

and calcium (S2) site in concanavalin A. Similarities in isotropic chemical shifts and in shielding tensor parameters for the parvalbumin calcium sites and for the S2 site in concanavalin A reflect similar metal-coordination environments in the two proteins. The significantly different isotropic shift and asymmetry parameter for the cadmium cation in the manganese (S1) site of concanavalin A is consistent with the distinctive coordination environment involving a cadmium-nitrogen bonding interaction at this site. The axially symmetric shielding tensor at the S1 site may be indicative of a higher cadmium site symmetry at the S1 site compared to that at the S2 site. Additional data are required in order to more fully understand cadmium-shielding tensors in metalloproteins. Such data should now be attainable with use of solid-state NMR techniques. With 7-mm rotors at 200 MHz,

it appears that proteins with molecular weights on the order of 100 000 are amenable to this approach.

Finally, these techniques have provided a sensitive and direct means of observing structural changes that occur at metal-binding regions in metalloproteins when such systems are dehydrated.

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## On the Singlet and Triplet Excited States of Nitrosamines

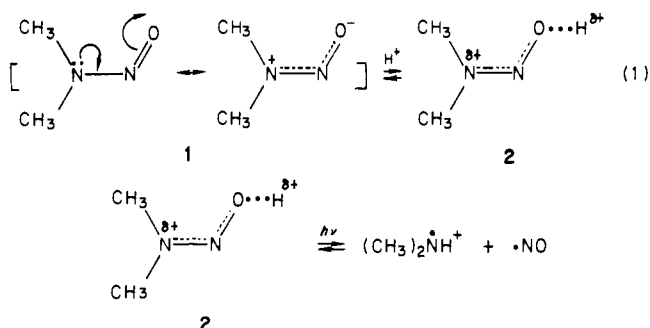
Yuan L. Chow,\* Zheng-Zhi Wu,<sup>1</sup> Ming-Pui Lau, and Rodrick W. Yip<sup>2</sup>

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6, and the Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1P 0R6. Received July 8, 1985

**Abstract:** With use of absorption and emission spectroscopy, flash photolysis, quenching experiments, and quantum yield determinations, the triplet and singlet excited-state energies of *N*-nitrosodimethylamine (NND) and *N*-nitrosopiperidine (NNP) were determined to be  $E_S = 72\text{--}73$  and  $E_T = 58\text{--}59$  kcal/mol and their chemical reactivities in the excited states were described. While the singlet excited state of nitrosamine-acid complexes rapidly dissociates to give aminium radicals and nitric oxide, with high quantum yields of  $>1$ , their triplet excited state shows no apparent chemical changes. In neutral conditions, nitrosamines photolytically dissociate equally efficiently to give amine radicals and nitric oxide that recombine to give nitrosamines leading to an efficient degradation of photoenergy. The  $S_0 \rightarrow T_1(n, \pi^*)$  electronic transition of NND was found in the 450-nm region and phosphorescence excitation spectra revealed the lack of the  $S_1 \rightarrow T_1$  intersystem crossing for NND. Low-temperature photolysis of NND has confirmed the reaction pattern and also revealed an intermediate species, assumed to be the nitrosodimethylammonium ion, which underwent irreversible photoreaction at  $-150$  °C and reverted readily to the NND-acid complex at  $-30$  °C.

The nitrosamine group<sup>3-5</sup> is theoretically interesting because of extensive electron delocalization to give a dipolar resonance hybrid with a partial N-N double bond character.<sup>5-7</sup> The association of the nitrosamine group with an acid<sup>8</sup> or metal<sup>7</sup> ion has been shown to occur at the oxygen atom. The association constant of *N*-nitrosodimethylamine (NND) in dilute sulfuric acid is determined to be  $0.18 \text{ M}^{-1}$ . In spite of this fact, nitrosamines rapidly photodissociate to aminium radicals and nitric oxides in the presence of an acid.<sup>9-11</sup> The chemistry of aminium radicals has

been well documented.<sup>9-12</sup> Since 1965, the world-wide concern with nitrosamines arises largely from the fact that many nitros-



amines are pernicious *animal carcinogens* (and, therefore, human carcinogens by extrapolation) with an organotropic action mode and that they are naturally formed in the human environmental samples with amazing facility.<sup>13</sup> Undoubtedly, their carcino-

(1) Visiting scientist from Shanghai Institute of Organic Chemistry, Academy of Sciences, P.R.C.

(2) R. W. Y. is located at the National Research Council of Canada. This paper is issued as NRCC contribution No. 25125. The other authors are from Simon Fraser University.

