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Absolute Kinetics of Aminium Radical Reactions with Olefins in Acetonitrile Solution[1]

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Abstract: Photolysis of *N*-nitrosamines in acidic acetonitrile produces aminium radical cations via protonation of the initially-formed aminyl radicals. The kinetics of these species can be monitored by transient UV spectroscopy via their absorption band which is found at *ca*. 300 nm in the case of the piperidinium radical, for example. By measuring the aminium radicals' lifetimes as a function of the concentration of added olefin, absolute values for the bimolecular rate constants for the addition reactions were obtained. In the case of the piperidinium radical, these rate constants varied from $<1 \times 10^6$ M^{-1} s^{-1} for acrylonitrile to $1.1 \pm 0.1 \times 10^9$ M^{-1} s^{-1} for 1,1-diphenylethylene and generally increased with decreasing ionization potential of the olefin, thus confirming the electrophilic nature of the piperidinium radical. The rate constants for analogous reactions of diethylaminium radicals were 1.5−25 times smaller indicating the importance of steric factors in aminium radical additions to olefins. The rate constant for the intramolecular 1,5-addition of the secondary aminium radical cation to an unactivated double bond is estimated to be *ca*. 1×10^6 s^{-1}, but the intramolecular addition rate constant increases to $>1 \times 10^8$ s^{-1} upon the phenyl substitution at the olefinic terminus.

Applications of nitrogen-centered radicals and their protonated counterparts, aminium cation radicals, in synthesis were investigated in detail several years ago.[4] It was established that protonation of neutral aminyl radicals affects strongly both their overall reactivity and the selectivity of their reactions, which makes aminium radicals considerably more attractive for synthetic purposes than their neutral counterparts. In contrast to the rather unreactive, nucleophilic aminyl radicals, aminium radicals, which are electrophilic, were shown to add readily to alkenes and arenes and to undergo synthetically useful intramolecular hydrogen atom abstraction reactions to form cyclic amines (the Hofmann−Löffler−Freytag reaction).[4]

The recent development of new methods for generating aminyl and aminium radicals has produced a renewed interest in these species as synthetically useful entities in free radical chain processes.[5,6] However, these synthetic applications, unlike those of carbon-centered radicals, are not augmented by any detailed knowledge of the kinetic properties of aminium radicals.[7] This lack of quantitative kinetic data is particularly true for additions of aminium radical cations to olefins. In this paper we present information obtained via a UV−visible laser flash photolysis (LFP) technique on the generation and spectroscopy of some alkyl and aryl secondary aminium radicals in acidic acetonitrile solutions and detailed information on the absolute kinetics of their reactions with olefins. In a recent article, Newcomb *et al*. also reported the absolute kinetics for reactions of some dialkylaminium radicals, using a different experimental approach.[8]

Results and Discussion

Generation of Aminium Radicals. Numerous methods have been reported for the generation of aminium radicals, e.g., electrochemistry[9,10] and pulse radiolysis.[11−14] There are also a number of photogeneration methods, which are of potential use in flash photolysis experiments. One method involves the reduction of sensitizers such as ketone triplets[15,16] or dicyanobenzene[17] by amines in an electron transfer quenching reaction, which generates the radical anion of the sensitizer and the radical cation of the amine. Aminium radicals have also been observed from the electron transfer quenching of aromatic radical cations.[18] All these methods have the disadvantage that sensitizer radical anion or other transient species is also formed,

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[16] Devadoss, C.; Fessenden, R. W. *J. Phys. Chem.* **1990**, *94*, 4540−4549.

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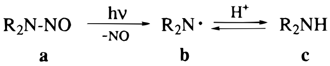
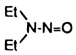
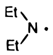
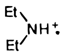
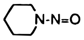
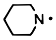
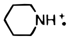
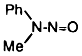
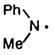
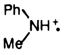
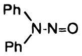
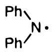
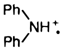
Scheme 1



$$\underset{\textbf{a}}{R_2N\text{-}NO} \xrightarrow[-NO]{h\nu} \underset{\textbf{b}}{R_2N\cdot} \xrightleftharpoons{H^+} \underset{\textbf{c}}{R_2NH^{+\cdot}}$$

Table 1. UV−LFP Characterization of the Radical Cations Generated from *N*-Nitrosamines in 0.05 M Malonic Acid/ Acetonitrile Solution

#	Precursor, **a**	Radical, **b**	Radical Cation, **c**	λ_{max}/nm	τ_0/μs
1				285	1.6
2				290	2.5
3				450	50
4				690	80

and this can complicate optical detection of the aminium radicals. A more useful group of methods involves the photolysis of an appropriate precursor to generate aminyl radicals directly, which are then very rapidly protonated in acidic media to yield the corresponding aminium radicals. Photochemical precursors which have been used include tetrazenes,[19] thione carbamates,[20] *N*-chloramines,[4,21,22] and *N*-nitrosamines.[4d,f,21,23,24] We decided to use *N*-nitrosamines as the precursors in our LFP experiments, because of the commercial availability of a wide range of substituted *N*-nitrosamines as well as the relatively clean photolysis reaction (cogeneration of NO radicals as compared with the much more reactive Cl atoms in the case of *N*-chloramines). Photolysis of nitrosamines in acetonitrile solutions containing added excess acid yields the desired aminium radicals via the mechanism shown in Scheme 1. However, it is important to note that this method can only be used to produce secondary aminium radicals, since R groups must be alkyl or aryl for the nitrosamine to be stable.

