Equipment. For the reaction, a multicompartmental trough (manufactured by Mayer-Feintechnic, Gottingen), essentially a modified Langmuir trough, was used.[4] This trough is made from PTFE and is circular, 24-cm outside diameter, 12-cm inside diameter, and 0.3-cm depth. The height of the partitioning walls is just below that of the inner and outer walls of the trough, allowing continuity of liquid surface but preventing any appreciable intermixing of the liquid between compartments. The PTFE trough was clamped securely onto an aluminum base through which water could be circulated from a thermostated bath. Two PTFE barriers are connected through separate shafts to an axle. The barriers could be either moved independently, to vary the enclosed surface area, or moved in concert from one part of the trough to another with a fixed area enclosed. The decoupled motion was used to bring a spread surface film to a given surface pressure; the film could then be transferred to the sulfuric acid subphase in adjacent compartments with a coupled motion of the barriers.

Near one barrier was a glass-slide Wilhelmy plate connected to the core of a linear variable differential transformer where the output signal could be calibrated in terms of the surface tension acting on the glass plate. Surface pressure could be measured to 0.1 mN m^{-1} via a digital display. Π–A isotherms were recorded on a Hewlett-Packard 7045B X–Y recorder using analog output signals corresponding to surface pressure and area from the trough assembly.

One of the compartments had a deep rectangular well (6 cm × 1.5 cm × 4.5 cm deep), originally intended for the deposition of Langmuir–Blodgett films. It was found convenient to quench our reaction mixtures by sweeping them into this reservoir containing water and 1 mL of hexane. The hexane layer was then removed by Pasteur pipet for analysis by high-performance liquid chromatography (HPLC).

HPLC analyses were performed with an LKB system, with a LKB 2151 variable-wavelength monitor and an LKB 2220 recording integrator.

Kinetics. In a typical run, the two barriers were positioned with three compartments (120 cm^2, digital display) between them, containing a measured amount of triply distilled water. The compression barrier was used to sweep and compress any surface impurity, which was then removed from the surface by suction. The compression barrier was then withdrawn, and a suitable quantity of the hexane solution of the alcohol (2.6×10^{-3} M) was added with a Hamilton microliter syringe. The solution was seen to spread, and after 1 min the compression barrier was moved to adjust the enclosed surface area to the desired area/molecule.

The film was then transferred over to a measured amount of the reaction subphase by coupled motion of the barriers. To minimize mixing of the water and the reaction subphase (aqueous sulfuric acid), the film was swept over an intermediate "buffer" compartment containing the acid subphase before being brought over the reaction compartments.

After reaction of the film for a given time, the reaction mixture was swept into the reservoir in the trough containing 1 mL of hexane and water by coupled motion of the barriers. The hexane solution was withdrawn using a Pasteur pipet and analyzed by HPLC.

The reaction mixture could be readily resolved by isocratic elution with 70% 2-propanol–30% water on a 25-cm LKB RP8 10-μm column. Both the alcohol **1** and the alkene **3** were detected in the UV at 210 nm, and the peak areas were measured electronically. Repeat injections of the same sample were reproducible within 2%.

Each point in Figure 2 represents a complete kinetic run, from spreading of the alcohol **1** to the analysis of product by HPLC. Thus the standard errors in the rate constants k given in Table I reflect the reproducibility of the measurement from run to run. In addition to the comparison of the value of k calculated for each run, reproducibility was also checked for the same reaction times in each of the three film types. Duplicates of measurements carried out for each of the three film types for two reaction times selected randomly showed that the error was better than ±5%. However, to ensure reproducible results it was imperative that the trough was meticulously cleaned between runs, first with concentrated sulfuric acid and then with copious quantities of water. Blank runs revealed no residual products from previous runs with this method.

To assess the efficiency of the trough operations, an absolute recovery experiment was performed by spreading an amount of the alcohol **1** on water and sweeping it into the reservoir containing 1 mL of hexane. HPLC analysis of the hexane solution showed that the alcohol recovered was 93% of the material spread originally. In addition to measuring the percentage of the spread alcohol that was recoverable, the mass balance was determined for reaction by comparing the peak areas, corrected for differing response of alcohol **1** and alkene **3** at various reaction times. In all cases (mol of unreacted alcohol **1**) + (mol of alkene product **3**) > 0.9(mol of starting material **1**).

The reactivity of the alkene product **3** under the reaction conditions employed in the study was determined by spreading a hexane solution of the alkene on 44% H_2SO_4. After 30 min the surface material was swept into the reservoir containing hexane. No trace of the alcohol **1** was found by HPLC analysis, indicating the absence of hydration under these conditions. This is an entirely expected result since the alkene does not form a monolayer.

By comparison with our previous work on the acid-catalyzed nerol cyclization, the current methodology represents a considerable enhancement. Owing to the relative instability of nerol and geraniol films (solubility and evaporation problems), the results obtained by GLC analysis of reaction products are only qualitative. Recoveries were not determined, but were assumed to be low and at best variable. However, the reaction times were maintained strictly constant and the relative reactivities of the film types were accurately determined.

Properties of Anions, Radicals, and Radical Cations Derived from 9-(Dialkylamino)fluorenes

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Abstract: Equilibrium acidities for seven 9-(dialkylamino)fluorenes together with their oxidation potentials and those of their conjugate bases have been measured in Me_2SO solution. These data are used to estimate (a) the homolytic bond dissociation energies (BDEs) of the 9-C–H bonds in these molecules, (b) the acidities of the corresponding radical cations, and (c) the relative stabilities of the radicals formed on deprotonation of their radical cations. Comparisons are made with similar estimates of the effects of 9-(1-imidazolyl), 9-(3-methyl-1-pyrazolyl), 2-Me_2N, and 2,7-$(Me_2N)_2$ groups. The 2-Me_2N and 2,7-$(Me_2N)_2$ groups decrease the acidity of the fluorene radical cation by 18 and 24 kcal/mol, respectively, but have little effect on the BDEs of the 9-C–H bonds. On the other hand, the 9-dialkylamino groups were found to lower the BDEs of the 9-C–H bonds by 5–12.8 kcal/mol relative to that of fluorene (79.5) and to decrease the acidity of the fluorene radical cation by an average of only 6.5 $pK_{HA^{\bullet +}}$ units. The latter decreases are the net result of making both $E_{ox}(HA)$ more negative (acid weakening) and $E_{ox}(A^-)$ more negative (acid strengthening). By contrast, the 9-imidazolyl group weakens the 9-C–H bond by only 3.3 kcal/mol and increases the acidity of the corresponding radical cation by 3.6 $pK_{HA^{\bullet +}}$ units, relative to that of fluorene. The Me_3N^+ moiety of 9-Me_3NFlH^+ increases the 9-C–H BDE by 5 kcal/mol.