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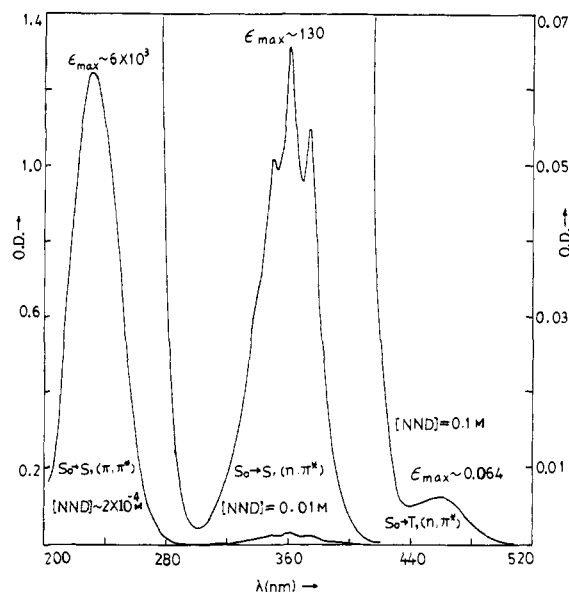
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**Table I.** Quenching of Aromatic Hydrocarbon Fluorescence by NND in CH<sub>3</sub>OH at 22 °C

ArH	$E_S^a$ (kcal/mol)	$\tau_0^a$ (ns)	$\lambda_{ex}$ (nm)	$\lambda_{em}^{max}$ (nm)	$k_q \times 10^9$ (M <sup>-1</sup> s <sup>-1</sup> )	[NND] (mM) <sup>b</sup>	$r$
naphthalene	92.0	96.0	300	323	12.4 <sup>c</sup>	0.5–4	0.999
anthracene	76.3	5.3	375	397	21.7	4–20	0.998
9,10-dimethylanthracene	71.8	16.2	400	425	1.53	7–35	1.000
perylene	65.8	6.0	430	465	0.185	10–60	0.993
tetracene	60.7	6.4	440	473	<i>d</i>	20–60	<i>d</i>

<sup>a</sup> Cited from ref 17. <sup>b</sup> The NND concentration range used. <sup>c</sup> This experiment was run in the presence of 0.012 M [HCl], using NNP as the quencher. <sup>d</sup> No quenching of fluorescence.

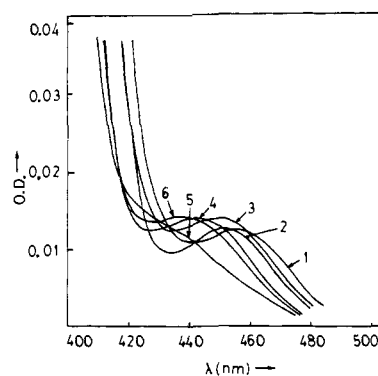
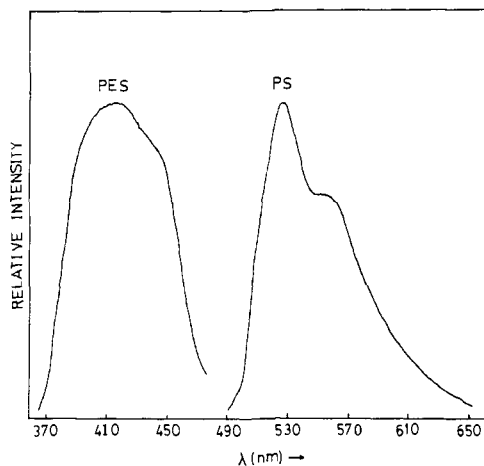
**Figure 1.** Absorption spectra of NND in methylcyclohexane.

genicity is prodoundly related to their chemical behavior.

The ground-state chemistry of nitrosamines has been investigated and summarized.<sup>3–5</sup> Excited-state behavior of nitrosamines is not readily elaborated because of the lack of emission in solution and their photostability under neutral conditions.<sup>11</sup> Using various indirect and direct methods, we have established the reaction patterns of their excited states. We wish to describe them in this report.

## Results

**Absorption Spectra.** The absorption spectra of NND in methylcyclohexane showed maxima at 234 and 342 nm for the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  electronic transitions that have been well-studied.<sup>14</sup> At high concentrations of NND ( $\approx 0.1$  M), it also showed a new absorption at 453 nm with a low extinction coefficient of  $0.064 \text{ M}^{-1} \text{ cm}^{-1}$ . Since this absorption maximum followed Beer's law at the 0.04–0.2 M concentration range of NND in methylcyclohexane and other solvents, it could not arise from dimer or polymer formations. As the maximum also blue-shifted considerably as the polarity of solvent was increased (Figure 2), this absorption must arise from the  $S_0 \rightarrow T_1 (n \rightarrow \pi^*)$  electronic transition. In agreement with this assignment, the external heavy-atom effect<sup>15,16</sup> on the intensity was relatively small (up to 70%) in changing solvent from methylcyclohexane to brominated or iodinated hydrocarbons.

**Figure 2.** The  $S_0 \rightarrow T_1$  absorption in various solvents: (1) methylcyclohexane, (2) toluene, (3) tetrahydrofuran, (4) methylene chloride, (5) methanol, (6) acetonitrile; [NND] = 0.20 M.**Figure 3.** The phosphorescence spectrum (PS) and phosphorescence excitation spectrum (PES) of NND in EPA at 77 K. For PS, NND (1.0 M) was excited at 440 nm, and for PES, NND was excited at 250–500 nm and monitored at 530 nm.

