

## Dynamic Behavior of Photoexcited Solutions of 4-Nitroveratrole Containing OH<sup>-</sup> or Amines

Alexander M. J. van Eijk,<sup>†</sup> A. Herbert Huizer,<sup>†</sup> Cyril A. G. O. Varma,<sup>\*,†</sup> and Jorge Marquet<sup>‡</sup>

Contribution from the Department of Chemistry, Leyden University, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leyden, The Netherlands, and Department of Chemistry, Universidad Autonoma de Barcelona, Bellaterra 08193, Barcelona, Spain. Received April 11, 1988

**Abstract:** Kinetics and mechanism of the photoinduced reactions of 4-nitroveratrole (NV) with OH<sup>-</sup> and a number of aliphatic amines have been studied by laser kinetic spectroscopy and by measurement of transient changes in electrical conductivity. In the case of OH<sup>-</sup> only reactions with NV in its lowest triplet state (T<sub>0</sub>) are observed and these lead to substitution of the OCH<sub>3</sub> group at atom C(2) of the aromatic molecule and to formation of a number of transient  $\sigma$ -complexes, which return to NV. In the case of the amines both excited singlet state and triplet state reactions are observed. The singlet state reactions with methylamine and with *n*-hexylamine lead to substitution of the OCH<sub>3</sub> group at atom C(2). Although piperidine quenches the excited singlet states involved, this does not lead to substitution at C(2). The triplet state reactions with the amines start with a discrete electron-transfer reaction in which the radical anion (E) of NV is formed. Subsequent reaction of E with the radical cation of the amine leads to substitution at C(1) and to a number of  $\sigma$ -complexes, which return to NV.

The photoinduced nucleophilic substitution reactions of aromatic molecules have been the subject of numerous studies since the discovery in 1956 of the photoreaction of nitrophenyl phosphates and sulfates with hydroxide ions.<sup>1,2</sup> Havinga and his co-workers reported that 3-nitroanisole is more reactive than 4-nitroanisole in the photoinduced reaction with OH<sup>-</sup>.<sup>3</sup> This led to the conclusion that the nitro group has a meta-directing influence toward nucleophilic substitution in the reactive excited triplet state. The meta-directing influence of the nitro group is encountered in the photoinduced substitution of a methoxy group in 4-nitroveratrole (NV, Figure 1) by the nucleophiles NH<sub>3</sub>,<sup>4</sup> OH<sup>-</sup>,<sup>5</sup> and methylamine.<sup>6</sup> The regioselectivity of the photoinduced substitution reaction of NV with amines depends on the ionization potential of the amine.<sup>7,8</sup> The photoreaction of NV and *n*-hexylamine yields a mixture of NV substituted at C(1) and C(2) in the ratio 5.9:1,<sup>8</sup> whereas in the photoreaction of piperidine and NV substitution takes place exclusively at C(1).<sup>9</sup> The involvement of two different excited states was suggested to explain the differences in regioselectivity.<sup>8,9</sup>

Time-resolved electronic absorption spectroscopy has been used successfully to unravel the mechanism of the photoinduced substitution of the methoxy group in 3-nitroanisole by OH<sup>-</sup> and hydroxyethylamine.<sup>10</sup> It has been established in this manner that the substitution reaction is completed in less than a few nanoseconds after the disappearance of the triplet state of 3-nitroanisole. The rate-determining step in this reaction is the addition of the nucleophile to the phenyl ring.

The aim of the present paper is to clarify the mechanism and the regioselectivity of the photoinduced substitution reaction of NV with OH<sup>-</sup> and amines by means of time-resolved electronic absorption spectroscopy and by studying photoinduced transient changes in electrical conductivity of the solutions.

In the discussion of the transient behavior of the photoexcited solution the following notation will be used. A particular set consisting of several types of molecular species A<sub>i</sub> will be denoted by {A}. A particular compound B in its electronic state, labeled J, will be referred to as B(J). The electronic ground state, the *n*th excited singlet state, and the lowest triplet state are referred to by J = S<sub>0</sub>, J = S<sub>n</sub>, and J = T<sub>0</sub>, respectively. The contribution to the transient change in optical density at wavelength  $\lambda$  induced by laser excitation of species B and arising from transient species {A} at time *t* is denoted by  $\Delta OD(B, A, \lambda, t)$ . The sum of all these contributions is denoted by  $\Delta OD(B, \lambda, t)$ . A reference electronic absorption spectrum, e.g., of stable species of type R will be denoted by OD(R,  $\lambda$ ).

### Experimental Section

The compound 4-nitroveratrole was prepared by nitration of veratrole with nitric acid in acetic acid.<sup>9</sup> Potassium hydroxide, *n*-hexylamine, methylamine, triethylamine (TEA), 1,3-dinitrobenzene (DNB), and *N,N'*-dimethyl-4,4'-bipyridinium dichloride (methylviologen, MV<sup>2+</sup>) were pure commercial products and were not purified further. Commercially available piperidine has been distilled prior to use. The compound 3,3,4,4-tetramethyldiazetidine dioxide (TMDD) was prepared according to the procedure given by Ullman and Singh.<sup>11</sup> Acetonitrile and 1,4-dioxane were of spectro-grade quality. Water was demineralized before use.

A mixture of H<sub>2</sub>O and CH<sub>3</sub>CN (80:20 v/v) was used as solvent in the majority of experiments. When another solvent was used, this is mentioned explicitly in the text.

The following compounds have been used as triplet state quenchers: TMDD, potassium sorbate, and 1,3-cyclohexadiene.

The concentration of the nucleophiles in solutions of NV amounted typically to 0.03 M. The pK<sub>b</sub> value of the amines was used to determine the amount of amine in its free base form. Rate constants for the excited state reactions of NV with amines are corrected for the competing reaction with OH<sup>-</sup> present in the solution.

Transient optical electronic absorptions have been measured with a kinetic spectrometer described previously.<sup>12</sup> The sample is excited with a pulse from an excimer laser (Lambda Physik, Model EMG100) of 308 nm, circa 7 ns fwhm, and integrated energy *I<sub>L</sub>* of typically 15 mJ. The transient species are probed by monochromatic light, emerging from a pulsed 500 W Xenon lamp, whose light passes through a monochromator. Absorption of this light by transient species is detected in real time by means of a system consisting of a photomultiplier and a 500-MHz transient digitizer (Tektronix, Model R 7912). A flow system is used to refresh the solution after each pulse to prevent interference of photo-products in the measurements.

(1) Havinga, E.; de Jong, R. O.; Dorst, W. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 378.

(2) (a) Cornelisse, J.; Havinga, E. *Chem. Rev.* **1975**, *75*, 353. (b) Döpp, D. O. *Top. Curr. Chem.* **1975**, *55*, 49.

(3) (a) Havinga, E.; de Jongh, R. O. *Bull. Soc. Chim. Belg.* **1962**, *71*, 803.

(b) de Vries, S.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 601.

(4) van Vliet, A. Thesis, Leiden, 1969.

(5) Stratenus, J. L. Thesis, Leiden, 1966.

(6) Kronenberg, M. E.; van der Heyden, A.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 254.

(7) Cervello, J.; Figueredo, M.; Marquet, J.; Moreno-Manas, M.; Bertran, J.; Lluch, J. M. *Tetrahedron Lett.* **1984**, *25*, 4147.

(8) Cantos, A.; Marquet, J.; Moreno-Manas, M. *Tetrahedron Lett.* **1987**, *28*, 4191.

(9) Cantos, A.; Marquet, J.; Moreno-Manas, M. *Tetrahedron* **1988**, *44*, 2607.

(10) van Zeijl, P. H. M.; van Eijk, A. M. J.; Varma, C. A. G. O. *J. Photochem.* **1985**, *29*, 415.

(11) (a) Singh, P.; Boocock, D. G. B.; Ullman, E. F. *Tetrahedron Lett.* **1971**, 3935. (b) Ullman, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077.

(12) Varma, C. A. G. O.; Plantenga, F. L.; Huizer, A. H.; Zwart, J. P.; Bergwerf, Ph.; van de Ploeg, J. P. M. *J. Photochem.* **1984**, *24*, 133.

<sup>†</sup>Leyden University.

<sup>‡</sup>Universidad Autonoma de Barcelona.

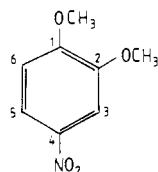


Figure 1. Structural formula for 4-nitroveratrole (NV).

