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Photochemical reactions of complexes of aromatic amines with polyhalomethanes

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Abstract. Data concerning the chemical processes occurring under light irradiation of complexes of aromatic amines with polyhalomethanes are critically reviewed. It is shown that electron transfer from an amine to a halomethane is the main photochemical reaction of the complexes. The properties and reactions of primary radical-ion species and secondary inter-mediates formed are discussed. The mechanisms of photo-induced formation of triphenylmethane dyes and acridine derivatives are considered in detail. The bibliography includes 234 references.

I. Introduction

Charge transfer complexes (CTC) are rather labile self-organising systems consisting of at least two components, an electron donor and an electron acceptor. The formation of a CTC manifests itself most clearly in the appearance of a new absorption band, the charge transfer (CT) band, in the electronic spectra of the mixtures of components. Electron transfer (ET) is the most typical reaction of such complexes. Depending on the properties of the donor and acceptor and on the external conditions, ET can occur either thermally or under light irradiation. Therefore, CTC provide a convenient model for studying the ET process.[1–6] In recent years, the attention of investigators has been attracted to molecular-bonded donor-acceptor systems.[7–13]

Of particular interest is the chemical aspect of ET, since this process is the primary step in many chemical transformations.[14–19] One can vary the rate of initiation of chemical reactions over a wide range and make them follow a required path by varying the properties of CTC components. This allows one to study reaction mechanisms, detect intermediate compounds, and determine their structures.

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In the present review we consider the photochemical reactions of complexes formed from aromatic amines (Am) with polyhalomethanes (PHM). The amine complexes have been known for a long time, but the use of PHM, particularly the chloro-substituted ones, in complexation reactions started only in the 1960s, when it was found that they could act as acceptors in complexes with comparatively strong donors, such as Am.[20] Since PHM correspond to 'sacrificial' acceptors (which decompose irreversibly when they capture an electron), irradiation of an Am + PHM mixture inevitably results in the initiation of chemical transformations. For this reason, studies of the photochemical properties of PHM started shortly after the discovery of their complexation ability.[21–26]

Two main aspects can be distinguished in the photochemical studies of Am – PHM systems: (1) the study of primary reactions and properties of primary photogenerated species; (2) the isolation of end products (dyes) formed under the irradiation of solutions simultaneously containing an Am and a PHM, and the determination of their structures and mechanisms of formation. Although the viewpoints of scientists on the first aspect are well founded and common, the data on the structures of dyes and the mechanisms of their formation are contradictory. The subject of the present review is analysis of these data, and we shall hardly deal at all with the rather broad and important aspect relating to study of the possibility of practical use of Am · PHM complexes, in particular in systems for information recording. These problems have been thoroughly discussed in works by Vannikov and Grishina.[27–30]

Prior to discussing the photochemical reaction of CTC we should also mention the complexation reaction itself, which occurs before light irradiation of the system is started. A detailed analysis of this reaction is a subject for special consideration. We shall note only the particular features of the donor – acceptor interaction of amines with PHM which affect considerably the photochemical properties of the complexes.

An important photochemical parameter is the action spectrum, i.e. the spectral region in which the irradiation results in light absorption and initiation of a chemical reaction. The action spectrum of Am · PHM complexes is generally located in the near UV region, e.g., in the 330–380 nm region for the CTC of diphenylamine (DPA) with CBr_4.[21,31] It has traditionally been accepted that CBr_4 forms 1:1 complexes with amines.[31–33] However, it was shown recently that DPA derivatives can form higher complexes, the so-called polycomplexes,

whose absorption spectra are shifted bathochromically relative to that of the 1:1 CTC.[34,35] Owing to the formation of such complexes, whose absolute content in an equilibrium mixture increases with increasing concentrations of the components, the action spectrum of the CTC of diphenylamine (and its derivatives) with CBr_4 expands significantly into the visible region up to 500–550 nm.[27,34] On the other hand, the relative content of polycomplexes in the mixture is small in comparison with that of the free amine, and hence they do not affect the kinetics of secondary chemical reactions initiated by light absorption.[36]

II. Primary photochemical processes during irradiation of amine–polyhalomethane systems

To date, it has been established unambiguously that the transfer of an electron from an amine to a halohydrocarbon (HC) is the primary photochemical act during the irradiation of mixtures of amines with PHM or, more widely, with HC. Depending on the structure of the donor and acceptor components, three routes for the photoinitiation of ET exist: excitation of CTC, selective excitation of Am, and selective excitation of HC. All three ways do not necessarily actually occur for any arbitrary Am–HC pair, since this would require that the absorption bands of Am, HC and CTC are sufficiently different.

Relatively strong donors (alkylarylamines, di- and triarylamines, diamines) and/or acceptors (polybromohydrocarbons, nitrohalo-derivatives, halocarbonyl compounds) form complexes whose absorption spectra are shifted bathochromically relative to the spectra of the components, since selective excitation of their complexes in the CT bands is possible.[27,37–39] In this case, ET occurs within the complex and, in essence, corresponds to an intramolecular process[40] (static quenching of Am luminescence,[41] or innersphere ET, according to the terminology accepted in the literatire[1,42]).

$$\mathrm{Am + RX} \rightleftharpoons \mathrm{(Am \cdot RX)} \xrightarrow{h\nu} \mathrm{(Am^{+\cdot} RX^{-\cdot})} \qquad (1)$$

Chlorohydrocarbons form weak complexes with amines (with stability constants $< 0.1\ \mathrm{l\ mol^{-1}}$), whose concentrations are much less than those of the starting components and whose absorption spectra almost coincide with those of the amines. When such mixtures are irradiated, an Am reacts with a HC to give a radical cation (RC) of the amine[43–48] (dynamic quenching of Am luminescence, outersphere ET).

$$\mathrm{Am} \xrightarrow{h\nu} \mathrm{(Am)^*} \xrightleftharpoons{RX} \rightleftharpoons \mathrm{[(Am)^* \cdot RX]} \longrightarrow \mathrm{(Am^{+\cdot} RX^{-\cdot})} \qquad (2)$$

Although it is assumed that reaction (2) occurs via quasistable intermediates, exciplexes,[44,45,49,50] their formation in the reactions of amines with alkyl halides has not been proved, unlike e.g. photochemical reactions of amines with carbonyl[51,52] or aromatic compounds,[53–57] including aryl halides.[58–62]

Selective excitation of a HC results in homolytic cleavage of a C–X bond (see Ref. 63)

$$\mathrm{RX} \xrightarrow{h\nu} \mathrm{R^{\cdot} + X^{\cdot}}, \qquad (3)$$

(heterolytic cleavage with formation of a carbonium ion is also possible for branched R).[64] Several authors assume that reaction (3) occurs when mixtures of aromatic amines with CX_4 (X = Cl, Br) are irradiated.[21,65,66] Probably, photoinitiation of Am + RX reactions by excitation of RX in their own absorption bands to a noticeable extent is possible only for aryl halides,[67–69] whose absorption spectra are shifted relative to those of the amines. Since the absorption spectra of alkylated HC overlap considerably with those of amines, selective excitation of the former in Am–HC mixtures is unlikely.

