

Photoinduced Wolff-Rearrangement of 2-Diazo-1-naphthoquinones: Evidence for the Participation of a Carbene Intermediate

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Abstract: Photolysis of sodium 2-diazo-1-oxo-1,2-dihydronaphthalene-5-sulfonate and 4-*tert*-butylphenylphenyl 2-diazo-1-oxo-1,2-dihydronaphthalene-5-sulfonate in aliphatic alcohols results in the formation of a high yield of the corresponding sodium 3-(alkoxycarbonyl)-1*H*-indene-5-sulfonate and 4-*tert*-butylphenyl 3-(alkoxycarbonyl)-1*H*-indene-5-sulfonate, respectively. 1-Hydroxy-2-alkoxynaphthalene-5-sulfonates are formed as side products in these photoreactions. The observed maximum molar yield of the latter products was 8.8%. Photolysis of a solution of sodium 2-diazo-1-oxo-1,2-dihydronaphthalene-5-sulfonate in water yields, apart from the main photoproduct, sodium 3-carboxy-1*H*-indene-5-sulfonate, approximately 15% of the sodium 1,2-dihydroxynaphthalene-5-sulfonate. Both the nature of the side products of the photoreaction, as well as their yield as a function of the concentration of alcohol and water in various solvent mixtures, are a strong indication for the presence of a carbene intermediate in the reaction mechanism. Picosecond transient absorption measurements show that the internal conversion and vibrational relaxation to the ground state in the two diazo compounds mentioned above, takes place within 8 ps after excitation. The photofragmentation and formation of indenylidene-ketene is also completed within this same time period. In the case of 2-diazonaphthalen-1(2*H*)-one, the vibrational relaxation and photofragmentation take place within 8 ps, but in this particular case, a precursor of the ketene could be observed. This precursor has a decay rate constant of $5 \times 10^{10} \text{ s}^{-1}$ and is proposed to be the carbene.

The photoactive compounds of photoresist materials which are used in the lithographic production of integrated electronic circuits are mainly derivatives of 2-diazo-1-naphthoquinone **1** (Scheme 1). Upon photolysis in the presence of water, the latter is converted into the indenecarboxylic acid **7**. The large change in polarity in connection with this photolysis is the basis of the working principle of these photoresist materials.¹ Although several papers have been published on this photoreaction,^{2–7} some aspects of its mechanism have still not been clarified. The photoreaction of diazonaphthoquinones (DNQ's) is widely accepted to proceed via an intramolecular rearrangement known as the Wolff-rearrangement, yielding the indenylidene-ketene intermediate **3**. In the presence of water, this ketene is converted into the indenecarboxylic acid enol **4**, which subsequently yields the indenecarboxylic acid **5** in an acid-catalyzed reaction.⁵ Evidence for the appearance of a ketene in the reaction sequence has been provided by low temperature IR-spectroscopic studies.² However, both the mechanism of formation of the ketene, as well as the mechanism of the reaction of the ketene to the

indenecarboxylic acid are still subject of discussion. This paper will deal with the mechanism of the photochemical *formation* of indenylidene-ketenes from 5-substituted DNQ's. Strong evidence will be provided for the formation of a carbene intermediate **2** as a first reaction step of the photolysis. A forthcoming publication will report a detailed study of the mechanism of the reaction of the ketene with water and aliphatic alcohols.⁸

For the mechanism of the formation of ketene intermediates from the photoreaction of diazonaphthoquinones and diazobenzoquinones, two different mechanisms have been suggested. Some authors have proposed the intermediacy of a carbene intermediate,⁴ while others are in favor of a concerted reaction^{9,10} (see Scheme I). In the latter case, a nitrogen molecule is released from the diazonaphthoquinone synchronously with the ring contraction, thus leading directly to the ketene, without intermediacy of a carbene. In the case of diazobenzoquinone this point of view has been supported by results from semiempirical MINDO/3 MO calculations⁹. Recently, Barra et al.¹⁰ supported the concerted mechanism since their attempts to trap a possible carbene intermediate by performing the photolysis in the presence of pyridine or methanol were not successful. They observed *almost* exclusively the formation of either the ylide, in the case of scavenging with pyridine, or of the ester, in the case of methanol. However, Barra et al. did not perform a complete analysis of the reaction products, as was performed by Ponomareva et al.¹¹ The latter studied both the photolysis

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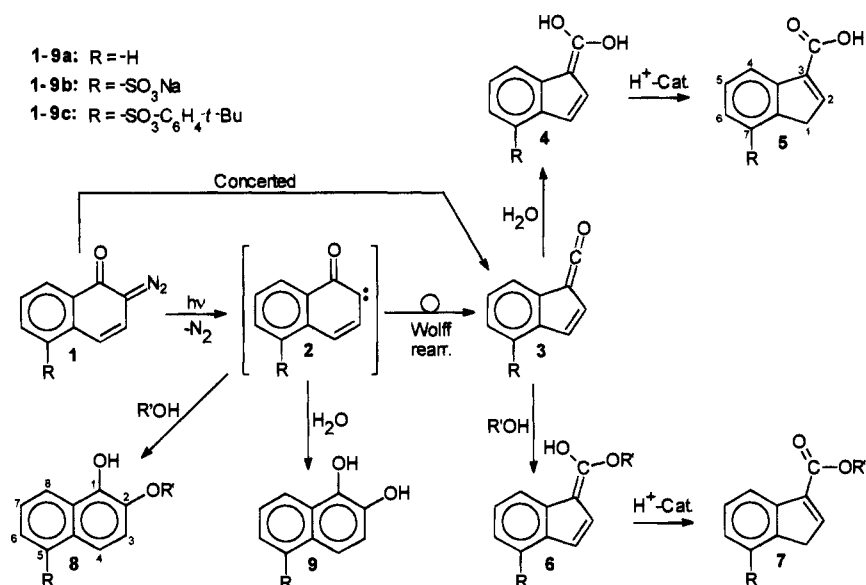
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Scheme 1



and thermolysis of 2-diazo-1-naphthoquinone (**1a**), and 1-diazo-2-naphthoquinone in aliphatic alcohols, and also reported the formation of the corresponding indenecarboxylic esters **7** ($R' = C_nH_{2n+1}$), as the main reaction product. Besides **7**, they also found 1-hydroxy-2-alkoxynaphthalenes **8** ($R' = C_nH_{2n+1}$) and 1-naphthol, as side products from the photoreaction, with total yields of up to 22%. They attributed these side products to reactions of the alcohol with both a singlet- and a triplet-state carbene. The yields of these products depended on the wavelength of the radiation used for the photolysis and on the type of alcohol used as solvent.

Besides trapping experiments and analysis of the photoproducts, time-resolved spectroscopy has also been used to identify a possible carbene intermediate. Tanigaki and Ebbesen⁴ performed such a study in the time domain between 5 ns and 1 ms. The first transient absorption which they detected had a maximum at a wavelength of 300 nm and they attributed this transient to the decay of a carbene-oxirene intermediate. However, this conclusion is disputable. Other authors assigned the same transient absorption to the ketene intermediate, by performing both IR and UV spectroscopic studies of the matrix isolated ketene.⁶ Delaire et al. observed a quadratic dependence of the reaction rate of this species on the concentration of water in the sample and also concluded that this transient absorption, attributed by Tanigaki and Ebbesen to the carbene-oxirene, arises from the ketene.³ The recent detailed kinetic investigations of Andraos et al.⁷ confirmed the propositions by Delaire et al. concerning the ketene, and by Shibata et al.,⁵ concerning the intermediacy of the carboxylic acid enol. Apparently the carbene is not observable in the nanosecond time domain. However, it might be detectable in the picosecond or subpicosecond time domain.