The four of the *N*-nitrosamines studied in the present work are listed in Table 1, as well as the structures, band maxima, and lifetimes of the corresponding radical cations generated upon 266 nm photolysis in 0.05 M malonic acid/acetonitrile solution.[25] The observed transient spectra of the radical cations are shown in Figure 1. In all cases, the spectra, top ΔOD's following the laser pulse, and lifetimes were unaffected by oxygen saturation of the solution, which is consistent with the assignment of these spectra to the aminium radical cations.[26] All four nitrosamines were also subjected to LFP in 2:1 MeOH:H_2O and in MeOH solutions containing 0.01 M HCl, in order to compare our findings with earlier work that was carried out mainly in aqueous or mixed aqueous solutions.[20,23] Spectra obtained in the three solvent systems were identical in all cases (both in the absence and presence of acid, *vide infra*), but the aminium radicals were found to live longer in 2:1 MeOH:H_2O than in acetonitrile. For example, the lifetime of the piperidinium radical (**2c**) was found to be 2.5 μs in acetonitrile and 4.0 μs in 2:1 MeOH:H_2O. In order to avoid solubility problems with some of the olefins used in the quenching studies, we chose 0.05 M malonic acid/ acetonitrile as our primary solvent system.

The two alkylaminium radicals **1c** and **2c** show absorption bands (Figure 1a,b) which appear to peak near 290 nm. However, these peaks may be a result of the strong bleaching of the absorption of the nitrosamine which begins in this region. That is, the true band maxima for these aminium radicals may occur at shorter wavelengths. For *N*-nitrosopiperidine the observed transient spectrum agrees well with that reported in acidic aqueous solution for the piperidinium radical.[21] No transient absorptions above 280 nm were observed upon photolysis of these two dialkylnitrosamines (**1a** and **2a**) in the absence of added acid. In contrast, LFP of *N*-nitroso-*N*-methylaniline (**3a**) and *N*-nitrosodiphenylamine (**4a**) in the absence of acid generates transient absorptions that on the basis of the previous studies[27] can be assigned to the corresponding aminyl radicals, **3b** and **4b**, respectively. However, very different spectra, which we assign to the aminium radicals **3c** and **4c**,[28] are observed for these two systems when the LFP is carried out in the presence of acid (Figure 1c,d). These phenyl-substituted aminium radicals were found to be much more stable than the dialkylaminium radicals under our experimental conditions, with lifetimes of *ca*. 50 and 80 μs, respectively, and with the decays in the absence of quenchers not following strictly first-order kinetics.

Chow *et al.* have suggested that *N*-nitrosamines form specific association complexes with acids in solution[4d,f,24] and that it is the photolysis of this complex which generates the aminium radical via the *N*-nitrosoammonium ion (Scheme 2), without the initial formation of a free aminyl radical as indicated in Scheme 1. The photolysis of *N*-nitrosodiphenylamine readily allows the direct study of the mechanism of aminium radical generation, since the diphenylaminyl and diphenylaminium radicals have strong and distinguishable visible absorptions. In order to distinguish between the mechanisms given in Schemes 1 and 2, the kinetics of the decay of the diphenylaminyl radical (**4b**, monitored at 430 nm) and the growth of the diphenylaminium radical (**4c**, monitored at 690 nm) were studied as a function of acid concentration. Initial studies using malonic acid showed upward-curving quenching plots (which is, perhaps, indicative of the role of dimeric or oligomeric acid species in this solvent system). However, studies with trifluoracetic acid (TFA) and methanesulfonic acid (MSA) gave excellent linear plots. The results using TFA are shown in Figure 2. At all acid concentrations, the diphenylaminyl radical was observed to be generated instantaneously (*i.e.* within the 10 ns laser pulse). The kinetics of decay of the diphenylaminyl radical (△) match perfectly with the kinetics of the growth of the diphenylaminium radical (●). These results strongly support the mechanism

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[19] Magdzinski, L. J.; Chow, Y. L. *J. Am. Chem. Soc.* **1978**, *100*, 2444−2448.

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[24] Lau, M. P.; Cessna, A. J.; Chow, Y. L.; Yip, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 3808−3809.

[25] Other less thoroughly examined *N*-nitrosamines studied included di-*n*-propylnitrosamine, 1-nitrosopyrrolidine, and *n*-propyl-*n*-butylnitrosamine which upon 266 nm LFP of 0.05 M maleic acid/acetonitrile solutions gave transient absorptions very similar to those shown in Figure 1a,b with aminium radicals lifetimes of 2.3, 2.6, and 1.8 μs, respectively.

[26] It has to be noted, however, that the spectra of the aminyl radicals **3b** and **4b** observed upon photolysis of the nitrosamines **3a** and **4a** (numbering system given in Table 1 and illustrated in Scheme 1) in the absence of acid (*vide infra*) were also unaffected by the presence of oxygen.

