$E_{1/2}$ for 2-aminophenol = 0.48 V vs. SCE at pH 7.4[33] and $E_{1/2}$ for catechol = 0.18 V vs. SCE at pH 7.0[34]).

The model 7_{ox} is able to oxidize primary amines (ethylamine and benzylamine) and amino acids and their derivatives (glycine and glycinamide) but does not oxidize a secondary (morpholine) or a tertiary amine (*N,N*-dimethylbenzylamine). This is surprising on the basis of amine oxidation potentials[19] which predict that *N,N*-dimethylbenzylamine would be much easier to oxidize than ethylamine. Also, *N,N*-dimethylbenzylamine and morpholine are oxidized by 3_{ox}. The finding that 7_{ox} reacts preferentially with primary amines and that some aminophenol **17** is formed supports these oxidations to occur via covalent addition-elimination mechanisms (eq 12 and 13). The absence of a kinetic isotope effect in the oxidation of benzylamine and benzylamine-d_2 by 7_{ox} shows that the rate-determining processes in the reaction must be carbinolamine and imine formation. Under the conditions of "aerobic autorecycling" oxidation of primary amines, the didecarboxymethoxatin (7_{ox}) and its ethyl ester (6_{ox}) are converted to redox inactive oxazoles (**20**) (eq 14).

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

Registry No. 1_{ox}, 72909-34-3; 3_{ox}, 84-12-8; 3_{ox} (urea adduct), 95912-06-4; **3** (aminophenol), 95912-15-5; 4_{ox}, 82701-91-5; 5_{ox}, 27318-90-7; 6_{ox}, 95911-95-8; 6_{ox} (methyl ester), 95912-14-4; 6_{ox} (hydrazone), 95911-98-1; 6_{ox} (urea adduct), 95912-05-3; 6_{red}, 95911-96-9; 6_{sem}, 95911-97-0; 7_{ox}, 95911-99-2; 7_{red}, 95912-00-8; 8_{ox}, 95912-01-9; **9**·2HCl, 21302-43-2; **9** (diazonium chloride), 95912-13-3; **10** (R = Me), 95912-02-0; **11** (R = Me), 95912-03-1; **12**, 95912-04-2; **15**, 95912-07-5; **17**, 95912-08-6; **20a**, 95912-09-7; **20a** (ethyl ester), 95935-32-3; **20b**, 95912-10-0; **20c**, 95912-11-1; **21**, 95912-12-2; $CH_3COCH(CH_3)CO_2Me$, 17094-21-2; $CH_3COCH(CH_3)CO_2Et$, 609-14-3; $(CH_3)_2CO$, 67-64-1; $(H_2N)_2CO$, 57-13-6; $H_2NCH_2CONH_2$·HCl, 1668-10-6; $PhCH_2NH_2$·HCl, 3287-99-8; $EtNH_2$·HCl, 557-66-4; $H_2NCH_2CO_2H$·HCl, 6000-43-7; $PhCONH_2$, 55-21-0; $PhCD_2NH_2$, 15185-02-1; 5-nitro-8-hydroxyquinoline, 4008-48-4.

(33) Bezuglyi, V. D.; Beills, Yu I. J. *Anal. Chem. USSR (Engl. Transl.)* **1965**, *20*, 1060.
(34) Pungor, E.; Szepesuary, E. *Anal. Chim. Acta* **1968**, *43*, 298.

Communications to the Editor

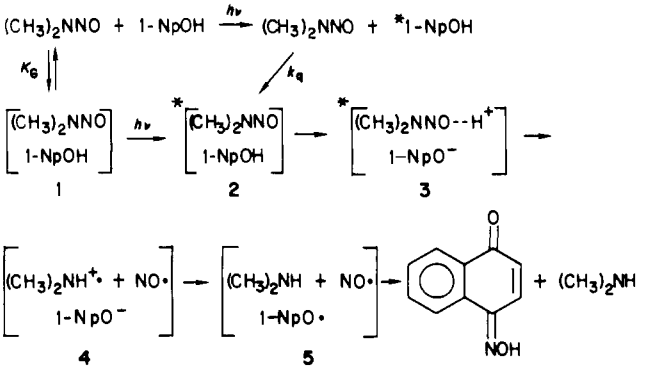
Photonitrosation Promoted by Enhanced Acidity of Singlet-State Phenols