Grasse et al.¹² and Sitzmann et al.¹³ produced arylcarbenes photochemically from diazocompounds and observed high singlet-triplet intersystem crossing rates for the initial singlet-state carbenes. They found rate constants for intersystem crossing of $2.5 \times 10^9 \text{ s}^{-1}$ for fluorenylidene (Grasse et al.) and $2.9 \times 10^9 \text{ s}^{-1}$ for diphenylcarbene (Sitzmann et al.). In the case of methanol as solvent, Grasse et al. report also the formation

of the methyl ethers with a yield of 95% resulting from the reaction of the singlet carbene with methanol. Note that if the formation of 1-naphthol from the photoreaction of DNQ's has to be attributed to a reaction of a triplet-state carbene, and if also the total lifetime of carbene **2** is of the order of a few picoseconds or less, the singlet-triplet intersystem crossing rate of this carbene would have to be much higher than in the cases of fluorenylidene and diphenylcarbene.

The transient absorption studies of the photolysis of DNQ's mentioned above were focused mainly on the band at 300 nm and on the band between 340 and 350 nm, attributed to the ketene **3** and the carboxylic acid enol **4**, respectively.⁵⁻⁷ Our spectroscopic observations in the time domain between 10 ns and 10 ms are in accordance with these results and therefore we will assume the assignments of the bands to be correct. However, we will discuss the mechanism of the formation of the ketene in detail and therefore we will pay only attention to the very first events in the photoreaction and especially to the involvement of a carbene in the formation of the ketene. The discussion will be based mainly on results from HPLC analysis of irradiated samples and on picosecond time-resolved spectroscopic studies. The results concerning three different 5-substituted DNQ's **1a-c** will be presented. The DNQ's with sulfonic substituents, **1b** and **1c**, have been chosen because the sulfonic substituent is essential for the application of DNQ's in photoresist materials. The ionic substituent in **1b** and nonionic substituent in **1c** make measurements possible in a large variety of solvents. Note that the nature of the substituents may strongly affect the kinetics of the various reaction steps.

Results and Discussion

HPLC Analysis of the Photolysis Products. Analytical and preparative high performance liquid chromatography (HPLC) were used to analyze the product mixture resulting from photolysis of solutions of 0.1 mM of **1b** and **1c** in different solvents. The solvents used are aliphatic alcohols, water, mixtures of alcohols and water, or mixtures of alcohols and 1,4-dioxane. The irradiated solutions were analyzed directly after the exposure. The reasons why **1a** has not been studied are that the quantum yields of the photoproducts from this molecule have been determined already by Ponomareva et al.,¹¹ and that the photoreaction of **1a**, depending on the pH of the solution, takes more than 1 h to yield the final product **5**.⁸

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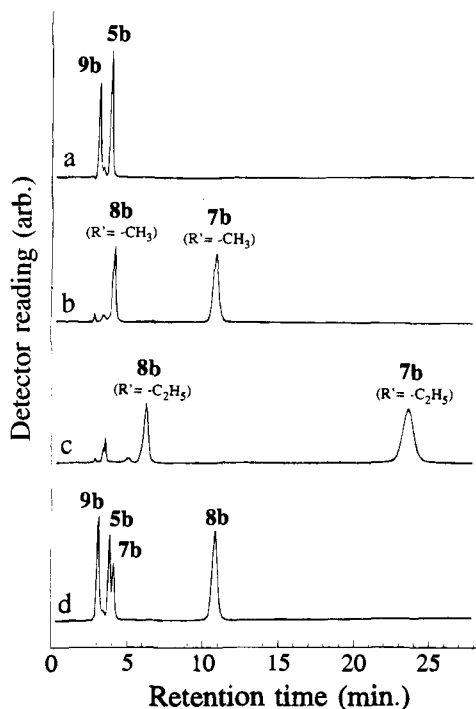


Figure 1. Typical HPLC-chromatograms of the reaction product mixture resulting from the photolysis of 0.1 mM **1b** in different solvents: (a) water, (b) methanol, (c) ethanol, (d) methanol/water (50/50 v/v). The probe wavelength is 256 nm.

Several mixtures of methanol and water, buffered with 0.1% (v/v) trifluoroacetic acid have been used as eluents in the HPLC experiments. These eluents do not affect the stability of the photoproducts and they give an excellent separation of the reaction products when used in combination with a reversed phase column.

Photolysis of 1b. A high yield of indenecarboxylic acid **5b** is obtained in the photoreaction of **1b** in water. Figure 1a shows a typical chromatogram of the product mixture resulting after photolysis of an aqueous solution of **1b**. In addition to **5b**, one specific side product is also observed. This is formed with a molar yield of 15%. Preparative separation of this side product combined with NMR shows that it is the sodium 1,2-dihydroxynaphthalene-5-sulfonate, **9b**.

Figures 1, parts b and c, show the chromatographic results obtained with irradiated solutions in neat methanol and ethanol. Here the indenecarboxylic esters **7b**, with an ester group corresponding to the alcohol used, appear as the main photoproducts, while only a trace amount of the acid **5b** can be observed. The HPLC analysis reveals one major side product in each of the irradiated solutions in an alcohol, namely the sodium 1-hydroxy-2-alkoxynaphthalene-5-sulfonate, **8b**. The highest yield of **8b** of 8.2% is obtained with neat methanol as the solvent. Solutions in higher aliphatic alcohols give a lower yield of **8b**. Neither of the irradiated solutions in alcohols contains a detectable amount of sodium 1-hydroxynaphthalene-5-sulfonate, contrary to the results of Ponomareva et al.¹¹

In the solutions in mixtures of an alcohol and water, four photoproducts are found as expected (Figure 1d). These are the compounds **5b** and **9b**, formed in a reaction involving water, and the compounds **7b** and **8b**, arising from a reaction in which the alcohol is involved. The molar yield of each photoproduct can be calculated from the corresponding peak surface in the HPLC chromatogram, taking into account the relative molar extinction coefficients of the photoproducts at the probe wavelength. Figures 2a,b give graphic representations of the yields of the products **9b** as a function of the concentration of

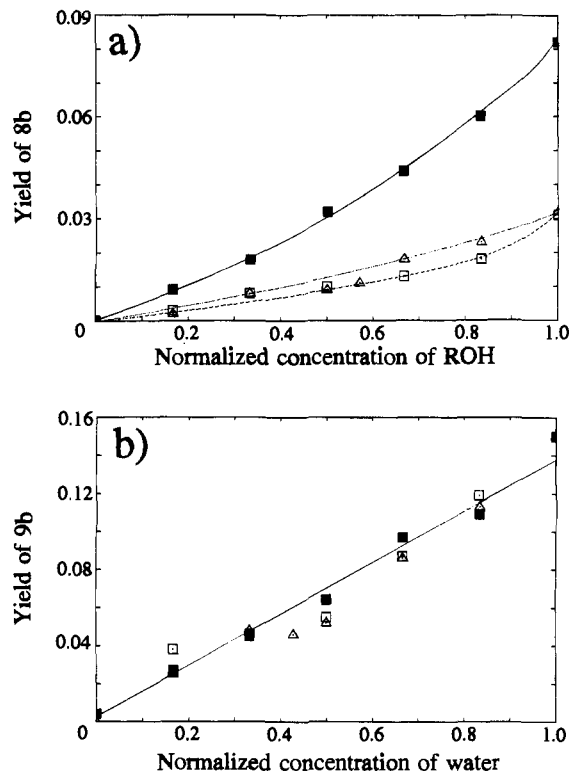


Figure 2. Product analysis of the photolysis of **1b** in alcohol/water mixtures: (a) dependence of the molar yield of **9b** on the normalized water concentration in mixtures with different alcohols and (b) molar yield of **8b** as a function of the normalized alcohol concentration in the corresponding mixture with water. The symbols used for the different mixtures are methanol/water (■), 1-propanol/water (△), and 2-propanol/water (□). The molar yields are given as a fraction of the total molar amount of **5b** + **7b** + **8b** + **9b**.

water and of **8b** as a function of a *normalized* concentration of alcohol in several solvent mixtures. The reason for this particular way of presenting the results is that when the yields of **8** are plotted as a function of the absolute alcohol concentrations, all data-points in the plots get mixed up, and the results of Figure 2 and Figure 4 become very unclear. The normalized concentrations are defined as the concentration of a particular solvent in the mixture, divided by the molarity of this solvent when pure. For example, in the case of water a relative concentration of 1 means an absolute concentration of 55.56 M; in the case of ethanol it means an absolute concentration of 17.16 M. Figure 2a shows that in alcohol/water mixtures, the yield of **8b** increases nonlinearly with the concentration of alcohol. Figure 2b shows that for all the three alcohol/water mixtures in the figure, the yield of **9b** increases almost linearly with the concentration of water.