In some cases, it was possible to determine the nature of the excited state involved in the ET process. It was shown by the chemically induced nuclear polarisation (CINP) method for the $Et_3N \cdot CCl_4$ complex that ET occurs by reaction (1) in a excited singlet state.[70,71] The reactions of arylamines with chloro-containing HC also occur by the singlet mechanism.[59,72–75]

A study of the photochemical properties of the system *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine–carbon tetrachloride showed that the reaction in a benzene solution occurs via an excited triplet state,[76] while in pure CCl_4 it probably occurs in a singlet state.[77] In both cases, the quantum yield of the contact ion pair $Am^{+\cdot}/Cl^-$ is close to unity and decreases somewhat when tetramethylbenzidine is used as the electron donor.[78]

It was found in a study of photo-ET from excited *N,N*-dimethylaniline (DMA) to chlorobenzene that both the singlet and the triplet states of DMA are reactive.[79,80] It was assumed that photodebromination of bromoanthracene by amines also occurs by the triplet pathway,[81] but recent studies by nanosecond laser photolysis has shown that an excited singlet state is reactive and that an intermediate anion radical ($RX^{-\cdot}$) is formed.[68]

A triplet mechanism was proposed[82–86] for the photochemical reaction of arylamines with CBr_4 in a polymer matrix. A reaction scheme was considered which involved transfer of triplet energy from the excited CTC to the free amine followed by the formation of a triplet exciplex, which gives the final dye.[82]

$$\begin{aligned} &\mathrm{Am \cdot CBr_4} \xrightarrow{h\nu} \mathrm{(Am \cdot CBr_4)^1} \longrightarrow \mathrm{(Am \cdot CBr_4)^3}, \\ &\mathrm{(Am \cdot CBr_4)^3 + Am} \xrightarrow{k_4} \mathrm{Am \cdot CBr_4 + (Am)^3}, \\ &\mathrm{(Am)^3 + CBr_4} \longrightarrow \mathrm{(Am)^3 \cdot CBr_4} \longrightarrow \mathrm{Dye}. \end{aligned} \qquad (4)$$

The authors assume that an additional reaction occurs in the presence of naphthol (NP)

$$\mathrm{(Am \cdot CBr_4)^3 + NP} \xrightarrow{k_5} \mathrm{Am \cdot CBr_4 + (NP)^3}, \qquad (5)$$

It was noted that $k_5[NP] \gg k_4[Am]$.[83] Such a relation of reaction rates is reasonable as the energies of the triplet levels are ~ 3.5 eV (CTC) and 2.5 eV (NP), respectively, i.e. NP is an effective triplet 'trap'. In this case, the formation of a dye should be suppressed completely at high NP concentrations, which contradicts the experimental data: at $[NP] \sim [Am] \sim 1\ \mathrm{mol\ l^{-1}}$, the quantum yield of the reaction (~ 0.1) is almost the same as that in the absence of NP.[83]

In the case when triplet energy is transferred from an excited CTC to the amine, the nature of this excited state and the reasons for its stability in comparison with the triplet exciplex remain unclear. Excitation of a weak CTC leads to the transfer of an electron from the donor to the acceptor, and formation of a radical-anion of the latter. Since the radical-anion of CBr_4 is unstable, excitation of an Am – CBr_4 CTC results in irreversible decomposition of the complex with formation of an amine radical-cation, a tribromomethyl radical and a bromide ion (see below).

Obviously, studies on the dependence of the quantum yield of photo-ET processes on the presence in solution of various admixtures, energy acceptors of various types, would throw light on the problem of the stability of excited CTC. But, although many studies on the primary processes in Am – PHM systems have been reported, unfortunately no data on the quantum yields φ_i of primary photochemical reactions are available for diarylamines.

If chain processes are absent in the system, φ_i cannot be lower than the sum of the quantum yields of all products of the photoinitiated reaction. Bearing in mind the wide variety of pathways in the transformation of primary photogenerated species, the fact that the quantum yield of dye formation exceeds 0.1,[27] and

that the quantum yield of acridines reaches 0.2,[87] one can assume that the quantum yield of the primary process involved in photo-ET during the excitation of Am–PHM complexes is close to unity, which is consistent with the dissociative nature of this process.

III. Reactions of radical-anions of halohydrocarbons

The properties of radical-anions of HC ($RX^{-\bullet}$) and the fact of their existence as separate species have been considered in a number of reports.[88–92] It was believed that when ET occurs to HC with R = Alk, the latter 'instantly' decompose releasing X^- (see Refs. 93, 94) ($HC^{-\bullet}$ exist only for a few vibration periods[95]). Therefore, the whole process was named (photo)dissociative transfer (capture) of an electron. When $RX^{-\bullet}$ is generated in frozen matrices (4–77 K), the problem discussed was: to what extent can we distinguish between a σ* ion ($RX^{-\bullet}$)[95] and a $R^{\bullet}\cdot X^-$ complex (see Ref. 96), which appears in a matrix 'cage' due to cleavage of a C–X bond.

To date, several anion radicals have been detected experimentally. The $CCl_4^{-\bullet}$ radical-anion absorbs at 354 nm (4.2 K)[97] or 365 nm (77 K).[98] According to the EPR spectrum and ab initio calculations, the unpaired electron in $CCl_4^{-\bullet}$ is located at the antibonding σ* orbital of a C–Cl bond.[99] At room temperature, $CCl_4^{-\bullet}$ decomposes in $\tau < 18$ ps.[100] The $C(NO_2)_4^{-\bullet}$ radical-anion, whose properties are similar, decomposes in less than 10 ps.[101] Recently the $CBr_4^{-\bullet}$ radical-anion was detected by mass spectroscopy of positive ions.[102] Perhaps femtosecond laser techniques would also make it possible to observe these species in the photoexcited state. In a solid matrix (77 K), absorption at 365 nm was ascribed to $CBr_4^{-\bullet}$.[103]

The location of negative charge in products of decomposition of a HC radical-anion can be estimated by comparing the electron affinities (EA) of the fragments. For example, the values of EA (eV) of radicals formed owing to decomposition of $CX_4^{-\bullet}$ are: Cl$^{\bullet}$ 3.61; Br$^{\bullet}$ 3.36 (see Ref. 104), $CCl_3^{\bullet}$ 1.88, $CBr_3^{\bullet}$ 0.57 (see Ref. 105), i.e. the formation of a halide anion is much more favourable energetically than the formation of a trihalomethyl anion. It should be noted that considerably different EA values are available in the literature for the starting CCl_4 and CBr_4: from 0.15 and 1.2 (see Ref. 106) to 2.12 and 2.06 eV.[107] Obviously, the data in Ref. 106 are more suitable for a consideration of the complexation properties of these compounds, since they have been obtained under similar conditions from the energies of excited complexes of CCl_4 and CBr_4 with tetramethylbenzene. According to the data in Ref. 107, the electron-accepting properties of CCl_4 and CBr_4 should almost coincide, which contradicts numerous experimental data on the properties of CTC of these PHM.

In quantum-chemical calculations, various authors considered, in essence, four different pathways of decomposition of PHM radicals.

$$RCH_nX_{3-n}^{-\bullet} \longrightarrow \begin{cases} RCH_nX_{2-n}^{\bullet} + X^- & (6) \\ RCH_nX_{2-n}^{-} + X^{\bullet} & (7) \\ RCH_nX_{3-n} + e^- & \\ RCH_{n-1}X_{3-n}^{-} + H^{\bullet} & (8) \end{cases}$$

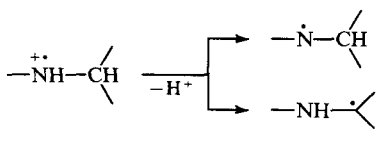
According to the data in Ref. 108, the most frequently occurring pathway (6) leading to a halide anion is characterised by the minimum energy. The formation of a halogen radical, pathway (7), is possible only through decomposition of iodine derivatives, since iodine has the lowest EA among halogens;[109] moreover, it is important that the remaining radical should contain strong electron-accepting substituents stabilising the anion. It has been shown by MNDO and AM1 methods for chloro- and bromomethanes[110] that for $n = 1, 2$, ET directly results in decomposition of the C–X bond by pathway (6). Decreasing n and the polarity of the medium favours stabilisation of the primary radical-anion as a kinetically independent species, which subsequently also decomposes by pathway (6). Fragmentation by pathway (8) is energetically unfavourable. According to the opinion of the authors,[110] it can occur by the mechanism of dissociative electron capture only in the presence of additional factors facilitating this reaction.