**Emission Studies.** No emission was observed of NND in various solvents at room temperature, either exciting the 234 or 342 nm transition band. NND in EPA glass at 77 K exhibited phosphorescence centered at 530 nm when the  $S_0 \rightarrow T_1$  transition band at 450 nm was excited (Figure 3); such phosphorescence emission was not observed when the  $S_0 \rightarrow S_n$  transition bands at 250 and 330 nm were excited. The phosphorescence peak decayed with a lifetime of 2.9 s in EPA glass at 77 K. Under the same conditions, the phosphorescence excitation spectrum was taken (Figure 3), which showed the absorption in the 400–480 nm region, very similar to the  $S_0 \rightarrow T_1 (n \rightarrow \pi^*)$  observed in Figure 2. The lowest triplet excited state energy level ( $E_T$ ) of NND estimated from

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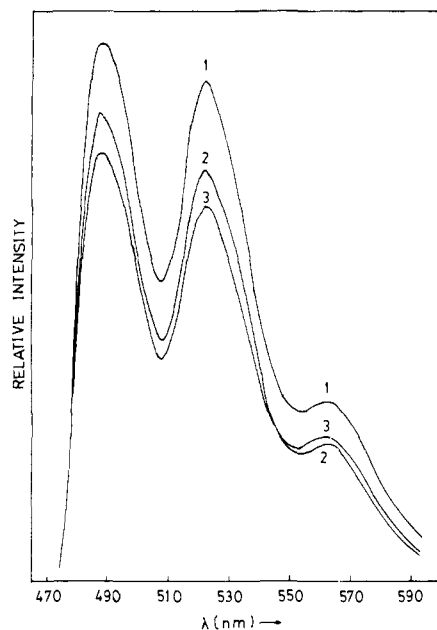
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**Figure 4.** The changes of phosphorescence spectra of 2-acetonaphthone (2 mM) in EEI (ether-ethanol-iodoethane) in the presence of NND (0, 4.8, and 9.6 mM). 2-Acetonaphthone was excited at 320 nm.

**Table II.** Aminium Radicals Generated from Flash Excitation

nitrosamine ( $\times 10^4$ M)	HCl ( $\times 10^2$ M)	solvent	aminium radicals lifetime ( $\mu$ s)
NNP (1.06)	1.2	CH <sub>3</sub> OH	16 $\pm$ 2; C <sub>5</sub> H <sub>10</sub> NH <sup>+</sup>
NNP (1.06) <sup>a</sup>	1.2	CH <sub>3</sub> OH	15 $\pm$ 2; C <sub>5</sub> H <sub>10</sub> NH <sup>+</sup>
NNP (0.62)	1.2	H <sub>2</sub> O	108 $\pm$ 4; C <sub>5</sub> H <sub>10</sub> NH <sup>+</sup>
NNP (0.62) <sup>a</sup>	1.2	H <sub>2</sub> O	112 $\pm$ 4; C <sub>5</sub> H <sub>10</sub> NH <sup>+</sup>
NND (1.00)	6.0	CH <sub>3</sub> OH	19 $\pm$ 2; (CH <sub>3</sub> ) <sub>2</sub> NH <sup>+</sup>
NND (1.00) <sup>a</sup>	6.0	CH <sub>3</sub> OH	24 $\pm$ 2; (CH <sub>3</sub> ) <sub>2</sub> NH <sup>+</sup>

<sup>a</sup> The solutions were saturated with oxygen.

$S_0 \rightarrow T_1$  transition bands in these absorption and phosphorescence spectra was about 58 kcal/mol (490–495 nm).

**Quenching Studies.** Fluorescence of some selected aromatic hydrocarbons was quenched with the rate constants shown in Table I. No new emission was observed in these quenching experiments. The gradual deviation in the quenching rate constants of 9,10-dimethylanthracene and perylene fluorescence from the near diffusion-controlled value indicated that the singlet-state energy  $E_S$  of NND could be 72–73 kcal/mol, which agreed well with that estimated from the “onset” of the  $S_0 \rightarrow S_1(n-\pi^*)$  transition band (at about 395 nm, see Figure 1), though a distinct 0–0 band at ca. 400 nm has not been recorded as yet.

Attempts to populate the triplet excited state of NND by benzophenone and acetophenone sensitizations in EPA glass were not successful, probably owing to strong overlapping phosphorescence of these sensitizers, though the intensity of which was reduced by NND. Phosphorescence of 2-acetylnaphthalene ( $E_T = 59.4$  kcal/mol) was quenched by NND efficiently in rigid EEI glass (Figure 4). The intensity enhancement in the 560-nm region in Figure 4 could arise from NND phosphorescence emission. Because of the overlap of both emissions, overall emission enhancement over the 500–600 nm range could not be obtained to confirm this point.

**Flash Excitation Studies.** The results pertaining to flash excitation of NND and *N*-nitrosopiperidine (NNP) in degassed or air-saturated solutions in methanol and water in the presence of hydrochloric acid are summarized<sup>18</sup> in Table II. For each nitrosamine, the transients decayed with pseudo-first-order kinetics and showed similar absorption curves under similar conditions.