The anion derived from 9-(dimethylamino)fluorene is only 0.14 kcal/mol less basic than the fluorenide ion, but has an oxidation potential, $E_{1/2}(A^-)$, that is about 8 kcal/mol more negative. This difference can be equated to an 8 kcal/mol weakening by the Me_2N moiety of the homolytic bond dissociation energy (BDE) of the 9-C–H bond in 9-Me_2NFlH, relative to that in HFlH, or to an 8 kcal/mol stabilization of the 9-$Me_2NFl^{\bullet}$ radical, relative to the $HFl^{\bullet}$ radical.[1] Similar large effects of α-R_2N groups on

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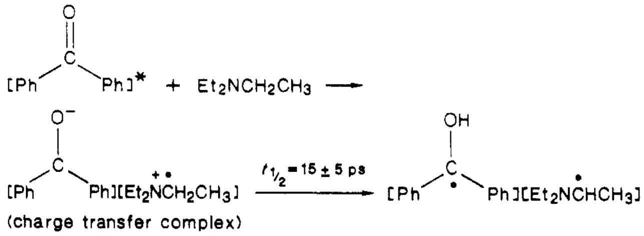
the stabilities of carbon radicals have aroused considerable interest of late, and some controversy. The first observation of this kind came in 1973, when mass spectral appearance potentials from electron-impact studies of amines revealed appreciable stabilization of radicals by α-amino groups, which increased along the series $H_2NCH_2^\bullet < EtNHCH_2^\bullet < Et_2NCH_2^\bullet$.[2a] This observation was supported a few years later by a study of the rate of rearrangement of vinylcyclopropane to cyclopentene, which showed that MeO and Me_2N groups in the cyclopropane ring lowered the activation energy by 11 and 18.5 kcal/mol, respectively, presumably because of stabilizing effects exerted by these substituents on incipient diradical intermediates.[2b] In 1981 a thermochemical study of the heats of formation of α-aminoalkyl radicals[3] gave satisfactory agreement with the stabilization energy E_s of the $H_2NCH_2^\bullet$ radical, relative to $CH_3^\bullet$, determined earlier by a kinetic method[4] and showed an increase in E_s values with *N*-methyl substitution [$H_2NCH_2^\bullet$ (10 kcal/mol) < $MeNHCH_2^\bullet$ (17 kcal/mol) < $Me_2NCH_2^\bullet$ (20 kcal/mol)] similar to that found by Sharma and Franklin.[2a] Also, the E_s values of 11 and 20 for MeO and Me_2N were close to the ΔE_a values obtained by Richkey and Shull.[2b] On the other hand, although ab initio SCF calculations gave an E_s value of 8–10 kcal/mol for the $H_2NCH_2^\bullet$ radical, they predicted a small decrease in E_s values on N-alkylation.[5] However, the subsequent full account of the thermochemical study contained references to studies of kinetics, ionization potentials, and spectral data all of which pointed to increasing radical stability of amino radicals on N-alkylation.[6]

There has also been considerable recent interest in the effect of R_2N groups on the acidities of the α-C–H bonds in $R_3N^{\bullet+}$ radical cations. The first such report appears to be that of Mann and his co-workers, who in 1970 concluded from electrochemical studies that the first two steps in the oxidation of a tertiary amine involve (a) removal of an electron from the lone pair to form a radical cation and (b) loss of a proton from the radical cation by heterolytic cleavage of an α-C–H bond, resulting in the formation of an α-dialkylamino radical.[7] Deprotonation has since been suggested as being an important step in reactions of the amine radical cations formed in chemical oxidations,[8] in biological oxidations,[9] and by photochemical routes, but differing accounts of the acid strengths of these species have been reported. Shaefer and Peters showed that the radical cation formed, as part of a charge-transfer complex, from the reaction of triplet benzophenone with triethylamine exhibited a high kinetic acidity, undergoing proton transfer within the complex with a half-life of 15 ± 5 ps.[10]



Lewis and his co-workers have observed similar facile proton transfers from the $[PhCH{=}CHPh]^{\bullet-}[R_2NCHR_2']^{\bullet+}$ exciplex formed from *trans*-stilbene and a tertiary amine under photostimulation.[11] They found, however, that proton transfer occurred exclusively via the exciplex intermediate. Exciplex solvation to form the solvent-separated radical ion pair or the free radical ions rendered the radical cation unreactive.[11c] These studies suggest that the *solvated radical cation* is not highly acidic, which agrees with the recent conclusion of Nelsen and Ippoliti that a tertiary amine is not a strong enough base to cause rapid deprotonation of its radical cation.[12] Nelsen and Ippoliti estimate $pK_{HA^{\bullet+}} \simeq 15$ in MeCN solution for the radical cation derived from 9-(2-adamantyl)-9-azabicyclo[3.3.1]nonane by using an equation derived by Nicholas and Arnold.[13] Their calculated value agrees reasonably well with a recently determined experimental value[14] of $pK_{HA^{\bullet+}} = 8$ in water for the $Et_3N^{\bullet+}$ radical cation.[15]

The direct measurement of the acidity of a radical cation presents a formidable problem because it requires determination of the concentrations of two highly reactive species in an equilibrium that is difficult to establish, i.e., $HA^{\bullet+} \rightleftarrows H^+ + A^\bullet$. We have found a simple method, which is based on a thermodynamic cycle,[13] to estimate the acidities of many radical cations ($HA^{\bullet+}$) in Me_2SO solution by combining pK_{HA} values for their acid precursors, HA, with the oxidation potentials of HA and those of their conjugate bases (eq 1).[17] It is also possible to combine pK_{HA} values with anion oxidation values, $E_{ox}(A^-)$, to estimate homolytic bond dissociation energies for H–A (eq 2).[18]

$$pK_{HA^{\bullet+}} = pK_{HA} + [E_{ox}(A^-) + E_{ox}(HA)]23.06/1.37 \qquad (1)$$

$$BDE = 1.37pK_{HA} + 23.06E_{ox}(A^-) + 55.86 \qquad (2)$$

Unfortunately, we cannot apply these equations to estimate the $pK_{HA^{\bullet+}}$ values and BDEs of simple amines because they are too weakly acidic to allow measurements of either the equilibrium acidities or the $E_{ox}(A^-)$ values in Me_2SO solution. We can apply the equations, however, to acidic hydrocarbons containing α-dialkylamino groups, such as 9-(dialkylamino)fluorenes. A series of $9\text{-}R_2NFl^-$ ions has recently been found to be useful in a test for the presence of single-electron transfer (SET) components in reactions with electrophiles.[19] For this and other reasons it was important to examine the effect of the structure of R_2N groups on (a) the acidities of 9-(dialkylamino)fluorenes, (b) their oxidation potentials, $E_{ox}(HA)$, and (c) the oxidation potentials of their conjugate bases, $E_{ox}(A^-)$. Also, we wished to obtain an esimate of the steric retardation factors, *r*, of the R_2N groups in S_N2 reactions by measuring the rates of reactions of $9\text{-}R_2NFl^-$ ions with $PhCH_2Cl$.[20]

