Laser Photolysis of Naphthoquinone Diazide in Cyclohexane – Two-Laser Chemistry

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The laser photochemistry of 1,2-naphthoquinone-diazide-(2)-5-sulfonic acid phenylester in cyclohexane has been investigated. The photolysis experiments have been done using a KrF laser pulse (generation pulse) and a nitrogen laser pulse (transformation pulse) with various time delay from 40 ns up to 1 s. At a time delay between the two laser pulses in the μs-region, the formation of indene and cyclohexyl-indene derivatives has been observed, additional to the corresponding indenecarboxylic acid. The laserspecific formation of these compounds is the result of the electronic excitation of the intermediately formed ketene and its reaction by decarbonylation. The time delay for getting a high yield of the indene and the cyclohexyl-indene derivatives correlates closely with the rise time and the life time of the ketene.

1. Introduction

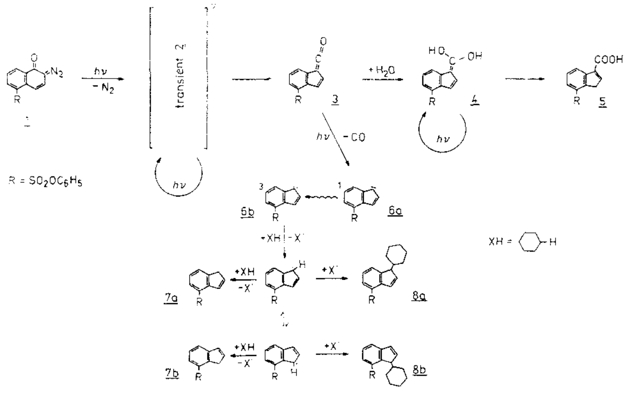
Positively acting photoresists based on naphthoquinone diazides (**1**) as the light-sensitive compound and Novolak as the polymeric binder are widely used in the manufacture of microelectronic devices [1]. The common photoreaction of the naphthoquinone diazide derivative takes place in the following manner [2]. The electronic excited naphthoquinone diazide (**1**) loses nitrogen and forms an short-living intermediate (**2**), which undergoes a Wolff rearrangement forming the ketene (**3**). The third intermediate observed, the ketene hydrate **4**, is the product of the reaction between the ketene and water present in Novolak layers (3 wt.%) and in the solvents at aerobic conditions. The final product of the photoreaction is the indenecarboxylic acid (**5**). The time scale of formation and life time of the intermediates were investigated by several authors in different solvents and matrices [2–5].

The results are controversy and a matter of some discussion. That means especially the appearance of the short-living intermediate (**2**). Scaiano et al. [5] did not observe any intermediate before the ketene and stated a concerted pathway from the excited naphthoquinone diazide to the ketene. But other authors observed on different conditions an additional transient (**2**) (Fig. 4) [2, 3]. However, the statements of carbene/oxirene formation were done without analytical data. The structure of the intermediate **2** is unknown.

At laser exposure of photoresist layers and solutions containing a naphthoquinone diazide, a non-reciprocity behaviour is observed [6, 7]. The given explanation of this phenomenon is of physical nature, depending on the excitation wavelength, the pulse laser exposure results in an optical switch-up or switch-down within the pulse duration attended with a higher or lower degree of photolysis.

The formation of a strongly absorbing transient within the pulse duration (arising of a filter effect) is connected with the electronic excitation of this transient compound. Nothing is known about the chemical consequences of the photoexcitation of this and the other intermediates.

In this paper we investigate the photochemistry of all three intermediates (**2**–**4**) formed on photolysis of naphthoquinone diazides in water-saturated cyclohexane solution. The results of this consecutive two-laser photolysis will be compared with those of *lamp excitation*.



Scheme 1: Reaction pathway of the one-photon and the consecutive two-photon chemistry of naphthoquinone diazide derivatives

2. Experimental Details

2.1 Materials

The synthesis of 1,2-naphthoquinonediazide-(2)-5-sulfonic acid phenylester (**1**) has been described in Ref. 8.

For the photolytic investigations, 50 μl solution of **1** ($1 \cdot 10^{-4}$ mol l^{-1}) in cyclohexane (Merck, fluorescence grade) was used in 1 mm quartz cells. The solution was changed after each two-laser experiment.