Yuan L. Chow* and Zheng-Zhi Wu

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

Received October 22, 1984

We wish to demonstrate that singlet-excited-state naphthols[1,2] and anthrols can induce decomposition of *N*-nitrosodimethylamine (NND) by dual proton and energy-transfer processes occurring from an exciplex within the lifetimes of these phenol-phenolate couples. Although intramolecular proton transfer of excited-state phenols has been demonstrated,[3] the claim that the enhanced acidity of singlet-state 2-naphthol nitrosation[4] has been disputed on the grounds of the short excited-state lifetimes.[5] Due to highly dipolar nature, nitrosamines are known to associate extensively with aromatic π-electron clouds[6] as well as Lewis acids.[7] Upon excitation, an acid complex of NND rapidly dissociates[8-10] ($>10^9$ s^{-1}) to the aminium radical and nitric oxide.[11,12] This paper describes the utilization of the enhanced acidity and excitation energy of singlet state phenols to cause the NND photodissociation as shown in **1** → **2** → **3** → **4**.



Photolysis of 1-naphthol (1-NpOH, 25 mM) and NND (25 mM) in a variety of neutral solvents, e.g., THF, dioxane, methanol, acetonitrile, or toluene, through a Pyrex filter, gave 1,4-naphthoquinone monooxime and dimethylamine, the former in limiting quantum yields Φ_{ox} of 0.14-0.02. The chemical yields of quinone monooximes from various phenols under similar reaction conditions are listed in Table I together with the pertinent data. With appropriate filter systems or monochromatic light, irradiation of NND at 360-380 nm under these conditions did not cause the reaction; irradiation of 1-NpOH at 290-310 nm caused the photonitrosation. In the presence of HCl, irradiation of a similar solution induced the decomposition of NND[9,10] but no nitrosation of 1-NpOH. That the reaction is initiated from singlet state 1-NpOH is indicated by the quenching of 1-NpOH fluorescence by NND (vide infra) and by the failure of xanthone triplet (E_T = 74 kcal/mol)[18] to sensitize the photoreaction. The participation of enhanced acidity in the singlet excited state of 1-NpOH was shown by the following evidence. First, irradiation

