vibrationally induced ring currents must remain a working hypothesis and a conceptual model. It can be stated, however, that more recent data obtained in our laboratory continue to be consistent with the ring current hypothesis.

(35) Barnett, C. J.; Drake, A. F.; Kuroda, R.; Mason, S. F. *Mol. Phys.* **1980,** *41,* 455.

of VCD intensity for glycine-C-d_1-N-d_3.

Intramolecular Selectivity of the Alkylation of Substituted Anilines by Gaseous Cations

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Abstract: The intramolecular selectivity of the electrophilic reactions of Et$^+$, i-Pr$^+$, and Me$_2$F$^+$ cations with substituted anilines, including m-toluidine, m-anisidine, and m- and p-fluoroaniline, has been investigated in the dilute gas state at pressures ranging from 100 to 720 torr by a radiolytic technique, complemented by chemical ionization mass spectrometry. The results indicate an appreciable kinetic bias for the nitrogen atom, leading to predominant N-methylation by Me$_2$F$^+$. The reactivity of the carbenium ions is complicated by the simultaneous occurrence of proton transfer, in particular to the NH$_2$ group, which increases the relative extent of ring alkylation. The positional selectivity is characterized, aside from the usual orienting effects of the substituents, by the enhanced reactivity of the ring positions ortho to an n-type substituent, irrespective of its activating or deactivating properties. The effect is traced to the preliminary formation of an electrostatic adduct between the aniline and the gaseous electrophile.

The current interest in gas-phase ionic reactions is largely associated with their recognized value as simplified and generalized models of the corresponding processes occurring in solution. In particular cases, experiments carried out in the dilute gas state may even represent the only practicable approach to the mechanistic study of specific reactions. A case in point is the attack of electrophilic carbon on aromatic amines, whose conventional study in solution is complicated by the ionization of the NH$_2$ group promoted by the acids used as reactants or catalysts in Friedel-Crafts reactions. As a consequence, the very nature of the substrate is affected, which largely precludes the mechanistic study of alkylation of *free* anilines.[1]

A recent paper from this laboratory has reported a radiolytic and mass spectrometric study of the alkylation of the model substrate, C$_6$H$_5$NH$_2$, with simple cations in the dilute gas state.[2] The radiolytic approach proved particularly useful, providing direct information on the positional selectivity of the substitution measured under conditions of kinetic control, a feature of paramount relevance to allow meaningful comparison with solution-chemistry studies. It should be noted in this connection that the results obtained with structurally diagnostic mass spectrometric techniques, e.g., MS/MS, have been found to reflect thermodynamic, rather than kinetic, control.[3]

The present paper reports extension of the study to substituted anilines, namely m-toluidine, m-anisidine, and m- and p-fluoroaniline, to focus the role of n-type substituents in dictating the

positional selectivity of the gas-phase alkylation and to gather additional evidence on the direct partecipation mechanism suggested by previous results.[2,4]

The reagents used, i.e., Et$^+$, i-Pr$^+$, and Me$_2$F$^+$ ions, have been obtained respectively from the radiolysis of CH$_4$ (or C$_2$H$_6$), C$_3$H$_8$, and CH$_3$F, according to a technique extensively applied to the study of gas-phase aromatic substitution, whose principles and results have been recently reviewed.[5]

Experimental Section

Materials. The gases uses were research grade products from Matheson Gas Products Inc., with a stated purity of 99.99 mol %. Fluka AG and Merk Co. were the source of the amines. m-Toluidine, m-anisidine, and m- and p-fluoroaniline were research-grade chemicals and were freshly redistilled before use, m-anisidine being further purified by preparative GLC. The alkylated anilines used as reference standards in the analysis of the products by GLC and GLC/MS were obtained from Fluka AG or synthesized according to unexceptional procedures.

Procedure. The gaseous samples were prepared by conventional vacuum techniques in a greaseless system as described elsewhere[5] and enclosed in sealed 250-mL Pyrex ampules. The γ irradiation was carried out to a total dose of 2.5 Mrad, delivered at the rate of 1.06 Mrad h^{-1}, in a 220 Gammacell from Nuclear Canada Ltd., within a thermostat set

(1) See for instance: Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1973,** *1,* 35.
(2) Attinà, M.; Cacace, F. *J. Am. Chem. Soc.* **1983,** *105,* 1122.
(3) Wood, K. V.; Burinsky, D. J.; Cameron, D.; Cooks, R. G. *J. Org. Chem.* **1983,** *48,* 5236.

