

PHOTOLYSIS OF QUINONEDIAZIDES IN ALCOHOLS AND IN WATER

Viktor ŘEHÁK, Jaroslav POSKOČIL, Jaroslav MAJER and Ivo DVOŘÁČEK

Institute of Chemical Technology, 532 10 Pardubice

Received February 8th, 1978

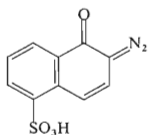
The photolysis of 9,10-phenanthrenequinonediazide and of 1,2-naphthoquinonediazide derivatives was studied; the spectral changes occurring during the photolysis and the quantum yields for various excitation wavelengths were measured, the order of the reaction was determined, and the effect of the exciting radiation intensity on the photolysis rate was investigated. A likely explanation of the different quantum yields in water and in ethanol is presented.

Photochemistry of quinonediazides has been studied so far predominantly from the qualitative point of view in attempts to make use of the light sensitivity of these compounds in reprography and in the synthesis of some otherwise hardly available compounds¹. Studies concerned with the quantitative aspects of photolysis of quinonediazides aiming at the determination of the factors controlling the mechanism of the reaction have not been made. Only scarce data on the photolysis quantum yields can be found in the literature²⁻⁵, these quantities having not been related in detail to the energy and structure of the molecule. The recently published papers have dealt with the nature of the excited states of *o*-quinonediazides⁶ and the solvent effect on their photolysis⁷.

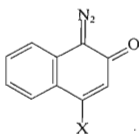
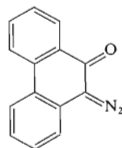
EXPERIMENTAL

Chemicals

1,2-Naphthoquinone-2-diazide-5-sulfonic acid (*I*), commercial product D215 (Fotochema, Hradec Králové) was twice recrystallized in darkness in a mixture acetone-water (6 : 1). 1,2-Naphthoquinone-1-diazide-4-sulfonic acid (*II*) was prepared by diazotation of 1-amino-2-naphthol-4-sulfonic acid with sodium nitrate in the presence of cupric sulphate. The product was isolated by acidifying out with sulphuric acid at 0–5°. The quinonediazide prepared was twice recrystallized from water at 50°C. 1,2-Naphthoquinone-1-diazide (*III*) was prepared by diazotation of 1-amino-2-naphthol hydrochloride with pentyl nitrite in ethanol saturated with hydrogen chloride⁸. The product prepared was twice recrystallized from ether; m.p. 94–96°C with decomposition. 9,10-Phenanthrenequinone-9-diazide (*IV*) was prepared according to the described procedure⁹.



I


 II, X = SO₃H
 III, X = H


IV

Methods

The purity of the quinonediazides was checked by chromatography on a thin layer of silica gel. Acetone served as the eluent and resorcinol in an alkaline solution as the detection reagent. The electronic absorption spectra were scanned on a spectrophotometer Specord UV VIS (Zeiss, Jena) in redistilled water and spectrally pure ethanol at room temperature. The spectral changes of the photolyte in preselected periods of irradiation¹⁰ and the kinetics of photolysis¹¹ were measured on the instruments described previously. The quantum yields were obtained with the precision ± 0.07 .

RESULTS AND DISCUSSION

A typical course of the spectral changes during the photolysis of the quinonediazides under study in alcohols as well as in water is shown in Fig. 1. In the region of the long-wavelength absorption band, the absorbance drops rapidly down to zero. The absorbance of the photoproducts is appreciable only in the range of higher energies (32000 cm^{-1} and more). From the point of view of the quantitative evaluation of the photolysis, no corrections for the absorption by the products are necessary; this applies both to the photolytic radiation (wavelengths 365, 405, and 436 nm) and to the analytical radiation (absorption maximum).

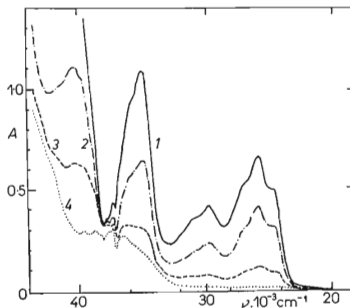


FIG. 1
 Spectral Changes Occurring During the Photolysis of 1,2-Naphthoquinone-1-diazide in Ethanol (10^{-4} M , 1 cm, 365 nm)
 1 Unirradiated, 2 6 s, 3 20 s, 4 40 s irradiation.