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(2) Förster, T. *Z. Electrochem.* **1950**, *54*, 42; **1950**, *54*, 531.
(3) Isaks, M.; Yates, K.; Kalanderopoulos, P. *J. Am. Chem. Soc.* **1984**, *106*, 2730.
(4) Saeva, F. D.; Olin, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 5631.
(5) Chandross, E. A. *J. Am. Chem. Soc.* **1976**, *98*, 1053.
(6) (a) Chow, Y. L.; Fesser, M. M. *Chem. Commun.* **1967**, 239. (b) Williams, D. H.; Wilson, D. A. *J. Chem. Soc. B* **1966**, 144.
(7) Layne, W. S.; Jaffe, H. H.; Zimmer, H. *J. Am. Chem. Soc.* **1963**, *85*, 435, 1816.
(8) It has not been possible to detect excited states of *N*-nitrosopiperidine associated with an acid by subnanosecond excitation, which implies the photodissociation process is faster than 10^9 s^{-1}.
(9) Chow, Y. L. *Acc. Chem. Res.* **1973**, *6*, 354.
(10) Cessna, A. J.; Sugamori, S. E.; Yip, R. W.; Lau, M. P.; Snyder, R. S.; Chow, Y. L. *J. Am. Chem. Soc.* **1977**, *99*, 4044.
(11) The photodissociation of NND in solution does not occur under neutral conditions.[9] In the gas phase NND is photolyzed at 363.5 nm to $(CH_3)_2N$· and NO· with Φ = 1, which recombine extremely rapidly leaving no net reaction; the rate constant of the singlet-excited-state decomposition is estimated to be $>8.5 \times 10^9$ s^{-1}.[12]
(12) Geiger, G.; Huber, J. R. *Helv. Chim. Acta* **1981**, *64*, 989. Geiger, G.; Stafast, H.; Brühlmann, Y.; Huber, J. R. *Chem. Phys. Lett.* **1981**, *79*, 521. Müller, R. P.; Murata, S.; Huber, J. R. *Chem. Phys.* **1982**, *66*, 237.
(13) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905.
(14) Harris, C. M.; Selinger, B. K. *J. Phys. Chem.* **1980**, *84*, 1366.
(15) Weller, A. *Z. Phys. Chem. (Munich)* **1958**, *15*, 438.
(16) Yamamoto, S. A.; Kikuchi, K.; Kokubun, H. *J. Photochem.* **1976**, *5*, 469.
(17) Young, J. F.; Schulman, S. G. *Talanta* **1973**, *20*, 399.
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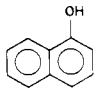
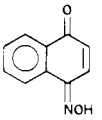
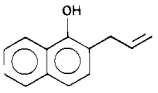
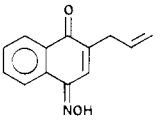
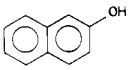
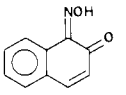
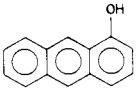
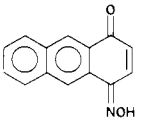
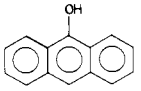
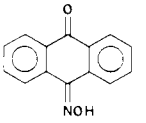
Table I. Sensitized Photonitrosation of Phenols with *N*-Nitrosodimethylamine

phenols (ArOH)	E_S(ArOH), kcal/mol	pK_a(S)	E_S(ArO$^-$),[d] kcal/mol	products	yields,[g] %	conversions[g] of ArOH, %
	91.3[a]	0.5[b] 2.5[c]	79 (360)		68	80 (dioxane)
	88.0[d]		77 (370)		64	74 (toluene)
	86.7[a]	2.8[c]	77 (370)		81	36 (dioxane)
	72.0[e]	−0.07[e]	62 (460)		64	42 (dioxane)
	72.0[d] (400)	0.6[f]	60 (480)		84[h]	(THF)

[a] Reference 13. [b] Reference 14. [c] Reference 15. [d] These values were calculated from the overlapping wavelengths (the figures in brackets) of absorption and fluorescence spectra for phenols (in MeOH) and phenolates (in MeOH-KOH) at room temperature by assuming that Stoke's shifts were small. [e] Reference 16. [f] Reference 17. [g] These percentages were obtained by GC and/or HPLC analysis, except that of anthraquinone monooxime. [h] The isolated yield.

of 1-methoxynaphthalene (E_S = 89.3 kcal/mol)[19] and NND under similar conditions caused no decomposition of NND. Second, the self-induced photonitrosation of 1-NpOH in methanol was retarded by the presence of 0.01 M sodium acetate because acetate ions compete for protons from excited-state 1-NpOH.[20] Third, in the presence of increasing amounts of water (10–30%) in dioxane, the oxime formation was retarded, and, also, 1-NpO$^-$ fluorescence at 450 nm increased at the expense of 1-NpOH fluorescence at 340 nm. Also, increasing the amount of triethylamine[21] decreased the monooxime formation in dioxane progressively; a Stern–Volmer analysis according to a simplified scheme gave $k_H' = 8.1 \times 10^8$ M^{-1} s^{-1} in the presence of [NND] = 0.02 M at 20 °C. For this calculation, $k_H = 6.8 \times 10^9$ M^{-1} s^{-1} was determined by following Φ_{ox} at various [NND] and from a $1/\Phi_{ox}$ vs. 1/[NND] plot. In the absence of NND, fluorescence of 1-NpOH in dioxane was quenched by triethylamine[22] (k_H') with an efficiency of 1.5×10^9 M^{-1} s^{-1} at 20 °C. The discrepancy between two values in the presence and absence of NND may arise from the complications of ground-state complex **1** formation between NND and 1-NpOH. The presence of **1** was shown by absorption compensated UV spectra (Figure 1) or upfield shifts of the NND NMR methyl signal[6] in the presence of 1-NpOH. The association constant K_G in dioxane calculated from the former method[23] at 400 nm was 6.1–6.2 M^{-1}.

