PHOTOLYSIS OF QUINONEDIAZIDES IN CYCLOHEXANE FORMATION OF COLOURED ADDUCT, HEAVY ATOM EFFECT

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Photolysis of 1,2-naphthoquinone-1-diazide and 9,10-phenanthrenequinonediazide in cyclohexane gives coloured products decomposing on further irradiation. Formation of the products and their concentration depends on the way of irradiation (short, continuous) and on the presence of 1-propanol in the solution. The products are presumed to be adducts of ketene with the starting quinonediazides. Rate constants of their formation have been determined. Influence of solvent containing a heavy atom (1-bromopropane, iodoethane) on quantum yield of the photolysis and influence of oxygen have been investigated.

The previous communication[1] dealt with photolysis of *o*-quinonediazides in alcohols and in water; the photolysis quantum yields were measured for various wavelengths of excitation, the reaction order was determined, and influence of intensity of the excitation radiation on the photolysis rate was investigated. In alcohols and water the photolysis course is relatively simple, since the ketene formed after elimination of nitrogen from the molecule of the excited quinonediazide reacts very rapidly with solvent to form indenecarboxylic acid or its ester[2]. In cyclohexane course of the reactions following photolysis is more complex, a coloured product being formed; the present report deals with its structure and conditions of its formation.

EXPERIMENTAL

Reagents

1,2-Naphthoquinone-1-diazide (*I*) and 9,10-phenanthrenequinonediazide (*II*) were prepared by known methods[3,4]. Cyclohexane for UV spectroscopy (Lachema, Brno) was rid of traces of benzene using annealed silica gel and then rectified on a column: the fraction boiling at 80·5°C was taken. 1-Bromopropane (Lachema, Brno) was rectified on a column before use: fraction boiling at 70·8°C was taken. Iodoethane was shaken with mercury and rectified on a column before use: fraction boiling at 72°C was taken.

Methods

Purity of the quinonediazides was checked by TLC on silica gel using acetone as eluent and alkaline resorcinol solution as detection agent. The electronic absorption spectra were measured at laboratory temperature with a Specord UV VIS spectrophotometer (Zeiss, Jena). Spectral changes of the photolyte were measured after certain intervals of irradiation[5], and the photolysis kinetics was measured at room temperature using the apparatus described previously[6]. The quantum yields were measured with the accuracy of $\pm 0{\cdot}07$. Kinetics of the reactions taking place in the solution after irradiation were followed with the use of a milisecond flash apparatus[7] combined with the Specord UV VIS spectrophotometer and an X—Y recorder BAK 4T (Aritma, Prague).

RESULTS AND DISCUSSION

Course of spectral changes during photolysis of *II* in cyclohexane is given in Fig. 1. In the region of the long-wavelength absorption band (30000 to 25000 cm^{-1}) there occurs an abrupt absorbance decrease to one half of the original value within the first minute of irradiation. In the course of further irradiation the decrease is slower, and after 15 min it drops to zero value. At the beginning of the photolysis a transient absorbance increase is encountered in the region 25000 to 21000 cm^{-1}. Further irradiation causes this absorption band to disappear. Similar behaviour can be observed during photolysis of cyclohexane solutions of *I*, too.

Quantitative evaluation of the photolysis carried out in usual way (the case when the photoproducts do not absorb) is loaded with considerable error. Therefore, the data for calculation of the quantum yields were taken from the initial irradiation intervals only (1 and 2 min). For the quinonediazide *I* the measured values were: $q_1 = 0{\cdot}62$ and $q_2 = 0{\cdot}59$ ($I_0 = 10{\cdot}9 \,.\, 10^{-7}$ e min^{-1}); for *II*: $q_1 = 0{\cdot}37$ and $q_2 = 0{\cdot}29$ ($I_0 = 15{\cdot}4 \,.\, 10^{-7}$ e min^{-1}). The quantum yield is obviously higher for *I* than for *II*, the same being true for ethanol[1], too. The both compounds exhibit higher quantum yields in ethanol than in cyclohexane. This fact can be due (to a certain extent) to absorption of photolytic radiation by the photolysis products. On the other hand, change in photoreactivity of the lowest excited state of the molecule is to be con-

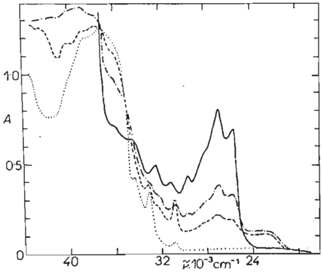


FIG. 1

Spectral Changes during Photolysis of 9,10-Phenanthrenequinonediazide in Cyclohexane ($5 \,.\, 10^{-5}$M, 1 cm, 365 nm)
——— Not irradiated, –·–·–·– 50 s, ------ 100 s, · · · · · · 900 s irradiation.

sidered, too. From the spectral measurements it is obvious that structure and energy position of the absorption bands are considerably sensitive to the solvent polarity.

