

## SPECTROSCOPIC AND KINETIC STUDY OF THE PHOTOINDUCED METHOXY SUBSTITUTION OF 3-NITROANISOLE AND 3,5-DINITROANISOLE

PIET H. M. VAN ZEIJL, LEX M. J. VAN EIJK and CYRIL A. G. O. VARMA

*Gorlaeus Laboratories, Department of Chemistry, The University of Leiden, P.O. Box 9502, 2300 RA Leiden (The Netherlands)*

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### Summary

The photoinduced nucleophilic substitution reactions of 3-nitroanisole (3-NA) in the presence of  $\text{OH}^-$  in mixtures of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$  and in the presence of  $\text{OCH}_3^-$  in  $\text{CH}_3\text{OH}$  were investigated by nanosecond time-resolved absorption spectroscopy. The absorption spectra of the solution recorded just after the triplet state of 3-NA has disappeared reveal that the formation of the substitution product is complete at that stage. We conclude that the addition of the nucleophile to the ring carbon atom C-1 is the rate-determining step in the methoxy substitution reactions of 3-NA in  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ . As well as the addition to C-1 there is at least one competing reaction of the nucleophile with the triplet state. This reaction, which reduces the overall quantum yield of the substitution reaction, leads to the formation of long-lived species ( $\lambda_{\text{max}} = 370 \text{ nm}$ ).

Analysis of previously reported results for the photosubstitution reactions of 3,5-dinitroanisole in the presence of  $\text{OH}^-$  and triethylamine shows that they can also be explained by the mechanism for the substitution reactions of 3-NA.

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### 1. Introduction

Investigations of the photoinduced nucleophilic substitution of the  $\text{OCH}_3$  group in 3,5-dinitroanisole (3,5-DINA) and 3-nitroanisole (3-NA) using steady state irradiation and a time-resolved spectroscopy study of this substitution reaction in 3,5-DINA have been reported earlier [1 - 4]. In the photoreaction with the nucleophiles  $\text{OH}^-$  and triethylamine (TEA) the only final products detected were 3,5-dinitrophenolate (3,5-DNP) and 3-nitrophenolate (3-NP). The time-resolved spectroscopy study of the substitution reaction of 3,5-DINA in the presence of  $\text{OH}^-$  and TEA revealed the existence of several transient species absorbing in the visible and near-UV spectral region. An attempt to identify these species led to the suggestion that the attack of the nucleophile on the substrate molecule in its

triplet state leads to the formation of an exciplex as well as addition to the ring carbon positions 2, 3 and 4. The anionic  $\sigma_1$  complex 1-hydroxy-1-methoxy-3,5-dinitrobenzene is formed from this exciplex by the addition of either an  $\text{OH}^-$  ion or an  $\text{H}_2\text{O}$  molecule. Elimination of the  $\text{OCH}_3^-$  group from this  $\sigma_1$  complex then yields the final product 3,5-DNP. The other adducts decompose back to the anisole.

The substitution reaction of 3-NA was assumed to proceed by a similar mechanism. This was suggested by the behaviour of the quantum yield of 3-NP in the presence of a quencher and by the variation in the quantum yield with the concentration of  $\text{CH}_3\text{CN}$  in the solvent mixture [2].

A time-resolved spectroscopy study, performed in our laboratory, of the photo-Smiles rearrangement of 3-nitrophenoxy- $\omega$ -alkylamines [5, 6], which represents an intramolecular version of the photoinduced nucleophilic substitution of 3-NA (an alkylamine-like nucleophile), revealed no transient absorption which could be attributed to an exciplex. This prompted us to examine the transient behaviour of solutions of 3-NA in the presence of nucleophiles upon laser excitation. Also, some of the earlier experiments on the photoreaction of 3,5-DINA have been repeated. In this paper we report the results obtained for the anisoles and conclude that the photosubstitution reaction starts from the triplet state of the anisole by direct formation of a  $\sigma$  bond between the nucleophile and the carbon atom bearing the methoxy group.

Deoxygenation of the solutions was achieved by purging with nitrogen.

## 2. Experimental details

The kinetics spectrometer described earlier [3] was slightly modified. The 308 nm emission of XeCl in an excimer laser (Lambda Physik EMG 500) (about 100 mJ; 10 ns) provided the initial excitation of the solution. The light intensity of the probe pulse from the xenon lamp was sampled just before the laser was fired. This signal, which was stored for 50  $\mu\text{s}$ , and the undisturbed photomultiplier signal were fed into a 125 MHz differential amplifier (Tektronix 7A13) which was connected to a transient digitizer (Tektronix 7912) controlled by a computer (PDP 11/10). Slow changes in the absorption ( $\tau > 50 \mu\text{s}$ ) were determined using a continuously burning xenon lamp and a photomultiplier load of 5 k $\Omega$ . The transient digitizer did not allow detection of responses at frequencies below 1 kHz. The absorption spectra of the ground state molecules were recorded on a Cary 14 spectrometer.

The  $\text{OH}^-$  concentration was varied by adding small quantities of a 0.25 N NaOH solution (pro analysis grade) to the sample. The concentrations were determined *in situ* using a pH meter which was calibrated with commercially available buffer solutions. When solvent mixtures of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$  were used the  $\text{OH}^-$  ion concentrations were calculated on the basis of the dilution factor.

Commercially available 3-NA was purified by recrystallization from a mixture of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ . 3,5-DINA and 3,3',4,4'-tetramethyldiazetinedioxide (TMDD) were available from previous experiments [3]. Ethanolamine was distilled just before use. Sodium methoxide solutions were made by reacting known amounts of sodium and methanol. Distilled water and spectroscopic grade methanol and acetonitrile were used.

### 3. Results

The optical transmission of a solution of  $1 \times 10^{-4}$  M 3-NA in  $\text{H}_2\text{O}$  ( $\text{pH} < 7$ ) or  $\text{CH}_3\text{OH}$  changes after excitation by the laser pulse. The spectral changes  $\Delta\text{OD}_0$  observed just after termination of the pulse are shown in Fig. 1. The low substrate concentration facilitated measurement of the absorption changes in the wavelength region where the ground state molecules absorb (280 - 400 nm;  $\lambda_{\text{max}} \approx 350$  nm;  $\epsilon_{\text{max}} \approx 2000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The part of the spectrum in  $\text{H}_2\text{O}$  for  $\lambda > 360$  nm is similar to the spectrum reported in ref. 3. The band at 405 nm is slightly broader for the spectrum in  $\text{CH}_3\text{OH}$  than for that in  $\text{H}_2\text{O}$ . The difference between the amplitudes of the bands at 300 nm in these solvents probably arises from small solvent shifts in the absorption maxima of the ground and excited state molecules.