$$*\text{1-NpOH} + (CH_3)_2NNO \xrightarrow{k_H} \text{monooxime}$$

$$*\text{1-NpOH} + NEt_3 \xrightarrow{k_H'} [*\text{1-NpO}^{-}\cdots{}^{+}HNEt_3]$$

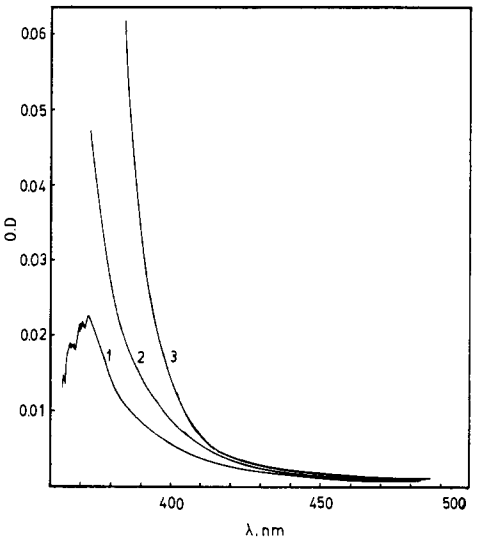


Figure 1. Differential absorption spectra of 1-naphthol (3×10^{-4} M)–NND in dioxane at 20 °C; [NND] are (1) 0.03, (2) 0.05, and (3) 0.15 M. The reference is a double-compartment cell, each compartment containing the double concentrations of 1-naphthol and NND as indicated above.

Fluorescence of 1-NpOH was efficiently quenched by NND in the 0.2–2.0 mM range giving excellent Stern-Volmer plots with k_q of 4.15×10^{10}, 5.94×10^{10}, and 5.01×10^{10} M^{-1} s^{-1} in dioxane, acetonitrile, and methanol, respectively. The values of k_q are considerably larger than the diffusion-controlled rate constant, indicating the intervention of a ground-state complex. The interaction of singlet-state 1-NpOH with NND in the concentration range 4–25 mM (Figure 2) demonstrated unambiguously exciplex **2** formation with λ_{max} 387–402 nm. Emission spectra normalized on the intensity of the exciplex peak (Figure 3) showed considerable bathochromic shifts of the exciplex emission maxima and a weak emission at the 450–460-nm region which could be assigned

(19) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York; 1973; Section 1.

(20) Weller, A. *Z. Elektrochem.* **1952**, *56*, 662; *Z. Phys. Chem. (Munich)* **1958**, *17*, 224.

(21) (a) Matsuzaki, A.; Nagakura, S.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1152. (b) Mataga, N.; Kaifu, Y. *Mol. Phys.* **1963**, *7*, 137. (c) Matsuyama, A.; Baba, H. *Bull. Soc. Chem. Jpn.* **1971**, *44*, 1162.

(22) The mechanism of the naphthol fluorescence quenching is probably more complex than just proton transfer to triethylamine. In the literature,[21] the observation of naphtholate fluorescence in these experiments is used as an indication of the formation of ion pairs, such as **3**. In the absence of the data on absolute fluorescence quantum yields, the involvement of other processes (e.g., electron transfer) cannot be ruled out.

(23) (a) Nagakura, S.; Gouterman, M. *J. Chem. Phys.* **1957**, *26*, 881. (b) Nagakura, S. *J. Am. Chem. Soc.* **1954**, *76*, 3070.