Aromatic radical-anions $RX^{-\bullet}$ are much more stable than aliphatic ones. For example, the rate constant for dissociative capture of a solvated electron measured for R = Ph ($l\ mol^{-1}\ s^{-1}$) increased in the series: Cl (5×10^8) < Br (4×10^9) < I (1.2×10^{10}).[111]

IV. Reactions of radical-cations of amines

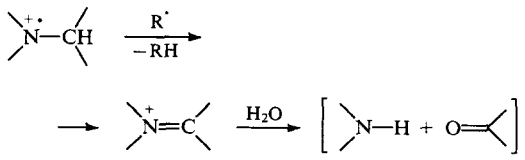
Unlike radical-anions of HC, the radical-cations of aromatic amines formed owing to ET during a chemical reaction have been reliably detected by many authors from their typical absorption spectra.[43,91,112–119] The radical-cations of monoarylamines, $(ArNRR')^{+\bullet}$, display absorption bands in the short-wave spectral region at 400–500 nm.[119–122] The radical-cations of diarylamines $Ar_2NR^{+\bullet}$ and triarylamines $Ar_3N^{+\bullet}$ absorb in the long-wave region at 600–800 nm.[123–126] In comparison with the $Ar_2NHm^{+\bullet}$ radical-cation, the spectra of the corresponding neutral radicals $Ar_2N^{\bullet}$ are shifted bathochromically and have lower intensities:[127,128] e.g., λ_{max} (nm) and ε_{max} ($l\ mol^{-1}\ cm^{-1}$) are 670 and 1.8×10^4, for $Ph_2NH^{+\bullet}$ (see Ref. 128) and 770 and 3.9×10^3 for $Ph_2N^{\bullet}$ respectively (see Ref. 129).

As is evident from the previous section, the reverse electron transfer from decomposition products of an HC radical-anion to an amine radical-cation is unlikely, since the latter cannot oxidise a halide anion or a $RCH_nX_{2-n}^{\bullet}$ radical. The amine radical-cation therefore undergoes various chemical reactions. The simplest one is deprotonation,[130] which, in the general case, can occur via two pathways.

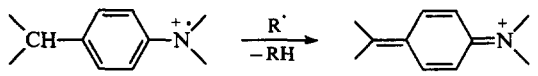


The acidity of the NH group does indeed increase considerably when an Am is oxidised into the radical-cation. For example, pK_a = 30.6 for $PhNH_2$ and 6.5 for $PhNH_2^{+\bullet}$ (see Ref. 131); 24.9 for Ph_2NH and 4.2 for $Ph_2NH^{+\bullet}$ (see Ref. 128). In both cases the acidity increases by more than 20 orders of magnitude. Values of the same order were obtained for the α-CH group in DMA: pK_a(DMA) is ~ 34, whereas pK_a($DMA^{+\bullet}$) is ~ 9 (Ref. 132). However, Nelsen and Ippoliti[133] consider that the acidity of the α-CH group in the radical-cation is usually unduly overestimated: for example, they obtained pK_a ~ 15 for the radical-cations of trialkylamines.

Not only heterolytic cleavage of the α-C–H bond is possible but also homolytic cleavage resulting in an iminium cation.

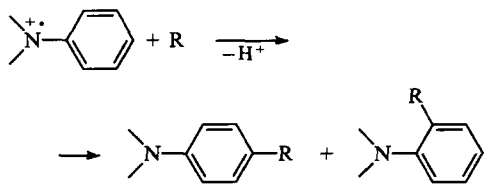


This is probably one of the pathways of dealkylation of radical-cations followed by hydrolysis.[140–142] Homolytic cleavage of a benzyl C–H bond with the formation of quinonoid compounds is known for radical-cations of amines that are toluidine derivatives.



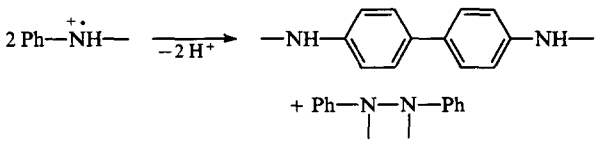
This class of reactions includes photooxidation of leuco-dyes with diverse structures in the presence of HC into the corresponding dyes.[46,143–146] It is suggested that the reaction may occur in two consecutive steps, first with abstraction of a proton and then of an electron, rather than by abstraction of a hydrogen atom.[147]

One of the typical and practically important reactions of radical-cations of aromatic amines is recombination, which occurs predominantly at the *ortho* and/or *para* positions of the benzene ring.



The ratio of reaction products is determined by the nature of the substituents on the nitrogen atom and on the aromatic ring and by the properties of radical R.[58,61,113,140,148–151]

The typical mode of recombination of radical-cations of aromatic amines with one another is C–C-dimerisation into benzidine derivatives (for radical-cations of amines having a free *para* position) and N–N-dimerisation into hydrazines (for radical-cations of primary and secondary amines).[125,152–157]

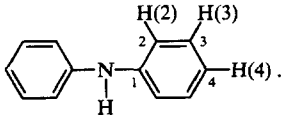


In addition to this, radical-cations of certain diarylamines dimerise into phenazines.[125,154,156]

It should be noted that C–C-dimerisation precedes deprotonation,[158] whereas N–N-dimerisation is likely to occur after deprotonation, i.e. it involves neutral radicals.[159] For example, it has been shown that protonation of the $Ar_2N^{\bullet}$ radical blocks the interaction at the reaction centre, the nitrogen atom.[160] In addition to C–C- and N–N-dimerisation, C–N-dimerisation is also observed for diarylnitrogen radicals.[161,162] According to quantum-chemical calculations and in agreement with the experiment, the labile N–N dimer is formed quickly and reversibly in one step, whereas stable C–N- and C–C-dimers are formed slowly and in two steps, the final step being irreversible.[163]

As to the electronic structure of the $Ar_2NH^{+\bullet}$ radical-cation and the neutral $Ar_2N^{\bullet}$ radical, the density distributions of the unpaired electrons in both radical species virtually coincide, judging from the coupling constants in the ESR spectra (Table 1). About 1/3 of the spin density is located on the nitrogen atom, while ~ 2/3 is located on the benzene rings at the *ortho* and *para* positions. Depending on the method, quantum-chemical calculations give somewhat differing results, but the preference for the *ortho* and *para* positions in delocalisation over the benzene rings is maintained. On the whole, one can conclude that the calculated data agree with the above main pathways in the interactions of these reactive species: the attack on the N, C(2) and C(4) atoms.

Table 1. EPR spectra (A) and data of quantum-chemical calculations (B) for radicals formed from DPA

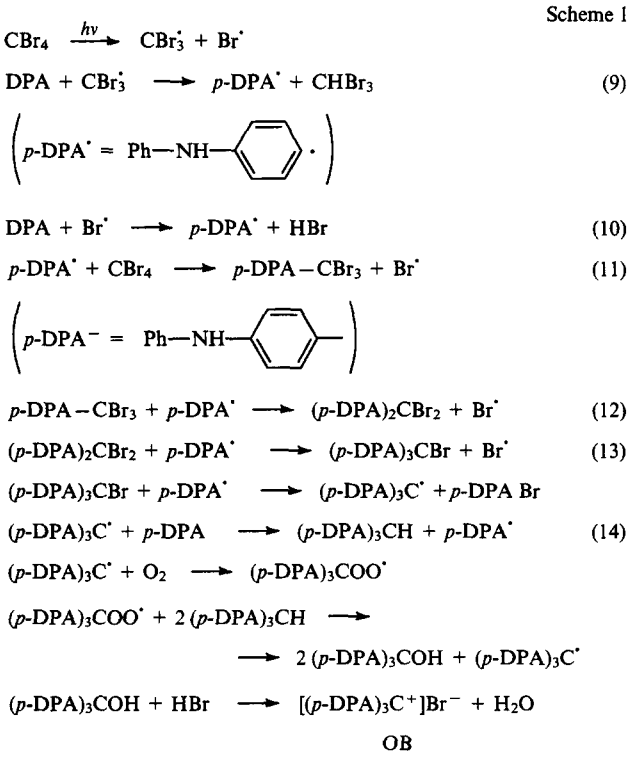


Radical	N	H(N)	H(2)	H(3)	H(4)	Ref.
A. Coupling constants (a_i, G)						
$Ph_2N^{\bullet}$	8.9	–	3.7	1.49	4.34	134
$Ph_2NH^{+\bullet}$	9.17	11.14	3.51	1.36	4.88	135
B. Spin densities (ρ_i)						
		C(1)	C(2)	C(3)	C(4)	
$Ph_2N^{\bullet}$	0.307	0.005	0.110	0.002	0.114	136
$Ph_2NH^{+\bullet}$	−0.29	0.25	0.22	−0.14	−0.48	158
	−0.801	0.096	−0.125	0.073	−0.115	137, 138
	0.501	0.006	0.080	0.002	0.079	139