In order to investigate conditions of formation of the coloured products, we carried out kinetic measurements with short-term excitation of the sample and followed the course of dark reaction in the region of absorption of the product (435 nm). Also we followed effect of 1-propanol on kinetic course of formation and decomposition of the photoproduct in cyclohexane. In the case of *II* absorbance increases abruptly within 2 min irradiation and further increase occurs even without excitation (the dark reaction). The absorbance increases to the value 0·57 after 22 min, whereafter it remains constant. Further irradiation results in a relatively fast photolysis of the formed product. On continuous irradiation (Fig. 2*a*) the absorbance increases to 0·19 after 5 min, whereafter it decreases again. In the case of *I* a similar absorbance increase was observed during the dark reaction, the only difference being in that photolysis of this product almost does not occur within the given time intervals.

Effect of 1-propanol on decomposition of the coloured product can be seen in Figs 2*b*, 2*c*. Presence of the alcohol in solution blocks the photolytically generated ketene by the reaction giving ester of carboxylic acid which is unable to react further.

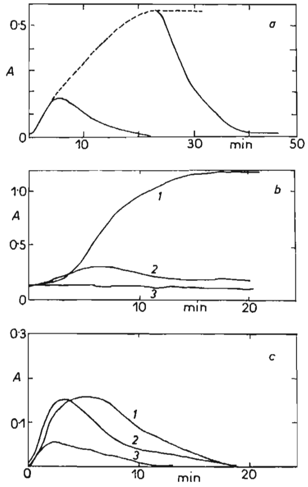


FIG. 2

a Kinetics of Formation and Photolysis of Adduct *IV* (exc. 365 nm, anal. 435 nm) ——— Irradiation, - - - - - dark reaction. *b* Influence of 1-propanol on kinetics of formation of adduct *III* (exc. 365 nm, anal. 435 nm)

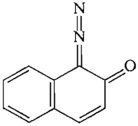
1 pure cyclohexane, *2* 1-propanol–cyclohexane 1 : 600, and *3* 1 : 200 by vol.

c Influence of 1-propanol on kinetics of formation of adduct *IV* (exc. 365 nm, anal. 435 nm)

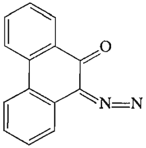
1 pure cyclohexane, *2* 1-propanol–cyclohexane 1 : 400, and *3* 1 : 200 by vol.).

In accord with refs[8,9] the coloured reaction product could be presumed to be the compound formed by condensation of ketene and carbene. These reactions were observed as thermolytical processes under the concentrations highly exceeding those in our experiments. It can be presumed that the mentioned reaction will not take place under the experimental conditions used by us due to high reactivity of carbene[10] (rapid conversion to ketene). Furthermore it can be presumed that the coloured product is an azo dyestuff formed by reaction of the quinonediazide with carboxylic acid[11]. This possibility is not likely, since this reaction occurs in aqueous media with such pH values when quinonediazides are present as diazonium salts. In cyclohexane this process cannot be expected. The dyestuff could be formed also by photocoupling mechanism involving interaction of the excited quinonediazide with the carboxylic acid. This possibility is practically out of question, since carboxylic acid cannot be formed in cyclohexane.

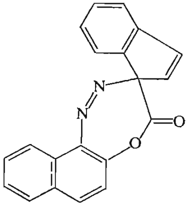
Experimental facts and the above considerations lead to the conclusion that the coloured product is an 1 : 1 adduct of ketene with the starting quinonediazide, most probably the compounds *III* and *IV*. These compounds have[12] absorption maxima about 415 nm in accord with those of the photolysis products. Attempts of isolation and structure determination of the adduct after irradiation of 10^{-3}M solutions in a preparative reactor failed due to its low stability (decomposition during crystallization and preparative chromatography).



