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Effect of silver ions on the photochemical properties of *N*-methyldiphenylamine

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Abstract

Silver(I) ions have been found to quench the fluorescence of *N*-methyldiphenylamine (**1**) and reduce the quantum yield of cyclization reaction of **1** to *N*-methylcarbazole (**3**). Comparison of relative quenching rate constants for the singlet- and triplet-excited states of **1** has enabled the evaluation of two components, physical and chemical, in silver(I) action on the triplet-excited **1** (^{3}**1**), namely: acceleration of the intersystem crossing processes ^{3}**1** → **1** and inhibition of the reaction of ^{3}**1** photocyclization to the triplet-excited *N*-methyldihydrocarbazole (**2**). © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Fluorescence; Photocyclization; Quenching; Diphenylamine; Silver ions

1. Introduction

Reaction of diphenylamine (DPA) to carbazole photocyclization and the effect of additives on this reaction have been studied for some decades [1–6]. The cyclization has been shown to proceed in the triplet-excited state; the primary (intermediate) product of the reaction is dihydrocarbazole (DHC), which is unstable and oxidized by oxygen or other suitable oxidant to carbazole. In the absence of oxidant, DHC disproportionates to tetrahydrocarbazole and carbazole and undergoes the reaction of cycle disclosure to initial DPA.

The quantum yield of photocyclization of DPA (φ_c) is increased by the addition of hydrogen-bonding agents due to increasing intersystem crossing rate constant for the transition ^{1}DPA → ^{3}DPA [4]. Chloromethanes show dual effect on the photocyclization reaction: they quench the lowest excited singlet and triplet states of DPA, thus retarding the photocyclization, but simultaneously, they take part in the dehydrogenation of DHC to carbazole, thus accelerating the photocyclization. As a result, the plot of the quantum yield φ_c versus chloromethane concentration shows a convex curvature [6].

Irradiation of DPA in aqueous Triton X-100 medium in the presence of silver nitrate leads to formation of the coloured silver sol [7]. The reaction is proposed for spectrophotometric determination of silver(I); it has not been studied whether DPA undergoes other photochemical transformations or serves only as an electron donor for reduction of silver ions.

Silver ions are known to form complexes with aromatic compounds both in the ground and in the excited states and affect the photophysical and photochemical properties of the compounds [8–10]. This influence is explained mainly by heavy atom effect, which consists of enhancement of spin–orbit coupling leading to acceleration of intersystem crossing [11,12]. Therefore, a priori silver ions can affect the DPA to carbazole photocyclization reaction in two contradictory mannerisms.

On one hand, due to acceleration of the $S_1 \rightarrow T_1$ intersystem crossing, they can enrich the population of the triplet-excited state of *N*-methyldiphenylamine (**1**), thus promoting the cyclization reaction. On the other hand, due to acceleration of the $T_1 \rightarrow S_0$ intersystem crossing, they can deplete the triplet-excited state, thus retarding the reaction.

In the present paper, we have investigated the effect of silver ions on the photochemical properties of **1**. Scheme 1 shows the sequence of reactions with participation of **1**, *N*-methyldihydrocarbazole (**2**) and *N*-methylcarbazole (**3**) being, respectively, the intermediate and final products in this case [2].

Comparison of the quenching rate constants, obtained for quenching of both the singlet and the triplet-excited **1**, with the corresponding rate constants of inherent intersystem crossing for **1**, has allowed us to conclude that diminution of the photocyclization quantum yield in the presence of silver ions is connected with the both acceleration of

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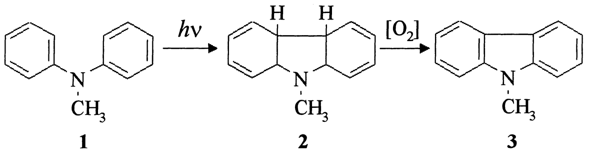

Scheme 1.

intersystem crossing and inhibition of the cyclization reaction itself.

2. Experimental details

Compound **1** was synthesized by alkylation of DPA with methyl iodide, and purified before use by distillation in vacuo. Acetonitrile (for HPLC grade, Reachim) was used as received. Experiments were carried out in quartz cuvettes with path length l=1 cm at room temperature in air-saturated solutions.