V. Photoinduced chain radical reactions

It has been suggested that several types of chain radical processes can be involved in photoinduced reactions of amines with PHM, but the existence of some of them has not been proven. For example, a scheme for the formation of a triphenylmethane dye (TPMD), Opal Blue (OB), in a photochemical reaction of DPA with CBr_4 has been proposed. The scheme involves the following radical-chain reactions (Scheme 1).[21]

Scheme 1



This scheme has been accepted by many authors (see, for example, the relevant reviews[164–167]), but the feasibility of these reactions is doubtful. Reactions (9), (10) and (14) are assumed to occur by the abstraction of a hydrogen atom from the aromatic ring, which is an unlikely process. In the case of reaction (14), this is a highly improbable process, since the stable triphenylmethane radical with a delocalised electron is transformed into an energy-rich unstable radical with an electron localised on an sp^2 orbital. For example, when benzophenone was used as acceptor instead of CBr_4 in the reaction with amines, it was found that the H atom was abstracted only from the α-carbon of the alkyl substituent, giving stable radicals of the type PhN(R)C$^{\bullet}$HR′ (see Ref. 168) or from the

N atom in Am, giving radicals of the $Ph_2N^{\bullet}$ type.[169,170] It was shown that similar radicals are formed in the reaction of DPA with $CCl_3^{\bullet}$ (see Ref. 43) and with fullerene.[171] However, the abstraction of an H atom from the aromatic ring has never been observed in these reactions.

Reactions (11) – (13), which involve radical substitution of a halogen radical at a saturated carbon atom, also look improbable (no reactions of this type have been reported in the literature).[172,173] If they occurred in the system under consideration, chain transfer (10) → (11) → (10) etc. would appear, and the quantum yield (φ) of the dye would exceed 1. It will be shown below that reactions of amines with HC can sometimes involve a chain process with $\varphi > 1$, but this is related to another reaction pathway, and the φ values for TPMD are always less than one.

A radical scheme for the formation of Opal Blue has been adopted in studies[43,44,50,114,115] dealing with reactions of Am with HC. Since the authors[114] have observed experimentally the formation of the $Ph_2N^{\bullet}$ radical, they tried to reconcile this result with the participation of the *p*-DPA$^{\bullet}$ radical, formed due to the inversion $Ph_2N^{\bullet} \rightarrow p$-DPA$^{\bullet}$, in the above reaction scheme. However, it was shown later that photochemical generation of the $Ph_2N^{\bullet}$ radicals resulted in their transformation into carbazole in a good preparative yield.[174] The reaction did not occur if methyldiphenylamine (MDPA) was used instead of DPA, also supporting the view that the formation of carbazole occurs via the $Ph_2N^{\bullet}$ radical. It is known that direct excitation of both DPA and MDPA results in carbazole by cyclisation directly in the excited state without the participation of radicals.[175]

However, the reactions of completely *N*-substituted amines with PMH also led to the isolation of TPMD, which confirms that *N*-radicals, whose generation from these amines occurs with difficulty, do not play a predominant role in TPMD formation.[43,176] It follows from the data in Ref. 177 that a dye results from the reaction of a $CX_3^{\bullet}$ radical with a radical-cation $Am^{+\bullet}$ (a dye does not form when $CX_3^{\bullet}$ is generated in the presence of neutral Am).

In the next section we present a scheme for the synthesis of TPMD, including OB, through a series of reactions of electrophilic aromatic substitution involving Am and intermediate dyes, together with experimental evidence for this scheme.

In the context of the discussion of chain radical reactions, it is of interest to consider a series of works by Latovskii et al.,[141,176,178–181] the purpose of which was to study the characteristics of the photochemical behaviour of the system of bonds Ph–N–Me in reactions with polychloromethanes. DMA and MDPA were used as reagents.

The reaction of DMA with CCl_4, as with many other compounds, gave a TPMD, Crystal Violet (CV). The quantum yields of many compounds were measured. The focus of attention of the authors was drawn to reactions related to the formation and transformations of an α-methylene radical $>N-CH_2^{\bullet}$, and they tried to explain the formation of all of the photoproducts on the basis of this radical. Although the quantum yield of the formation of CV did not exceed unity, the authors proposed a scheme of chain radical reactions,[141] which, although it differs from Scheme 1, is also rather unlikely.[182]

During the studies of simpler systems of DMA with CH_2Cl_2 (Ref. 179) and $CHCl_3$ (Ref. 180), results were obtained suggesting that interaction of $Cl_nH_{3-n}C^{\bullet}$ type radicals with the benzene ring of the DMA radical-cation, rather than with the α-methylene radical, is important (these results are considered in more detail in the following section).

However, chain reactions still occur in the DMA–CCl_4 system, which is evident from the experimentally found high quantum yields for the formation of HCl and the disappearance of DMA, $\varphi(HCl) \approx \varphi(DMA) > 10$. This fact was explained[183] by reactions involving an α-radical, a CTC, and an amine.

$$Ph(Me)NCH_2^{\bullet} + PhNMe_2 \cdot CCl_4 \longrightarrow$$
$$\longrightarrow Ph(Me)NCH_2C_6H_4NMe_2\text{-}p + HCl + CCl_3^{\bullet}$$

$$CCl_3^{\bullet} + PhNMe_2 \longrightarrow Ph(Me)NCH_2^{\bullet} + HCCl_3$$

However, this scheme seems doubtful. First, it is more likely that a radical would attack a free amine rather than a CTC, since the concentration of the former is much higher, [DMA] ≫ [CTC]. Second, it is unlikely that a CCl_4 molecule can accept an H atom giving the $CCl_3^{\bullet}$ radical; more probably, the latter captures H to give chloroform. Third, if the assumption in Ref. 183 is valid, the DMA · CCl_4 complex is the chain carrier. In this case, increasing DMA concentration should lead to elongation of the chain. But, the authors observed a reverse dependence: when the concentration of DMA in CCl_4 increased, the quantum yield decreased,[183] and conversely, when the reaction was carried out in dioxane, the quantum yield increased with increasing CCl_4 concentration.[178] It follows from these data that a CCl_4 molecule is the chain carrier.

$$Ph(Me)NCH_2^{\bullet} + CCl_4 \longrightarrow Ph(Me)NCH_2Cl + CCl_3^{\bullet}$$

$$CCl_3^{\bullet} + PhNMe_2 \longrightarrow Ph(Me)NCH_2^{\bullet} + HCCl_3$$

A similar sequence of transformations occurs in reactions of CX_4 with alkylamines, which do not contain an aromatic ring but contain an H atom in the α-position relative to the nitrogen atom; the quantum yields of these reactions can be as high as 100.[184–186]

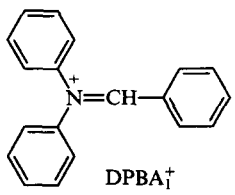
It should be emphasised once more that a $\varphi > 1$ in reactions of DMA and isomeric toluidines with CCl_4 is observed only for HCl formation and results from a different reaction, which is a side reaction with respect to CV formation. The φ value for the latter, like the values for the formation of other dyes from amines, is always less than one.

VI. Formation reactions of triphenylmethane dyes

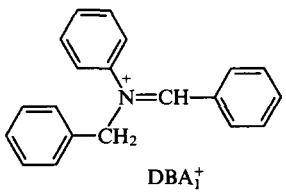
To date, the formation of two types of dyes during the photolysis of complexes of aromatic amines with PHM has been proved reliably. These include triphenylmethane dyes, which absorb light at 600–700 nm, and acridine dyes absorbing light at 450–550 nm and possessing luminescent properties. Studies on the mechanisms of their formation revealed a number of common features. Of the primary reactions, we should mention the formation of radical-cations or, in some instances (for secondary amines), neutral amine radicals on irradiation of CTC and the recombination of these radicals with halomethyl radicals. Their participation in the electrophilic alkylation of the free amine (which is present in excess in the reaction mixture) is a general feature. As noted in the Introduction, different viewpoints exist concerning the structure of the intermediates and the mechanism of their transformation into the final dyes, as well as for the structure of the dyes absorbing in the region of 600–700 nm. Below we present these viewpoints and make a reasoned choice of one of them.

