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Characterization and Reactivity of the [*N*,*N*-Dimethyl(thioformamidyl)]-9-fluorenyl Cation[1]

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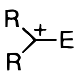
The 9-[*N*,*N*-dimethyl(thioformamidyl)]-9-fluorenyl cation was generated under stable ion conditions and characterized by UV/visible and NMR spectroscopy and methanol trapping reactions. The same cation was generated by laser excitation of the appropriate chloride precursor in 2,2,2-trifluoroethanol, and rate constants for nucleophilic quenching by alcohols and several anions were measured. The quenching data for this and other 9-fluorenyl cations demonstrate that the reactivity decreases for 9-substituents in the order H > carbomethoxy > *N*,*N*-dimethyl(thioformamidyl), demonstrating that the thioamidyl group imparts substantial kinetic stabilization to an adjacent cationic center. Both steric and electronic factors are suggested to be important in determining this reactivity order.

Introduction

It is now well established that carbocations that have a formally electron-withdrawing group (e.g., **1** where E = carboxy, ester, keto, trifluoromethyl) directly attached to the cationic center can be readily generated under solvolytic and stable ion conditions.[4−9] This is despite the long-held belief that such intermediates were intrinsically unstable and would require very forcing conditions for their formation. In fact, there is now a substantial volume of data that demonstrates that many of these "electron-deficient" carbocations are more stable than their corresponding hydrogen-substituted analogues. Most of these data come from comparison of relative rates of solvolysis and from indirect measurements of rates of nucleophilic addition using azide clock techniques.[9−12] In addition, we and others have recently used time-resolved methods to provide the first absolute rate constants for addition of nucleophiles to α-carbalkoxy-substituted cations;[13,14] the results confirm previous conclusions that an α-ester group dramatically lowers the reactivity of arylmethyl cations.[15]



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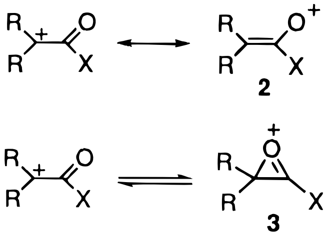
A number of factors have been used to explain the stabilizing effects of α-carbonyl groups.[8,9,16] The two most common are π-resonance stabilization by the carbonyl group (**2**) and neighboring group participation by the carbonyl group to give a cyclic oxiranyl ion (**3**). Both steric effects and increasing resonance stabilization by aryl groups as a result of increased electron demand have also been postulated. Several theoretical studies have addressed the question of the relative stability of structures **2** and **3** and their importance in stabilizing α-carbonyl cations.[17−21] The most recent of these concludes that the cyclic oxiranyl cation is lower in energy than the open form for a variety of acylcarbenium ions with the general structure H_2C^+COX.[20] By contrast, the open structure is preferred for $(CH_3)_2C^+COX$. However, there is currently no compelling experimental evidence for the involvement of cyclic oxiranyl cations.



Several α-(thiocarbonyl) cations have also been generated as intermediates in solvolysis reactions and have been detected directly at low temperature under stable ion conditons.[22−25] These cations are of particular interest since replacing oxygen by sulfur is expected to increase the charge delocalization associated with struc-

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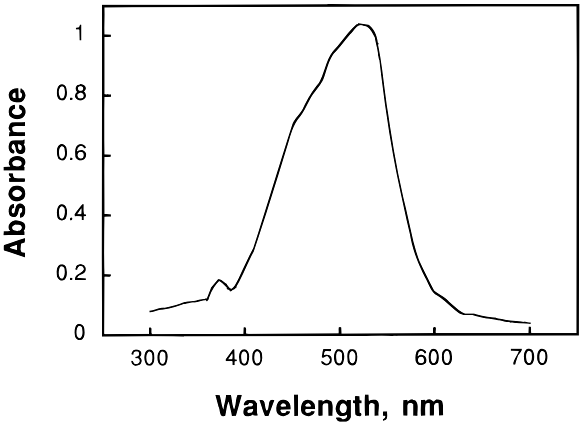
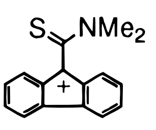


Figure 1. UV−vis absorption spectrum of cation **4** at −78 °C in CH_2Cl_2. The cation was generated by $AgBF_4$ dehalogenation of the chloride precursor.

