

Chemistry of Amido Radicals. Flash Photolysis of *N*-Nitroso-*N*-Alkylacetamides^{1,2}

Josiah N. S. Tam,^{3a,b} Roderick W. Yip,^{3c} and Yuan L. Chow*^{3b}

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada, and the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada.
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Abstract: The mechanism of *N*-nitroso-*N*-methylacetamide (NMA) photolysis and the kinetic behavior of the *N*-methylacetamido radical were studied by the flash excitation method and by steady state quantum yield determination. The results were interpreted that the lowest singlet excited NMA decayed to give the acetamido radical; the absorption spectrum of the latter transient species was determined. From both methods, it was demonstrated beyond any doubt that the acetamido radical primarily reacted with NMA with the rate constant of $3.96 \times 10^6 M^{-1} \text{sec}^{-1}$ and also underwent unimolecular decay with the rate constant of $2.09 \times 10^4 \text{sec}^{-1}$. The flash excitation studies showed that both the lowest singlet excited NMA species and the acetamido radical abstracted hydrogen from hydrocarbon substrate. The bimolecular rate constants of the reactions of the amido radical with cyclohexane and *trans*-piperylene were determined to be 1.85×10^4 and $2.45 \times 10^5 M^{-1} \text{sec}^{-1}$, respectively. The singlet excited NMA reacted with cyclohexane and *trans*-piperylene (but not with NMA) by estimated rate constants of 1.87×10^8 and $4.04 \times 10^9 M^{-1} \text{sec}^{-1}$, respectively. Determination of the quenching rate constants of the aromatic triplet transients by NMA placed its E_T at 51 kcal/mol. The steady state kinetic analysis showed that 61% of the incident light energy was converted to the generation of the acetamido radical. The failure of *trans*-stilbene to quench the NMA photodecomposition was interpreted as evidence that the lowest singlet excited state decayed to the amido radical so rapidly that none crossed over by an intersystem pathway to the triplet state. Benzophenone, a triplet sensitizer, sensitized the NMA photodecomposition indicating that the triplet reaction of NMA was similar to the singlet one.

Photolytic or thermal decompositions of *N*-halo- and *N*-nitrosoamides have been reported to follow a wide range of overall reaction patterns. However, there is a general agreement that the primary photochemical process is the homolysis to generate an amido radical. It has been recognized that the ground state electronic configuration of an amido radical may exist either as a Π or as a Σ radical.⁴ These possibilities raise a wide range of questions regarding their chemical behavior. It is expected that the reactivity of the ground state Π and Σ radical configurations can be modified by the electronic and structural interactions of an amido radical and that chemistry of these radicals may differ considerably. Recently, Danen and Gellert^{4a} have obtained esr evidence consistent with the Π radical configuration for the ground states of some simple *N*-alkylamido radicals. In a previous communication,^{5a} we have demonstrated that an amido radical primarily reacts as an N radical but have not been able to throw any light on the electronic configuration of ground state amido radicals. As a part of the long-range investigation addressing these questions, we have undertaken flash photolysis studies of *N*-nitroso-

N-alkylacetamide in order to elucidate the kinetic behavior of a simple amido radical and the photolysis mechanisms.

Among other routes available for generation of amido radicals, *N*-alkylnitrosamide photolysis⁵⁻⁷ was chosen for the following reasons. Photolysis of *N*-haloamides⁸ presents the following drawbacks for kinetic studies: (i) difficulty in purifying *N*-haloamides, (ii) a complication of the kinetic analysis from radical chain reactions, and, finally (iii), intrusion of a possible side reaction from halo atoms. On the other hand, photolysis of tetrazenes⁹ suffers from a low quantum yield due to the *cis-trans* isomerization and polyacylhydroxylamine photolysis¹⁰ requires a quartz apparatus. The nitrosamide photolysis, as we have discovered, also presents an unexpected complication from the side reaction of nitric oxide (NO) generated from the $\pi-\pi^*$ band excitation^{6,11,12} during which NO disproportionates to form NO₂, N₂, and NO₃ radicals. Fortunately, this disproportionation process can be circumvented by limiting the irradiation at the nitrosamide $n-\pi^*$ transition band.¹² In this paper, we wish to discuss the photochemical processes of *N*-nitroso-*N*-methylacetamide (NMA) and the kinetics of the amido radical reactions.

(1) (a) Taken in part from the Ph.D. Thesis of J. N. S. Tam, Simon Fraser University, January, 1970. (b) Issued as NRC publication No. 14080.

(2) Photoreactions of Nitroso Compounds in Solution. XXVI. For part XXV, see Y. L. Chow, *Accounts Chem. Res.*, **6**, 354 (1973).

(3) (a) NRC Postdoctoral Fellow, 1970-1971, Division of Chemistry, National Research Council, Ottawa, Canada; (b) Simon Fraser University; (c) National Research Council of Canada.

(4) (a) W. C. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, **94**, 6853 (1972); see also T. Koenig, J. A. Hoobler, and W. R. Mabeay, *ibid.*, **94**, 2514 (1972); (b) E. Hedaya, R. L. Hinman, U. Schomaker, S. Theodoropoulos, and L. M. Kyle, *J. Amer. Chem. Soc.*, **89**, 4875 (1967).

(5) (a) Y. L. Chow and T. C. Joseph, *J. Chem. Soc., Chem. Commun.*, 490 (1969); (b) Y. L. Chow, J. N. S. Tam, and A. C. H. Lee, *Can. J. Chem.*, **47**, 2441 (1969).

(6) L. P. Kuhn, G. G. Kleinspehn, and A. C. Duckworth, *J. Amer. Chem. Soc.*, **89**, 3858 (1967).

(7) O. E. Edwards and R. S. Rosich, *Can. J. Chem.*, **45**, 1287 (1965).

(8) For a summary, see the recent review by R. S. Neale, *Synthesis*, **1** (1971).

(9) P. Tordo, E. Flesia, and J. M. Surzur, *Tetrahedron Lett.*, 183 (1972).