Results and Discussion

Estimates of Steric Retardation Factors (*r*) in Reactions of $9\text{-}R_2NFl^-$ Ions with $PhCH_2Cl$. In earlier papers we have used a Brønsted line obtained for a plot of rate constants (log *k*) for S_N2

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(15) The Nelsen–Ippoliti estimate is lowered to about $pK_{HA^{\bullet+}} = 11$ when the oxidation potential is referred to the standard hydrogen electrode, as prescribed by the Nicholas and Arnold equation, rather than the SCE electrode. In water an 7–10 unit lower value would be expected by analogy with the ΔpK_{HB^+} value for R_3NH^+ in MeCN.[16]

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Table I. Acidities of 9-(Dialkylamino)fluorenide Ions, Rate Constants, and Steric Retardation Values (r) for Their Reactions with $PhCH_2Cl$ and Oxidation Potentials ($E_{1/2}$) (All in Me_2SO Solution at 25 °C)

R_2N	pK_a[a]	k_{obs}[b]	r[c]	$E_{1/2}$[d]
dimethylamino	22.5	1.85	−1.5	−0.535
piperidinyl	22.5	1.29	−1.6	−0.518
pyrrolidinyl	22.5	2.9	−1.2	−0.680
azetidinyl	21.8	22.4	−0.17	−0.740
diethylamino	21.4			−0.511
2-methylpiperidinyl	21.4	0.073	−2.5	−0.473
diisopropylamino	20.8	0.0069	−3.4	−0.360
2,2,6,6-tetramethylpiperidinyl	18.2	0.0034	−2.9	−0.313
3-methyl-1-pyrazolyl	18.45	0.65	−0.68	−0.178[e]
1-imidazolyl	17.3	0.099	−1.1	−0.145[e]

[a] Measured in Me_2SO solution by the overlapping indicator method as described in earlier papers; see: Bordwell, F. G.; Margolin, Z.; Olmstead, W. N. *J. Org. Chem.* **1980**, *45*, 3295–3299 and references cited therein. [b] $M^{-1}\ s^{-1}$; standard deviations were usually ±10% or lower. [c] Calculated with eq 1. [d] Reversible oxidation potentials (unless otherwise noted) measured by cyclic voltammetry under the conditions previously described with a Ag/AgI reference electrode.[25] [e] E_p value for an irreversible potential.

reactions between $PhCH_2Cl$ and a family of 9-MeFl^- ions (2-Br- and $2,7\text{-Br}_2\text{MeFl}^-$ and 9-MeFl^-) as a reference for estimating steric retardation factors (r) for substituent, G, in 9-GFl^- ions, relative to G = Me. In order to estimate r at the same basicity, we have used eq 3, where β is the Brønsted coefficient for the 9-MeFl^- ion family (0.31), k^{Me} is the rate constant for the reaction of $PhCH_2Cl$ with 9-MeFl^- ion in Me_2SO at 25 °C (49.4 $M^{-1}s^{-1}$), and k^G is the rate constant for the reaction of the 9-GFl^- ion in question with $PhCH_2Cl$ in Me_2SO at 25 °C. The following are representative r values: Me (0.0), $PhCH_2$ (−0.10), $t\text{-BuCH}_2$ (−0.11), $MeCH_2$ (−0.17), MeO (−0.56), Ph (−0.58), $c\text{-C}_6H_{11}$ (−1.2), *o*-Tol (−2.2), *t*-Bu (−2.6), and Mes (−3.1); the negative values indicate the size of the steric retardation of rate, relative to Me, in logarithmic units.[20] The rates of reactions of the series of $9\text{-R}_2\text{NFl}^-$ ions with $PhCH_2Cl$ in Me_2SO solution are summarized in Table I.

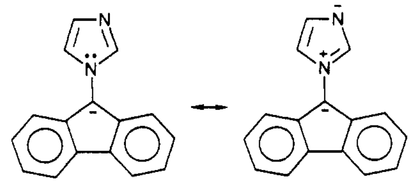
$$r = \beta(\Delta pK_{HA}) - \log (k^{Me}/k^G) \quad (3)$$

Examination of Table I shows that most of the dialkylamino groups cause strong steric retardation of the S_N2 reactions with $PhCH_2Cl$. All are more sterically retarding than methyl, and two have larger negative r values than does *t*-Bu, which has the largest retarding effect of the alkyl groups.[20] The azetidinyl group is noteworthy in having much smaller steric demands than the other R_2N groups (r = −0.17).

Equilibrium Acidities of 9-(Dialkylamino)fluorenes. 9-(Dimethylamino)-, 9-piperidinyl-, 9-pyrrolidinyl-, 9-azetidinyl-, 9-(diethylamino)-, and 9-(2-methylpiperidinyl)fluorenes are 0.4–1.5 pK_a units more acidic than fluorene (statistically corrected); their acidities are close to that of 9-MeFlH (22.3). Examination of scalar molecular models shows that interference of the alkyl groups with the C-1 and C-8 hydrogen atoms in the fluorene ring causes the p orbital on nitrogen in these groups to be essentially orthogonal to the p orbital of the C-9 carbanion. The repulsions of the lone pairs on nitrogen and the carbanion are thereby minimized, allowing the stabilization of the carbanion by the small electron-withdrawing field effect of nitrogen (σ_F = 0.10 for Me_2N)[21] to become the dominant factor.