(4) Participation of an n-type substituent in gas-phase aromatic substitution has been suggested originally by the following: (a) Attinà, M.; Giacomello, P. *Tetrahedron Lett.* **1977,** 2373; (b) *J. Am. Chem. Soc.* **1979,** *101,* 6040. Predominant ortho substitution has been reported in the gas-phase alkylation of anisole and phenol: (c) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* **1977,** *99,* 4401; (d) *J. Chem. Soc., Perkin Trans. 2,* **1979,** 891; (e) Pepe, N.; Speranza, M. *J. Chem. Soc., Perkin Trans. 2,* **1981,** 430; (f) Attinà, M.; de Petris, G.; Giacomello, P. *Tetrahedron Lett.* **1982,** *34,* 3525.
(5) (a) Cacace, F. *Radiat. Phys. Chem.* **1982,** *20,* 99 and references therein. (b) Speranza, M. *Gazz. Chim. Ital.* **1983,** *113,* 37.

Table I. Alkylation of Anilines by Gaseous Ethyl Ions

substrate	system composition[a] (torr)		k_N/k_{ring}[b]	isomeric composition[c] of ring alkylated products (%)			absolute yields $G_{(+M)}$	
							nitrogen	ring
aniline[d]								
	CH$_4$: 720		0.29	63	~2	35		
	CH$_4$: 720	NMe$_3$: 3.0	0.28	57		43		
	CH$_4$: 200		0.24	57	~1	42		
	C$_2$H$_6$: 720		0.47	82		18		
m-toluidine								
	CH$_4$: 720		0.27	30	36	34	0.11	0.41
	C$_2$H$_6$: 720		0.34	40	37	23	0.15	0.44
	C$_2$H$_6$: 720	NMe$_3$: 3.0	0.43	39	45	16	0.068	0.16
	C$_2$H$_6$: 720	NMe$_3$: 5.0	1.7				0.088	0.052
	C$_2$H$_6$: 100		0.44	38	35	27	0.28	0.64
m-anisidine								
	CH$_4$: 720		0.18	53	29	18	0.034	0.19
	C$_2$H$_6$: 720		0.084	51	28	21	0.016	0.19
	C$_2$H$_6$: 720	NMe$_3$: 3.0	0.45	46	29	25	0.020	0.044
	C$_2$H$_6$: 100		0.23	45	27	28	0.089	0.38

[a] All systems contained the aromatic amine (ca. 2 torr) and O$_2$ (1–4 torr, depending on the total pressure). [b] Standard deviation ca. 10%. [c] Isomers other than those listed were below detection limit, ca. 1%. [d] Data from ref 2.

at 80 °C. In order to allow the relatively unvolatile anilines to reach a constant concentration in the gas phase, the sealed bulbs were maintained at 80 °C during a period of 1 h, just before being irradiated.

Blank runs were carried out to exclude the occurrence of "dark" chemical reactions between the aromatic amines and other components of the gaseous systems, in particular MeF. The blanks were performed under conditions identical with those prevailing in the actual runs, except for the γ irradiation. No detectable "dark" reactions could be demonstrated, with the exception of the systems containing MeF and *m*-anisidine, where traces of alkylated products were formed on standing for a few hours at 80 °C.

Analysis of the Products. The reaction products, recovered from the irradiated vessels according to a procedure described elsewhere,[6] were analyzed by GLC with a Perkin-Elmer Sigma 1 or a Hewlett-Packard Model 5700 chromatograph, equipped with FID units. The identity of the products, established by comparison of their retention volumes with those of authentic samples, was confirmed by GLC/MS, using a Hewlett-Packard Model 5982 A quadrupole mass spectrometer, connected to a 5934 A data system, or a VG ZAB-2F magnetic mass spectrometer. The following columns were used: (i) a 50 m long, fused quartz capillary column, coated with Carbowax 20 M deactivated methyl silicone (SP-2100) fluid, operated at 120–140 °C; (ii) a 10 ft long, $^1/_8$ in. i.d. stainless steel column, packed with 10% SP-2100 + 0.1% Carbowax 1500 on 100–120 mesh Supelcoport, operated at 125–140 °C; (iii) a 6 ft long, $^1/_4$ in. i.d. glass column, packed with 10% Carbowax 20 M + 2% KOH on 80–100 mesh Chromosorb W, operated at 135–160 °C; and (iv) a 6 ft long, $^1/_4$ in. i.d. glass column, packed with 3% SP-2100 DB on 100–120 mesh Supelcoport, operated at 60 °C.