tures analogous to **2** and **3** and to lead to enhanced stabilization. For example, *ab initio* molecular orbital calculations on the thioformyl methyl cation have shown that the cyclized species is significantly more stable than the open form.[20] However, calculations for $RR'CCSNH_2^+$ demonstrate that both the stabilizing effect of the thioformamidyl substituent and the preference for cyclic vs open structures depend on the nature of R.[21] In fact, an α-(thioformamidyl) substituent is found to be slightly destabilizing in the benzyl cation. The calculations are inconclusive as to the relative stability of the cyclic and open structures for diaryl systems.[21] Enhanced rates of solvolysis relative to α-H or α-CH_3 have been observed for several substrates that yield α-[*N*,*N*-dimethyl(thioamidyl)] cations.[24] Product studies suggest that π-delocalization is responsible for the stabilizing effects for the α-(thioamidyl)-1-phenethyl cation while bridged structures are important in α-(thioamidyl)benzyl cations.[24] These studies have also led to the conclusion that the thermodynamic cation-stabilizing ability of the α-(thioamidyl) group exceeds that of methyl and approaches that of the phenyl group.

Our continuing interest in the study of electron-deficient carbocations under stable ion and laser flash photolysis conditions has prompted us to examine α-(thioamidyl)-substituted cations. We report herein the direct observation of the 9-[*N*,*N*-dimethyl(thioformamidyl)]-9-fluorenyl cation (**4**) by laser flash photolysis (LFP) in neutral solution and by UV−vis and NMR spectroscopy under stable ion conditions. We also report the first absolute rate constants for the reactivity of this cation under solvolytic conditions.



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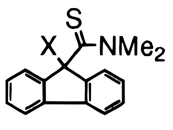
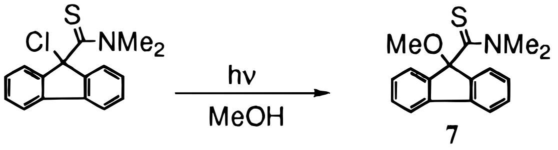


5 X = Cl
6 X = OH

Results and Discussion

The chloride precursor (**5**) to cation **4** was synthesized from the corresponding alcohol (**6**) by standard chlorination techniques, as outlined in the Experimental Section. Preparative irradiation (medium pressure Hg lamp through Pyrex) of chloride **5** in methanol (4 mM) resulted in the formation of a 60% yield of the methyl ether, reaction 1, as well as a second product that was not characterized but that may be a dimer. Dimeric products have been isolated from the preparative photolysis of methyl 9-bromofluorene-9-carboxylate.[13] Control experiments demonstrated that chloride **5** is stable under the conditions used for the preparative irradiations and the flash photolysis experiments described below.



(1)

Cation **4** was generated at low temperature under stable ion conditions for comparison of its UV−vis characteristics to those for the same species obtained by LFP. The cation was generated by mixing chloride **5** with $AgBF_4$ in dichloromethane at −95 °C and has the spectrum shown in Figure 1 with λ_{max} at 520 nm. The observed λ_{max} is in good agreement with that observed for the 9-fluorenyl cation and a number of its 9-substituted derivatives.[26−28] Quenching of the solution containing cation **4** with methanol at −70 °C resulted in the formation of methyl ether **7** as the only product.

The ^{13}C NMR spectrum of cation **4** was recorded using the alcohol precursor in chlorosulfonic acid/CD_2Cl_2 and shows two low-field signals at δ 187 and 175 ppm associated with the thiocarbonyl and cationic carbons. The multiciplicity of peaks in the aromatic region (six peaks between δ 120 and 145 ppm) suggests a structure with $C2_v$ symmetry. This is consistent with molecular orbital calculations at the 6-31G* level for the 9-(thioformamidyl)-9-fluorenyl cation, which predict that the CCS group is orthogonal to the plane of the fluorene ring, with a CCS bond angle of ∼114°.[21]

The transient absorption spectrum generated by 308 nm excitation of chloride **5** in 2,2,2-trifluoroethanol (TFE) has a strong visible absorption at 520 nm with weaker bands at 440 and 370 nm (Figure 2). Decay kinetics are identical at all wavelengths and give lifetimes of ∼5 μs. This transient is assigned to cation **4**, on the basis of the similarity to the spectrum for this species under stable ion conditions and its reactivity toward nucleophiles. A similar transient is observed in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP); in this case, the transient is much longer-lived (lifetime of ∼1 ms). However, no transients assignable to cations were observed in acetonitrile, presumably due to the short lifetime of the cation in this solvent.