**Table III.** Quenching of Triplet Signals Generated by Flash Photolysis by NNP

sensitizers (concn)	solvent	lifetime of sensitizers ( $\mu$ s)	quenching rate constant ( $M^{-1} s^{-1}$ )	$E_T^a$	$E_S^a$
xanthone ( $10^{-5}$ M)	H <sub>2</sub> O, HCl (50 mM)	10	$1.4 \times 10^9$	74	78
naphthalene ( $2 \times 10^{-4}$ M)	CH <sub>3</sub> OH, HCl (84 mM)	101	$1.4 \times 10^9$	61	92
2,2'-binaphthyl ( $4.2 \times 10^{-5}$ M)	CH <sub>3</sub> OH, HCl (84 mM)	57	$7.5 \times 10^7$	56	(85)

<sup>a</sup> kcal/mol.

The transients were shown to be identical with those obtained from *N*-chlorodimethylamine<sup>19,20</sup> and *N*-chloropiperidine and were confirmed as the corresponding aminium radicals. The transient lifetimes monitored at several wavelengths in the 300–400 nm region remained constant. The excitation of either  $\pi \rightarrow \pi^*$  (Vycor filter) or  $n \rightarrow \pi^*$  (Pyrex filter) transition band produced similar transient, though that from the latter was weaker. Oxygen ( $\approx 1 \times 10^{-3}$  M) did not affect the absorption shape and intensity nor the decay kinetics of aminium radicals, indicating that the precursorial excited state disappeared rapidly and was not intercepted by oxygen at that concentration. With an improved apparatus, the rising time of the aminium radical was determined to be  $< 0.1 \mu$ s from an oscilloscopic trace. These two observations placed the lifetime of the excited state at  $< 10^{-7}$  s. Recently, this lifetime in the gas phase has been estimated<sup>21,22</sup> to be  $< 10^{-10}$  s (vide infra). In the absence of an acid, no transient was obtained nor nitrosamine absorption maxima decreased after more than 30 flashes.

The triplet-state xanthone signal generated in aqueous acidic solution was quenched by NNP with  $k_q = 1.4 \times 10^9 M^{-1} s^{-1}$  (Table III) without showing any enhancement of the signal due to the aminium radical. The naphthalene and 2,2'-binaphthyl triplet signals generated in acidic methanol solution were also quenched by NNP with  $k_q$  of  $1.4 \times 10^9$  and  $7.5 \times 10^7 M^{-1} s^{-1}$ ; in the naphthalene case, the signals of the piperidinium radical was concurrently observed. However, in the absence of an acid, this signal was not observed. In both cases, after repeated flashes, the optical density of NND at 340–400 nm decreased considerably.

The low rate constant of quenching of the binaphthyl ( $E_T = 56$  kcal/mol) triplet signal suggested that  $E_T$  of NNP could be higher than 56 kcal/mol but lower than  $E_T$  of naphthalene (61 kcal/mol). Assuming reversibility of energy transfer and using the Sandros estimation method, the  $E_T$  of NNP was calculated to be 58–59 kcal/mol.

Both naphthalene ( $E_S = 92$  kcal/mol and  $\tau_S = 96$  ns)<sup>17</sup> and binaphthyl ( $E_S = 85 \pm 1$  kcal/mol from  $\lambda_{\text{emission}}$ , 342 nm) are capable of sensitizing nitrosamines to their singlet excited state, while xanthone and acetophenone are not capable of doing so. The precursor of (or the excited state responsible for) the aminium radicals must be the singlet excited state of nitrosamines.

**Quantum Yields.** The quantum yields of NNP disappearance in acidic methanol solution, either in the presence or absence of an olefin, were lower in lower NNP concentrations, ranging from 2.7 to 3.6, showing short chain nature of the photodecomposition (Table IV). At lower concentrations of NNP, the margin of error arising from low optical density was too great to allow reliable determinations of the quantum yields that decreased  $< 2$  below  $10^{-3}$  M of NNP. Since the quantum yield of NND decomposition in the gas phase has been shown to be unity<sup>21,22</sup> (vide infra), the singlet excited state NNP decomposition in solution must also be very efficient in approaching unity, which could account for the lack of emission on excitation of the 234- or 342-nm band. As expected, the quantum yields were not significantly reduced in

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Table IV. Quantum Yield Measurement in Methanol

reaction no.	[NNP] ( $\times 10^3$ M)	others	[HCl] (M)	excitation wavelength	$\Phi$
1	7.03		0.10	366	3.6
2	2.06		0.06	366 <sup>a</sup>	2.6
3	2.06	cyclohexene (2.6 mM)	0.06	366 <sup>a</sup>	2.7
4	2.06	1,3-pentadiene (3.2 mM)	0.06	360 <sup>a</sup>	3.1
5	4.36	naphthalene (0.56 mM)	0.06	366	3.8
6	4.36	naphthalene (1.1 mM)	0.06	366	4.1
7	4.36	naphthalene (1.1 mM)	0.06	310	2.3
8	10.00	naphthalene (8 mM)	0.10	310 <sup>a,b</sup>	2.6
9	10.00	acetophenone (5 mM)	0.06	360 <sup>a,b</sup>	2.5
10	10.00	acetophenone (10 mM)	0.06	310 <sup>a,b</sup>	<0.01

<sup>a</sup>These data are cited from ref 36. <sup>b</sup>The solutions of these experiments contained 10 mM of cyclohexene.

the presence of naphthalene (nos. 5 and 6) or acetophenone (no. 8), indicating the lack of quenching of the photodecomposition by these compounds. The photodecomposition was efficiently sensitized by naphthalene (Table IV, nos. 6 and 7) but not by acetophenone (no. 9). As acetophenone is a typical triplet sensitizer owing to the fast intersystem crossing, experiment no. 9 confirms that nitrosamine triplet states do not undergo decomposition. Nitrosamine photoreactivity was further confirmed by the ready photoaddition of NNP to cyclohexene in the presence of naphthalene as a sensitizer under acidic conditions. 2-Piperidinocyclohexanone oxime was isolated in good yields.<sup>23,24</sup> This photoaddition could not be sensitized by acetophenone or benzophenone.