2.2 Laser Photolysis Apparatures

Fig. 1 shows the two-laser flash apparature. The KrF laser (EMG 1003i, Lambda Physik) was used for the pulse

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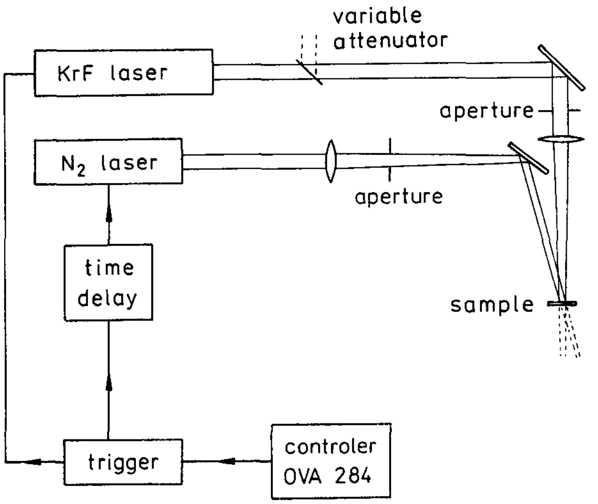

Fig. 1
Experimental arrangement for the two-laser photolysis

photolysis of the naphthoquinone diazide (*generation* of the intermediates) at $\lambda = 248$ nm. The nitrogen laser ($\lambda = 337$ nm) was used for the excitation of the intermediate (*transformation* of the transient). The pulse energy was 15 to 16 mJ (KrF) and 2.2 to 2.4 mJ (N_2), respectively. The pulse energy was measured at the probe position, deviations were less than 5%.

The realized time delays between KrF laser pulse and nitrogen laser pulse were from 40 ns up to 1 s. The time delay has an accuracy of 10%. Each photolysis experiment was carried out five times. The collected solutions (250 µl) were used for the chromatography.

2.3 High Performance Liquid Chromatography (HPLC)

HPLC was carried out using the following conditions: Knauer HPLC pump 64, Knauer injection valve with 20 µl sample loop; mobile phase, methanol-water (75:25); flow rate 0.5 ml min^{-1}; Knauer column (250×4 mm) filled with LiChrosorb RP18 (5 µm); UV-visible detector LCD 2563 (Laborni Pristroje Praha); detection wavelength, 248 nm.

Each photolyzed solution was analyzed three times. The differences of the peak intensities of corresponding signals were less than 5%.

2.4 UV-Visible Spectroscopy

UV spectra were recorded using a UVICON 930 (Kontron Instruments).

2.5 Mass Spectra

The solvent of the collected fractions resulting from HPLC was removed by rotating evaporation. The solid residues were analyzed by mass spectroscopy.

Mass spectra were measured using a Gas Chromatograph/Mass Spectrometer 5935 (Hewlett Packard). At comparison, spectra of corresponding indenecarboxylic acid and indene derivatives are described in Ref. 9.

3. Results

Using the arrangement shown in Fig. 1, solutions of **1** in cyclohexane were photolyzed by two laser pulses (KrF, N_2) with time delay of 40 ns, 100 ns, 300 ns, 1 µs, 3 µs, 10 µs, 30 µs, 100 µs, 300 µs, 1 ms, 3 ms, 10 ms, 30 ms, 100 ms, 300 ms, 1 s. The absorbance of the solution ($c = 1 \cdot 10^{-4}$ mol l^{-1}) and the laser pulse energy (see 2.2) were chosen to get a compromise of high product yield and uniform excitation energy distribution within the irradiated volume. The degree of photolysis of **1** by the KrF laser pulse was about 50% in the irradiated volume.

The UV spectra of the non-photolyzed and photolyzed solution of **1** are shown in Fig. 2. The irradiation spectra of the one-laser photolysis and of the two-laser exposure are very similar. No pronounced spectral change is observed at different laser pulse intensity and at different time delay. The final product of the one-laser photolysis and the two-pulse exposure with $\Delta t \geq 10$ ms, the indenecarboxylic acid **5**, absorbs at shorter wavelength. Therefore, a decrease of the absorption spectrum in the long wavelength region is observed.

