Kinetic stabilizing effect of the 4-*N*methylacetamido substituent on the phenylnitrenium ion

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Abstract: Photolysis of 4-(*N*-methylacetamido)phenyl azide in aqueous solution results in quantitative formation of the 4-(*N*-methylacetamido)phenylnitrenium ion, this cation arising from solvent protonation of an initially formed singlet arylnitrene. The cation is observed by flash photolysis, and is identified through characteristic quenching by azide ion and by 2'-deoxyguanosine, both excellent nucleophiles for arylnitrenium ions in water. The nitrenium ion is protonated in acidic solutions to form the 4-(*N*-methylacetamido)aniline dication, whose pK_a is determined to be 1.5 based on the rate–pH profile. This means that the nitrenium ion is relatively basic, which suggests that there is significant positive charge on the *N*-methylacetamido group. Further evidence for this is seen in the remarkably long lifetime (5 ms) of the nitrenium ion in water. In fact, the 4-(*N*-methylacetamido)phenylnitrenium ion is 5000-fold longer-lived than the 4-methoxy-substituted analog. A 4-methoxy substituent on a phenyl ring is more electron donating according to σ^+ values (–0.78 for MeO vs. –0.60 for NMeAc). The dramatic reversal in the arylnitrenium ions is another example of the failure of these to follow the carbocation scale.

Key words: nitrenium ion, flash photolysis, amide substituent.

Résumé : La photolyse de l'azoture de 4-(*N*-méthylacétamido)phényle, en solution aqueuse, conduit à la formation quantitative de l'ion 4-(*N*-méthylacétamido)phénylnitrénium qui découle de la protonation par le solvant de l'arylnitrène singulet qui se forme originalement. On observe ce cation par photolyse éclair et on l'a identifié par un piégeage caractéristique à l'aide de l'ion azoture ou de la 2'-désoxyguanosine qui sont deux excellents nucléophiles pour les ions arylnitrénium dans l'eau. L'ion nitrénium se protone en solutions acides pour former le dication 4-(*N*-méthylacétamido)aniline qui, sur la base d'un profil vitesse–pH, aurait un pK_a de 1,5. Ce résultat indique que l'ion nitrénium est relativement basique et ceci suggère que le groupe *N*-méthylacétamido porte une charge positive importante. Cette suggestion est confirmée par le temps de vie relativement long (5 ms) de l'ion nitrénium dans l'eau. En fait, le temps de vie de l'ion 4-(*N*-méthylacétamido)phénylnitrénium est 5000 fois plus long que celui de son analogue portant un substituant 4-méthoxy. Un substituant 4-méthoxy sur un noyau phényle est plus électrorépulsif selon les valeurs de σ^+ (-0,78 pour MeO vs. -0,60 pour NMeAc). Cette inversion dramatique dans les ions arylnitrénium est un autre exemple du fait que ces entités ne suivent pas l'échelle des carbocations.

Mots clés : ion nitrénium, photolyse éclair, substituant amide.

[Traduit par la Rédaction]

The carcinogenicity observed with many aromatic amines is now recognized to be the result of metabolic activation (1-3). This bioactivation involves oxidation to a hydroxylamine derivative 2 followed by *O*-esterification, with either an acetyl or a sulfate transferase. Heterolysis of the N—O bond of the acetate or sulfate ester 3 yields a nitrenium ion 4, which reacts with DNA, principally at the C-8 position of guanine. Adducts such as the C-8 adduct 5 have been characterized in both biological and model systems (Scheme 1) (4–6).

Arylnitrenium ions have not been spectroscopically characterized in super acids (7–9), although there have been reports of their observation in electrochemical experiments (10–12). Our group (13–23), as well as others (24–27), have recently reported their observation using laser flash photolysis (LFP) with aryl azides serving as the photochemical precursors. Nitrenium ions have also been observed with LFP by the Falvey group (28–31) using other photochemical methods. As shown in Scheme 1, the nitrenium ion from the aryl azide arises through protonation of a singlet nitrene 7. The latter is the initial product of photolysis, being formed by loss of nitrogen from the azide. Singlet nitrenes are highly reactive species (32), but they are also remarkably basic (14). The singlet 4-biphenylylnitrene 7 (R = Ph), for example, is protonated by a solvent water molecule on the ps time scale in 20% acetonitrile:80% water (14).