**Low-Temperature Irradiation.** A transparent glass of NND in anhydrous EtOH-MeOH (9:1) in the presence of  $\text{CF}_3\text{CO}_2\text{H}$  at  $-150^\circ\text{C}$  showed structured UV absorption (Figure 5) at 367, 343, and 333 nm. On irradiation with monochromatic light (313 nm) at this temperature a new set of peaks at 391, 375, and 362 nm appeared which disappeared on warming to  $-30$ – $0^\circ\text{C}$ . This solution was cooled to  $-150^\circ\text{C}$  to show the original NND spectra with the same intensity. If the new species were irradiated at 365 nm, these new peaks simultaneously decreased irreversibly. The warming of this solution did not restore the original intensity. When a similar NND solution was irradiated at room temperature with 313-nm monochromatic light, the broad NND absorption at  $\lambda_{\text{max}}$  345 nm decreased irreversibly with zero-order kinetics without showing new peaks. This is the ordinary photodecomposition pattern reported.<sup>11</sup>

Since similar irradiation at  $-150^\circ\text{C}$  in a mixture of 2,2-dimethylbutane and pentane (8:3) did not show the peaks of the new species, the requirement of acid to observe the new species was reconfirmed.

## Discussion

The quenching studies with the monitor of emission spectra and the aminium radical signal, the quantum yields of nitrosamine decompositions, and the formation of nitrosamine decomposition products indicate (i) that the photodecomposition of nitrosamines to aminium radicals occurs from the singlet excited state, (ii) that the singlet excited state of nitrosamine dissociates rapidly with a very high quantum efficiency, affording no chance for intersystem crossing to the triplet excited state, and (iii) that the triplet excited state nitrosamines do not lead to an irreversible chemical change. The last conclusion is unexpected but is clearly demonstrated by the lack of chemical reactions on excitation of the  $S_0 \rightarrow T_1$  bands also by triplet sensitization with aromatic carbonyl sensitizers. This is also supported by the failure of dienes, as high as 0.1 M, to quench the photodecomposition. At this diene concentration, any triplet-state molecules would have been quenched.<sup>24</sup> It is assumed that triplet-state nitrosamines depopulate themselves by intersystem crossing or by a reversible chemical change to the ground state.

The efficient photodecomposition of nitrosamines, either by direct excitation or singlet state sensitization of aromatic hy-

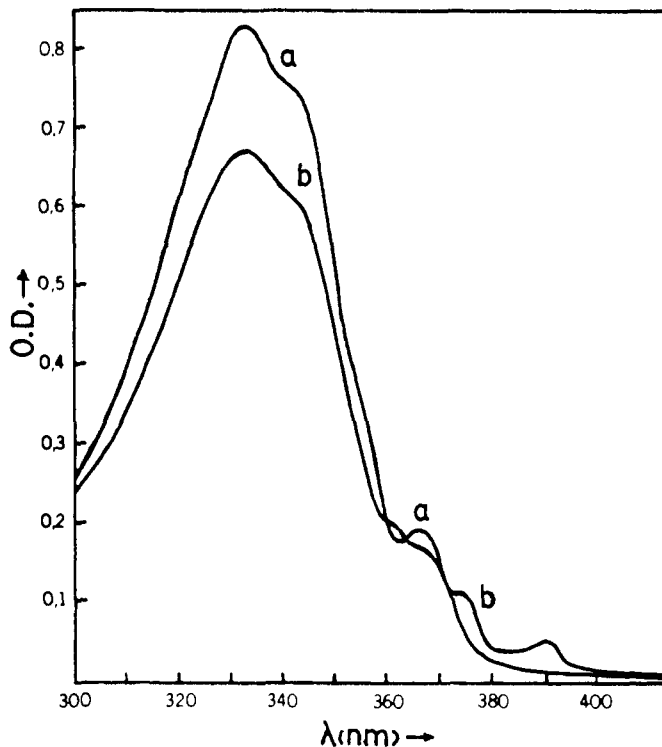


Figure 5. Monochromatic photolysis of NND (10 mM) in EtOH-MeOH (9:1) in the presence of  $\text{CF}_3\text{CO}_2\text{H}$  (10 mM) at  $-150^\circ\text{C}$ . Curve b was obtained after 10 min of irradiation at 313 nm.