(10) (a) B. Danielli, P. Manitto, and G. Russo, *Chem. Ind. (London)*, 329 (1969); 203 (1971); (b) F. R. Stermitz and D. W. Neiswander, *J. Amer. Chem. Soc.*, **95**, 2630 (1973).

(11) Y. L. Chow and J. N. S. Tam, *J. Chem. Soc. C*, 1138 (1970).

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

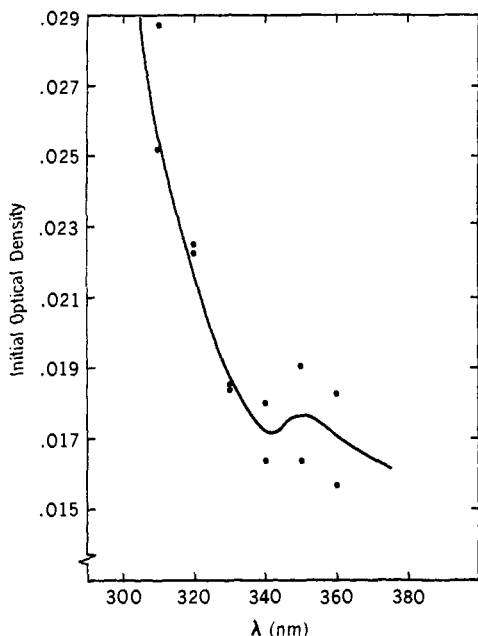


Figure 1. The absorption curve of the transient *N*-methylacetamido radical in benzene solution. A degassed solution $4 \times 10^{-3} M$ in NMA was flash excited with 98 J of energy per flash and a 0.85 μ sec flash duration.

Flash Excitation Studies

When a degassed benzene solution of NMA (10^{-3} – $10^{-5} M$) was flash excited in a 0.85 or 0.5 μ sec flash photolysis apparatus, the oscilloscope registered a transient signal which exhibited uv absorption in the 300–400-nm region. The excitation flash was filtered through NaNO_2 /potassium acid phthalate solution¹² so that only the n - π transition band (λ_{max} 390, 407, and 426 nm) of NMA above 400 nm was irradiated; the energy input per flash was in the range of 98 J. The oscilloscopic trace, monitored at several wavelengths, decays with first-order kinetics varying the half-life due to a pseudo-first-order component ranging from 5 to 50 μ sec. When an undegassed solution of NMA was flash excited, no transient signal was observed indicating either rapid quenching of the transient or its precursors.

The absorption curve of the transient (Figure 1) was obtained by a point-by-point plot of the observed initial optical densities (OD) from the oscilloscopic traces at various wavelengths; the transient was generated under a standard set of conditions using a $4 \times 10^{-3} M$ NMA solution in benzene. At this nitrosamide concentration, the region between 300 and 360 nm was transparent which allowed us to observe the absorption due to the transient. The absorption exhibits a small maximum at 350 nm and a minimum at about 340 nm (Figure 1).

For the kinetic studies, the decay of the transient was monitored at 340 nm. Some kinetic rates were also measured at 330 and/or 350 nm as controls. The observed decay rate constant (k_{obsd}) of the transient was obtained from the slope of the first-order plot and was related to the lifetime (τ_{obsd}) by the relation $k_{\text{obsd}} = 1/\tau_{\text{obsd}}$. As shown in Figure 2, k_{obsd} varied with the initial NMA concentration [S], obviously following the relation^{13,14}

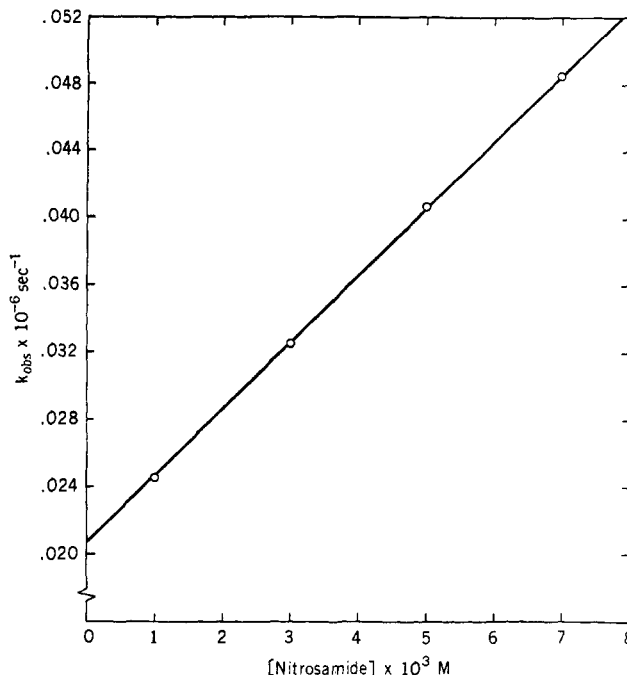


Figure 2. The observed decay rate of the *N*-methylacetamido radical as a function of NMA concentration in benzene.

$$k_{\text{obsd}} = k_1 + k_2[S] \quad (1)$$

where k_2 is the bimolecular rate constant of the reaction between the transient and NMA, and k_1 is the first-order decay rate of the transient. From Figure 2, k_2 was calculated from the slope to be $3.96 \pm 0.05 \times 10^6 M^{-1} \text{sec}^{-1}$ and k_1 from the intercept to be $2.09 \pm 0.02 \times 10^4 \text{sec}^{-1}$. The lifetime of the transient calculated from the latter is 48 μ sec. From the results, it could not be decided whether the observed k_1 represented a truly unimolecular decomposition or a bimolecular reaction of the transient (*vide infra*). The initial OD increased rapidly up to 0.004 M nitrosamide concentration due to the increase of the absorbancy of NMA in the region >400 nm. Between the concentration of 0.004 and 0.008 M , the increases were small and uneven; the initial OD, within experimental error, could be regarded as constant.