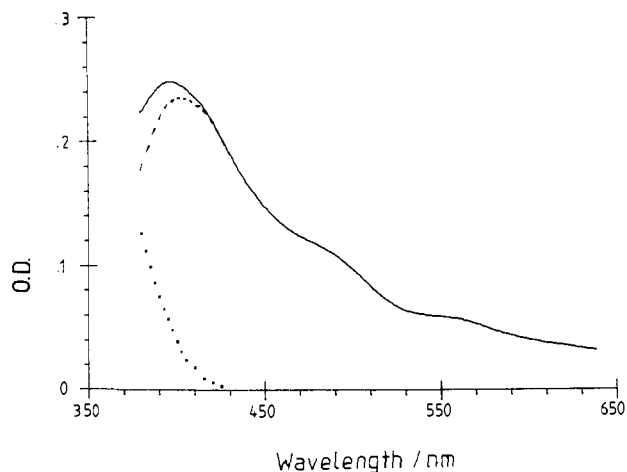


Figure 2. Electronic absorption spectra of a solution of 4-nitroveratrole (NV) in  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  (80:20 v/v), before and after laser excitation. Curve a,  $\text{OD}(\text{NV}, S_0, \lambda)$  (···); curve b,  $\Delta\text{OD}(\text{NV}, \lambda, t_L)$  (---); curve c,  $\Delta\text{OD}(\text{NV}, X, \lambda, t_L)$  (—).

Solutions of NV with an optical density of 1.0 at 308 nm were used in the time-resolved electronic absorption experiments. The solutions were not degassed. Only the lifetime of the triplet state of NV was affected noticeably by the presence of oxygen. The compounds DNB and  $\text{MV}^{2+}$  in the solutions of NV and amines absorb part of the laser pulse, but this does not yield transient species that interfere with the photoinduced reaction of NV.

The measurement of photoinduced transient electrical conductivity has been described previously.<sup>13</sup> The apparatus consists of a conduction cell in which a rectangular voltage pulse is applied across the two electrodes. The solution between the electrodes in the cell is excited with a pulse from an excimer laser (Lambda Physik, Model EMG500) of 308 nm, circa 15 ns fwhm, and integrated energy  $I_L$  of typically 50 mJ. An RC network consisting of a resistor R in parallel with a variable capacitor C is used to compensate for the permanent conductance. One terminal of the RC network is connected to one of the electrodes and to the inner conductor of a coaxial cable through which the transient signal is transmitted to the transient digitizer, mentioned above.

The solutions of NV in  $\text{CH}_3\text{CN}$  used in the study of photoinduced transient electrical conductivity had an optical density of 0.3 at 308 nm. The use of mixtures of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$  (80:20 v/v) as solvent was impossible due to the high permanent conductance.

## Results and Discussion

**1. The Triplet State of 4-Nitroveratrole.** The electronic absorption spectrum  $\text{OD}(\text{NV}, S_0, \lambda)$  of NV ( $S_0$ ) is represented by the dotted line in Figure 2. The dashed line in Figure 2 represents the transient electronic absorption spectrum  $\Delta\text{OD}(\text{NV}, \lambda, t_L)$  of a solution of NV in  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  (80:20 v/v) at time  $t_L$ . Time  $t_L$  denotes the point of time just after termination of the laser pulse. The transient spectrum overlaps the spectrum of NV in its ground state for  $\lambda \leq 430$  nm. In this region a negative absorption  $\Delta\text{OD}(\text{NV}, S_0, \lambda, t_L)$ , caused by the partially depleted ground-state population, contributes to  $\Delta\text{OD}(\text{NV}, \lambda, t_L)$ . In principle the transient absorption may contain contributions from several yet unidentified species  $X_i$ . This set of species will be denoted by  $\{X\}$  and their contribution to  $\Delta\text{OD}(\text{NV}, \lambda, t_L)$  will be indicated by  $\Delta\text{OD}(\text{NV}, X, \lambda, t_L)$ . The contribution  $\Delta\text{OD}(\text{NV}, X, \lambda, t_L)$  is represented by the solid line in Figure 2. The spectrum  $\Delta\text{OD}(\text{NV},$

Table I. Values of the Rate Constant  $k_D$  for the Decay of  $\text{NV}(T_0)$  in Various Solvents, When the Solution Does Not Contain Any Nucleophile

solvent	$10^6 k_D$ ( $\text{s}^{-1}$ )
$\text{H}_2\text{O}$	0.45
$\text{H}_2\text{O}/1,4\text{-dioxane}$ (80:20 v/v)	0.50
$\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (80:20 v/v)	0.55
1,4-dioxane	2.70
$\text{CH}_3\text{CN}$	2.99

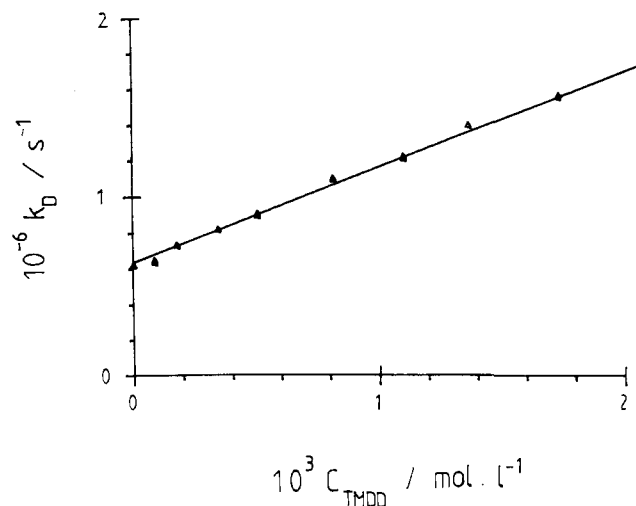


Figure 3. Variation of the rate constant  $k_D$  for the decay of  $\text{NV}(T_0)$  as a function of  $C_{\text{TMDD}}$ .

$X, \lambda, t_L$ ) is obtained by subtracting  $\Delta\text{OD}(\text{NV}, S_0, \lambda, t_L)$  from  $\Delta\text{OD}(\text{NV}, \lambda, t_L)$ . The contribution  $\Delta\text{OD}(\text{NV}, S_0, \lambda, t_L)$  is given by

$$\Delta\text{OD}(\text{NV}, S_0, \lambda, t_L) = \epsilon(V, S_0, \lambda) \Delta C(\text{NV}, S_0, t_L) \quad (1)$$

where

$$\Delta C(\text{NV}, S_0, t_L) = \phi_T(\text{NV}) \Delta C(\text{NV}, S_0, t_0) \quad (2)$$

and

$$\Delta C(\text{NV}, S_0, t_0) = C(\text{NV}, S_0, t_0) - C(\text{NV}, S_0, t < 0) \quad (3)$$

In eq 2  $\phi_T(\text{NV})$  is the triplet quantum yield of NV, which under these conditions amounts to 0.31.<sup>9</sup> The quantity  $\Delta C(\text{NV}, S_0, t_0)$  is the concentration of molecules initially removed from the ground-state population by the laser pulse. In order to determine the magnitude of  $\Delta C(\text{NV}, S_0, t_0)$  we have used naphthalene (N) as an actinometer for the laser intensity by measuring the laser-induced triplet-triplet absorption  $\Delta\text{OD}(\text{N}, T_0, \lambda, t_L)$  in the same setup. The triplet state quantum yield  $\phi_T(\text{N})$  of naphthalene is known, as well as the molar extinction coefficient  $\epsilon(\text{N}, T_0, \lambda)$  for the absorptions of naphthalene in its lowest triplet state.<sup>14</sup> A solution of naphthalene in  $\text{CH}_3\text{CN}$  with the same optical density at 308 nm as the NV solution is used as the actinometer. The optical density  $\Delta\text{OD}(\text{N}, T_0, \lambda, t_L)$  yields

$$\Delta C(\text{NV}, S_0, t_0) = \Delta C(\text{N}, S_0, t_0) = \frac{\Delta\text{OD}(\text{N}, T_0, \lambda, t_L)}{\epsilon(\text{N}, T_0, \lambda) \phi_T(\text{N})} \quad (4)$$

The point of time at which the transient absorption  $\Delta\text{OD}(\text{NV}, X, \lambda, t)$  has vanished practically completely (i.e.,  $\Delta\text{OD}(\text{NV}, X, \lambda, t) < 0.001$ ) will be denoted by  $t_X$ . The time interval  $t_L \leq t < t_X$  will be indicated by period I. The decay of  $\Delta\text{OD}(\text{NV}, X, \lambda, t)$  in period I is described by a single exponential function

$$\Delta\text{OD}(\text{NV}, X, \lambda, t) = \Delta\text{OD}(\text{NV}, X, \lambda, t_L) \exp[-k_D(t - t_L)] \quad (5)$$

Since  $\Delta\text{OD}(\text{NV}, X, \lambda, t)$  vanishes completely after a single exponential decay,  $\{X\}$  is taken to contain a single species X. The values of the decay constant  $k_D$  obtained for NV in various solvents are listed in Table I.