Photolysis of 1c. The solubility of **1c** in water is too low to enable a study of the photolysis of solutions in pure water. The solubility of **1c** in a mixture of water and alcohol is sufficient when the mixture contains a fair amount of alcohol (the concentration of **1c** used is 0.1 mM). Therefore the normalized concentration of water is kept below 0.7 in all mixtures. Irradiation of **1c** in neat aliphatic alcohols leads mainly to the formation of the corresponding indenecarboxylic ester **7c**, and, depending on the alcohol, of up to 8.8% of **8c**. Typical HPLC chromatograms of **1c** irradiated in methanol, ethanol, and a mixture of methanol and water (50:50 v/v) are shown in Figures 3a–c. Irradiation of **1c** in mixtures of an alcohol and water mainly yields four different photoproducts, similar to the case of **1b**. HPLC analysis combined with NMR reveals that these products are **5c**, **7c**, **8c**, and **9c**. The dependence of the molar yields of **8c** and **9c** as a function of the normalized concentration

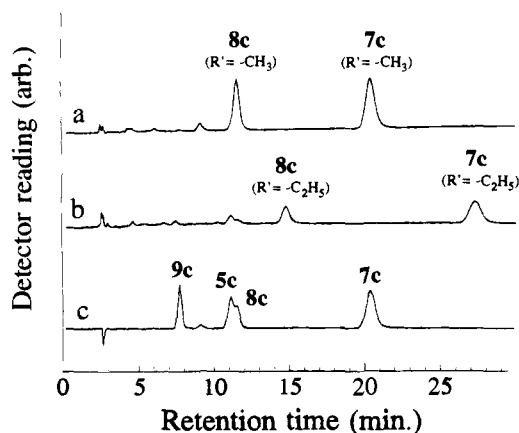


Figure 3. Typical HPLC-chromatograms of the reaction mixture resulting from the exposure of 0.1 mM **1c** in different solvents: (a) methanol; (b) ethanol; and (c) methanol/water mixture (50:50 v/v).

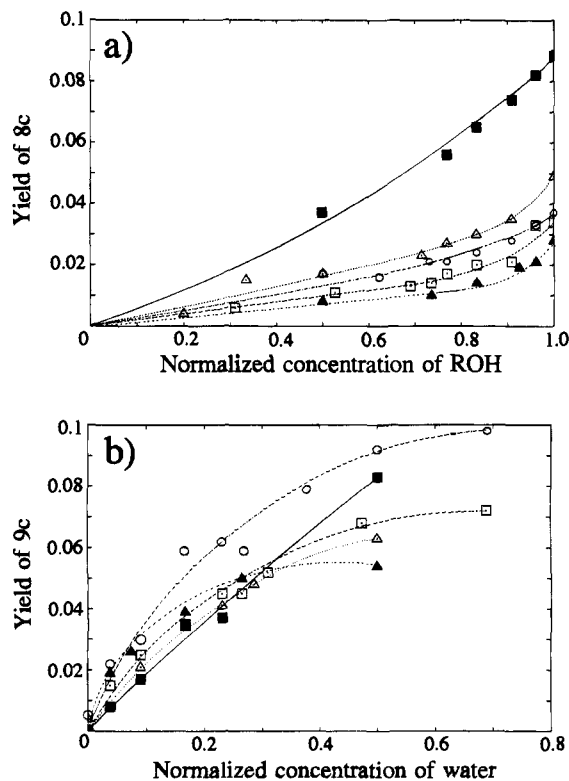


Figure 4. Product analysis of the photoreaction of **1c** in alcohol/water mixtures: (a) yield of **8c** on the normalized alcohol concentration in alcohol/water mixtures and (b) molar yield of **9c** as a function of the normalized water concentration in the mixtures with the different alcohols. The symbols used for the different mixtures are methanol/water (■), ethanol/water (△), 2-propanol/water (□), *tert*-butyl alcohol/water (▲), and trifluoroethanol/water (○). The molar yield is given as a fraction of the total amount of **5c** + **7c** + **8c** + **9c**.

of water or alcohol is shown in Figure 4. As can be seen, the obtained amount of **8c** increases with increasing concentration of alcohol. The curvature in the plots of Figure 4a,b is stronger in mixtures containing alcohols of larger molecular size.

When the mixtures of water and methanol are strongly diluted in 1,4-dioxane, such that the total concentration of water and methanol remains below 2.5 M, irradiation of **1c** in this three-component solvent does not produce a significant amount of photoproducts **8c** and **9c**. The combined yields of photoproducts **5c** and **7c** is constant, but the individual yields vary with the concentration of water and alcohol. The yield of **5c** increases linearly with the concentration of water and decreases with the concentration of alcohol, while the yield of **7c** shows the

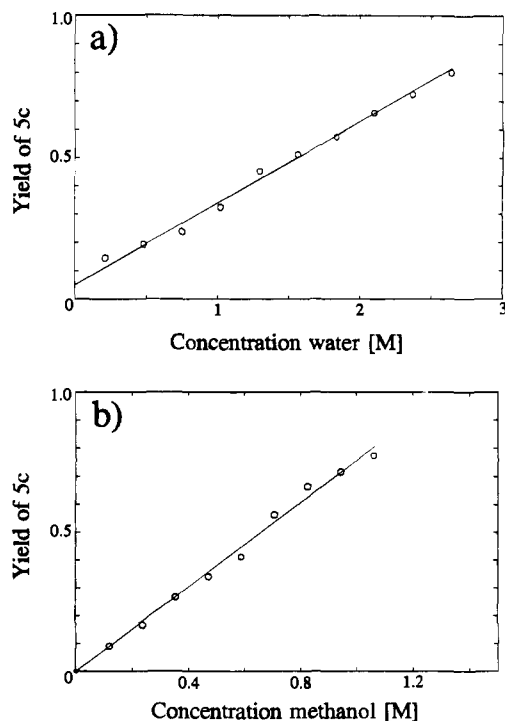


Figure 5. Dependence of the yield of **7c** on the alcohol concentration and the yield of **5c** on the water concentration in methanol-water mixtures strongly diluted in 1,4-dioxane (total concentration of water + alcohol < 2.65 M).

opposite behavior (Figure 5). In addition to the products **5c** and **7c**, small amounts of unidentified side products are also observed.

The formation of **7c** and **8c** could be followed in the absence of water as a function of the concentration of alcohol, by studying the photoreaction of DNQ in alcohol/1,4-dioxane and alcohol/cyclohexane mixtures. The behavior in the case of mixtures of ethanol with either 1,4-dioxane or cyclohexane is shown in the Figure 6, parts a and b. The figures show that a relatively high amount of **7c** is formed in both types of mixtures even at low concentrations of alcohol. With increasing concentration of alcohol, the amount of **7c** decreases slightly, while the yield of **8c** increases. The increase in the yield of **8c** shows a very different curvature in both solvent mixtures. In the case of solutions in ethanol/cyclohexane (Figure 6a) this yield is rather high at low concentrations ethanol and increases only slowly by increasing the concentration further. In the case of 1,4-dioxane/ethanol the yield of **8c** is very low at low concentrations of ethanol. Solution mixtures of both types also yield small amounts of other side products, which could not be identified because of their small individual yields. These products are probably formed in the reaction involving a carbene and dioxane or cyclohexane, and their yields vary with the composition of the solvent mixture.