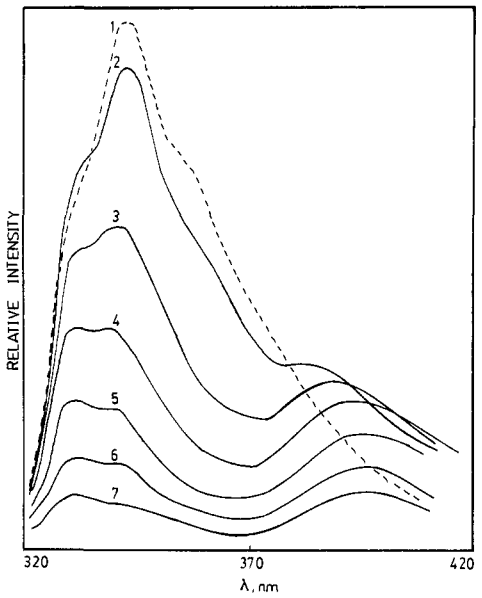


Figure 2. Fluorescence spectra of 1-naphthol (2.0×10^{-4} M) in the presence of 0, 4, 8, 12, 16, 20 and 25 mM of NND for curves 1-7, respectively, in dioxane at 20 °C.

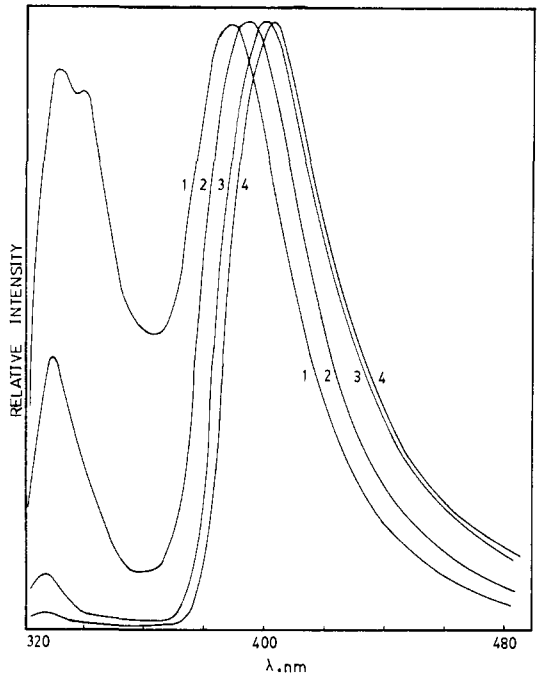


Figure 3. Fluorescence spectra of 1-naphthol (2.0×10^{-4} M) in the presence of [NND] at 0.01, 0.03, 0.07, and 0.10 M for curves 1-4, respectively, in acetonitrile at 20 °C: curves 2-4 were normalized at 390-410 nm with respect to curve 1.

to the 1-naphtholate fluorescence in the ion pair **3**. Its intensity is low probably owing to the rapid decomposition to the aminium and nitric oxide radicals as in **3** → **4**. The precise mechanism of this step is unclear but may be regarded as energy migration within the ion pair **3** to cause the homolysis of proton associated NND.[24] Within exciplexes, the lowest singlet-excited-state phenolates certainly possess enough energy to cause the homolysis of the N-N bond of NND (≈40 kcal/mol).[25]

(24) The energy level of the lowest singlet-state NND is calculated from the longest absorption maximum of NND (375 nm) at −150 °C in ethanol–methanol to be 76 kcal/mol. However, within exciplexes, the classical collisional energy transfer is not necessarily the only way for the energy migration.

(25) (a) Gowenlock, B. G.; Pritchard-Jones, P.; Major, J. R. *Trans. Faraday Soc.* **1961**, *57*, 23. (b) Fisher, I. P.; Henderson, E. *Trans. Faraday Soc.* **1967**, *63*, 1342.

While there are a number of mechanisms that can be written for the nitrosation step from 4, electron transfer followed by radical coupling as in **4** → 5 → monooxime is the simplest route. In conclusion, singlet-state phenols can provide enhanced acidity and excitation energy to promote a substantial chemical transformation if such reactions occur within the lifetimes of phenol–phenolate couples.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for generous financial support and to Professor S. Nagakura, Okazaki Institute of Molecular Science, for stimulating discussions.