The extensive experimental data concerning the photochemical reactions of Am with CBr_4 and $CBr_3SO_2CBr_3$ in solution and in polymer layers are presented in studies by Vannikov and Grishina et al.[27,82,83,187–196] DPA, diphenylbenzylamine (DPBA), and dibenzylaniline (DBA) were used mainly as the amines. It was found that irradiation of all three amines with CBr_4 first gave dyes with $\lambda_{max} \sim 665$ nm, which were given a general conventional designation D665, and which were then thermally ('in the dark') transformed into dyes with $\lambda_{max} \sim 605$ nm (D605). The activation energy for the D665 → D605 transformation for DPA was found to be half of that for DPBA (43 and 86 kJ mol^{-1}, respectively), whereas the activation energies for the sensitised formation of D665 were the same for all three amines (24 kJ mol^{-1}).[189]

The quantum yields for the formation of dyes D665 measured during direct photolysis of the complexes were $\varphi = 0.14$ (DPBA) and $\varphi = 0.07$ (DBA).[27] As shown above, the D605 formed from DPA is Opal Blue. The structures of D605 dyes obtained in the reactions with DPBA and DBA, and the D665 obtained from DPA, are not reported in the works cited. The authors [27] propose diarylmethyleneiminium structures (Am_I^+) for the D665 formed from DPBA and DBA. Diarylmethyleneimines are formed due to abstraction of H atoms from the benzyl groups of the amine radical-cations.



$DPBA_I^+$



DBA_I^+

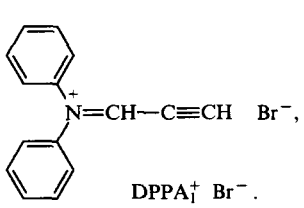
To substantiate the structures of the Am_I^+ type, the authors drew an analogy with photochemical reactions of amines with CBr_4 and with the Methylene Blue dye (MB^+). It was found that MB^+ was reduced on illumination by various benzylamines through the transfer of an H atom from the CH_2 group.[197,198]

$$MB^+ + Am \xrightarrow{h\nu} MB^{\cdot} + Am^{+\cdot} \longrightarrow MBH + Am_I^+$$

The reactivity of the amines in this reaction increases with increasing number of benzyl groups, i.e., DPBA is less reactive than DBA. However, judging from the quantum yields of D665 formation, a reverse order of reactivity is observed in the reaction with CBr_4: DPBA > DBA, in agreement with the number of phenyl groups, which are obviously involved in formation of the dyes.

In addition, it is clear that an Am_I^+ structure is not feasible for DPA, although its photochemical properties coincide with those of DPBA and DBA. Probably the structures of all three dyes (based on DPA, DPBA, and DBA) should be similar, hence the Am_I^+ structure is inappropriate for them.

To confirm the Am_I^+ type structure for D665, the authors of a book (Ref. 27) cite the previously published data (Ref. 199), where a dye with $\lambda_{max} = 670$ nm, obtained from diphenylpropargylamine and CBr_4, is assigned the following structure:



$DPPA_I^+ Br^-$.

Let us consider the arguments presented in Ref. 199 in order to confirm this structure: (1) the retention of phenyl groups and an acetylene group, according to IR and ^1H NMR spectral data; (2) instead of the signal of two methylene group protons, the appearance of a new broadened signal around 5.2 ppm, which disappeared in a deuteriated solvent; (3) the presence of bromine, according to mass spectrometric data. Strictly speaking, the first argument does not confirm the structure $DPPA_I^+$ but merely does not contradict it, as well as many other possible structures. The second argument is qualitatively consistent with the structure $DPPA_I^+$; however, it follows from various known data [200–202] for the chemical shifts of the methine proton in the iminium moiety that the value of 5.2 ppm is too low for such a structure, since the normal signal for this proton is found at 9–9.5 ppm. The third argument in the form presented is inconsistent with the structure of $DPPA_I^+$, since the presence of bromine in the molecular ion implies that the bromine atom is covalently bonded to the skeleton of the molecule. However, $DPPA_I^+$ does not incorporate the bromide ion, and the latter is merely the counterion of the dye cation. Unfortunately, the authors do not report the m/z value measured experimentally.

It is known that phenyliminium salts have absorption bands in the middle UV region,[203–205] spectra considerably different from the postulated spectrum of Am_I^+. Diphenylmethyleneaniline $Ph_2C{=}NPh$ and triphenylethene $Ph_2C{=}CHPh$, whose molecules are isoelectronic with DPBA, also absorb in the UV region: $\lambda_{max} = 346$ and 298 nm, respectively.[206] Thus, the validity of the structure $DPPA_I^+Br^-$ for the dye with $\lambda_{max} = 670$ nm obtained in Ref. 199 and the structure Am_I^+ for D665 described in Vannikov and Grishina's book [27] is doubtful.

The Am_I^+ type structure for D665 also contradicts flash photolysis data.[119] The formation of Am_I^+ should involve abstraction of an H atom from an $Am^{+\cdot}$ radical-cation, hence the accumulation of Am_I^+ should occur in parallel with the disappearance of $Am^{+\cdot}$ and over the same time interval. Such a reaction occurs during photooxidation of leuco-dyes in the presence of HCs. The final dye is formed in <100 μs, which is comparable with its lifetime.[207] When a D665 is formed in the system $Am \cdot CBr_4$, the lifetime of $Am^{+\cdot}$ also does not exceed 100 μs, but the appearance and increase of D665 absorption occurs over seconds,[119] and even more slowly (over minutes) at low concentrations of the amine.[36] The time difference between the two processes is several orders of magnitude. Obviously, the transformation of $Am^{+\cdot}$ into D665 is a more complex reaction (or a sequence of reactions) than simple removal of a hydrogen atom from the benzyl group.

In order to determine the structural moiety of amines involved in the formation of D665 and D605, photochemical reactions of CBr_4 with several groups of amines, differing in the presence of an unsubstituted benzene ring and an *N*-benzyl group in their molecules, were studied.[208] It was found that dyes are formed only from amines whose molecules contain a benzene ring unsubstituted at the *para*-position and linked to the amine nitrogen atom (an 'aniline' ring). If the *para*-position is blocked, dyes are not formed, irrespective of the presence of a *N*-benzyl group. For example, irradiation of the complex of CBr_4 with MDPA, which does not contain an *N*-benzyl substituent, resulted in the formation of a dye. However, the reaction of *N*-benzyl-di(*p*-tolyl)amine under the same conditions did not give products absorbing in the visible region, although a benzyl group was present.

Based on an analysis of experimental data on primary reactions, reactions in solutions and in polymer layers, and taking into account analogies with photochemical and thermal reactions of Am with PHM, we proposed a general scheme for the photochemical synthesis of dyes (Scheme 2; for simplicity, the positive charge is shown as localised at one of nitrogen atoms),[182] which was then confirmed experimentally [209] for all of the above aromatic amines whose reactions gave D665 and D605 (the latter are di- and triphenylmethane dyes, respectively).

Scheme 2 shows reaction initiation by excitation of a CTC, which is easily performed for X = Br by irradiation of the reaction mixture by light with $\lambda > 350$ nm. The free components virtually do not absorb in this region, hence selective excitation of the CTC occurs, since the absorption spectra of the $Am \cdot CBr_4$ complexes are shifted bathochromically relative to the spectra of the components. Then the first steps of the process (15) – (17) correspond to the sequence of the static quenching [reaction (1)] and dissociation [reaction (6)] reactions discussed above. During amine photoexcitation ($\lambda < 300$ nm), which is the more probable in the case of X = Cl, the ET changes somewhat in nature and occurs by the dynamic quenching pathway (2).