Kinetic behavior of the transient reaction was studied further in the presence of cyclohexane and *trans*-piperylene. The results, as summarized in Table I, indicated that in both cases while k_{obsd} increased according to a pseudo-first-order type reaction the initial OD decreased proportionally as the substrate concentration was increased. The plots of k_{obsd} against the concentrations (Figure 3) gave reasonable straight lines, the slopes of which represented the bimolecular rate constants of the reactions between the transient with cyclohexane ($k_3 = 1.85 \times 10^4 M^{-1} \text{sec}^{-1}$) and with *trans*-piperylene ($k_4 = 2.48 \times 10^5 M^{-1} \text{sec}^{-1}$), respectively. These bimolecular rate constants fall in the range of those for H-atom abstraction by various radicals¹⁵ as shown in Table II. The comparison is confirmatory

(13) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, Chapter 5.

(14) A. A. Lamola in "Energy Transfer and Organic Photochemistry, Technique of Organic Chemistry," Vol. 14, P. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, p 17.

(15) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 627.

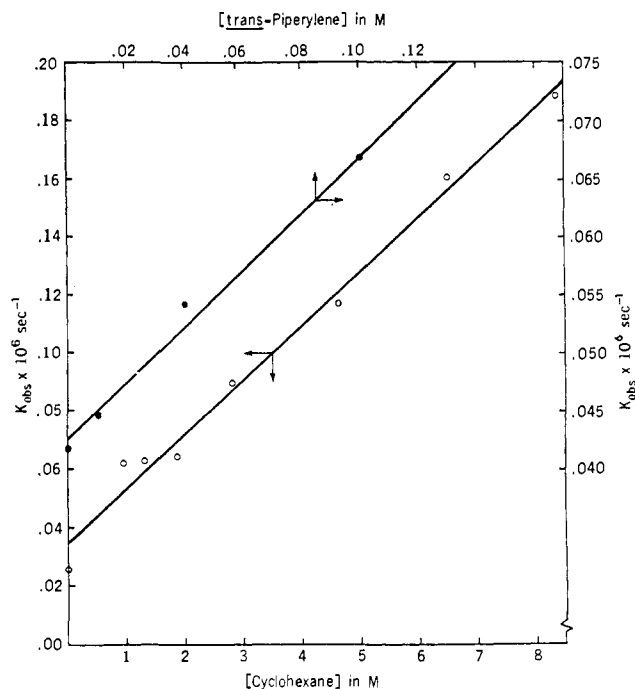


Figure 3. The observed decay rates of the *N*-methylacetamido radical as a function of the concentrations of cyclohexane (○) and of *trans*-piperylene (●); the concentrations of NMA were 0.001 and 0.004 *M*, respectively.

Table I. Reaction of the *N*-Methylacetamido Radical with Hydrocarbon Substrate^a

Concn of cyclohexane, <i>M</i>	Lifetime, μsec	$k_{\text{obsd}} \times 10^{-6}$, sec^{-1}	Initial OD	$(\text{OD})_0/(\text{OD})$
(1) With Cyclohexane; Concentration of NMA is 0.001 <i>M</i>				
0.00	40.2	0.0249	0.0241	1.00
0.93	16.1	0.0619	0.0212	1.14
1.30	15.9	0.0631	0.0205	1.18
1.85	15.6	0.0643	0.0190	1.27
2.78	11.2	0.0892	0.0153	1.58
4.63	8.6	0.1165	0.0135	1.79
6.48	6.2	0.1608	0.0103	2.34
8.33	5.3	0.1875	0.0099	2.43
(2) With <i>trans</i> -Piperylene; Concentration of NMA is 0.004 <i>M</i>				
Concn of <i>trans</i> -piperylene, <i>M</i>				
0.00	24.1	0.0415	0.0183	1.00
0.01	22.5	0.0444	0.0176	1.04
0.04	18.5	0.0542	0.0164	1.13
0.10	15.1	0.0664	0.0131	1.40

^a Degassed benzene solutions of nitrosamide 1 were excited with 98 J of flash energy and the transient was monitored at 340 nm. The excitation flash was filtered with NaNO_2 /potassium acid phthalate solution.

evidence in favor that the transient is the *N*-methylacetamide radical and, therefore, the measured rate constants represent those of the intermolecular H-atom abstraction of the amido radical from the respective substrates.

The systematic decrease of initial OD in both cases indicated that the precursor of the amido radical also reacted with the substrates, cyclohexane and *trans*-piperylene. The term $(\text{OD})/(\text{OD})_0$, where (OD) and $(\text{OD})_0$ are the initial OD of the amido radical in the

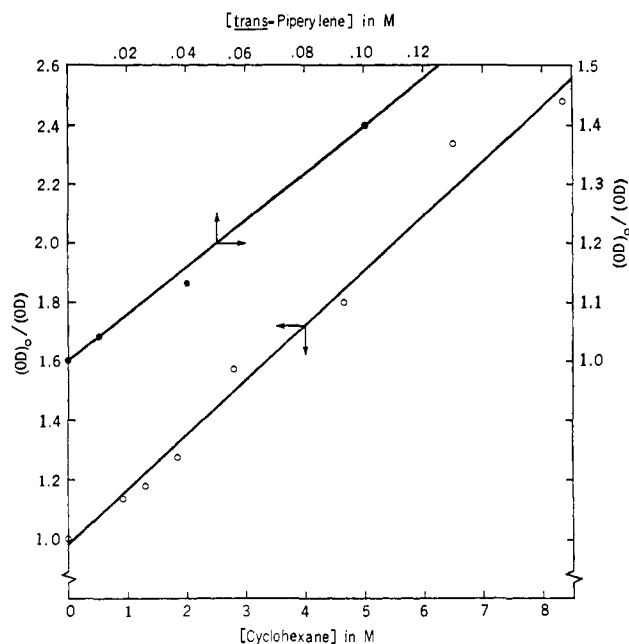


Figure 4. Stern-Volmer plots for the reaction of the singlet state of NMA (precursor) with cyclohexane (○) and with *trans*-piperylene (●) in benzene.