Included amongst the intermediates that we have studied were a series of 4-alkoxyphenylnitrenium ions (15, 19). The

Received July 12, 2001. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on December 10, 2001.

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Scheme 1.



4-ethoxyphenylnitrenium ion would be derived from the carcinogen phenacetin, an analgesic long removed from the market. These cations were obtained essentially quantitatively upon irradiation of the appropriate azide in aqueous solutions; they had lifetimes in water of the order of 1 ms.

In this paper, we report a study of the *N*-(methylacetamido) phenylnitrenium ion, generated from the appropriate azide. This represents the first spectroscopic detection of an arylnitrenium ion bearing a 4-acetamido substituent. A para amido substituent, on the σ^+ scale, is substantially electron donating ($\sigma^+ = -0.60$) but it is not as good as *p*-methoxy ($\sigma^+ = -0.78$). One of the objectives of our work was to see if the σ^+ order was also observed when these substituents were present on nitrenium ions.

Experimental section

4-Acetamidophenyl azide $(6, R = NHCOCH_3)$

4'-Aminoacetanilide (0.1 mol) was dissolved in 95% ethanol (100 mL) and, with cooling in an ice bath, 5.0 mL of concentrated sulfuric acid was added. After 10 min, amyl nitrite (6.0 mL) was added in small portions. The reaction temperature was raised to 35-40°C for 20 min, and after cooling, the aryldiazonium salt was precipitated by the addition of ether (200 mL). The resultant precipitate was washed repeatedly with ether until the ethereal washings gave no coloration. The semiwet precipitate with ether was treated at 0°C with a solution of sodium azide (5.0 g) and sodium acetate (10 g) in 50 mL of water. After stirring for 1 h, the product was extracted into ether, which was washed with dilute sulfuric acid, water, 10% sodium carbonate, and water. The ethereal extract was dried over magnesium sulfate and the solvent was evaporated under reduced pressure. 4-Acetamidophenyl azide was obtained as a solid with mp 114-118°C which was judged sufficiently pure to proceed to the next reaction stage. ¹H NMR (200 MHz, DMSO- d_6) & 10.02 (s, 1H, disappeared in D_2O), 7.63 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 2.04 (s, 3H).

4-(*N*-Methylacetamido)phenyl azide (6, $R = N(CH_3)COCH_3$)

The 4-acetamidophenyl azide (2.5 mmol) and methyl iodide (3.0 mmol) were dissolved in anhydrous dimethyl sulfoxide (50 mL) and sodium hydride hydride (95%, 3.0 mmol) was added under argon. After stirring for 1 h at room temperature, the reaction mixture was diluted with ether (150 mL) and the organic layer was washed with water, dried over magnesium sulfate, and the solvent evaporated under reduced pressure to give an oily residue which solidified on standing. The crude product was purified by column chromatography on silica gel eluting with 50:50 ethyl acetate:hexanes. 4-(N-Methylacetamido)phenyl azide decomposed on heating above 100°C. HRMS m/z 190.0859; C₉H₁₀N₄O requires 190.0855. IR (cm⁻¹): 2219. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$ & 7.62 (d, J = 8.5 Hz, 2H), 7.10 (d, J =8.5 Hz, 2H), 3.26 (s, 3H), 1.94 (s, 3H). HPLC (see below) showed only a single peak.

Laser flash photolysis experiments involved ca. 20 ns pulses at 248 nm (60–120 mJ per pulse) from a Lumonics excimer laser. A pulsed Xenon lamp providing monitoring light. The sample was placed in a $4 \times 1 \times 1$ cm cuvette, irradiated with the laser on the 4×1 face, and monitored perpendicular so that the path length was 4 cm. The cuvette was replaced with a fresh solution after each irradiation. After passing through a monochromator, the signal from the photomultiplier tube was digitized and sent to a computer for analysis.