[27] Leyva, E.; Platz, M. S.; Niu, B.; Wirz, J. *J. Phys. Chem.* **1987**, *91*, 2293−2303.

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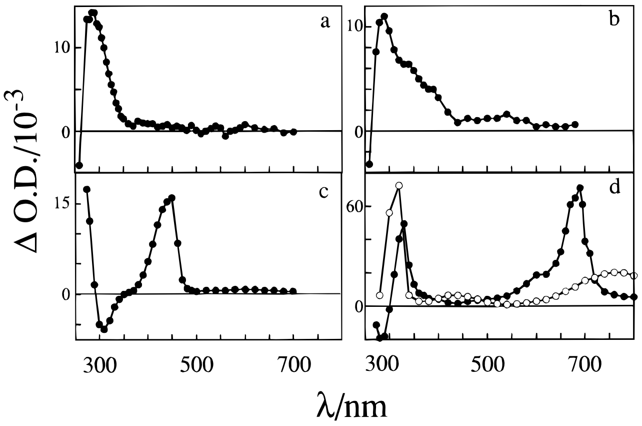


Figure 1. Transient spectra of the aminium radicals generated by 266 nm LFP from (a) *N*-nitrosodiethylamine, (b) *N*-nitrosopiperidine, (c) *N*-nitroso-*N*-methylaniline, and (d) *N*-nitrosodiphenylamine in 0.05 M malonic acid/acetonitrile solutuion. The open circles in d show the observed transient spectrum of the diphenylaminyl radical in the absence of added acid.

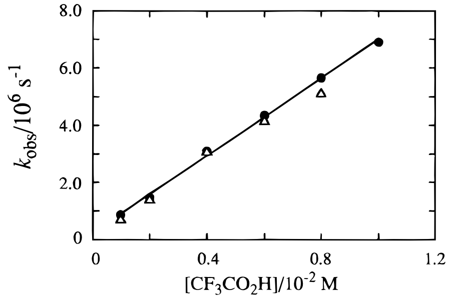
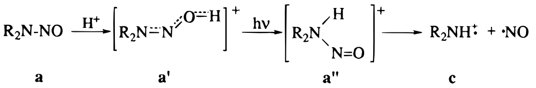


Figure 2. Observed first-order rate constant for the decay of the diphenylaminyl radical (monitored at 430 nm, △) and the growth of the diphenylaminium radical (monitored at 690 nm, ●) observed upon photolysis of *N*-nitrosodiphenylamine in acetonitrile as a function of the concentration of CF_3CO_2H.

Scheme 2



shown in Scheme 1 with the formation of a free aminyl radical as a distinct intermediate which is then protonated under our experimental conditions to give the aminium radical. Similar plots of aminium radicals' growth rate as a function of TFA concentration were made for the other three nitrosamines. The measured apparent second-order rate constants for reaction of the aminyl radicals with TFA to generate the aminium radicals were $(1.3 \pm 0.1) \times 10^9$, $(2.6 \pm 0.5) \times 10^9$, $(1.2 \pm 0.1) \times 10^9$, and $(6.8 \pm 0.5) \times 10^8$ M^{-1} s^{-1} for diethylaminyl, piperidinyl, phenylmethylaminyl, and diphenylaminyl, respectively. In the case of the diphenylaminyl radical, reaction with MSA yielded an apparent rate constant of $(5.7 \pm 0.5) \times 10^8$ M^{-1} s^{-1}. Thus, our results demonstrate that *if N*-nitrosamines form association complexes with acids, then these complexes are destroyed upon photolysis, generating the free aminyl and NO radicals, and that the aminium radicals are formed by the protonation of the free aminyl radicals, as shown in Scheme 1.

Intermolecular Reactions of Aminium Radicals with Olefins. The rate of decay of the dialkylaminium radicals **1c** and **2c** can be increased by addition of an olefin; this is illustrated in Figure 3, which shows the decay of the piperidinium radical in the absence (●) and presence (○) of 1 mM ethyl vinyl ether. However, the lifetimes of arylaminium radicals **3c** and **4c** were unchanged upon additions of any of the olefins we used in our studies, indicating that the rate constants for any corresponding reactions must be less than 10^6 M^{-1} s^{-1}.

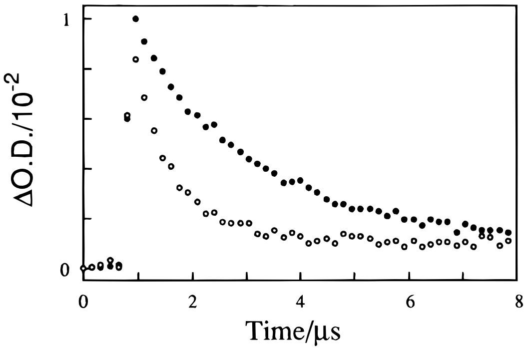
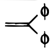
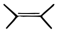
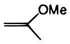
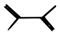
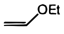
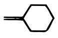
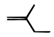
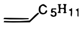
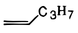
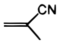


Figure 3. Transient absorption decay traces observed at 310 nm upon photolysis of *N*-nitrosopiperidine in 0.05 M malonic acid/acetonitrile solution in the absence of quencher (●) and in the presence of 1 × 10^{-3} M ethyl vinyl ether (○).