Electronic absorption spectra were recorded on a Specord M40 spectrophotometer; fluorescence spectra were recorded on Elumin-2 spectrofluorimeter. The concentration of **1** was maintained within $0.8–1.7\times10^{-5}$ mol dm^{-3}, and that of $AgClO_4$ varied in the range 0–0.1017 mol dm^{-3}.

Irradiations were performed with a high pressure mercury lamp; the line at 313 nm was selected using appropriate glass filters. The intensity of the incident light was measured by a PP-107 actinometer and kept in the region $2.9–3.1\times10^{-6}$ einstein dm^{-3} s^{-1}.

3. Results and discussion

Under the concentrations used, no modifications of absorption spectra were observed upon addition of $AgClO_4$ to solutions of **1**. This indicates the absence or low extent of interaction between the salt and the amine in the ground state. At the same time, the fluorescence of **1** reduced appreciably in the presence of $AgClO_4$, thus testifying quenching of the amine singlet-excited state by silver ions. Quantum yields of fluorescence of **1** at various concentrations of $AgClO_4$ are shown in Table 1.

Table 1
Fluorescence and photocyclization quantum yields for *N*-methyldiphenylamine (**1**) in acetonitrile

[$AgClO_4$] (mol dm^{-3})	φ_f	[$AgClO_4$] (mol dm^{-3})	φ_c
0	0.035[a]	0	0.29
0.0054	0.032	0.0054	0.25
0.0077	0.029	0.0110	0.23
0.0079	0.028	0.0138	0.20
0.0205	0.023	0.0249	0.16
0.0361	0.018	0.0403	0.14
0.0753	0.012	0.0753	0.080
0.1017	0.009	0.1017	0.062

[a] Measured relative to φ_f (DPA)=0.05 [3].

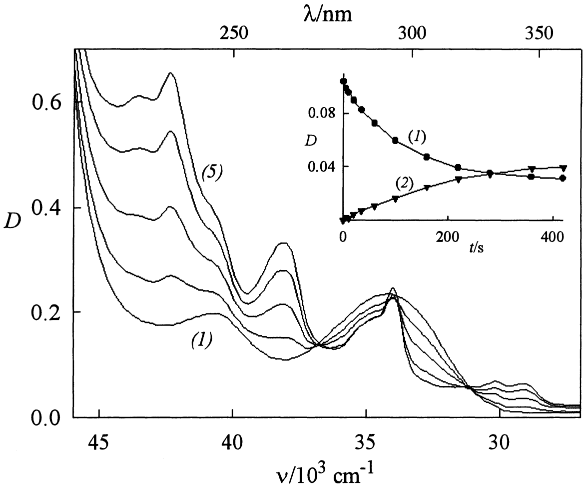

Fig. 1. Spectral changes during irradiation of a 1.657×10^{-5} mol dm^{-3} acetonitrile solution of **1** in the presence of 0.0241 mol dm^{-3} $AgClO_4$: irradiation time (1)–(5) (in s): 0, 35, 100, 220, 420. Insert: kinetics of the optical density change at (1) 313 nm and (2) 346 nm.

On irradiation of **1** solutions, identical spectral changes were observed independently of $AgClO_4$ presence; however, the rate of changes decreased with increasing concentration of the salt; the isosbestic points at 272 and 320 nm were maintained for high conversion percentage. In Fig. 1, the spectral changes observed by irradiation in presence of the salt are represented.

Reaction kinetics was monitored at two wavelengths: at 313 nm, where amine **1** absorbs mainly and where optical density decreased, and at 346 nm, where carbazole **3** absorbs mainly and where optical density increased during irradiation (insert in Fig. 1, curves (1) and (2), respectively). Inasmuch as thin optical layers were used (at irradiation wavelength $D_{313}<0.1$), the quantum yield of cyclization (φ_c) was calculated by rectification of kinetic curves in terms of the equation

$$\ln\left[\frac{D_t - D_\infty}{D_0 - D_\infty}\right] = -2.3\varepsilon_{313}\varphi_c l I_0 t$$

where D_t is the optical density of the reaction mixture at the wavelength of observation (313 or 346 nm) at time moment t, ε_{313} the absorption coefficient (6230 dm^{-3} mol^{-1} cm^{-1}) of **1** at the irradiation wavelength, and I_0 the intensity of incident light (einstein dm^{-3} s^{-1}). Table 1 shows quantum yields of cyclization of **1** at different concentrations of $AgClO_4$. At the same concentrations, addition of $LiClO_4$ does not affect the fluorescence or cyclization quantum yields. Therefore, within the concentration range investigated, the effects observed are not connected with the influence of the ionic strength of the solution.