Chemical Ionization (CI) Spectra. The spectra were recorded with the quadrupole instrument, at a source temperature of 153 °C, using CH$_4$, C$_3$H$_8$, and CH$_3$F as the reactant gases. The gaseous samples, contained the anilines at approximately the same concentration as in the radiolytic experiments, were maintained at 80 °C in a thermostat and introduced into the ion source via a heated transfer line. The source pressure was measured with a Bourdon-type mechanical gauge whose readings must be considered as largely approximate in the absence of an absolute calibration. The major features of the CI spectra can be outlined as follows. The protonated adduct of the substrate M, namely the species (M + H)$^+$, is invariably the most abundant ion in the CH$_4$ and C$_3$H$_8$ spectra of the anilines, while the alkylated adducts, (M + Et)$^+$ and (M + C$_3$H$_7$)$^+$, are also major products, their relative abundance increasing with the pressure. As a typical example, the (M + C$_3$H$_7$)$^+$/(M + H)$^+$ intensity ratio

in the C$_3$H$_8$ spectra of *m*-toluidine increases from 0.05 at a *nominal* pressure of ca. 0.3 torr to a maximum value of 0.30 at pressures of 0.5–0.6 torr. Closely similar trends prevail in the CI spectra of the other anilines, e.g., *m*-anisidine, reflecting the stabilization of a higher fraction of the excited alkylated adducts at higher pressures, consistent with previous observations.[7] The CH$_3$F spectra are characterized by the methylated and the protonated adducts as major ionic species, with a much lower abundance of the fluoromethylated adduct. As a typical example, the CH$_3$F CI spectrum of *m*-toluidine recorded at a *nominal* pressure of 0.7 torr contains the (M + Me)$^+$, (M + H)$^+$, and (M + CH$_2$F)$^+$ ions in the ratio of 1.00:0.62:0.13.

Results

Nature and Yields of the Products. Both ring- and N-alkylated anilines are formed from all systems investigated, as shown in Tables I–III, which include the $G_{(+M)}$ values of the products, i.e., the number of molecules formed per 100 eV absorbed by the gaseous system. Comparison of the $G_{(+M)}$ values of the products with those of their ionic precursors allows one to estimate the *absolute* yield of the alkylation. While the yields depend on the nature of the substrate and the electrophile, the total pressure, the presence of additives, etc., they are in general sufficiently large to characterize the alkylation of anilines as a major reaction channel of the radiolytically formed cations. As a typical example, the combined yields of ring- and N-isopropylated *m*-toluidines account for 25 to 30% of the *i*-Pr$^+$ ions from the radiolysis of neat C$_3$H$_8$ at 720 torr. Such values are remarkably high, if one considers that the ionic reactant can protonate, as well as alkylate, *m*-toluidine, and that the latter must compete with other nucleophiles, either initially present as impurities in the gas or formed during its radiolysis. Comparable yields are obtained from other anilines, with the exception of *m*-anisidine, which undergoes N-alkylation at a remarkably low extent.

The ionic character of the alkylation is ensured by the presence of an effective radical scavenger (O$_2$), whose concentration is comparable to, or even higher than, that of the aromatic amine. Further support for the ionic nature of the alkylation is provided by the direct observation of the postulated charged intermediates in the appropriate CI mass spectra of the anilines, and by the effect of a gaseous base (NMe$_3$) on the yields. In fact, the absolute

(6) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* **1977**, *99*, 5027.

(7) Bone, L. I.; Futrell, J. H. *J. Chem. Phys.* **1967**, *47*, 4366.

