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Acid-controlled photoreactivity of 9-(4′-azidophenyl)acridine

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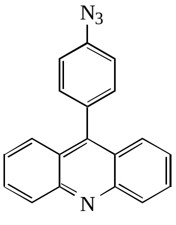
The possibility to control the photodissociation quantum yield of aromatic azide within two orders of magnitude by varying acid concentration is demonstrated using 9-(4′-azidophenyl)acridine as an example.

The problem of adjusting the photochemical quantum yield is of great importance for the development of light-controlled molecular devices. Aromatic azides, due to their photochemical activity, could be used as photosensitive elements in these nanoscale systems. However, the quantum yield (φ) of azido group photodissociation, being determined by arylazide structure, possesses a discrete value and is little dependent on the conditions of photolysis.[1] This restricts the possibility to regulate smoothly the properties of a molecular device.

Here we describe a system where the observed quantum yield of arylazide decomposition can be smoothly changed within two orders of magnitude.



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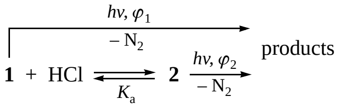
The quantum yield of decomposition of 9-(4′-azidophenyl)acridine **1**[†] was measured at different HCl concentrations. In an acid medium, we observed the disappearance of a neutral azide absorption band at 359 nm (Figure 1, spectrum *1*) and the appearance of a new longwave band at 420 nm (Figure 1, spectrum *2*). The latter band is characteristic of the acridinium cation with a substituent at an endocyclic nitrogen atom.[2,3] Figure 1 (curves 2–7) shows the spectral changes upon irradiation of the reaction mixture.[‡] Evidently, in this case, two photochemical reactions take place simultaneously: the decomposition of free (neutral) azide **1** and acridinium chloride **2** with quantum yields φ_1 and φ_2, respectively (Scheme 1).



Scheme 1

To obtain the quantitative dependence of the observed quantum yield of azide decomposition (φ_{obs}) on acid concentration, we should take into account that, firstly, the concentrations of free (nonprotonated) and protonated azide are connected through the acidity constant K_a and, secondly, the ground-state equilibrium between the free and protonated azide is not shifted during steady-state photolysis since the rate of azide decomposition upon light intensities used is several orders of magnitude lower than that of equilibrium attainment. Under these conditions, the kinetics of absorbance (D) changes is expressed as follows (in the case of a thin optical layer at irradiation wavelength, $D_{365} < 0.1$):

$$dD/dt = -2.3\varepsilon_{365}\varphi_{obs}lI_0,$$

Table 1 Observed quantum yield (φ_{obs}) of 9-(4′-azidophenyl)acridine dissociation at different HCl concentrations (EtOH, error ±20%).

[HCl]×100/mol dm^{-3}	φ_{obs}×100
0	82
0.063	32
0.211	18
0.302	14
0.64	8.8
1.36	4.6
1.38	4.7
1.52	4.2
2.19	3.7
3.7	2.8
6.25	2.0
9.95	1.5

or in the integral form

$$\ln[(D_0 - D_\infty)/(D_t - D_\infty)] = 2.3\varepsilon_{365}\varphi_{obs}lI_0t,$$

where the observed quantum yield is

$$\varphi_{obs} = \beta\varphi_2 + (\varphi_1 - \beta\varphi_2)/(1 + \beta[\mathrm{HCl}]/K_a). \qquad (1)$$

Here, ε_{365} (= 7720 dm^3 mol^{-1} cm^{-1}) is the absorption coefficient of azide at the irradiation wavelength (365 nm), β (= 1.09) is the ratio of the absorption coefficients of protonated and neutral azide at the same wavelength, l is an optical path (= 1 cm), and I_0 is the intensity of incident light (einstein dm^{-3} s^{-1}). The insert in Figure 1 shows the kinetics of absorbance changes at a band maximum (360 nm) and its anamorphosis in semilogarithmic coordinates. The observed quantum yields of azide dissociation at different HCl concentrations calculated from kinetic curves are summarised in Table 1.

