Effect of diphenylamine on photodissociation of aryl azides

M. F. Budyka, M. M. Kantor, and R. M. Fatkulbayanov*

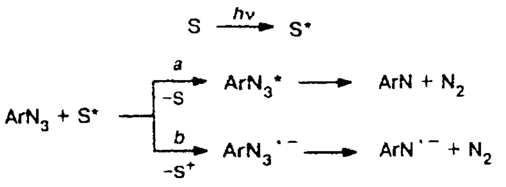
Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: 007 (096) 515 3588

The charge-transfer complexes of aromatic azides with diphenylamine (DPA) were studied. Irradiation of 4-nitrophenyl azide in the presence of DPA was found not to give rise to the dissociation of the azido group in the azide radical anion *via* intracomplex electron transfer. The photodissociation slows down due to both the static (the formation of a photostable complex with diphenylamine) and dynamic quenching. When 4-azidoacetophenone is irradiated in the presence of DPA, the amine-sensitized decomposition of azide and the photodecomposition of the azide—DPA complex occur along with the direct photolysis of azide, which results in acceleration of the photodissociation due to an increase in the efficiency of the light absorption by the reaction system. A possible sensitization of photodecomposition of aromatic azides *via* an electron transfer mechanism by irradiation of the azide—donor complex is shown.

Key words: aryl azide; photodissociation, sensitization; charge-transfer complex.

Aromatic azides are widely used in scientific research and technology due to their photochemical activity.[1,2] The quantum yield of decomposition of many azides under UV irradiation is close to unity, but it decreases for irradiation with the visible light even when azide has absorption bands in this spectral range.[3,4]

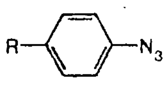
A way to increase the sensitivity of azides in the visible spectral range is the use of sensitizers (S),[5—8] which act *via* a mechanism of energy (route *a*) or electron (route *b*) transfer. In both cases, azide decomposes.



Aryl azides have been previously decomposed both by intra- and intermolecular electron transfer.[8,9]

It is known that electron transfer (ET) occurs when charge-transfer complexes (CTC) are excited. We supposed that the photodecomposition of azide can be sensitized when it is used as a component of CTC. Since there are examples of decomposition of azides when an electron is trapped,[6,8,9] azide was chosen as the acceptor component of the complex. When the CTC forms, a charge-transfer band, which is bathochromically shifted relative to absorption bands of the initial complexes, appears in the electronic spectrum. Thus, if ET occurring in the excitation of CTC results in the decomposition of azide, the formation of the complex results in an extension of the region of spectral sensitivity.

In this work, the photochemical properties of the donor-acceptor systems are studied for two simplest aromatic azides with electron-withdrawing substituents in the ring (4-azidoacetophenone (AA) and 4-nitrophenylazide (NPA)) using diphenylamine (DPA) as the donor.



AA: R = MeCO,
NPA: R = NO_2

Experimental

Aromatic azides were synthesized using a standard procedure by diazotization of the corresponding amines followed by treatment with NaN_3. The photolysis was carried out in a quartz cell (l = 0.095 cm) with the light of a high-pressure mercury lamp. The photolysis of 4-azidoacetophenone and 4-nitrophenylazide was carried out at 365 and 405 nm, respectively. The combination of glass and interference filters was used to separate lines of 365 and 405 nm.

The observed quantum yield was calculated as the ratio of the rate of the azide decomposition to the rate of the light absorption by the whole system. The rate of decomposition of azide was determined chromatographically by measuring the concentration of azide in a cell during photolysis. The change in the overall optical density in the system was simultaneously monitored spectrophotometrically. Chromatographic analysis was performed on a Millikhrom chromatograph (column Separon S18, 5.0 mm, gradient regime, acetonitrile—water system). Acetonitrile of the "for liquid chromatography" grade was used in the experiments.