Fig. 2 shows a typical shape of the kinetic curves of I for different excitation wavelengths. The dependence of $\log A_0/A$ on the time is plotted as well; its linearity confirms that the reaction is first order with respect to the concentration of the reacting compound. Alike shapes have been found also for the other compounds examined, both in water and in ethanol.

The photolysis is fastest if excited by light of the wavelength 405 nm. The increase of the rate can be ascribed to the high radiation intensity ($29 \cdot 10^{-7}$ e/min) and also to the high absorption of this radiation. More slowly proceeds the photolysis in the case of excitation by light of the wavelength 365 nm, and it is the slowest with the excitation by light of the wavelength 333 nm, where the intensity is about ten times weaker though the absorption is comparable with that at 405 nm.

The effect of the photolytic radiation intensity on the photolysis rate and quantum yield was examined for the quinonediazides I and II in water as well as in ethanol. Linear dependences of the photolysis rate on the exciting radiation intensity for different degrees of conversion were obtained in all cases (Fig. 3); the photolysis quantum yield virtually does not change with the intensity of the photolytic radiation. It can be thus concluded that a one-photon process takes place, the energy of a single photon being sufficient for the initiation of the reaction.

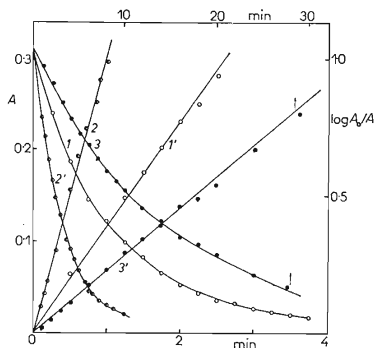


FIG. 2

Kinetics of the Photolysis of I in Water

Excitation wavelength: 1, 1' 365 nm, 2, 2' 405 nm, 3, 3' 333 nm; analytical wavelength 400 nm.

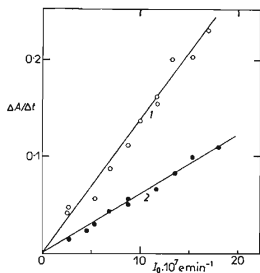


FIG. 3

Dependence of the Photolysis Rate of I in Water on the Intensity of the Exciting Radiation of the Wavelength 365 nm

Degree of conversion: 1 35.4%, 2 66.7%.

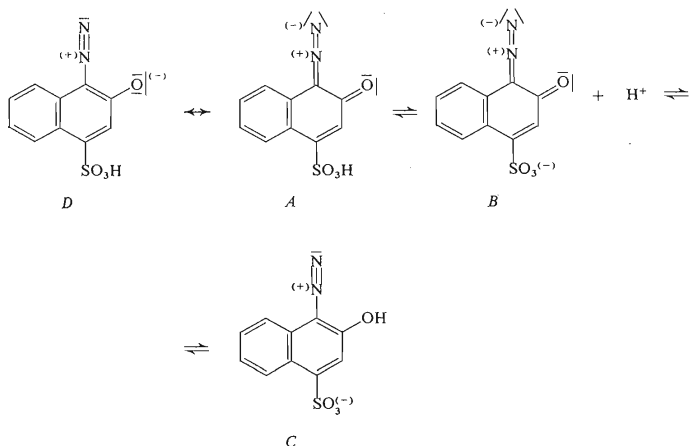
Table I gives the values of the quantum yields of photolysis of the quinonediazides in water and in ethanol in different conditions of excitation. The highest quantum yields can be achieved by using excitation by light of the wavelengths 365 and 405 nm, hence by excitation to the absorption band which very probably corresponds to the $\pi \rightarrow \pi^*$ vibronic transition⁶. Excitation by radiation of the wavelength 436 nm results in a lowering of the quantum yield, particularly appreciably in ethanolic solutions. This can be explained in terms of the increased population of the $n\pi^*$ states whose photochemical reactivity or possibilities of relaxation are different from those for the population of the $\pi\pi^*$ states. The quantum yields of photolysis of *III* in ethanol given in the paper⁷ are lower than those obtained by us. We suppose that the difference may be due to the different evaluation of the intensity of the exciting radiation absorbed by the system: in the paper⁷ the intensity absorbed by the complete system (quinonediazide, intermediate products) is taken into the calculation, whereas our calculations involve the intensity absorbed by the quinonediazide solely.

