## DETERMINATION OF THE QUANTUM YIELDS OF PHOTODISSOCIATION OF

ANILINE DERIVATIVES

Sh. Ruziev, Ya. N. Malkin, and V. A. Kuz'min

A sharp increase in the quantum yield of photodissociation of the N-H bond in solutions of aromatic amines -1,2-dihydro- and 1,2,3,4-tetrahydroquinolines - was previously found with an increase in the excitation energy [1-3].

Strictly speaking, the quantum yield of rupture of the N-H bond with formation of an H atom and an aminyl radical is the quantum yield of photodissociation:

$$RNH + hv \rightarrow RN + H \tag{1}$$

UDC 530.145:541.141.7:547.551

111

The quantum yield of photodissociation of the N-H bond has not been directly determined for aromatic amines (as for any other system) (with the exception of the estimation in [4], where the method used was not reported). It was shown in [5, 6] that the quantum yield of photodissociation of the N-H bond in solutions of aniline in water and hydrocarbons should not differ from the quantum yield of liberation of hydrogen, since the H atoms formed in dissociation of the N-H bond can cleave an H atom from the solvent with the formation of a molecule of  $H_2$ ; however, H atoms are also capable of forming adducts with theaniline, which can decrease the quantum yield of formation of  $H_2$ .

The quantum yields of the photodecomposition of aniline and its derivatives in heptane  $(\phi_{decomp})$ , the formation of hydrogen  $(\phi_{H_2})$ , and the formation of aminyl radicals  $(\phi_{rad})$ , and their dependence on the excitation energy were determined in the present study.

#### EXPERIMENTAL

The quantum yields of photodecomposition of the amines in heptane for  $\lambda = 254$  and 300 nm were determined on a setup consisting of steady-state irradiation with a DRSh-500 lamp; light with  $\lambda = 254$  nm was separated with a light filter (gaseous Cl<sub>2</sub>, atmospheric pressure, 5 cm cell length), and light with  $\lambda = 300$  nm was separated by a combination of UFS-5 and ZhS-20 light filters (Fig. 1).

The intensity of the light falling on the cell was determined by an F-4 photocell calibrated with a ferrioxalate actinometer (for  $\lambda = 254$ , 300, and 366 nm) and with an Aberchrome-540 actinometer (for  $\lambda = 300$  and 360 nm). The agreement was satisfactory in both cases (Table 1). The temperature of the measurements was  $22 \pm 2^{\circ}$ C. The solutions were blown through with nitrogen or argon for 20 min or evacuated. Aniline, N-ethylaniline, and 2,6-dichloroaniline were purified according to [7].

The amount of converted aniline was determined by the change in the intensity of its fluorescence during irradiation (Fig. 2). The quantum yields of the formation of H<sub>2</sub> were determined in a specially designed cell (Fig. 3) which permitted simultaneously recording the transformation of the starting aniline and the amount of H<sub>2</sub> formed with a PMT-2 lamp. After irradiation at 22°C, the solution was frozen in liquid nitrogen and the H<sub>2</sub> pressure was determined at 77°K (the PMT-2 lamp was specially calibrated for H<sub>2</sub>). Preliminary mass spectrometry showed that H<sub>2</sub> was the only gas liberated during irradiation. The precision of the measurements was  $\geq 20\%$ . The absorption spectra were recorded on a Specord UV-VIS spectrophotometer, and the fluorescence spectra were recorded on an Aminco-Bowman spectrofluorimeter. The absorption spectra of the short-lived intermediate products were recorded on a pulsed photolysis instrument with a resolution time of 20 µsec [3].

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 537-541, March, 1986. Original article submitted September 30, 1984.

	Iinc. photons/sec			
Type of actinometer	λ 254	λ 300	λ 360	
Ferrioxalate actinometer Aberchr <b>ome-</b> 540	0,238.1016	1,067 · 10 <sup>15</sup> 1,015 · 10 <sup>15</sup>	$\begin{array}{c c} 1,97 \cdot 10^{16} \\ 2,5 \cdot 10^{16} \end{array}$	

TABLE	1.	Intensity of	the Light	Falling on	the	Cell '
under	the	Measurement*	Conditions	$s (\lambda, nm)$		

\*The intensity of the light falling on the cell from a height of 3 cm was measured.



Fig. 1. Spectra: 1) absorption of aniline in heptane,  $C = 10^{-4}$  M; 2) transmission of filter with  $Cl_2$  for separation of the  $\lambda = 254$  nm line; 3) transmission of the combination of UFS-5 and ZhS-20 filters for separation of the  $\lambda = 300$  nm line; 4) absorption of the Aberchrome-540 actinometer  $(0.92 \cdot 10^{-3} \text{ M})$ .