Table II. Some Absolute Rates of H-Atom Abstraction of Various Radicals

Substrate	Temp, $^{\circ}\text{C}$	Solvent	$k \times 10^{-4}$, $\text{M}^{-1} \text{sec}^{-1}$	Ref
(i) <i>N</i> -Methylacetamido Radical				
Ac(CH ₃)NNO	25	C ₆ H ₆	396 ± 5 (k_2)	This work
Cyclohexane	25	C ₆ H ₆	1.85 ± 0.09 (k_3)	This work
<i>trans</i> -Piperylene	25	C ₆ H ₆	24.8 ± 9.1 (k_4)	This work
(ii) <i>tert</i> -Butoxy Radical				
Cyclohexane	24	CCl ₄	10	<i>a</i>
Toluene	24	CCl ₄	2	<i>a</i>
(iii) Triplet Benzophenone Diradical				
Cyclohexane	20–25	C ₆ H ₆	42	<i>a</i>
Toluene	20–25	C ₆ H ₆	19	<i>a</i>
Propan-2-ol	20–25	C ₆ H ₆	180	<i>a</i>
(iv) Piperidinium Radical				
Methanol	25	H ₂ O	0.48	<i>b</i>
Decanoic acid	30	4 <i>M</i> H ₂ SO ₄ AcOH	0.032	<i>c</i>

^a J. A. Howard, *Advan. Free-Radical Chem.*, **4**, 49 (1970). ^b M. P. Lau, A. J. Cessna, Y. L. Chow, and R. W. Yip, *J. Amer. Chem. Soc.*, **93**, 3808 (1971). ^c J. Spanswick and K. U. Ingold, *Can. J. Chem.*, **48**, 544 (1969); V. Malatesta, and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6400 (1973).

presence and the absence of a substrate, was plotted against the substrate concentration $[S]$ (Figure 4) according to the Stern-Volmer equation¹³

$$(\text{OD})/(\text{OD})_0 = 1 + k_s \tau_s [S] \quad (2)$$

where k_s is the bimolecular rate constant of the reaction between the precursor and the substrate, and τ_s is the lifetime of the precursor. The slope of the Stern-Volmer plot corresponds to $k_s \tau_s$, where the unknown quantity τ_s must be estimated in order to calculate k_s .

Quenching experiments (*vide infra*) led us to suggest that the precursor was the lowest singlet excited state of NMA which decomposed to give the amido radical.

Table III. Reaction of the Precursor with Substrate

	Slope of Stern-Volmer plot, M^{-1}	Bimolecular rate constant, $M^{-1} \text{sec}^{-1}$
Cyclohexane	0.187 ± 0.011	$k_5 = 1.87 \times 10^8$
<i>trans</i> -Piperylene	4.04 ± 0.36	$k_6 = 4.04 \times 10^9$

Table IV. Decay Rate Constant of the Triplet Transient of Aromatic Compounds in the Presence (k_{obsd}) and in the Absence (k_0) of NMA ($5.68 \times 10^{-6} M$)

Sensitizer	Concn in M , $\times 10^6$	Monitoring wavelength, nm	$k_{\text{obsd}} \times 10^{-4}$, sec^{-1}	$k_0 \times 10^{-4}$, sec^{-1}	E_T , kcal/mol ^a	$k_q \times 10^{-9}$, $M^{-1} \text{sec}^{-1}$
Naphthalene	1.14	415, 375	>50	0.41	61	>10
1-Acetonaphthone	1.06	450, 475, 500	~50	0.41	59	~9
Pyrene	1.29	450, 500	3.31	0.67	49	0.46
Anthracene	1.00	425	0.39	0.28	42	0.019

^a The triplet energy was quoted from ref 13-15.

On the basis of this assumption, τ_s in eq 2 becomes the mean lifetime of the lowest nitrosamide singlet state and can be estimated from the relation¹³ of $\tau_0 = \tau_s/\Phi_f$ in which τ_0 is the natural fluorescence lifetime of the singlet excited state and Φ_f is the fluorescence quantum yield of NMA. Since under various conditions we have not been able to detect the fluorescence of NMA, Φ_f is approximated¹⁶ to be $<2 \times 10^{-4}$. The natural singlet lifetime obtained for the longest absorption peak of NMA in benzene (λ_{max} 426 nm, ϵ 160), using the modified Förster equation,¹⁷ is $\tau_0 \cong 5 \mu\text{sec}$. Thus, τ_s is estimated to be $\sim 10^{-9}$ sec. The slopes calculated from Figure 4 and the estimated k_5 values for cyclohexane (k_5) and for *trans*-piperylene (k_6) are summarized in Table III. One may note that the k_6 values approach the diffusion-controlled rate in benzene which is calculated by the simplified Debye expression to be¹⁵ $5 \times 10^9 M^{-1} \text{sec}^{-1}$ at 25°.

When a benzene solution of NMA ($4.5 \times 10^{-5} M$) was flash excited in a quartz vessel (unfiltered), the absorption curve of the transient showed a distinct maximum at 333 nm and a shoulder at 348 nm. Attempts to study the decay kinetics of the transient at the 330-nm region gave erratic and nonreproducible pseudo-first-order rates when the concentration of NMA or that of cyclohexane was varied. This led us to believe that more than one, probably two, transients having comparable lifetimes (in the microsecond region) were simultaneously involved in the reaction.

For comparison, photolysis of *N*-nitroso-*N*-pentylacetamide¹⁸ was studied by the flash excitation technique. In benzene solution this nitrosamide gave a very weak transient signal which did not allow us to investigate the decay kinetics. The absence of any meaningful transient is not surprising since rapid intramolecular δ -hydrogen abstraction could presumably either quench the singlet excited state or the amido radical.