The light intensity measured by an RTN-20 bolometer was equal to (3—4) $\cdot 10^{-9}$ Einstein s^{-1} cm^{-2}. Electronic absorp-

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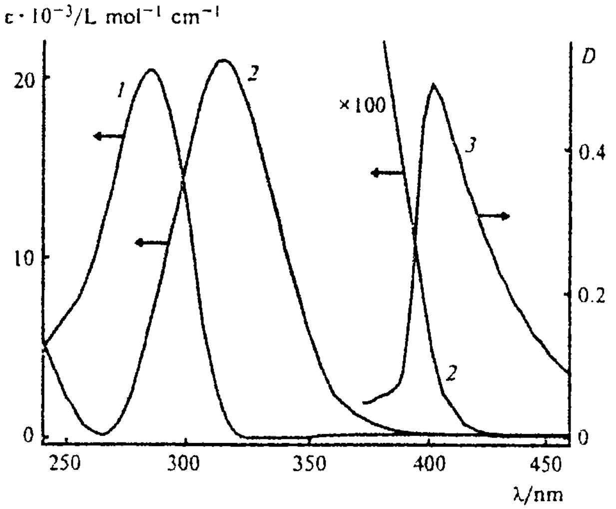

Fig. 1. Electronic absorption spectra: (left axis) *1*, DPA; *2*, NPA; *3*, (right axis) differential spectrum of a mixture of NPA and DPA, ([NPA] = 0.05 mol L^{-1}, [DPA] = 0.3 mol L^{-1}, 0.5-cm cell, acetonitrile).

tion spectra were measured on a Specord UV-VIS spectrophotometer.

Results and Discussion

The absorption spectra of DPA (spectrum *1*) and NPA (spectrum *2*) are presented in Fig. 1 as an example. The differential spectrum of a mixture of NPA and DPA (spectrum *3*) is also presented in Fig. 1. It can be seen that the formation of CTC manifests itself as the appearance of a charge-transfer band shifted to the long-wave spectral region compared to the absorption of azide at 6810 cm^{-1}. A similar effect is also observed in the case of AA, and the bathochromic shift is equal to 7220 cm^{-1}.

We attempted to determine the stability constant of the CTC by the Benesi—Hildebrandt method,[10] and the values of constants close to zero were obtained for both systems (Fig. 2). This is usually explained by the fact that contact pairs, rather than classic (equilibrium) complexes, are present in the solution.[10] On the other hand, according to Person's criterion,[11] for the reliable measurement of the complex formation constant (K), the concentration of a donor in the most concentrated solutions should be > 0.1(1/K). Therefore, in our case, when the constants are lower than 0.1—0.2 mol L^{-1}, a linear dependence of the optical density on the concentration of diphenylamine should be observed, which corresponds to the experimental data. The following empirical ratios between the overall optical density (D_{ov}) of the solution and the concentrations of azide (C_{az}) and amine (C_{am}) were obtained from these dependences:
for AA (365 nm):

$$D_{ov} = C^0_{az} \cdot \varepsilon_{az} \cdot l \cdot (1 + 0.92 \cdot C_{DPA}) + \varepsilon_{DPA} \cdot l \cdot C_{DPA}, \quad (1)$$

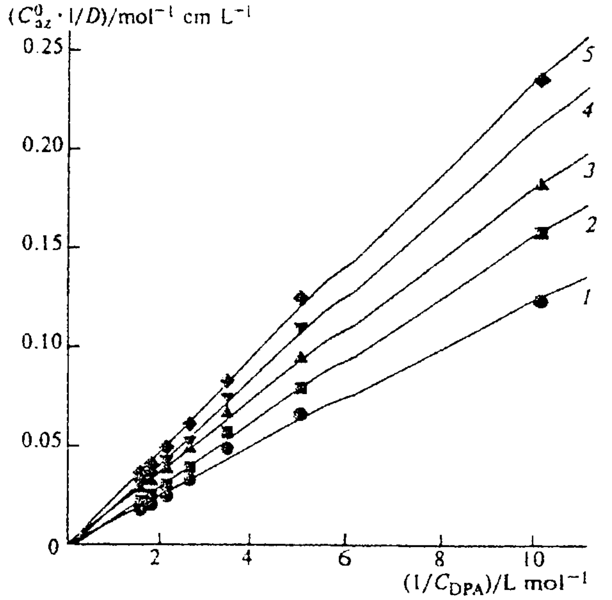

Fig. 2. Application of the Benesi—Hildebrandt method for the NPA—DPA system at different wavelengths: 401 (*1*), 405 (*2*), 412 (*3*), 415 (*4*), and 421 nm (*5*) ([NPA] = 0.01 mol L^{-1}, [DPA] = 0.1—0.7 mol L^{-1}, 1-cm cell, acetonitrile).