In the introduction it was discussed that formation of **8** and **9** is a strong indication for the participation of a carbene in the reaction mechanism. Evidently **8** and **9** may arise from the reaction of the intermediate carbene with water and alcohol, respectively. This is then in agreement with the observed increase in the amounts of **8** and **9** with increasing concentration of water and alcohol, respectively. Nevertheless, it remains worthwhile to examine if the observed yields of the various photoproducts are in agreement with the widely accepted scheme for the reaction (Scheme 1). According to this scheme, **8** and **9** are formed from the carbene intermediate and **5** and **7** are obtained from the ketene. The curvature in the Figures 2 and 4 cannot be readily explained with the reaction scheme. It is

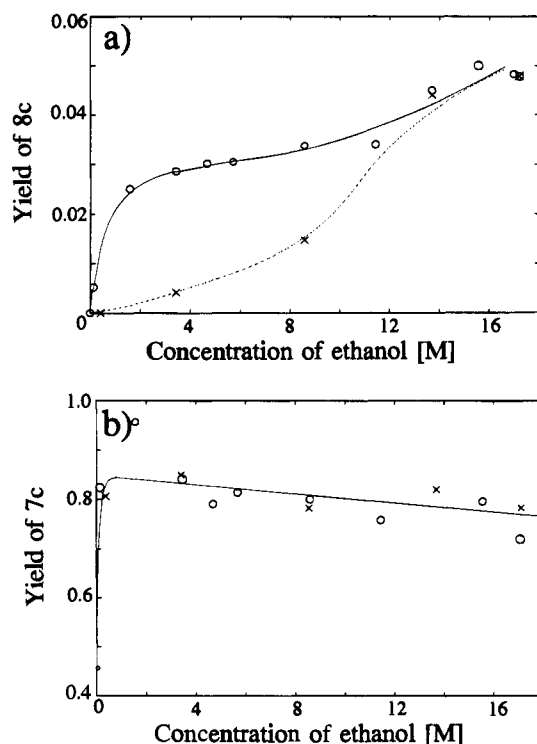


Figure 6. (a) Yield of **8c** in ethanol/1,4-dioxane mixtures (x) and in ethanol/cyclohexane mixtures (o) as a function of the ethanol concentration. (b) Yield of **8c** in the mixtures as in (a) as a function of the ethanol concentration.

obvious to try to attribute the curvatures to differences in reactivity of the carbene towards either water or the alcohol. However, when the yields of **8b** and **8c** in neat alcohols are plotted as a function of the concentration of alcohol, an almost linear relationship is observed in Figure 7. Even the molar yield of **9b** in pure water lies on this line when plotted as a function of the concentration of water. This relation supports the idea that the reaction products **8b,c** and **9b,c** arise from reaction of the carbene with the solvent and that it reacts with a single solvent molecule. The relation indicates furthermore that the reactivity of the carbene toward the alcohols does not depend on the nature of the alcohol, but only on its concentration. The curvature in the plots of the yields of **8b,c** and **9b,c** in mixtures of water and higher alcohols (like 2-propanol and *tert*-butyl alcohol) can therefore not be attributed to differences in the reactivity of the alcohol. This nonlinearity is very likely caused by specific solute-solvent and solvent-solvent interactions in these mixtures. Considering that the lifetime of the carbene is less than 8 ps (see the section dealing with picosecond pump-probe spectroscopy), it can react in a bimolecular way only with a nearest neighbor alcohol molecule. It is therefore reasonable to attribute the curvature in Figures 2 and 4 to variations in the availability of an alcohol in the immediate neighborhood of the carbene. The infrared spectrum of solutions of **1c** shows that in solvents containing alcohols, a large part of the C=O group of the DNQ is H-bonded to the alcohol. This bonding is observed as a shift of the absorption peak from the C=O stretching vibration from 1626 to 1614 cm^{-1} . The H-bonded alcohol molecule is already very close to the reaction center at the moment of excitation, so this alcohol molecule may be considered as the reaction partner of the carbene in the reaction yielding **8**. The availability of the alcohol partner from a hydrogen bonded solute-solvent complex varies in alcohol/water mixtures due to the competition of the alcohol and the water molecules to form a hydrogen bond with the carbonyl group of the DNQ. The supply of an alcohol or water molecule from the solvent to the carbene may vary also with the solvent

Table 1. Quantum Yields of the Photoreaction of DNQ in Methanol for Different Substituents

| | quantum yield of photolysis |
|-----------|-----------------------------|
| 1a | 0.54 |
| 1b | 0.37 |
| 1c | 0.49 |

composition, because this is governed by the distribution of hydrogen bonded alcohol-, water-, and mixed alcohol/water clusters in the solvent shell. Either one or both of the latter two effects cause the nonlinear variation of the yields with the concentration of alcohol or water in alcohol/water mixtures.

The results concerning solutions in 1,4-dioxane/alcohol and in cyclohexane/alcohol also support the validity of Scheme 1. A negligible amount of **8** is formed in both solvent mixture types when concentration of alcohol is very small. This agrees with the ideas proposed above in which formation of **8** requires an alcohol molecule to be in the immediate neighborhood of the carbene. When this requirement is not satisfied, only the ketene is expected to be formed from the carbene. If reactions of 1,4-dioxane with the ketene can be ruled out, only **7** would have to be expected as final product. Therefore a higher yield of **7** is expected at lower concentrations of alcohol, which is exactly what is observed in Figure 6b. However, formation of small amounts of other photoproducts probably arising from the reaction of the carbene with the 1,4-dioxane or cyclohexane causes slight deviations of the yields to be expected purely on the basis of the reaction scheme. Some deviations may arise also from solvent effects such as described above. In the case of ethanol/cyclohexane mixtures the formation of a relatively high amount of **8** is observed at low concentrations of ethanol. At low ethanol concentrations in ethanol/cyclohexane, the DNQ is expected to be more strongly hydrogen bonded to ethanol than in ethanol/1,4-dioxane, because the cyclohexane solvent bulk is very apolar. For this reason, the probability that the carbene finds an alcohol molecule in the direct vicinity is higher than is expected purely on basis of the concentration of alcohol. This will result in a relatively high yield of **8** at low concentrations of alcohol in cyclohexane.

Quantum Yield of Photolysis. The quantum yields of the photoconversion of several DNQ's have been measured by various authors.^{14,3} The reported values range from 0.2 to 0.7. The large spread in the values from different authors for the same DNQ in the same solvent made it necessary to examine the quantum yield of the photolysis of the specific DNQ's discussed here. The quantum yield of the photolysis given here is defined as the number of DNQ molecules photolyzed (regardless of the products formed) per absorbed photon. The obtained quantum yields are given in Table 1 and are in the range of 0.35 to 0.54. These values agree well with those found by Delaire et al.³ The fact that the quantum yield is always lower than 0.54 shows that a relatively large fraction of the excited DNQ molecules do not get involved in any chemical reaction and return to the original ground state. It is conceivable that the carbene and the N_2 molecule formed in the photodissociation recombine and form an original molecule again. However, this has to be considered highly improbable, because N_2 is a relatively inert molecule. Experimental evidence against this recombination reaction is obtained by studying the quantum yield of photolysis of **1a** in methanol saturated with either nitrogen or oxygen. In these two cases, the observed quantum yields are the same. It may therefore be concluded that the

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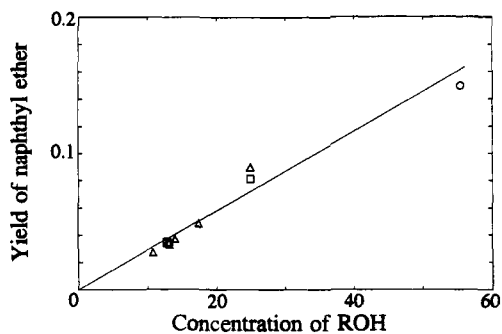


Figure 7. Molar yield of **8b** (\square) and **8c** (Δ) as a function of the alcohol concentration in the neat alcohols. The numbers are taken from Figures 2 and 4. Included also is the molar yield of **9b** in neat water (\circ).

excitation of DNQ's does not always lead to photoinduced fragmentation. If the fragmentation takes place directly from an electronically excited state, the deactivation of the primary excited state of the DNQ's must involve at least two pathways. Since the photodissociation is expected to proceed with a rate constant of 10^{12} s^{-1} or larger, and since no fluorescence from the DNQ has been observed,¹⁵ extremely fast internal conversion and vibrational relaxation must be involved besides photodissociation. The possibility that photodissociation occurs from a vibrationally excited electronic ground state has to be taken into account, because DNQ's can fragment thermally.^{11,16} The thermal reaction also leads to Wolff-rearrangement.