Energy Levels of the Excited States

NMA gave no detectable luminescence spectrum;

(16) This was estimated from the quantum yield of 0.01 and the signal-to-noise ratio for fluorescence of biacetyl in aqueous solution obtained with our instrument.

(17) Th. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck und Ruprecht, Göttingen, 1951, p 158.

(18) (a) Irradiation of this nitrosamide in toluene solution >400 nm gave the dimer of *N*-(4-nitrosopentyl)acetamide in 42 and 45% yields in separate experiments. Besides *N*-pentylacetamide, no other by-product was isolated. (b) J. N. S. Tam, Ph.D. Thesis, Simon Fraser University, January, 1970.

this did not allow us to directly determine the energy levels of the excited states. Fortunately, it was found that NMA did quench the triplet transients generated by flash photolysis of some aromatic compounds. In Table IV, the detail of the quenching experiments was summarized. Some transients of these sensitizers had

been studied by others and assigned to the corresponding triplet excited species.^{19,20} Conditions of these flash photolyses were so adjusted that the concentrations of the aromatic compounds in benzene (degassed) were low (10^{-5} – $10^{-6} M$) to ensure no self-quenching of the transient and the flash energy was kept as low as 80–50 J to avoid triplet-triplet annihilation.^{21–25} In this respect a good first-order decay kinetics of the transient was used as a guide. The occurrence of quenching by NMA ($5.7 \times 10^{-5} M$) was indicated by the decreases in the lifetime of the sensitizer triplet in the presence of the nitrosamide (Table IV). The quenching of naphthalene and 1-acetonaphthone triplets by NMA is about equal to the limiting rate constant controlled by the diffusion process in benzene,¹⁵ while anthracene triplet was not quenched efficiently. If an electronic energy transfer was the sole process of quenching, the lowest triplet energy of NMA was fairly close to but higher than that of pyrene. The difference in triplet energy (ΔE_T) can be calculated by the relation²⁴

$$k = k_d \exp(-\Delta E_T/RT) \quad (3)$$

where k_d is the diffusion-controlled rate constant ($5 \times 10^9 M^{-1} \text{sec}^{-1}$)¹⁵ and k is the observed rate constant; ΔE_T is calculated to be ~ 2 kcal/mol. This places the lowest triplet energy of NMA at 51 kcal/mol.

Assuming that the fluorescence spectrum of NMA is symmetrical with its absorption spectrum, the 0–0 band of fluorescence could be approximated by the longest absorption peak at 426 nm from which the energy level of the lowest singlet manifold E_s was calculated to be 67 kcal/mol. It should be noted that the lowest singlet-triplet energy split is 16 kcal/mol.

Quenching and Sensitization

The quantum yield (Φ) of the disappearance of var-

(19) G. Porter and M. W. Windsor, *Discuss. Faraday Soc.*, No. 17, 178 (1956).

(20) R. Livingston and D. N. Tanner, *Trans. Faraday Soc.*, 54, 765 (1958).

(21) B. Stevens and M. Wolker, *Proc. Roy. Soc., Ser. A*, 281, 420 (1964).

(22) C. C. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, 59, 284 (1963).

(23) C. Tanaka, J. Tanaka, E. Hutton, and B. Stevens, *Nature (London)*, 198, 1192 (1963).

(24) K. Sandros, *Acta Chem. Scand.*, 18, 2355 (1964).

(25) A. Beckett and G. Porter, *Trans. Faraday Soc.*, 59, 2038 (1963).

ious nitrosamides was determined using potassium ferrioxalate actinometry.²⁶ Two irradiation methods were employed: one utilizing a merry-go-round apparatus and the other a split beam irradiation apparatus;²⁵ the latter method is primarily utilized to check the accuracy of the quantum yields obtained by the former method. The light source was filtered through a Corning filter CS 5-60 or a NaNO_2 /potassium acid phthalate solution. The rate of disappearance of the nitrosamide was followed by the decrease of the uv absorption maxima at 405 and 426 nm. The quantum yield of the disappearance of NMA was shown to vary with the concentration. For the purpose of performing a steady state kinetic analysis $1/\Phi$ was plotted against $1/[\text{NMA}]$ as shown in Figure 5. For comparisons, the similar quantum yield determinations of *N*-nitroso-*N*-hexylacetamide and *N*-nitroso-*N*-methylcaproamide no longer yielded a reasonable straight line obviously due to the subsequent chain reactions of alkyl radicals.

In the presence of *trans*-piperylene (10^{-4} – $3 M$), Φ of NMA increased gradually. The recovered diene was shown to be isomerized to a mixture of *cis*- and *trans*-piperylene with the ratio of 44:56. The photolysate gave the parent amide and a complex mixture of diene oxime which was not investigated further. Energetically piperylene cannot quench the excited states of NMA by a classical energy transfer mechanism. Obviously the allylic hydrogen abstraction by the amido radical prevailed to form the piperilyl radical as indicated by the kinetic studies above. No doubt the piperilyl radical mediated the isomerization of the diene and the formation of the oximes.

As a triplet quencher, *trans*-stilbene ($E_s = 89$ kcal/mol and $E_T = 49$ kcal/mol)¹⁵ having no abstractable hydrogen atom was an ideal one. In the presence of up to $4 \times 10^{-3} M$ *trans*-stilbene, Φ of the photodecomposition of NMA was not affected within experimental errors. Both *trans*- and *cis*-stilbene were not isomerized in benzene solution in which NMA was decomposed to the extent of 30% by >400-nm irradiation. The results strongly indicated that in the direct photolysis the singlet state NMA rapidly decomposed to amido radical, the process of which is so much faster than the intersystem crossing that no triplet NMA was formed.²⁷

Benzophenone ($E_T = 69$ kcal/mol),¹³ a good triplet sensitizer, did photosensitize the decomposition of nitrosamides. For this experiment, the light was filtered through nickel sulfate solution and soft glass so that only the benzophenone $n-\pi^*$ transition band in the 300–330-nm region was irradiated. The sensitized photodecomposition of nitrosamides proceeded smoothly; the pattern of the products distribution was virtually the same with that obtained in the direct photolysis in a Pyrex apparatus.^{5,11} A simplistic interpretation of the results is that a triplet state of nitrosamides²⁸ also undergoes a homolytic cleavage to form amido radicals and $\cdot\text{NO}$ similar to that of the singlet

(26) C. G. Hatchard and C. C. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 578 (1956).