for NPA (405 nm):

$$D_{ov} = C^0_{az} \cdot \varepsilon_{az} \cdot l \cdot (1 + 2.25 \cdot C_{DPA}), \quad (2)$$

where ε_{az} and ε_{DPA} are the extinction coefficients of azide and amine (mol^{-1} L cm^{-1}), respectively, at the excitation wavelength; $C_{az}{}^0$ and C_{DPA} are the initial concentrations of azide and amine (mol L^{-1}), respectively; and l (cm) is the length of the cell.

Based on Person's criterion, the upper boundary of the complex formation constants can be estimated for the systems studied as $K < 0.14$ mol^{-1} L (0.1/0.7).

The study of the kinetics of the photodissociation of NPA and AA in the presence of DPA showed that the photochemical properties of these systems differ sharply. In the case of AA, an increase in the photolysis rate was observed as the concentration of DPA increased, and in the case of NPA, the rate of photodecomposition decreased as the concentration of the donor increased (Fig. 3). The rate of decomposition of azide $v = -dC/dt$ was determined by chromatographic analysis of the reaction mixture during irradiation with a constant intensity of the incident light.

Based on the measured rate of the photodecomposition of azides, the values of the observed quantum yields Φ_{obs}, determined per light absorbed by the whole system (Table 1) were estimated.

The effect of DPA on the rate of photodecomposition of azide can be determined by the following factors: a) amine forms a complex with azide, which decomposes under the action of light or is photoinert; b) amine photosensitizes the decomposition of azide; c) amine

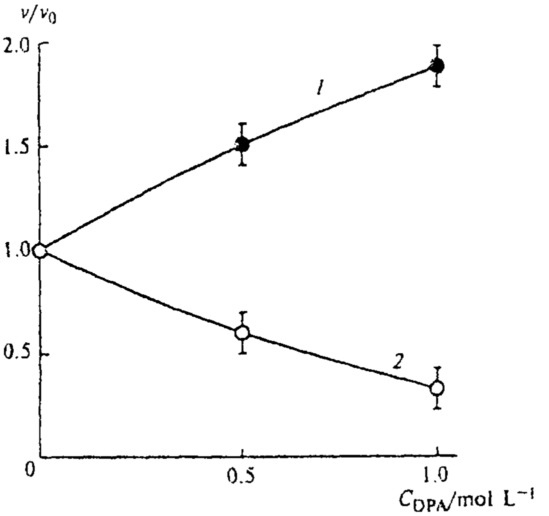

Fig. 3. Dependence of the relative rate of photodissociation of azide on the concentration of DPA: *1*, AA (irradiation at the wavelength of 365 nm); *2*, NPA (irradiation at 405 nm); acetonitrile.

quenches the excited state of azide. The effect of the second factor should appear as an increase in the observed rate of photodecomposition, and the effect of the third factor should be manifested in its decrease. The change in the rate of the first process is determined by the ratio of the quantum yields of the photodecomposition of the free azide and the complex. In the case of the photoactive complex, an increase in the rate of photolysis of azide should be observed due to the increase in the efficiency of light absorption. Otherwise, the existence of the complex will result in a decrease in the rate of the photodecomposition of azide due to the fact that a portion of azide is bound in the complex and is not photoactive at the moment of irradiation.

The processes mentioned can be presented as a general scheme.