For any initiation pathway, the primary reactive species are an amine radical-cation $Am^{+\cdot}$, a $CX_3^{\cdot}$ radical, and an X^- anion. Subsequently, reaction (18) involves recombination of radicals into a *p*-amino-substituted trihalotoluene, which undergoes ionization giving a *p*-quinonoid ('monophenylmethane') dye

Scheme 1

$$PhNR'R'' + CX_4 \rightleftharpoons PhNR'R'' \cdot CX_4 \quad (15)$$

$$PhNR'R'' \cdot CX_4 \xrightarrow{h\nu} (PhNR'R'' \cdot CX_4)^* \quad (16)$$

$$(PhNR'R'' \cdot CX_4)^* \longrightarrow (PhNR'R'')^{+\cdot}\,CX_3^{\cdot}, X^- \quad (17)$$

$$(PhNR'R'')^{+\cdot} + CX_3^{\cdot} \xrightarrow[-H^+]{} R'R''N\text{-}C_6H_4\text{-}CX_3 \longrightarrow R'R''\overset{+}{N}{=}C_6H_4{=}CX_2, X^- \quad (18)$$

ICI DI

$$DI + Am \xrightarrow[-HX]{} R'R''N\text{-}C_6H_4\text{-}CX_2\text{-}C_6H_4\text{-}NR'R'' \longrightarrow R'R''N\text{-}C_6H_4\text{-}CX{=}C_6H_4{=}\overset{+}{N}R'R'', X^- \quad (19)$$

ICII DII

$$DII + Am \xrightarrow[-HX]{} \left[R'R''N\text{-}C_6H_4\right]_3CX \longrightarrow \left[R'R''N\text{-}C_6H_4\right]_2C{=}C_6H_4{=}\overset{+}{N}R'R'', X^- \quad (20)$$

ICIII DIII

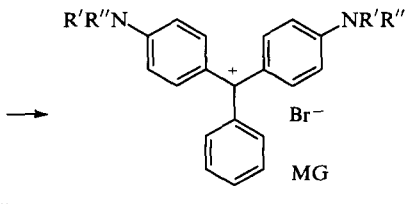
X = Cl, Br; R', R'' = H, Alk, Ar.

DI; ionisation is facilitated by the strong mesomeric effect of the nitrogen atom and the thermodynamic stability of the halide ion. It was noted in studies by flash photolysis [50,65,114,115] dealing with the primary steps of the reactions of Am with CBr_4 that the destruction of $Am^{+\cdot}$ obeys second-order kinetics, which corresponds to a recombination of the two radical species present in solution in equal concentrations.

After that, the amine present in excess acts as a nucleophile with respect to DI [reaction (19)]. In turn, this is an electrophilic aromatic substitution (alkylation) reaction with respect to the amine, in which DI is the alkylating agent. This results in diphenylmethane dye DII (named as D665 owing to its spectral properties [27]). Subsequently, DII reacts as an electrophile with respect to a new Am molecule in reaction (20), which is similar to reaction (12), giving the final TPMD — DIII, i.e. D605.

The lability of compounds such as DI and DII and the ease of their reaction with Am were described in Ref. 210, where a TPMD was obtained in the cold simply by mixing an amine with the corresponding halo-derivative. The reaction of Am with tribromotoluene, which is, in essence, the simplest model of intermediate compound (IC) I without an amino group in the *para*-position, also occurs readily to give dyes like Malachite Green (MG). The reaction can occur both thermally and under light irradiation. [36]

$$PhNR'R'' + PhCBr_3 \xrightarrow{\Delta\ (\text{or } h\nu)}$$



R' = R'' = Me.

Thermal synthesis of di- and triphenyl dyes directly from Am and PHM is carried out under pressure at an elevated temperature in the presence of metal salts. [211,212] The reaction occurs as a Friedel–Crafts alkylation of Am. [213] The amino group, which is a type I substituent, directs the attack predominantly to the *ortho*- and *para*-positions. The behaviour of aromatic amines in thermal reactions of arylamines with PHM, as in photochemical reactions, is exactly the same, irrespective of the presence or absence of the *N*-benzyl group in their molecules.

The spectral properties of arylmethane dyes are characterised by a clear relation between the positions of the absorption band maxima and the number of donor (amine) groups in the benzene rings for related mono- (λ_I), di- (λ_{II}) and triphenylmethane dyes (λ_{III}): introduction of the second substituent into the molecule results in a marked red shift of the colour — the maximum shifts considerably towards longer wavelengths, whereas introduction of the third substituent causes a slight blue shift of the colour, and the maximum slightly shifts towards shorter wavelengths, i.e. $(\lambda_I) < (\lambda_{III}) < (\lambda_{II})$. [212,214,215] For example, for Crystal Violet and its analogues (Scheme 2, R' = R'' = Me), the values of λ_I, λ_{II}, and λ_{III} are ~ 415, ~ 610, and ~ 590 nm, respectively. [182]

According to Scheme 2, when the number of halogen atoms in an HC molecule is gradually decreased from 4 to 1, the reaction can be terminated at any of steps (18)–(20), since the absence of a halogen atom in the corresponding intermediate makes the latter unable to participate in subsequent substitution reactions with Am. All of the six possible compounds, ICI–ICIII and DI–DIII, have been obtained in the case of DMA in the above studies by Latovskii et al. Along with the *para*-substituted derivatives shown in Scheme 2, similar *ortho* isomers were also obtained, in agreement with the directing effect of the amino group in aromatic electrophilic substitution reactions. When the free amine is present in deficit, the reaction stops at the recombination step (18), since subsequent reactions of electrophilic alkylation become impossible under these conditions. [112,182]

The process presented in Scheme 2 can be controlled by varying the temperature and by using matrix effects. For example, if the reaction is carried out at 77 K in frozen solutions, irradiation leads only to ET and generation of an amine radical-cation, [43,115,119] which is stable under these conditions. When the reaction is carried out at −15 °C in a polystyrene matrix, recombination (18) already occurs giving DI; however, further reaction is impossible owing to limited diffusion of the reagents. [209] When polystyrene layers containing a CTC of Am with CBr_4 are irradiated at room temperature, reaction (19) occurs in several minutes, and DII is detected immediately. A longer time or heating are required for reaction (20) to occur. [189,209]

Obviously the difference in the rates of reactions (19) and (20) involving the same amine is explained by the different alkylating power of DI and DII. The reactivity of these compounds depends on the positive charge on the reaction centre, the exocyclic carbon atom. The conjugation chain in DII, which stabilises the charge, is twice as long as that in DI, which results in a decrease in the charge on DII in comparison with DI and manifests itself by reaction (20) being slower than reaction (19).

The difference between the alkylating activities of DI and DII was used for determining the rate constants for reactions (19) and (20) during the formation of Opal Blue in a toluene solution.[216] Since the process was carried out with a great excess of DPA, pseudounimolecular constants were measured which were directly proportional to amine concentration. Relatively low activation energies (16.8 and 40 kJ mol^{-1}) and high negative entropies of activation (−187 and −155 J mol^{-1} K^{-1}), typical of bimolecular processes, were found for reactions (19) and (20), respectively.

Interesting results were obtained by comparing the rates of formation of DII and DIII during the photoionisation of DPA and DPBA with CBr_4 in polystyrene.[36] It was found that the rate constants for reaction (19) are ca. 10^{-2} for both amines, and those for reaction (20) are ca. 10^{-4} l mol^{-1} s^{-1}. For reactions (19) and (20), the ratio of the reaction rate constants for the two amines is $k_i(DPA)/k_i(DPBA) \approx 3$, and the ratio of the rate constants for both reactions is $k_{19}/k_{20} \approx 90$ for both amines. Obviously such a coincidence of kinetic parameters indicates the similarity of the reactions of formation of D665 and D605 from these amines.