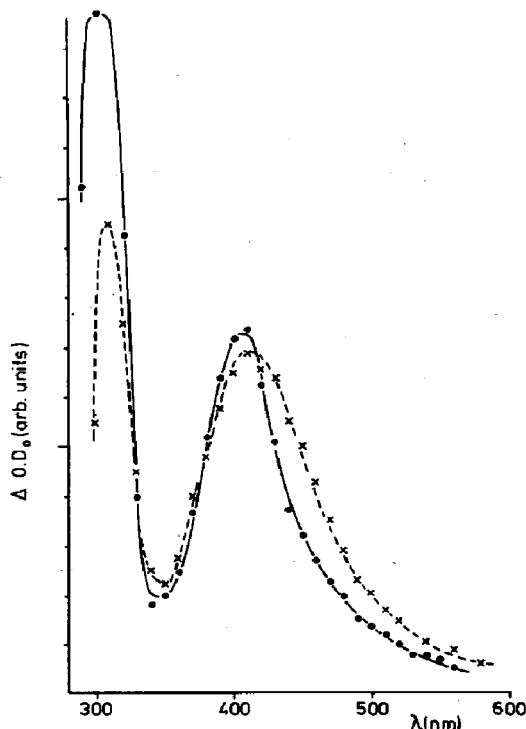


Fig. 1. Difference spectra of the triplet and ground states of 3-NA ( $1 \times 10^{-4}$  M) in  $\text{H}_2\text{O}$  (—) and  $\text{CH}_3\text{OH}$  (---) just after excitation of the solution with a 10 ns laser pulse ( $\lambda = 308$  nm).

The decay of the initial absorption change is single exponential and wavelength independent. The time constant of the decay was evaluated from a fit to the sum of a single exponential and a constant term [7]. The decay constants for air-saturated and oxygen-free solutions are given in Table 1.

The laser-induced change in the absorption of the aqueous solutions has been attributed to the lowest electronic state of 3-NA [3]. From the close resemblance of the behaviour of the aqueous and methanolic solutions we conclude that the absorption change in CH<sub>3</sub>OH can be attributed to the population of the lowest electronic triplet state of 3-NA. A very weak absorption R remains after the triplet has disappeared (less than 1% of the triplet signal ( $\lambda_{\max} \approx 410$  nm)).

When TMDD is added to the solutions of 3-NA in mixtures of H<sub>2</sub>O and CH<sub>3</sub>CN, the triplet lifetime is reduced but the same transient spectrum is observed. If the reduction in the triplet lifetime is attributed to a bimolecular quenching reaction of the triplet molecule with TMDD, the triplet decay constant is given by

$$\frac{k}{k_0} = 1 + \frac{k_Q}{k_0} [Q] \quad (1)$$

where  $k$  and  $k_0$  are the decay constants for solutions in the presence and absence of quencher,  $k_Q$  is the second-order rate constant for quenching and  $[Q]$  is the concentration of the quencher.

In Fig. 2 the ratio  $k/k_0$  is plotted as a function of the concentration of TMDD for various solvent compositions. The values for  $k_Q$  obtained from the slopes of the lines in Fig. 2 and  $k_0$  are listed in Table 2.

To verify whether the magnitude of  $k_Q$  is affected by the presence of OH<sup>-</sup> ions we have also measured the rate constants for quenching of the triplet state absorption of 3-NA by TMDD in alkaline aqueous solutions at pH  $\approx$  10.9 - 12.1. The results of these experiments are shown in Fig. 3. The slopes of the lines in Fig. 3 need to be corrected for the dilution of the OH<sup>-</sup> ion concentration caused by addition of the neutral TMDD solution. The corrected slopes were used to calculate the values of  $k_Q$ . Apparently, these values of  $k_Q$  are independent of the OH<sup>-</sup> ion concentration between pH 4 and pH 12.1.

TABLE 1

Decay constants of the triplet state of 3-nitroanisole in oxygen-free and oxygen-containing H<sub>2</sub>O and CH<sub>3</sub>OH solutions

Solvent	O <sub>2</sub>	$k$ (s <sup>-1</sup> )
H <sub>2</sub> O (pH 4)	+	$0.72 \times 10^6$
CH <sub>3</sub> OH	+	$5.0 \times 10^6$
H <sub>2</sub> O (pH 4)	-	$0.35 \times 10^6$
CH <sub>3</sub> OH	-	$1.4 \times 10^6$

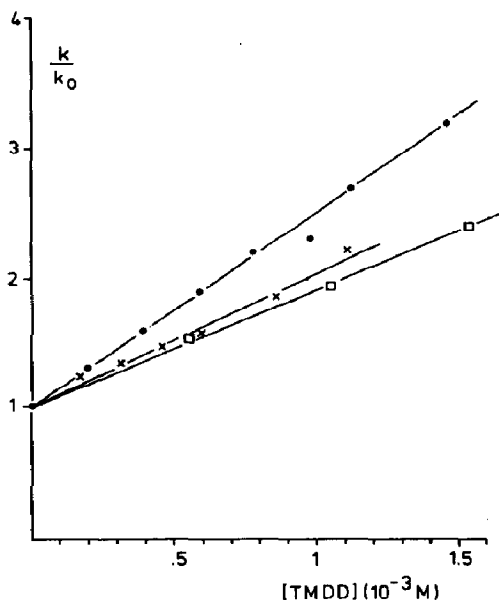


Fig. 2. Normalized decay constant of the triplet-triplet absorption at 410 nm of 3-NA ( $2 \times 10^{-4}$  M) dissolved in  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  mixtures as a function of the TMDD concentration: ●, pure  $\text{H}_2\text{O}$ ; x, 40 mol.%  $\text{CH}_3\text{CN}$ ; □, 80 mol.%  $\text{CH}_3\text{CN}$ .

TABLE 2

Effect of the concentration of  $\text{CH}_3\text{CN}$  on the decay and reaction rate constants of the triplet state of 3-nitroanisole in mixed  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  solvents (non-oxygenated)

[ $\text{CH}_3\text{CN}$ ] (mol.%)	$k_0$ ( $\times 10^6 \text{ s}^{-1}$ )	$k_Q$ ( $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )	$k_{\text{OH}}$ ( $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )
0	0.72	0.46	0.35
26	1.02		0.64
40	1.26	1.28	0.77
80	3.4	3.23	

The photoinduced substitution of the methoxy group in 3-NA by  $\text{OH}^-$  requires the presence of  $\text{OH}^-$  ions. We have studied the kinetics and the spectral changes for a wide range of  $\text{OH}^-$  ion concentrations in the 3-NA solutions. In aqueous solutions of 3-NA the pH was increased up to 12.3 at which value the limiting quantum yield of formation of 3-NP is reached. The magnitude of  $\Delta\text{OD}_0$ , corrected for dilution, does not change when NaOH is added to the solution. The spectrum of  $\Delta\text{OD}_0$  of an aqueous solution of 3-NA at pH 12 is the same as that shown in Fig. 1. The triplet decay constant, however, increased with the  $\text{OH}^-$  ion concentration. After the triplet population had disappeared another long-lived spectrum was observed between 300 and 500 nm. This spectrum did not show any changes for at least 50  $\mu\text{s}$ . At 410 nm no change was detected for at least 1 ms.

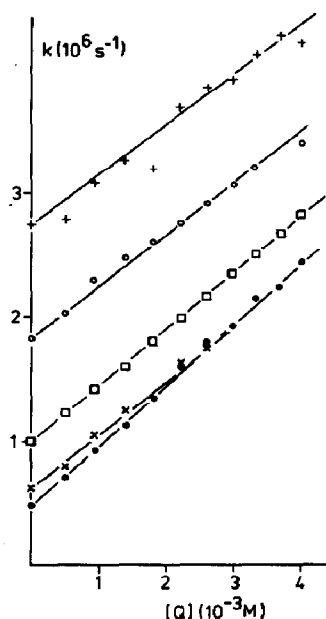


Fig. 3. Decay constant of the triplet-triplet absorption at 410 nm of aqueous solutions of 3-NA ( $2 \times 10^{-4}$  M) as a function of the TMDD concentration at various pH values ( $k$  is not corrected for dilution by the quencher solution): +, pH 11.9; o, pH 11.7; □, pH 11.0; ●, pH 10.7; x, pH 2.5.