Fig. 2 shows the Stern–Volmer dependence (straight line (1), r=0.999) plotted using the data of Table 1, relevant to the quenching of emission; the Stern–Volmer constant K_{sv} is obtained to be 27 dm^3 mol^{-1}. The absence of curvature of the Stern–Volmer plot indicates that the quadratic terms,

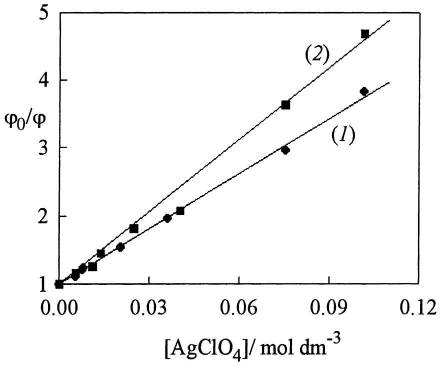

Fig. 2. Dependence of relative quantum yields of (1) fluorescence $\varphi_{f,0}/\varphi_f$ (Stern–Volmer plot) and (2) cyclization $\varphi_{c,0}/\varphi_c$ of **1** on $AgClO_4$ concentration.

which arise in the Stern–Volmer equation in the case of both dynamic and static quenching, are negligible in the range of salt concentration explored. This result corroborates the conclusion about low extent of **1**–Ag(I) interaction in the ground state (static quenching), made on the basis of absence of changes in the absorption spectrum of **1** on addition of $AgClO_4$.

The ratio $\varphi_{c,0}/\varphi_c$, where $\varphi_{c,0}$ is quantum yield of the reaction without additive, shows straight-line dependence on $AgClO_4$ concentration too (Fig. 2, straight line (2), $r=0.996$); the slope of plot $K_c=36\,dm^3\,mol^{-1}$. The results obtained can be rationalized within the framework of the following simplified scheme of photocyclization of amine **1** to carbazole **3** (Scheme 2); in the scheme, silver ions are assumed to mainly affect the intersystem crossing processes:

In Scheme 2, ^{1}**1** and ^{3}**1** are the singlet- and triplet-excited **1**, respectively, Q is the quencher-silver ion, and every reaction (n) is characterized by the rate constant k_n. Silver ions can also accelerate intersystem crossing in the intermediate **2** — Reaction (8); however, this process has no effect on the cyclization quantum yield and is not taken into account.

$$\mathbf{1} + h\nu \rightarrow {}^1\mathbf{1}$$

$${}^1\mathbf{1} \rightarrow \mathbf{1} + h\nu' \tag{1}$$

$${}^1\mathbf{1} \rightarrow \mathbf{1} \tag{2}$$

$${}^1\mathbf{1} \rightarrow {}^3\mathbf{1} \tag{3}$$

$${}^1\mathbf{1} + \mathrm{Q} \rightarrow {}^3\mathbf{1} + \mathrm{Q} \tag{4}$$

$${}^3\mathbf{1} \rightarrow {}^3\mathbf{2} \tag{5}$$

$${}^3\mathbf{1} \rightarrow \mathbf{1} \tag{6}$$

$${}^3\mathbf{1} + \mathrm{Q} \rightarrow \mathbf{1} + \mathrm{Q} \tag{7}$$

$${}^3\mathbf{2} \rightarrow \mathbf{2} \tag{8}$$

$$\mathbf{2}(+\mathrm{O_2}) \rightarrow \mathbf{3} \tag{9}$$

Scheme 2.

According to Scheme 2, the lifetimes of the singlet- and triplet-excited states of **1** without quencher are $\tau_s=1/k_s=1/(k_1+k_2+k_3)$ and $\tau_t=1/k_t=1/(k_5+k_6)$, correspondingly. Therefore, the Stern–Volmer constant K_{sv} is expressed as $k_4\tau_s$, from which one can calculate the value of quenching rate constant $k_4=7.1\times10^9\,dm^3\,mol^{-1}\,s^{-1}$ (τ_s is known to be 3.8×10^{-9} s [3]). It should be noted that, for reasons of simplicity, the reactions of quenching of the excited states of **1** by oxygen are not depicted in Scheme 2; however, they are taken into account automatically by using data for τ_s and τ_t (see below) obtained in the air-saturated solutions [3].