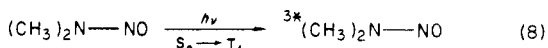
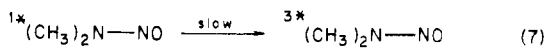
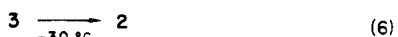
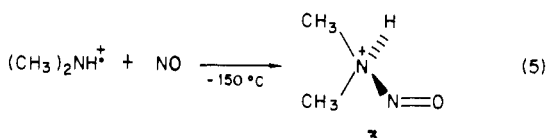
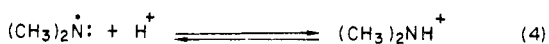
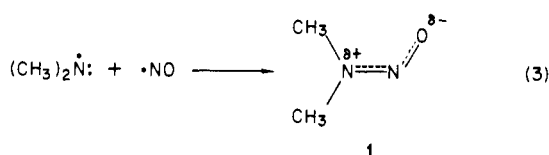
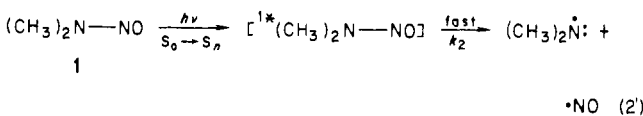
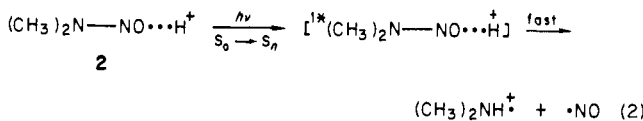
drocarbons, with quantum yields of higher than unity suggests that the singlet state nitrosamine-acid complex dissociates very fast and with high efficiency to the aminium radicals and nitric oxide. This conclusion is indicated by various observations. The failure of oxygen ( $10^{-3}$  M) to quench the nitrosamine-acid complex singlet state is demonstrated here by flash excitation, quantum yield measurements, and preparative studies.<sup>25</sup> The failure to observe fluorescence and phosphorescence emission on excitation of  $S_0 \rightarrow S_1(n-\pi^*$  or  $\pi-\pi^*)$  hints that the singlet excited state dissociation of a nitrosamine-acid complex dominates the reactivity and that no other channels of reactions can be observed. Recently, Huber and co-workers<sup>21,22</sup> have demonstrated that the excitation of the 363.5-nm band in the gas phase causes NND to dissociate from the lowest singlet excited state to the amine radical and nitric oxide in the absence of an acid (eq 2'), with  $\phi = 1.03$  and  $k_2 > 8.5 \times 10^9 \text{ s}^{-1}$ . The two radicals recombine (eq 3) with a rate constant of  $k_3 \leq 10^6 \text{ torr}^{-1} \text{ s}^{-1}$ . This places the lifetime of the singlet excited state at  $< 1.2 \times 10^{-10} \text{ s}$ . The results substantiate our observations that photolysis of nitrosamines under neutral conditions causes no chemical changes and that the singlet excited state of a nitrosamine-acid complex rapidly and exclusively dissociates to give aminium and  $\text{NO}\cdot$  radicals. A direct proof of the photodissociation of NND at 77 K has also been gained by

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(24) (a) Chow, Y. L.; Colon, C. J.; Chang, D. W. L. *Can. J. Chem.* **1970**, *48*, 1664. (b) Chow, Y. L.; Colon, C. J.; Quon, H. H.; Mojselsky, T. *Can. J. Chem.* **1972**, *50*, 1065.

(25) Chow, Y. L.; Colon, C. J.; Tam, J. N. S.; Pillay, K. S. *Can. J. Chem.* **1973**, *51*, 2469.

the ESR detection of the dimethylaminium radical.<sup>26</sup> Indirectly, photolysis of nitrosamines under neutral conditions has been proven to cause no net chemical reaction except the syn and anti-isomerization.<sup>27</sup> Both observations could be explained by NND photodissociation established by Huber.<sup>21,22</sup> This information, together with what is learned in this paper, allows us to present the following reaction schemes using NND as the model.



The acid-base equilibrium of eq 4 has been determined by ESR spectroscopy to be  $\text{pK} = 6.5$  and the rate constant  $k_4$  is expected to be ultrafast, being an acid-base equilibrium in hydroxylic media.<sup>29</sup> In water, aminium radicals have a lifetime of  $\approx 100\ \mu\text{s}$ , which means that eq 5 is a very slow process. Since this reaction does not occur efficiently in neat methanol,<sup>11,19</sup> the bimolecular rate constant of eq 5 is estimated to be  $k_5 < 10^{-4}\ \text{M}^{-1}\ \text{s}^{-1}$ , e.g., slower than that of the H abstraction from methanol. In theory, the rate of eq 5 should be slower than that of the corresponding unprotonated species of eq 3 because of the availability of resonance stabilization of **1**, which should serve as a driving force in the latter. This is shown experimentally by the fact that preparative or flash photolysis of nitrosamines in methanol under neutral conditions does not cause any chemical changes owing to exclusive recombination<sup>11</sup> as in eq 3. The N-protonated species **3** is isomeric to **2** and must possess a higher energy than the corresponding O-protonated species. With use of INDO closed-shell calculations, **3** is estimated to be about 25–30 kcal/mol higher<sup>30</sup> than **2**.