The relation between  $k$ , measured at 410 nm, and  $[\text{OH}^-]$  in mixtures of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$  are shown in Fig. 4. The rate constant  $k_{\text{OH}}$  is calculated from the slopes of the lines in Fig. 4 by using the equation

$$k = k_0 + k_{\text{OH}}[\text{OH}^-] \quad (2)$$

where  $k_0$  is the decay constant at very low  $\text{OH}^-$  concentrations (e.g. at pH 4),  $k_{\text{OH}}$  is the second-order rate constant for the reaction of  $\text{OH}^-$  with the molecule in its triplet state and  $[\text{OH}^-]$  is the  $\text{OH}^-$  ion concentration determined from the pH meter reading or by calculation (the dilution factor was applied when  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  mixtures were used).

A rate constant  $k_{\text{OH}}$  of  $0.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  is obtained in  $\text{H}_2\text{O}$ , whereas  $k_{\text{OH}} = 0.77 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  is obtained when the solution contains 40 mol.%  $\text{CH}_3\text{CN}$ . Figure 5, curve A, shows the spectrum of the long-lived absorption 1  $\mu\text{s}$  after excitation of an aqueous solution of 3-NA at pH 12, i.e. after the triplet has disappeared. The difference spectrum of 3-NP and 3-NA obtained after a period of continuous irradiation is shown in Fig. 5, curve B. The two spectra are scaled such that they have equal amplitudes at 400 nm. The positions of the isosbestic points near 325 nm and 345 nm in the laser experiments are inaccurate because the optical changes are small in this wavelength region ( $\Delta\text{OD}(320 \text{ nm}) = (2 \pm 0.5) \times 10^{-3}$ ) and were measured for a spectral bandwidth of 5 nm.

The magnitude of the long-lived absorption varied with the  $\text{OH}^-$  ion concentration. We denote the species responsible for the absorption at

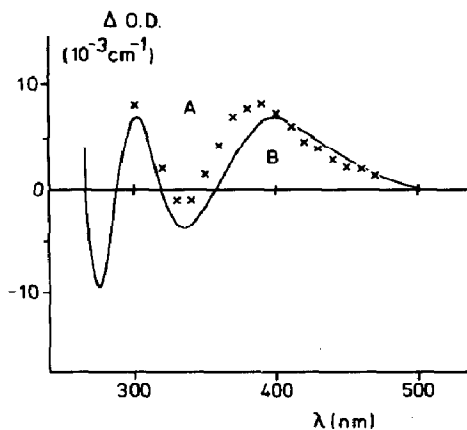
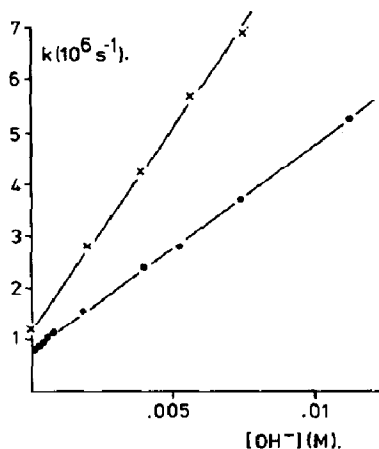


Fig. 4. Decay constant of the triplet-triplet absorption at 410 nm of 3-NA ( $2 \times 10^{-4}$  M) dissolved in  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  mixtures as a function of the  $\text{OH}^-$  concentration: ●, pure  $\text{H}_2\text{O}$ ; x, 40 mol.%  $\text{CH}_3\text{CN}$ .

Fig. 5. Curve A, difference spectrum 1  $\mu\text{s}$  after excitation of an aqueous solution of 3-NA ( $1 \times 10^{-4}$  M) (pH 12); curve B, difference spectrum of 3-NP and 3-NA obtained after continuous irradiation.

410 nm by I and its contribution to the optical density change by  $\Delta\text{OD}_I$ . If I is formed from the anisole in the triplet state by attack of  $\text{OH}^-$  the following equation holds:

$$\Delta\text{OD}_I = \alpha_I \frac{k_{\text{OH}'}[\text{OH}^-]}{k_0 + (k_{\text{OH}'} + k_{\text{OH}''})[\text{OH}^-]} = \alpha_I \frac{k_{\text{OH}'}[\text{OH}^-]}{k} \quad (3)$$

where  $\alpha_I$  is a proportionality constant,  $k_{\text{OH}'}$  is the second-order rate constant for the reaction yielding I and  $k_{\text{OH}''}$  is the sum of all rate constants of reactions of the triplet state with  $\text{OH}^-$  which do not lead to species absorbing at 410 nm. A plot of  $k\Delta\text{OD}_I$  as a function of  $[\text{OH}^-]$  should give a straight line. We have plotted these quantities for two solvent compositions in Fig. 6. The small value of the intercept of the line in Fig. 6 for the aqueous solution reflects the small absorption  $R$  which remained after the triplet had disappeared in the acidified solution (see above). This absorption could arise from products formed by a reaction of the excited molecules with the solvent. A ratio  $k_0/(k_{\text{OH}'} + k_{\text{OH}''}) = 2.1 \times 10^{-3}$  M is obtained from a plot of  $(\Delta\text{OD}_I - R)^{-1}$  against  $[\text{OH}^-]^{-1}$ . The same value for this ratio is obtained from the triplet decay constants. Analysis of  $\Delta\text{OD}_I$  in the experiments where TMDD was added at various concentrations at fixed pH (see above) yielded values for the ratios of  $k_0/k_{\text{OH}}$  and  $k_Q/k_{\text{OH}}$  which are consistent with the determinations discussed above.

In order to identify the chemical nature of the transient species in the photoreaction of 3-NA with  $\text{OH}^-$  we have also studied the kinetics of the photoreaction of 3-NA in  $\text{H}_2\text{O}$  in the presence of ethanolamine (EA) and in  $\text{CH}_3\text{OH}$  containing  $\text{NaOCH}_3$ .

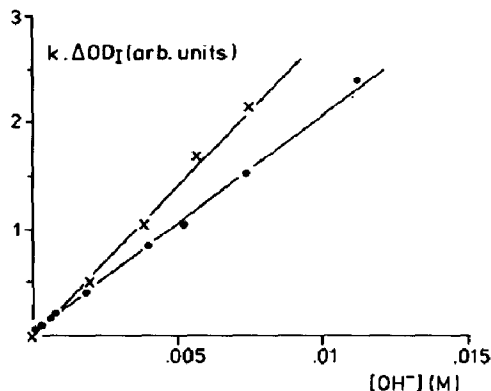
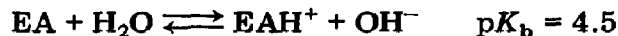


Fig. 6. Experimental values of  $k\Delta OD_T$  from eqn. (3) as a function of  $[OH^-]$  for 3-NA ( $1 \times 10^{-4}$  M)  $H_2O-CH_3CN$  mixtures; ●, pure  $H_2O$ ; x, 40 mol.%  $CH_3CN$ .

