

comparison with an authentic sample:<sup>18</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.92 (q,  $J = 7.5$  Hz, 4 H), 2.43 (m, 4 H), 2.49 (m, 4 H), 5.59 (m, 2 H).

**Flash Vacuum Thermolysis of Monoazoalkanes 11a and 11d.** The azoalkanes **11a** and **11d** (2 mg of each) were thermolized as described above. The results are shown in Table IV.

**Flash Vacuum Thermolysis of Bibicyclopentane 12a.** The bibicyclopentane **12a** was thermolized as described above. The results are summarized in Table III.

**X-ray Structure Analysis of the Bis-Azoalkane 5.** A clear colorless crystal of **5** with dimensions  $0.12 \times 0.28 \times 0.08$  mm was optically centered on a Syntex P3 four-circle diffractometer. The orientation matrix and cell parameters were determined on the basis of 15 reflections. The intensities of 1313  $hkl$  reflections were measured according to the  $\omega$  method (Mo K $\alpha$ , graphite monochromator) using a scan range of  $1^\circ$  and a scan speed between  $0.5$  and  $24.0^\circ/\text{min}$  as a function of the intensity of the reflections. In the range  $3.0^\circ \leq 2\theta \leq 55.0^\circ$ , 656 reflections were obtained that were utilized in the structure determination. For the evaluation, SHELXTL on an Eclipse S/250 at the Max-Planck-Institut für Festkörperforschung was employed. The structure was solved by direct-phase determination. The phases of 297 strong reflections were determined, and on the resulting  $E$  map approximate positions of all C, N, and O atoms could be easily determined. Positional and thermal parameters could be refined by anisotropic least-squares cycles to  $R = 0.113$ .

The bis-azoalkane **5** crystallizes orthorhombically in the space group  $P_{nma}$  (No. 62) with  $a = 1705.9$  (4) pm,  $b = 986.9$  (2) pm, and  $c = 562.9$

(1) pm. The unit cell contains  $z = 4$  formula units, and the density was calculated to be  $1.333 \text{ mg cm}^{-3}$ . The labeling of the atoms is shown in Figure 1. All atomic parameters are given in Table VI and the bond distances and bond angles in Table VII.

**X-ray Structure Analysis of the Monoazoalkane 11a.** A clear colorless crystal of the monoazoalkane **11a** with dimensions  $0.19 \times 3.69 \times 0.07$  mm was analyzed by the same procedure described above. The intensities of 951  $hkl$  reflections were determined, and 951 of these used in the structure determination. The phases of 232 strong reflections were determined. Positional and thermal parameters could be refined by anisotropic least-squares cycles to  $R = 0.060$ .

The monoazoalkane **11a** crystallizes monoclinically in the space group  $P2_1$  (No. 4) with  $a = 774.8$  (3) pm,  $b = 969.1$  (5) pm,  $c = 600.7$  (2) pm, and  $\beta = 95.78$  (2) $^\circ$ . The unit cell contains  $Z = 2$  formula units, and the density was calculated to be  $1.201 \text{ mg cm}^{-3}$ . The labeling of the atoms is shown in Figure 2. All atomic parameters are given in Table VIII and the bond distances and bond angles in Table IX.

**Acknowledgment.** Financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, The National Science Foundation, and the North Atlantic Treaty Organization made this collaborative research project possible and are most gratefully acknowledged.

**Registry No.** **5**, 96412-10-1; **9a**, 108943-58-4; **10**, 108868-13-9; **11a**, 96479-38-8; **11b**, 96412-11-2; **11c**, 96479-37-7; **11d**, 96479-39-9; **12a**, 96479-40-2; **12b**, 96412-12-3; **12c**, 96479-41-3; **13**, 934-02-1.

## Light-Induced Self-Nitrosation of Polycyclic Phenols with Nitrosamine. Excited State Proton Transfer

Yuan L. Chow\* and Zheng-Zhi Wu

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada, V5A 1S6. Received February 24, 1987

**Abstract:** Photoexcitation of polycyclic phenols in the presence of *N*-nitrosodimethylamine caused the self-nitrosation of the phenols to give 1,2- or 1,4-quinone monooximes. With use of naphthols as models, the key step of the photonitrosation was shown to be a dual sensitization process from the lowest singlet excited state of naphthols by proton transfer followed by energy migration within an exciplex to cause the known homolysis of the nitrosamine; it is assumed that the resulting radical species undergo nitrosation of naphtholates. The crucial requirement of the excited state proton transfer (ESPT) reaction is established by quenching of the photonitrosation by general bases, such as water and TEA, with quenching rate constants close to those of naphthol fluorescence by these bases.

Förster<sup>1</sup> pioneered the theoretical work on excited state acidity as a thermodynamic property. On the basis of both steady-state and time-resolved measurements, Weller<sup>2</sup> has demonstrated the validity of acid dissociation constants in excited states ( $pK_a^*$ ). This stimulates much interest on the mechanism of the most basic acid-base equilibria. Particularly, the advent of fast kinetic spectrometry enables the precise measurements of the various parameters of excited state proton transfer (ESPT) reactions in water and protic solvents. While literally hundreds of examples of ESPT reactions<sup>3,4</sup> have been described, most of the mechanistic investigations utilize naphthols as model compounds.<sup>5-14</sup> Most

of these reactions are concerned about acid-base equilibria in the singlet excited state manifold in aqueous or protic solution rather than dealing with substantive chemical transformations that may be promoted by enhanced excited state acidity (EESA).<sup>15-17</sup> Such EESA-promoted reactions are severely limited by the short lifetimes of singlet excited states, typically in the order of 10 ns or shorter.<sup>16</sup> That is, a substantive chemical transformation must occur within the lifetime of singlet excited states so that the

(1) (a) Förster, Th. *Naturwissenschaften* **1949**, *36*, 186. (b) Förster, Th. *J. Electrochem.* **1950**, *54*, 531.

(2) (a) Weller, A. *Z. Electrochem.* **1952**, *56*, 662. (b) Weller, A. *Prog. React. Kinet.* **1961**, *1*, 187.

(3) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.

(4) Martynov, I. Yu.; Demyashkevich, A. B.; Uzhinov, B. M.; Kuzmin, M. G. *Usp. Khim. (Engl. Trans.)* **1977**, *46*, 3.

(5) Harris, C. M.; Selinger, B. K. *J. Phys. Chem.* **1980**, *84*, 891.

(6) Harris, C. M.; Selinger, B. K. *J. Phys. Chem.* **1980**, *84*, 1366.

(7) Rosenberg, J. L.; Brinn, I. *J. Phys. Chem.* **1972**, *76*, 3558.

(8) Tsutsumi, K.; Shizuka, H. *Z. Phys. Chem. (Wiesbaden)* **1983**, *122*, 129.

(9) Tabita, S.; Shizuka, H. *Chem. Phys. Lett.* **1980**, *75*, 140.

(10) Shizuka, H.; Tobita, S. *J. Am. Chem. Soc.* **1982**, *104*, 6919.

(11) Webb, S. P.; Phillips, L. A.; Yeh, S. W.; Tolbert, L. M.; Clark, J. H. *J. Phys. Chem.* **1986**, *90*, 5154.

(12) Lee, J.; Robinson, G. W.; Webb, S. P.; Phillips, L. A.; Clark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 6538.

(13) Webb, S. P.; Yeh, S. W.; Phillips, L. A.; Tolbert, M. A.; Clark, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 7286.

(14) Lee, J.; Griffin, R. D.; Robinson, G. W. *J. Chem. Phys.* **1985**, *82*, 4920.

(15) Saeva, F. D.; Olin, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 5631. The proposal of an excited state acidity catalyzed reaction described in this paper remains unconfirmed upon a different opinion expressed in ref 16.

(16) Chandross, E. A. *J. Am. Chem. Soc.* **1976**, *98*, 1053.

(17) Kalanderopoulos, P.; Yates, K. *J. Am. Chem. Soc.* **1986**, *108*, 6290.

Table I. Spectroscopic Data<sup>a</sup> of Some Phenols (ArOH)

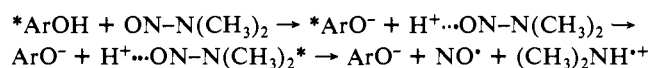
ArOH	$E_s$ kcal/mol <sup>i</sup>	$\phi_f$	$\tau_f$ (ns)	$pK(S_1)$	$E_s$ (ArO <sup>-</sup> ) <sup>g</sup> kcal/mol <sup>i</sup>
1-naphthol (1)	91.3 (313)	0.18	10.6	$0.4 \pm 0.2^b$ $0.5 \pm 0.2^c$	79 (360)
2-naphthol (3)	86.7 (330)	0.27	13.3	2.8 <sup>c</sup>	77 (370)
1-anthrol (5)	72.0 <sup>d</sup> (400)		19 <sup>b</sup>	-0.07 <sup>d</sup>	62 (460)
9-anthrol (7)	72.0 <sup>e</sup> (400)			0.6 <sup>e</sup>	60 (480)
9-phenanthrol (9)	73.4 <sup>e</sup> (365)			1.8 <sup>f</sup>	64 (450)

<sup>a</sup>Unless specified the spectroscopic data are cited from ref 23. <sup>b</sup>References 11 and 12;  $pK(S_0)$  for 1-NpOH is 9.20. <sup>c</sup>References 5 and 6;  $pK(S_0)$  for 2-NpOH is 9.45. <sup>d</sup>Reference 24. <sup>e</sup>Reference 3. <sup>f</sup>Reference 25. <sup>g</sup>These values were calculated from the overlapping wavelengths (in parentheses) of absorption and fluorescence spectra for phenols in MeOH and phenolate in MeOH-KOH at room temperature, assuming that the Stoke's shifts were small. <sup>h</sup>See ref 26. <sup>i</sup>nm are in parentheses.

probability of leading to products does exist.