Table II. Alkylation of Anilines by Gaseous Isopropyl Ions

substrate	system composition[a] (torr)		k_N/k_{ring}[b]	isomeric composition[c] of ring alkylated products (%)			absolute yields $G_{(+M)}$	
							nitrogen	ring
aniline[d]								
	C₃H₈: 720		0.25	74	~1	25		
	C₃H₈: 720	NMe₃: 10.0	0.46	70		30		
	C₃H₈: 100		0.31	63	~2	35		
m-toluidine								
	C₃H₈: 720		0.28	44	37	19	0.24	0.85
	C₃H₈: 720	NMe₃: 3.0	0.43	49	37	14	0.26	0.61
	C₃H₈: 720	NMe₃: 5.0	1.0	46	40	14	0.20	0.20
	C₃H₈: 100		0.43	39	34	27	0.61	1.43
m-anisidine								
	C₃H₈: 720		0.075	56	32	22	0.024	0.32
	C₃H₈: 720	NMe₃: 3.0	0.18	50	24	26	0.067	0.37
	C₃H₈: 720	NMe₃: 5.0	0.25				0.015	0.060
	C₃H₈: 100		0.22	42	28	30	0.19	0.85
m-fluoroaniline								
	C₃H₈: 720		0.11	36	26	38	0.063	0.58
	C₃H₈: 720	NMe₃: 3.0	0.28	40	26	34	0.23	0.82
	C₃H₈: 720	NMe₃: 5.0	0.49				0.094	0.19
	C₃H₈: 100		0.22	29	21	50	0.32	1.46
p-fluoroaniline								
	C₃H₈: 720		0.52	>90%			0.25	0.48

[a–d] See the corresponding footnotes for Table I.

Table III. Alkylation of Anilines by Gaseous Me₂F⁺ Ions

| substrate	system composition[a] (torr)		k_N/k_{ring}[b]	isomeric composition[c] of ring alkylated products (%)			absolute yields $G_{(+M)}$	
							nitrogen	ring
aniline[d]								
	MeF: 720		1.2	76		24		
	MeF: 720	NMe₃: 720	1.7	75		25		
	MeF: 100		0.86	72		28		
m-toluidine								
	MeF: 720		1.9	46	29	25	0.56	0.30
	MeF: 720	NMe₃: 3.0	3.8	46	27	27	0.65	0.17
	MeF: 100		1.7	45	24	32	0.96	0.58
m-fluoroaniline								
	MeF: 720		1.1	41	27	32	0.67	0.61
	MeF: 720	NMe₃: 3.0	3.8	56	25	19	0.61	0.16
p-fluoroaniline								
	MeF: 720		2.8	>90			2.1	0.75
	MeF: 720	NMe₃: 3.0	3.5	>90			1.6	0.46

[a–d] See the corresponding footnotes for Table I.

Table IV. Exothermicity of Proton Transfer from Et$^+$ and *i*-Pr$^+$ Ions to Substituted Anilines

aniline X–C$_6$H$_4$–NH$_2$ X	ΔH° value		
	from Et$^+$	from *i*-Pr$^+$	ref
H^a	−48	−27	10,11
m-Me^b	−50	−29	10, 11
m-OMe^b	−54	−33	10, 11
m-F^a	−45	−24	10, 11
p-F^a	−46	−25	12

^{a} Nitrogen protonation. ^{b} Ring Protonation.

overall yields of the products from ionic reactions can be expected to be depressed by NMe$_3$, to an extent increasing with its concentration, owing to the recognized ability of the base to intercept the alkylating cations. The data of Tables I–III, which portray the effects of NMe$_3$ upon the absolute yield, largely support the ionic nature of the alkylation process. In addition, sufficiently high concentrations of NMe$_3$ or other gaseous bases have been found to depress the yields of alkylated anilines below detection limit.

Intramolecular Selectivity. The relative rate of alkylation at the N atom and at the ring, expressed in Tables I–III by the apparent k_N/k_{ring} ratio, depends on the nature of the substrate and of the electrophile, as well as on the reaction conditions (pressure, presence and concentration of additives, etc.).

The Et$^+$ and *i*-Pr$^+$ cations lead to predominant ring substitution, while Me$_2$F$^+$ promotes predominant N-methylation. The most pronounced bias for the ring is observed in the ethylation and isopropylation of *m*-anisidine, the most basic substrate investigated. Taking into account the absolute yields, one can conclude that the low k_N/k_{ring} ratio reflects the inefficiency of N-alkylation, rather than an exceptionally high reactivity of the *m*-anisidine ring.

The presence of NMe$_3$ invariably enhances the *relative* rate of N-alkylation, to a degree which increases with the concentration of the additive. Small amounts of the latter (3 torr) enhance, in most cases, even the *absolute* yields of N-alkylated anilines, a mechanistically noteworthy feature if one considers that NMe$_3$ intercepts a considerable fraction of the alkylating cations. Finally, a decrease of total pressure of the irradiated gas leads to enhanced N-ethylation and isopropylation of all substrates investigated.