In view of the equilibrium



the solution contains both EA and  $OH^-$  as nucleophiles. The concentrations of EA and  $OH^-$  were varied independently by factors of up to  $10^4$ . The decay constant of the triplet state in the aqueous solution in the presence of EA can be analysed according to

$$k = k_0 + k_{OH}[OH^-] + k_{EA}[EA]_0 \frac{[OH^-]}{K_b + [OH^-]} \quad (4)$$

where  $k_{EA}$  is the second-order rate constant for the reaction of the triplet molecule with EA,  $[EA]_0$  is the sum of the concentrations of EA and  $EAH^+$  ( $2 \times 10^{-4}$  -  $2 \times 10^{-1}$  M) and  $K_b$  is the base-acid equilibrium constant of EA. The plots of  $k - k_0 - k_{OH}[OH^-]$  versus the pH of the solution have the same shape as that of the titration curve of EA. Such a plot for a solution with  $[EA]_0 = 5 \times 10^{-2}$  M (ionic strength, 0.5 M NaCl) is shown in Fig. 7. In the calculation of  $k - k_0 - k_{OH}[OH^-]$  we have used  $k_0 = 0.72 \times 10^6 \text{ s}^{-1}$  and  $pK_b = 4.1$  (for 0.5 M NaCl). The deviation in Fig. 7 indicates that  $k_0$  is larger than  $0.72 \times 10^6 \text{ s}^{-1}$ ; this is probably owing to the external heavy atom effect of  $Cl^-$ .

After the disappearance of the triplet state from the solution containing EA, we observed a long-lived absorption as in the case of aqueous solutions containing NaOH. In the present case the absorption arises from several species formed in parallel reactions of the two nucleophiles with anisole in the triplet state. The yields of these species depend on the competition of the two nucleophiles in the reaction with the triplet state molecule.

3-NA may exchange its methoxy group in a photoreaction with methoxide ions [8]. After completion of the exchange reaction, there are no further changes in the absorption spectrum. Therefore all laser-induced absorption changes must be attributed to transient species.



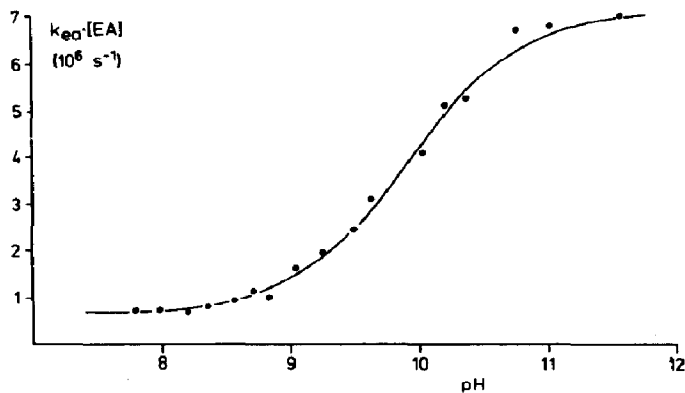


Fig. 7. Contribution of EA ( $5 \times 10^{-2}$  M) to the decay constant of the triplet absorption of an aqueous solution of 3-NA ( $2 \times 10^{-4}$  M; ionic strength, 0.5 M NaCl).

As in the previous cases we find that the decay constant of the triplet state increases with the concentration of the nucleophile. This is shown in Fig. 8. The second-order rate constant  $k_{Me}$  for the reaction of the triplet state of 3-NA with  $OCH_3^-$  has a value of  $3.4 \times 10^9$  M $^{-1}$  s $^{-1}$ . The absorption which remains after the triplet state has disappeared shows different behaviour from that in the cases with  $OH^-$  or EA in the solution. After about 100 ns the spectrum in Fig. 1 evolves to that shown by the full curve in Fig. 9. Within 5  $\mu$ s the spectrum changes further to that shown by the broken curve in Fig. 9 and then remains constant for at least 50  $\mu$ s.

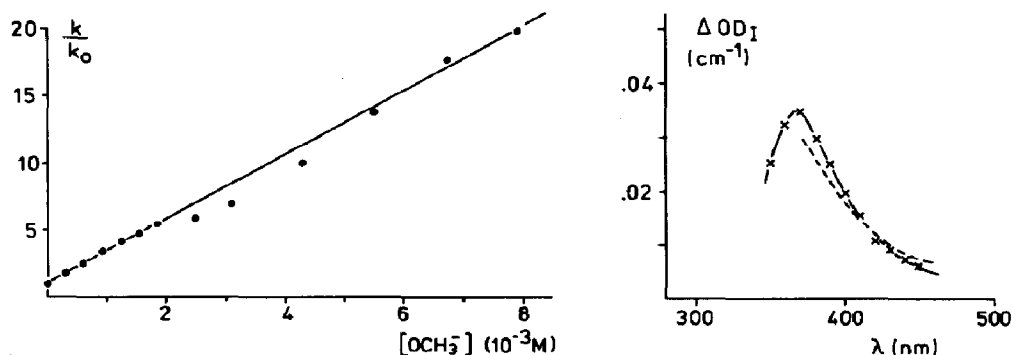


Fig. 8. Normalized decay constant of the triplet absorption at 410 nm of 3-NA ( $2 \times 10^{-4}$  M) dissolved in methanol as a function of the  $OCH_3^-$  concentration.

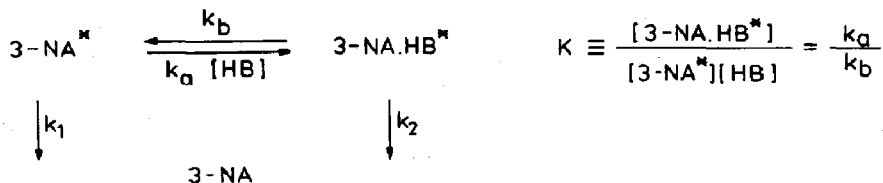
Fig. 9. Difference spectrum of a methanolic solution of 3-NA ( $2 \times 10^{-4}$  M) containing  $3 \times 10^{-3}$  M  $OCH_3^-$  immediately after the disappearance of the triplet-triplet absorption (—) and 5  $\mu$ s later (---).