In order to confirm that there were no complications due to either radicals or radical cations in our results for cation **4**, these intermediates were generated independently. Thus, 266 nm photolysis of chloride **5** in hexane gave a transient with λ_{max} at 510 nm, in good agreement with the reported spectrum for the 9-fluorenyl radical, which has λ_{max} at 500 nm.[29] Radical cation $\mathbf{5}^{\bullet+}$ was produced by electron transfer from triplet chloranil

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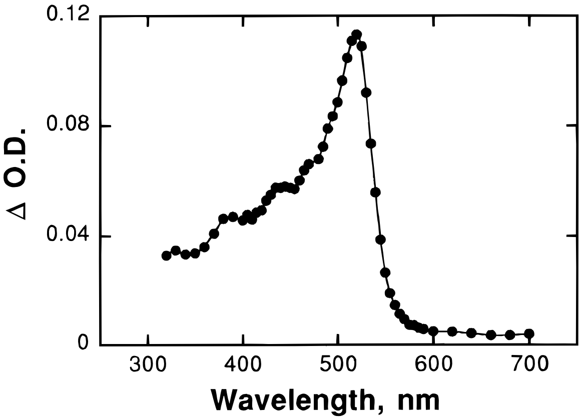


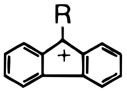
Figure 2. Transient absorption spectrum of cation **4** obtained by 308 nm excitation of chloride **5** in aerated 2,2,2-trifluoroethanol.

in acetonitrile using 355 nm excitation. The spectrum of $\mathbf{5}^{\bullet+}$ has a maximum at approximately 645 nm, in good agreement with the known spectra for radical cations of several substituted fluorenes.[13,27,30]

The rate constants for reaction of cation **4** with several nucleophiles were determined by measuring the observed rate constant for decay (k_{obs}) of the cation at 520 nm as a function of the concentration of added nucleophile. The data were fit according to eq 2, where k_0 is the lifetime of the cation in the absence of quencher (Q).

$$k_{\mathrm{obs}} = k_0 + k_{\mathrm{q}}[\mathrm{Q}] \qquad (2)$$

The data are listed in Table 1, along with literature data for the parent and α-carbomethoxy-9-fluorenyl cations (**8**, **9**). Representative quenching plots for reaction of **4** with methanol and ethanol are shown in Figure 3. The rate constants for cation **4** have been measured in TFE; by contrast, quenching studies for cations **8** and **9** can only be carried out in HFIP due to their short lifetimes in TFE. Since the observed rate constants for addition of most of the nucleophiles to **4** in TFE are already quite slow and require high concentrations to obtain accurate kinetic data, only the rate constant for methanol has been measured in both TFE and HFIP.



8 R = H
9 R = CO_2CH_3
10 R = CH_3

Table 1. Rate Constants (M^{-1} s^{-1}) for Quenching of Substituted 9-Fluorenyl Cations with Nucleophiles in TFE or HFIP at 20 °C

nucleophile	**4** (TFE)	**8** (HFIP)	**9** (HFIP)
water	$(4.14 \pm 0.06) \times 10^4$	1.5×10^6 [a,b]	2.4×10^5 [a,d]
TFE	2.4×10^5 [c,e]	$\sim 4.6 \times 10^6$ [a,c]	$\sim 2 \times 10^5$ [a,c,d]
2-propanol	$(4.43 \pm 0.07) \times 10^5$	3.9×10^6 [a]	2.3×10^6 [a]
ethanol	$(8.15 \pm 0.09) \times 10^5$	1.3×10^7 [a]	4.6×10^6 [a]
methanol	$(1.53 \pm 0.04) \times 10^6$ $(3.4) \times 10^4$ (HFIP)[d]	1.8×10^7 [a]	6.7×10^6 [a]
bromide	$(4.9 \pm 0.2) \times 10^7$ [d]	9.6×10^9 [a]	3.9×10^9 [a]
azide	$(1.5 \pm 0.1) \times 10^9$	*f*	*f*

[a] Reference 13. [b] Reference 27. [c] Based on one point. [d] Plot curves at high concentrations. [e] First-order decay rate constant, s^{-1}. [f] Azide quenching data were not measured in HFIP due to the potential protonation of N_3^-.

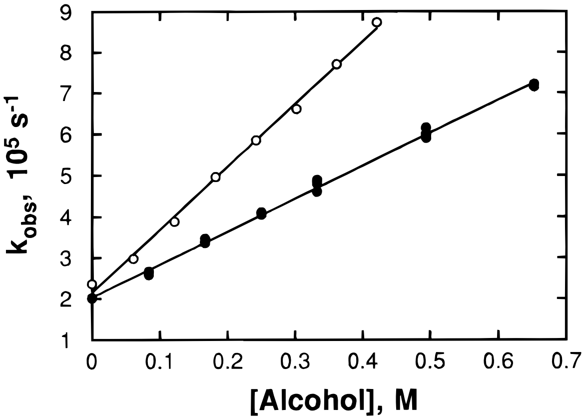


Figure 3. Plots of the observed rate constants for decay of cation **4** in TFE as a function of the concentration of added methanol (○) and ethanol (●).