The isomeric composition of ring-substituted products, which appears less sensitive than the k_N/k_{ring} ratio to changes of pressure or to addition of NMe$_3$, is characterized by a high degree of selectivity. Thus, no substitution occurs at position 5 of *m*-toluidine, *m*-anisidine, and *m*-fluoroaniline, consistent with the lack of reactivity already reported for the meta position of aniline,[2] the alkylation of *p*-fluoroaniline occurs predominantly ortho to the activating NH$_2$ group, etc.

The isomeric composition of ethylated products obtained from the radiolysis of CH$_4$ and C$_2$H$_6$ is appreciably different. Since the internal energy of the Et$^+$ ions formed by different processes is known to affect to a minor extent the reactivity of the cation,[8] the different isomeric composition can probably be traced to the diverse quenching ability of the two gases, or to their different ability to "solvate" the Et$^+$ ions via the reversible formation of gaseous adducts.[9]

Discussion

The Alkylation Process. Formation of the reactants, Et$^+$, H_f° = 219 kcal mol^{-1},[10a] *i*-Pr$^+$, H_f° = 192 kcal mol^{-1},[10a] and Me$_2$F$^+$, H_f° = 161 kcal mol^{-1},[10b] from the radiolysis of appropriate precursors has been previously discussed.[2,5]

The general reactivity pattern of the cations, deduced from CI and radiolytic results, is outlined in Scheme I, which refers specifically to carbenium ions but can accommodate, with obvious modifications, Me$_2$F$^+$ as well.

(8) Solka, B. H.; Harrison, A. G. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *14*, 125.

(9) On the formation of Et$^+$·CH$_4$ adduct see: Field, F. H.; Beggs, D. P. *J. Am. Chem. Soc.* **1970**, *92*, 1585.

Scheme I. Reactions Promoted by the Attack of Gaseous Carbenium Ions, R$^+$, on Substituted Anilines^a
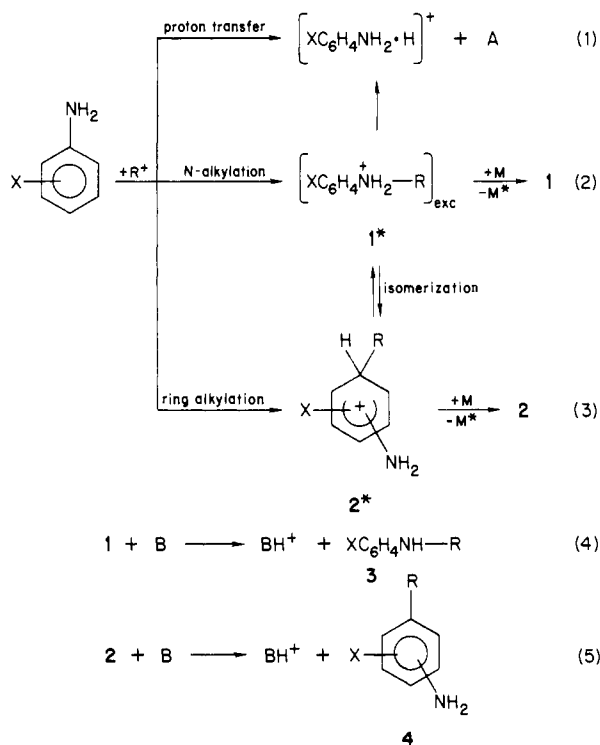
^{a} A indicates the conjugate base of R$^+$ and B is a gaseous base.

Proton transfer (reaction 1) from Et$^+$ and *i*-Pr$^+$ to anilines is exothermic, as shown in Table IV. Lack of the necessary data prevents analogous calculations for processes 2 and 3, whose highly exothermic character can nevertheless be inferred from the ΔH° values calculated for the corresponding reactions of aniline, −67 and −83 kcal mol^{-1}, respectively for methylation by Me$_2$F$^+$ and ethylation by Et$^+$.[2]

Ionic species having m/z ratios corresponding to those of all intermediates postulated in Scheme I are major peaks in the appropriate CI spectra of the anilines, and the abundance of the ions identifiable with the alkylated adducts **1** and **2** is observed to increase with the pressure to maximum values consistent with the absolute yields of alkylated products from radiolytic reactions. The comparison between the two set of experiments, if significant, is nevertheless of qualitative nature, owing to the lack of structural discrimination of the CI spectra and especially to the differences of the reaction conditions, 80 °C and 100–720 torr in the radiolytic experiments and 153 °C and <1 torr in the CI ion source.