## 4. Discussion

### 4.1. The photoreaction of 3-nitroanisole

Tamminga [2] deduced the magnitude of the rate constants  $k_{OH}$  and  $k_Q$  in  $H_2O$  in an indirect manner from the results of his work on the photo-reaction of 3-NA in the presence of  $OH^-$  and TMDD. The plots of the inverse of the quantum yield  $\Phi$  of 3-NP as a function of the TMDD concentration yield straight lines at various  $OH^-$  concentrations. The ratio of the intercept and slope of each of the lines depends linearly on the  $OH^-$  concentration. The coefficients in the latter linear relation are  $k_0/k_{OH}$  and  $k_Q/k_{OH}$  and are obtained from a least-squares fit. The fit yields  $k_0/k_{OH} = 0.29 \times 10^{-3} M$  and  $k_Q/k_{OH} = 0.8$ . On the basis of a triplet decay constant  $k_0 = 0.7 \times 10^6 s^{-1}$ , Tamminga obtained  $k_{OH} = 2.6 \times 10^9 M^{-1} s^{-1}$ . From the change in the decay constant of the initial laser-induced absorption in an aqueous solution of 3-NA in the presence of  $OH^-$  and TMDD, we obtain  $k_{OH} = 0.35 \times 10^9 M^{-1} s^{-1}$  and  $k_Q = 0.49 \times 10^9 M^{-1} s^{-1}$ . These values are significantly smaller than those obtained by Tamminga. However, in the case of an aqueous solution of 3,5-DINA such differences between the results of continuous and flash irradiation experiments, which both yield virtually diffusion-limited values [3] ( $k_{OH} = 2.7 \times 10^9 M^{-1} s^{-1}$  and  $k_Q = 2.5 \times 10^9 M^{-1} s^{-1}$ ), are not observed. These results suggest that in the case of 3-NA it may be incorrect to assign the initial laser-induced absorption to the population of the lowest triplet state, but rather it should be assigned to an intermediate emerging from it. Moreover, if the quenching of triplet state molecules by TMDD is caused by energy transfer as assumed by Ullman and Singh [9] the value of  $k_Q$  for 3-NA would imply that the triplet state energy  $E_T$  of 3-NA is approximately  $180 kJ mol^{-1}$  [9]. This is a remarkably low value compared with  $E_T > 220 kJ mol^{-1}$  for 3,5-DINA in aqueous solution, and is also surprising in view of the fact that a value of about  $250 kJ mol^{-1}$  for the  $E_T$  of 3-NA in a 4:1 methylcyclohexane-isopentane mixture at 77 K [1] is derived from the phosphorescence maximum at 520 nm. Despite these objections we maintain our assignment of the initial laser-induced absorption to population of the triplet state because the spectrum of this initial absorption does not change when  $H_2O$ ,  $CH_3OH$  (Fig. 1) or  $CH_3CN$  are used as solvents and is not affected by the presence of nucleophiles such as  $OH^-$ ,  $OCH_3^-$  and EA. Furthermore, the initial spectrum is similar to the spectrum of transient species formed by energy transfer from the triplet state of toluene in the pulse radiolysis of 3-NA in toluene [10].

The triplet state of nitroanisoles in hydrogen-bonding solvents is assumed to be hydrogen bonded to a solvent molecule [2, 11]. In the specific case of 3-NA in  $H_2O$  it is not clear whether this hydrogen bond results in a much lower value of  $E_T$  energy or whether the quenching by TMDD does not proceed by the energy transfer mechanism. Nevertheless, we can relate the increase of  $k_Q$  with increasing concentration of  $CH_3CN$  in the mixed aqueous solution to the hydrogen-bonded triplet state. An equilibrium, as shown in Scheme 1, exists between the hydrogen-bonded



Scheme 1

triplet state and the bare triplet state with  $k_1 > k_2$  [11]. If  $k_a[\text{HB}] + k_b > k_1$  and the two triplet states have similar absorption bands, the observed decay constant of the triplet-triplet absorption is given by

$$k_{\text{obs}} = \frac{k_1}{1 + K[\text{HB}]} \quad (5)$$

It can be seen from this equation that  $k_{\text{obs}}$  increases with decreasing  $[\text{HB}]$  provided that  $K$  does not depend on the solvent composition. If the hydrogen-bonded triplet state cannot be quenched and the quenching of the bare triplet state molecule is diffusion controlled, the observed value of  $k_Q$  will vary with the solvent composition according to eqn. (5).

We mentioned above that a small value of the ratio  $k_0/k_{\text{OH}}$  has been obtained from the indirect analysis of  $\Phi$  in the presence of both  $\text{OH}^-$  and TMDD. For the case with  $[\text{TMDD}] = 0$  we obtain  $k_0/k_{\text{OH}} = 2.2 \times 10^{-3}$  M from the linear fit to  $\Phi^{-1}$  as a function of  $[\text{OH}^-]^{-1}$ . This value is almost equal to that determined in our study of transient absorption and also to that obtained by Duddell and Richards [10]. However, the behaviour observed by Duddell and Richards for the long-lived absorption as a function of the  $\text{OH}^-$  concentration is quite different from our observations. The mechanism which they propose for the production of 3-NP from 3-NA does not agree with the dependence of  $\Phi$  on the  $\text{OH}^-$  concentration reported by Tamminga [2] and de Jongh [12].

The  $k_0/k_{\text{OH}}$  ratios obtained in the steady irradiations and the time-resolved experiments and the stability of the long-lived absorption indicate that the formation of 3-NP is complete within a few microseconds of initiation of the photoreaction by the laser. This assumption is justified by examination of Fig. 5. Spectrum A represents the difference between the optical densities of the laser-induced photoproduct(s) from 3-NA and the amount of 3-NA converted  $1 \mu\text{s}$  after the primary excitation. If the formation of 3-NP is complete in the solution for which spectrum A is recorded, we should be able to make spectra A and B almost coincide by appropriate magnification along the vertical axis. In Fig. 5 the spectra obtained in aqueous solution are scaled to have equal amplitudes at 400 nm. This shows that A has a major component with the shape of B and a minor component which is an absorption band with its maximum near 370 nm. In the case of the photoinduced exchange of  $\text{OCH}_3$  in 3-NA with  $\text{OCH}_3^-$  in  $\text{CH}_3\text{OH}$  a transient difference spectrum analogous to A has been recorded (Fig. 9). In this spectrum only the band with a maximum near 370 nm is observed. Since the main photoproduct in this reaction is identical with

the starting compound, we conclude that the major component in spectrum A is due to the presence of 3-NP in the solution. Furthermore, as spectrum A is observed 1  $\mu$ s after the primary excitation, *i.e.* just after the triplet has disappeared, we conclude that the addition of OH<sup>-</sup> to the triplet state of 3-NA is the rate-determining step in the formation of 3-NP.

In view of the regiospecificity of the photoreaction it is probable that the addition of OH<sup>-</sup> to the triplet state leads to the formation of the  $\sigma_1$  complex 1-hydroxy-1-methoxy-3-nitrobenzene. The OCH<sub>3</sub><sup>-</sup> group and the hydroxy proton are rapidly released from this  $\sigma_1$  complex either in separate steps or together (as CH<sub>3</sub>OH) to yield the most stable product in alkaline solutions. The effect of OH<sup>-</sup> on the initial laser-induced absorption cannot be attributed to the deprotonation of the 1-hydroxy substituent in either the  $\sigma_1$  complex or 3-nitrophenol. In the photoreaction of 3-NA in the presence of EA, the magnitude of the product  $k\Delta OD_1$  at equal values of  $k$  is much smaller than that in the presence of OH<sup>-</sup> only. This indicates that the amine reacts as a nucleophile with the triplet state leading eventually to the formation of nitroaniline rather than acting as a base which abstracts the proton from the 1-hydroxy substituent.