The data in Table 1 demonstrate that the rate constants for nucleophilic addition are substantially lower for the 9-(thioformamidyl)-9-fluorenyl cation than for the parent or the α-carbomethoxy-substituted analogues. For example, the relative rate constants for methanol addition are 1:200:530 for thioformamidyl, carbomethoxy, and hydrogen. Bromide reacts ~100 times more slowly with **4** than with either the parent or the 9-carbomethoxy-9-fluorenyl cation. Note that this difference is expected to be even larger if cation **4** had been measured in HFIP rather than TFE, since rate constants are typically significantly faster in TFE.[13,27,31] The data in Table 1 confirm that the thioamidyl group imparts a substantial kinetic stabilization to the 9-fluorenyl cation. It is interesting to compare these results to those for methyl- and phenyl-substituted 9-fluorenyl cations. The measured rate constant for addition of bromide ion to the 9-methyl-9-fluorenyl cation (**10**) in HFIP of 4.5×10^9 M^{-1} s^{-1} is approximately 2 orders of magnitude faster than that for **4**. A comparison of the reported rate constant of 6.8×10^8 M^{-1} s^{-1} for addition of bromide to the 9-phenyl-9-fluorenyl cation in TFE[28] with our rate constant of 4.9×10^7 M^{-1} s^{-1} for bromide addition to **4** indicates that the α-(thioformamidyl)-substituted cation is also less reactive than the phenyl derivative. The increased kinetic stabilization of the thioamidyl group relative to either methyl or phenyl is of interest in light of the previous suggestion that the thermodynamic stabilization of the thioamidyl group is larger than that of methyl and comparable to that of phenyl.[24] It should, of course, be noted that the calculated structure for **4** indicates that thermodynamic stabilization will be unimportant for this particular cation.[21]

Conclusions

The α-[*N*,*N*-dimethyl(thioformamidyl)]-9-fluorenyl cation, **4**, has been observed under stable-ion conditions and by laser flash photolysis in neutral solutions and has λ_{max} at 520 nm. The close agreement between the spectra for **4** and a variety of other 9-fluorenyl cations suggests that **4** exists in an open rather than a cyclic structure. This cation is less reactive toward nucleophilic addition than the corresponding methyl carboxylate-substituted cation,

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which in turn is less reactive than the parent 9-fluorenyl cation. Steric factors may be involved in determining the relative reactivities as the reactivity towards nucleophiles decreases with increasing steric bulk of the α-substituent. However, electronic factors may contribute in some cases since charge delocalization by either bridging or resonance effects for these substituents would be expected to increase in the order H >carbomethoxy > dimethyl(thioformamidyl), resulting in less available charge at the cationic site. The present results demonstrate that the thioamidyl group imparts significant kinetic stabilization to an adjacent cationic center.

Experimental Section

Materials and General Techniques. All the solvents used were reagent grade and were dried before use. UV−vis spectra were obtained on a HP-8451A diode array spectrophotometer. Low-temperature UV−vis spectra were measured on an Optical Waveguide spectrum analyzer, Model 100. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 or ARX-400 spectrometer using samples dissolved in $CDCl_3$ or CD_2Cl_2. Chemical shifts are measured in parts per million (δ) relative to TMS as internal standard. Mass spectra were obtained on a VG Micromass 16F or Kratos Profile spectrometer at 28 eV for EI ionization. The continuous photolyses were performed using a Hanovia 450 W medium-pressure mercury arc lamp in a water-cooled quartz immersion well. Pyrex test tubes containing the samples were strapped around this well and the assembly immersed in an ice−water bath. Microanalyses were carried out by Guelph Chemical Laboratories Limited.

Preparation of *N,N*-Dimethyl-9-hydroxy-9-fluorenecarbothioamide (6). A solution of fluorenone (0.9 g, 5 mmol) and *N,N*-dimethylthioformamide (0.445 g, 5 mmol) in dry THF (5 mL) was added to a solution of LDA (prepared from 5 mmol of *n*-butyllithium and 5 mmol of diisopropylamine in 50 mL of dry THF) at −80 °C. The reaction mixture was allowed to warm to room temperature over 2 h. The reaction was quenched by the addition of saturated ammonium chloride solution (50 mL). The organic layer was separated and dried over $MgSO_4$. After evaporation of the solvent the residual material was purified by flash chromatography (silica gel; CH_2Cl_2 eluent) and recrystallization to give 1.06 g (79% yield) of a crystalline product: mp 158.5−159 °C; ^{1}H NMR δ 7.66−7.63 (d, 2H), 7.34−7.24 (m, 6H), 6.74 (s, 1H, OH), 3.49 (s, 3H), 2.40 (s, 3H); IR (KBr) ν 3450 (OH), 1520, 1250, 1210 cm^{-1}; MS *m/e* 269 (62), 181 (100), 88 (100); HRMS calcd for $C_{16}H_{15}NOS$ 269.0874, found 269.0900. Anal. Calcd for $C_{16}H_{15}NOS$: C, 71.37; H, 5.58. Found: C, 71.35; H, 5.61.

