with quantum yields of 0.035–0.080. The yield of DAAA is linearly dependent on the light intensity. An intermediate (IM1) with a lifetime varying from several minutes to tens of minutes is observed. IM1 is transformed into DAAA with pseudo-first-order kinetics, the observed rate constant being proportional to the amine concentration. A detailed examination of the spectral and kinetic properties of IM1, and a comparison with the reaction of amines with $CHBr_3$, leads to the conclusion that an intermediate (IM2) is formed during the transformation of IM1 to DAAA. The general reaction scheme of the photoinduced formation of DAAA is assumed to involve five principal stages: the formation of an electron donor–acceptor complex between the reactants; photodissociative electron transfer from the amine to CBr_4 on irradiation of the complex; recombination of the $CBr_3{}^{\cdot}$ radical predominantly on the nitrogen atom of the amine cation radical and/or neutral radical, resulting in the formation of IM1; interaction of IM1 with the second amine molecule and formation of IM2 (this is the rate-limiting state); fast cyclization of IM2 to DAAA.

Keywords: Charge transfer complex; Photoinduced reaction; Diarylamine; CBr_4; Aminoacridine; Reaction mechanism

1. Introduction

The formation of 9-diphenylaminoacridine (DPAA) by photochemical reaction of diphenylamine (DPA) with CBr_4 was discovered a decade ago [1,2]. The last two compounds form an electron donor–acceptor (EDA) complex [3]. Irradiation of this complex at the charge transfer (CT) band results in the formation of the DPA cation radical [4], which is the primary product in the photoinduced formation of DPAA. Different proposals have been put forward for the subsequent reactions of the primary products and the reaction scheme of DPAA formation as a whole [1,2].

The reaction of photoinduced formation of 2,7-dimethylacridine from di-*p*-tolylamine (DTA) and bromoform can be regarded as a simplified model of the formation of diarylaminoacridine (DAAA) from this amine and CBr_4. As intermediates with lifetimes in the microsecond to second time range have been observed in this model reaction [5], we propose that similar rather long-lived reactive particles should also be formed in the reaction of aromatic amines with CBr_4.

This paper reports the results of an investigation of the mechanism of the photochemical reaction of diarylamines with CBr_4. Particular attention has been given to the study of the spectral properties and kinetic behaviour of the secondary intermediates. The primary stages of the reaction have been studied previously by flash photolysis, and the formation of an amine cation radical $Ar_2NH^{\cdot +}$ and, probably, a neutral radical $Ar_2N^{\cdot}$ has been proposed [6].

In order to avoid the formation of triphenylmethane dyes in this reaction system [3] and to facilitate the spectral observation of the intermediate and final reaction products, the derivatives of DPA with substituents in the para positions of the benzene rings were used, i.e. DTA and di(*p*-cumylphenyl)amine (DQPA). In reactions of these amines with CBr_4, derivatives of DPAA, i.e. DAAAs, are formed and are the only coloured reaction products (Scheme 1).

2. Experimental details

Amines and CBr_4 were purified by crystallization prior to use. Toluene (spectrograde, Reachim) was used
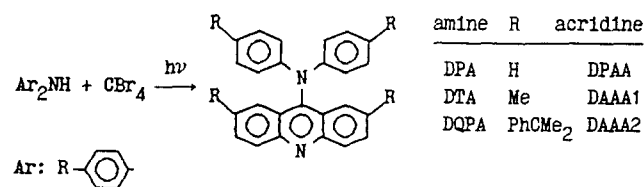
Scheme 1.

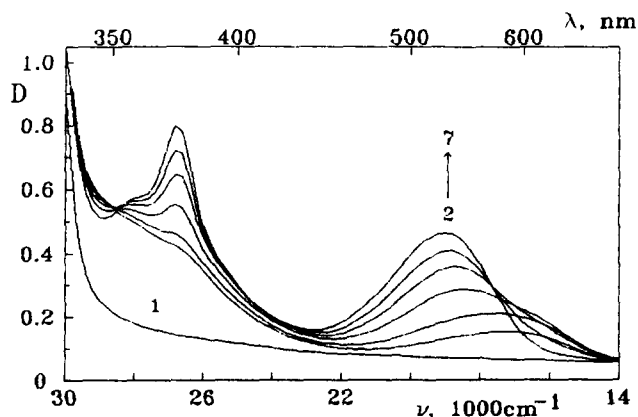Fig. 1. Absorption spectra of a degassed toluene solution, containing [DQPA] = 0.01 M and [CBr₄] = 0.025 M, before (1) and after (2) irradiation; (2)–(7) spectral change during thermal stage of photoinduced reaction (13 °C, 0–50 min).

as received. Experiments were carried out in thermostatically controlled quartz cuvettes (path length, 0.5 cm); if necessary, solutions were degassed by repeated freeze–pump–thaw cycles.