We have already mentioned two parallel reactions of the triplet state molecule with the nucleophile N for the particular case of OH<sup>-</sup>. We indicate the rate constants of the parallel reactions for the general case by  $k_N'$  and  $k_N''$ . The rate constant  $k_N'$  is associated with the formation of the  $\sigma$  bond between N and atom C-1 of the carbon ring, yielding the  $\sigma_1$  complex which is ultimately transformed into the substitution product. The rate constant  $k_N''$  has at least one component which is associated with the formation of the metastable species absorbing at 370 nm and which is transformed later into the starting material. There may be other components of  $k_N''$  arising from other quenching processes of the triplet state by N. In this picture the quantum yield of the photosubstitution is given by

$$\Phi = \Phi_T \frac{k_N'}{k_N' + k_N''} \Phi_P$$

where  $\Phi_T$  is the quantum yield of the triplet state and  $\Phi_P$  is the fraction of the number of  $\sigma_1$  complexes converted to the substitution product. Although no exact values of  $\Phi_T$  are known, we have assumed that it is at least 50% in our solutions. Van Riel *et al.* [8] obtained  $\Phi = 0.08$  for the symmetrical methoxy exchange. Since in this case the leaving abilities of the two substituents on C-1 are equal ( $\Phi_P = 0.5$ ), we can conclude from  $\Phi = 0.08$  that only 16% of the excited molecules react with the  $\sigma_1$  complex and therefore that  $k_{Me}' < k_{Me}''$ . The value of  $\Phi$  attained at high OH<sup>-</sup> concentrations in aqueous solutions of 3-NA is 0.30. Consequently, at least 30% of the excited molecules must have reacted with the  $\sigma_1$  complex. This means that  $k_{OH}' \approx k_{OH}'' \Phi_P$ . If we assume on the basis of  $k_{Me} = 10k_{OH}$  that OCH<sub>3</sub><sup>-</sup> has a higher reactivity than OH<sup>-</sup> for addition to C-1, we can conclude that the small quantum yield in the symmetrical exchange reaction

arises from a stronger enhancement of  $k_N''$  than of  $k_N'$  when  $\text{OCH}_3^-$  is used instead of  $\text{OH}^-$  as the nucleophile.

In mixtures of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$  the value of  $\Phi$  at high  $\text{OH}^-$  concentrations increases with the  $\text{CH}_3\text{CN}$  concentration. When the  $\text{CH}_3\text{CN}$  concentration is 26 mol.%,  $\Phi = 0.50$ . This behaviour of  $\Phi$  can be explained by assuming that the change in  $k_{\text{OH}}$  is mainly due to the increase of  $k_{\text{OH}}'$  with the concentration of  $\text{CH}_3\text{CN}$  and that  $\Phi_P$  does not depend on the solvent composition. The value of  $k_{\text{OH}}$  obtained in aqueous solutions shows that the addition of  $\text{OH}^-$  is slower than that characterizing a diffusion-controlled reaction. Therefore the increase in  $k_{\text{OH}}$  cannot be due to the change in the viscosity of the solvent mixture. Apparently, the addition of  $\text{OH}^-$  to the triplet state of 3-NA needs a small activation energy. The increase in  $k_{\text{OH}}$  then reflects a decrease in this activation energy, probably owing to a change in the solvation energy of  $\text{OH}^-$  with the solvent composition.

#### 4.2. The photoreaction of 3,5-dinitroanisole in the presence of triethylamine

It is interesting to determine whether the mechanism which we proposed above for the photoreaction of 3-NA in the presence of  $\text{OH}^-$  also applies to the photoreaction of 3,5-DINA when  $\text{OH}^-$  or TEA are present in the solution.

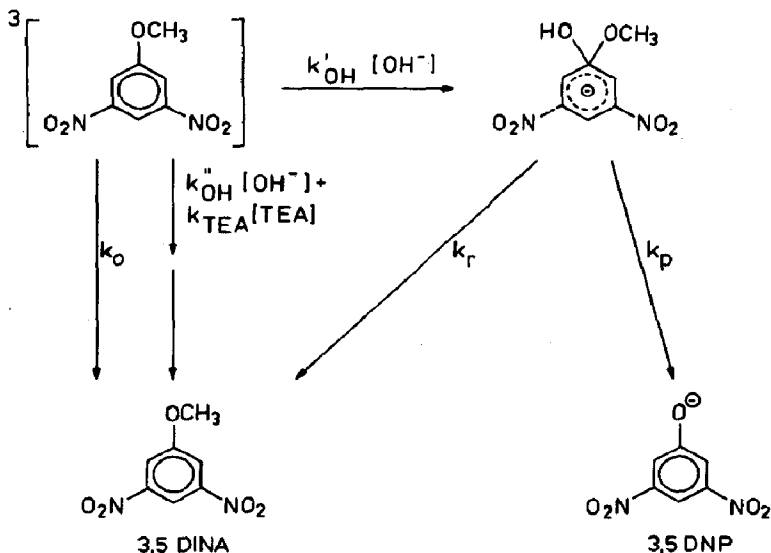
Irradiation of an aqueous solution of 3,5-DINA in the presence of TEA yields 3,5-DNP as the only reaction product. The quantum yield of 3,5-DNP increases with the concentration of TEA added to the solution until the TEA concentration is about  $1.2 \times 10^{-3}$  M, above which the quantum yield decreases with a further increase of the amine concentration [2]. This behaviour of the quantum yield of 3,5-DNP as a function of the added concentration of TEA can be simulated more accurately by the mechanism shown in Scheme 2 than has been possible using previously proposed mechanisms [2, 3].

In Scheme 2 we assume that the encounter between TEA and excited 3,5-DINA leads to deactivation of the excited molecule without the formation of any intermediate from which 3,5-DNP could be formed. By analogy with the case of 3-NA we assume that only attack of  $\text{OH}^-$  on atom C-1 of the carbon ring at the triplet molecule leads to production of 3,5-DNP. The rate constant for the formation of a  $\sigma$  bond between  $\text{OH}^-$  and C-1 is denoted by  $k_{\text{OH}}'$ . The sum of the rate constants for all other possible reactions of  $\text{OH}^-$  with the triplet molecule is denoted by  $k_{\text{OH}}''$ . These other reactions do not lead to formation of 3,5-DNP. According to Scheme 2, the quantum yield  $\Phi$  of 3,5-DNP is given by

$$\frac{1}{\Phi} = \alpha \left( 1 + \beta \frac{1}{[\text{OH}^-]} + \gamma \frac{[\text{TEA}]}{[\text{OH}^-]} \right) \quad (6)$$

where

$$\alpha = \Phi_T^{-1} \Phi_P^{-1} \left( 1 + \frac{k_{\text{OH}}''}{k_{\text{OH}}'} \right)$$



Scheme 2

$$\beta = \frac{k_0}{k_{\text{OH}'} + k_{\text{OH}}''}$$

$$\gamma = \frac{k_{\text{TEA}}}{k_{\text{OH}'} + k_{\text{OH}}''}$$

$\Phi_{\text{T}}$  is the quantum yield of the triplet state of 3,5-DINA,  $\Phi_{\text{P}} \equiv k_{\text{p}} / (k_{\text{p}} + k_{\text{r}})$ , and  $[\text{OH}^-]$  and  $[\text{TEA}]$  are the concentrations of the  $\text{OH}^-$  ions and the free base form of TEA which result from the base-acid equilibrium [13]



The experimental values of  $\Phi^{-1}$  for the concentration range  $0.45 \times 10^{-3} < [\text{TEA}] + [\text{TEAH}^+] < 0.3 \text{ M}$  are given in Table 3 which also lists values of  $\phi^{-1}$  obtained from a simulation based on eqn. (6) in which  $\alpha = 2.94$ ,  $\beta = 0.49 \times 10^{-3} \text{ M}$  and  $\gamma = 0.8$ . These values were obtained by numerically fitting the results of eqn. (6) to the experimental values of  $\Phi$  in a few iterations in which the coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  were varied and  $K_{\text{b}}$  was kept fixed. Owing to the uncertainty in the temperature of the samples for which the quantum yields were determined, the accuracy of our fit is expected to be limited by a possible inappropriate choice of the value of  $K_{\text{b}}$ .