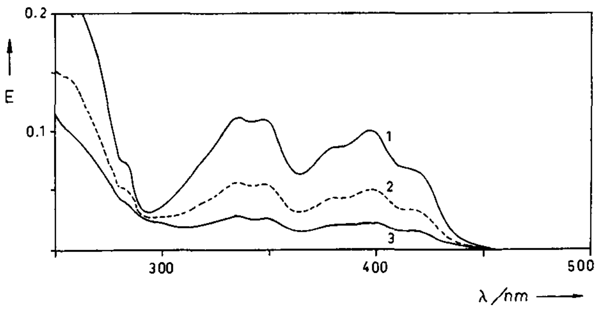

Fig. 2
Irradiation spectra of **1** in cyclohexane ($d = 0.1$ cm); 1-non-irradiated solution; 2-ratio of photolysis 50% (two-laser photolysis with a laser pulse delay of 1 s, compare Fig. 3); 3-ratio of photolysis 78%

The photolyzed solutions were analyzed using the HPLC. In Fig. 3 the obtained chromatograms are shown in dependence on the time delay between the two laser pulses. At very short (≤ 100 ns) and at very long (≥ 10 ms) delay between generation and transformation pulse only two compounds are detected, the starting compound **1** and the indenecarboxylic acid derivative **5**, determined using the corresponding reference probe [9, 10]. Within the time delay region $\Delta t = 1$ µs...1 ms peaks of further photoproducts are observed at longer retention time (rt). Using the combined gas chromatography/mass spectroscopy the mass spectra of these additional formed compounds are measured. The results are summerized in Tab. 1. The mass of the mole peaks (272, 354) show that the compounds **7a** and **7b** are phenoxysulfonyl substituted indenes and the compounds **8a** and **8b** are cyclohexyl substituted phenoxysulfonyl indenes. The fragmentation of these compounds and their UV spectra measured using the eluated solutions confirm that.

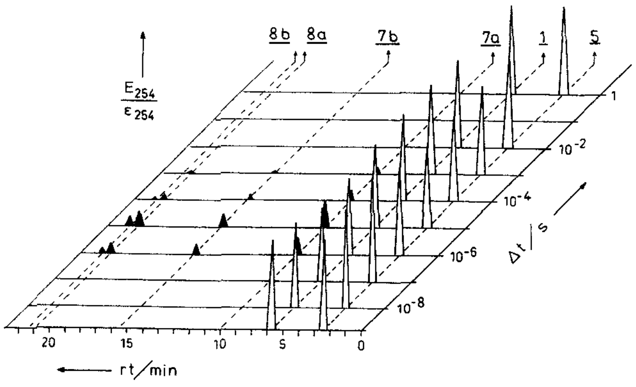

Fig. 3
Chromatograms of the photolyzed solutions of **1** at different laser pulse delay

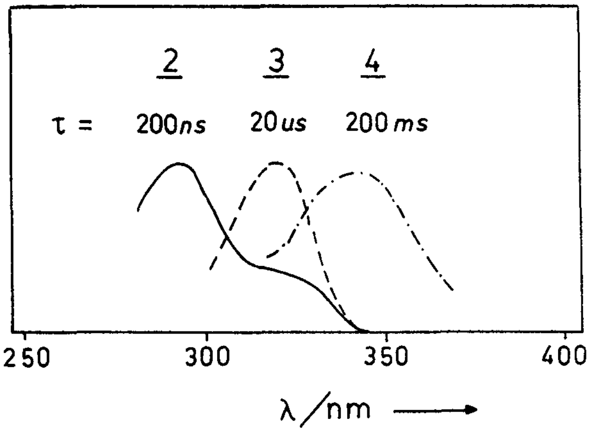

Fig. 4
UV spectra of the observed transients at photolysis of **1** [2]

The classification of the indene isomers (**7a**, **7b**) showing peaks at 9.95 and 15.4 min, respectively, was done corresponding to [9, 11] using the model compounds 4-phenoxysulfonyl-indene (**7a**) and 7-phenoxysulfonyl-indene (**7b**) prepared by preparative photochemistry and analyzed by NMR. A reliable distinction of the structurally isomeric cyclohexylindenes **8a** and **8b** was not possible on the basis of the mass spectroscopic data only. NMR spectra were not available. We assume the same sequence in retention time for the isomeric cyclohexyl substituted phenoxysulfonyl-indenes (**8a**, **8b**) like the compounds **7a** and **7b** (rt(a) > rt(b)), but the assignment may be changed.