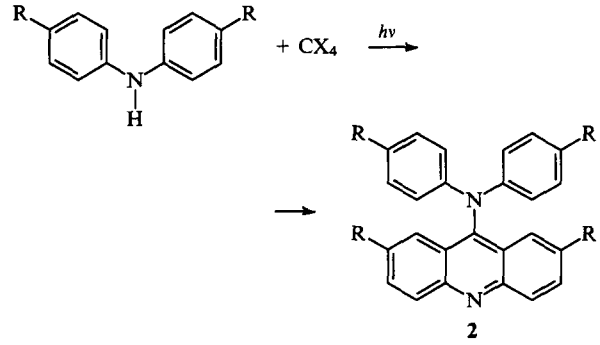
Although an analogy exists between aromatic amines with respect to the formation of TPMD, this reaction, as shown in the previous section, is not the only possible process during the photochemical irradiation of amine – CBr_4 complexes. Therefore, the experimentally observed difference in, say photochemical behaviour and photographic properties of DPA·HC and DPBA·HC complexes,[217] can be explained by various side processes in these systems, which occur in parallel with the formation of dyes but are not related to them. For example, in the case of DPBA these can be reactions involving the α-aminyl radical, which is readily formed from DPBA but not from DPA, whereas in the case of DPA these are reactions involving the amine hydrogen atom, which is absent in DPBA. The side processes result in sets of products possessing different properties and specific to different amines. However, it should be emphasised once more that these features refer to side processes, whereas, as shown experimentally, the formation of TPMD from all amines studied, whose molecules contain a benzene ring unsubstituted in the *para*-position and linked to an amine nitrogen atom ('aniline' ring), react via a common mechanism giving D665 and D605, i.e. DII and DIII (Scheme 2), respectively.[208,218]

VII. Formation reactions of acridine compounds

The formation of acridine compounds upon irradiation of DPA·CX_4 complexes was found in the early 1980s independently by two scientific groups.[219,220] In both studies, the authors reported that 9-diphenylaminoacridine (DPAA) was isolated as one of the reaction products, and the possible pathways for its formation were considered. Scheme 3 shows the sequence of reactions suggested in Ref. 219. This sequence involves recombination of primary radicals into intermediate **1** of *o*-quinonoid structure, which undergoes cyclisation directly into 9-bromoacridine. The latter reacts with a second amine molecule to give DPAA, which (like bromoacridine) exists in the reaction medium as a hydrobromide.

As already noted, direct irradiation of DPA results in carbazole through unimolecular photocyclisation.[221] Unlike this reaction, the formation of the acridine ring involves at least two molecules, an Am and a PHM, and several consecutive reactions result in photoinduced bimolecular cyclisation.

A study of the preparative possibilities of this reaction showed that DPAA analogues, the corresponding 9-diarylaminoacridines **2**, can be obtained in up to 40% yield and in up to 0.08 quantum yield from DPA derivatives substituted in the *para*-position.[36,222]

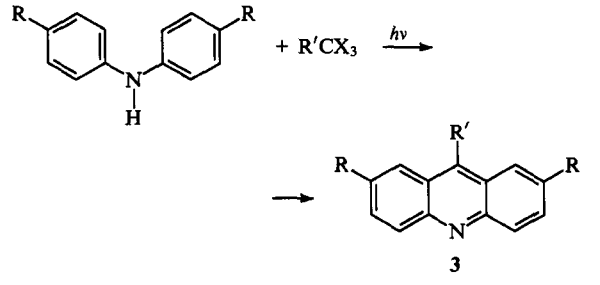


2

R = Me, $PhCMe_2$; X = Cl, Br.

The use of *para*-substituted derivatives instead of DPA increases the yields of cyclisation products considerably, since in this case the above TPMD formation reaction, which is a side process with respect to cyclisation, is blocked.[223]

A similar effect, i.e. an increase in the yield of acridine to 50% and above with R ≠ H, has been observed in reactions of diarylamines with trihalomethanes.[224] In this case acridines **3** containing no amino-substituent in position 9 are the end products. Thus, as in the case of the formation of TPMD, a decrease in the number of halogen atoms in a PHM molecule results in a decrease in the number of steps in the chain of consecutive photoinduced reactions, and the whole process ends at the ring closure step due to the absence of a halogen atom in the acridine molecule after cyclisation.

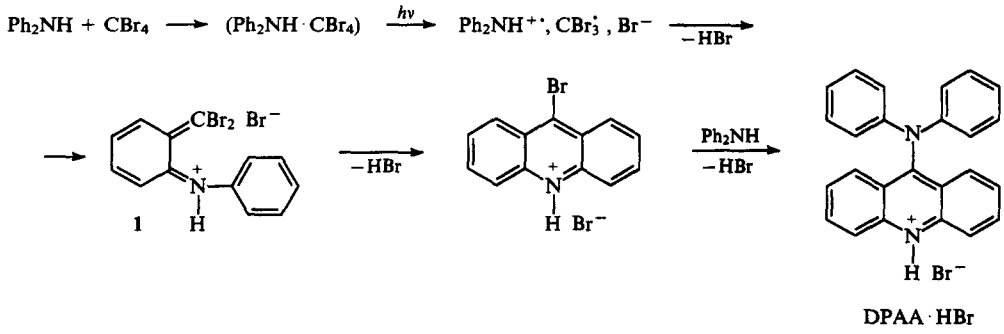


3

R = H, Me, Br; R′ = H, Ph; X = Cl, Br.

The reaction of amines with tribromotoluene occurs not only photochemically but also thermally to give the corresponding 9-phenylacridines (R′ = Ph).[225]

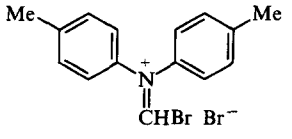
Scheme 2



DPAA·HBr

Although the experimental data considered above were consistent with Scheme 3 and even seemed to confirm it, data were accumulated during studies of photoinduced bimolecular cyclisation that could not be completely explained within the process described. According to Scheme 3, the last step of the reaction is nucleophilic substitution of a halogen atom by an amine molecule. Modelling this step by examples of reactions of 9-bromo- or 9-chloroacridine with various aromatic amines showed that only primary amines undergo the reaction at room temperature.[225] Thermal reaction involving diarylamines occurred only at high temperatures (>100 °C), which differed from the conditions of the photoinduced reaction (< 25 °C). In addition, according to Scheme 3, *N*-methylated amines should give *N*-methylated acridines, but the latter were not found in the reaction mixture.[226] Thus, both the structures of the intermediates and the overall mechanism of the formation of aminoacridines proved to be doubtful.

A study of photochemical reactions of complexes of di-*p*-tolylamine (DTA) with tetra- and tribromomethane by pulse methods showed that in both cases an amine radical-cation absorbing around 700 nm was formed as the primary product.[227,228] As a subsequent intermediate in the reaction with bromoform, a product was detected which absorbed at 540 nm. It was formed by a pseudo-first-order reaction with a rate constant proportional to the amine concentration and was then transformed into acridine by a unimolecular reaction.[228] A comparison of spectral and kinetic properties of the intermediates detected and the time scales of the transformations of compounds into each other led to the conclusion that one more intermediate, which does not absorb in the visible region, exists on the coordinate of the photoinduced reaction of DTA with $CHBr_3$. This intermediate was assigned the bromomethyleneiminium structure **4**.[87]



4

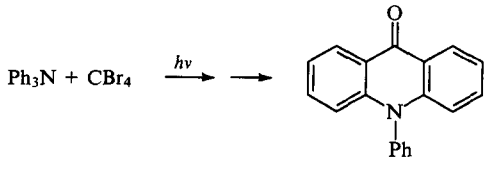
This compound is formed by recombination of primary radicals with participation of the nitrogen atom in $Am^{+\cdot}$ rather than of the *ortho*-positions of the benzene ring, as was assumed according to Scheme 3. Since methyleneimine salts possess pronounced electrophilic properties,[229] compound **4** readily reacts with a new amine molecule to give the next intermediate, which was detected by spectral methods.

Attempts were made to detect a similar intermediate in the reaction of DTA with CBr_4, but only data on the kinetics of the formation of aminoacridine **2** (R = Me) were obtained in this case.[230,231] However, analysis of the kinetic curves of spectral changes in various wavelength ranges confirmed the assumption of the absence of a haloacridine as an intermediate compound during the formation of aminoacridine.

The results of the works cited can be generalised as Scheme 4, where (for DTA as an example) the sequence of photoinduced reactions that occur during the interaction of diarylamines with tri- or tetrahalomethanes to give acridine compounds is shown. The scheme shows: first, that the incident light can be absorbed both by the complex and by the free amine (this is determined by the spectral range of the incident light), and second, that the methyleneiminium intermediate can really be formed owing to recombination involving not the nitrogen atom of the amine radical-cation but a neutral diarylnitrogen radical formed after deprotonation of the radical-cation (see Section IV). Since the data available are insufficient for making an unambiguous choice, both possible recombination pathways are shown.