Our values of  $\alpha$ ,  $\beta$  and  $\gamma$  agree with those calculated from other experimental data. The values  $\alpha = 2.64$  and  $\beta = 0.35 \times 10^{-3} \text{ M}$  were obtained from the results of the continuous irradiation of 3,5-DINA in the presence of  $\text{OH}^-$  [2], and a value of  $\gamma \approx 1$  was obtained from the time-resolved study of the photoreaction of 3,5-DINA in the presence of TEA [3]. These results provide evidence that the formation of an exciplex between TEA

TABLE 3

Reciprocal values of the experimental quantum yields of formation of 3,5-dinitrophenolate and the results according to eqn. (6) for the photohydrolysis of aqueous solutions of 3,5-dinitroanisole in the presence of triethylamine ( $pK_b$  3)

[TEA] ( $\times 10^{-3}$ M)	[OH <sup>-</sup> ] ( $\times 10^{-3}$ M)	$1/\Phi_{\text{calc}}^a$	$1/\Phi_{\text{exp}}^b$	$\Delta^c$ (%)
0.11	0.34	7.98	8.02	0
0.18	0.42	7.32	7.4	-1
0.33	0.57	6.78	6.7	1
0.50	0.70	6.63	5.9	12
0.68	0.82	6.57	6.3	4
1.27	1.13	6.85	6.7	2
1.70	1.3	7.11	7.1	0
2.82	1.68	7.76	7.7	1
4.00	2.00	8.38	9.1	-8
6.46	2.54	9.50	9.1	4
9.00	3.00	10.50	10.8	-3
14.1	3.76	12.19	13.2	-8
19.6	4.42	13.69	13.8	-1
25.0	5.00	15.03	15.9	-5
30.5	5.52	16.23	16.7	-3
36.0	6.00	17.33	17.2	1
41.6	6.44	18.36	18.9	-3
55.5	7.45	20.71	20	4
99	9.95	26.57	25	6
110	10.5	27.76	27.8	0
138	11.8	30.79	30	3
206	14.3	36.88	37	0
254	15.9	40.62	40	1
283	16.8	42.72	43	-1

<sup>a</sup>Results according to eqn. (6).

<sup>b</sup>From refs. 2 and 3.

<sup>c</sup>Deviation of  $1/\Phi_{\text{calc}}$  relative to  $1/\Phi_{\text{exp}}$ .

and 3,5-DINA, previously denoted by  $X^u(\text{TEA})$  [3], does not precede the formation of the  $\sigma_1$  complex 1-hydroxy-1-methoxy-3,5-dinitrobenzene. We assumed above that the encounter between TEA and the excited 3,5-DINA leads to deactivation of the nitroanisole. There are two conceivable mechanisms for this deactivation: (1) electron transfer from TEA to the triplet state of 3,5-DINA resulting in a triplet radical ion pair which subsequently crosses to the singlet radical pair state and finally decays to the ground state; (2) the formation of the 1-TEA-1-methoxy-3,5-dinitrobenzene complex. The  $\sigma$  complex in the second mechanism will undoubtedly decompose by releasing TEA, because TEA is a much better leaving group than  $\text{OCH}_3^-$  [14].

### 4.3. The photoreaction of 3,5-dinitroanisole in mixtures of $H_2O$ and $CH_3CN$ in the presence of $OH^-$

The quantum yield of 3,5-DNP formation at various  $OH^-$  concentrations has been studied for several solvent mixture compositions [2]. We obtain a linear relation between  $\Phi^{-1}$  and  $[OH^-]^{-1}$  of the form

$$\Phi^{-1} = \text{intercept} + \text{slope} \times [OH^-]^{-1}$$

for each composition. The coefficients intercept and slope and the correlation coefficient of the fit are listed in Table 4 for various solvent mixtures. The following three ratios are also given in Table 4:  $R_1 = \text{slope}/\text{intercept}$ , the ratio  $R_2$  of the triplet decay constant  $k_0$  to the rate constant  $k_{OH}$  obtained from the time-resolved experiments [2] and  $R_3 = R_1/R_2$ .

If, in the presence of  $OH^-$ , 3,5-DINA reacts according to 2 the ratios  $R_1$  and  $R_2$  should have equal values and there should be a linear relation between  $\Phi^{-1}$  and  $[OH^-]^{-1}$ . Apparently only the latter condition is satisfied. A previous attempt to explain the differences between  $R_1$  and  $R_2$  and to identify the transient absorptions which were observed in the time-resolved experiments led to the suggestion that an exciplex is formed between  $OH^-$  and 3,5-DINA prior to the formation of the  $\sigma_1$  complex 1-hydroxy-1-methoxy-3,5-dinitrobenzene [2]. An absorption band at  $\lambda > 600$  nm, which was reported to appear for alkaline solutions after the decay of the triplet population, was attributed to this exciplex. However, we could not reproduce this absorption band, but instead observed a monotonic decline in the absorption spectrum between 600 and 660 nm. From this observation and from the fact that the formation of 3,5-DNP in the presence of TEA does not proceed via an intermediate complex with TEA, we conclude by analogy with the case of 3-NA that the  $\sigma_1$  complex is formed readily when the triplet state of 3,5-DINA encounters  $OH^-$ . The differences between  $R_1$  and  $R_2$ , which are determined from the results of steady irradiation and time-resolved experiments, can be attributed to inaccuracies in the experimental data. Since  $k_0$  depends strongly on the concentration of  $CH_3CN$

TABLE 4

Effect of the  $CH_3CN$  concentration in the  $H_2O-CH_3CN$  mixed solvents on the intercept and slope of the linear relation between  $\Phi^{-1}(3,5\text{-DNP})$  and  $[OH^-]^{-1}$  and on  $R_2^a$

$[CH_3CN]$ (mol.%)	Intercept <sup>b</sup>	Slope <sup>b</sup> ( $\times 10^{-3}$ M)	Correlation coefficient <sup>b</sup>	$R_1$ ( $\times 10^{-3}$ M)	$R_2^c$ ( $\times 10^{-3}$ M)	$R_3$
0	2.64	0.9	0.997	0.35	0.27	1.3
4	2.48	1.01	0.951	0.41	0.29	1.4
15	2.05	2.69	0.991	1.3	1	1.3
26	1.52	13.95	0.99996	9.17	6	1.5
41	1.36	40.7	0.99997	30	20	1.5

<sup>a</sup>See text for details.

<sup>b</sup>From ref. 2, p. 100.

<sup>c</sup>From ref. 2, p. 126.



in the solvent mixtures, the temperature and the oxygen concentration in the sample [2, 11], slight differences between the values of these parameters in the two different experiments result in large deviations of the ratio  $R_1/R_2$  from unity.

In contrast with the reaction of 3-NA, it is not clear in the reaction of 3,5-DINA whether the final product 3,5-DNP is still being formed after the triplet state of 3,5-DINA has disappeared, *i.e.* whether the addition of  $\text{OH}^-$  to C-1 is the rate-determining step in the formation of 3,5-DNP. The transient spectrum of alkaline solutions of 3,5-DINA, seen just after the disappearance of the triplet population of 3,5-DINA and denoted previously by {X} shows maxima at 395 nm and 570 nm. A few microseconds later this spectrum has changed to that denoted by {Y} which has maxima at 410 nm and 505 nm. Spectrum {Y} changes slowly to the final stable spectrum.