Table 2. Second-Order Rate Constants for the Intermolecular Quenching of the Radicals **1c** and **2c** by Various Olefins in 0.05 M Malonic Acid/Acetonitrile Solution at 295 ± 2 K (Errors Correspond to the 95% Confidence Level Limits of the Slopes of the Relevant Quenching Plots)

#	Quencher	IP(eV)[a]	$k_q/10^8$, $M^{-1}s^{-1}$	
			1c	**2c**
1		8.0	0.37 ± 0.06	11 ± 1
2		8.27	0.37 ± 0.06	3.2 ± 0.3
3		8.64	1.6 ± 0.2	3.8 ± 0.6
4		8.62	0.93 ± 0.02	10 ± 3
5		8.80	1.9 ± 0.2	3.1 ± 0.6
6		8.93	0.60 ± 0.01	2.3 ± 0.3
7		8.95	<0.01	0.12 ± 0.04
8		9.13	0.26 ± 0.03	1.8 ± 0.3
9		9.38	<0.01	0.19 ± 0.01
10		9.50	0.08 ± 0.02	0.32 ± 0.03
11		10.34	-	< 0.01

[a] For consistency all the IPs were taken from the NIST Standard Database 25. *NIST Structures Properties Database and Estimation Program 1991*; U.S. Department of Commerce: Gaitherburg, MD 20899, 1991.

In the usual manner, a number of rate constants for the reactions of radicals **1c** and **2c** with series of olefins were determined in quenching experiments and are presented in Table 2. A given rate constant, k_q, can be obtained as the slope of plot of k_{obs} *vs* [Q] according to the simple relationship

$$k_{obs} = k_0 + k_q[Q] \tag{1}$$

where k_0 is the observed first-order decay rate constant for the radical in the absence of added quencher and k_{obs} is the observed rate constant in the presence of a given quantity of a quencher Q.

The kinetic analysis described above is only valid if the aminyl radicals are completely protonated under our conditions, *i.e.* if the equilibrium shown in Scheme 1 lies entirely to the right. Our experimental conditions for the quenching studies were chosen on the basis of a series of measurements in which we monitored the top ΔOD (at 300 nm) of the piperidinium radicals as a function of acid concentration for both trifluoro-

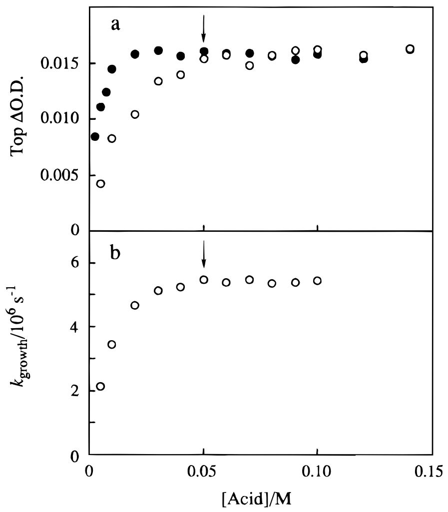


Figure 4. (a) Top ΔOD of the piperidinium radical cation absorption (measured at 300 nm) observed upon 266 nm photolysis of **2a** in acetonitrile as a function of acid concentration for trifluoroacetic acid (●) and malonic acid (○). (b) Observed rate of growth of the diphenylmethyl radical (measured at 330 nm) upon 308 nm photolysis of **2a** in acetonitrile in the presence of 4 mM 1,1-diphenylethylene as a function of malonic acid concentration. The arrows on these plots indicate the malonic acid concentration at which all of the quenching studies were performed.

acetic (TFA) and malonic acid (MA). The results, shown in Figure 4a, indicate that the necessary conditions are attained at above *ca.* 0.015 M TFA and *ca.* 0.05 M MA.[29] It is significant that the same limiting top ΔOD (*i.e.* at high acid concentration) is obtained with the two acids since this supports our conclusion that the piperidinyl radicals are fully protonated to give the radical cation. As a further test of the experimental conditions used to obtain complete protonation, the observed first-order rate constant for growth of the 2-piperidinyl-1,1-diphenylethyl radical formed by reaction of the piperidinium radical with 4 mM diphenylethylene (*vide infra*) was monitored at 330 nm as a function of malonic acid concentration. These results are shown in Figure 4b in which it can be seen that the measured rate constant for the growth reaches a plateau at [MA] ≥ 0.05 M. This verifies that protonation of piperidinyl is complete at this acid concentration. Since some of the olefins were found to react with trifluoroacetic acid even at low acid concentrations, we chose 0.05 M malonic acid/acetonitrile as our standard solvent for the quenching experiments. Under these conditions our quenching plots of k_{obs} *vs* [olefin] were linear, yielding the rate constants for the reaction of the piperidinium radicals with a series of 10 olefins. These data are summarized in Table 2. As a final test of the validity of these measurements, quenching experiments were also done with **2c** at a much higher MA concentration (cyclohexene, 0.20 M MA: $k_q = (0.17 \pm 0.04) \times 10^8$ M^{-1} s^{-1} and with TFA (methylenecyclohexene, 0.02 M TFA: $k_q = (2.9 \pm 0.3) \times 10^8$ M^{-1} s^{-1}). Both of these rate constants are in good agreement with those listed in Table 2.