(27) It is unlikely that the NMA triplet lifetime is shorter than 0.5 μsec , the highest limit of allowed lifetime estimated from the quencher concentration assuming a diffusion-controlled quenching.

(28) An attempt to use anthracene as the quencher gave ambiguous results since anthracene reacted with the amido radical to form what appeared to be *N*-methyl-*N*-acetyl-9-aminoanthracene.^{18b}

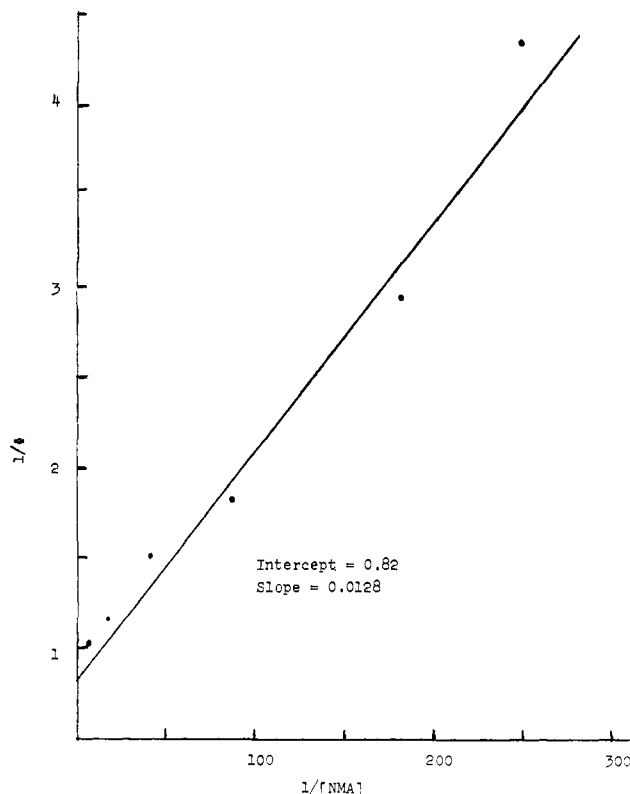


Figure 5. Variations of the reciprocals of the quantum yields vs. the reciprocals of the concentration of NMA.

excited as described above. However, in view of the fact that E_T of benzophenone is higher than E_s of NMA, we cannot rule out the possibility that the sensitized NMA may undergo intersystem crossing to the singlet state where it takes the same reaction pathway.

Reaction Mechanism

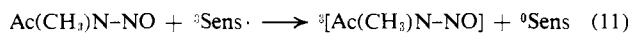
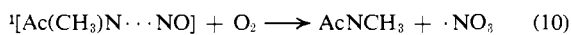
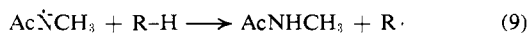
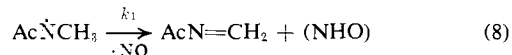
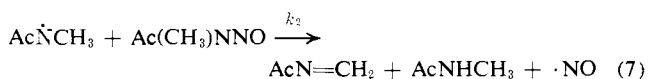
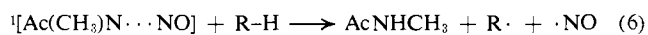
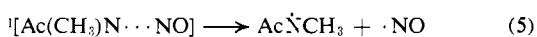
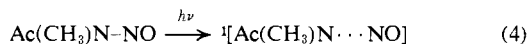
The following evidences are in agreement with the assignment of the observed transient to the *N*-methylacetamido radical. First of all the transient reacts with cyclohexane and *trans*-piperylene with the rate constants within the range of those observed for various radical hydrogen abstraction (Table III). Second, flash excitation of a benzene solution of NMA in the presence of benzhydrol generates strong uv absorption typical of the diphenyl ketyl radical showing λ_{max} in the 425-nm region²⁹ while the amido radical transient is completely absent. As the control flash of benzhydrol solution does not yield the transient absorption, the facile transfer of the benzyl hydrogen atom to the amido radical (or to the precursor) must have occurred verifying the radical nature of the reaction. Finally, the photolysis of NMA in the presence of cyclohexane or other hydrogen atom donating hydrocarbon gives intermolecular hydrogen atom nitroso group exchange products that can only be interpreted by radical processes.^{5,11,12} The observed isomerization of *trans*-piperylene where the sensitization is unfavorable also supports the formation of a radical intermediate. Coupled with the direct kinetic proofs of the transients reacting with these hydrocarbons, the assignment of the amido radical to transient appears convincing.

As the transient is the *N*-methylacetamido radical,

(29) E. J. Land, *Progr. React. Kinet.*, **3**, 369 (1965).

the precursor must be a reactive state of undissociated NMA; the lowest singlet excited state has been ascribed to the precursor (*vide supra*). In view of the fact that *trans*-stilbene ($E_T = 49$ kcal/mol) failed to quench the quantum yield of the nitrosamide photodecomposition and itself is not isomerized at all during the photolysis, it should be concluded that the triplet state of NMA is not formed in the direct photolysis. In other words, the singlet excited state NMA rapidly decays to the amido radical. The high bimolecular rate constant ($k_5 = 1.87 \times 10^8 M^{-1} \text{sec}^{-1}$) of the reaction between the precursor and cyclohexane suggests³⁰ that the reactive species is an electronically excited state nitrosamide rather than an ordinary ground state radical. Their interaction, however, is apparently similar to an intramolecular hydrogen abstraction in *N*-nitroso-*N*-pentylacetamide photolysis and possesses radical nature. It is suggested that the lowest singlet excited state of nitrosamide may have a metastable structure in which the N-N bond is stretched while the bonding electrons are held apart in an interacting distance. Summarizing the discussion, the detailed reaction mechanism is presented in Scheme I.