The  $\sigma_1$  complex can be observed when  $k_0 + k_{\text{OH}}[\text{OH}^-]$  is larger than its decay constant. This condition is expected to be satisfied because the value of  $k_{\text{OH}}$  is approximately eight times larger than that obtained in the case of 3-NA.

It is known that the stability of  $\sigma$  complexes formed in thermal reactions of nitrobenzenes with nucleophiles such as  $\text{OH}^-$  and  $\text{OCH}_3^-$  increases with the number of  $\text{NO}_2$  substituents on the aromatic ring [15]. Therefore the appearance of  $\sigma_1$  complexes in the photoreaction of 3,5-DINA is probable. Knyazev *et al.* [16] observed the  $\sigma_1$  complex 1-methoxy-1- $\beta$ -methoxyethoxy-3,5-dinitrobenzene in the thermal reaction of 1- $\beta$ -methoxyethoxy-3,5-dinitrobenzene with  $\text{OCH}_3^-$ . This  $\sigma$  complex, which resembles the  $\sigma_1$  complex of 3,5-DINA with  $\text{OH}^-$ , has an absorption maximum at 420 nm. Therefore the maximum at 395 nm in spectrum {X} may be due to the  $\sigma_1$  complex formed during the photoconversion of 3,5-DINA to 3,5-DNP. However, photoreactions of nitroanisoles and nitroveratroles with  $\text{OH}^-$  or  $\text{OCH}_3^-$  yield products in which the substituent para to the  $\text{NO}_2$  group is replaced [8]. We must therefore consider the possibility that the addition of  $\text{OH}^-$  is not restricted to the C-1 position in the excited nitroanisole. We attribute the long-wavelength absorption maximum in spectrum {X} to a  $\sigma_4$  complex between  $\text{OH}^-$  and 3,5-DINA. Similar complexes formed in thermal reactions of dinitrobenzene compounds with  $\text{OH}^-$  or  $\text{OCH}_3^-$  all show two maxima in the near-UV-visible wavelength region [17-19]. The long-wavelength band appears between 535 and 610 nm and the short-wavelength band appears between 350 and 400 nm. On these grounds we identify the band at 400 nm in spectrum {X} with the second band of the  $\sigma_4$  complex between 3,5-DINA and  $\text{OH}^-$ . We therefore suggest that the transformation from {X} to {Y} corresponds to the disappearance of the  $\sigma_4$  complex only. Consequently the decay constants of the transient absorption bands at 395 nm and 570 nm must be equal. This has been observed experimentally [3]. In the description just suggested, we must conclude that the  $\sigma_1$  complex is absent from both species {X} and species {Y}. The  $\sigma_1$  complex must have disappeared before we observe

spectrum {X} in accordance with its stability which is less than that of the  $\sigma_4$  complex. Consequently, 3,5-DNP is among the species giving rise to spectrum {X}.

The spectral change from {X} to {Y} is probably due to the conversion of the  $\sigma_4$  complex to the isomeric  $\sigma_2$  complex. The  $\sigma_2$  complex is known to be the most thermodynamically stable of all the  $\sigma$  complexes detected in thermal reactions between dinitrobenzene compounds and a specific nucleophile [18, 19]. However, the activation energy for the formation of the  $\sigma_2$  complex is higher than that for the formation of the  $\sigma_4$  complex. For 4-X-2,6-dinitroanisoles (X = H or an electron-withdrawing substituent) with  $\text{OCH}_3^-$  the rearrangement from the less stable  $\sigma$  complex ( $\sigma_3$  in this case) to the stable  $\sigma$  complex ( $\sigma_1$ ) can be observed by nuclear magnetic resonance [20]. It has also been observed that the isomerization of these systems is strongly catalysed by methanol. From this we infer that in our system the  $\sigma_2$  complex can be formed directly from the  $\sigma_4$  complex and that the formation does not require nucleophilic attack on the C-2 atom of the excited nitroanisole. The  $\sigma_2$  complex has two absorption maxima in the near-UV-visible wavelength region: the short-wavelength band appears between 350 and 400 nm, and the long-wavelength band appears between 480 and 530 nm [21]. The maxima of spectrum {Y} are within these ranges. The transformation of {Y} to the stable final spectrum involves the decomposition of the  $\sigma_2$  complex. Some of the long-lived  $\sigma_2$  complexes may be deprotonated at high  $\text{OH}^-$  concentrations [22] and may then cause slight absorption changes and result in an  $\text{OH}^-$ -dependent decay constant for {Y}.

## References

- 1 G. P. de Gunst and E. Havinga, *Tetrahedron*, 29 (1973) 2167.  
G. P. de Gunst, *Thesis*, Leiden, 1979.
- 2 J. J. Tamminga, *Thesis*, Leiden, 1979.
- 3 C. A. G. O. Varma, J. J. Tamminga and J. Cornelisse, *J. Chem. Soc., Faraday Trans. II*, 78 (1982) 265.
- 4 J. den Heyer, T. Spee, G. P. de Gunst and J. Cornelisse, *Tetrahedron Lett.*, (1973) 1261.
- 5 G. G. Wubbels, P. H. M. van Zeijl and C. A. G. O. Varma, *Proc. 9th Symp. on Photochemistry, Pau, 1982*.
- 6 P. H. M. van Zeijl, G. G. Wubbels and C. A. G. O. Varma, to be published.
- 7 L. A. McLachlan, *J. Magn. Res.*, 26 (1977) 223.
- 8 H. C. H. A. van Riel, G. Lodder and E. Havinga, *J. Am. Chem. Soc.*, 103 (1981) 7257.
- 9 E. Ullman and P. Singh, *J. Am. Chem. Soc.*, 94 (1972) 5077.
- 10 D. A. Duddell and J. T. Richards, in M. A. West (ed.), *Lasers in Chemistry*, Elsevier, Amsterdam, 1977, p. 349.
- 11 F. L. Plantenga, *Thesis*, Leiden, 1982.
- 12 R. O. de Jongh, *Thesis*, Leiden, 1966.
- 13 *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, OH, 60th edn., 1980.

- 14 C. F. Bernasconi, *Acc. Chem. Res.*, *11* (1978) 147.
- 15 F. Terrier, *Chem. Rev.*, *82* (1982) 77.
- 16 V. N. Knyazev, V. N. Drozd and A. A. Klimov, *J. Org. Chem. U.S.S.R.*, *12* (1976) 2319.
- 17 R. J. Pollitt and B. C. Saunders, *J. Chem. Soc.*, (1965) 4615.
- 18 M. R. Crampton and H. A. Khan, *J. Chem. Soc., Perkin Trans. II*, (1973) 710.
- 19 C. A. Fyfe, M. Cocivera and S. W. H. Damji, *J. Am. Chem. Soc.*, *97* (1975) 5707.
- 20 K. L. J. Servis, *J. Am. Chem. Soc.*, *89* (1967) 1508.
- 21 M. J. Strauss, *Chem. Rev.*, *70* (1970) 667.
- 22 B. Gibson and M. R. Crampton, *J. Chem. Soc., Perkin Trans., II* (1979) 648.