9-(Diisopropylamino)- and 9-(2,2,6,6-tetramethylpiperidinyl)fluorenes are more acidic than fluorene by 2.1 and 4.7 pK_a units, respectively. These much larger effects must have a steric origin. In both instances methyl groups in the R_2N moiety are held over the face of the p orbital of the carbanion. They are therefore in a position to stabilize the carbanion by a polarizability effect. A second contributing or alternative effect causing this increase in acidity may be relief of strain on forming the anion from the highly strained hydrocarbon.[22]

9-(3-Methyl-1-pyrazolyl)- and 9-(1-imidazolyl)fluorenes are more acidic than fluorene by 4.45 and 5.6 pK_a units, respectively. These heteroaromatic amino groups can stabilize the carbanion formed on acid dissociation by polarization. The imidazolyl moiety of 9-imidazolylfluorenide in (**1**) is evidently more effective in stabilizing the carbanion in this way than is the Ph group in the 9-PhFl^- ion, as judged by the relative acidities of their conjugate acids. (The pK_{HA} values are 17.3 and 17.9, respectively.)



1a **1b**

Reversible Oxidation Potentials of $9\text{-R}_2\text{NFl}^-$ Ions. The eight $9\text{-R}_2\text{NFl}^-$ ions for which $E_{1/2}$ potentials are given in Table I are unusual for 9-GFl^- ions in that the radicals formed have sufficient lifetimes in solution to be reduced back to the anion in a reverse CV sweep. The $E_{1/2}$ values thus obtained are more negative than their E_p values by 30–70 mV (average 42 mV). The longer lifetimes of these radicals are no doubt due to two factors, their greater stability, which is imparted by the presence of the $\alpha\text{-R}_2N$ group, and steric hindrance to dimerization. The importance of radical stability is indicated by the reversibility of the oxidation potential for 9-azetidinylfluorenide ion, which has the smallest steric r value in Table I. On the other hand, the importance of steric hindrance is brought out by the observation that the $9\text{-}i\text{-Pr}_2\text{NFl}^\bullet$ radical is persistent, and that its rate of formation can be monitored in measuring the rate of reaction of $9\text{-}i\text{-Pr}_2\text{NFl}^-$ with F_3CCH_2I.[24] Addition of a solution of $1,1\text{-c-C}_6H_{10}(NO_2)_2$ to a solution of 9-pyrrolidinylfluorenide ion gave an ESR signal for the $9\text{-c-C}_4H_8\text{NFl}^\bullet$ radical.

Effects of Dialkylamino Moieties on Radical Cation Acidities. Acidities (pK_{HA}) and oxidation potentials for 9-(dialkylamino)fluorenes and related compounds are given in Table II. The r values, BDEs, and $pK_{HA^{\bullet+}}$ values for the corresponding radical cations have been collected in Table III.

Dialkylamino groups are among the most powerful groups known for stabilizing cations and radicals. As such, they exert profound effects on radical cation acidities. An R_2N group, when present on the aromatic ring in a fluorene radical cation, can affect the position of its dissociative equilibrium both by stabilizing the radical cation (acid weakening) and by stabilizing the radical formed on loss of the proton (acid strengthening). An estimate made by using eq 1 indicates that the fluorene radical cation is a super acid with a $pK_{HA^{\bullet+}}$ in Me_2SO solution of about −17. It has been estimated that introduction of a 2-MeO group lowers its acidity by 6 units, and that introduction of a second MeO group into the 7-position causes a further 5-unit decrease. Methoxyl substituents in the 3- and 3,6-positions have similar, but smaller, effects.[25] We see by examination of Table III that a 2-Me_2N group in the fluorene radical cation decreases its acidity by 18 $pK_{HA^{\bullet+}}$ units (25 kcal/mol), an effect greater than that of both MeO groups in the $2,7\text{-(MeO)}_2\text{FlH}_2^{\bullet+}$ radical cation. The presence of a second Me_2N group in the $2,7\text{-(Me}_2N)_2\text{FlH}_2^{\bullet+}$ radical cation (**2**) decreases its acidity by another 6 $pK_{HA^{\bullet+}}$ units. These large stabilizing effects must be associated with the extensive delocalization of the positive charge and odd electron in the radical cation (e.g., **2**) formed by loss of an electron from 2,7-

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(22) These effects are similar to that observed for 9-neopentylfluorene, which is a stronger acid than fluorene by 2.6 pK_a units.[23]

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Table II. Acidity and Oxidation Potentials for (Dialkylamino)fluorenes in Me_2SO Solution

		$E_{ox}(HA)^b$		$E_{ox}(A^-)^b$	
fluorene	pK_{HA}^a	MeCN	Me_2SO	MeCN	Me_2SO
fluorene (FlH_2)	22.6	2.15			−0.194
2-$MeOFlH_2$	22.7	1.79 (40)	1.8		−0.189 (40)
2,7-$(MeO)_2FlH_2$	22.95	1.55^c	1.60	−0.176	−0.195
2-Me_2NFlH_2	24.2	1.14^c (60)	1.13^c (60)		−0.248 (40)
2,7-$(Me_2N)_2FlH_2$	25.4		0.80^c (60)		0.298^c (55)
9-Me_2NFlH	22.5	1.47 (65)	1.45	-0.504^c (65)	-0.507^c
9-Et_2NFlH	21.4		1.43		-0.470^c
9-*i*-Pr_2NFlH	20.8	1.48 (60)	1.36 (60)	-0.348^c (60)	-0.297^c (55)
9-azetidinyl-FlH	21.8	1.51 (60)	1.52	-0.715^c (60)	-0.700^c (45)
9-pyrrolidinyl-Fl	22.2	1.35 (75)	1.33	-0.606^c (75)	−0.625
2,7-$(MeO)_2$-9-pyrrolidinyl-FlH	22.2	1.33	1.30	-0.62^c	-0.595^c
9-piperidinyl-FlH	22.5	1.49 (75)	1.48	-0.508^c (60)	−0.485
9-(2,6-dimethylpiperidinyl)-FlH	19.4		1.41		−0.305
9-imidazolyl-FlH	17.3	2.23			−0.020
2,7-$(MeO)_2$-9-imidazolyl-FlH	18.1	1.68^d (55)	1.67 (70)	−0.069 (50)	−0.024 (50)
n-BuNHFlH	21.5				-0.74^d
9-$Me_3NFlH^+Br^-$	17.8				+0.312

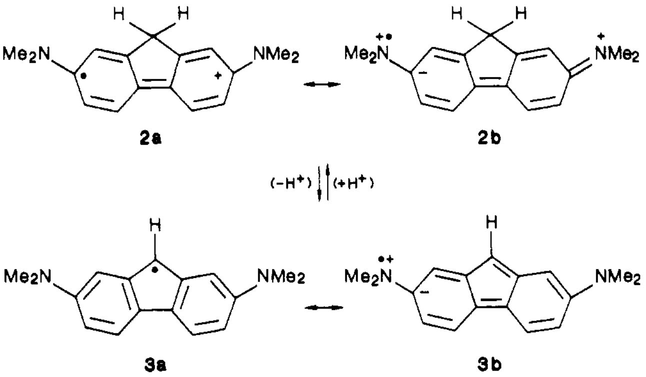
[a] Measured in Me_2SO by the overlapping indicator method, usually with two standard acids or indicators. [b] E_p values in volts measured by cyclic voltammetry under the conditions previously described (ref 25) with a Ag/AgI reference electrode; wave widths in millivolts. [c] Reversible potential; E_p is reported. [d] Partially reversible potential; E_p is reported.