(13) (a) Warman, J. M.; de Haas, M. P.; Hummel, A.; Varma, C. A. G. O.; van Zeyl, P. H. M. *Chem. Phys. Lett.* **1982**, *87*, 83. (b) de Haas, M. P.; Warman, J. M. *Chem. Phys.* **1982**, *73*, 35.

(14) Birks, J. B., Ed. *Organic Molecular Photophysics*; John Wiley & Sons: London, 1973; Vol I, p 310; Vol II, p 481.

The transient spectrum  $\Delta OD(NV, X, \lambda, t_L)$  cannot be attributed to an intermediate in a photochemical reaction, because solutions of NV do not change noticeably by UV irradiation. The transient absorption may be quenched by TMDD and oxygen. This is illustrated by the Stern-Volmer plot, shown in Figure 3, for quenching of the transient absorption of a solution of NV by TMDD. The rate constant  $k_q(\text{TMDD})$  for quenching amounts to  $0.54 \times 10^9 \text{ s}^{-1}$ .

The decay constant  $k_D$  is not affected by variation of the laser energy  $I_L$  between 15 and 1.5 mJ. Therefore bimolecular reactions between two transient species as well as between transient species and  $NV(S_0)$  may be excluded. The decay constant  $k_D$  does not change when the concentration of NV is varied. This means that excited states of multimers are not involved in the transient absorption. However, the composition of the solvent has a strong influence on  $k_D$ , as shown in Table I. The lowest value of  $k_D$  is observed, when pure water is used as the solvent and  $k_D$  amounts then to circa  $0.45 \times 10^6 \text{ s}^{-1}$ . When the solution contains acetonitrile or 1,4-dioxane,  $k_D$  is larger and it reaches a value of circa  $3.0 \times 10^6 \text{ s}^{-1}$  in pure 1,4-dioxane or acetonitrile. A similar influence of the  $H_2O$  concentration in aqueous solvent mixtures has been observed in the case of the decay constant of the lowest triplet states of 3,5-dinitroanisole and 3-nitroanisole. This behavior has been attributed to hydrogen bonding to an  $NO_2$  group of the triplet state molecule.<sup>15</sup>

The observed behavior of the decay constant of the transient absorption of NV indicates therefore that the transient absorption  $\Delta OD(NV, X, \lambda, t_L)$  is due to the population of  $NV(T_0)$ .

**2. The Reaction of 4-Nitroveratrole with  $OH^-$ .** The acid-base equilibrium of amines in aqueous solutions involves the formation of hydroxide ions. The hydroxide ions are nucleophiles and react with NV. The substitution products will be denoted by  $P_n-N$ , where  $n$  refers to the label of the ring carbon atom at which the substitution takes place and  $N$  refers to the nucleophile. The photoreaction of NV and  $OH^-$  leads almost exclusively to the formation of  $P_2-OH$ , 2-hydroxy-4-nitroanisole.<sup>16</sup> We studied this reaction in order to be able to distinguish between effects due to  $OH^-$  and due to the free base form of the amines.

The presence of  $0.167 \times 10^{-3} \text{ M } OH^-$  in a solution of NV causes no changes in  $\Delta OD(NV, T_0, \lambda, t_L)$ . The triplet decay constant  $k_T$  increases with the hydroxide ion concentration. This is due to the reaction of  $NV(T_0)$  with  $OH^-$ . The relation between  $k_T$  and the concentration  $C_{OH}$  of hydroxide ions is

$$k_T = k_D + k_q(OH)C_{OH} \quad (6)$$

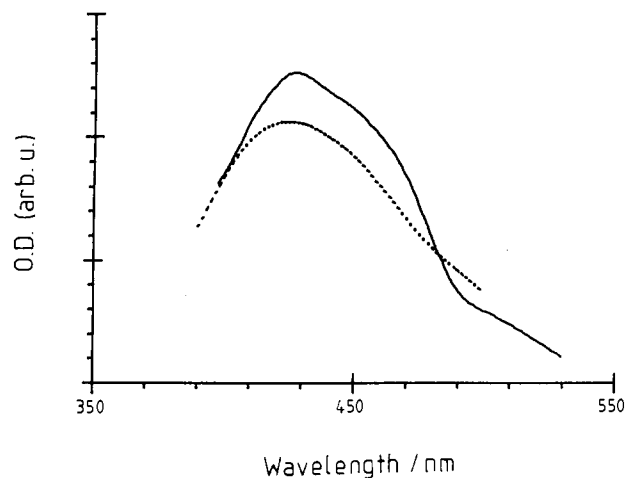
where  $k_q(OH)$  is the second-order rate constant for the reaction of  $OH^-$  with  $NV(T_0)$ . The rate constant  $k_q(OH)$  amounts to  $44.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

Starting at time  $t_X$ , when the triplet state absorption has become negligible, i.e., at  $t_X \approx 0.5 \mu\text{s}$ , a new spectrum  $\Delta OD(NV, Y_1, \lambda, t_X)$  is observed. The new spectrum, which is represented by the solid line in Figure 4, is obtained by applying the following procedure to subtract the contribution  $\Delta OD(NV, S_0, \lambda, t_X)$  from  $\Delta OD(NV, \lambda, t_X)$ . The contribution  $\Delta OD(NV, S_0, \lambda, t_X)$  may be expressed as

$$\Delta OD(NV, S_0, \lambda, t_X) = \Delta OD(NV, S_0, \lambda, t_L) \left( 1 - \frac{k_D \beta(t_X)}{k_D + k_q(OH)C_{OH}} \right) \quad (7)$$

where  $\beta(t_X)$  is the fraction of  $NV(T_0)$  that has disappeared at  $t = t_X$ .

The optical density  $\Delta OD(NV, Y_1, \lambda, t_X)$  increases with  $C_{OH}$  but decreases with the concentration  $C_{TMDD}$  of TMDD in the solution.



**Figure 4.** (—) Transient absorption spectrum  $\Delta OD(NV, Y_1, \lambda, t_X)$  of the laser-excited solution of NV in  $H_2O/CH_3CN$  (80:20 v/v) containing  $OH^-$ . (---) Absorption spectrum  $OD(P_2-OH, \lambda)$  of the final reaction product.

A linear relationship between  $\{\Delta OD(NV, Y_1, \lambda, t_X)\}^{-1}$  and  $\{C_{TMDD}\}^{-1}$  is observed. Therefore  $\Delta OD(NV, Y_1, \lambda, t_X)$  must be attributed to a collection  $\{Y_i\}$ , consisting of species  $Y_{1i}$  formed by reactions of  $OH^-$  with  $NV(T_0)$ .

At this point we introduce a time interval, referred to as period II, defined by  $t_X \leq t < t_E$ , where  $t_E$  is the instant when the absorption spectrum of the solution has become time independent on our time scale, which extends up to 1 ms. The value of  $t_E$  is about 0.7 ms. The decay of spectrum  $\Delta OD(NV, Y_1, \lambda, t)$  in period II can be reproduced with a function of the form

$$\Delta OD(NV, Y_1, \lambda, t) = G_Y + H_Y \exp\{-k_{Yq}(t - t_X)\} \quad (8)$$

The term  $G_Y$  has to be identified with the absorption by species  $Y_{1p}$  that do not decay significantly within period II, i.e.

$$G_Y = \sum_p \Delta OD(NV, Y_{1p}, \lambda, t_X) \quad (9)$$

The parameter  $G_Y$  is about 5 times larger than  $H_Y$ . The second term of eq 8 describes the absorption by species  $Y_{1q}$  which decay in a monoexponential manner with a rate constant  $k_{Yq}$  equal to  $10^4 \text{ s}^{-1}$ .

The disappearance of spectrum  $\Delta OD(NV, Y_{1q}, \lambda)$  coincides with the termination of period II. At times  $t > t_E$  the spectrum  $\Delta OD(P, \lambda)$  of the final products  $P$  of the reaction is observed. The shape of  $\Delta OD(P, \lambda)$  is almost the same as the shape of  $\Delta OD(NV, Y_1, \lambda, t_X)$  and  $OD(P_2-OH, \lambda)$ , the absorption spectrum of the final product of the reaction. The latter spectrum is represented by the dashed curve in Figure 4.