Conventional flash photolysis experiments were performed using an apparatus previously described (33) with the sample being irradiated with a broad band flash lamp of ca. 100 µs duration.

Product analyses were performed with a Waters HPLC system using a C^{18} column with 2 mL per minute flow rate and the UV-vis detector set at 260 nm. Elution was carried out with isocratic 60:40 acetonitrile:water. The 4-(Nmethylacetamido)phenyl azide was dissolved in water and dilute aqueous buffers to give solutions of concentration 5 \times 10⁻⁴ M. Injection of these solutions before irradiation gave only one peak in the chromatogram. As discussed in the Results section, irradiation of this aqueous solution at 254 nm in a Rayonet reactor resulted in clean conversion to a peak for an unstable species, which thermally converted over time to a third peak with a retention time identical to that of pbenzoquinone. That this peak did correspond to benzoquinone was verified from a scaled-up reaction where the product was isolated and its ¹H NMR spectrum recorded. The conversions of the azide to the benzoquinone were quantitatively analyzed by determining the response factors for the two, and using these to correct peak areas of the irradiated solutions.

Results and discussion

As shown in Fig. 1, 248 nm laser irradiation of an aqueous solution of 4-(*N*-methylacetamido)phenyl azide resulted in a strong absorbance with a λ_{max} at 310 nm. This absorbance was quite stable, showing only a small decay at the longest times available with our laser apparatus (1 ms). Addition of small concentrations of sodium azide accelerated the decay, resulting in excellent first-order plots proceeding to the baseline above 290 nm. A plot of the decay

Fig. 1. Transient spectrum obtained on 248 nm laser irradiation of a solution of 4-(*N*-methylacetamido)phenyl azide $(2 \times 10^{-4} \text{ M})$ in water. (Note that this is a difference spectrum, i.e., the optical density after the laser pulse – the optical density before the pulse).



rate constants k (obs) vs. the concentration of azide was linear, with a slope of 3.9×10^9 M⁻¹ s⁻¹.

Highly efficient quenching by azide ion is a characteristic of carbocations and aryInitrenium ions (34). More compelling evidence for the 4-(N-methylacetamido)phenylnitrenium ion comes in the analysis of the products of irradiation in aqueous solutions. Protonation of a singlet arylnitrene is obvious in the products (14), since the nucleophilic adducts derived from the further reactions of a nitrenium ion are very different in nature from the products associated with other reactions of singlet arylnitrenes, such as intersystem crossing to a triplet or ring expansion to a didehydroazepine. In the case of the nitrenium ion in question in this study, we anticipated that the reaction with water would follow the course outlined in Scheme 2. The solvent should react at the position para to the formal nitrenium center, the normal fate of simple arylnitrenium ions in water (14, 35-37). This would give an intermediate 8 which would eliminate Nmethylacetamide to give the monoimine of benzoquinone 9. This species is unstable in aqueous solutions, undergoing hydrolysis of the imine to give p-benzoquinone 10 (38).

Indeed irradiation of 4-(*N*-methylacetamido)phenyl azide at 254 nm in aqueous solutions for times up to 75% conversion resulted in the formation of benzoquinone as the only stable product that could be observed by HPLC. The yield of this product, based upon quantitative HPLC analysis, was 100% (95 \pm 5%). A second peak could be seen at early times. This peak disappeared and was replaced by the peak for the benzoquinone. The material responsible for this early peak can be identified as the quinoneimine **9**. This assignment is based upon an identical UV spectrum and, in particular, kinetic behavior for this material with that previously published for an authentic sample of the quinoneimine (38). This same imine was also observed in our earlier studies with the *p*-alkoxyphenyl azides (19). The nitrenium ions derived from these azides react in an analogous manner, with **Fig. 2.** Log rate vs. pH for the 4-(*N*-methylacetamido)phenylnitrenium ion. Points are experimental and have been extrapolated to zero buffer concentration where measurements were performed in buffers. The line through the experimental points has been drawn according to the equation $k_{OH}[OH^-] + (k_w^{+2}[H^+] + k_w^{+}K_a)$: $([H^+] + K_a)$ using the values for the parameters given in the text. It can be noted that the plateau in acid decreases slightly. This may be related to a specific salt effect, as was observed in a previous study (14).



water reacting at the para position to give an adduct that eliminates an alcohol to give the same imine 9.