Scheme 1

$$ArN_3 \xrightarrow{h\nu} ArN_3{}^*$$

$$ArN_3 \cdot Ph_2NH \xrightarrow{h\nu} (ArN_3{}^{\cdot -}, Ph_2NH^{\cdot +})$$

$$Ph_2NH \xrightarrow{h\nu} Ph_2NH^* \xrightarrow{+ArN_3} ArN_3{}^* + Ph_2NH$$

$$ArN_3{}^* \longrightarrow ArN_3$$

$$(ArN_3{}^{\cdot -}, Ph_2NH^{\cdot +}) \longrightarrow ArN_3 \cdot Ph_2NH$$

$$ArN_3{}^* + Ph_2NH \longrightarrow \longrightarrow ArN_3 + Ph_2NH$$

$$ArN_3{}^* \longrightarrow ArN + N_2$$

$$ArN_3{}^{\cdot -} \longrightarrow ArN^{\cdot -} + N_2$$

Table 1. Observed quantum yields (Φ_{obs}) of photodissociation of azides for different concentrations of DPA

C^0_{az}	C_{DPA}	Φ_{obs}	
mol L^{-1}		AA	NPA
0.005	0.0	0.85	0.95
0.005	0.5	0.65	0.26
0.005	1.0	0.55	0.095
0.050	1.0	0.67	—

The first three reactions include possible routes of the photoactivation of azide, the next three reaction describe all routes of deactivation of the reactive state, and the last two reactions represent the dissociation of the excited azide and radical anion.

In the case of AA, the acting light (365 nm) is absorbed by all components of the reaction mixture. Therefore, taking into account the photodissociation of azide, the photodecomposition of the complex, and the amine-sensitized decomposition of azide, the following equation can be written for the rate of the photodecomposition:

$$v = -dC/dt = \Phi_{obs} \cdot I = \Phi_1 \cdot D_{az} \cdot I/D_{ov} + \\ + \Phi_2 \cdot D_c \cdot I/D_{ov} + \Phi_3 \cdot D_{DPA} \cdot I/D_{ov}, \qquad (3)$$

where the intensity of the absorbed light $I = I_0 \cdot (1 - 10^{-D_{ov}})$, I_0 is the intensity of the incident light; Φ_{obs} is the observed quantum yield of the photodecomposition of azide; Φ_1, Φ_2, and Φ_3 are the quantum yields of the photodecomposition of azide in the absence of diphenylamine, the photodecomposition of the complex, and the diphenylamine-sensitized photodecomposition of azide, respectively; D_{ov}, D_{az}, D_c, and D_{DPA} are the optical densities (overall) of the solution at the excitation wavelength, of azide at the excitation wavelength, of the complex at the excitation of the wavelength, and of diphenylamine at the excitation wavelength, respectively.

Assuming that the probability of the decomposition of the excited azide is independent of the method of excitation, the quantum yield of the photosensitized decomposition of azide can be estimated as

$$\Phi_3 = \Phi_1/(1 + 1/(K_s \cdot C_{az})), \qquad (4)$$

where K_s is the quenching constant of azide excited by amine. Hence we obtain

$$\Phi_{obs} = (\Phi_1 \cdot D_{az} + \Phi_2 \cdot D_c + \Phi_3 \cdot D_{DPA})/D_{ov}. \qquad (5)$$

Since in our case $C_{DPA} \gg C^0_{az}$, the optical density of azide is determined as

$$D_{az} = C^0_{az} \cdot \varepsilon_{az} \cdot l \cdot (1/(1 + K \cdot C_{DPA})), \qquad (6)$$

the optical density of amine is

$$D_{DPA} = \varepsilon_{DPA} \cdot C_{DPA} \cdot l, \qquad (7)$$

where D_{ov} is determined from empirical equation (1), and the optical density of the complex is determined from the difference

$$D_c = D_{ov} - D_{az} - D_{DPA}. \quad (8)$$

Using the experimental values of Φ_{obs} (see Table 1) and the following values of the initial parameters: I = 0.095, K < 0.14, ε_{az} = 20, and ε_{DPA} = 0.1, the possible values of the parameters were estimated by the numerical solution of Eq. (5), taking into account Eqs. (4), (6)—(8), by the least-squares method: Φ_1 = 0.85, Φ_2 = 0.49, K_s = 160 mol^{-1} L. It is noteworthy that when K < 0.1 the K value has no effect on the calculated values of Φ_1 and Φ_2.