We conclude from the resemblance of  $\Delta OD(NV, Y_{1p}, \lambda, t_X)$  and  $OD(P_2-OH, \lambda)$  that the photoinduced substitution of NV by  $OH^-$  is completed at time  $t_X$ , i.e., just after the disappearance of  $NV(T_0)$ . Species  $Y_{1p}$  is therefore to be associated with  $P_2-OH$ . This conforms to the observation of van Zeijl et al.,<sup>10</sup> who found that the encounter of the nucleophile  $OH^-$  and triplet state 3-nitroanisole is the rate-determining step in the photohydrolysis of the latter.

Species  $Y_{1q}$  have to be identified with  $\sigma$ -complexes  $\sigma[C_n]$ , which do not yield  $P_2-OH$ . The subscript  $n$ , labeling the ring carbon atom to which the nucleophile is attached, may have the values 1, 3, 4, 5, and 6.

Scheme I shows the pathway for the reaction of NV and  $OH^-$ .

### 3. Photoinduced Reaction of 4-Nitroveratrole with Piperidine.

In the photoreaction of NV and piperidine (Pip) the methoxy group at carbon atom C(1) gets substituted.<sup>7</sup> Since the formation of this product, denoted as  $P_1$ -Pip, is strongly inhibited by triplet state quenchers such as potassium sorbate or 1,3-cyclohexadiene,<sup>8</sup> the reaction is considered to proceed via  $NV(T_0)$ .<sup>9</sup> In accordance with this, the decay constant  $k_T$  of  $NV(T_0)$  increases with the piperidine concentration. The rate constant  $k_q(\text{Pip})$ , for the bimolecular reaction of  $NV(T_0)$  with the free base form of piper-

(15) Tamminga, J. J. Thesis, Leiden, 1979.

(16) van Riel, H. C. H. A.; Lodder, G.; Havinga, E. *J. Am. Chem. Soc.* **1981**, *103*, 7257.

(17) Bernasconi, C. F. *J. Org. Chem.* **1970**, *35*, 1214.

(18) Yokoyama, K.; Nakagaki, R.; Nakamura, J.; Mutai, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2472.

(19) Duonghong, D.; Borgarello, E.; Graetzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 4685.

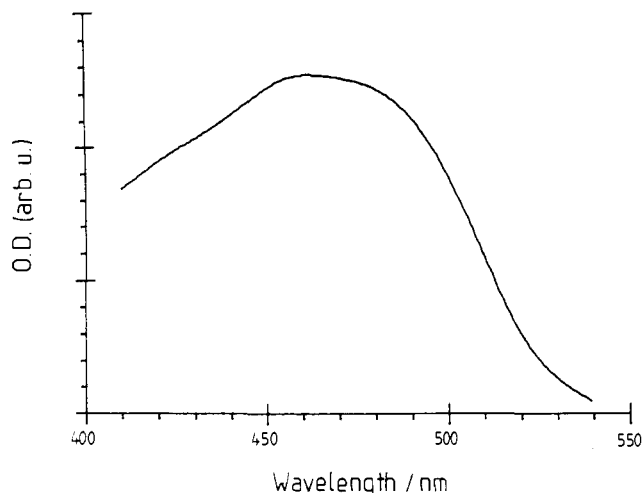
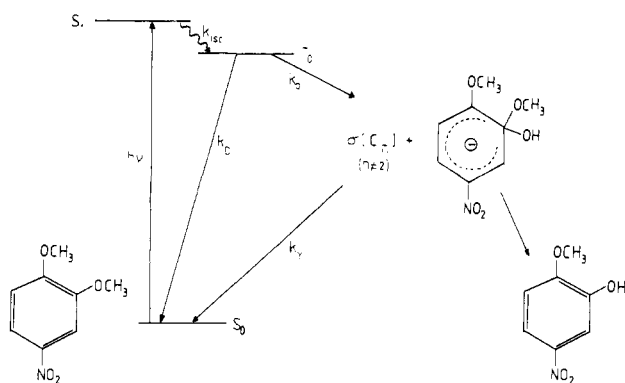


Figure 5. Transient absorption spectrum  $\Delta OD(NV, Y_2, \lambda, t_X)$  of the laser-excited solution of NV in  $H_2O/CH_3CN$  (80:20 v/v) containing piperidine.

Scheme I. Mechanism of the Reaction of  $OH^-$  with Photoexcited NV



idine, obtained from a Stern-Volmer plot, has the value  $0.11 \times 10^9 M^{-1} s^{-1}$ .

**a.  $\sigma$ -Complexes of Piperidine and 4-Nitroveratrole as Transient Species.** Just as in the case of the photoinduced reaction with  $OH^-$ , new and longer lived species are observed after the disappearance of  $NV(T_0)$ . To indicate both the resemblance and the difference with the former case, they will be denoted as  $\{Y_2\}$ .

Figure 5 shows the transient absorption spectrum  $\Delta OD(NV, Y_2, \lambda, t_X)$  of a solution of NV and 0.029 M piperidine. The wavelength region of this spectrum had to be limited to  $\lambda \geq 410$  nm, because of a substantial negative contribution from the depleted ground state population of NV to the induced change in absorption at shorter wavelengths.

The optical density due to species  $\{Y_2\}$  is being reduced by the presence of TMDD in the solution. The plot of  $\{\Delta OD(NV, Y_2, \lambda, t_X)\}^{-1}$  versus  $\{C_{TMDD}\}^{-1}$  is linear and this means that species  $\{Y_2\}$  are formed by a reaction of piperidine with  $NV(T_0)$ .

As in the case of the photoreaction with  $OH^-$ , the period II refers to the time interval  $t_X \leq t < t_E$ . Species  $\{Y_2\}$  decay monoexponentially with decay constant  $k_{Y_2}$  equal to  $14 \times 10^3 s^{-1}$  and as a result the transient absorption vanishes completely at the end of period II. If  $\{Y_2\}$  consists of several types of species they must establish a dynamic equilibrium with rate constants  $k_+$  and  $k_-$  which are both large compared to  $k_{Y_2}$ .

The species in  $\{Y_2\}$  decay mainly to  $NV(S_0)$ . Unlike the case of the photoreaction with  $OH^-$ , no indication could be obtained for the presence of the final product ( $P_1$ -Pip) among the species in  $\{Y_2\}$ . The main reason for this is that the first electronic absorption band of  $P_1$ -Pip coincides practically with that of  $NV(S_0)$ .

Considering the resemblance of  $\Delta OD(NV, Y_2, \lambda, t_X)$  and of the value of  $k_{Y_2}$  with respectively the absorption spectra<sup>17</sup> and decay rate constants<sup>18</sup> of  $\sigma$ -complexes of trinitroanisole and piperidine,

Scheme II. Structural Formulas of the  $\sigma$ -Complexes  $\sigma_0[C_1]$  and  $\sigma_-[C_1]$  between NV and Piperidine

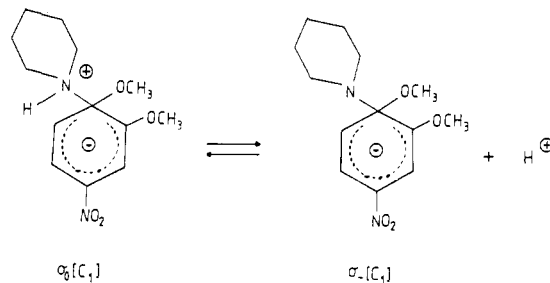


Table II. Ionization Potential IP of Various Compounds Q; Rate Constant  $k_q$  for the Reaction of Q with  $NV(T_0)$ ; Rate Constant  $k_Y$  for the Establishment of the Equilibrium  $\sigma_0[C_n] \leftrightarrow \sigma_-[C_n]$  between the  $\sigma$ -Complexes with Q and the Rate Constant  $k_Y$  for the Decay of These  $\sigma$ -Complexes

compd Q	IP (eV)	$10^6 k_q (s^{-1})$ $H_2O/CH_3CN$	$10^6 k_Y (s^{-1})$ $H_2O/CH_3CN$	$10^3 k_Y (s^{-1})$	
				$CH_3CN$	$CH_3CN$
TMDD		540			
$OH^-$		44.2		30	
methyl-amine	8.90	90.6	0.24	18	
n-hexyl-amine	8.63	99.6	0.20	17	330
piperidine	7.95	113	>1	14	930
triethyl-amine	7.15	460		12	

$\{Y_2\}$  is identified with an ensemble consisting of a number of  $\sigma$ -complexes, to be denoted by  $\sigma_m[C_n]$ . The subscript  $m$  can be either 0 or  $-$ , with the former referring to the free base form and the latter to a deprotonated form of the amine in the  $\sigma$ -complex. Scheme II shows  $\sigma_0[C_1]$  and  $\sigma_-[C_1]$ , which are the two  $\sigma$ -complexes, which could lead to the substitution product of NV and piperidine. They are probably not contained in  $\{Y_2\}$ , because their conversion into the final product  $P_1$ -Pip is expected to be as rapid as the product formation from  $\sigma[C_2]$  in the case of the photoreaction with  $OH^-$ .