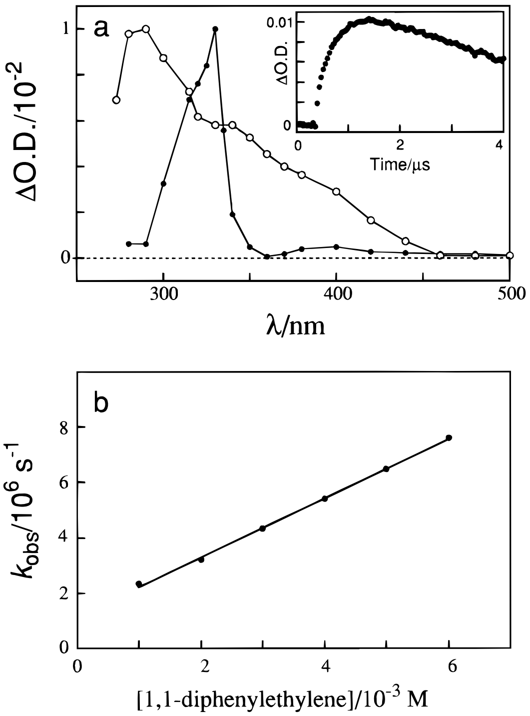
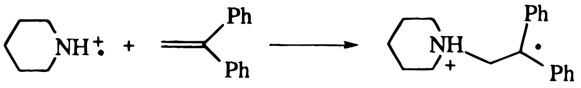


Figure 5. (a) Absorption spectra observed upon 308 nm LFP of **2a** in 0.05 M malonic acid/acetonitrile solution in the absence (○) and presence (●) of 3×10^{-3} M 1,1-diphenylethylene. The inset shows the transient absorption trace in the latter case measured at 330 nm. (b) Plot of k_{obs} for the growth of the 2-piperidinyl-1,1-diphenylethyl radical *vs* [1,1-diphenylethylene]. The slope gives $k_q = (1.1 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, with a correlation coefficient of 0.999.

Quenching of the piperidinium radical by 1,1-diphenylethylene (DPE) (which was studied with 308 nm LFP of **2a** due to strong DPE absorption at 266 nm) gave an absorption which grew at 330 nm and was much stronger than the absorption of the piperidinium radical at this wavelength. The spectra and growth at 330 nm are shown in Figure 5a. The new 330 nm absorption can readily be assigned to the 2-piperidinyl-1,1-diphenylethyl radical,[30] which proves that quenching occurs (at least in part) via addition as shown in eq 2. The observed rate constant for the growth of this 2-piperidinyl-1,1-diphenylethyl radical absorption depended linearly upon the concentration of the olefin (Figure 5b), and the derived quenching rate constant k_q was equal to $(1.1 \pm 0.1) \times 10^9$ M^{-1} s^{-1} (see Table 2).



(2)

Aminium radical quenching experiments for most of the olefins were also carried out with the diethylaminium radical in order to assess the influence of the aminium radical structure on reactivity. The kinetics results which suggest a significantly lower reactivity of diethylaminium radical cation in comparison with the piperidinium radical are listed in Table 2.

To our knowledge the results in Table 2 constitute the first reasonably comprehensive set of absolute kinetic data for the reactions of aminium radicals with olefins. We are aware of only three literature values for such reactions, *viz.*, piperidinium plus cyclohexene and 1,3-pentadiene in 2:1 MeOH:H_2O solution, $(2.4 \pm 0.1) \times 10^7$ and 5.3×10^7 M^{-1} s^{-1}, respectively,[21] and 2,2,6,6-tetramethylpiperidinium plus cyclohexene, $(1.1 \pm 0.1) \times 10^4$ M^{-1} s^{-1} in 10% CH_3CN:H_2O.[22] The first of the rate constants compares quite well with the value of $(1.2 \pm 0.4) \times 10^7$ M^{-1} s^{-1} obtained in our study of this reaction in acidic acetonitrile solution.

Our measurements demonstrate the relatively high reactivity of the aminium radicals toward olefins. The measured rate constants for piperidinium radicals range from 10^6 to 10^9 M^{-1}

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(29) Rough estimates of the equilibrium constants for the protonation reaction of piperidinyl radical can be made from these data yielding values of *ca.* 60 and 400 M^{-1} for TFA and MA, respectively. More precise measurements of these and other related equilibrium constants will be presented later.

(30) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1984**, *106*, 3056−3057.