In view that nitrosamines, such as *N*-nitrosodimethylamine (NND), require proton association as well as electronic excitation (singlet excited state) to undergo homolytic scission to yield aminium radicals and nitric oxide,<sup>18-21</sup> we envisage that singlet excited state polycyclic phenols (ArOH), by virtue of their EESA, might provide both ESPT as well as energy transfer in sequence to promote such homolysis as shown in Scheme I. This scheme

#### Scheme I



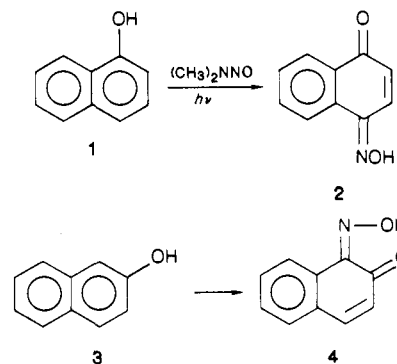
requires a dual sensitization process from singlet excited state \*ArOH undergoing a sequential proton transfer and energy transfer. This paper demonstrates the feasibility of such a sensitization process.<sup>22</sup> The ground- and excited-state properties of some phenols to be used in this investigation are summarized in Table I. Some important excited state parameters of 1- and 2-naphthols can be found in publications.<sup>11,12,27,28</sup>

#### Results

Irradiation of a solution containing a phenol (Table I) and NND in a neutral solvent through a Pyrex filter under nitrogen rapidly gave dimethylamine and the corresponding quinone monooxime (Table II) which also absorbed in the region similar to the starting materials. The progress of photolysis was retarded after 2-3 h and over-irradiation produced amorphous materials. In the presence of dilute hydrochloric acid the same quinone monooxime was also produced but another byproduct was also formed as the

minor component. Photolysis of an aromatic hydrocarbon (such as naphthalene, anthracene, pyrene, etc.) and NND under the similar conditions caused no photodecomposition of NND; the photoaddition of NND to these hydrocarbons was shown to occur *only in the presence of dilute acid* previously.<sup>18-20</sup> Quinone monooximes were isolated and identified from their physical data (Experimental Section) and by direct comparisons with authentic samples in some cases. The presence of the quinone monooxime moiety was demonstrated by the characteristic IR absorptions at 3100-3400 (OH), 1620 (C=O), 1580 (C=N), and 980 (N-OH)  $cm^{-1}$ . Dimethylamine was identified as its *p*-nitrobenzamide. The quinone monooxime **4** and **10** probably possess the syn geometry on the basis of a low field OH signal at  $\sim 17$  ppm arising from intramolecular H-bonding.

While the pattern of photonitrosation varied from case to case, generally the monooxime formations were faster in aprotic solvents than in alcohols and rapid in the initial 1-2-h period and tapered off on continuing irradiation during which phenol percentages steadily decreased. Typically, the photoreaction of 1-naphthol (1-NpOH, **1**) with NND proceeded in the decreasing order of



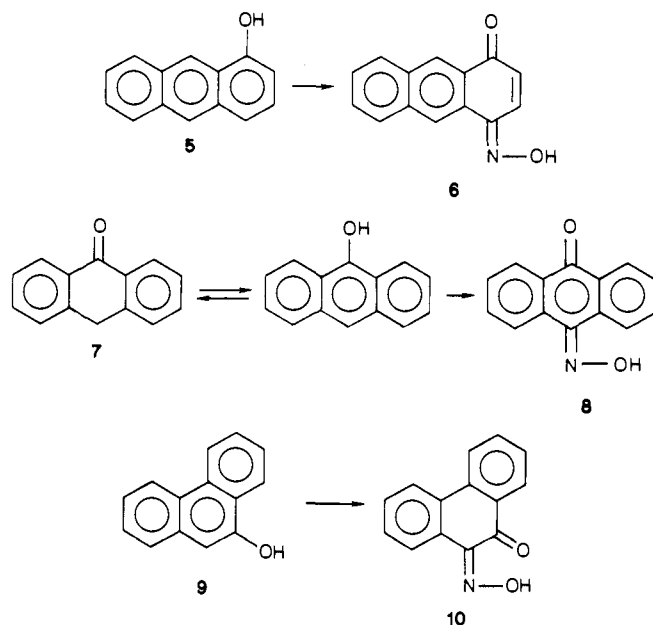
rates in dioxane, THF, acetonitrile, and methanol. Quinone monooxime **2** in either methanol or dioxane was rapidly photodecomposed on irradiation in a Pyrex apparatus to form amorphous material. This explained the formation of ether insoluble material and the sluggish formation of **2** after the initial stage. It was fortunate that 1-NpOH acted as an internal filter to allow the buildup of **2** during the initial stage. However prolonged irradiation offered no advantage since it contributed to form complex product mixtures. The photoinduced self-nitrosation of 2-naphthol (2-NpOH, **3**) was slow with a Pyrex filter and was carried out with a Corex filter in prolonged irradiation; this also caused the formation of at least six byproducts. Under oxygen, instead of nitrogen, the photoreaction of 1-NpOH and NND gave a small amount of 2-nitro-1-naphthol and other minor products in addition to quinone monooxime **2**.

Rapid keto  $\rightleftharpoons$  enol tautomeric equilibria of anthrone in solution are well established.<sup>29</sup> Photolysis of anthrone-NND solution was carried out with a filter solution (NaNO<sub>2</sub> and sodium hydrogen phthalate) to cutoff <400 nm so that only 9-anthrol ( $\lambda_{max}$  410 nm) was excited; anthrone solution does not have absorption<sup>30</sup> >390 nm. It was also noted that the photoinduced self-nitrosation of 1-anthrol gave only monooxime **6** without a trace of the addition products to the 9,10-positions.

In contrast, 1-naphthyl methyl ether (1-NpOCH<sub>3</sub>) and NND, when photolyzed under similar conditions, did not initiate self-nitrosation nor the decomposition of NND. The singlet excited state of \*1-NpOCH<sub>3</sub> ( $E_s = 89.3$  kcal/mol,  $\Phi_f = 0.36$ , and  $\tau_f = 13$  ns)<sup>23</sup> possesses properties very similar to those of \*1-NpOH with the exception of the lack of dissociable hydrogen. As fluorescence of the naphthyl ether was efficiently quenched by NND even at the  $<10^{-3}$  M level, the failure to cause NND photodecomposition and self-nitrosation must be related to the EESA of the OH group. The mechanistic implication of this photoreaction was investigated further by using 1-NpOH as a

- (18) Chow, Y. L. *Acc. Chem. Res.* **1973**, *6*, 354.  
 (19) Chow, Y. L.; Colon, C. J.; Quon, H. H.; Mojelsky, T. *Can. J. Chem.* **1972**, *50*, 1065.  
 (20) Chow, Y. L.; Colon, C. J.; Chang, D. W. L.; Pillay, K. S.; Lockhart, R. L.; Tezuka, T. *Acta Chem. Scand.* **1982**, *B36*, 623.  
 (21) Chow, Y. L.; Wu, Z.-Z.; Lau, M. P.; Yip, R. W. *J. Am. Chem. Soc.* **1985**, *107*, 8196.  
 (22) Part of the results has been communicated previously: Chow, Y. L.; Wu, Z.-Z. *J. Am. Chem. Soc.* **1985**, *107*, 3338.  
 (23) Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973.  
 (24) Yamamoto, S.; Kikuchi, K.; Kokubun, H. *J. Photochem.* **1976**, *5*, 469.  
 (25) Dogra, S. K.; Swaminathan, M. *J. Chem. Soc., Perkin Trans. 2* **1984**, 947.  
 (26) Lifetimes of 1-NpOH and 1-AnOH in some organic solvents were determined by Professor M. Thewalt and Dr. T. W. Steiner (Department of Physics, Simon Fraser University) with their time-resolved fluorimetry machine modified for solution spectroscopy. We are much indebted to them for these data.  
 (27) Brinn, I. Doctoral Dissertation, University of Pittsburgh, 1968.  
 (28) Higasi, K.; Ogata, S. *Oyo Denki Kenkyusho Hokoku* **1967**, *19*, 28.

- (29) Baba, H.; Takemura, T. *Tetrahedron* **1968**, *24*, 4779, 5311.  
 (30) Scaiano, J. C.; Lee, C. W. B.; Chow, Y. L.; Buono-Core, G. E. *J. Photochem.* **1982**, *20*, 327.



model. A solution of 1-NpOH and NND was irradiated at  $\sim 300$  nm region by using a window provided by a NND filter solution (see Figure 1); this set-up caused the photoexcitation of 1-NpOH and induced the rapid decomposition of NND and the formation of quinone monooxime 2. The same solution, when irradiated at NND by using a GWA filter (cutoff  $< 340$  nm), afforded no decomposition of NND. That the photoexcitation of 1-NpOH caused the reaction was further demonstrated by pulsing of 1-NpOH with an Excimer laser at 308 nm where NND absorbs  $< 1\%$ : quinone monooxime 2 was formed. Under similar conditions laser excitation of 2-NpOH also showed comparable results.