When  $CH_3CN$  is used as solvent instead of the mixture  $H_2O/CH_3CN$  (80:20 v/v), this causes the dramatic increase of the value of  $k_{Y_2}$  shown in Table II. The explanation of this behavior is that  $\{Y_2\}$  consists of zwitterionic species  $\sigma_0[C_n]$  and ionic species  $\sigma_-[C_n]$ , which are both less stable in the less polar solvent, i.e., in  $CH_3CN$ .

The presence of ionic species in  $\{Y_2\}$  could be verified for the solution of NV and piperidine in  $CH_3CN$ . In that case a transient electrical conductance signal is observed. The transient conductance signal, shown in Figure 6, cannot be generated in the same manner by excitation of the pure solvent or solutions containing only one of the reactants. The conductance signal decays over the whole time range of about 100  $\mu s$  according to second-order kinetics, corresponding to homogeneous charge neutralization of oppositely charged ions with time-independent mobilities. If  $\sigma_-[C_1]$  was among the species in  $\{Y_2\}$ , breaking of the bond between  $C_1$  and the leaving  $OCH_3$  group would yield the anion  $OCH_3^-$  with a substantially higher mobility than its precursor and would consequently lead to a deviation from the observed time profile of the conductance signal. The observed decay of the conductance signal is in conformity with the proposition of formation of the final product prior to period II. Since the time range of the conductance signal lies within period II, we conclude that there are deprotonated  $\sigma$ -complexes of the type  $\sigma_-[C_n]$  ( $n \neq 1$ ) among the species  $\{Y_2\}$ .

**b. Radical Ion Pairs of Piperidine and 4-Nitroveratrole as Transient Species.** The photoinduced substitution reaction of NV with piperidine may be inhibited by the presence of the electron acceptor 1,3-dinitrobenzene (DNB) in the reaction mixture. When the concentration of the latter is high enough to inhibit the reaction

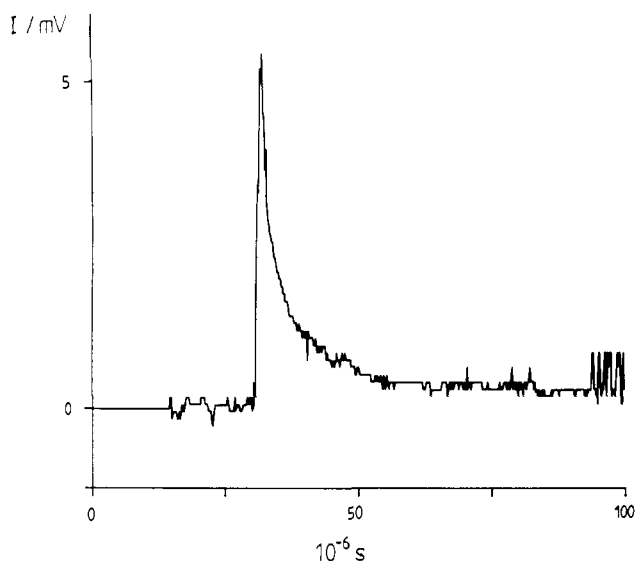


Figure 6. Transient conductance signal observed in the laser-excited solution of NV and piperidine in  $\text{CH}_3\text{CN}$ .

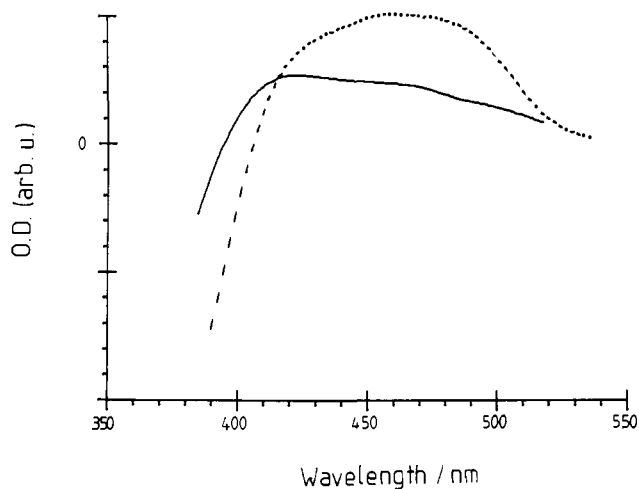


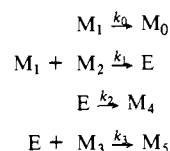
Figure 7. Transient absorption spectrum  $\Delta\text{OD}(\text{NV}, \lambda, t_x)$  of the laser-excited solution of piperidine and NV in  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  (80:20 v/v): (---) solution without DNB; (—) Solution containing DNB.

completely, only reduction products of DNB are obtained.<sup>9</sup>

The presence of the electron acceptor DNB or methylviologen ( $\text{MV}^{2+}$ ) in the reaction mixture does not cause changes in either the spectrum  $\Delta\text{OD}(\text{NV}, T_0, \lambda, t_L)$  or the value of the triplet decay constant  $k_T$ . However, it causes a drastic change in the spectrum  $\Delta\text{OD}(\text{NV}, \lambda, t_x)$ , as shown in Figure 7. A rather flat spectrum with reduced absorbances is observed instead of the spectrum for a reaction mixture without DNB, which is more intense and has a maximum. The negative magnitudes in the spectra  $\Delta\text{OD}(\text{NV}, \lambda, t_x)$  at  $\lambda < 410$  nm are caused by a substantial depletion of  $\text{NV}(S_0)$ . The presence of DNB in the reaction mixture results in an increase of the absorbance at  $\lambda < 410$  nm, which compensates to a large extent for the negative absorbance due to ground-state depletion. This behavior means that the production of species  $\{Y_2\}$  is markedly reduced by the presence of the electron acceptor and that this is accompanied by the formation of yet not encountered species  $\{Y_2'\}$  with an electronic absorption band in the region  $\lambda \leq 410$  nm. Since this band is identical with the first electronic absorption band of  $\text{NV}(S_0)$ , species  $\{Y_2'\}$  and the latter are identical.

When  $\text{MV}^{2+}$  is present in the reaction mixture a transient absorption band is observed with a maximum at  $\lambda = 602$  nm, just as in the spectrum of the radical cation  $\text{MV}^+$ .<sup>19</sup> However, this band is not observed when piperidine is not present in the solution. Apparently  $\text{MV}^{2+}$  gets reduced in a reaction with a product (E) formed by reaction of piperidine and  $\text{NV}(T_0)$ . This is in ac-

**Scheme III.** Reduction of Methylviologen (See Text for the Labeling of the Species)



cordance with the fact that the formation of  $\text{MV}^+$  may be inhibited by TMDD.

The transient absorption band  $\Delta\text{OD}(\text{MV}^+, \lambda, t)$  due to  $\text{MV}^+$  grows from zero to its maximum intensity within period  $I$ , i.e., in the period coinciding with the decay period of  $\text{NV}(T_0)$ . Although  $\text{MV}^+$  is not formed directly from  $\text{NV}(T_0)$ , the growth of  $\Delta\text{OD}(\text{MV}^+, \lambda, t)$  in period  $I$  can unexpectedly be described by the single exponential function

$$\Delta\text{OD}(\text{MV}^+, \lambda, t) = \Delta\text{OD}(\text{MV}^+, \lambda, t_x) \{1 - \exp[-k_M(t - t_L)]\} \quad (10)$$

The rise time  $k_M$  has the value  $4.33 \times 10^6 \text{ s}^{-1}$  at the particular value of  $3 \times 10^{-3} \text{ M}$  for the concentration  $C_{\text{MV}}$  of  $\text{MV}^{2+}$  used. Keeping the concentration  $\text{MV}^{2+}$  fixed at this value, the triplet decay constant  $k_T$  has been varied in the range  $5.5 \times 10^5 \leq k_T \leq 3.3 \times 10^6 \text{ s}^{-1}$  by variation of the concentration  $C_{\text{Pip}}$  of piperidine. The growth of  $\text{MV}^+$  remained monoexponential and the value of  $k_M$  is observed to be equal to that of  $k_T$ .