Comparison of Low Temperature Matrix UV Spectra and Nanosecond Transient Absorption Spectra at Ambient Temperature. The product analysis and the considerations concerning the quantum yields of photolysis in the previous paragraph have led to the ideas about the nature of the very first steps in the photoinduced reactions of DNQ's. Time-resolved spectroscopy may now reveal the time domains in which these steps take place. It is convenient to review briefly the spectral data of the ketene intermediate, because this until now is the first intermediate in the photoreaction which has been observed by spectroscopic techniques. These data will be needed to follow the history of the ketene with picosecond transient absorption spectroscopy. Spectral data concerning the carbene intermediate are not available.

Pacansky showed with IR spectroscopy² that the photoreaction does not proceed beyond formation of the ketene, when the DNQ is irradiated in a glassy matrix at 77 K. Figure 8 shows the electronic absorption spectra before and after irradiation of the different DNQ's in an ethanol glass at 77 K. A strong bleaching of the first electronic absorption band of the DNQ around 400 nm can be observed in all cases. Depending on the substituents on the DNQ, either an increased absorption or bleaching is observed at other wavelengths in the UV region. The spectra in Figure 8a–c have been used to construct difference spectra which show the difference in the spectrum before and after irradiation of each DNQ in the glassy solution. These difference spectra are shown in Figure 9a–c (solid lines). Also shown in Figure 9 are the corresponding difference spectra for liquid solutions of the DNQ's at 293 K, recorded immediately after photolysis with a 308 nm excimer laser. The solvents in the latter case were selected in such a manner that the disappearance of the ketene is not too rapid and that its absorptions can be observed. For instance the ketene derived from **1b** reacts so fast with the solvent molecules in methanol or ethanol that it is virtually converted completely to **4b** at the

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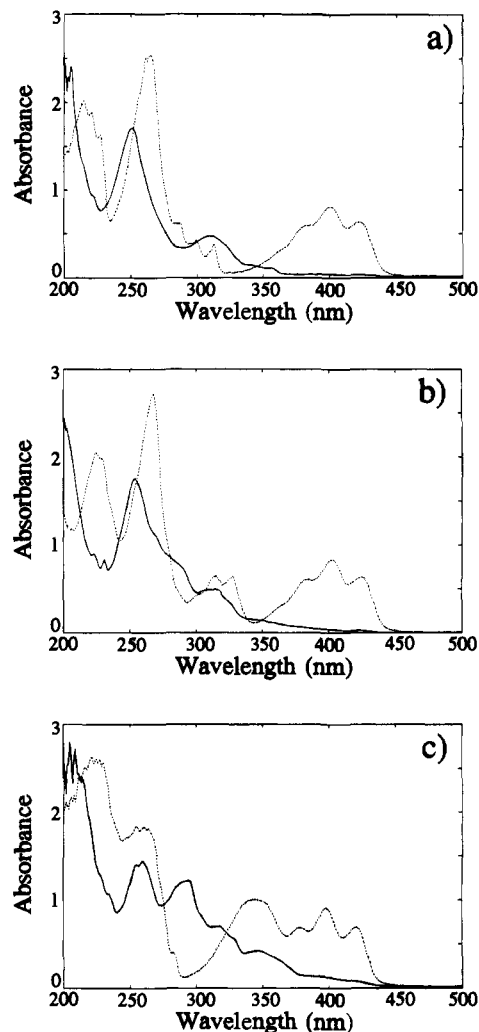


Figure 8. (a) Spectra of unexposed **1a** (dotted line) and the corresponding ketene **3a** (solid line) formed after the exposure ($\lambda_{\text{exp}} > 385 \text{ nm}$); (b) **1b** and **3b**; and (c) **1c** and **3c**. All spectra are recorded in ethanol glass at 77 K.

end of the excimer laser pulse. Water satisfied the conditions for a suitable solvent in the case of **1b**. The difference spectra of the glassy solution and of the liquid solution are practically identical. The small differences are due to differences in solvation, and due to narrowing of bands and the appearance of more structure in a spectrum when a sample is cooled substantially.

The striking resemblance of the two types of difference spectra of the various DNQ's is evidence for the presence of the ketene immediately after excitation with the excimer laser pulse. Observation of the process of formation of the ketene requires a spectroscopic study on a faster time scale. Such a study is described in the next section.

Picosecond Pump-Probe Spectroscopy. 1a in Methanol. A solution of **1a** in methanol has been studied with picosecond time-resolved absorption spectroscopy at a number of discrete wavelengths between 295 and 457 nm. The results are presented in Figure 10. Figure 10a concerns a correlation experiment in which the convolution of the probe pulse and the excitation pulse is determined. The width of the convolution shows that the time resolution of our setup is approximately 8 ps. The absorption changes in the sample of **1a** in methanol is shown in Figures 10b–f. Depending on the probing wavelength, either positive or negative changes in the absorbance are observed directly after the excitation. At 357 nm and at 400 nm (Figure 10d,e) an immediate bleaching of the ground state absorption

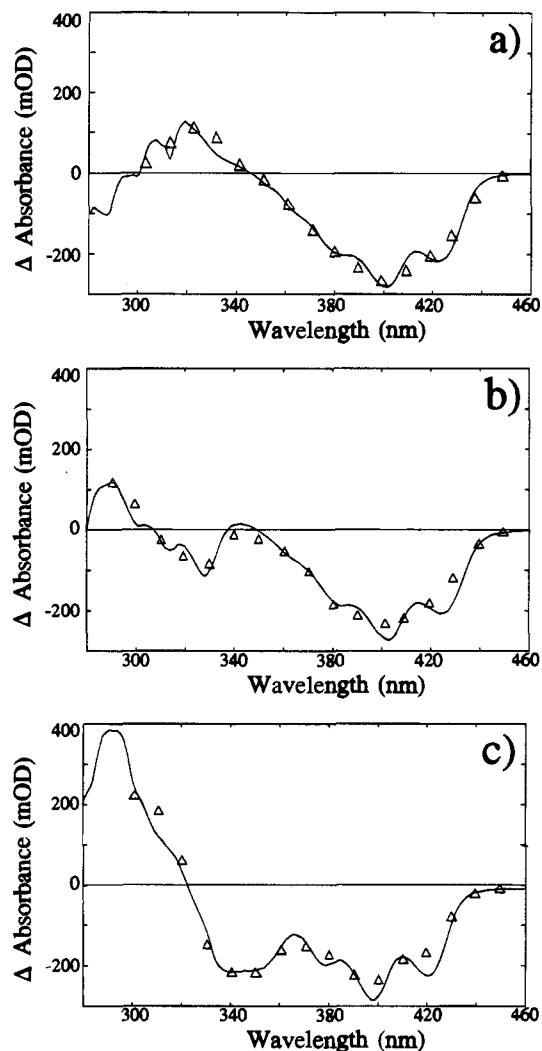


Figure 9. Differential spectra of the exposure of DNQ. The solid lines show spectral changes of the three different DNQs in ethanol glass at 77 K (constructed from the data in Figure 8 and scaled in the vertical direction). The triangles represent the observed spectral changes in nanosecond transient absorption measurements at room temperature, directly after a 308 nm excimer laser exposure: (a) **1a** in methanol; (b) **1b** in water; and (c) **1c** in 1,4-dioxane with 1 M water.

is observed without any further transient behavior. At 295 nm (Figure 10b), a small increase in absorption appears when pump- and probe-pulse are overlapping. This effect might be due to coherent interaction between the pump and probe beam, which is observed sometimes when pump- and probe-wavelength are identical.¹⁷ The only transient behavior in the absorption that is observed *after* the period of excitation is around 323 nm (Figure 10c). Figure 11 presents enlargements of the traces in Figure 10, parts c and e. Numerical fits to these traces are also shown. The fits are based on the convolution of the known pulse shape and single exponential dynamics of the absorption decay. At 323 nm, the absorption increases instantaneously during the period of overlap of pump- and probe-pulse, whereafter the absorption decays with a rate constant of $5 \times 10^{10} \text{ s}^{-1}$. The trace for 400 nm shows that the bleaching is immediate and remains constant in time.