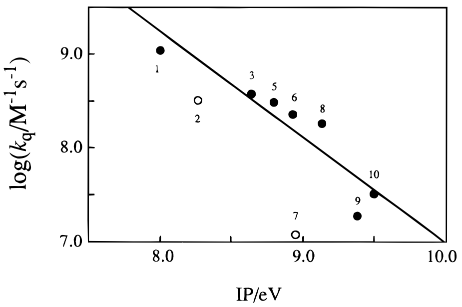


Figure 6. Plot of $\log(k_q/M^{-1}\ s^{-1})$ *vs* the olefin ionization potential for the reactions of the piperidinium radicals with olefins listed in Table 1. The line is the best fit through the data points represented by the filled circles.

s^{-1}, with $10^6\ M^{-1}\ s^{-1}$ representing the lower limit measurable under our experimental conditions. It should be stressed that these rate constants refer to the overall reactions of the aminium radical with the olefin. It seems reasonable to assume on the basis of the earlier product studies that addition to terminal olefins will be much more important than allylic hydrogen atom abstraction[4f] (when the latter is possible). It is also likely that addition is favored over abstraction for the unsaturated ethers since the previously measured rate constants for reactions of piperidinium radicals with alcohols and dioxanes are very low (e.g. $1.4 \times 10^4\ M^{-1}\ s^{-1}$ and $9.3 \times 10^3\ M^{-1}\ s^{-1}$ for ethanol and dioxane, respectively)[21] compared with those we obtain for vinyl ethers. There is a general trend of increasing reactivity of the olefin with decreasing ionization potential (IP) as would be expected for electrophilic radicals.[31] That is, in the absence of steric effects, addition to an olefin should be dominated by the interaction of the SOMO with the HOMO of the olefin, the energy of the latter being reflected in the olefin's IP. Figure 6 shows a plot of log ($k_q/M^{-1}\ s^{-1}$) *vs* IP for quenching of the piperidinium radicals by nine monoolefins. For terminal olefins the correlation coefficient is 0.92 (slope = −1.1) which is reasonable, though not as good as the correlations for similar plots with perfluoro-*n*-alkyl radicals, ($r = 0.97$)[33] and with azidyl radicals ($r = 0.991$).[32] All three of these radicals are strongly electrophilic. The two rate constants that deviate significantly from the linear relationship shown in Figure 6 correspond to the reactions with tetramethylethylene and cyclohexene, which indicates that steric hindrance retards these addition reactions. The importance of steric hindrance in the additions of aminium radicals to olefins becomes apparent if we compare the rate constants reported for the addition to cyclohexene of piperidinium (*viz.*[21] ($2.4 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$) and 2,2,6,6-tetramethylpiperidinium (*viz.*[22] ($1.1 \pm 0.1) \times 10^4\ M^{-1}\ s^{-1}$). Our own data, Table 2, indicate that the piperidinium radical is more reactive than the sterically more crowded diethylaminium radical. It is interesting to compare the present piperidinium radical data with similar data for the much less sterically demanding azidyl radicals,[32] see Figure 7. For reactions with the more reactive olefins, including tetramethylethylene, the correlation between two sets of kinetic data is remarkably good. However, the two reactions with cyclohexene appear to be governed by very different steric demands, the piperidinium radicals showing a much decreased reactivity.

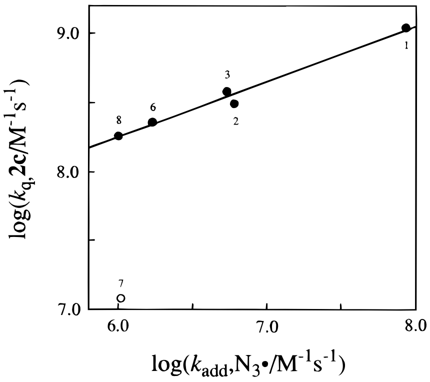
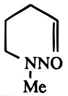
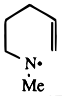
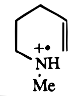
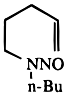
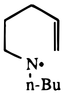
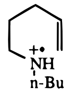
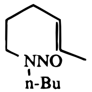
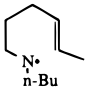
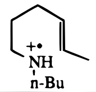
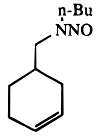
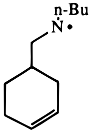
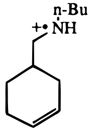


Figure 7. Plot of $\log(k_q/M^{-1}\ s^{-1})$ for the reactions of the piperidinium radicals with the olefins listed in Table 1 *vs* log ($k_{add}/M^{-1}\ s^{-1}$) for the reactions of azidyl radicals with the same olefins (data from ref 32). The line is the best fit through the data points represented by the filled circles.