Table III. Estimates of Radical Cation Acidities and Bond Dissociation Energies of (Dialkylamino)fluorenes

fluorene	pK_{Ha}	$pK_{HA^{\bullet+}}{}^a$	BDE^c	*r*
fluorene (FlH_2)	22.6	−17	79.5	
2-$MeOFlH_2$	22.7	−11	79.7	
2,7-$(MeO)_2FlH_2$	22.95	−6.0	79.9	
2-Me_2NFlH_2	24.2	+1.0	80.4	
2,7-$(Me_2N)_2FlH_2$	25.4	+6.9	80.9	
9-Me_2NFlH	22.5	−10.5	72.1	−1.5
9-Et_2NFlH	21.4	−10.5	71.5	
9-*i*-Pr_2NFlH	20.8	-7.1^b	74.6^d	−3.4
9-azetidinyl-FlH	21.8	−15.5	66.7	−0.17
2,7-$(MeO)_2$-9-pyrrolidinyl-FlH	22.2	−10	69.7	
pyrrolidinyl-FlH	22.2	−10	69	−1.2
9-piperidinyl-FlH	22.5	−10.5	72.6	−1.6
9-(2,6-dimethylpiperidinyl)-FlH	19.4	−9.3	72.5	
9-imidazolyl-FlH	17.3	−20.5	76.2	
2,7-$(MeO)_2$-9-imidazolyl-FlH	18.1	−10.5	77.2	
n-BuNHFlH	21.5		65.4	
9-$Me_3NFlH^+Br^-$	17.8		84.5	

[a] Calculated from eq 1 and the Me_2SO data in Table II; relative $pK_{HA^{\bullet+}}$ values are estimated to be ±1. [b] Using $E_{ox}(HA)$ in MeCN gives −9.1. [c] Calculated from eq 2 and the data in Table II; using E_p values (using the $E_{1/2}$ values in Table I gives BDEs lower by about 1 kcal/mol). For this calculation −0.125 must be added algebraically to $E_{ox}(A^-)$. [d] Using $E_{ox}(A^-)$ in MeCN gives 73.5.

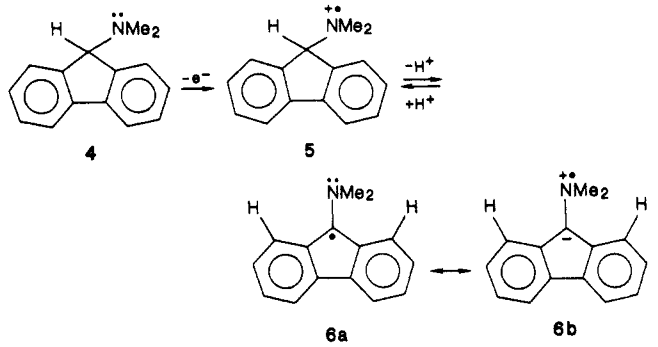
$(Me_2N)_2FlH_2$. The radical formed by loss of a proton from **2** has its electron density concentrated at the 9-position (3a). It is possible to delocalize the odd electron in the radical partially into the Me_2N groups (e.g., **3b**), but a calculation by a ΔAOP method (eq 4)[26] suggests that the effects of the ("meta") Me_2N groups will be slightly destabilizing.



$$\Delta AOP = 1.37\Delta pK_{HA} + 23.06\Delta E_{ox}(A^-) \qquad (4)$$

The two Me_2N groups in 2,7-$(Me_2N)FlH_2$ enrich the electron density of the aromatic system to the point where its oxidation potential, $E_{ox}(HA)$, is 1.35 V less positive than that of fluorene (Table I). The resulting 31 kcal/mol stabilization of the radical cation is sufficient to place this point on the line of the plot of $E_{ox}(HA)$ vs $pK_{HA^{\bullet+}}$ for remotely substituted fluorenes.[25]

The presence of a dialkylamino group at the 9-position of fluorene (e.g., **4**) does not enrich the electron density of the fluorene ring because the Me_2N group is isolated therefrom. Nevertheless, $E_{ox}(HA)$ for **4** is 0.7 V (16 kcal/mol) less positive than that of fluorene (Table II). The reason is that the electron lost on oxidation comes from the lone pair on nitrogen rather than from the fluorene π system. Loss of a proton from the resulting radical cation (**5**) leads to radical **6**, which is strongly stabilized by the α-9-Me_2N group.



The stabilizing effect of the Me_2N moiety of **6** is estimated by the ΔAOP method to be 8 kcal/mol, relative to fluorene (eq 5). This acid-strengthening effect counteracts to a considerable extent the 16 kcal/mol (acid weakening) stabilizing effect of Me_2N on the radical cation **5**, relative to fluorene; the net results is an 8 kcal/mol (6 $pK_{HA^{\bullet+}}$) decrease in acidity.

$$\Delta AOP\ (\text{for } 6^{\bullet}) = 1.37(22.5 - 22.6) + 23.06(-0.535 + 0.194) = -8\ \text{kcal/mol} \qquad (5)$$

Examination of scalar molecular models indicates that steric interference with the C-1 and C-8 hydrogen atoms on the fluorene ring with the R groups in 9-$R_2NFl^{\bullet}$ radicals inhibits effective overlap between the p orbital on nitrogen and the p orbital at C-9. Estimation of radical-stabilizing effects by eq 4 suggests that overlap decreases along the series c-C_3H_6N (13) > c-C_4H_8N (10) > c-$C_5H_{10}N$ (7), Me_2N (7.5), Et_2N (8), 2,6-$(Me)_2$-c-$C_5H_{10}N$ (7) > *i*-Pr_2N (6) (parenthetical numbers in kcal/mol). We see that the acidity of the 9-c-$C_3H_6NFlH^{\bullet+}$ radical cation is nearly as high as that of the $FlH_2^{\bullet+}$ radical cation ($pK_{HA^{\bullet+}}$ = −15 vs −17), but for a different reason. For $FlH_2^{\bullet+}$ the high acidity is caused by the low stability of the radical cation, whereas for 9-c-$C_3H_6NFlH^{\bullet+}$ it is caused primarily by the high stability of the radical formed on deprotonation.