On basis of the ground state absorption spectrum, the maxima in the $S_1 \rightarrow S_n$ absorption spectra are estimated to appear at 485 and 790 nm. No positive absorption changes could be observed in the wavelength range from 450 to 700 nm.

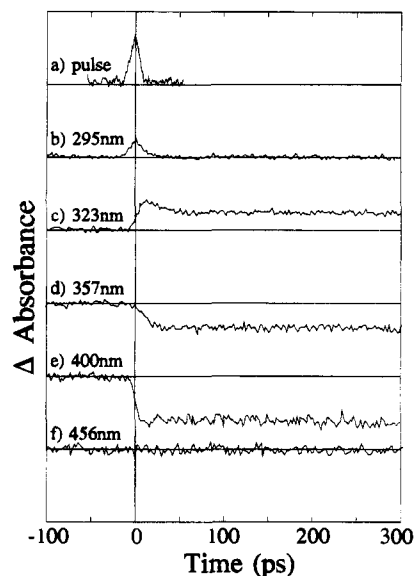


Figure 10. Picosecond transient absorption signals of 250 mg/L of **1a** in methanol at different probe wavelengths: (a) convolution of pump and probe pulse and (b–f) transient absorption signals at 295, 323, 357, 400, and 456 nm.

Bleaching is also not observed because the ground state molecule does not absorb in this spectral region.

At 400 nm the DNQ has a strong absorption due to the $S_0 \rightarrow S_1$ transition. Since the quantum yield of photolysis is 0.54 (Table 1), a time dependence in the absorption at 400 nm is expected due to repopulation of the ground state. In the picosecond pump-probe experiment this could not be observed in the time domain of 8 ps to 1 ns. It has also been searched for in the time domain between 1 ns and 1 s and has not been found. Therefore it may be concluded that electronic relaxation to the electronic ground state and subsequent vibrational relaxation is completed in less than 8 ps. Note that the photo-induced fragmentation has also been completed within this period of less than 8 ps. All the spectroscopically observed changes from Figure 10 observed after ca. 50 ps are in agreement with the spectral changes expected on basis of the difference spectra between the ketene and the DNQ parent molecule which are shown in Figure 9a.

1b in Water and Methanol. Figure 12b–f show the transient absorption behavior of **1b** in water at several wavelengths of interest. A fast bleaching is observed in the wavelength region from 310 to 450 nm, whereas a strong increase in absorption is observed around 300 nm. No positive changes in optical density are observed within the wavelength range from 450 to 700 nm. Excitation of **1b** does not lead to any observable transient absorptions in the picosecond time domain, except those appearing during the period of overlap between pump- and probe pulse. At 313 nm, an increased transmission is observed directly after laser excitation. Figure 13 shows a similar experiment at 310 nm which was performed with a femtosecond laser setup with a time-resolution of approximately 135 fs. A sharp spike is observed during pump- and probe-pulse overlap. After this period, increased transmission is immediately observed.

All the absorption changes observed after the period of pump- and probe-pulse overlap are in agreement with the absorption changes expected on the basis of the ketene formation shown in Figure 9b. We therefore conclude that the ketene is formed within 8 ps after preparation of the excited state. The femtosecond experiment reveals that a bleaching exists already after 135 fs. Since only a single experiment has been done and the noise level is relatively high, it is not possible to distinguish

(17) Flemming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford University Press: New York, 1986; pp 66–82.

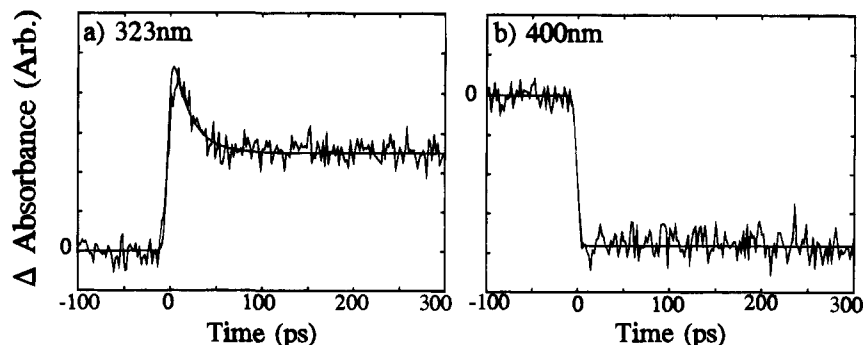


Figure 11. Vertical enlargements of the experimental absorption traces of **1a** in methanol at (a) 323 and (b) 400 nm. The data are fitted assuming a Gaussian convolution of the pump and probe pulse of 8 ps length. In the case of the signal at 323 nm an additional exponential absorption decay is fitted.

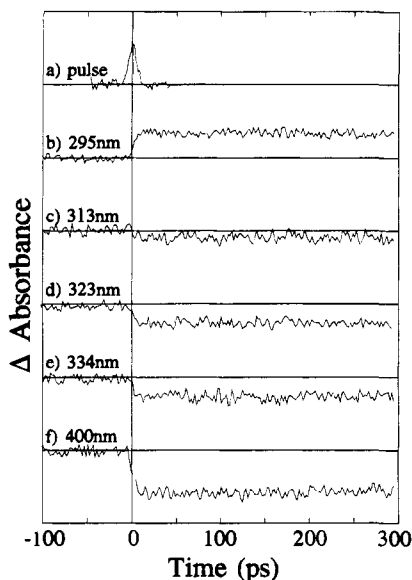


Figure 12. Picosecond transient absorption signals of 280 mg/L of **1b** in water at different probe wavelengths: (a) convolution of pump and probe pulse and (b–f) and transient absorption signals at 295, 313, 323, 334, and 400 nm.

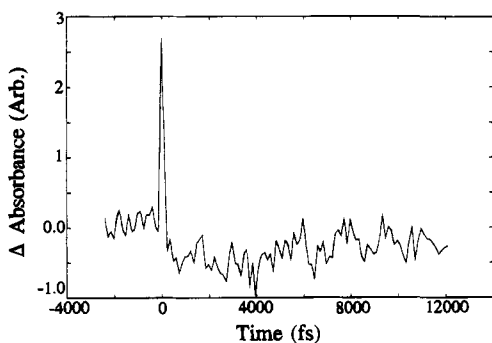


Figure 13. Femtosecond transient absorption signal from **1b** in water at 310 nm. The pump-wavelength in this experiment is also 310 nm.

clearly between the possibilities of bleaching due to ground state depopulation or to immediate carbene or ketene formation. The positive spike which is observed in Figure 13 could be a coherent spike or could arise from an optical transition of the excited intact DNQ. The former may be ruled out, because coherent interaction of the pump- and probe-pulse would create a coherent spike and an absorption change of the same sign.¹⁷

Transient absorption changes similar to those shown in Figure 12 are observed in the case of solutions of **1b** in methanol. When these changes are compared with the transient absorption spectrum of the same solution 30 ns after excimer laser excitation, large differences are observed. In the latter case, a

strong absorption band with a maximum around 350 nm is found,⁴ which may be ascribed to the enol of the indenecarboxylic acid methyl ester, **6b** ($R' = \text{CH}_3$). As was already mentioned above, the reaction from **3b** to **6b** is too fast to be measured by excimer laser flash photolysis. However, the reaction rate can be measured on the timescale of a few nanoseconds, by slightly modifying the transient absorption setup. Instead of an excimer laser pulse for excitation, a frequency-quadrupled YAG pulse of 80 ps and 266 nm is used. The rate constant for the reaction from **3b** to **6b** found by this method is $2.0 \times 10^7 \text{ s}^{-1}$. The absorption changes observed in the latter experiment agree with the picosecond transient experiments and the transient absorption spectrum of the ketene (Figure 9b). The obvious conclusion from these observations is that excitation of **1b** leads to the formation of **3b** within 8 ps.