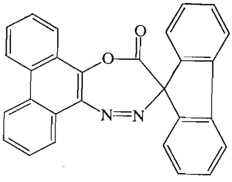
I



II



III



IV

Investigation of spectral changes during continuous irradiation showed rapid absorption increase in UV region and subsequent rapid decrease which can be observed as early as during measurement of spectra. Flash-photolytic measurements in this and in visible regions recorded kinetic course of pseudofirst order with respect to absorption decrease and formation of the adduct. Table I gives rate constants of these processes. Immediately after the flash a steep absorbance increase is observed with the both quinonediazides ($c = 5 . 10^{-5}$M) in the region 35000 cm^{-1} from the initial value 0·57 to 1·02 (for *I*) and 0·58 to 1·13 (for *II*). The rate constants were calculated from the data taken from the beginning of the kinetic processes, where absorption of the original quinonediazide and that of the products formed in the reaction play no important role. For the both quinonediazides the rate constants for UV and visible region do not differ much. Therefrom it can be concluded that the kinetic course in UV region and the steep absorbance increase after the flash will be due to the ketene which reacts further with excess amount of the starting quinonediazide.

Heavy atoms can considerably influence by external (solvent with a heavy atom) or internal (substituent) effects the probability of inter-system crosssing through the mechanism of spin-orbital interaction. From the viewpoint of photochemical reactivity possibilities are shown to investigate mechanisms of primary photochemical processes with respect to the photoreactive excited state. We followed effect of 1-bromopropane and iodoethane on kinetics and quantum yields of photolysis of the mentioned quinonediazides in non-deareated ethanol and cyclohexane solutions. From Fig. 3 it is seen that the both solvents with heavy atom have roughly the same effect. The most significant decrease of quantum yield is found in cyclohexane where it dropped from the original value 0·62 for *I* to 0·20 (iodoethane). In ethanol the decrease is not so important. In the case of photolysis of *II* under similar conditions

TABLE I

Rate Constants of Ketene Decrease and Formation of Adduct

Compound		$\nu . 10^{-3}$, cm^{-1}	$k . 10^2$, s^{-1}
I	ketene	34·8	3·84
	adduct	29·0	3·20
II	ketene	35·0	1·68
	adduct	22·0	1·46

the influence of the heavy-atom solvent is not so marked. The greatest decrease was found in cyclohexane in the presence of 0·6M iodoethane (from 0·37 to 0·18). The presumed linear Stern–Volmer relation between q_0/q and concentration of the heavy-atom solvent is approximatively valid only in the concentration range below 0·3M. The given results can be interpreted (in accord with theoretical views[13]) as it follows: external mechanism of the spin–orbital interaction results in increase of probability of non-radiative intersystem crossing from the lowest excited singlet S_1 to the lowest excited triplet T_1. As the quantum yield decreases, the lowest excited singlet S_1 can be presumed to be the photoreactive excited state. This presumption agrees with the reports[14,15], even though, in contrast to these reports, we did observe the effect of heavy-atom solvents. The difference can be due to different method of calculation of quantum yield (we involve only the quanta absorbed by quinonediazide) and to higher sensitivity of the measurements.

The presence of oxygen has no substantial influence on the photolysis rate and quantum yield. In some cases a mild decrease was observed in the absence of oxygen varying within experimental error. The process of damping of the excited states and of the increased probability of intersystem crossing due to interaction of the excited molecules with paramagnetic triplet oxygen in the ground state or with the heavy-atom solvents is predominantly influenced by diffusion. If the concentration relations are taken into account, the normal oxygen concentration[16] is of the order 10^{-3}M, whereas concentration of the heavy-atom solvents producing observable

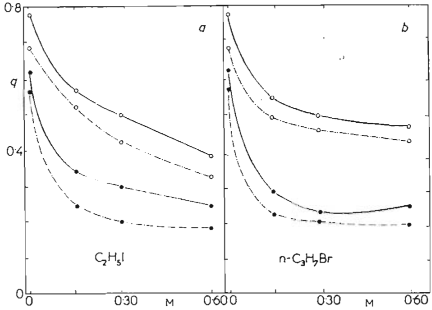


FIG. 3

Influence of Solvent with Heavy Atom (*a* iodoethane, *b* 1-bromopropane) on Quantum Yield of Photolysis of 1,2-Naphthoquinone-1-diazide

○ Ethanol, ● cyclohexane, ——— 60 s and –·–·–· 120 s of irradiation.

decrease of quantum yield is of the order 10^{-1}M. As far as the quinonediazide molecules are not directly solvated by molecules of the heavy-atom solvent, the rate constants of the both diffusion-controlled processes will vary about the value 10^9M^{-1} . . s^{-1}. A decisive role will also be played by concentration of the molecules in the interacting excited state. This concentration is given by life-time of this state and intensity of the excitation radiation. The life-time of S_1 states of quinonediazides is probably very low (10^{-12} s), hence the given reasons suggest that influence of oxygen on the photolysis could be expected at concentrations by several orders of magnitude higher than those of the dissolved oxygen under normal experimental conditions.

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