# DISCUSSION OF RESULTS

The quantum yields of the formation of aminyl radicals have only been previously determined for indole and tryptophan [8]. The quantum yield  $\varphi_{rad}$  of the formation of aminyl radicals from the anilines were determined in the present study as follows: the amount of radicals formed in the cell 20 µsec after the exciting pulse ("immediately after the flash") was recorded by pulsed photolysis, the solution of Aberchrome-540 in toluene was then irradiated in the same cell, and the yield of aminyl radicals formed was calculated with the equation

$$\varphi_{\rm rad} = \varphi_{\rm Ab} (\Delta D \cdot D_{\lambda}^{\rm A0} \varepsilon_{\rm Ab} / \Delta D_{\rm Ab} D_{\lambda} \varepsilon) \tag{2}$$

where  $\varphi_{Ab} = 0.20$  [8] is the quantum yield of the formation of the colored form of Aberchrome;  $\Delta D_{Ab}$  and  $\Delta D$  are the changes in the optical density in absorption maximum of Aberchrome-540 and the aminyl radical immediately after the flash;  $\varepsilon_{Ab}$  and  $\varepsilon$  are the extinction coefficients at these maxima,  $\varepsilon_{Ab} = 8200$  liters/mole•cm. Pulsed photoexcitation was conducted through a combination of UFS-5 and ZhS-20 glass light filters. As Fig. 1 shows, the fraction of absorbed light for the anilines and Aberchrome is proportional to the integral transmission (determined by the area under the absorption spectrum) due to the close coincidence of the absorption spectra of the anilines and Aberchrome-540 in the narrow region of transmission of the light filters, and no correction is required for the emission spectrum of the pulsed xenon lamp.

The extinction coefficients ( $\varepsilon$ ) of the aminyl radicals were determined by the method previously used for determining the extinction coefficients of the aminyl radicals from 7-azaindolines [9]: the induced optical density in photoexcitation of benzophenone in benzene with  $10^{-3}$  M of aniline in the presence and absence of oxygen was recorded by the method of pulsed photolysis. Ketyl and aminyl radicals are formed in the same concentrations in the absence of oxygen (the triplet states of benzophenone are completely quenched with these concentrations of aniline). In the presence of oxygen, the ketyl radicals are totally quenched during the flash, and only the absorption spectrum of the aminyl radicals is recorded by pulsed photolysis. It was assumed that the amount of aminyl radicals formed is equal to the amount of ketyl radicals which appear in the absence of oxygen [10] (i.e., the oxygen in the air has no effect on the yield of formation of ketyl radicals, since they are totally quenched by the aniline). Knowing the extinction coefficient of the ketyl radicals from benzophenone,  $\varepsilon_{545} = 3220$  litters/ mole.cm, it is possible to determine the amount and extinction coefficients of the aminyl rad-





Fig. 2. Dependence of the degree of conversion of a solution of aniline in heptane  $C = 10^{-4}$  M on the time of irradiation with 254 nm light (in the absence of oxygen): 1) decrease in the optical density of the solution at a wavelength of 300 nm; 2) decrease in the intensity of the fluorescence at the maximum of the fluorescence spectrum of aniline.

Fig. 3. Cell for simultaneously recording the amount of converted aniline and the amount of liberated hydrogen: 1) PMT-2 lamp, 2) cock for connection to the vacuum installation; 3) quartz cell for irradiation and measurement of the fluorescence.

icals. The good coincidence of all three values obtained for aniline (Table 2) and their correspondence to the data in [6] should be noted.  $\varphi_{\rm H_{2}}$  = 0.09 ± 0.02 for ( $\lambda$  = 254 nm).

The  $\varphi_{\text{decomp}}$  and  $\varphi_{\text{H}_2}$  obtained in the present study coincide within the limits of precision of the experiment, and dissociation of the N-H bond is thus the only process of phototrans-formation of anilines with concentrations of the aniline of <9.5 \cdot 10^{-5} M. We note that the quantum yield  $\varphi_{\text{decomp}}$  also decreases with an increase in the concentration of the aniline, as for  $\varphi_{\text{H}_2}$  (Table 3), and this event is consequently not due to the formation of adducts of the H atom with the aniline as hypothesized in [6].

The values of  $\varphi_{\text{H}_2}$  obtained are in agreement with the data in [6], and it is thus possible to consider it solidly established that cleavage of the N-H bond is the only photochemical process in the irradiation of solutions of anilines in heptane with light, and this results in the formation of H atoms and aminyl radicals (quantum yield of side reactions  $\leq 10^{-3}$ ). It should be noted that in our opinion, this is the only photochemical system of photodissociation for which such a finding has been precisely established. The subsequent transformation of the photoinduced aminyl radicals is not totally clear. The kinetics of quenching of aminyl radicals obeys a second-order law. Dimerization of aminyl radicals in water results in the formation of aminodiphenyl, azobenzene, and benzidine derivatives [5], but the nature of the final products has not been studied in organic solvents.