Irradiations were performed with a high pressure mercury lamp; the line at 365 mn was selected using appropriate glass filters. For quantum yield determinations, the intensity of the incident light, measured using a PP-107 actinometer, was 1.2×10^{-6} W cm^{-2}. Electronic absorption spectra were recorded on a Specord UV–visible spectrophotometer.

The rate constants of the thermal stages were calculated provided that the kinetic order observed was within the time region of two or more half-lives (error limits, ±20%).

3. Results

3.1. Quantum yields

Identical spectral changes were observed on irradiation of the DTA–CBr₄ and DQPA–CBr₄ EDA complexes. As an example, Fig. 1 shows the spectra of DQPA–CBr₄ in toluene. Spectrum 1 corresponds to that of the EDA complex (the CT band can be obtained by difference spectroscopy). The transient spectra 2–6 were registered at different reaction times after irradiation and testify to the transformations of the primary photoinduced intermediates. The final spectrum 7 corresponds to that of the protonated form of DAAA, i.e. the acridinium cation DAAAH$^+$.

The quantum yield of DAAA formation was defined as the linear slope of the D–$I_0 t$ plot [5]; the optical density D was measured at 525 nm ($\epsilon = 14\,000$ M^{-1} cm^{-1}) during the formation of DAAA1 from DTA and at 515 nm ($\epsilon = 18\,700$ M^{-1} cm^{-1}) during the formation of DAAA2 from DQPA after completion of the thermal stages of the reactions. Straight lines were obtained for both amines in the initial stages of irradiation. The quantum yields were calculated to be: aerated solutions, 0.035 ± 0.007 for both amines; degassed solutions, 0.063 ± 0.012 (DTA), 0.080 ± 0.016 (DQPA).

The dependence of the quantity of aminoacridine formed on the light intensity was measured with constant irradiation time (Fig. 2).

3.2. Kinetics of the thermal stages

Fig. 3 shows the kinetic curves, measured at different wavelengths, corresponding to the transformation of spectra 2–7 in Fig. 1. The optical density changes in the short-wave and long-wave spectral regions (curves
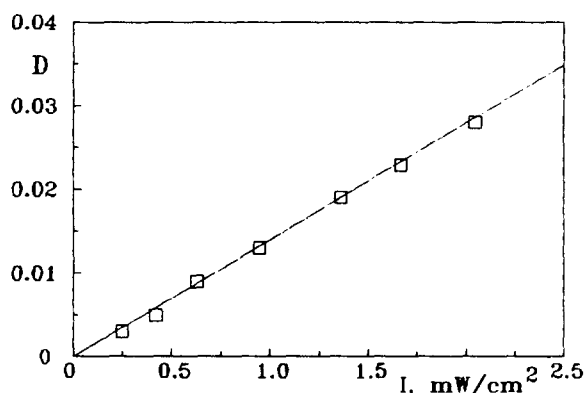

Fig. 2. Optical density of DAAA1 formed vs. light intensity for constant irradiation time; [DTA] = 0.02 M, [CBr₄] = 0.098 M, aerated solution in toluene, 22 °C.
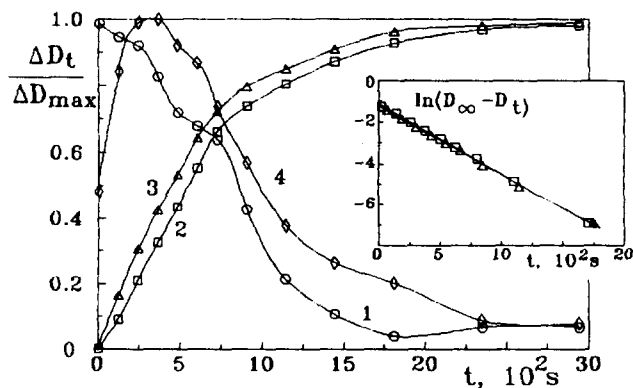

Fig. 3. Time dependence of the absorbance (ratio to maximum D change) at 345 (1), 375 (2), 515 (3) and 610 nm (4), corresponding to the transformation of spectra 2–7 in Fig. 1. The inset shows the semilogarithmic plot of curves 2 and 3.

1 and 4 respectively) do not obey a simple kinetic low, testifying to the superimposition of the absorption of different reaction products in these regions.