Nitrogen vs. Ring Alkylation. Deducing the intramolecular selectivity of the gaseous cations from the isomeric composition of neutral products relies on the assumption that the latter is kinetically controlled.

In this connection, a preliminary problem arises, as the composition of the products is found to change appreciably with the reaction conditions.

The major change observed, i.e., the increase of the apparent k_N/k_{ring} ratio at low pressure, could conceivably be traced to isomerization processes, e.g., **2*** → **1**, affecting the population of excited intermediates from the exothermic reactions 2 and 3, and whose extent is expected to increase at lower pressures, owing to the reduced efficiency of collisional deactivation.

However, isomerization processes alone could not account for the increase of the *combined* yields of ring- and N-alkylated products observed at low pressure, and especially for the effects of added NMe$_3$, that should decrease the extent of isomerization, reducing the lifetime of **1** and **2** by a faster deprotonation. The experimental evidence shows instead that addition of NMe$_3$ affects the composition of products *in the same direction* as a decrease of the pressure. These observations speak against an exclusive or a major role of isomerization in determining the observed

changes of the products composition. In order to account for the peculiar combination of the pressure and NMe$_3$ effects, there is very little alternative but to suggest that, in the absence of a gaseous base of sufficient proton affinity (PA), the rate of formation of the neutral products is limited by the rate of the deprotonation steps 4 and 5. Under these conditions, in fact, the starting aniline is the only base whose strength is adequate to accomplish deprotonation of the alkylated adducts. However, the relevant proton transfer processes

$$1 + XC_6H_4NH_2 \rightarrow 3 + [XC_6H_4NH_2 \cdot H]^+ \qquad (4')$$

$$2 + XC_6H_4NH_2 \rightarrow 4 + [XC_6H_4NH_2 \cdot H]^+ \qquad (5')$$
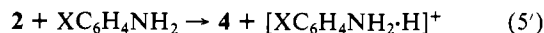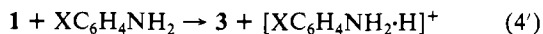
have different energetics, which could lead to a partial and biased conversion of the charged intermediates into the corresponding neutral products. Reactions 4' are appreciably endothermic, e.g., $\Delta H° \simeq 6$ kcal mol^{-1} when R = Me, X = H,[10a] since the basicity of the starting aniline is appreciably enhanced by N-alkylation. Reactions 5' are probably thermoneutral, or just slightly endothermic, since the basicity of the starting aniline is less affected, if at all, by ring alkylation. Thus, the PA of the methyl-substituted position of toluene has been calculated to be *lower* than,[14] or comparable to,[15] that of benzene, and the measured PA of *m*-toluidine, the most basic among the isomers from the standpoint of ring protonation, exceeds that of aniline by less than 2 kcal mol^{-1}.[11]

The low rate of processes 4' and, if to a minor degree, of processes 5' can account for the concurrent effects of added NMe$_3$ and of decreasing the pressure on the absolute yields of neutral products, in particular the N-alkylated ones. Addition of a base, such as NMe$_3$, whose PA exceeds those of alkylated anilines,[11] removes the bias in the deprotonation of 1 and 2, making both (4) and (5) equally fast and thus increasing the measured k_N/k_{ring} ratio. As to the absolute yields, the base has two opposite effects, since the conversion into neutral products of an larger fraction of the anilinium ions is counteracted by the interception of an increasing aliquot of the alkylating reactant. Consequently, the *absolute* yields of the N-alkylated neutral products can be expected to *increase* at low NMe$_3$ concentrations and to decline at higher concentrations, consistent with the peculiar experimental trend.

Lowering the pressure causes a larger fraction of the excited adducts 1* to retain sufficient internal energy to overcome the (modest) endothermicity of their deprotonation processes, thus increasing the absolute yields as well as the measured k_N/k_{ring} ratios.