1c in Dioxane/Water and in Methanol. Transient spectroscopic studies of aqueous solutions of **1c** were not possible due to its low solubility in water. Therefore the photoinduced reaction of **1c** with water has been studied by taking solutions in 1,4-dioxane/water mixtures. The ketene does not react with 1,4-dioxane and can exist for seconds in absolutely dry dioxane. Since the reaction of the ketene with water is taking place on a timescale longer than several nanoseconds, the addition of water is not strictly needed in the studies on picosecond timescale. Nevertheless, the solutions contained water also in these studies in order to let the reaction proceed to its end quickly and thus to inhibit the well known dimerization reactions of ketenes.⁴

The absorption behavior in the time domain below 300 ps of a solution in a 1,4-dioxane/water mixture is presented in Figure 14b–f. Again there is no transient behavior in this time domain, with the exception of the period of the laser excitation. The observed spectral changes agree with the transient absorption spectrum of the ketene. Use of the 80 ps/266 nm pulse for primary excitation does also not reveal any transient behavior in the time domain between 1 and 30 ns. Therefore formation of **3c** within less than 8 ps after photolysis of **1c** must be proposed.

The transient absorption spectrum at 30 ns after photolysis of **1c** in methanol is identical with the spectrum of the enol of the indenecarboxylic acid methyl ester. Using the 80 ps/266 nm pulse for excitation, the decay of the ketene could be observed at 310 nm with a rate constant of $1.3 \times 10^8 \text{ s}^{-1}$, but the growth could not be resolved. The time dependence of the absorptions in the picosecond time domain is identical to that shown by the solution in 1,4-dioxane with 1 M H_2O (Figure 14). Also in this case, no transient behavior is seen in this time domain, except during the overlap between the pump- and probe-pulse. The changes in the absorbance at the different

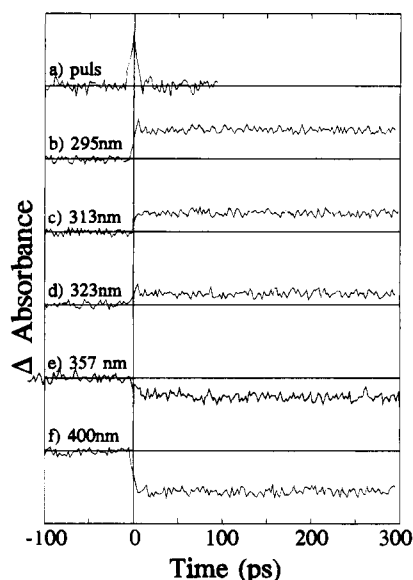


Figure 14. Picosecond transient absorption signals of 480 mg/L of **1c** in dioxane/water: (a) convolution of pump and probe pulse at 295 nm and (b–f) and transient absorption signals at 295, 313, 323, 357, and 400 nm.

wavelengths agree with the transient absorption spectrum of the ketene.

Deactivation of the Primary Excited State. The spectroscopic and kinetic results covering the picosecond time domain indicate clearly that **1** loses the azo-chromophore certainly in less than 8 ps after photoexcitation. Two observations show that the observed bleaching is not caused by transfer of population from the ground state to the excited state of intact DNQ, but by an irreversible reaction taking place within this very short time. The first one is that no absorption recovery is observed in the ground state absorption bands. The second one is that no transient increase in absorbance is observed in the range from 450 to 700 nm. At least one absorption band of the S_1 -state is expected in this region. The quantum yield of approximately 0.5 for the photolysis indicates that the rate constants for internal conversion and for photofragmentation are nearly equal, and that both are larger in magnitude than $1.3 \times 10^{11} \text{ s}^{-1}$ in all the three DNQ compounds discussed here.

Only in the case of **1a**, transient behavior is observed in the picosecond time domain. This is the absorption decay at 323 nm, with a rate constant of $5 \times 10^{10} \text{ s}^{-1}$. This value is smaller than the lower limit of the decay constant of the primary excited DNQ ($1.3 \times 10^{11} \text{ s}^{-1}$) and much larger than the rate constant of the decay of the ketene observed in the nanosecond time domain ($5.5 \times 10^6 \text{ s}^{-1}$). Therefore the transient absorption arising from **1a** at 323 nm in the picosecond domain must be attributed to an intermediate between the primary excited state of **1a** and the ketene **3a**. This rules out the possibility of a concerted rearrangement in which the excited DNQ is converted directly to the ketene. In the case of **1b** and **1c** the observations are somewhat different. Absorption transients cannot be observed in the time domain from 8 ps to 1 ns. Also all observed spectroscopic changes during excitation are in agreement with the ketene absorption. It is therefore clear that the intact excited state of **1b** and **1c**, as well as the corresponding carbenes must have a lifetime of less than 8 ps. Although there is no spectroscopic evidence for carbene intermediacy in this case, the chemical analysis of side products from the reaction provides evidence for carbene involvement in the photoreaction of these molecules.

The nature of the substituent in the 5-position has a strong effect on the reactivity of almost all reaction intermediates. For

instance, the rate constant of the reaction of the ketene with methanol has a value of $5.5 \times 10^6 \text{ s}^{-1}$ for **3a**, $2 \times 10^7 \text{ s}^{-1}$ for **3b**, and $1.3 \times 10^8 \text{ s}^{-1}$ for **3c**. It is to be expected that the reactivity of the carbene is also influenced by the substituent in a similar manner as in the case of the ketene. This would explain that **2b** and **2c** cannot be observed in the experiments described if the rate constant is larger than in the case of **2a** by a factor of more than 2.6. The variation of the rate constant for the conversion of the carbene to the ketene among the different DNQ's may be attributed to reduction of electron density in the carbene by action of the sulfonic substituent in the 5-position as an electron acceptor. The sulfonic substituent is moderately electrophilic and is likely to cause charge transfer from the aromatic π -system to the substituent which can cause lower bond order in the π -system and therefore a lower stability of the carbene intermediate. In this way the shorter lifetime of **2b** and **2c** compared to that of **2a** can be explained. Significant substituent effects of the reactivity of ring-substituted phenyl-carbenes have been reported previously.¹⁸

The previous papers dealing with time-resolved spectroscopy of DNQ's have neither dealt with the formation of side products from the photoreaction, nor with the nature of the latter. Barra et al.⁹ showed that the ester is formed as the main photoproduct in the solutions in methanol. They searched without success for the formation of **8**. When NMR is used as the only technique to analyze the mixture of reaction products directly, the formation of less than 9% of side product in methanol may be overlooked easily. However, in the case of the photoreaction of **1b** in water, the NMR spectrum of the product mixture clearly shows lines arising from the main product as well as from a side product. HPLC proved to be a much more sensitive technique than NMR for the detection of side products. The advantage is due to the possibility to increase the detection sensitivity for side products, by probing at wavelengths where they have a much higher extinction coefficient than the main photoproduct.

The yields of photoreaction products **1b** and **1c** are consistently lower than those observed by Ponomareva et al.¹¹ for **1a**. In contrast with their results, not a trace of the sulfonic derivatives of 1-naphthol is found in the present study. The discrepancy can be attributed to the major difference between two methods of irradiation. In the present study the irradiation time is kept below approximately 2 s by irradiating only a small amount of sample in a continuous flow, whereas Ponomareva et al. irradiated the whole solution batchwise over a prolonged time. It is likely that the formation of 1-naphthol observed in the latter case occurs by a photoinduced reaction of one of the photoproducts of the DNQ, for instance through photolysis of the azo-coupling products such as have been described by Süs.¹⁹

Conclusions. Product analysis and time-resolved spectroscopy provide strong evidence for the participation of a carbene in the conversion of photoexcited DNQ's into ketenes. The small values of the yields of side products are due to the very short lifetime of the carbene. The carbene **2a** has a lifetime of approximately 20 ps in methanol. In the case of **2b** and **2c** it must be less than 8 ps. The amount of side products formed from the reaction of the carbene with aliphatic alcohols and water implies that the reaction rate constants must be larger than, approximately $3.5 \times 10^8 \text{ s}^{-1}$. The results in 1,4-dioxane/alcohol and cyclohexane/alcohol mixtures show that the DNQ is solvated specifically by alcohol molecules and that the reaction of these two involves a single nearest-neighbor alcohol molecule. The specific solvation causes the observed curvature in the yields of photoproducts as a function of the concentration

(18) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042.