In the case of NPA, only azide and CTC are the components absorbing the light (because at 405 nm $\varepsilon_{DPA} \approx 0$); therefore, the rate of photodecomposition of azide is determined by the photolysis of azide, photolysis of the complex, and the quenching of the excited state of azide by diphenylamine:

$$-dC/dt = \Phi_{obs} \cdot I = \Phi_1 \cdot D_{az} \cdot I/(1 + K_q \cdot C_{DPA})/D_{ov} + \Phi_2 \cdot D_c \cdot I/D_{ov}, \quad (9)$$

where K_q is the quenching constant of the excited azide by amine. Hence, as in the case of AA, we obtain

$$\Phi_{obs} = (\Phi_1 \cdot D_{az}/(1 + K_q \cdot C_{DPA}) + \Phi_2 \cdot D_c)/D_{ov}, \quad (10)$$

where D_{ov} is determined from empirical Eq. (2), and the other parameters are similar to those in the case of AA.

The numerical solution of Eq. (10), using the values of the initial parameters (I = 0.095, K < 0.14, ε_{az} = 28) and experimental values of Φ_{obs} (see Table 1), result in the following values of the quantum yields and constants: Φ_1 = 0.95, Φ_2 = 0, and K_q = 1.3 mol^{-1} L.

The results obtained are presented in Fig. 4, where the experimental values of the observed quantum yield of the photodissociation of AA and NPA for different concentrations of DPA are shown by points, and solid lines demonstrate the theoretical dependences obtained by Eqs. (5) and (10) using the calculated constants.

Based on the data obtained, we can conclude that when NPA is irradiated in the presence of diphenylamine, the intracomplex electron transfer does not result in the dissociation of the azido group in the radical anion of azide, and the rate of the photodissociation decreases due to both static (the formation of a photostable complex with diphenylamine) and dynamic quenching.

In the case of AA when the irradiation is carried out in the presence of diphenylamine, the diphenylamine-sensitized decomposition of azide and the photodecomposition of the azide—diphenylamine complex probably occur along with the direct photolysis of azide, which results in an increase in the observed reaction rate due to an increase in the efficiency of the absorption of the acting light by the reaction system.

Thus, in the present work, the possibility of sensitization of the photodecomposition of aromatic azides *via* the electron transfer mechanism by irradiation of CTC of azide and donor has been shown.

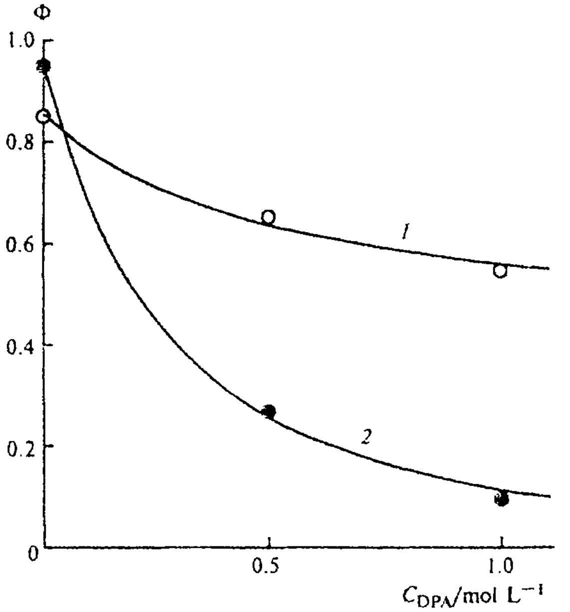

Fig. 4. Dependence of the observed quantum yield (Φ_{obs}) of photodecomposition of azides (points) on the concentration of DPA: *1*, AA (irradiation at the wavelength of 365 nm); *2*, NPA (irradiation at 405 nm); acetonitrile; solid curve shows the calculation by Eqs. (5) and (10).

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