Registry No. 1-NpO⁻, 17545-30-1; NND, 62-75-9; 1-NpOH, 90-15-3; 2-allyl-1-naphthalenol ion (1−), 95739-59-6; 2-naphthalenol ion (1−), 15147-55-4; 1-anthracenol ion (1−), 22718-00-9; 9-anthracenol ion (1−), 56709-95-6; 2-allyl-1-naphthalenol, 28164-58-1; 2-naphthalenol, 135-19-3; 1-anthracenol, 610-50-4; 9-anthracenol, 529-86-2; 1,4-naphthalenedione monooxime, 4965-30-4; 2-allyl-1,4-naphthalenedione 4-oxime, 95739-60-9; 1,2-naphthalenedione 1-oxime, 2636-79-5; 1,4-anthracenedione monooxime, 31619-42-8; 9,10-anthracenedione monooxime, 14090-75-6.

Supplementary Material Available: Tables of analytical data for oximes, a graph of the quenching of 1-naphthol fluorescence, and a plot of the fluorescence spectra of 2-naphthol (4 pages). Ordering information is given on any current masthead page.

syn-[2.2]Metacyclophane: Synthesis and Facile Isomerization to *anti*-[2.2]Metacyclophane. The use of (Arene)chromium Carbonyl Complexes To Control the Stereochemistry of Cyclophanes[1]

Reginald H. Mitchell,* Thottumkara K. Vinod, and Gordon W. Bushnell

Department of Chemistry, University of Victoria Victoria, British Columbia, Canada V8W 2Y2

Received December 27, 1984

anti-[2.2]Metacyclophane (**1**) was probably prepared as early as 1899,[2] though definitely in 1950,[3] and since that time has been the subject of much study.[4] *syn*-[2.2]Metacyclophane (**2**), however, has remained unknown. We now report its preparation and facile isomerization to **1**.

In 1970,[5] we thought that we had prepared a bis(methylthio) derivative of **2**, but on reinvestigation we have found that this compound was a mixture of two *anti*-cyclophanes **4**, whose 100-MHz ^{1}H NMR fortuitously was consistent with the syn structure previously assigned. Repeated careful chromatography separated the mixture, and 250 MHz ^{1}H NMR spectra then led to their assignment as the 1(e),3(e) and 1(e),4(e) anti isomers **4A** and **4B**, respectively. Thus the only authentic *syn*-[2.2]metacyclophane derivatives known[5b,6] are those with internal methyl substituents, where the substituent raises the barrier for the syn → anti isomerization. interestingly even there the parent compound has not yet been prepared.

It has been observed that the presence of electron-withdrawing substituents on one benzene ring favors *syn*-2,11-dithia[3.3]-metacyclophane formation over that of the anti conformer.

(1) Presented in part at the 66th Chemical Institute of Canada Conference, Calgary, Alberta, Canada OR7-2, June 6, 1983, and the 38th American Chemical Society Northwest Regional Meeting, Honolulu, HI, paper 138, Dec. 29, 1983.

(2) Pellegrin, M. M. *Recl. Trav. Chim. Pays-Bas* **1899**, *18*, 458.

(3) Baker, W.; McOmie, J. F. W.; Norman, J. M. *Chem. Ind. (London)* **1950**, *77*; *J. Chem. Soc.* **1951**, 1114-1118.

(4) Reviews: (a) Griffin, R. W. *Chem. Rev.* **1963**, *63*, 45-54. (b) Smith, H. B. "Bridged Aromatic Compounds"; Academic Press: New York, 1964. (c) Vögtle, F.; Neumann, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 73-83. (d) Keehn, P., Rosenfeld, S., Eds. "Cyclophanes"; Academic Press: New York, 1983.

(5) (a) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3510-3512; (b) *Ibid.* **1974**, *96*, 1547-1557.

(6) Kamp, D.; Boekelheide, V. *J. Org. Chem.* **1978**, *43*, 3470-3475.

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