Table 2 shows that a more significant increase in the quantum yield of photodissociation with an increase in the excitation energy (by 30-80 times) is characteristic of anilines in comparison to dihydro- and tetrahydroquinolines. For aniline and N-ethylaniline, this is accompanied by a decrease in the quantum yield of fluorescence with an increase in the excitation energy  $(\beta - \phi S_2 / \phi S_1 = 0.58$  for aniline and 0.70 for N-ethylaniline [6]).

In [6], the decrease in  $\varphi_{f1}$  with an increase in the excitation energy was attributed to the effective occurrence of photodissociation through the higher excited levels of the molecule, and photodissociation competes with the internal conversion of  $S_2 \rtimes S_1$ . It was also hypothesized in [6] that the effective photodissociation of aniline with excitation in the  $S_2$ state is related to the transition to the Rydberg potential surface and photodissociation from the n, 3S-Rydberg states located between the  $S_2$  and  $S_1$  ( $\pi\pi^*$ ) states of aniline. However, the calculations with the CNDO/S method did not confirm the possibility of the occurrence of the homolytic dissociation from Rydberg states [11], and dissociation from the higher T ( $\sigma$ ,  $\pi^*$ ) state is most probable for aromatic amines.

It should be noted that, strictly speaking, even the values of  $\varphi_{rad}$  determined by pulsed photolysis correspond to the amount of aminyl radicals found in the solution 20 µsec after the

Compound	<sup>φ</sup> decomp		$\varphi_{\mathrm{H}_{2}}$		φrad
	λ 254	λ 300	λ 254	λ 300	λ 254
Aniline N-Ethylaniline 2,6-Dichloroaniline	0,082 0,041 0,032	$\begin{vmatrix} <10^{-3} \\ <10^{-3} \\ <10^{-3} \end{vmatrix}$	0,076 0,021 0,0185	$\begin{array}{c c} 5,5\cdot10^{-3} \\ <10^{-3} \\ <10^{-3} \end{array}$	0,086 0,071 0,0387

TABLE 2. Quantum Yields of the Photodissociation of Anilines at Different  $(\lambda_{exc}, nm)$  (experimental details in text)

TABLE 3. Dependence of  $\phi_{\mbox{ decomp}}$  on the Concentration of the Starting Anilines

Compound	С, М	<sup>φ</sup> decomp	Compound	С, М	φ. decomp
Aniline	$9,7 \cdot 10^{-5} \\ 8,8 \cdot 10^{-4} \\ 1,43 \cdot 10^{-2}$	0,082 0,0055 0,0015	N-Ethylaniline	$\begin{vmatrix} 1,84 \cdot 10^{-4} \\ 1,66 \cdot 10^{-3} \\ 1,02 \cdot 10^{-2} \end{vmatrix}$	0,021 0,0078 0,0032

exciting pulse and cannot only reflect the efficiency of photodissociation but also the efficiency of the intracage recombination of the H atoms and aminyl radicals formed (for example, the increase in the quantum yield of photodissociation with an increase in the temperature was attributed in [6] to the presence of a cage effect, more probable than its dependence on the viscosity). Nevertheless, there are data in the literature on the absence of a cage effect for the H atom [12], although these data were undoubtedly only obtained for photolysis of water by HI and only concern the photodissociation of HI into atoms and cannot be extrapolated to polyatomic molecules which have a larger number of vibrational degrees of freedom.

The previously found effect of H atom acceptors (unsaturated hydrocarbons) on the quantum yield of photodissociation of hydrogenated quinolines [2] indicates the presence of the cage effect for hydrogen atoms in photolysis of aromatic amines. However, a direct response to the question of whether the observed quantum yield of formation of aminyl radicals is only a reflection of the efficiency of photodissociation or is a function of the cage effect (i.e., the properties of the medium) can only be given by using picosecond photolysis for studying the kinetics of recombination of the radicals formed.

We would like to thank S. N. Kozlova for calibration of the PMT-2 lamp with respect to  $\rm H_2.$ 

## CONCLUSIONS

1. Cleavage of the N-H bond with the formation of H atoms and aminyl radicals is the only photochemical process in the irradiation of anilines in heptane with light) the quantum yields of this process were determined.