Preparation of *N,N*-Dimethyl-9-chloro-9-fluorenecarbothioamide (7). Alcohol **9** (100 mg, 0.37 mmol) was dissolved in 35 mL of dry CCl_4. To this solution was added 150 mg of $CaCO_3$, and the solution was kept under nitrogen. After 5 min thionyl chloride (0.05 mL) was added and the reaction mixture was stirred for 10 min. The ionic salts were filtered off, and the filtrate was evaporated to yield the chloride. Excess trace thionyl chloride was removed by pumping under high vacuum: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72−7.69 (d, 2H), 7.58−7.33 (6H, m), 2.9 (br. s, 3H), 2.05 (br. s, 3H).

Preparation of Carbocation 4 under Stable Ion Conditions. (a) UV−vis Spectroscopy Studies. A solution of cation **4** was prepared by dissolving 5 mg of the chloride precursor **5** in 5 mL of dry CH_2Cl_2 cooled to liquid nitrogen temperature. A cooled (−78 °C) solution consisting of 5 mg of $AgBF_4$ in 15 mL of CH_2Cl_2 was added to the mixture. The solution was warmed to −78 °C and allowed to stand and mix until homogeneous. The UV−vis spectrum was recorded at −78 °C and gave λ_{max} 520 nm for carbocation **4**.

(b) ^{13}C NMR Spectroscopy Studies. A solution of 80 mg of alcohol **6** in 3 mL of SO_2 in a 10 mm NMR tube was cooled to liquid nitrogen temperature. Chlorosulfonic acid (1 mL) was added, and the mixture was warmed to −78 °C and shaken until homogeneous. A dark pink solution was obtained: ^{13}C NMR (SO_2, acetone-d_6 external reference) δ 187.0 (C=S or C$^+$), 175.6 (C$^+$ or C=S), 143.0, 141.0 (quaternary aromatic C), 134.9, 130.2, 125.2, 123.2 (aromatic C), 46.7, 44.5 (N-CH_3).

Product Studies from Quenching of Carbocation 4 in Methanol. Chloride **5** (15 mg) was dissolved in 20 mL of CH_2Cl_2 and cooled to −78 °C. Silver tetrafluoroborate (20 mg) in 5 mL of CH_2Cl_2 was added to this solution. A dark red solution and the immediate formation of precipitate were observed. The reaction mixture was poured into methanol (10 mL) and filtered. The filtrate was evaporated under reduced pressure to give a solid product, *N,N*-dimethyl-9-methoxy-9-fluorenecarbothioamide (**7**): yield 13.0 mg (84%); mp 177−179 °C; ^{1}H NMR δ 7.72−7.67 (d, 2H), 7.49−7.28 (d, 6H), 3.53 (br. s, 3H), 2.85 (s, 6H); IR (KBr) ν 1508, 1247 (C=S), 1150 (C-O) cm^{-1}; MS *m/e* 283 (32), 195 (100), 163 (29); HRMS calcd for $C_{17}H_{17}NOS$ 283.1031, found 283.1048.

Continuous Irradiation of Chloride 5. A solution of **5** (5 mg) in 50 mL of methanol was irradiated for 3.5 h. The reaction mixture was evaporated to dryness, and the residue was applied to a preparative TLC plate (silica gel) and eluted with CH_2Cl_2. Photoproduct **7** (60%) was identified by comparison with the sample prepared above.

Laser Flash Photolysis. The laser system has been described in detail elsewhere.[32] Either a Lumonics HY750 Nd:YAG laser (266 or 355 nm, 10-ns pulses, ≤50 mJ/pulse) or a Lumonics EX-510 excimer laser (XeCl, 308 nm, 6-ns pulses, ≤40 mJ/pulse) was used for sample excitation. Solutions were contained in 7 × 7 mm^2 Suprasil quartz cells for the quenching experiments and in 7 × 7 mm^2 flow cells connected to a sample reservoir with Teflon tubing for spectra. Unless otherwise noted, aerated samples were used for all the experiments.

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