Curves 2 and 3 (Fig. 3), measured at 375 and 515 nm respectively, obey a first-order kinetic law and are practically coincident in the semilogarithmic form (Fig. 3, inset). Since they characterize the increase in the optical density at the two main maxima of the DAAA absorption spectrum, the rate constant found can be regarded as the constant k_f of DAAA formation.

In order to determine the real nature of k_f (i.e. monomolecular or pseudo-monomolecular), the effect of the solution composition on the k_f value was studied by carrying out the photolysis using varying amine concentrations. In Fig. 4, the measured first-order rate constants for DAAA formation from DTA and DQPA are plotted as a function of the amine concentration $(2.5 \times 10^{-3} - 8.0 \times 10^{-2}$ M). From the slopes of the straight lines, the second-order rate constants k_2 were obtained as (20 °C, toluene, M^{-1} s^{-1}): 0.33 (DTA) and 0.21 (DQPA).

The dependence of the constant k_f on the temperature was also measured (Table 1). The calculated enthalpy and entropy of activation of the rate-limiting stage are given in Table 2.
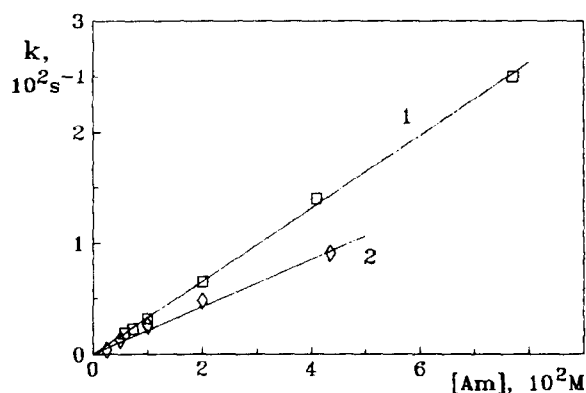

Fig. 4. First-order dependence of the observed rate constants of aminoacridine formation (at 525 nm for DTA and 515 nm for DQPA) on the amine concentration.

Table 1
The dependence of the observed rate constant k_f of aminoacridine formation on temperature; k_f was measured at 525 nm for DTA and at 515 nm for DQPA ([Am] = 0.01 M, [CBr$_4$] = 0.025 M, toluene)

| DTA		DQPA	
T (K)	$k_f \times 10^3$ (s^{-1})	T (K)	$k_f \times 10^3$ (s^{-1})
279	2.0	279	1.2
286	2.6	286	1.6
293	3.2	293	2.6
300	4.3	300	3.6
307	5.7	307	5.3
314	7.3		

Am, amine.

Table 2
Activation enthalpy and entropy of the rate-limiting stage in the photoinduced formation of aminoacridine from diarylamine and CBr$_4$

Amine	ΔH^* (kJ mol^{-1})	$-\Delta S^*$ (J/K^{-1} mol^{-1})
DTA	24.6 ± 1.9	169 ± 6
DQPA	36.0 ± 3.7	133 ± 13

4. Discussion

Taking into account the results obtained in this study and those in the simplified model reaction of amine with CHBr$_3$ [5], the reaction scheme of aminoacridine formation from diarylamine and CBr$_4$ is assumed to involve at least five principal stages (Scheme 2).
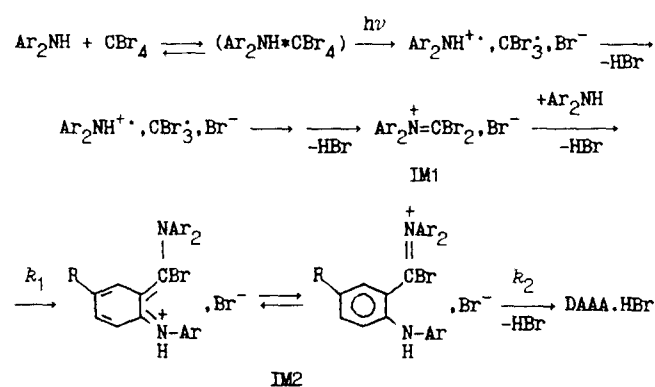
Scheme 2. Photoinduced aminoacridine formation from diarylamine and CBr$_4$.

Scheme 2 does not show the detailed pathway of IM1 formation. This may be formed on recombination of the CBr$_3$· radical directly with the amine cation radical Ar$_2$NH·$^+$ or with the neutral radical Ar$_2$N· obtained after deprotonation of the former. In both of these species, the spin density on the nitrogen atom predominates over that on the benzene ring carbon atoms [7,8], so that the attack of CBr$_3$· should be predominantly directed towards this atom. Therefore recombination with the participation of both Ar$_2$NH·$^+$ and Ar$_2$N· is possible. In order to distinguish between these two possibilities, the spectral and kinetic properties of the primary radical particles must be analysed in detail by laser photolysis.