For the relative quantum yield of cyclization, we obtain

$$\frac{\varphi_{c,0}}{\varphi_c} = k_3\frac{\{(k_s+k_4[\mathrm{Q}])(k_t+k_7[\mathrm{Q}])\}}{\{k_s k_t(k_3+k_4[\mathrm{Q}])\}} \tag{10}$$

After some simplifications, one can show that Eq. (10) can be approximated by the straight line

$$\frac{\varphi_{c,0}}{\varphi_c} \sim 1 + \left(\frac{k_3 k_7}{k_s k_t}\right)[\mathrm{Q}] = 1 + (k_3 k_7 \tau_s \tau_t)[\mathrm{Q}]$$

Thus, the slope of the straight line (2) in Fig. 2 is $K_c=k_3k_7\tau_s\tau_t$. The product $k_3\tau_s$ characterizes the quantum yield of intersystem crossing from the S_1 state of **1**. Knowing this value (0.89) and the triplet lifetime $\tau_t=1.36\times10^{-8}$ s [3], one can calculate the value of the quenching rate constant $k_7=3.0\times10^9\,dm^3\,mol^{-1}\,s^{-1}$.

It should be noted here that photophysical parameters, used for calculations of the quenching constants, were obtained in apolar solvents, whereas quenching experiments were conducted in acetonitrile. Some dependence of intersystem crossing rate constant on solvent has been observed for DPA and explained by the formation of hydrogen-bonding complex with the solvent molecule in which DPA acts as a proton donor [4]. This kind of interaction is impossible for *N*-substituted DPA derivatives, so one should not expect substantial solvent dependence of photophysical constants for **1**.

Quenching rate constants of aromatic compounds quenched with silver ions have been shown to be related to the rate constants of inherent intersystem crossing of the compounds [12]. We can correlate the quenching rate constants obtained with the corresponding rate constants of intersystem crossing (to obtain a non-dimensional quantity, one should compare the quenching ability at $[Q]=1\,mol\,dm^{-3}$): $k_4[Q]/k_3=30$ and $k_7[Q]/k_6=286$ (calculated using $k_5=6.3\times10^7\,s^{-1}$ [1], from which $k_6=k_t-k_5=1.05\times10^7\,s^{-1}$). From the comparison, one can see that the relative quenching ability of silver ions with respect to the triplet-excited **1** is an order of magnitude greater than that with respect to the corresponding excited singlet.

If one assumes that quenching of the triplet-excited **1** by silver ions is conditioned only by enhancement of the spin–orbit coupling, which is proportional to the rate constant of intersystem crossing k_6, then the slope of the straight line (2) in Fig. 2 should be K_c=3.8 dm^3 mol^{-1}, that is an order of magnitude less than observed one.

A relatively high value of quenching rate constant k_7 can be rationalized taking into account that it was measured with reduction of the cyclization quantum yield. Therefore, the k_7 observed can include two components: physical, connected with enhancement of spin–orbit coupling and acceleration of intersystem crossing, and chemical, connected with retardation of the cyclization reaction.

There are some possibilities for Ag(I) to retard the cyclization reaction itself. In the encounter complex (exciplex), the silver ion can be localized predominantly between two aromatic rings of **1**, thus hindering C–C bond formation upon cyclization. The other possibility is connected with formation of radical-cation $\mathbf{1}^{\bullet+}$. As has been mentioned above, excited DPA serves as an electron donor for silver ions [7]; obviously, electron transfer gives rise to formation of the amine radical cation. On the other hand, comparison of oxidative and excited state cyclization of DPA derivatives, both experimental and theoretical, shows faster and more energetically favourable cyclization of *N*-substituted DPAs from the triplet state than from radical cation [13]. Thus, electron transfer from excited **1** to Ag(I), which results in the formation of radical-cation $\mathbf{1}^{\bullet+}$, should give rise to retardation of the cyclization reaction. Application of time-resolved technique will evidently allow one to discriminate different components in silver ions action on triplet-excited **1**.

Acknowledgements

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