Scheme I



The validity of the mechanistic proposal is further checked by the steady state kinetic analysis (Figure 5) when NMA is photolyzed alone at various concentrations, [S]. Assuming fraction α of the incident light intensity I leads to the successful amido radical formation as represented in eq 4 and 5, the rate of the formation is αI . A steady state treatment of the quantum yield of NMA disappearance Φ with respect to the radical reaction 7 and 8 gives

$$\frac{1}{\Phi} = \frac{1}{2\alpha} + \frac{k_1}{2\alpha k_2[S]} \quad (12)$$

The intercept and the slope in Figure 5 give $k_1/k_2 = 0.015$, which is in fair agreement within an order of magnitude with $k_1/k_2 = 0.0052$ obtained from eq 1 of flash photolysis. The fraction of the amido radical formation α in the irradiation is calculated from the intercept to be 61%. The kinetic results are further substantiated by a quantitative determination of >400-nm photolysis of NMA in benzene in which 25% of AcNHCH_3 and 47% of the products derived from $\text{AcN}=\text{CH}_2$ (isolated as $\text{AcNHCH}_2\text{OC}_2\text{H}_5$ and AcNHCH_2OH) are obtained.^{18b}

Conspicuously missing in Scheme I is the intersystem crossing of the singlet excited state nitrosamide

(30) An alternative suggestion that if the transient has a Π configuration of the ground state amido radical⁴ the precursor may be the corresponding Σ configuration cannot be excluded at this stage.

to the corresponding triplet state which can be generated by a triplet sensitization reaction (eq 11). The reaction of the singlet state with a hydrogen atom donating hydrocarbon (eq 6) is assumed to generate alkyl radical $\text{R}\cdot$ and nitric oxide, but other modes of reactions are not excluded.³¹ Judging from the relative constancy of the initial OD in flash photolysis of NMA over the range 0.004–0.008 M solution, the singlet state is apparently not reacting with NMA as the amide radical does in reaction 7. Among several possible pathways to the formation of $\text{AcN}=\text{CH}_2$, the present result unambiguously proves that reaction 7 is the major one responsible. The nature of the first-order decay (k_1) may be expressed by reaction 8 in which the counter radical $\cdot\text{NO}$ is utilized as a hydrogen atom scavenger.

We have observed the efficient photooxidation of nitrosamides in the presence of oxygen to form nitrate derivatives and have suggested that at some stage oxygen reacts with the $\cdot\text{NO}$ moiety without quenching excited states of nitrosamides.^{11,12} If the result from the flash photolysis of the undegassed solution of NMA are assumed as oxygen quenching of the singlet state, eq 10 can be written. In view of the high reaction rate constants for the singlet state NMA reaction (eq 6) (k_5 and k_6 in Table III), the oxidation rate constant in reaction 10 can well be equal to the diffusion-controlled rate ($5 \times 10^9 M^{-1} \text{sec}^{-1}$). Taking the oxygen concentration in benzene³² at 25° as $4.5 \times 10^{-2} M$, the upper limit of the decay rate constant of the singlet state in (5) is calculated to be $2.25 \times 10^8 \text{sec}^{-1}$ which is equivalent to the lifetime (τ_s) of $4.5 \times 10^{-9} \text{sec}$. This lifetime value is in general agreement with that estimated from the modified Förster equation (10^{-9}sec).

From the benzophenone sensitization experiment the reactions of the triplet state nitrosamide are expected to be similar to those of the singlet state. However, there is no information to propose the triplet reaction mechanisms. It is very likely that both singlet and triplet state NMA undergo electronic transitions and cascade down the vibronic levels to reach the same dissociation potential energy surface from where the irreversible homolysis of the N-NO bond occurs.

Experimental Section

N-Nitroso-*N*-methylacetamide¹¹ was prepared as described previously and distilled at 0.05 mm of pressure. Benzophenone, piperylene (*trans* and a mixture of *cis-trans*), *trans*-stilbene, and 1,10-phenanthroline were purified by distillation or recrystallization from C.P. grade chemicals. Other sensitizers were taken from the Sensitizer and Quencher kit (Baker Chemicals) without further purification. For benzophenone-sensitized photolysis, nickel sulfate solution ($\text{NiSO}_4 \cdot 10\text{H}_2\text{O}$, 276 g/l.) and a soft glass were used as a filter system which possess a narrow transparent window in the 350–300-nm region. Other working conditions are the same as reported.^{11,12}

The quantum yield measurements and the flash photolysis are briefly described below. A detailed description of the apparatus and procedures as given in the thesis of the coauthor.¹⁸

Quantum Yield Determination. Benzene solutions containing NMA and the necessary substrate were treated with purified nitro-

(31) A singlet excited state abstracting a hydrogen atom from a hydrogen is conceptually more difficult to understand than a triplet excited state hydrogen abstraction. It is not inconceivable that the singlet state nitrosamide may react with a cyclohexane C-H bond by a concerted mechanism controlled by orbital symmetry. A comparison of the reaction pattern of the singlet state with that of the triplet state nitrosamide may provide a valuable insight.

(32) J. Horiuti, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **17**, 341, 125 (1931).

gen or degassed and were irradiated in a "merry-go-round" apparatus using a PEK No. 202 high-pressure Hg arc lamp with the light collection system. The collimated light was filtered through a water jacket (20-cm length) and either a Corning filter (CS 5-60) or a NaNO_2/K acid phthalate solution to provide a transparent window in the 405–436-nm region. The potassium ferric oxalate actinometry described by Hatchard and Parker²⁶ was adapted. The duration of irradiation was usually 2–3 hr during which the optical density of the monitoring peaks (405 and 425 nm) decreased by 15–25%.