It can be noted that there is an alternative mechanism for the formation of **9** from the *N*-methylacetamidophenyl nitrenium ion. This involves hydrolytic deacylation of the nitrenium ion, rather than water addition at the para position. This route can be ruled out on two grounds. The first is that this reaction results in an intermediate bis-imine, 1-imino–4-methyliminobenzoquinone. According to data for the analog without the methyl group (38) this should be long-lived, particularly at higher pH. The second is that the bis-imine is likely to hydrolyze both imino groups at comparable rates, so that there would be two different monoimine intermediates, **9** and the *N*-methyl analog of **9**. Thus, this route predicts that there is only one such intermediate.

While the decay of the nitrenium ion in water alone was too slow for the apparatus, it could be observed by irradiating an aqueous solution of 4-(*N*-methylacetamido)phenyl azide with a lamp flash photolysis apparatus. This showed an excellent first-order decay occurring on the ms time scale with a rate constant of 2×10^2 s⁻¹. The rate constant for quenching by azide ion is interesting in this regard, since the value, 3.9×10^9 M⁻¹ s⁻¹, is still quite close to the maximum value of 9 to 10×10^9 M⁻¹s⁻¹ found for more reactive nitrenium ions (16). This maximum is associated with the azide–nitrenium combination becoming diffusion controlled, i.e., the rate-limiting step is encounter (16, 34). Combinations of azide and short-lived benzylic-type carbocations are also diffusion-controlled (34, 39). What is interesting is that

Scheme 2.



the break to rate-limiting bond formation as the carbocation becomes less reactive occurs at a much earlier point then it does with a nitrenium ion. For example, a triphenylmethyl cation that reacted with water with a rate constant of $2 \times 10^2 \text{ s}^{-1}$ would react with azide ion with a rate constant around $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, well below the diffusion limit (39).

Figure 2 provides further kinetic information about the behavior of the nitrenium ion in the form of the dependence of its rate constant for decay as a function of pH. This figure was constructed through a combination of experiments with laser and lamp flash photolysis, the latter being used for the solutions with pH 2-10, and the former for the faster reactions in the acidic and basic solutions. It can be seen that there is a pH-independent region from pH 4–10. This represents the reaction of the cation with water. In more basic solutions, this breaks to a linear dependence on hydroxide ion, with the slope $k_{\text{OH}} = 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. This is clearly explained by reaction with hydroxide ion. The acceleration in acid is a feature of nitrenium ions that we have observed previously (14, 19). It is explained by the mechanism of Scheme 3, whereby under acidic conditions, reaction occurs via the dication 11, the conjugate acid of the nitrenium ion.

The levelling below pH 2 indicates that the protonation equilibrium actually shifts to the dication. The experimental data can be fit to eq. [1],

[1]
$$k_{\text{obs}} = \frac{F(k_{\text{w}}^{+2}[\text{H}^+] + k_{\text{w}}^+K_{\text{a}})}{[\text{H}^+] + K_{\text{a}}}$$

where k_w^{+2} and k_w^+ are the rate constants for the reaction of water with the dication and monocation, respectively, and K_a is the acidity constant of the dication. Parameters obtained from this fit are provided in Table 1, where they are also compared with values obtained from other systems.

The basicity of the NH group of an aryInitrenium ion is one indicator that the structure $Ar-N^+H$ is only a very minor resonance contributor. There must, in fact, be little positive charge at this nitrogen, i.e., that the cation is better written as a cyclohexadienyl cation with an imine substituent, as in the resonance structure **4'** in Scheme 3. Recent time-resolved IR (30, 31) and resonance Raman (27) spectra have provided excellent evidence for this. The data in Table 1 show that the Scheme 3.



nitrenium ion of this study is one of the more basic examples, although it is not nearly as basic as the nitrenium ion derived from benzidine (23). This suggests that the N-methylacetamido group in the cation bears a considerable fraction of the positive charge. This is clearly also evident in the kinetic stability of this cation.