It is abundantly clear that, owing to the fast reaction in eq 2, intersystem crossing of the singlet excited state NND (or its acid complex, eq 7) cannot compete efficiently to give the phosphorescing triplet excited state (see Figure 3). The latter state is fortunately accessible by direct excitation of the  $\text{S}_0 \rightarrow \text{T}_1$  transition

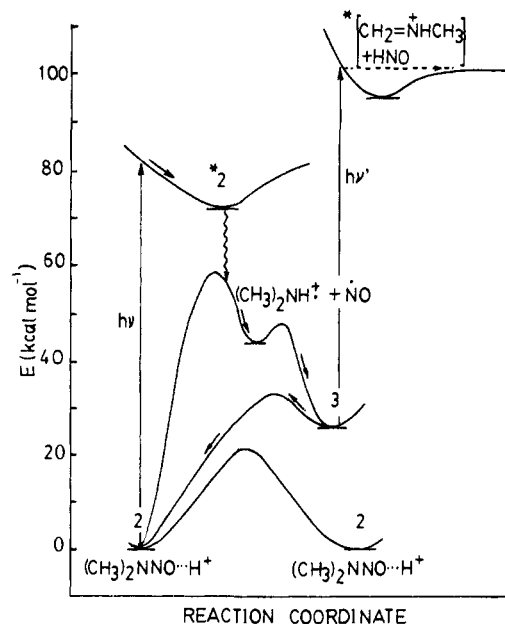
(26) (a) Jukubowski, E.; Wan, J. K. S. *Mol. Photochem.* **1973**, *5*, 439. (b) Adelke, B. B.; Wan, J. K. S. *Mol. Photochem.* **1974**, *6*, 329.

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(30) In the absence of experimental proof, **3** is assumed to be the N-protonated species which possesses higher energy levels than the O-protonated NND by 25 kcal/mol, as indicated by INDO calculations (see T. Mojelsky, Ph.D. Dissertation, Simon Fraser University, 1978).

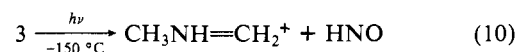
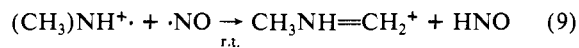


**Figure 6.** Schematic representation of singlet-state reactions of NND. The arrows indicate the cycle of energy dissipation.

band at 450 nm. The energy level of the lowest singlet excited state of NND and NNP is determined<sup>31</sup> to be  $E_S = 72\text{--}73$  kcal/mol and that of the lowest triplet excited state  $E_T = 58\text{--}59$  kcal/mol, both obtained by a combination of spectroscopy and quenching methods.

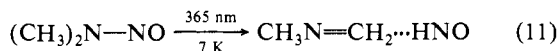
Low-temperature photolysis of NND further elaborates the reactivity of the singlet state of NND. The chemical consequences upon excitation of **2** can be conceptually expressed in Figure 6, which maps the pathways of energy dissipation in low temperature photolysis. The new species with  $\lambda_{\text{max}} 391, 375,$  and  $362\ \text{nm}$  obtained at  $-150\text{ }^\circ\text{C}$  in the presence of an acid (Figure 5) is most likely **3**, a NND with a tetrahedral configuration of the amine N atom, which can readily revert to the more stable **2** by proton migration at  $-30\text{ }^\circ\text{C}$ . Indeed, two species have very similar vibrational progressions of  $900\text{--}1000\ \text{cm}^{-1}$ .

The excitation of **2** is rapidly followed by vibrational relaxation and surface crossing in the weakly avoided region (internal conversion) to form  $(\text{CH}_3)_2\text{NH}^{\dot{+}}$  and  $\cdot\text{NO}$  carrying residual vibrational energy. It is believed that the excess vibrational energy of two species is rapidly dissipated by collisional deactivation at  $-150\text{ }^\circ\text{C}$ , leading to the recombination of them as the only accessible channel of reactions. In room-temperature solution photochemistry, as we have demonstrated here and in preparative work,<sup>11</sup> two radicals are "hot" species and reacted irreversibly as shown in eq 9. The irreversible photodecomposition of **3** on irradiation at 360 nm even at  $-150\text{ }^\circ\text{C}$  must be the elimination of HNO, similar to that shown in eq 9, occurring from a pre-dissociative manifold of an excited state of **3** (eq 10). Indeed, when irradiation



of **2** is carried out with 360-nm monochromatic light, instead of 313 nm, weak absorption peaks of **3** are also observable but on warming and recooling, the intensity of **2** is reduced, no doubt owing to the operation of the consecutive excitation of eq  $2 \rightarrow \text{eq } 5 \rightarrow \text{eq } 10$ . Huber's group has proposed a direct photodissociation of NND in pulsed laser photolysis of an argon matrix at 7 K (see eq 11).<sup>22</sup> We believe that the reaction in eq 11 may occur by a two-photon sequence, similar to that proposed above.

(31) These values may be compared with those of theoretical calculations: Cimragna, R.; Persico, M.; Tomas, J. *J. Am. Chem. Soc.* **1985**, *107*, 1617.



The transformation of **1** to **3** is a diabatic process which is not possible by an adiabatic process because the input of thermal energy is consumed by pumping the barrier of the rotation around the partial N-N double bond (23 kcal/mol)<sup>6</sup> in **1** and **2** by continuous processes. It should be noted that there is no direct access to  $(\text{CH}_3)_2\text{NH}\cdot^+ + \cdot\text{NO}_2$  and **3** from **1** by a ground-state thermal process because of the high-energy barriers<sup>31,32</sup> though the dissociation energy of the N-N bond has been estimated to be only<sup>33</sup> 40.5 kcal/mol.