One can see that the value of φ_{obs} decreases by a factor of 50 as the acid concentration increased up to 0.1 mol dm^{-3}. The limiting value lim(φ_{obs}) = 0.0075, provided [HCl] → ∞, according to equation (1), is equal to $\beta\varphi_2$ and it was obtained as an intercept from the dependence of φ_{obs} on reciprocal HCl concentration. Since β is known, we can calculate the quantum yield of

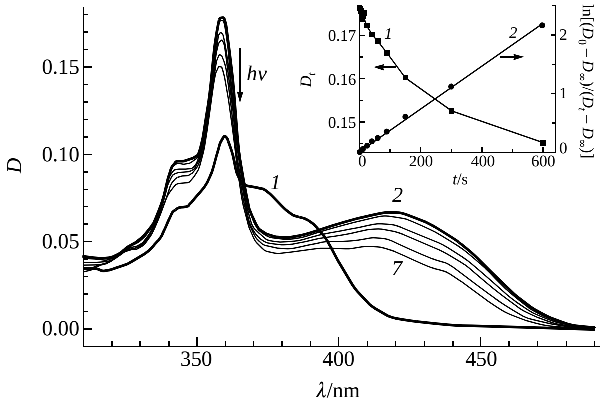


Figure 1 (*1*) Absorption spectrum of 9.5×10^{-6} mol dm^{-3} solution of 9-(4′-azidophenyl)acridine in EtOH; (*2*) the spectrum in the presence of 0.0219 mol dm^{-3} HCl. Spectral changes upon irradiation of the solution, irradiation time, s: (*2*) 0, (*3*) 25, (*4*) 90, (*5*) 150, (*6*) 300, (*7*) 600; light intensity, 4.88×10^{-6} einstein dm^{-3} s^{-1}. Insert: (*1*) kinetic curve at 360 nm and (*2*) its anamorphosis in semilogarithmic coordinates.

[†] The synthesis of 9-(4′-azidophenyl)acridine **1** was described earlier.[2]

[‡] *Typical photochemical procedure*: an air-saturated ethanol solution of **1** in 1 cm quartz cuvette adjusted by conc. HCl to an appropriate acid concentration was irradiated by 365 nm Hg line [light intensity (4.5–5)×10^{-6} einstein dm^{-3} s^{-1}]; (0.8–1.2)×10^{-5} mol dm^{-3} azide concentrations were used.

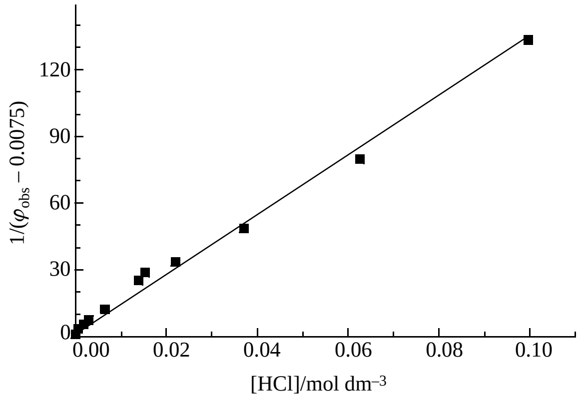


Figure 2 Reciprocal quantum yield of azide **1** decomposition *vs.* [HCl], experimental points and theoretical straight line plotted using equation (2).