An estimate by the ΔAOP method suggests a 3.4 kcal/mol stabilization by the imidazolyl group in the 9-ImFl$^{\bullet}$ radical, relative

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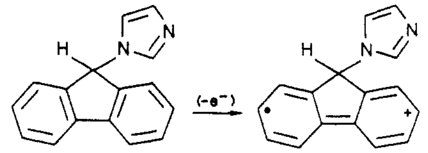
[26] Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985.

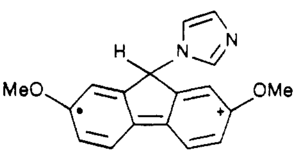
to HFl$^\bullet$, whereas the ΔE_{ox}(HA) value points to a 1.8 kcal/mol stabilization of the radical cation, relative to $FlH_2^{\bullet+}$. The higher acidity for 9-ImFlH$^{\bullet+}$ than for $FlH_2^{\bullet+}$ therefore appears to be caused by a small radical-stabilizing effect. Loss of the electron from 9-ImFlH is no doubt from the fluorene π system (**7** → **8**) rather than from a nitrogen lone pair. This view is confirmed by the fact that introduction of MeO groups at C-2 and C-7 in 9-ImFlH decreases E_{ox}(HA) by 13 kcal/mol (Table I) causing a 10 p$K_{HA^{\bullet+}}$ unit decrease in the acidity of the radical cation (**9**). On the other hand, introduction of MeO groups into the 2- and 7-position of 9-c-C_4H_8NFlH has only a small effect on E_{ox}(HA) because in this instance the electron is being removed at the electrode from the lone pair on nitrogen, and the acidity of the radical cation remains the same (within experimental error).



7

8

(p$K_{HA^{\bullet+}}$ = −20)



9

(p$K_{HA^{\bullet+}}$ = −10)

Effects of 9-Dialkylamino Groups on the Homolytic Bond Dissociation Energies (BDEs) of the 9-C–H Bond in Fluorenes. The radical-stabilizing effects of R_2N groups in 9-R_2NFl$^\bullet$ radicals estimated, relative to that of the HFl$^\bullet$ radical (eq 4), are equivalent to the ΔBDEs estimated by eq 2. The absolute BDEs in Me_2SO solution calculated by eq 2 are more meaningful, however, since they allow direct comparisons to be made with gas-phase values. The BDEs given in Table III are estimated to be accurate to about ±2–3 kcal/mol but the *relative* BDEs are more accurate. The results obtained from eq 2 are therefore given to three significant figures for purposes of comparison. The BDE of fluorene itself of 79.5 ± 3 kcal/mol is in good agreement with the gas-phase number of 80 ± 5 kcal/mol.[27] The largest effects observed are the 10.5 and 12.8 kcal/mol ΔBDEs for 9-c-C_4H_8NFlH and 9-c-C_3H_6NFlH, respectively, relative to fluorene. In an earlier paper we presented a plot of ΔAOP values for 9-Gfluorenes (G = H, MeOCO, Me, CN, MeO, fluoradene, and Me_2N) vs gas-phase BDEs for GCH_2H methanes, with a slope of about 0.5, which suggested that ΔBDEs relative to fluorene will be about 50% as large as ΔBDEs relative to methane.[26] When viewed in this light, the average ΔBDE of about 8 kcal/mol for 9-R_2NFlH indicated by the present data are consistent with the ΔBDE of 20 kcal/mol found by Griller and Lossing for Me_2NCH_2H.[3] On the other hand, the BDE for 9-*n*-BuNHFlH is 6 kcal/mol *less* than that for 9-Et_2NFlH, which is not consistent with the N-alkylation effect observed.[3] Measurements on other 9-RNHFlH compounds are underway to test the effect of N-alkylation on BDEs.

It will be noted that in Table III the largest ΔBDE relative to FlH_2 (12.8 kcal/mol) is observed for the least sterically demanding R_2N group (c-C_3H_6N), i.e., that with the least negative *r* value (−0.17), and that the smallest ΔBDE (4.9 kcal/mol) is observed for the most sterically demanding R_2N group (*i*-Pr_2N) with the largest *r* value (−3.4). This is consistent with the size of ΔBDE in the incipient radicaloid α-C–H bonds being controlled by the effectiveness of the overlap of the p orbital on carbon containing the odd electron and the p orbital on nitrogen containing the lone pair. When the lone pair on nitrogen in 9-Me_2NFlH is tied up by methylation to form 9-$Me_3NFlH^+Br^-$ the BDE is increased by 12.4 kcal/mol. Now the C–H BDE is *stronger* by 5 kcal/mol than that in fluorene itself (Table III). This effect is similar, but larger than that observed for 9-$PhSO_2$FlH, which has a BDE 2 kcal/mol greater than that of fluorene.[26]

Summary and Conclusions. The rates of reaction with $PhCH_2Cl$ of a series of 9-(dialkylamino)fluorenide ions have been shown to decrease progressively over a range of 3.2 log units from 9-c-$C_3H_6NFl^-$ to 9-*i*-Pr_2NFl^-. Stereoelectronic effects cause the oxidation potentials of these ions to become less negative by about 9 kcal/mol over this range and the homolytic bond dissociation energies of the 9-C–H bonds in their conjugate acids to decrease by nearly 13 kcal/mol. The acidities of the radical cations derived from these 9-R_2NFlH fluorenes are decreased by an average of 6.5 p$K_{HA^{\bullet+}}$ units, relative to the fluorene radical cation; a decrease of 18 p$K_{HA^{\bullet+}}$ units was observed for the 2-$Me_2NFlH^{\bullet+}$ radical cation, relative to HFlH$^{\bullet+}$. These acidity decreases are explained by the powerful stabilizing effect of R_2N groups on radical cations.

Experimental Section

Materials. 2-Methoxy- and 2,7-dimethoxyfluorenes have been described earlier.[25] 2,7-Bis(dimethylamino)fluorene was prepared from 2,7-diaminofluorene (Aldrich) by the method of Giumanini.[28] Purification by vacuum sublimation and crystallization (EtOH) gave material of mp 188–190 °C (lit.[29] mp 190 °C).