Marked is the increase of the quantum yield for all wavelengths in ethanol. At present it is questionable whether quinonediazides possess the *o*-quinoid structure or whether the diazonium form prevails. The elementary quantum chemical calculations favour the diazonium structure^{6,12}, whereas the chemical reactivity corroborates the *o*-quinoid structure¹³. Naturally, the preference of the two structures will be controlled by the substitution and medium, the polarity of the solvent, and the pH; particularly the pH value has a considerable effect upon the quinonediazide structure and photolysis quantum yield¹⁴. In the case of the quinonediazides *I* and *II* a ready dissociation of the sulfo group can be assumed in aqueous medium, which results in a decrease of the pH of the solution and establishing of the equilibrium. The equilibrium $B \rightleftharpoons C$ must bring about significant changes in the electronic absorption spectrum taken in water as compared with that in ethanol, where the equilibrium establishes in different concentration conditions. The experiment shows, however, that the spectral

TABLE I
Photolysis Quantum Yields

Quinonediazide	Medium	365 nm	405 nm	436 nm
<i>I</i>	H ₂ O	0.47	0.44	0.48
	C ₂ H ₅ OH	0.66	0.60	0.52
<i>II</i>	H ₂ O	0.29	0.25	0.13
	C ₂ H ₅ OH	0.41	0.40	0.19
<i>III</i>	C ₂ H ₅ OH	0.79	0.72	0.72
<i>IV</i>	C ₂ H ₅ OH	0.38	0.32	—

differences are negligible; this implies that either the two media exert the same effect upon the equilibrium, or the equilibrium processes play an important part only after the excitation of the molecule.



In the sense of the Wolff rearrangement the quinoid structure is preferred¹⁵, the nitrogen being easily detached in the excited state with the formation of carbene¹⁶. We suppose that this structure is formed in ethanol, bringing about a rise of the photolysis quantum yield.

REFERENCES

1. Dinaburg M. S.: *Svetochuvstvitel'nost' Diazosoidinonii i Ikh Primenenie*. Khimiya, Moscow 1964.
2. De Jonge J., Dijkstra R., Wiggerink G. L.: *Rec. Trav. Chim. Pays-Bas* 71, 846 (1952).
3. Schröter W.: *Z. Wiss. Photogr.* 28, 1 (1930).
4. Eggert J.: *Z. Elektrochem.* 34, 602 (1928).
5. Kirmse W., Horner L.: *Justus Liebigs Ann. Chem.* 625, 34 (1959).
6. Maksimova L. I., Kuznetsov V. A., Talnikova E. V., Fedorov J. I.: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1975, 149.
7. Komagorov A. M., Ponomareva R. P.: *Zh. Org. Khim.* 12, 1758 (1976).
8. Anderson L. C., Roedel M. J.: *J. Amer. Chem. Soc.* 67, 955 (1945).
9. Sűs O., Steppan H., Dietrich R.: *Justus Liebigs Ann. Chem.* 617, 20 (1958).

10. Řehák V., Majer J., Poskočil J.: Chem. Listy 69, 990 (1975).
11. Řehák V., Novák F., Čepčiansky I.: Chem. Listy 66, 875 (1972).
12. Bochvar D. A., Gambaryan N. P., Mishchenko V. V., Kazitsyna L. A.: Dokl. Akad. Nauk SSSR 175, 829 (1967).
13. Stepanova B., Sakharova N. A.: Zh. Org. Khim. 11, 138 (1975).
14. Böttcher H., Werner R., Becker H. G. O.: Z. Chem. 13, 374 (1973).
15. Meier H., Zeller K. P.: Angew. Chem. Int. Ed. 14, 32 (1975).
16. Dürr H.: *Topics in Current Chemistry*, Vol. 55, p. 87. Springer, Berlin 1975.

Translated by P. Adámek.