2. The quantum yields of photodissociation increase sharply with an increase in the excitation energy.

### LITERATURE CITED

- 1. Ya. N. Malkin, N. O. Pirogov, and V. A. Kuzmin, J. Photochem., 26, 193 (1984).
- Ya. N. Malkin, N. O. Pirogov, O. T. Kasaikina, and V. A. Kuzmin, Oxidation Commun., 6, 293 (1984).
- 3. N. O. Pirogov, Ya. N. Malkin, and V. A. Kuz'min, Dokl. Akad. Nauk SSSR, 264, 636 (1982).
- 4. E. J. Land and G. Porter, Trans. Faraday Soc., <u>59</u>, 2027 (1963).
- 5. J. Zechner, L. St. Prangova, G. I. Grabner, and N. Getoff, Z. Phys. Chem., 102, 137 (1976).
- 6. G. Kohler and N. Getoff, J. Chem. Soc. Faraday Trans. 1, <u>76</u>, 1576 (1980).
- 7. A. Weissberger, E. Proskauer, J. A. Riddick, and E. Toops, Organic Solvents, Physical Properties, and Methods of Purification, 1st ed., in: Technique of Organic Chemistry, (ed. by A. Weissberger), Wiley, New York.
- 8. H. G. Heller and J. R. Langan, J.Chem. Soc. Perkin Trans. 1, 341 (1981).

9. Ya. N. Malkin, A. S. Dvornikov, and V. A. Kuzmin, J. Photochem., <u>27</u>, 343 (1984).
10. P. P. Levin and T. A. Kokrashvili, Izv. Akad. Nauk SSSR, Ser. Khim., 1234 (1981).
11. Ya. N.Malkin and S. P. Makarov, Izv. Akad. Nauk SSSR, Ser. Khim., 1282 (1985).
12. J. S. Lorand, Progr. Inorg. Chem., 17A, 207 (1973).

PHOTOLYSIS OF INDOLINE

Sh. Ruziev, A. S. Dvornikov, Ya. N. Malkin, and V. A. Kuz'min UDC 541.144.8:547.754

Earlier we showed [1-4] that the photodissociation of the N-H bond in aromatic amines obeys the following law: photodissociation occurs with low yields from the lower singlet or triplet state, and the quantum yield of photodissociation increases sharply with increasing energy of excitation, while the quantum yield of fluorescence decreases. We attribute this phenomenon to the appearance of a new channel for the photodissociation reaction — through higher excited states (for 1,2-dihydroquinolines, this photochemically active state has been identified as  $T_8$  ( $\sigma$ ,  $\pi$ \*) [2]). The indicated pattern is fulfilled for anilines [3, 5], indoles [5], and 1,2-dihydro- and 1,2,3,4-tetrahydroquinolines [1-4]. In [5] an analogous increase in the yield for anilines is attributed to dissociation through a Rydberg state. We should note that the dependence of the quantum yield of photodissociation on the wavelength of excitation is observed only at ~20°C; at 77°K in 3-methylpentane, the quantum yields of fluorescence and photodissociation do not depend on the wavelength [4]. The onlygroup of compounds that do not obey this law are the 7-azaindolines [6], for which  $\varphi_{f1}$  and  $\varphi_{dis}$  do not depend on the excitation energy, and photodissociation occurs from the lower T<sub>1</sub> state.

In this work we studied the photochemical properties of indoline (I), which is an analog of 7-azaindolines, but does not contain the N atom in the six-membered ring.

The instruments used and the methods of determination of the quantum yields of fluorescence ( $\varphi_{fl}$ ), photodissociation ( $\varphi_{H_2}$ ), and photodecomposition of the initial amine ( $\varphi_{dec}$ ) were described in our earlier studies [1-3]. Indoline from Merck was purified by vacuum redistillation over NaOH and recrystallized from water.

Pulse photoexcitation of a solution of (I) in heptane in the absence of oxygen by UV light leads to cleavage of the N-H bond and the formation of the corresponding aminyl radical with an absorption spectrum (Fig. 1) similar to the spectra of the radicals generated by 7-azaindoline and 1,2,3,5-tetrahydroquinoline:



In the presence of oxygen, the formation of aminyl radicals does not occur, i.e., the photodissociation of (I) occurs from the  $T_1$  state, quenchable by oxygen (just as for 7-azain-dolines and tetrahydroquinolines). The quantum yield of the formation of aminyl radicals for (I) could not be determined, since the method used in [6] cannot be used to determine the co-efficients of extinction of the aminyl radical for (I) (evidently on account of the interaction of aminyl radicals with benzophenone or ketyl radicals). However, the quantum yields of the liberation of H<sub>2</sub> for light with  $\lambda$  254 and 300 nm, equal to 0.06 and 0.01, respectively, at 22°C could be determined according to the method described in [3]; here the quantum yield  $\varphi_{H_2}$  also increases with increasing excitation energy, and the quantum yield of fluorescence falls from 0.09 (300 nm) to 0.064 (254 nm). The quantum yield of the photodecomposition of (I) also doubles when the energy of excitation is increased from 254 to 300 nm, and it was shown

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 542-543, March, 1986. Original article submitted January 24, 1985.