Table 3. UV−LFP Characterization of the Alkenylaminium Radical Cations Generated from Alkylalkenyl-*N*-nitrosamines in 0.05 M Malonic Acid/Acetonitrile Solution

#	Precursor, a	Radical, b	Radical Cation, c	$\tau_0/\mu s$
5				0.77
6				0.60
7				0.91
8				0.48

Theory seems to be of little help in understanding the subtleties of the intermolecular additions of the aminium radicals to olefins. In recent *ab initio* calculations (at the MP2/6-311G** level of the theory) for the addition of $NH_3^{\bullet+}$ to ethylene, no transition state could be located and the reaction was predicted to proceed without any barrier and to be highly exothermic.[34]

Intramolecular Reactions of Aminium Radicals with Olefins. Intramolecular alkenylaminium radical cyclizations have been shown to be very useful in constructing the pyrrolidine nucleus.[4f,g,5] Such reactions proceed with high regioselectivity and with no Hoffmann−Löffler−Freytag reaction derived products. Until now there have been no relevant absolute kinetic data for this important unimolecular rearrangement,[5,7] although product studies and competition kinetic experiments indicate,[4,5] that these reactions are irreversible and dramatically more efficient than the corresponding aminyl radical cyclizations.

Detection of the dialkylaminium radicals using the LFP technique(*vide supra*) offered promise of a direct measurement of the absolute rate constants for intramolecular addition reactions. As expected, 266 nm LFP of nitrogen-saturated acetonitrile solutions of the alkylalkenyl-*N*-nitrosamines listed in Table 3 did not produce any detectable transients. However, upon 266 nm LFP of 0.05 M malonic acid/acetonitrile nitrogen-

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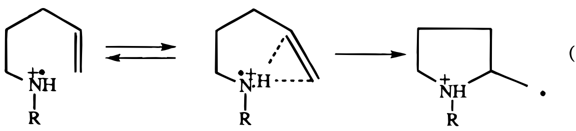
[31] The very strong electrophilic nature of the aminium radicals was demonstrated in the reactions of piperidinium radicals with substituted styrenes. The log of relative rate constants for these reactions plotted against the Hammett σ constants yields the value of $\rho = -1.34$.[23] For comparison $\rho = -1.5$ and -0.53, respectively, for the same reactions for azidyl[32] and n-$C_8F_{17}^\bullet$ radicals.[33]

[32] Workentin, M. S.; Wagner, B. D.; Lusztyk, J.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 119−126.

[33] Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Dolbier, W. R., Jr.; Pan, H.-Q.; Muir, M. *J. Am. Chem. Soc.* **1994**, *116*, 99−104.

[34] Maxwell, J. B.; Schiesser, C. H.; Smart, B. A.; Tsanaktsidis, J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2385−2387; *J. Chem. Soc., Perkin Trans. 2* **1995**, 1245.

saturated solutions of the same nitrosamines, transient absorptions which were very similar to those observed for the dialkylaminium radical cations (Figure 1a,b) were formed. The structures and lifetimes of these alkylalkenylaminium radicals are listed in Table 3. Surprisingly, the decays of these alkylalkenylaminium radicals, unlike those of their dialkyl counterparts (*vide supra*), were accelerated in the presence of oxygen. The only plausible explanation that we are able to offer for this experimental observation is based on the recent *ab initio* calculation of the 1,5-cyclization of *N*-pent-4-enylaminium radical cation[34] for which the ground state structure was suggested to have the nitrogen proton coordinated to the tethered double bond. One can envisage that such coordination would substantially alter the spin distribution within the radical and as a result alter its reactivity toward oxygen.



(3)

Comparison of the lifetimes of the alkylalkenylaminium radical cations (Table 3) with those of the dialkylaminium radical cations (Table 1) shows that the former species decay substantially more rapidly. On the basis of earlier product studies,[4f,g,5] this acceleration of the decay rate can confidently be attributed to the 1,5-cyclization reaction. The measured rate constants always correspond to all possible reactions of the aminium radicals. Thus for alkylalkenylaminium radical cations,

$$k_{\mathrm{obs}} = k_{1,5} + \sum k_x$$

where $\sum k_x$ represents all the modes of decay other than cyclization, including radical−radical self-reactions, reactions with NO generated upon nitrosamine photolysis, and, where possible, hydrogen atom abstractions. If we assume that all contributions to the decay of dialkyl- and alkylalkenylaminium radicals other than the cyclization reaction are similar under identical experimental conditions, we can use the decay data for the former and subtract them as a background in order to estimate the rate constants for cyclization of the latter. We assume (Table 1 and ref 25) that decay of an dialkylaminium radical can, on average, be represented by $\sum k_x = 5 \times 10^5$ s^{-1} under our experimental conditions. This assumption yields rate constants for the cyclization reaction of **5c** and **6c** of 8 × 10^5 and 9 × 10^5 s^{-1}, respectively. The rate constant for **6c** can be compared with a rate constant of 1 × 10^4 s^{-1} at 50 °C[35] determined for cyclization of the corresponding neutral aminyl radical, **6b**. The two rate constants serve to demonstrate the large increase in the intramolecular reactivity of aminium radicals compared with their aminyl counterparts.

The 266 nm LFP of *N*-methyl(5-phenylpent-4-enyl)nitrosamine, **9a**, in acetonitrile solution generates transient species (Figure 8a) that can be readily assigned to the substituted benzyl radical product of the 1,5-cyclization of the *neutral* aminyl radical **9b** (eq 4). The kinetics of benzyl radical growth can be represented by the first-order rate constant, $k_{\mathrm{growth}} = 3.8 \times 10^5$ s^{-1} which, of course, corresponds to the upper limit for the rate constant for cyclization of this aminyl radical. This rate constant can be compared with a rate constant of 4 × 10^5 s^{-1} estimated recently by Newcomb et al.[35] for the cyclization of the diphenyl-substituted analog of **9b**.