(19) Süs, O; *Ann. Chem.* **1944**, 65.

of alcohol in water/alcohol mixtures (Figures 2 and 4). The internal conversion and the relaxation to the ground state is shorter than 8 ps in all three excited state DNQ molecules. The rate of photofragmentation must be of the same magnitude as this relaxation process.

Experimental Section

Materials. **1b** was purchased from by Fluka A. G. and was purified by recrystallization from methanol. **1c** was prepared according to procedures described previously.²⁰ It was recrystallized twice from a methanol/acetone (2:1) mixture. **1a** was kindly supplied by Philips Research and recrystallized twice from heptane. Millepore water was used in the experiments involving water. The alcohols (methanol, ethanol, 1-propanol, 2-propanol, *tert*-butyl alcohol, trifluoroethanol) were dried and purified by distillation from Mg/I₂ or Na. 1,4-Dioxane was distilled from Na.

Nanosecond Time Resolved UV/vis. Absorption Spectroscopy. Studies of transient absorptions with a time resolution of 30 ns were performed by using either a Questec 2120 KrF excimer laser (248 nm, 15 ns) or a Lambda Physik EMG 100 XeCl excimer laser (308 nm, 20 ns) for the photolysis. A cw 500 W Xe-lamp which could be boosted pulsewise to a power of 10 kW generated the probing light. The sample was placed between two monochromators transmitting the probing wavelength. The first one selected the probing wavelength and the second one acted as an optical filter in front of the photomultiplier to eliminate laser light and fluorescence from the sample. The transient signal from the photomultiplier was recorded on a computer-interfaced Yokogawa 2100 digital oscilloscope. The flash photolysis is carried out in a 10 mm × 2 mm quartz flow cell in which the sample is refreshed after each laser shot by a dosage pump. To achieve a time resolution of 1 ns, the experiment could be modified by using 80 ps pulses for the primary excitation, instead of the 15–20 ns excimer laser pulses. These pulses were generated by amplifying a pulse from a cw mode-locked Nd-YAG laser (Coherent Antares) in a regenerative amplifier (Quantel RGA-60) and subsequent quadrupling of the frequency. The resulting 80 ps pulses, with a wavelength of 266 nm, had an energy of 1.5 mJ. Fairly good results could be obtained in this way by signal accumulation (200 shots).

Picosecond Time-Resolved UV/vis Absorption Spectroscopy. Absorption changes in the picosecond time domain were studied with pump-probe techniques.¹⁷ Pulses of 3 ps and a wavelength of 590 nm are produced in a synchronously pumped dye laser oscillator (Coherent 702 dye), using rhodamine-6G as laser dye and DODCI as a saturable absorber. The dye oscillator is pumped by the second harmonic of the pulses from a cw mode-locked Nd-YAG laser (Coherent Antaris 76-s). These pulses were amplified in a 3-stage dye laser amplifier (Quantel PTA-10) pumped by the second harmonic of pulses from the Nd-YAG laser which were amplified in a regenerative amplifier (Quantel RGA-60, 10 Hz). The amplified dye laser pulses, with a width of about 5 ps, were frequency doubled to pulses of 295 nm having an energy of 200 μJ and were used as the pump-source. The excitation was tunable from 290–300 nm. Probing light was generated in several ways, depending on the required wavelengths. A fraction of the excitation beam was used for probing in the range of 290–300 nm. A picosecond spectral continuum was used to probe in the region 380–700 nm. The spectral continuum was generated in D₂O by the 5 ps laser pulse of 590 nm. In the range of 300–360 nm, the probing light was generated using stimulated Raman scattering of the pulse of 595 nm, which remained after it had been used for second harmonic generation of the pump pulse of 295 nm. The pump beam for the stimulated Raman scattering was focused in a cuvette of 5 cm length filled with either benzene or acetone. The Stokes shifted Raman light was mixed with the 590 radiation in a 1 mm BBO crystal. The desired wavelength could be selected by angle tuning the BBO such that a second harmonic or the sum frequency of two input wavelengths was produced. By Stokes shifting the 595 nm pulse for instance in benzene and subsequent frequency upconversion probing wavelengths of 295, 305, 313, 323, and 334 nm were generated. The pump and probe beams had an angle of 5° with respect to each other. A flow cell of quartz with a 2 mm optical path was used to hold the sample. The flow cell

was refreshed by a Teflon "merry go round"-apparatus incorporating a 250 mL sample reservoir. Concentrations of the solutions were adjusted to achieve an optical density of the sample of **1** at the pump wavelength. The pump and probe beams were focused to cross sections of about 3 mm² and 1 mm², respectively. The directions of polarization of the beams were at magic angle. The convolution of pump and probe pulse was recorded before and after each recording of the time profile of a transient absorption.

The technique for time resolved absorption in the femtosecond time domain has been described elsewhere.²¹

Quantum Yields of the Photoproducts. The samples have been photolyzed by irradiating them with the focused light from a continuous high pressure xenon lamp, which passed through either optical cutoff filters or a monochromator. The photolysis of analytical experiments was performed in a 3 mL quartz cuvette during a uniform exposure of 10 s of a solution of 0.1 mM DNQ. Preparative photolysis was performed during a single pass through a 1 mm thick quartz flow cell of 250 mL of a 1 mM DNQ solution. In this way, the actual exposure time could be kept as low as approximately 2 s. A preparative high performance liquid chromatography system from Merck was used in the HPLC studies. The system consists of a L-6250 gradient pump equipped with an automatic sample injection system, an analytical (2.5 mm) or a semipreparative (10 mm) RP-18 column, a variable wavelength L-4200 UV/vis detector, and sample collector. The detection wavelength used for all experiments was 256 nm. The eluent flow was either 1 mL/min with the analytical column, or 5 mL/min with the semipreparative column. Two methanol/water mixtures were used as eluents. Eluent 1 consisted of 25% methanol (Baker, HPLC grade) and 75% millepore water and was buffered by 0.1% (v/v) trifluoroacetic acid. Eluent 2 consisted of 80% methanol and 20% water and was also buffered with 0.1% (v/v) trifluoroacetic acid. All retention times reported are recorded with the semipreparative column with 5 mL/min flow. The product yields were determined with an accuracy of approximately 10%. NMR spectra were recorded on a JEOL Model FX200 200 MHz FT-NMR spectrometer. Molecular masses were determined by injection of the sample through a liquid chromatograph into a Finnigan Model MAT TSQ-70 mass spectrometer provided with a Hewlett Packard 59980A particle beam interface with a pneumatic nebulizer. Methane chemical ionization was used in standard EI-CI source housing.

Quantum Yield of Photolysis. The quantum yield of photolysis was determined by irradiating the sample in the same manner as in the determination of the quantum yields of the photoproducts, but with lower intensity. The number of photons entering the sample was measured with the Aberchrome chemical actinometer.²²

For data on the chemical analysis such as product yields, HPLC retention times, and NMR spectra, the reader is referred to the supplementary material.

Acknowledgment. These investigations have been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Technology Foundation (STW). Prof. H. G. Heller from Cardiff University provided a sample of the Aberchrome actinometer. The time profile in the femtosecond time domain was recorded by Mr. E. Lenderink and Dr. K. Duppen from Groningen University. Mr. R. A. M. van der Hoeven recorded the mass spectra, and Mr. P. Schakel from Gorlaeus Laboratories designed and manufactured the electronic equipment.

Supplementary Material Available: Tables S1–S8 contain numerical data on the yields of photoproducts **5b,c**, **7b,c**, **8b,c**, and **9b,c**. Also available are NMR spectra, HPLC data, and mass spectroscopic data from the preparative product isolation (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see current masthead page for ordering information.

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