Methyleneiminium salts are electrophilic and react smoothly with aromatic amines [9]. As it is a methyleneiminium derivative, compound IM1, on reaction with a second amine molecule, produces the intermediate IM2. The intramolecular cyclization of IM2 results in the formation of aminoacridine.

Taking into account the large difference between the rates of formation and subsequent transformation of IM1 (the reactions of recombination and substitution respectively), the following set of kinetic equations can be written (Am, amine)

$d[IM1]/dt = -k_1[IM1][Am]$

$d[IM2]/dt = k_1[IM1][Am] - k_2[IM2]$

$d[DAAAH^+]/dt = k_2[IM2]$

On condition that $k_2 \gg k_1[Am]$, the observed rate constant $k_f = k_1[Am]$ should be assigned to the interaction of IM1 with Am, and the activation parameters, measured from the temperature dependence of k_f (Table 2), are also attributed to this reaction. The rather large negative activation entropy and low activation enthalpy are characteristic of bimolecular reactions of nucleophilic substitution.

The kinetics of the secondary "dark" stages of the photoinduced reaction and the spectral properties of the intermediates and final reaction products are similar in aerated and degassed solutions, but the quantum yields of DAAA formation are greater in degassed solutions. The reduction of the quantum yields in the presence of air appears to be associated with side reactions of oxygen with excited or primary ion radical particles.

Attention is drawn to the fact that, in degassed solution, the quantum yield of DAAA2 formation is somewhat higher than that of DAAA1 formation. The difference in the quantum yields appears to be associated with the difference in the structures of the para substituents in the molecules of the starting amines. Methyl groups in the DTA molecule contain mobile hydrogen atoms of the benzyl type. For example, $CBr_3^{\cdot}$ can abstract hydrogen atoms from amine or its cation radical, giving rise to the side products
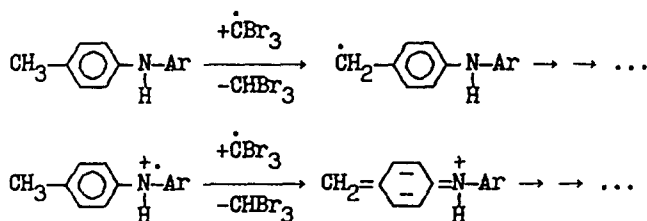
The molecule of DQPA is free of mobile hydrogen atoms; therefore on reaction of this amine in degassed solution, the photoinduced reactive particles are not wasted. In the presence of oxygen, the distinction between the photochemical reactivities of the two amines disappears.

Scheme 2 as a whole is coincident with the scheme of acridine formation from diarylamines and $CHBr_3$ [5]. In order to determine the distinguishing feature of the reaction with CBr_4, the last stage in Scheme 2 must be discussed in more detail. The transformation of IM2 to acridine comprises at least two steps: cyclization to dihydroacridine derivative and aromatization of the latter (Scheme 3). In the reaction with $CHBr_3$ ($X \equiv H$), aromatization occurs by splitting of the diar-

ylamine molecule, whereas in the reaction with CBr_4 ($X \equiv Br$), only HBr is split from dihydroacridine. Therefore, in the reaction with CBr_4, the final acridine molecule includes two molecules of the starting amine, compared with only one amine molecule in the reaction with $CHBr_3$.
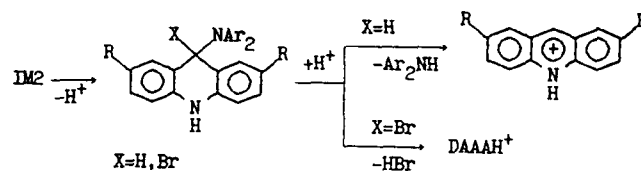
Scheme 3.

The linear dependence of the aminoacridine yield on the light intensity (Fig. 2) testifies that the reaction is induced by the absorption of a single quantum, and that subsequent stages involving complex transformations of the intermediates proceed "in the dark".

5. Conclusions

The reaction mechanism of photoinduced formation of aminoacridine derivatives (DAAAs) from derivatives of DPA and CBr_4 was studied. An intermediate IM1 with a lifetime of about 1 min was registered. The spectral and kinetic properties of IM1, i.e. the dependence of the observed rate constant of transformation to DAAA on the amine concentration and the values of the enthalpy and entropy of activation, lead us to conclude that an additional intermediate exists on going from IM1 to DAAA.

In view of the previous investigation of the primary stages of the reaction and the results of a model reaction with $CHBr_3$, a general scheme was proposed for the bimolecular photocyclization reaction of diarylamines to acridines in the presence of halogenomethanes.

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