Sensitization of the photoreactions of 1-NpOH and NND with triplet sensitizers, such as xanthone ( $E_T = 74.1$  kcal/mol)<sup>23</sup> and 2-acetonaphthone ( $E_T = 59.4$  kcal/mol)<sup>23</sup> failed to induce any chemical changes. As these experiments were run with equal concentrations of 1-NpOH ( $E_T = 58.6$  kcal/mol)<sup>23</sup> and NND ( $E_T = 57$ – $59$  kcal/mol),<sup>21</sup> at least a half of excitation energy transfer should have occurred with 1-NpOH. The photonitrosation was not quenched by 1,3-cyclohexadiene, a triplet quencher ( $E_T = 52.4$  and  $E_s = 97$  kcal/mol). These experiments established that the lowest singlet excited state of 1-NpOH by sensitization processes caused the decomposition of NND and led to the nitrosation of 1-NpOH.

We have demonstrated that NND shows no emission except under special conditions.<sup>21</sup> Nor was fluorescence of quinone monooxime 2 detected. Owing to the overlap of the fluorescence of 1-NpOH (Figure 2) and absorption of NND (Figure 1), the fluorescence spectra of 1-NpOH is distorted from "trivial" as well as real quenching by NND if standard emission spectroscopic technique was used.<sup>31,32</sup> These led us to prematurely assign the irregular emission in the  $> 400$ -nm region to the exciplex emission band. While this region showed weak emission, this assignment remains to be confirmed due to the complex structure of the emission spectra (see Figure 1 in ref 22). By using a "front-face illumination" technique<sup>31,32</sup> to minimize reabsorption by NND, the quenching of 1-NpOH fluorescence intensities in dioxane is shown in Figure 2. The corresponding Stern-Volmer plot monitored at 342 nm ( $I^0/I$  vs. [NND]) gave a straight line with  $k_q\tau_0 = 117$  M<sup>-1</sup> and  $k_q = 11.0 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> by using  $\tau_0 = 10.6$  ns. In methanolic KOH solution 1-naphtholate<sup>33</sup> (1-NpO<sup>-</sup>) exhibited an emission maximum at  $\lambda_{em}$  460 nm. However, the fluorescence intensity above 400 nm in the [NND]  $> 0.01$  M range (Figure 2) was too weak to afford a conclusion.

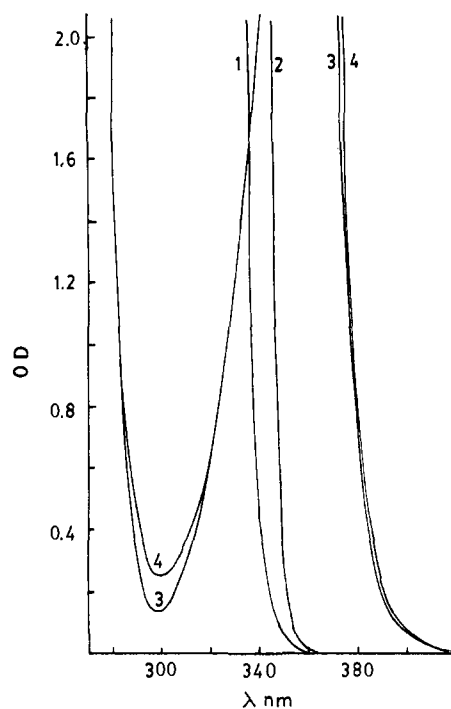


Figure 1. Absorption spectra in dioxane of (1) 1-NpOH (0.050 M), (2) 2-NpOH (0.050 M), and (3) NND (0.025 M).

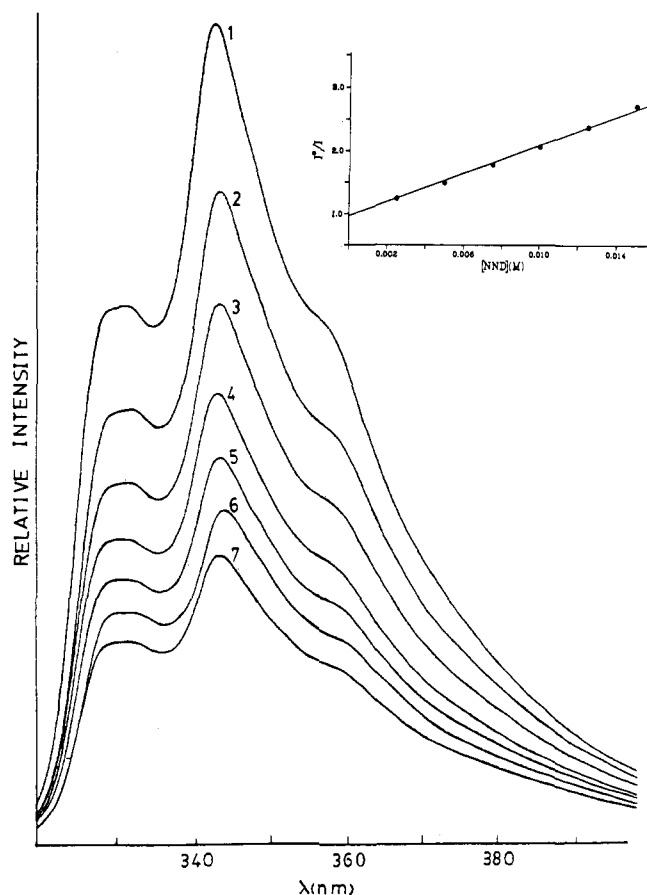


Figure 2. Quenching of 1-NpOH (0.002 M) fluorescence by NND in dioxane at 22 °C,  $\lambda_{ex}$  300 nm by using the "front-face illumination" technique: curves 1–7 contain [NND] 0, 0.0025, 0.0050, 0.0075, 0.0100, 0.0125, and 0.0150 M. Insert: the corresponding Stern-Volmer plot of  $I^0/I$  vs. [NND] at 342 nm.

(31) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; p 43.

(32) Parker, C. A. *Photoluminescence of Solution*; Elsevier: New York, 1968; pp 83, 225.

(33) Wu, Z.-Z. Ph.D. Thesis, Simon Fraser University, 1986.

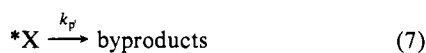
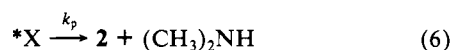
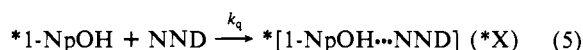
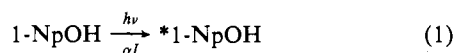
The information gained so far allows the assumption of the following reaction scheme for kinetic analysis by using 1-NpOH

Table II. Photonitrosation of Phenols (ArOH) with NND<sup>a</sup>

ArOH	product	yield, <sup>b</sup> % (convsn. %)	$k_q\tau_0$ (M <sup>-1</sup> )	$\frac{k_b^f}{k_p + k_p'}$	$\Phi_N(\text{lim})^f$
1-naphthol (1-NpOH, 1)	1,4-naphthoquinone-1-oxime (2)	52 (80)	74 ± 7 89 ± 9 <sup>e</sup>	5.7 4.3	0.15 ± 0.01 0.19 ± 0.01
2-naphthol (2-NpOH, 3)	1,2-naphthoquinone-1-oxime (4)	60 (36)	79 ± 10 <sup>e</sup>	13.2	0.071 ± 0.005
1-anthrol (1-AnOH, 5)	1,4-anthraquinone-1-oxime (6)	53 (61)	34 ± 8	4.4	0.19 ± 0.04
9-anthrol (9-AnOH, 7)	9,10-anthraquinone-9-oxime (8)	85 (100) <sup>c</sup>	79 ± 8	3.4	0.23 ± 0.01
9-phenanthrol (9-PnOH, 9)	9,10-phenanthraquinone-9-oxime (10)	34 (100) <sup>d</sup>	38 ± 6 <sup>e</sup>	4.7	0.18 ± 0.02

<sup>a</sup>Unless specified the reactions were carried out in dioxane. <sup>b</sup>The percentages were determined by GC and/or HPLC analysis with an internal standard. <sup>c</sup>Run in THF <sup>d</sup>Run in benzene. <sup>e</sup>Run in CH<sub>3</sub>CN. <sup>f</sup>Calculated from eq 10.