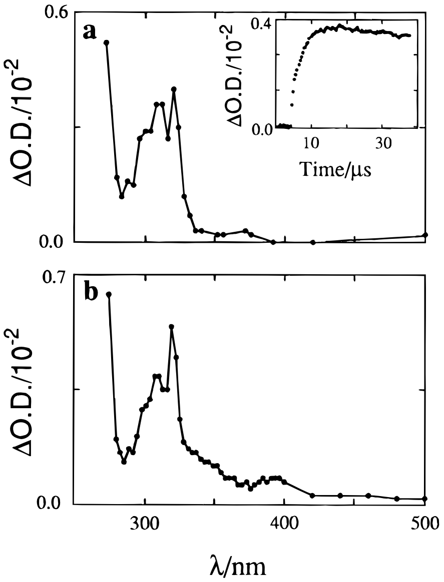
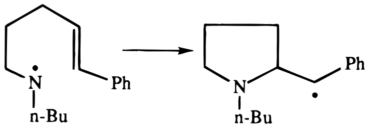
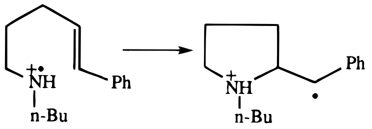


Figure 8. Absorption spectra observed upon 266 nm LFP of acetonitrile solution of **9a** (a) in the absence and (b) in the presence of 0.05 M of malonic acid. Inset shows the growth of the transient absorption monitored at 320 nm.



9b

(4)



9c

(5)

When the experiment was repeated in the presence of 0.05 M of malonic acid, a very similar transient spectrum was obtained (Figure 8b) and was readily assigned to the distonic radical cation formed upon cyclization of **9c** (eq 5). The growth of this species, however, was much faster; it occurred within the duration of our laser pulse, that is in less than 10 ns (corresponding to $k_c > 1 \times 10^8$ s^{-1}), once again indicating the dramatic acceleration in the rates of cyclization of aminium radicals relative to their neutral counterparts.

Experimental Section

N-Nitrosodiethylamine (Sigma), *N*-nitrosophenylmethylamine (Sigma), *N*-nitroso-*N*-methylaniline, (Sigma), *N*-nitrosodiphenylamine (Sigma), malonic acid (Aldrich), trifluoroacetic acid (Aldrich), and methanesulfonic acid (Aldrich) were used as received. *N*-Nitrosopiperidine (Sigma) was distilled under reduced pressure (T_b = 110 °C at 42 Torr). Olefins used as quenchers were available from Aldrich (>99%) and were purified by passing them through activated alumina immediately prior to use. Solvents were spectroscopic grade and were used without further purification. *N*-Nitrosoamines **5**−**9** were prepared with the use of sodium nitrite in standard reaction[36] from the corresponding

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(35) Newcomb, M.; Horner, J. H.; Shahin, H. *Tetrahedron Lett.* **1993**, *35*, 5523−5526.

(36) White, E. H. *J. Am. Chem. Soc.* **1955**, *77*, 6008−6010.

alkenylamines that were obtained following previously described precedures.[37−39]

Nanosecond laser flash photolysis experiments employed the pulses from a frequency-quadrupled Lumonics HY-750 Nd:YAG laser (266 nm; 8 ns pulse width; *ca*. 45 mJ/pulse) or from a Lumonics EX-530 excimer laser (308 nm; 8 ns pulse width; *ca*. 45 mJ/pulse) and a computer-controlled detection system previously described.[40] Solutions used in the LFP experiments were prepared to give an optical density at the excitation wavelength of *ca*. 0.3; this corresponded to precursor concentrations in the range of $10^{-4}-10^{-5}$ M (with the exception of the 308 nm LFP experiments in which 1,1-diphenylethylene was employed that required a much higher concentration of a nitrosamine to attain an OD of 0.3). The range of concentrations of olefins used in quenching studies varied depending on the quenching rate and was adjusted in a way so as not to absorb significantly at the laser line. The samples were contained in rectangular 7 × 7 mm^2 Suprasil quartz cells. Transient absorption spectra were measured employing a flow system which ensured that a fresh volume of sample was irradiated by each laser pulse.

Acknowledgment. The authors wish to thank Drs. Linda Johnston and Keith Ingold for stimulating discussions and Professor Martin Newcomb for sharing his data prior to submission.

JA950133Y

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(37) Perry, R. A.; Chen, S.; Menon, B. C.; Hanaya, K.; Chow, Y. L. *Can. J. Chem*. **1976**, *54*, 2385−2401.

(38) Krapcho, A. P.; Jahngen, E. G. E.; Lovey, A. J. *Tetrahedron Lett*. **1974**, 1091−1094.

(39) Tokuda, M.; Miyamoto, T.; Fujita, H.; Suginome, H. *Tetrahedron Lett*. **1991**, *47*, 747−756.

(40) Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem*. **1991**, *95*, 4430−4435.