9-(Dialkylamino)fluorenes. General Procedure. A 2-g sample of 9-bromofluorene (Aldrich) was added to excess amine. If 9-bromofluorene was soluble in the amine, no solvent was added; otherwise, enough acetonitrile was added to dissolve the 9-bromofluorene. The solution was refluxed for various lengths of time (1 day for nonhindered amines, up to 2 weeks for severely hindered ones). The progress of the reaction was followed by TLC. The solution was then poured into acidic H_2O and extracted with ether. The aqueous extract was neutralized with NaOH and again extracted with ether. Removal of the solvent resulted in precipitation of the desired amines. Solids were crystallized from EtOH unless otherwise noted. Since all of the compounds were made by the same method and gave NMR, mass spectral, pK_{HA}, E_{ox}(HA), $E_{ox}(A^-)$, and rate data[19] in agreement with the assigned structures, microanalytical data were obtained on only four compounds as being representative. Three of these gave satisfactory analyses. The carbon analysis of 9-diisopropylfluorene was 1.1% low. We have frequently observed low carbon analyses for fluorenes bearing bulky 9-substituents, however, presumably because of facile fragmentation during combustion. Note in this connection that for 9-diisopropylfluorene the molecular ion peak is weak (4.7%) and the largest peak is for mass 165, corresponding to loss of the *i*-Pr_2N fragment.

The following appear to be new compounds (NMR in $CDCl_3$).

9-(2,2,6,6-Tetramethylpiperidinyl)fluorene: mp 93–94 °C; ^{1}H NMR δ 0.7 (s, 6 H), 1.3 (m, 2 H), 1.5 (s, 6 H), 1.7 (m, 4 H), 5.2 (s, 1 H), 7.2–7.8 (m, 8 H); MS, *m/e* 305 (molecular ion, 1.0), 290 (10.3), 165 (100).

9-(2-Methylpiperidinyl)fluorene: mp 62–63 °C; ^{1}H NMR δ 1.4 (d, 3 H), 1.5–2.2 (m, 8 H), 3.2 (m, 1 H), 5.2 (s, 1 H), 7.2–7.8 (8 H); MS, *m/e* 263 (molecular ion, 5.2), 248 (25.8), 165 (100%).

9-(Diisopropylamino)fluorene:[30] mp 104.5–105 °C; ^{1}H NMR δ 1.1 (d, 12 H), 2.8 (m, 1 H), 4.9 (s, 1 H), 7.2–7.8 (1 H); MS, *m/e* 265 (molecular ion, 4.7%), 250 (13.5), 165 (100). Anal. Calcd for $C_{19}H_{23}N$: C, 86.1; H, 8.7; N, 5.3. Found: C, 85.0; H, 8.9; N, 5.1.

9-(3-Methyl-1-pyrazolyl)fluorene: mp 126–128 °C; ^{1}H NMR δ 2.4 (s, 3 H), 5.9 (d, 1 H), 6.3 (s, 1 H), 6.8 (d, 1 H), 7.1–7.8 (m, 8 H); MS, *m/e* 246 (molecular ion, (42.4), 245 (46.7), 204 (11.9), 165 (100).

9-Azetidinylfluorene. Azetidine (0.25 g, Aldrich) was placed in a flask under nitrogen, 0.5 g of diisopropylamine was added, followed by 9-bromofluorene (0.75 g) dissolved in a minimum amount of acetonitrile. On warming at 50 °C for 10 min the amine salt precipitated. The solution was poured into 25 mL of water and the solid was collected on a filter. Vacuum sublimation gave a white powder: mp 94–95 °C; GLC gave a single peak; ^{1}H NMR ($CDCl_3$) δ 2.1 (q, 2 H), 3.4 (t, 4 H), 4.5 (s, 1 H) 7.2–7.7 (m, 8 H); MS, *m/e* 221 (50.7), 220 (58%), 192 (19.1), 165 (100). Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83. Found: C, 87.05; H, 6.83.

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(28) Giumanini, A. G.; Chiavatti, G.; Musiani, M. M.; Rossi, P. *Synthesis* **1980**, 743–746.

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(30) Synthesized by Daniel Gombos.

9-Pyrrolidinylfluorene: colorless needles (MeOH), mp 93 °C; ^{1}H NMR δ 7.5 (m, 8 H), 5.1 (s, 1 H), 2.7 (t, 4 H), 1.7 (m, 4 H). Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.29. Found: C, 87.02; H, 7.34.

9-Piperidinylfluorene: colorless needles (MeOH), mp 89 °C; ^{1}H NMR δ 1.43 (br m, 6 H), 2.5 (br t, 4 H), 5.72 (s, 1 H), 7.2–7.7 (m, 8 H).

9-(Diethylamino)fluorene: Bright yellow oil, bp 138–140 °C (1 mm); ^{1}H NMR δ 1.1–0.9 (t, 6 H), 2.7–2.4 (q, 4 H), 4.81 (s, 1 H) 7.65–7.05 (m, 8 H); MS, *m/e* 237 (M^+, 8.3), 222 (8.7), 166 (14.9), 165 (100).

9-(2,6-Dimethylpiperidinyl)fluorene: mp 83.5–84.5 °C; ^{1}H NMR δ 7.1–7.8 (m, 8 H), 5.2 (5, 1 H), 3.1 (m, 1 H), 1.3–1.8 (m, 6 H), 0.6–0.8 (d, 6 H); MS, *m/e* 277 (2.2), 262 (12.9), 166 (22.1), 165 (100).

9-Imidazolylfluorene: mp 151–151.5 °C; ^{1}H NMR δ 7.2–7.7 (m, 9 H), 7.0 (s, 1 H), 6.6 (s, 1 H), 6.0 (s, 1 H); MS, *m/e* 232 (19.5), 166 (14.5), 165 (100.0). Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.22; N, 12.07. Found: C, 82.92; H, 5.22; N, 12.08.

2,7-Dimethoxy-9-pyrrolidinylfluorene. 2,7-Dimethoxyfluorenone (0.36 g, 1.5 mmol) was dissolved in 5 mL of methanol and reduced with $NaBH_4$ (0.084 g, 2 mmol). The crude alcohol obtained as a colorless solid on workup was suspended in benzene and treated with 0.6 mL of acetyl bromide in 5 mL of acetonitrile. After 1 h at 45 °C the solvent was removed and the solid was washed with water and crystallized from EtOH. The bromide (0.15 g, yellow crystals) was refluxed in 1.5 mL of pyrrolidine for 1 h. After quenching with water, extraction with ether and evaporation of the solvent yielded colorless needles: mp 122.5–123 °C (EtOH); ^{1}H NMR δ 1.78 (m, 4 H), 2.76 (m, 4 H), 3.91 (s, 6 H), 6.96 (dd, 2 H), 7.25 (d, 2 H), 7.57 (d, 2 H).