as a model. The key step is the formation of a complex (\*X) from collisional interaction (eq 5), which can dissipate by reverting to



starting material (eq 8) and collapsing to unidentified byproducts and the major product 2 (eq 6 and 7). The latter processes will be elaborated. A steady-state treatment gave eq 9 and 10 where  $\Phi_{\text{OX}}$  and  $\Phi_N$  are the quantum yield of the quinone monooxime formation and that of NND decomposition, respectively;  $\tau_0$  is the lifetime of the singlet excited state of 1-NpOH, i.e.,  $\tau_0 = 1/(k_f + k_t + k_{ST})$ . In eq 1,  $\alpha$  is the efficiency of the formation of \*1-NpOH upon absorption of the light intensity of  $I$  and is assumed to be unity

$$1/\Phi_{\text{OX}} = 1/\beta + 1/[\beta k_q\tau_0[\text{NND}]] \quad (9)$$

where  $\beta = \Phi_{\text{OX}}(\text{lim}) = k_p/(k_p + k_b + k_p')$

$$1/\Phi_N = 1/\beta' + 1/[\beta' k_q\tau_0[\text{NND}]] \quad (10)$$

where  $\beta' = \Phi_N(\text{lim}) = (k_p + k_p')/(k_p + k_b + k_p')$ . The limiting quantum yields,  $\Phi_{\text{OX}}(\text{lim})$  and  $\Phi_N(\text{lim})$ , are obtained at high concentrations of NND. The relation of reactions 6, 7, and 8 can be expressed as in eq 11 and 12.

$$k_p/k_p' = \beta'/\beta - 1 \quad (11)$$

$$k_b/k_p = (1 - \beta')/\beta \quad (12)$$

The  $\Phi_{\text{OX}}$  values for 1-NpOH self-nitrosation as a function of [NND] were determined at 19 °C by using a Hanovia lamp-Pyrex filter setup. The  $\Phi_{\text{OX}}$  and  $\Phi_N$  values were also determined at 31 °C with the light source of RPR 3000-Å lamps. A typical plot of  $1/\Phi$  vs.  $1/[\text{NND}]$  in dioxane is shown in Figure 3; the slope and intercept of the linear plot give  $k_q\tau_0$  and the reciprocal of the limiting  $\Phi$  value according to eq 9 and 10. For 1-NpOH,  $k_q\tau_0$  obtained by this method is smaller by a factor 0.63 than that obtained from fluorescence intensity quenching; this may arise from concurrent photolysis as well as absorption or incident light by the product 2 contributing as the major errors in quantum yield determinations. Conditional to the correctness of this assumption,

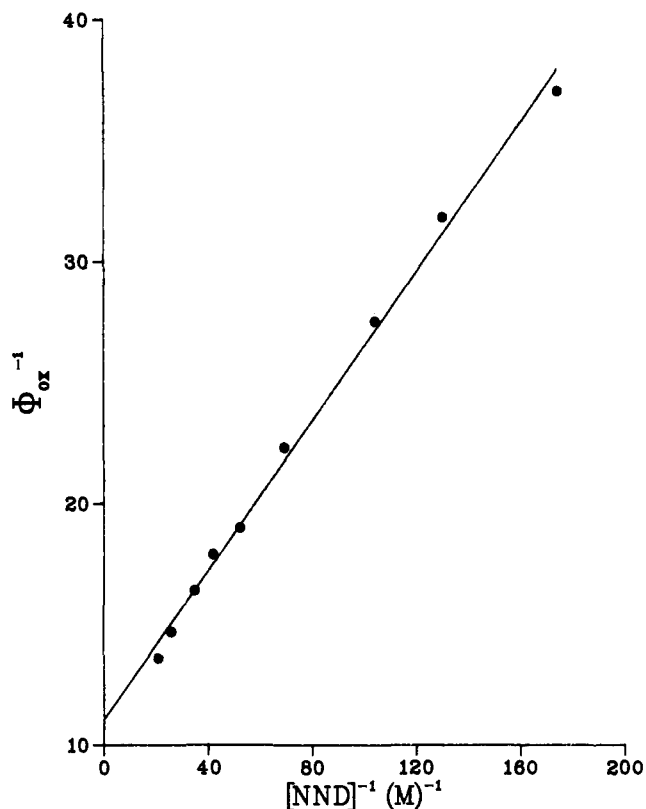


Figure 3. A plot of  $1/\Phi_{\text{OX}}$  against  $1/[\text{NND}]$  in dioxane according to eq 9; slope =  $0.154 \pm 0.004$ , intercept =  $11.1 \pm 0.4$ ,  $r = 0.998$ .

Table III. Kinetic Parameters of the Photonitrosation of 1-NpOH with NND at 19 °C from  $\Phi_{\text{OX}}$  Determinations<sup>a</sup>

solvent	$k_q\tau_0$ (M <sup>-1</sup> )	$k_q \times 10^{-9}$ (M <sup>-1</sup> s <sup>-1</sup> )	$(k_p + k_b)/k_p^d$	$\Phi_{\text{OX}}(\text{lim})$	$r$
dioxane <sup>b</sup>	72 ± 4	6.8 ± 0.4	10.0 ± 0.3	0.091 ± 0.003	0.998
	79 ± 6 <sup>c</sup>	7.0 ± 0.5	9.3 ± 0.4	0.097 ± 0.004	0.998
acetonitrile <sup>c</sup>	81 ± 9	11.0 ± 1.0	11.5 ± 0.6	0.080 ± 0.004	0.993
benzene <sup>b</sup>	33 ± 4	3.1 ± 0.4	21.7 ± 2.0	0.044 ± 0.004	0.998
toluene <sup>b</sup>	45 ± 9	4.3 ± 0.8	30.3 ± 4.0	0.032 ± 0.004	0.993
methanol <sup>c</sup>	85 ± 5	11.1 ± 0.6	58.8 ± 3.5	0.017 ± 0.001	0.996

<sup>a</sup>[1-NpOH] = 0.050 M, [NND] = 0.008–0.050 M; the conversions of 1-NpOH were 5–15%. <sup>b</sup> $\tau_0 = 10.6$  ns in nonpolar solvents (ref 23). <sup>c</sup> $\tau_0 = 7.7$  ns in methanol was adapted and assumed to be the same in acetonitrile. <sup>d</sup>Calculated from eq 9. <sup>e</sup>O-deuterio-1-naphthol (1-NpOD) was used.

we concluded that the lowest singlet excited state of 1-NpOH initiated the reaction. The relevant data in various solvents are summarized in Tables III and IV. Photoinitiated self-nitrosation of other phenols was also studied with respect to their quantum efficiencies as the function of NND concentrations and were analyzed similarly. The quenching parameters are included in Table II. It is noted that the quantum efficiency of quinone monooxime is not only determined by the Stern–Volmer parameter

**Table IV.** Kinetic Parameters of Photonitrosation of 1-NpOH with NND at 31 °C from  $\Phi_{\text{OX}}$  and  $\Phi_{\text{N}}$  Determinations<sup>a</sup>

solvent	$\Phi_{\text{OX}}$ -monitoring			$\Phi_{\text{N}}$ -monitoring			$k_p:k_p:k_b^b$
	$k_q\tau_0$ (M <sup>-1</sup> )	$\Phi_{\text{OX}}(\text{lim})$	$r$	$k_q\tau_0$ (M <sup>-1</sup> )	$\Phi_{\text{N}}(\text{lim})$	$r$	
dioxane	74 ± 7	0.08 ± 0.01	0.997	93 ± 9	0.15 ± 0.01	0.996	1.0:0.9:11.0
MeCN	89 ± 9	0.089 ± 0.005	0.995	74 ± 9	0.19 ± 0.01	0.993	1.0:1.0:9.0
THF	69 ± 9	0.094 ± 0.006	0.993	60 ± 5	0.24 ± 0.01	0.999	1.0:1.6:8.0
EtOH	60 ± 5	0.034 ± 0.002	0.997	110 ± 20	0.081 ± 0.005	0.990	1.0:1.6:26.4
MeOH	82 ± 13	0.020 ± 0.002	0.991	c			

<sup>a</sup> [1-NpOH] = 0.030 M, [NND] = 0.007–0.022 M; the conversions of 1-NpOH were 3–20% with irradiation at 300 nm at 31 °C. <sup>b</sup> Calculated from eq 11 and 12. <sup>c</sup> The change of [NND] during irradiation was too small.

**Table V.** Quenching of Photonitrosation and Fluorescence of 1-NpOH (0.03 M)

quencher	[NND] (M)	plot	$k_c\tau_0$ (M <sup>-1</sup> )	$\tau^e$ (ns)	$10^{-7}k_c$ (M <sup>-1</sup> s <sup>-1</sup> )
H <sub>2</sub> O <sup>a</sup>	0.02	$\Phi_{\text{OX}}^\circ/\Phi_{\text{OX}}^c$	0.188 ± 0.011	3.9	4.8 ± 0.3
	0.02	$\Phi_{\text{N}}^\circ/\Phi_{\text{N}}^c$	0.233 ± 0.012	3.9	6.0 ± 0.3
	0.0	$I^\circ/I^f$	0.325 ± 0.010	9.3	3.5 ± 0.1
TEA <sup>b</sup>	0.02	$\Phi_{\text{OX}}^\circ/\Phi_{\text{OX}}^{d,i}$	3.08 ± 0.01	4.1	75 ± 2
	0.006	$I^\circ/I^{f,g}$	13.9 ± 0.6	6.7	208 ± 8
	0.0	$I^\circ/I^f$	17.0 ± 0.7	10.7	160 ± 8
DMF <sup>b</sup>	0.01	$\Phi_{\text{OX}}^\circ/\Phi_{\text{OX}}^c$	0.34 ± 0.02	5.7	6 ± 0.4
	0.01	$I^\circ/I^{f,g}$	5.4 ± 0.3	5.7	95 ± 5
	0.0	$I^\circ/I^f$	10.1 ± 0.3	10.7	94 ± 3

<sup>a</sup> In THF solution. <sup>b</sup> In dioxane solution. <sup>c</sup> Irradiated with RPR 3000-Å lamps at 31 °C to cause 5–15% 1-NpOH conversion. <sup>d</sup> Irradiated with 450-W Hanovia lamp at 18 °C to cause 5–15% 1-NpOH conversions. <sup>e</sup> These  $\tau_0$  values were determined in THF and dioxane with a time-resolved fluorescence decay apparatus (ref 26). <sup>f</sup> Solutions were excited at 300 nm and monitored at 344 nm at room temperature. <sup>g</sup> The "front-face-illumination" technique was used. <sup>h</sup> This experiment was carried out at 31 °C. <sup>i</sup> [TEA] < 0.1 M.