Photolysis of NND in hydrocarbon media (neutral conditions) at  $-150\text{ }^\circ\text{C}$  can now be interpreted with some certainty since related work has been published.<sup>21,22,26,27</sup> The photoexcitation of NND rapidly follows the sequence of eq 2' and 3, leaving no net chemical transformation. A similar pattern has been observed in preparative photolysis<sup>11</sup> and no aminium radical signal can be observed in flash photolysis under comparable conditions. In the absence of an acid, the recombination of amine and nitric oxide radicals should be rapid leading to an unstable N-nitroso compound with the tetrahedral amine nitrogen which must mutate immediately to the resonance-stabilized nitrosamine **1**.

### Experimental Section

**General Conditions.** The general experimental conditions and chemicals were the same as those reported in the previous publications.<sup>19,20,34</sup> Phosphorescence and fluorescence spectra were taken with a Perkin-Elmer MPF44B spectrophotometer.

**Flash Photolysis.** The apparatus and procedures were the same as those described previously.<sup>19,20</sup> Nitrosamines were prepared by vacuum distillation in a fumehood (Caution! THEY ARE CARCINOGENS). Liquid sensitizers were distilled under vacuum and solid ones were recrystallized and sublimed. The treatment of data is described in the thesis presented by M.P.L.<sup>35</sup> The absorption curve of the piperidinium radical has been published.<sup>19</sup>

For the sensitization of NNP decomposition by naphthalene, a solution containing NNP ( $5.2 \times 10^{-3}\text{ M}$ ) and HCl (0.01 M) in the presence and absence of naphthalene ( $1.08 \times 10^{-2}\text{ M}$ ) was flashed with a potassium acid phthalate solution filter (irradiation of NNP) or without the filter

(irradiation of both NNP and naphthalene). The OD of the aminium radical at 10  $\mu\text{s}$  after photoflash was measured at 400, 410, and 420 nm and the percent enhancement of OD was calculated. The average enhancement is 30%.

**Quantum Yield Measurements.** The quantum yields of nitrosamine disappearance were determined by the split-beam irradiation apparatus described previously.<sup>34</sup> The light source is a PEK (No. 202) 200-W high-pressure mercury lamp. A Corning glass filter CS 7-60 (No. 5840, 4.5 mm) and soft glass filter were used for irradiation in the 366-nm region. A Pyrex filter, coupled with 0.02 M NND in water, was used for irradiation in the 300–310 nm region. Irradiation was carried out in a "merry-go-round" to cause 10–15% disappearance of nitrosamines and quantum yields were calculated with ferric oxalate actinometry.<sup>17</sup> The concentrations of NNP and NND were determined from the decrease of the absorption band at 340 nm. In some cases, the measurements were supplemented with VPC analysis on a Varian Model 1200 gas chromatograph, fitted with FID and a SE-30 (8 ft  $\times$  1/8 in.) column.

**Sensitized Photoaddition of NNP to Cyclohexene.** A solution containing NNP (0.34 g, 3 mmol), cyclohexene (0.82 g, 10 mmol), concentrated hydrochloric acid (3.6 mmol), and naphthalene or acetophenone (10 mmol) in methanol (40 mL) was irradiated in a Rayonet photoreactor equipped with RPR 3000-Å lamps. The light was filtered through a solution of 0.02 M NND which was externally cooled and circulated through the jacket. The workup of the photolysate followed well-established methods.<sup>23</sup>

**Low-Temperature Photolysis of NND.** A solution of NND (0.01 M) and  $\text{CF}_3\text{CO}_2\text{H}$  (0.01 M) in anhydrous EtOH–MeOH (9:1) was placed in a 1-cm square UV cell and purged with nitrogen for 5 min and sealed. The sample was placed in a homemade apparatus with a temperature regulator and the spectrum (280–450 nm) was recorded. It was then cooled to  $-150\text{ }^\circ\text{C}$  and spectra were recorded after each 5 (or 10) min irradiation at 313 nm (Figure 5). On warming to  $-30\text{ }^\circ\text{C}$  and above, the new absorption at 362, 375, and 391 nm and the original spectra disappeared and the original spectrum (curve a) was restored. The light source was a PEK No. 202 high-pressure mercury arc lamp with a quartz collimation system. The light beam was filtered through a Pyrex filter and an interference filter (Oriel at 313.0 and 365.0 nm).

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**Registry No.**  $\text{C}_3\text{H}_{10}\text{NH}^+$ , 59095-50-0;  $(\text{CH}_3)_2\text{NH}^+$ , 85234-70-4; NND, 62-75-9; NNP, 100-75-4; naphthalene, 91-20-3; anthracene, 120-12-7; 9,10-dimethylanthracene, 781-43-1; perylene, 198-55-0; tetracene, 92-24-0; xanthone, 90-47-1; 2,2'-binaphthyl, 612-78-2; 2-acetylnaphthalene, 93-08-3.

(32) An ab initio study also indicated that a singlet excited nitrosamine merges with the dissociative surface: see ref 31.

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