The observed time-dependence of  $\Delta\text{OD}(\text{MV}^+, \lambda, t)$  may be explained by the following formal kinetic scheme, in which ground and triplet state NV, piperidine,  $\text{MV}^{2+}$ , species  $\{Y_2\}$ , and  $\text{MV}^+$  have to be identified respectively with  $M_0, M_1, M_2, M_3, M_4,$  and  $M_5$ . Indicating the concentration of  $M_i$  by  $C_i$ , we may write the condition under which we want to know the time dependence of the concentration of  $\text{MV}^+$  as

$$C_2(t) = \text{constant} \quad (11)$$

$$C_3(t) = \text{constant} \quad (12)$$

Introducing rate constants  $k_1$  and  $k_3$  defined by

$$k_1 \equiv k_T = k_0 + k_1 C_2 \quad (13)$$

$$k_3 \equiv k_3 C_3 \quad (14)$$

the required time dependence may be written as

$$C_5(t) = \alpha C_1(0) \{f_1(t) - f_2(t)\} \quad (15)$$

where

$$\alpha = k_3 / \{(k_3 + k_2)(k_3 + k_2 - k_1)\} \quad (16)$$

$$f_1(t) = (k_3 + k_2) \{1 - \exp(-k_1 t)\} \quad (17)$$

$$f_2(t) = k_1 \{1 - \exp(-[k_3 + k_2] t)\} \quad (18)$$

From the relation

$$f_2(\infty) / f_1(\infty) = k_1 / (k_3 + k_2) \quad (19)$$

it follows that if

$$k_2 \gg k_1 \quad (20)$$

the contribution from  $f_2(t)$  to  $C_5(t)$  is negligible compared to that from  $f_1(t)$ . Then the growth of  $C_5(t)$  is practically described by a monoexponential growth with rate constant  $k_1$ .

An experimental justification that relation 20 is satisfied is the fact that formation of all species  $\{Y_2\}$  is completed in period  $I$  and E is then not observed. In view of the formation of  $\text{MV}^+$  from E, we identify E as the radical anion of NV. The reaction step in which E is formed then involves an electron transfer from the amine (e.g., piperidine) to  $\text{NV}(T_0)$ .

**4. Reactions of Methylamine and *n*-Hexylamine with Photoexcited 4-Nitroveratrole.** The photoinduced reactions of NV with methylamine (MA) and with *n*-hexylamine (HA) lead to substitution at both carbon atoms C(1) and C(2). The ratio  $\phi_{R1}/\phi_{R2}$  of overall quantum yields for substitution at C(1) and

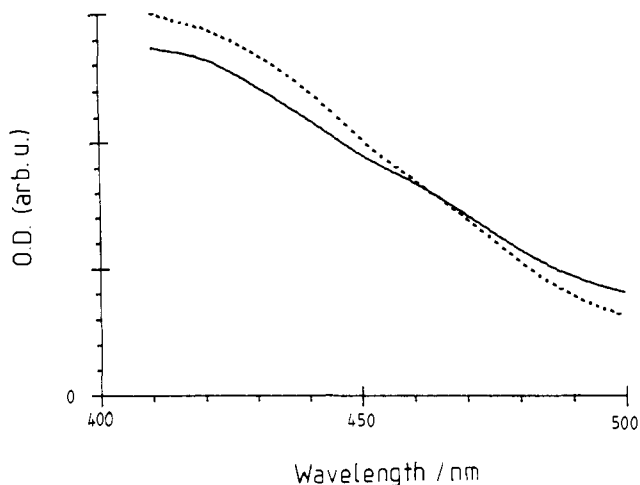


Figure 8. Transient absorption spectra of the photoexcited solution of methylamine and NV in  $H_2O/CH_3CN$  (80:20 v/v): curve a,  $\Delta OD(NV, Y_3, \lambda, t_X)$  (—); curve b,  $\Delta OD(NV, Y_3' + Y_3'', \lambda, t_Y)$  (---).

C(2) by the nucleophiles MA and HA amounts to 0.11 and 0.17, respectively.<sup>6,9</sup> For both reactions  $\phi_{R1}/\phi_{R2}$  decreases when triplet state quenchers or electron acceptors are present in the reaction mixture.<sup>8,9</sup> By determination of the absolute values of the quantum yield for the reaction of NV and *n*-hexylamine, the decrease of  $\phi_{R1}/\phi_{R2}$  is found to arise from a decrease in  $\phi_{R1}$ , while  $\phi_{R2}$  is not affected.<sup>9</sup> This indicates that  $NV(T_0)$  is an intermediate only in the reaction leading to substitution at C(1), while substitution at C(2) results from reaction of the amine with  $NV(S_n)$ .<sup>8,9</sup>

**a. Reaction of 4-Nitroveratrole in Its  $T_0$  State with Methylamine.** The bimolecular reaction with rate constant  $k_A(MA)$  between  $NV(T_0)$  and methylamine causes an increase in the decay constant  $k_T$  with increasing concentration MA in the solution. The value  $90.6 \times 10^6 M^{-1} s^{-1}$  has been obtained for  $k_q(MA)$  from a Stern-Volmer plot of  $k_T$  versus concentration  $C_{MA}$  of the free base form of methylamine.

Excitation of solutions of NV, methylamine, and  $MV^{2+}$  leads to formation of the  $MV^+$  cation. The formation of  $MV^+$  may be inhibited by TMDD. The growth of  $\Delta OD(MV^+, \lambda, t)$  during period I is reproduced adequately by eq 10, when  $k_M = 3.95 \times 10^6 s^{-1}$  is used. At concentrations  $C_{MV} = 3 \times 10^{-3} M$  and  $C_{MA} = 0.303 \times 10^{-3} M$  the values of  $k_M$  and  $k_T$  have been determined and have been found to be equal. We assume that the equality pertains when  $C_{MA}$  is varied, just as in the case of piperidine. This means that Scheme III applies also in the present case and that methylamine leads also to formation of the anion of NV (E in Scheme III) via an electron-transfer reaction with  $NV(T_0)$ .

After the disappearance of  $NV(T_0)$ , new and longer lived species are observed, just as in the cases of the photoinduced reaction with  $OH^-$  and piperidine. These will be denoted as  $\{Y_3\}$ .

The solid line in Figure 8 represents the transient absorption spectrum  $\Delta OD(NV, Y_3, \lambda, t_X)$  of a solution of NV and methylamine. The wavelength region covered in the spectrum  $\Delta OD(NV, Y_3, \lambda, t_X)$  had to be limited to  $\lambda \geq 410$  nm, because of substantial depletion of  $NV(S_0)$  as in the case of  $\Delta OD(NV, Y_2, \lambda, t_X)$  for the photo-reaction with piperidine. The absorption  $\Delta OD(NV, Y_3, \lambda, t_X)$  may be decreased by TMDD. This means that species  $\{Y_3\}$  are formed via  $NV(T_0)$ .

The shape of  $\Delta OD(NV, Y_3, \lambda, t - t_X)$  changes as a function of elapsed time  $t - t_X$ . This means that new species, to be denoted as  $\{Y_3''\}$ , are formed. The time interval  $t_X \leq t \leq t_Y$ , where  $t_Y$  is the instant when the formation of  $\{Y_3''\}$  is completed, will be referred to as period IIa. The next time interval within period II, i.e.,  $t_Y < t < t_E$ , will be referred to as period IIb. The evolution of  $\Delta OD(NV, \lambda, t)$  in period IIa may be expressed as

$$\Delta OD(NV, \lambda, t) = \Delta OD(NV, Y_3, \lambda, t_X) \exp[-k_{Y3}(t - t_X)] + \Delta OD(NV, Y_3'', \lambda, t_Y) [1 - \exp[-k_{Y3}(t - t_X)]] \quad (21)$$

The value of the decay constant  $k_{Y3}$  amounts to  $0.24 \times 10^6 s^{-1}$ . An isosbestic point appears at 460 nm in the spectrum  $\Delta OD-$

$(NV, \lambda, t)$  during period IIa. It indicates that some of the species in  $\{Y_3\}$  are converted into species  $\{Y_3''\}$ . The collection of other species in  $\{Y_3\}$  will be denoted by  $\{Y_3'\}$ . The spectrum  $\Delta OD(NV, Y_3' + Y_3'', \lambda, t_Y)$  is represented by the dashed curve in Figure 8.

The absorption due to species  $\{Y_3'\}$  and  $\{Y_3''\}$  decays during period IIb in a monoexponential manner with a rate constant  $k_{Y3}$  equal to  $18 \times 10^3 s^{-1}$  and, as shown in Table II, almost equal to the value of  $k_{Y2}$  in the reaction of NV and piperidine. The end of period II coincides with the instant when  $\Delta OD(NV, Y_3' + Y_3'', \lambda, t)$  has become negligible.