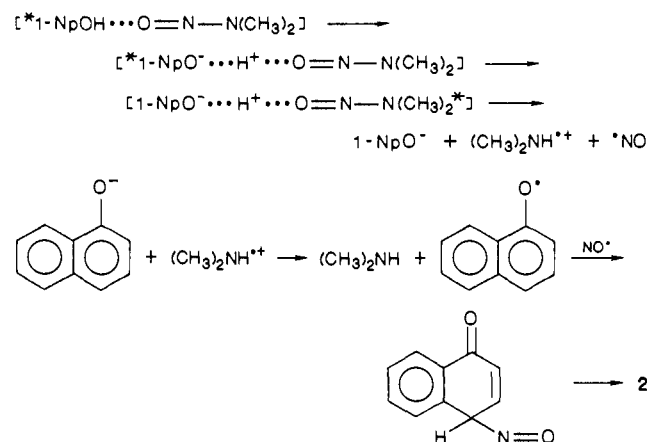
$k_q\tau_0$  but also by the subsequent competing reaction of the complexes. Tables III and IV show the solvent effects on these two parameters; protic solvents give low  $\Phi_{\text{OX}}(\text{lim})$  value while aprotic polar solvents tend to give larger  $k_q\tau_0$  and  $\Phi_{\text{OX}}(\text{lim})$  values. The second experiment in Table III was carried out by using O-deuterated 1-naphthol (1-NpOD); the close similarity of the kinetic parameters with those of 1-NpOH indicated the lack of deuterium isotope effects in the self-nitrosation. This observation is consistent with the fact that the activation energy of the \*1-NpOH deprotonation in water<sup>11,12</sup>  $\Delta H^\ddagger = 0$ .

In order to examine the crucial water-transfer step, the photoreaction of 1-NpOH and NND in the presence of a general base, such as water, dimethylformamide (DMF), and triethylamine (TEA), was investigated. The quantum yield  $\Phi_{\text{OX}}$  and  $\Phi_{\text{N}}$  in THF solutions containing various concentrations of water but fixed concentrations of 1-NpOH and NND were determined, and  $\Phi_{\text{OX}}^\circ/\Phi_{\text{OX}}$  or  $\Phi_{\text{N}}^\circ/\Phi_{\text{N}}$  were plotted against water concentrations to obtain quenching parameter  $k_c(\text{H}_2\text{O})\tau$ . The quenching parameter,  $k_c(\text{H}_2\text{O})\tau_0$  of 1-NpOH fluorescence by water in THF was also determined by the standard method. The quenching rate constants by water,  $k_c(\text{H}_2\text{O})$ , in both cases were calculated by using  $\tau_0$  and  $\tau$ , the 1-NpOH singlet state lifetime in the absence and presence of NND, obtained from time-resolved fluorimetry.<sup>26</sup> The quenching data by water, TEA and DMF are summarized in Table V. The agreement in the quenching rate constants of self-nitrosation and fluorescence intensities of 1-NpOH by water is excellent, while the corresponding quenching rate constants by TEA show only reasonably good agreement; but those corresponding data by DMF differed by more than an order of magnitude. It was observed that in these steady-state quenchings of \*1-NpOH fluorescence, no new emission was observed in the presence of water, TEA, and DMF.<sup>33</sup> The details of spectrometry and calculations were described in the thesis submitted.<sup>33</sup>

## Discussion

The pattern of photoinduced self-nitrosation of various polycyclic phenols with NND clearly shows that the reaction is initiated from the lowest singlet excited state, but not the triplet state, of the phenols. Since the photoreaction does not occur from exci-

## Scheme II



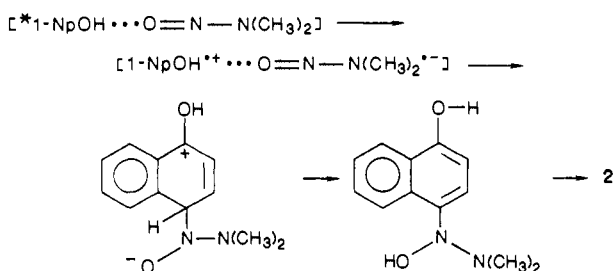
tation of methyl 1-naphthyl ether, it is assumed that the enhanced acidity of excited state 1-NpOH, and also other phenols, initiates the reaction by transferring its proton to NND followed by energy migration to cause photodissociation of NND to the dimethylammonium radical and nitric oxide. The formation of quinone monooxime from these radical species and phenolates can be described by various mechanisms; one of them is shown. The exciplex \*X proposed in eq 5 may be elaborated as in Scheme II. It should be mentioned that an alternative sensitization sequence (i.e., energy transfer as the first step) would de-excite \*1-NpOH and lead to no net reaction since ground-state 1-NpOH is not acidic enough to serve as a proton source in photodecomposition of NND.<sup>18–21</sup>

The data summarized in Tables III and IV represent the solvent effects on the event leading to photodecomposition of NND (eq 1–8) since the subsequent reactions do not reproduce NND. The quenching rate constants in various solvents (Table III) approach the diffusion rate constants and appear to be higher in polar solvents than in benzene or toluene. However, the low quantum yields in alcoholic solvents as compared to those in aprotic polar solvents are believed to arise from much faster reversion to the ground state (eq 8) in competition with the successful reaction (eq 6). It may be suggested that a protic molecule in a solvent shell competes the excited state proton in \*X and reduces the probability of ESPT to NND since ESPT to oxygen bases is well known.<sup>11,12</sup>

The crucial questions in the proposed mechanism are, first, that proton transfer from \*1-NpOH is the key step that initiates the process and, second, energy migration is necessary to cause NND photodissociation. Owing to fast proton quenching of naphtholates by external protons,<sup>5–13</sup> the quantum yields of naphtholate emission is low in particular in acidic aqueous solution. In our case emission from naphtholate or its complexes in the presence of NND could not be confirmed because of weak emission in the >400-nm region, most likely owing to the subsequent energy migration as a competing step within the complex \*X. Indeed it is shown that the emission peak of \*1-NpO- is quenched by NND efficiently.<sup>33</sup>

The requirement of the ESPT step is nicely demonstrated by the quenching of the self-nitrosation by general bases that are not likely to quench \*1-NpOH by other ways, e.g., electron or energy transfer. The ESPT of \*1-NpOH to water is a well-established phenomenon<sup>5,6,11–13</sup> by fast kinetic spectroscopy. The ESTP step

## Scheme III



to TEA at 77 K has been shown<sup>34,35</sup> by the shift of emission to ca. 400 nm assigned to emission of hydrogen-bonded  $*1\text{-NpO}^-$ . The occurrence of a ESPT step to TEA in acetonitrile and dioxane was confirmed<sup>33</sup> by observing a low quantum yield emission peak at 460–470 nm with an isosbestic point at 440 nm at room temperature. Under similar conditions, 2-NpOH emits a new peak at 450–460 nm with an isosbestic point at 415 nm.<sup>33,36</sup> While another quenching mechanism (e.g., electron transfer) may also be possible for the interaction of TEA with  $*\text{NpOH}$ , the appearance of the new emission can be taken as a proof of the quenching of  $*\text{NpOH}$  by ESPT; the low intensity of the new emission has precedence in a similar quenching by water.<sup>6,12</sup> This conclusion is consistent with the previous workers who have arrived at the same conclusion.<sup>35–38</sup> *The reasonable agreements in the quenching rate constants by water and TEA of the self-nitrosation of 1-NpOH in one hand and those of  $*1\text{-NpOH}$  fluorescence by ESPT in the other indicate that indeed the ESPT step initiates the nitrosation process.* DMF also interacts with  $*1\text{-NpOH}$  causing the fluorescence peak to shift to 360 nm, at 77 K, which has been assigned as hydrogen-bonded exciplex emission.<sup>34,35</sup> DMF is also known to form ground-state complexes through hydrogen bonding<sup>39</sup> with a high equilibrium constant of  $60 \text{ M}^{-1}$  in  $\text{CCl}_4$ . It is possible that owing to the competing ground-state complex formations, the self-nitrosation is not quenched by DMF as efficiently as  $*1\text{-NpOH}$  fluorescence intensities.