Some quantum yields obtained by the above method were checked by a split beam irradiation apparatus similar to that described by Beckett and Porter.²⁵ The agreements of the results by two methods were within $\pm 2\%$.

Flash Photolysis. The preliminary experiment was carried out with a 5 μsec dual beam flash kinetic apparatus using a pulsed monitoring light source as previously described. The subsequent kinetic studies utilized an improved apparatus with 0.8 and 0.5 μsec flash durations. This consists of two independent, synchronously triggered capacitor-spark gap lamp circuits. The 0.8- μsec apparatus used two 0.3- μF 25-kV capacitors (one in each circuit).³³ For the 0.5- μsec apparatus, two 0.05- μF 35-kV capacitors were used.³⁴ The lamp configuration and the procedure were

(33) R. W. Yip, W. D. Riddell, and A. G. Szabo, *Can. J. Chem.*, **48**, 987 (1970).

(34) G. Porter, R. W. Yip, J. M. Dunstin, A. J. Cessna, and J. E. Sugamori, *Trans. Faraday Soc.*, **67**, 3149 (1971).

the same as that reported.³⁵ The decay curve of the transient was analyzed by plotting the logarithm of the optical density *vs.* time which gave a straight line. The data were processed by a computer program made available by Dr. A. G. Szabo, Division of Biology, National Research Council, Ottawa. The optical density of the transient 2 μsec after the termination of photoflash is taken as the initial OD.

Quenching of NMA. Decomposition by Stilbenes and Pterylenes. Commercial *trans*-stilbene in benzene was irradiated in a Pyrex apparatus under nitrogen. A vpc analysis (Apiezon N column, 8 ft \times $\frac{1}{8}$ in.) showed that the retention times for *cis*- and *trans*-stilbene were 3.8 and 8.2 min and the ratio was 90.5:9.5.

Solutions containing NMA (4.7×10^{-3} M) and *trans*-stilbene (4.07×10^{-6} M to 4.07×10^{-3} M) were degassed and irradiated as described in the quantum yield determination. The nitrosamide absorptions at 403 and 426 nm decreased by 25% in 2.5 hr of irradiation.

The variation of the quantum yield was less than 10% when the concentration of *trans*-stilbene was less than 10^{-3} M. The ratio of *cis*- to *trans*-stilbenes was shown to be 1.5:98.5 before the irradiation and 1:99 after the irradiation. When *cis*-stilbene was used for a similar quenching experiment, the result was the same; the ratio of *cis*- to *trans*-stilbenes was 90.2:9.8 before and after the irradiation, during which 30% of NNO had decomposed.

The ratio of *cis*- to *trans*-pterylene was analyzed by vpc on a 30% AgNO_3/TEG on 25% firebrick (5 ft \times $\frac{1}{8}$ in.) at 42°.

(35) R. W. Yip, *Rev. Sci. Instrum.*, **40**, 1035 (1969).

Polar Effects of the Aminium Radical Addition to Styrenes¹

Thomas Mojelsky and Yuan L. Chow*

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada. Received January 3, 1974

Abstract: In order to study the polar effects of the aminium radicals generated by the photolysis of nitrosamines, the relative reactivities of eight meta- and para-substituted styrenes toward the piperidinium radical addition were determined by the competitive method in methanol containing dilute hydrochloric acid. The electric requirements were shown to correlate better with σ constants giving the ρ value of -1.34 but not with σ^+ constants. Comparisons of the known ρ values for various radical addition reactions led us to conclude that the polar effects were caused by ground state electrostatic attraction between the positive charge of the aminium radical and the π electron of styrenes rather than resonance stabilization at the transition state. The quantum yield of the *N*-nitroso-piperidine photoaddition to styrene was dependent on the nitrosamine concentration but not on the styrene concentration indicating the presence of chain processes.

In the recent years, polar effects of radical reactions² have been a subject of intense investigations in a hope to delineate nonrandom reactivity of radicals. For a quantitative treatment of the polar effects, Hammett-type substituent effect-reactivity correlation has been widely utilized to unravel the radical reaction mechanism. Competitive hydrogen abstractions of various radicals from meta- and para-substituted toluenes have been widely used techniques to obtain Hammett correlations with considerable success.² However, there are only a few cases of the similar correlation on radical addition to meta- and para-substituted styrenes and the corresponding stilbenes in the literatures.^{3–5} All of the radicals studied in these hydrogen

abstraction and addition reactions give negative reaction constants (ρ values) of various size and generally correlate better with σ^+ constants than with σ constants.

We have established that photolysis of a *N*-nitrosodialkylamine in dilute acid solution generates nitric oxide and the aminium radical, the latter of which undergoes hydrogen abstraction or addition to a double bond.⁶ Aminium radicals have been generated by a metal ion catalyzed decomposition⁷ or photolysis⁸ of *N*-chloramines under strongly acidic conditions (for example, 4 M H_2SO_4 in AcOH). There exists good evidence that an aminium radical is an electrophilic species

(1) Photoreactions of Nitroso Compounds in Solution. XXVII. For part XXVI, see J. N. S. Tam, R. W. Yip, and Y. L. Chow, *J. Amer. Chem. Soc.*, **96**, 4543 (1974).

(2) For a general review of this subject, see the recent monograph by G. A. Russell in "Free Radicals," Vol. 1, J. Kochi, Ed., Wiley, New York, N. Y., 1973, p 275.

(3) H. Sakurai, S. Hayashi, and A. Hosomi, *Bull. Chem. Soc. Jap.*, **44**, 1945 (1971).

(4) J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc. B*, 1191 (1966).

(5) G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

(6) M. P. Lau, A. J. Cessna, Y. L. Chow, and R. W. Yip, *J. Amer. Chem. Soc.*, **93**, 3808 (1971).

(7) F. Minisci, *Synthesis*, 1 (1973), and the previous papers quoted therein.

(8) R. S. Neale and E. Gross, *J. Amer. Chem. Soc.*, **89**, 6579 (1967), and the preceding papers from this research group.