The 4-(*N*-methylacetamido)phenylnitrenium ion was also generated from the azide in the presence of 2'-deoxyguanosine. The nucleoside did quench the cation, with a rate constant k_{dG} of $9.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Efficient quenching by guanine derivatives is also a characteristic of aryl-nitrenium ions. We have previously determined k_{dG} values for a series of biphenylylnitrenium ions (17). The reactive derivatives in this series combined at the diffusion limit with a constant k_{dG} of $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The less reactive derivatives react more slowly, and showed a constant k_{dG} : k_w selectivity of 2 to $3 \times 10^4 \text{ M}^{-1}$. The value of k_{dG} : k_w for the cation of this study is $4.5 \times 10^4 \text{ M}^{-1}$. Thus, this cation is behaving in a similar manner as the biphenylyl derivatives.

One of the remarkable features of the 4-(N-methylacetamido)phenylnitrenium ion is its long lifetime in water. This is dramatically illustrated in Fig. 3 in terms of a Hammett plot of the rate constants for water addition vs. σ^+ . As originally noted by Novak et al. (35) this correlation is scattered. What is particularly notable is that the lifetime of the 4-NMeAc derivative is 5000-fold longer than that of the 4-methoxy-substituted cation, despite the fact that 4-MeO is more electron donating according to its σ^+ value (-0.78 for MeO vs. -0.60 for NMeAc (40)). As noted above, there is now excellent evidence that aryInitrenium ions have substantial cyclohexadienyl cation character. With heteroatom substituents such as oxygen and nitrogen, the positive charge will be further significantly delocalized onto the heteroatom. Thus, the 4-methoxyphenylnitrenium ion is probably best described as an oxocarbocation (C=O⁺Me), and the cation of this study as a acyliminium ion (C=N⁺MeAc). Since σ^+ calibrates the effect of a substituent on the transition state for a developing positive charge on a benzylic carbon, it is therefore not surprising that the aryInitrenium correlation is poor. There is in fact some evidence that intrinsic barriers for addition to oxocarbocations are low, i.e., that the cations are inherently reactive (41). No such data exists for acetylated iminium ions. The present study suggests that this class of cation is inherently less reactive.

In conclusion, this paper further describes the remarkable basicity of singlet nitrenes, especially those bearing an electron-donating group in the 4- position. The results provide further confirmation that aryInitrenium ions are better described as imino cyclohexadienyl cations. The 4-*N*methylacetamidophenylnitrenium ion is in fact remarkably long lived in aqueous solution especially when compared to

Constant	Α	В	С	D	Е
$pK_a (ArNH_2)^{+2}$	5.0	1.5	0.6	0.1	<-0.3
$k_{\rm w}^{+2} ({\rm ArNH_2})^{+2} ({\rm s}^{-1})$	$8 imes10^{-5}$	1.4×10^4	1.9×10^{6}	6.0×10^{7}	$>4 \times 10^8$
$k_{\rm w}^+$ (ArNH) ⁺ (s ⁻¹)	1×10^{-2}	2.2×10^{2}	1.3×10^{4}	1.1×10^{6}	1.1×10^{6}

Table 1. Acidity constants for aniline dications, and rate constants for reaction of the dications and their nitrenium conjugate bases with water.

Note: A: Ar = 4 'aminobiphenylyl (23); B: Ar = 4-(*N*-methylacetamido)phenyl (this work); C: Ar = 2-fluorenyl (14); D: Ar = 4-biphenylyl (14); E: Ar = 4-methoxyphenyl (19).

Fig. 3. Hammett plot for the hydration of arylnitrenium ions 4- $XC_6H_4NH^+$. Data for H (37), 4-Me (36), and 4-Cl (36) are based on a clock method. Other rate constants are directly measured: 4-Ph (14), 4-MeO (19), 4-PhO (19), 4-NH₂ (monoprotonated benzoquinone bis-imine) (38).



other aryl nitrenium ion bearing electron-donating groups in the para position such as alkoxy. Their long lifetimes in water make them viable intermediates in mechanistic models that explain biological effects associated with monoamides of p-benzenediamines.

Acknowledgement

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

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