Distinctly sluggish photoinitiated self-nitrosation with NND of 2-NpOH in comparison to that of 1-NpOH must arise from differences in their properties in the lowest singlet excited state. While some similarities exist, it is shown recently that  $*1\text{-NpOH}$  undergoes deuterium exchange at the 5- and 8-positions in acidic solution while  $*2\text{-NpOH}$  shows no tendency of the exchange.<sup>8–12</sup> The lowest singlet excited state of  $*1\text{-NpOH}$  exhibits lower  $\text{pK}_a(\text{S}_1)$  by two units, a faster deprotonation rate constant in water by 300 times,<sup>5–12</sup> and a higher dipole moment by about 2 Debye units<sup>27</sup> than those of  $*2\text{-NpOH}$ . The higher acidity and faster proton-transfer rate for  $*1\text{-NpOH}$  clearly support the ESPT step as the critical driving force pumping the self-nitrosation of 1-NpOH. The effects can be explained by stronger charge-transfer character in  $*1\text{-NpOH}$ , than that in  $*2\text{-NpOH}$ , causing a larger electron density depletion on oxygen atom:<sup>10,12</sup> the larger dipole moment of  $*1\text{-NpOH}$  confirms this postulation.

The photolabile state (i.e., the lowest singlet state) of NND has  $E_s = 72 \text{ kcal/mol}$ .<sup>21</sup> As this value is higher than  $E_s$  of the conjugated bases of 1-AnOH, 9-AnOH, and 9-PnOH, normal course of classical energy transfer via collision complexes will be highly endothermic and is not expected to occur. The fact that these phenols undergo photoinitiated self-nitrosation smoothly suggested that other mechanisms exist to transmit excitation energy to proton-associated NND. It is proposed that the exciplex

(34) At 77 K in isopentane–methylcyclohexane, 1-NpOH in the presence of TEA or DMF emits fluorescent peaks at 400 and 360 nm and has been assigned to the  $*1\text{-NpO}^-$  species hydrogen bonded to TEA and DMF ( $*1\text{-NpO}^- \cdots \text{H}^+ \cdots \text{S}$ ), respectively (ref 35).

(35) Matsuyama, A.; Baba, H. *Bull. Chem. Soc. Jpn.* 1971, 44, 1162.

(36) Matsuzaki, A.; Nagakura, S.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* 1974, 47, 1152.

(37) Mataga, N.; Kaifu, Y. *J. Chem. Phys.* 1962, 36, 2804.

(38) Mataga, N.; Kawasaki, Y.; Torihashi, Y. *Theor. Chim. Acta* 1964, 2, 168.

(39) Devaure, J.; Huong, P. V. *Bull. Soc. Chem. Fr.* 1971, 11, 3917.

Table VI.  $^1\text{H}$  NMR Parameters of Quinone Monooximes in  $\text{CDCl}_3$ 

comps	chemical shifts in ppm
2	6.67 (d, 1 H, $J = 11 \text{ Hz}$ ), 7.58 (t, 1 H, $J = 8 \text{ Hz}$ ), 7.64 (t, 1 H, $J = 8 \text{ Hz}$ ), 8.02 (d, 1 H, $J = 11 \text{ Hz}$ ), 8.17 (t, 2 H, $J = 8 \text{ Hz}$ ), 8.41 (s, 1 H, $\text{D}_2\text{O}$ exch)
4	6.57 (d, 1 H, $J = 10 \text{ Hz}$ ), 7.74 (d, 1 H, $J = 10 \text{ Hz}$ ), 7.52–7.56 (m, 3 H), 8.37 (d, 1 H, $J = 8 \text{ Hz}$ ), 17.52 (s, 1 H, $\text{D}_2\text{O}$ exch)
6	6.74 (d, 1 H, $J = 10 \text{ Hz}$ ), 7.57 (t, 1 H, $J = 9 \text{ Hz}$ ), 7.63 (t, 1 H, $J = 9 \text{ Hz}$ ), 7.97 (d, 1 H, $J = 9 \text{ Hz}$ ), 8.06 (d, 1 H, $J = 9 \text{ Hz}$ ), 8.11 (d, 1 H, $J = 10 \text{ Hz}$ ), 8.22 (s, 1 H, $\text{D}_2\text{O}$ exch), 8.69 (s, 1 H), 8.74 (s, 1 H)
8	7.59 (t, 1 H, $J = 8 \text{ Hz}$ ), 7.65 (t, 2 H, $J = 8 \text{ Hz}$ ), 7.73 (t, 1 H, $J = 8 \text{ Hz}$ ), 8.20 (d, 1 H, $J = 8 \text{ Hz}$ ), 8.27 (d, 1 H, $J = 8 \text{ Hz}$ ), 8.43 (d, 1 H, $J = 8 \text{ Hz}$ ), 8.69 (s, 1 H, $\text{D}_2\text{O}$ exch), 9.02 (d, 1 H, $J = 8 \text{ Hz}$ )
10	7.52 (m, 3 H), 7.80 (t, 1 H, $J = 8 \text{ Hz}$ ), 8.13 (d, 1 H, $J = 8 \text{ Hz}$ ), 8.20 (d, 1 H, $J = 8 \text{ Hz}$ ), 8.35 (d, 1 H, $J = 8 \text{ Hz}$ ), 8.43 (d, 1 H, $J = 8 \text{ Hz}$ ), 17.06 (s, 1 H, $\text{D}_2\text{O}$ exch)

$*\text{X}$  is a tightly bound ion pair through hydrogen bonding that allows energy to migrate and localize in the nitrosamino moiety. As the dissociation energy of the N–NO bond is only 40 kcal/mol,<sup>40</sup> these anions possess enough energy to cause the scission.

One prominent alternative mechanism which must be considered for the quenching step of eq 5 is the electron-transfer process from  $*1\text{-NpOH}$  to NND as shown in Scheme III. While such electron transfer is feasible on the basis of Weller's empirical relation,<sup>33</sup> this pathway is not a serious contender because of the fact that it can not explain quenching by water or TEA.

The present photoinduced self-nitrosation of phenols proceeds better in aprotic polar solvents, and their ESPT process must be different from those in water which has cluster of hydrogen bonding. In organic solvent the interaction of an excited state phenol with NND must be essentially diffusion controlled as shown by  $k_q$  values in these experiments. Thus the ESPT process in organic solvents is diffusion controlled and must occur within the exciplex.

## Experimental Section

**General Conditions.** Unless otherwise specified, the following experimental conditions prevailed. Infrared spectra (IR) were recorded with a Perkin-Elmer 559B spectrophotometer with use of Nujol mull or KBr pellet. Ultraviolet and visible spectra (UV) were taken with a Varian Cary 210 spectrophotometer. Mass spectra (MS) and gas chromatography mass spectra (GC-MS) were obtained on a Hewlett-Packard 5985 GC-MS system by electron ionization (at 70 eV). Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded with a Bruker WM-400 spectrometer in  $\text{CDCl}_3$  solution. Chemical shifts are reported in  $\delta$  values in ppm and coupling constants ( $J$ ) in Hz. Elemental analyses were carried out by M. K. Yang. Gas chromatography (GC) analyses were performed on a Hewlett-Packard 5790A chromatograph (FID), equipped with an OV-1 capillary column and a Hewlett-Packard 3390A chart integrator. High-pressure liquid chromatography (HPLC) analyses were performed on a Waters Associates HPLC system, equipped with a Bondapak  $\text{C}_{18}$  column and a Waters Associates Model-440 UV detector at 254 or 340 nm. Fluorescence spectra were taken with a Perkin-Elmer MPF 44B spectrophotometer and uncorrected.

**Chemicals and Apparatus.** For the preparative photochemical reactions, reagent grade solvents were distilled prior to use. For spectroscopy, spectroscopic grade solvents were used as supplied. Methylcyclohexane (BDH) and isopentane (Mallinckrodt) were carefully purified according to standard methods.<sup>41</sup> NND was prepared and purified according to the procedure described elsewhere.<sup>42</sup> *It should be noted that nitrosamines are powerful carcinogens and appropriate caution was exercised on handling in the laboratory.* *O*-Deuterio-1-naphthol (1-NpOD) was prepared by repetitive exchange of the hydroxylic proton by shaking with  $\text{D}_2\text{O}$ .<sup>33</sup> Commercially available reagent grade chemicals were purified by recrystallization, vacuum sublimation, or a combination of the both. Nitrogen gas (Union Carbide) was purified by scrubbing through a Fieser

(40) Fisher, I. P.; Henderson, E. *Trans. Faraday Soc.* 1967, 63, 1342.

(41) Perrin, D. D.; Arinarego, W. L. L.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1966.

(42) Vogel, A. I. *Practical Organic Chemistry*; Longmans Green: New York, 1956; p 426.