The similarity between the behavior of the photoexcited solutions of NV with piperidine on the one hand and with methylamine on the other hand leads to the conclusion that the amines behave mechanistically in the same manner in each of the reaction steps which follow after their encounter with  $NV(T_0)$ . However, kinetically there is a difference between the two amines. In the case of piperidine the achievement of the dynamic equilibrium between  $\sigma_0[C_n]$  and  $\sigma_-[C_n]$  ( $n \neq 1$ ) is kinetically governed by the relation

$$k_+, k_- \gg k_q(\text{Pip})C_{\text{Pip}} \gg k_{Y2} \quad (22)$$

but in the case of methylamine it is governed by the relation

$$k_q(\text{MA})C_{\text{MA}} \gg k_+, k_- \gg k_{Y3} \quad (23)$$

Relation 23 takes care of the fact that by transient absorption one observes immediately after the disappearance of  $NV(T_0)$  only species  $\sigma_0[C_n]$ . Remember that the final stable substitution product  $P_1\text{-MA}$  is already formed but that it makes a negligible contribution to  $\Delta OD(NV, \lambda, t_X)$ . Therefore  $\{Y_3\}$  has to be identified with  $\sigma_0[C_n]$  ( $n \neq 1$ ). The conversion of certain species from  $\{Y_3\}$  into  $\{Y_3''\}$  has to be identified with the establishment of the equilibrium between  $\sigma_0[C_n]$  and  $\sigma_-[C_n]$ . The establishment of this type of equilibrium in the case of piperidine is so fast that it falls entirely within period I. The difference between piperidine and methylamine in this respect must be attributed to their action in a general base catalyzed reaction step. The difference in their base strength results in a deprotonation of  $\sigma_0[C_n]$ , which is faster in the case of piperidine ( $pK_b = 2.88$ ) than in the case of methylamine ( $pK_b = 3.44$ ).

**b. Reaction of Methylamine with 4-Nitroveratrole in Its Excited Singlet State.** The presence of 0.05 M methylamine in the photoexcited solution of NV causes an average intensity reduction of about 10% and a change in the shape of spectrum  $\Delta OD(NV, X, \lambda, t_L)$ . Note that, when methylamine is absent, this is the triplet state spectrum just after termination of the laser pulse. Such a modification in this spectrum is not induced by the presence of  $OH^-$  or piperidine. The modification must be attributed to a reduction in the triplet quantum yield  $\phi_T(NV)$  and to the formation of absorbing species  $\{Z\}$  by reaction of methylamine and  $NV(S_n)$ , prepared directly or via electronic relaxation. In conformity with this the spectrum  $\Delta OD(NV, X, \lambda, t_L)$  for the solution with methylamine is expressed as

$$\Delta OD(NV, X, \lambda, t_L) = \Delta OD(NV, Z, \lambda, t_L) + \gamma \Delta OD(NV, T_0, \lambda, t_L) \quad (24)$$

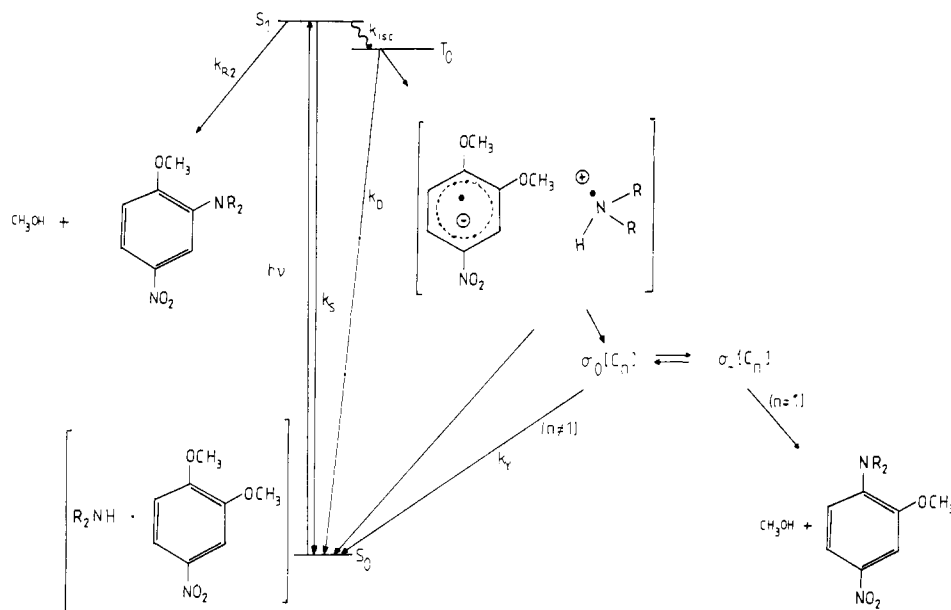
where

$$\gamma = \frac{\Delta OD(NV, T_0, \lambda, t_L)}{\Delta OD(NV, X, \lambda, t_L)} \quad (\lambda \geq 480 \text{ nm}) \quad (25)$$

The spectrum  $\Delta OD(NV, Z, \lambda, t_L)$ , obtained on the basis of eq 24, is shown in Figure 9. It has a band with a maximum around 400 nm. The compound  $P_2\text{-MA}$  has been isolated as a photo-product.<sup>6</sup> Since the maximum of the first band in its electronic absorption spectrum is at  $\lambda = 390$  nm,<sup>9</sup> it must be identical with  $\{Z\}$ . The absorption by  $P_2\text{-MA}$  could be observed in the transient spectrum, because the quantum yield  $\phi_{R2}$  for substitution at C(2) is large compared to  $\phi_{R1}$  for substitution at C(1).

**c. Reaction of *n*-Hexylamine with Photoexcited 4-Nitroveratrole.** The photoreaction of NV with *n*-hexylamine has been studied with the same experimental detail as its photoreactions with piperidine and methylamine. Nevertheless, we will not discuss

Scheme IV. Mechanism of the Reaction of Amines with Photoexcited NV



the results in detail, because the mechanism of this reaction is found to be the same in all respects as that in the case of methylamine. The relevant kinetic information is provided in Table II.

#### 5. Reaction of Triethylamine with Photoexcited 4-Nitroveratrole.

No stable photosubstitution products are formed when solutions of NV and triethylamine (TEA) are irradiated with UV light, at least not when the wavelength is longer than 290 nm. Nevertheless, the value of the triplet decay constant  $k_T$  increases with increasing concentration  $C_{TEA}$  of TEA in the solution. The rate constant  $k_q(TEA)$  for the bimolecular quenching of NV( $T_0$ ) by TEA is found from a Stern–Volmer plot of  $k_T$  versus  $C_{TEA}$  to be equal to  $0.46 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

Immediately after the disappearance of NV( $T_0$ ) the spectrum represented by the solid line in Figure 10 and denoted by  $\Delta OD(NV, Y_4, \lambda, t_X)$  is observed. The species that give rise to this spectrum will be denoted by  $\{Y_4\}$ . As in the case of the amines encountered already, the wavelength region had to be limited to  $\lambda \geq 400 \text{ nm}$  due to considerable depletion of NV( $S_0$ ). The spectrum  $\Delta OD(NV, Y_4, \lambda, t_X)$  resembles the spectrum of the radical anion E of NV<sup>20</sup> with respect to both the maximum of the band at 450 nm and the tail of the UV band. Therefore we identify  $\{Y_4\}$  with E. A further justification for this is the observation of  $MV^+$  in the transient spectrum of a photoexcited solution, containing NV, TEA, and  $MV^{2+}$ . The quantum yield of  $MV^+$  is reduced, when TMDD is also present in the solution.

In the case of the photoreactions with the other amines discussed so far, the formation of E had been deduced indirectly. Apparently E can be observed in the present case, because it has a lifetime that is now longer than in the previous cases. The lifetime extension of E could arise, in conformity with the lower ionization energy of TEA, from a reduction in the rate constant for charge neutralization between E and the radical cation of the amine, which competes with the formation of  $\sigma$ -complexes from E. However, a reduction in the rate constant of the latter reaction, due to steric hindrance, seems to be important also, because the higher value of  $k_q(TEA)$  does not lead to a higher quantum yield for the  $\sigma$ -complexes.

Within a few microseconds after time  $t_X$  species in the set  $\{Y_4\}$  are converted into new species  $\{Y_4'\}$ , whose spectrum  $\Delta OD(NV, Y_4', \lambda, t_Y)$  is also shown in Figure 10. Time  $t_Y$  denotes the instant when the conversion is completed, i.e.,  $t_Y \approx t_X + 5 \mu\text{s}$ .