Electrochemistry. The measurements of cyclic voltammograms were carried out as previously described.[25]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work. We thank Dr. A. V. Satish for the preparation of 2,7-bis(dimethylamino)fluorene and for the acidity and oxidation potential measurements made with this compound.

Registry No. $PhCH_2Cl$, 100-44-7; 9-Me_2NFl^-, 83936-70-3; 9-piperidinyl-Fl^-, 111933-72-3; 9-pyrrolidinyl-Fl^-, 111933-71-2; 9-azetidinyl-Fl^-, 111933-70-1; 9-Et_2NFl^-, 116997-61-6; 9-(2-methylpiperidinyl)Fl^-, 111933-73-4; 9-*t*-Pr_2NFl^-, 109495-02-5; 9-(2,2,6,6-tetramethylpiperidinyl)Fl^-, 111933-74-5; 9-(3-methyl-1-pyrazolyl)Fl^-, 116997-62-7; 9-(1-imidazolyl)Fl^-, 116997-63-8; FlH_2, 86-73-7; 2-$MeOFlH_2$, 2523-46-8; 2,7-$(MeO)_2FlH_2$, 42523-30-8; 2-Me_2NFlH_2, 13261-62-6; 2,7-$(Me_2N)_2FlH_2$, 13261-63-7; 9-Me_2NFlH, 53156-46-0; 9-Et_2NFlH, 108975-83-3; 9-*i*-Pr_2NFlH, 109495-00-3; 9-azetidinyl-FlH, 116997-64-9; 9-pyrrolidinyl-FlH, 7596-59-0; 2,7-$(MeO)_2$-9-pyrrolidinyl-FlH, 116997-65-0; 9-piperidinyl-FlH, 3333-06-0; 9-(2,6-piperidinyl)-FlH, 116997-66-1; 9-imidazolyl-FlH, 35214-35-8; 2,7-$(MeO)_2$-9-imidazolyl-FlH, 116997-67-2; 9-*n*-BuNHFlH, 46880-06-2; 9-$Me_3NFlH^+Br^-$, 6634-60-2; FlH^-, 12257-35-1; 2-$MeOFlH^-$, 100858-88-6; 2,7-$(MeO_2)FlH^-$, 100858-87-5; 2-Me_2NFlH^-, 113533-33-8; 2,7-$(Me_2N)FlH^-$, 116997-68-3; 2,7-$(MeO)_2$-9-pyrrolidinyl-Fl^-, 116997-69-4; 9-(2,6-dimethylpiperidinyl)-Fl^-, 116997-70-7; 2,7-$(MeO)_2$-9-imidazolyl-Fl^-, 116997-71-8; 9-*n*-$BuFl^-$, 116997-72-9; 9-$Me_3N^+Fl^-Br^-$, 116997-73-0; $FlH_2^{\bullet+}$, 34985-70-1; 2-$MeOFlH_2^{\bullet+}$, 101631-12-3; 2,7-$(MeO)_2FlH_2^{\bullet+}$, 51548-21-1; 2-$Me_2NFlH_2^{\bullet+}$, 113533-40-7; 2,7-$(Me_2N_2)FlH_2^{\bullet+}$, 116997-74-1; 9-$Me_2NFlH^{\bullet+}$, 117065-69-7; 9-$Et_2NFlH^{\bullet+}$, 116997-75-2; 9-*i*-$Pr_2NFlH^{\bullet+}$, 116997-76-3; 9-azetidinyl-$FlH^{\bullet+}$, 116997-77-4; 2,7-$(MeO)_2$-9-pyrrolidinyl-$FlH^{\bullet+}$, 116997-78-5; 9-pyrrolidinyl-$FlH^{\bullet+}$, 116997-79-6; 9-piperidinyl-$FlH^{\bullet+}$, 116997-80-9; 9-(2,6-dimethylpiperidinyl)-$FlH^{\bullet+}$, 116997-81-0; 9-imidazolyl-$FlH^{\bullet+}$, 116997-82-1; 2,7-$(MeO)_2$-9-imidazolyl-$FlH^{\bullet+}$, 116997-83-2; 9-(2,2,6,6-tetramethyl)-FlH, 116997-84-3; 9-(2-methylpiperidinyl)FlH, 116997-85-4; 9-(3-methyl-1-pyrazolyl)FlH, 116997-86-5; 9-BrFlH, 1940-57-4; azetidine, 503-29-7.

Competing Reactions of the Acetone Cation Radical: RRKM–QET Calculations on an ab Initio Potential Energy Surface[†]

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Abstract: Two parallel unimolecular dissociations of the acetone cation radical, (1) methyl loss and (2) methane elimination, were studied by means of RRKM–QET calculations on an ab initio potential energy surface. The ab initio calculations demonstrated the existence of a hydrogen-bridged complex as an intermediate for both reaction paths. Sets of reactant and transition structure frequencies, as well as energetics based on high-level ab initio (MP3/6-31G(d,p)//6-31G(d)+ZPVE) calculations, were employed in the RRKM-QET calculations. By invoking tunneling in the CH_4 elimination channel, we were able to reproduce several experimental observations: (a) reaction channel 2 is the major channel for so-called "metastable ion" fragmentations in the microsecond lifetime range; (b) channel 1 becomes the major reaction channel at high internal energies of the reactant ion. Photoionization efficiency (PIE) curves for the two competing channels calculated on the basis of RRKM-QET microcanonical rate coefficients, $k(E)$, reproduce rather well recent experimental results by Traeger, Hudson, and McAdoo.

There have been two successful approaches in treating unimolecular fragmentations of polyatomic cations in recent years,[1] ab initio calculations of potential energy profiles and RRKM-QET calculations of microcanonical rate coefficients, $k(E)$. The latter require accurate knowledge of the energetics of the reaction in the form of the critical energy of activation, E_0, and the vibrational frequencies of the reactant and transition structures. While the vibrational frequencies of the reactant ion can be guessed, on the basis of those of the neutral molecule, and more recently there

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[†] Dedicated to Professor F. W. McLafferty on the occasion of his 65th birthday.

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