Table VII. UV, IR, and Mass Spectral Data of Quinone Monooximes

compds	$\lambda_{\max}$ in nm ( $\epsilon$ )	$m/e$ (% fragment)	$V_{\max}$ in $\text{cm}^{-1}$
<b>2</b>	214 (22 000)	173 (100, $\text{M}^+$ )	3160 (br), 3070 (br), 1627 (s)
	282 (24 000)	143 (10, M-NO)	1573 (m), 1443 (m), 1340 (m)
	345 (13 000)	115 (54)	1320 (m), 1160 (w), 1095 (m)
<b>4</b>	215 (26 300)	173 (100, $\text{M}^+$ )	978 (s), 850 (m), 800 (w), 760 (s)
	261 (15 $\mu\text{tc}$ 700)	156 (60, M-OH)	3440 (br), 1620 (s), 1525 (m)
	368 (6 000)	143 (10, M-NO)	1455 (m), 1406 (w), 1377 (m)
		128 (48)	1333 (w), 1260 (w), 1218 (m)
		115 (64)	1075 (s), 965 (m), 855 (s)
<b>6<sup>a</sup></b>	290 (39 700)	223 (100, $\text{M}^+$ )	768 (m), 760 (m), 720 (m)
	297 (41 800)	206 (45, M-OH)	3220 (br), 3130 (br), 1645 (m)
	412 (6 100)	193 (10, M-NO)	1620 (s), 1585 (m), 1465 (s)
<b>8</b>	231 (37 000)	177 (8), 165 (22)	1380 (m), 1320 (m), 1030 (w)
	244-250 (18 000)	223 (100, $\text{M}^+$ )	970 (7), 845 (m), 760 (m)
	279 (16 000)	193 (258, M-OH)	3270 (br), 1648 (s), 1595 (m)
	340-350 (5 200)	177 (10)	1465 (m), 1323 (s), 1315 (s)
<b>10</b>	254 (41 000)	165 (20)	1175 (w), 1020 (m), 940 (w)
	306 (shoulder, 6 200)	223 (70, $\text{M}^+$ )	780 (w), 680 (m)
	385 (6 000)	206 (100, M-OH)	3440 (br), 1635 (w), 1600 (m)
	414 (2 600)	178 (50)	1535 (s), 1455 (m), 1280 (m)
		165 (60), 151 (40)	1120 (m), 990 (s), 845 (m)
			765 (s), 725 (s)

<sup>a</sup>UV spectra were taken in  $\text{CH}_3\text{OH}$  except this one which was taken in dioxane.

solution, concentrated sulfuric acid, and then potassium hydroxide pellets.

**Preparative Photonitrosation. General Procedures.** For preparative purposes, either Hanovia lamp (450 or 200 W) in immersion apparatus or a Rayonet Photochemical Reactor equipped with RPR 3000 Å were used. Sometimes a small scale reaction was carried out in a flat cylindrical cell placed near a Hanovia immersion jacket. Unless otherwise specified, the following general procedures were followed. A solution of NND and a phenol was placed in a vessel which was cooled in a water bath and purged with nitrogen. A sample of the photolysate was withdrawn at intervals for GC or HPLC analysis. A zero-hour sample was kept in the dark at the same temperature and analyzed by GC or HPLC as a control. When the color of photolysates turned red-brown, the irradiation was stopped. The solvent was evaporated under reduced pressure, and the residue was separated into a small amount of an ether-insoluble black solid and ether-soluble fraction. The former was filtered from the ethereal solution of the residue and was not investigated further. The latter was washed with a 5% aqueous NaOH solution (2  $\times$  10 mL). The combined basic phase was neutralized immediately with acetic acid, and the precipitate was filtered and purified by recrystallization to afford quinone monooxime. The percent yields of the quinone monooximes were calculated on the basis of the phenolic compounds, and the pertinent spectral data were summarized in Tables VI and VII.

**1-NpOH (1).** Photolysis of 1-NpOH (30 mg, 0.2 mmol) and NND (45 mg, 0.6 mmol) in 5-mL aliquots of THF, dioxane, methanol, or acetonitrile in Pyrex tubes (1.1  $\times$  12 cm) for 3 h gave **2** (retention time 3.16 min by HPLC) in 52%, 66%, 32%, and 49%, respectively. The crude product was recrystallized from  $\text{MeOH-H}_2\text{O}$  twice to afford yellow needles of 1,4-naphthoquinone-1-oxime (**2**), mp 189-191 °C (dec). Anal. Calcd for  $\text{C}_{10}\text{H}_7\text{NO}_2$ : C, 69.36; H, 4.05; N, 8.09. Found: C, 69.09; H, 3.71; N, 7.92.

A similar dioxane solution was irradiated under oxygen at 15 °C for 3 h. The dark-brown photolysate was shown by GC-MS to contain four compounds; 1-NpOH (180 °C, 2.57 min,  $m/e$  144  $\text{M}^+$ ), 2-nitro-1-naphthol (180 °C, 4.68 min;  $m/e$  189  $\text{M}^+$ , 172 M-OH, 143 M- $\text{NO}_2$ ), **2** (180 °C, 6.61 min;  $m/e$  174  $\text{M}^+$ ), and an unknown compound (180 °C, 11.46 min;  $m/e$  212  $\text{M}^+$ ) in the peak ratio of 2.5:1.00:13.9:1.6. 2-Nitro-1-naphthol was identified by the matching of its GC peak with that of an authentic sample. The yields of 2-nitro-1-naphthol, **2**, and the unknown were calculated to be 5%, 67%, and 8%.

**2-NpOH (3).** A solution of 2-NpOH (288 mg, 2 mmol) and NND (720 mg, 10 mmol) in 40 mL of dioxane was irradiated through a Corex filter under  $\text{N}_2$  for 5 h to give a dark red-brown photolysate. A fraction obtained from chromatography on silica gel was recrystallized from  $\text{MeOH-H}_2\text{O}$  and then from benzene/petroleum ether (30-60 °C) to give **4** as brown prisms: mp 107-108 °C. Anal. Calcd for  $\text{C}_{10}\text{H}_7\text{NO}_2$ : C, 69.36; H, 4.05; N, 8.09. Found: C, 69.24; H, 4.07; N, 7.98.

**1-Anthrol (5).** 1-AnOH was prepared according to the method of Ferrero and Conzetti.<sup>43</sup> A dioxane solution (25 mL) containing 1-AnOH (194 mg, 1 mmol) and NND (300 mg, 4.05 mmol) was irradiated through a Pyrex filter under nitrogen at about 15 °C for 14 h. The ether-insoluble fraction was a black solid (90 mg), and the ether-soluble

fraction afforded the brown solid (43 mg), which was recrystallized from  $\text{MeOH-H}_2\text{O}$  to give orange crystals (13 mg): 1,4-anthraquinone-1-oxime (**6**), mp 174-176 °C dec. Anal. Calcd for  $\text{C}_{14}\text{H}_9\text{NO}_2$ : C, 75.34; H, 4.04; N, 6.28. Found: C, 75.46; H, 4.03; N, 5.93.

**9-Anthrol (7).** A solution of anthrone (388 mg, 2 mmol) and NND (400 mg, 5.4 mmol) in THF (35 mL) was irradiated through a Pyrex filter under nitrogen at about 15 °C for 3 h. The crude product afforded a yellow solid (460 mg) which was recrystallized from ethanol-water to give yellowish crystals (373 mg, 84%), identified as 9,10-anthraquinone-9-oxime (**8**), mp 228-230 °C dec. Anal. Calcd for  $\text{C}_{14}\text{H}_9\text{NO}_2$ : C, 75.34; H, 4.04; N, 6.28. Found: C, 75.14; H, 4.02; N, 5.99.

**9-Phenanthrol (9).** A solution of 9-phenanthrol (120 mg, 0.062 mmol) and NND (89 mg, 1.2 mmol) in benzene (25 mL) was irradiated with RPR 3000Å lamps (21 W  $\times$  16) under nitrogen at 31 °C for 8 h. The residue (80 mg) obtained from the ether solution was chromatographed on silica gel to give 9,10-phenanthraquinone-9-oxime (**10**) as orange crystals (26 mg): mp 157-158 °C. Anal. Calcd for  $\text{C}_{14}\text{H}_9\text{NO}_2$ : C, 75.34; H, 4.04; N, 6.28. Found: C, 75.52; H, 3.76; N, 6.55.

**Laser Photolysis.** These experiments were performed in Professor G. B. Porter's laboratory, Department of Chemistry, University of British Columbia. The laser pulses (about 8-12 ns at 308 nm and maximum pulse energy of 80 mJ) were generated from a Lumonics TE-861-T<sub>3</sub> excimer laser with HCl, H<sub>2</sub>, and Xe as the operating gas mixture. The pulse frequency was adjusted to give 0.3 W. The sample solution in a quartz tube (1.1  $\times$  12 cm) was sealed with a septum and purged with nitrogen.

**1-NpOH.** The following sample solutions were prepared in quartz tubes: no. 1, a 7.5-mL dioxane solution containing 1-NpOH (54 mg, 0.375 mmol) and NND (54 mg, 0.73 mmol); no. 2, a 1.2-mL THF solution containing 1-NpOH (9 mg, 0.0625 mmol) and NND (30 mg, 0.208 mmol); no. 3, a 1.2-mL methanol solution containing 1-NpOH (9 mg, 0.0625 mmol) and NND (30 mg, 0.208 mmol).

The deaerated solutions were irradiated with laser pulses at 30-35 °C for 10 min (no. 1) and 20 min (no. 2 and no. 3). GC analysis (at 180 °C) of light brown photolysate of no. 1 showed three peaks for 1-NpOH at 2.55 min, an unknown compound at 3.05 min, and **2** at 6.55 min in the ratio of 10:1.0:4.1. The conversion of 1-NpOH and the yield of **2** were determined to be 11.5% and 80%, respectively. Similar analysis of brownish photolysate of no. 2 also showed three peaks for 1-NpOH at 2.56 min, an unknown compound at 2.67 min, and **2** at 6.67 min in the peak-area ratio of 28.8:1.8:1.0. The conversion of 1-NpOH and the yield of **2** were determined to be 9.2% and 38%, respectively. GC analysis of yellowish photolysate of no. 3 showed only one peak for 1-NpOH at 2.57 min.