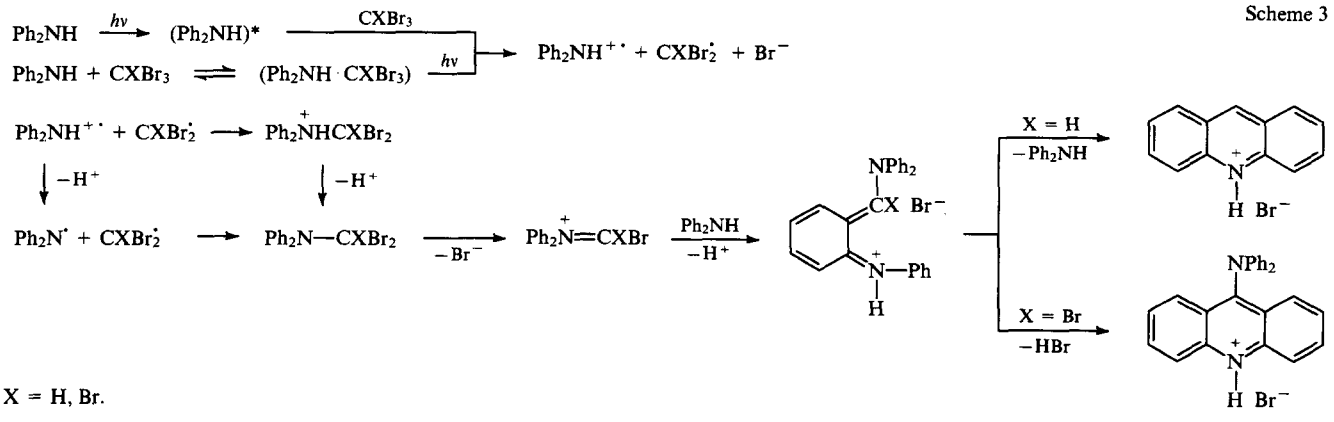
It should be noted that Scheme 4 reflects the main but not the only pathway for the formation of acridine compounds in photochemical reactions of amines with PHM. As shown above (see Table 1), in agreement with quantum-chemical calculations and in conformity with EPR spectra, the maximum density of the unpaired electron in radicals of the type $Ph_2NH^{+\cdot}$ and $Ph_2N^{\cdot}$ is located at the central nitrogen atom, which serves as the main reaction centre for the recombination of primary radicals. The recombination involving the carbon atoms of benzene rings also occurs, although with a lower probability. But, if the nitrogen atom is blocked by a third substituent, this becomes the main reaction pathway, e.g. as in the formation of TPMD.

Obviously recombination in the *ortho*-position of the benzene ring is also the only pathway in the photochemical reaction of triphenylamine with CBr_4, which results in *N*-phenylacridone (from the intermediate *N*-phenylbromoacridinium after treatment of the reaction mixture with water).[33]



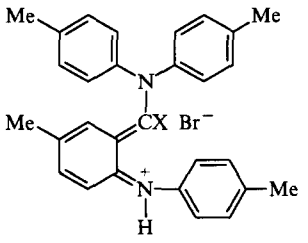
Interesting data were obtained by comparing the rates of the formation of intermediate compounds **5a,b** in reactions of DTA with $CHBr_3$ (**5a**, X = H) and CBr_4 (**5b**, X = Br). These compounds are formed by alkylating DTA with type **4** methyleneiminium salts. It was found that the rate constant for the formation of compound **5a** is more than an order of magnitude higher than the constant for compound **5b**; these constants were 10.8 and 0.32 $l\ mol^{-1}\ s^{-1}$ (toluene, 20 °C), respectively.[232] The activation enthalpies ($kJ\ mol^{-1}$) and entropies ($J\ mol^{-1}\ K^{-1}$) for the formation of compounds **5a** and **5b** were found to be 36.3 and −101 (**5a**) and 24.6 and −169 (**5b**), respectively. It follows from these data that the entropy factor makes the greatest contribution to

Scheme 3



X = H, Br.

the retardation of the reaction for compound **5b** compared with compound **5a**, and the entropy decreases so much that the simultaneous decrease in the activation enthalpy does not compensate for the former effect.



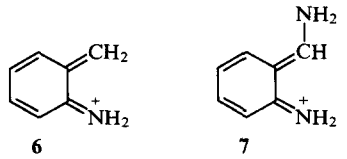
5

X = H (**a**), Br (**b**).

In comparison with the alkylation reaction, the intramolecular cyclisation of compound **5a** into 2,7-dimethylacridine is characterised by a higher activation energy (68 kJ mol^{-1}) but a lower magnitude of entropy of activation (−58 J mol^{-1} K^{-1}).

As mentioned above, the efficiency of the processes shown in Scheme 3 (formation of *N*-substituted diarylamines) is lower than that of the reactions shown in Scheme 4 (for Ar_2NH diarylamines). A comparison of Schemes 3 and 4 shows that, in both cases, *ortho*-quinonoid compounds are the key structures in the cyclisation process. An analysis of the structures of these compounds and a comparison of this process with similar processes of thermal intramolecular cyclisation[233,234] leads to the conclusion that cyclisation is possible only in *cis*-isomers, whereas compounds **5a** and **5b** obviously exist at room temperature in the *trans*-forms, which are thermodynamically more stable. Thus, the general sequence of reactions should include a step involving the isomerisation of the C=N double bond, omitted in Schemes 3 and 4.

The potential barrier to rotation about the C=N bond was calculated for model compounds **6** and **7** by the MNDO method. It was found that the activation energy for isomerisation is twice as high for compound **6** as that for compound **7**: 77.5 and 44.4 kJ mol^{-1}, respectively.[232]



6 **7**

This effect is related to a decrease in the multiplicity of the C=N bond in compound **7** in comparison with compound **6** due to delocalisation of the positive charge onto the second nitrogen atom. It should be noted here that isomerisation of compounds of type **1** and **5** can occur not only by rotation around the C=N double bond, but also by inversion of the sp^2-orbital of the nitrogen atom in the neutral compound after deprotonation. As a result, the energy barrier to isomerisation decreases. The isomerisation of *N*-substituted diarylamines can result only in type **1** *o*-quinonoid compounds, in which, owing to the impossibility of deprotonation, the only isomerisation pathway is rotation in which a high potential barrier is overcome. This makes it possible to explain the low effectiveness of *N*-substituted diarylamines in the photoinduced bimolecular cyclisation.

VIII. Conclusion

The review of the available data on the photochemical reactions of complexes of aromatic amines with halohydrocarbons shows that these systems attract the attention of researchers because of two factors. First, they are convenient systems for studying the process of electron transfer, the main primary chemical reaction occurring upon the irradiation of complexes. Second, they provide a broad range of compounds, including triphenylmethane dyes (reactions of photoinduced consecutive aromatic substitution), acridine derivatives (photoinitiated bimolecular cyclisation), carbazoles (intramolecular cyclisation of diarylamines on their direct excitation), benzidines (photooxidation of amines), etc. The ratio of reaction products is primarily determined by the structures of the amine and the halohydrocarbon, and also by the spectral range of the incident light (excitation of the complex, local excitation of the amine or the acceptor) and by the ratio of reagent concentrations.

In many cases, the nature of the excited state (singlet or triplet) involved in the reaction and the structures of the reacting primary species (radical-cation or neutral amine radical) remain unclear. The mechanism of secondary thermal reactions occurring after irradiation of the complexes has been studied in more detail. Reaction schemes have been proposed that are confirmed by direct observation of the corresponding intermediates, their spectral and kinetic properties, and by modelling separate steps in the general sequence of photoinitiated reactions.

We may note that the photoinitiated formation reactions of triphenylmethane dyes and acridine compounds involve common photochemical and some thermal stages. In both cases, the reactions start as photo-transfer of an electron due to excitation of a charge transfer complex or a free amine. One of the intermediate stages involves electrophilic alkylation of the amine by cations of dyes or by iminium salts. The alkylation reactions are characterised by relatively low activation energies (no higher than 40 kJ mol^{-1}) and high negative entropies of activation (up to −190 J mol^{-1} K^{-1}) typical of bimolecular reactions of this class.

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