An isosbestic point at 430 nm is observed in this spectrum during the conversion. The set of species  $\{Y_4'\}$  decays in a monoexponential manner with a decay rate constant  $k_{Y_4'}$  equal to  $12 \times 10^3 \text{ s}^{-1}$ . The disappearance of  $\{Y_4'\}$  defines the end of period II.

The approximately equal lifetime ( $k_Y$  in Table II) of  $\{Y_4'\}$  and of the set  $\{Y_3'\} + \{Y_3''\}$  suggests that  $\{Y_4'\}$  must be identified with  $\sigma$ -complexes of TEA and NV. Obviously, this set of  $\sigma$ -complexes does not contain the type  $\sigma_-[C_n]$ , simply because TEA does not have an H-atom available for deprotonation. The set consists only of  $\sigma$ -complexes of the type  $\sigma_0[C_n]$ .

#### Concluding Remarks

No indication has been found for chemical reactions between  $\text{OH}^-$  and NV( $S_n$ ), prepared by 308-nm excitation. In Scheme I the sequence of reaction steps is shown, which follow upon encounter of an  $\text{OH}^-$  ion and NV( $T_0$ ). No indication has been found for a discrete step involving electron transfer between NV( $T_0$ ) and  $\text{OH}^-$ , and the main reaction product results from substitution at atom C(2) of the aromatic molecule. The formation of the reaction product is completed at the stage when a collection of  $\sigma$ -complexes is seen by transient spectroscopy. These complexes yield NV.

In certain respects the behavior of solutions with amines is different from that of the solution with  $\text{OH}^-$ . The interaction of amines with NV( $S_n$ ) leads to enhanced electronic relaxation, sometimes accompanied by formation of new chemical products, resulting from substitution at atom C(2). The encounter of the amines and NV( $T_0$ ) leads to a discrete electron-transfer reaction, in which the radical anion (E) of NV is formed. The subsequent reaction of E with the amine yields a stable product, resulting from substitution at atom C(1) and a collection of unstable  $\sigma$ -complexes that return to NV.

An ESR study of the photoreaction of NV and TEA in  $\text{CH}_3\text{CN}$ ,<sup>21</sup> using stationary illumination, has revealed that E does not react with the neutral amine. In this study the radical cation of TEA could not be observed. This means that the lifetime of this cation is much shorter than that of E as a consequence of reactions that proceed more efficiently than its reaction with E. Therefore the disappearance of E, certainly after the concentration of the radical cation has vanished, must involve reactions other than the one with the cation. Since E is formed via electron transfer between a triplet state molecule and a singlet state molecule, the formation of a singlet state  $\sigma$ -complex from E and the radical cation of the amine is retarded by the time required by the radical pair to evolve into a singlet state. The retardation, governed by the hyperfine couplings in the radicals and amounting to about 10 ns, enables the radicals in a fraction of the geminate

(20) Mutai, K.; Yokoyama, K.; Kanno, S.; Kobayashi, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1112.

(21) Van Eijk, A. M. J.; Huizer, A. H.; Varma, C. A. G. O., to be published.

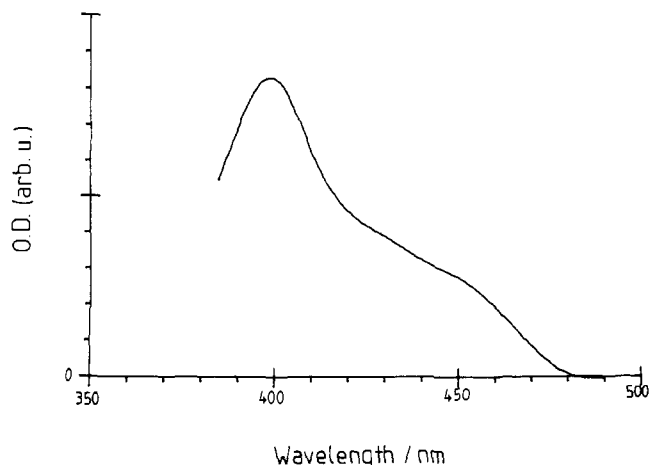


Figure 9. Absorption spectrum  $\Delta OD(NV, Z, \lambda, t_L)$  of the photoexcited solution of methylamine and NV in  $H_2O/CH_3CN$  (80:20 v/v).

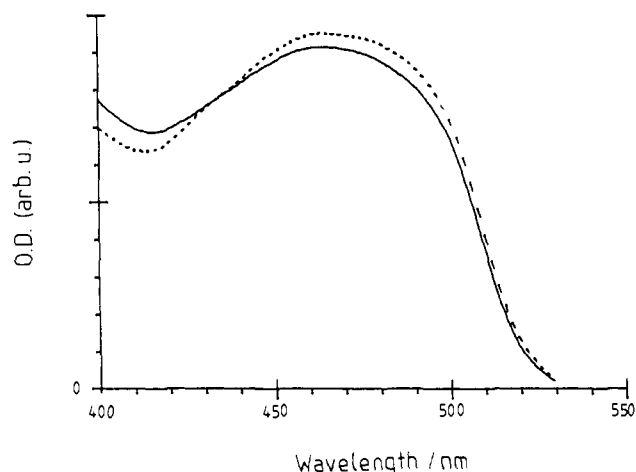


Figure 10. Transient absorption spectra of the photoexcited solution of TEA and NV in  $H_2O/CH_3CN$  (80:20 v/v): curve a,  $\Delta OD(NV, Y_4, \lambda, t_X)$  (—); curve b,  $\Delta OD(NV, Y_4', \lambda, t_Y)$  (---).

pairs to separate and to enter into the bulk of the solvent. The anions E which are observed are those which escaped from reaction within the cage in which they were formed.

The difference in regioselectivity of the triplet state reactions with  $OH^-$  and amines must be related to the direct formation of

the required  $\sigma$ -complex in the former case and via the anion E in the latter case. These facts are incorporated in Scheme IV, which presents the sequence of steps following electronic excitation of the solutions containing amines.

The reaction of  $NV(S_n)$  with methylamine or *n*-hexylamine leads to substitution at carbon atom C(2). However, the reaction with piperidine does not yield substitution at this position, although the intensity of  $\Delta OD(NV, T_0, \lambda, t_L)$  decreases with increasing  $C_{PIP}$  as a result of quenching of the excited singlet states in competition with intersystem crossing. Since the ionization energy of piperidine is much smaller than that of methylamine, the lack of a C(2)-substitution product of piperidine in the excited singlet state reaction must be due to a reduction in the rate constant for formation of the required  $\sigma$ -complex arising from steric hindrance. Apparently, at least in the case of piperidine, an excited complex or exciplex is formed as a precursor of the  $\sigma$ -complex, depending on whether the quenching is static or dynamic in nature. Dynamic quenching may be ruled out on the basis of the quantum yield  $\phi_{R2}$  of the C(2) substitution product. The quantum yield is given by

$$\phi_{R2} = \frac{k_{R2}C_A}{k_S + k_{R2}C_A} \quad (26)$$

where  $k_{R2}$  is the rate constant for the bimolecular excited singlet state quenching by the amine,  $C_A$  is the concentration of the amine, and  $k_S$  is the rate constant for decay of the population of excited singlet states. As a reasonable lower limit for the value of  $k_S$ , we take the lower limit found for the rate constant for decay of the excited state  $S_1$  of several nitroanisoles dissolved in  $H_2O/CH_3CN$  (80:20 v/v).<sup>12</sup> This amounts to  $k_S \geq 10^{11} s^{-1}$ . Using eq 26 and the experimental values  $\phi_{R2} = 0.022$  at  $C_A \approx 0.1$  M in the case of *n*-hexylamine we find  $k_{R2} \geq 10^{10} s^{-1}$ . The value of  $k_{R2}$  exceeds the value for a diffusion limited reaction rate constant and is therefore an indication for quenching within excited complexes generated by excitation of ground-state complexes. The difference in behavior of  $OH^-$  and of amines in the photoexcited solution must be related to the absence of such ground-state complexes in the former case.

**Acknowledgment.** The investigations were supported in part by the Foundation for Chemical Research in the Netherlands (S.O.N.) with financial aid from the Netherlands Organization for Scientific Research (N.W.O.). J.M. acknowledges financial support from CAICYT (Ministerio de Educación y Ciencia of Spain) through project 0343/84.

**Registry No.** TEA, 121-44-8; TMDD, 34493-89-5; 4-nitroveratrole, 709-09-1; potassium hydroxide, 1310-58-3; hexylamine, 111-26-2; methylamine, 74-89-5; piperidine, 110-89-4.