**Sensitization by Xanthone and 2-Acetonaphthone.** Two dioxane solutions of 1-NpOH (18 mg, 0.125 mmol), NND (10 mg, 0.135 mmol) containing either xanthone (196 mg, 1 mmol) or 2-acetonaphthone (85 mg, 0.5 mmol) were sealed in a quartz tube (1.1  $\times$  12 cm). The solution was purged by nitrogen and irradiated through a GWA filter (cutoff < 350 nm) at 15 °C for 6 h. GC analysis (at 180 °C) of the photolysate showed that the peak-area ratios of 1-NpOH and the standard (1-nitronaphthalene) were not changed (0.35 and 0.31 before and after irradiation, respectively). No peak at 6.55 min for the compound **2** was detected.

(43) Ferrero, P.; Conzetti, A. *Helv. Chim. Acta* 1928, 11, 1152.

**Triplet Quenching by Cyclohexadiene.** Seven THF solutions (5 mL) of 1-NpOH (0.030 M) and NND (0.030 M) containing varied concentrations of cyclohexadiene (CHDE, 0-0.009 M) were degassed and irradiated on a merry-go-round in a Rayonet photochemical reactor with 3000-Å lamps (21 W × 16) for 20 min at 31 °C. The actinometer solution of benzophenone (0.050 M)-benzohydro<sup>14</sup> (0.10 M,  $\Phi = 0.74$ ) in 5 mL of benzene was irradiated under the same conditions, but for 5 min. The concentration of quinone monooxime **2** was determined by HPLC (C<sub>18</sub> column, MeOH/H<sub>2</sub>O = 70/30 by volume) with 1-nitro-

naphthalene as the internal standard.

**Fluorescence Spectra and Fluorescence Intensity Quenching.** Fluorescence spectra were either recorded with the standard technique of the right angle configuration of incident and emitting light or by a "front-face" illumination technique.<sup>31-33</sup> If both quencher and quenchee absorb at the wavelength excitation, emission intensities were corrected according to light energy absorbed by two for calculations of  $I^0/I$ .

**Acknowledgment.** We are grateful to the Natural Science and Engineering Research Council of Canada, Ottawa, for generous financial support. Z.Z.W. thanks Simon Fraser University for an award of a SFU Open Scholarship.

(44) Hammond, G. S.; Leermakers, P. A. J. *Phys. Chem.* 1962, 66, 1148.

## Communications to the Editor

### Reduction of Silicon-Hydrogen Bond Strengths<sup>1</sup>

J. M. Kanabus-Kaminska, J. A. Hawari, and D. Griller\*

Division of Chemistry  
National Research Council of Canada  
Ottawa, Ontario, Canada K1A 0R6

C. Chatgililoglu\*

Consiglio Nazionale delle Ricerche, Ozzano Emilia  
Bologna, Italy 40064

Received January 9, 1987

The factors which moderate carbon-hydrogen bond dissociation energies (BDE), eq 1 and 2, are now reasonably well understood. Bond dissociation energies are lowered when conjugated radicals



$$BDE(R-H) = \Delta H_f(R^{\cdot}) + \Delta H_f(H^{\cdot}) - \Delta H_f(R-H) \quad (2)$$

are formed (e.g., R = allyl or benzyl),<sup>2,3</sup> when the radical center has an adjacent heteroatom,<sup>2-6</sup> or when the dissociation relieves steric compression in R-H.<sup>7</sup> The underlying principles of these and other effects have been the subject of extensive debate and discussion.<sup>2,7</sup> However, there is hardly any information on the factors which influence the strengths of silicon-hydrogen bonds.

Almost all of the available thermochemical data on Si-H bond dissociation energies are due to the pioneering work of Walsh and his colleagues.<sup>8</sup> To a large extent, they have shown that the factors which dominate the thermochemistry of the C-H bond are essentially unimportant in the silicon congeners. For example, BDE(H<sub>3</sub>Si-H) = 90.3, BDE(Me<sub>3</sub>Si-H) = 90.3, and BDE(PhSiH<sub>2</sub>-H) = 88.2 kcal mol<sup>-1</sup> whereas the corresponding series of bond strengths in hydrocarbon chemistry<sup>2</sup> would span a range of 26 kcal mol<sup>-1</sup>! Despite the uniformity of most Si-H bond strengths, there are some interesting anomalies. For example, the presence of three fluorines has a profound strengthening effect,<sup>8</sup> BDE(F<sub>3</sub>Si-H) = 100.1 kcal mol<sup>-1</sup>, whereas the presence of a second silyl group has a moderate weakening effect,<sup>8</sup> BDE(H<sub>3</sub>SiSiH<sub>2</sub>-H) = 86.3 kcal mol<sup>-1</sup>. We have pursued this last result and have found that it holds the key to the systematic reduction of Si-H bond strengths.

Silicon-hydrogen bond dissociation energies were measured by a photoacoustic technique which has been described in detail elsewhere.<sup>9,10</sup> Pulses from a nitrogen laser (337 nm; pulse width

**Table I.** Bond Dissociation Energies and Related Kinetic Data for the Si-H Bonds in Silanes

	$\Delta H_{\text{obsd}}$ kcal mol <sup>-1</sup>	$k_4$ M <sup>-1</sup> s <sup>-1</sup>	$k_8$ M <sup>-1</sup> s <sup>-1</sup>	BDE(R <sub>3</sub> Si-H) <sup>a</sup> kcal mol <sup>-1</sup>
Et <sub>3</sub> SiH	76.3	$5.7 \times 10^6$ <sup>b</sup>	$1.0 \times 10^6$ <sup>c</sup>	90.1
Me <sub>3</sub> Si(Me) <sub>2</sub> SiH	84.9	$1.7 \times 10^7$ <sup>d</sup>	$1.5 \times 10^6$ <sup>e</sup>	85.3
(Me <sub>3</sub> Si) <sub>3</sub> SiH	95.9	$1.1 \times 10^8$ <sup>f</sup>	$5.9 \times 10^6$ <sup>g</sup>	79.0

<sup>a</sup>Relative error  $\pm 1$  kcal mol<sup>-1</sup>. Absolute error  $\pm 2$  kcal mol<sup>-1</sup>. <sup>b</sup>Reference 21. <sup>c</sup>Reference 22. <sup>d</sup>Reference 23. <sup>e</sup>Reference 24. <sup>f</sup>Reference 20. <sup>g</sup>Reference 25.

10 ns;  $h\nu = 84.8$  kcal mol<sup>-1</sup>) were used to photolyze deoxygenated solutions containing di-*tert*-butyl peroxide (4-16% v/v) and an appropriate silane in isoctane, which were flowed through a standard UV flow cell. The photolysis gave rise to reactions 3 and 4, and the net heat evolved in these processes caused a shock



wave in the solution that was detected by a piezoelectric transducer that was clamped to the cell wall. The laser light intensity used in the experiments was sufficiently low that the concentrations of the reagents were essentially unaffected by the photolysis. The signals from the transducer were stored and averaged in an oscilloscope, and their amplitude was found to be proportional to the light absorbed by the peroxide in the solution. The system was calibrated by using *o*-hydroxybenzophenone, which efficiently and rapidly converts light into heat.<sup>9,11</sup>

Since the rate constants for reaction 4 are known (Table I) it was a simple matter to adjust the silane concentrations (0.2-1.0 M) so that reaction 4 was complete in a time which was short compared to the ca. 2- $\mu$ s response of the system.<sup>9</sup> At the same time this response was long compared to the lifetimes for bimolecular decay of the silyl radicals. The observed heat deposition,  $\Delta H_{\text{obsd}}$ , therefore reflected the contribution from the laser pulse (84.8 kcal mol<sup>-1</sup>) and that from  $\Delta H_f$ , the combined heats of reactions 3 and 4. The relationship between the experimental result and the heats of formation of the reactants and products is defined in eq 5 and 6, where  $\Phi$  is the quantum yield for peroxide

$$-\Delta H_{\text{obsd}} = 84.8 - \Delta H_R \Phi \text{ kcal mol}^{-1} \quad (5)$$

$$\Delta H_R = 2\Delta H_f(t\text{-BuOH}) + 2\Delta H_f(R_3\text{Si}^{\cdot}) - \Delta H_f(t\text{-BuOOBu-}t) - 2\Delta H_f(R_3\text{SiH}) \quad (6)$$

(1) Issued as NRCC publications No. 27883.

(2) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* 1982, 33, 493.

(3) Grell, M. A.; Colussi, A. J. *Int. J. Chem. Kinet.* 1985, 17, 257.

(4) Burkey, T. J.; Castelhan, A. L.; Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* 1983, 105, 4701.

(5) Grell, M. A.; Colussi, A. J. *J. Phys. Chem.* 1984, 88, 5995.

(6) Kondo, O.; Benson, S. W. *Int. J. Chem. Kinet.* 1984, 16, 949.

(7) Ruchardt, C. *Angew. Chem., Int. Ed. Engl.* 1970, 9, 830.

(8) Walsh, R. *Acc. Chem. Res.* 1981, 14, 246.

(9) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* 1986, 108, 2218.

(10) Grabowski, J. J.; Simon, J. D.; Peters, K. S.; *J. Am. Chem. Soc.* 1984, 106, 4615 and references cited therein.

(11) Allen, N. S. *Polym. Photochem.* 1983, 3, 167.