The photolytic formation of the compounds **7a**, **7b**, **8a**, **8b** is the result of the combined two-pulse excitation at specific time delay. To understand the role of the second laser pulse (transformation pulse), it is necessary to investigate the pathway of the complex reaction and to analyze, which compound (transient) exists at the specific time delay $\Delta t = 1$ µs...1 ms. In Fig. 4, using earlier data [2], the transient spectra of the corresponding intermediates (first intermediate **2**, ketene **3**, ketene hydrate **4**) and the time of their highest concentration are presented. All three intermediates are able to absorb the excitation pulse of the nitrogen laser. But the formation of the indene (**7a**, **7b**) and the cyclohexyl-indene derivatives (**8a**, **8b**) are observed only at the excitation of the ketene (time delay in the µs-region). The excitation of both, the first intermediate (ns-region) and the ketene hydrate (ms-region), do not result in a *new photochemistry*. The transients **2** and **4** are "non-reactive", the ketene **3** (1-carbonylene-4-phenoxysulfonyl-indene) is photoreactive.

4. Discussion

After excitation of **1** using the laser pulse (KrF) the transient **2** is generated within the ps-time scale [2, 3]. It was impossible to analyze this primary process, the limit of time resolution of the used equipment (Fig. 1) was only a few ns. The primary formed intermediate **2** reacts via the further transients **3** and **4** to the indenecarboxylic acid **5**. At all two-laser experiments the percentage of photolyzed compound **1** is about 50%, but the specific time delay values differ significantly from this average value (c_∞). At a time delay in the ns-region, lower concentration of **1** is measured in the photolyzed solution combined with a higher yield of formed **5** (Fig. 5). The reason of this phenomenon is the lower absorbance of **2** compared with that of **1** (Figs. 2, 4). At the formation of **2** an optical switch-up of the solution at 337 nm goes on [2]. Within this ns-time scale the second laser pulse is absorbed very effectively by the remaining non-photolyzed **1**. This explains the enhanced formation of **5**.

At two-pulse photolysis with a time delay within the µs-region other phenomena are observed:

- the formation of **5** decreases (Fig. 5), and
- the formation of the additional compounds goes on (Figs. 6, 7).

A comparison of the Figs. 5, 6 and 7 shows that both, the formation of the indene derivatives **7a**, **7b** (Fig. 6) and the reaction to the cyclohexylindene derivatives **8a**, **8b** (Fig. 7), correspond with the reduction of the yield of **5**. That means, in the case of two-laser photolysis with a time delay within 1 µs...1 ms the photoreaction of the naphthoquinone

Table 1
Chromatographic and mass spectra data of the additional formed compounds **7a**, **7b**, **8a**, and **8b**

rt/min	Mole peak (M^+)	Characteristic fragments	Compound
7a 9.95	272	179, 115, 92, 77, 65, 64	4-phenoxysulfonyl-indene
7b 15.4	272	179, 115, 92, 77, 65, 64	7-phenoxysulfonyl-indene
8a 20.85	354	261, 197, 179, 115, 92, 83, 77	1-cyclohexyl-4-phenoxysulfonyl-indene
8b 21.4	354	261, 197, 179, 115, 92, 83, 77	1-cyclohexyl-7-phenoxysulfonyl-indene

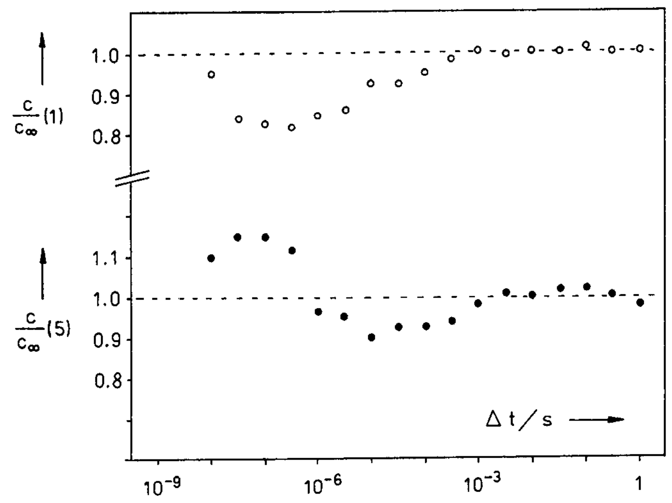

Fig. 5
Relative concentration of non-photolyzed **1** and formed **5** at different laser pulse delay