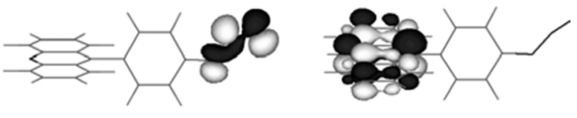
protonated azide decomposition: $\varphi_2 = 0.0069$, which is of the same order of magnitude as previously found for *N*-methyl-9-(4′-azidophenyl)acridinium methyl sulfate.[2]

Knowing the product $\beta\varphi_2$, equation (1) can be reduced to the linear form

$$1/(\varphi_{obs} - \beta\varphi_2) = 1/(\varphi_1 - \beta\varphi_2) + [\beta/K_a(\varphi_1 - \beta\varphi_2)][\text{HCl}]. \qquad (2)$$

Figure 2 shows the experimental data in the coordinates of equation (2) and the theoretical straight line plotted using the following parameters: $\beta = 1.09$, $K_a = 10^{-3}$ mol dm^{-3},[§] $\varphi_1 = 0.82$ and $\varphi_2 = 0.0069$. The coincidence of experimental points with the theoretical line testifies that the test system is adequately described by Scheme 1, and equation (1) or (2) can be used for the calculation of an acid concentration that is necessary for obtaining a given value of φ_{obs}.

On going from neutral azide **1** to its cation **2**, the photodissociation quantum yield decreases by more than two orders of magnitude. This can be explained taking into account the results of a quantum-chemical study of the dissociation of aromatic azides in the ground and lowest excited states.[1(*b*),4] The photoreactivity of aromatic azides depends on the nature of the molecular orbital (MO) that is filled in the excited state. The azide decomposes with a high quantum yield ($\varphi > 0.1$) if in the excited state the MO of a definite type, namely, σ_{NN} MO, is filled. This orbital is antibonding in respect to the $N–N_2$ bond and its filling is a prerequisite for the facile dissociation of the azido group. If the σ_{NN} MO remains empty upon excitation, the φ value decreases below 0.01.



1 **2**

Figure 3 Structure of HSOMO of **1** and **2**.

Figure 3 shows the structure of the highest semi-occupied MO (HSOMO) for **1** and **2** in the lowest excited singlet (S_1) state calculated using the PM3 quantum-chemical method.[¶,5] In **1**, the σ_{NN} MO is filled, whereas this MO remains empty in **2** and an aromatic MO localised on the acridine nucleus is filled instead. This explains the high photochemical reactivity of azide **1** and the low activity of its cation **2**.

Thus, the possibility to control the photodissociation quantum yield of an aromatic azide by varying acid concentration is demonstrated for the first time. The acidity can be controlled using photoacids, which release protons under irradiation.[6] Combined together in a supramolecular system, a proton photoreleasing compound and an acid-controlled photosensitive compound create a light-adjustable photosensitive system, which can be used for 3-D optical information recording and storage.

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References

1 (*a*) *Azides and Nitrenes*, ed. E. F. V. Scriven, Academic Press, Orlando, 1984; (*b*) M. F. Budyka, T. S. Zyubina and M. M. Kantor, *Zh. Fiz. Khim.*, 2000, **74**, 1115 (*Russ. J. Phys. Chem.*, 2000, **74**, 995).
2 M. F. Budyka, M. M. Kantor and R. M. Fatkulbayanov, *Khim. Geterotsikl. Soedin.*, 1997, 1504 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1997, **33**, 1301].
3 (*a*) B. Zhou, K. Kano and S. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1633; (*b*) T. Pedzinski, B. Marciniak and G. L. Hug, *J. Photochem. Photobiol. A: Chem.*, 2002, **150**, 21.
4 M. F. Budyka and T. S. Zyubina, *J. Mol. Struct. (Theochem)*, 1997, **419**, 191.
5 (*a*) J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 208; (*b*) J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.
6 (*a*) E. M. Kosower and D. Huppert, *Ann. Rev. Phys. Chem.*, 1986, **37**, 127; (*b*) L. M. Tolbert and K. M. Solntsev, *Acc. Chem. Res.*, 2002, **35**, 19.

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[§] The K_a value was measured spectrophotometrically.

[¶] The structures of azides **1** and **2** in the S_1 state were calculated with the full geometry optimization using the MOPAC 93 program package; cation **2** was calculated without counterion.