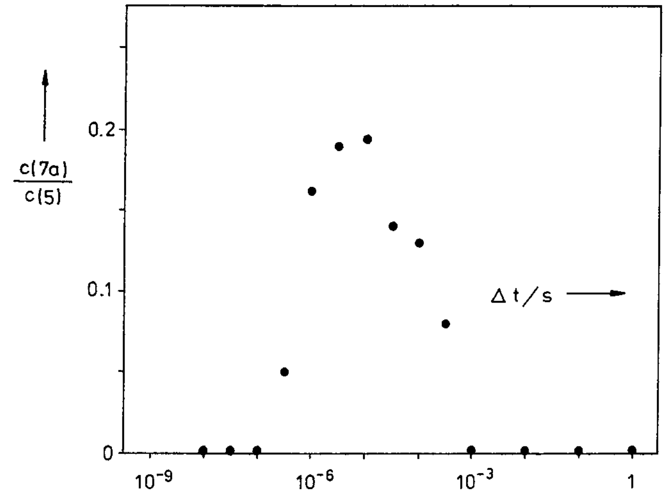

Fig. 6
Relative concentration of formed **7a** at different laser pulse delay

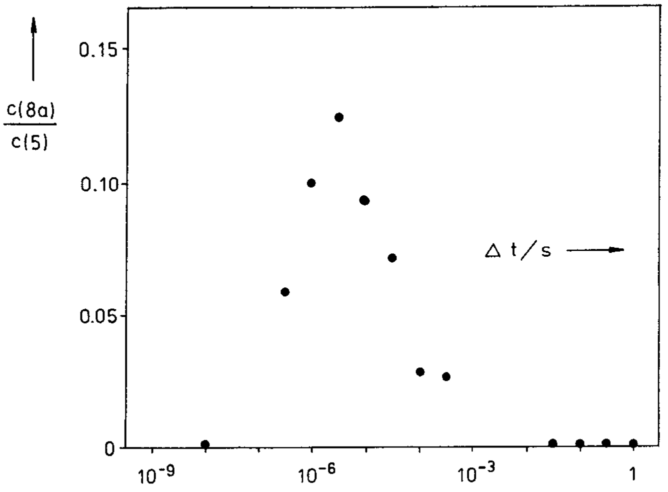

Fig. 7
Relative concentration of formed **8a** at different laser pulse delay

diazide does not only occur in the common way (**1**→**5**) but also a laser specific photochemistry is observed (**1**→**7a**, **7b**, **8a**, **8b**).

In [12, 13] photoreactions of ketoketenes similar to **3** are described. Diphenyl ketene decarbonylates after electronic excitation (Eq. 1).

$$\begin{matrix}R\\R\end{matrix}\!\!>C{=}C{=}O \xrightarrow{h\nu} \begin{matrix}R\\R\end{matrix}\!\!>C| + CO \qquad (1)$$

The formed carbene reacts with the solvent, with reagents and/or with another carbene in the well-known manner [14]. So on photolysis of the diphenyl ketene in cyclohexene 3-diphenyl-methyl-cyclohexene is formed as the result of the insertion/pseudo insertion reaction, tetraphenylethylene is obtained from the dimerization of the primary carbene and the bis-[cyclohexen-yl-(3)] is formed by combination of the allyl-like solvent radicals resulting from the H-abstraction reaction [12].

At excitation of the ketene **3** a decarbonylation takes place forming a carbene **6**. The carbene **6** reacts as a triplet carbene and abstracts a hydrogen atom from the solvent. Scheme 1 illustrates the reaction pathways of the highly reactive triplet carbene and the radicals formed intermediately by H-abstraction from the solvent. A radical combination of the indenyl and the solvent radical (pseudo insertion) results in the synthesis of the cyclohexyl derivatives **8a** and **8b**. At double H-abstraction the carbene reacts in two steps to the phenoxysulfonyl indenes **7a** and **7b**. Due to the tautomerization equilibrium of the indenyl radical both isomers of **7** and **8** are formed. A possible reaction of the carbene **6** with water forming hydroxy substituted indene derivatives did not observed, the mole peaks of the chromatographically detected products do not agree with the corresponding alcoholes.

5. Summary

At two-laser photolysis of naphthoquinone diazide derivatives, a consecutive two-photon chemistry is observed. In the first step (generation pulse) the ketene is formed, in the second step (transformation pulse) the ketene is decarbonylized and the resulting carbene reacts by H-abstraction and pseudo insertion. The success of this two-laser excitation requires a specific time delay regime determined by the rise time and the life time of the ketene. The absence of this two-laser chemistry at ns-delay between the two pulses is in good agreement with the observation of a „first" transient at the flash photolysis experiments.

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