The above considerations suggest that the closest correspondence between the isomeric composition of the neutral products and that of the charged intermediates can be expected from the systems at the highest pressure, in the presence of NMe$_3$. The diverse behavior of carbenium ions, characterized by an apparent k_N/k_{ring} ratio well below unity, and of Me$_2$F$^+$, leading to predominant nitrogen substitution, is traced to the ability of Et$^+$ and *i*-Pr$^+$ to protonate as well as alkylate the anilines, the competition between the two processes shifting in favor of protonation when attack occurs at the N atom. As a matter of fact, the reactions leading to the lowest k_N/k_{ring} ratios are characterized as well by low overall yields, showing that the carbenium ions largely undergo processes other than alkylation. This behavior is consistent with general kinetic trends, aptly epitomized by the hard–soft acid–base

principle, dictating predominant alkylation of the ring and protonation of the NH$_2$ group by Et$^+$ and *i*-Pr$^+$ cations. The simultaneous occurrence of alkylation and proton transfer complicates the reactivity pattern of carbenium ions,[17] obscuring the effects of the substituents.

Alkylation by Me$_2$F$^+$ is largely free of competitive protonation, and the isomeric composition of the products obtained at a high MeF pressure in the presence of NMe$_3$ is likely to reflect with reasonable accuracy the kinetically controlled abundances of 1 and 2. Such a contention is based on the effective collisional deactivation in MeF, a polar gas at atmospheric pressure (collision intervals <10^{-9} s), on the fast and unbiased deprotonation of 1 and 2 by NMe$_3$, and on earlier evidence against isomerization of gaseous anilinium ions, formed in a highly excited state by protonation of alkylated anilines.[2]

In conclusion, the reactivity of a purely alkylating cation toward gaseous anilines seems characterized by a distinct kinetic bias for the N atom.

The meager data[19] concerning the effect of substituents on the k_N/k_{ring} ratio in methylation do not allow a detailed discussion. Nevertheless, ring deactivation caused by an electron-withdrawing substituent is apparent in methylation of fluoroanilines.

Positional Selectivity. The isomeric composition of the ring-alkylated products appears to depend on two factors, namely the usual orienting effects of substituents and the enhanced reactivity of the positions ortho to an n-type substituent, a feature typical of gas-phase aromatic alkylation.[2,4] Operation of the first factor is discernible in aniline, *m*-toluidine, and *m*-anisidine, where no appreciable alkylation occurs at position 5, meta to the activating substituents, in *p*-fluoroaniline, where substitution occurs predominantly ortho to NH$_2$, etc. The second effect can be easily appreciated if one compares the extent of alkylation at position 2 of *m*-anisidine, ortho to *both* substituents, with that at the equally activated positions 4 and 6, ortho to *one* substituent. The same effect is observed in *m*-fluoroaniline.

In principle, the high reactivity of the positions ortho to the amino or methoxy group could be traced to their activating effect without invoking peculiar mechanistic features. In fact, the calculated electrostatic potential of aniline is characterized by a highly negative region associated with the N atom and attributed to the effect of its lone pair, which incidentally provides a reasonable explanation of the kinetic bias for N-alkylation.[18] A considerable extent of negative potential is located above the ring, affecting in particular the ortho positions, which could well justify their high reactivity, especially toward gaseous cations free of solvation and counterions. However this interpretation fails to account for the enhanced reactivity of the positions ortho to *deactivating* n-type substituents, such as F. Consequently, the present results are not inconsistent with the view that the *local* concentration of the electrophile at the ortho positions is enhanced by the preliminary formation of an adduct between the charged electrophile and the ambient substrate.[4a,b] A pictorial representation of the postulated species is provided by the following hypothetical structures

5   **6**   **7**
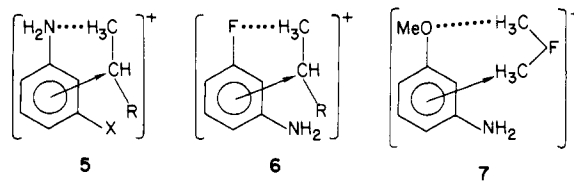
where the cation is envisaged as electrostatically (not covalently)

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bound to the n electrons of the substituent and to the π system of the ring, thus attaining a high degree of stability via charge delocalization.

The case for the formation of electrostatic adducts between aniline and gaseous carbenium ions is considerably strengthened by recent mass spectrometric observations. In fact, analysis of the high-energy dissociation spectra of the ions formed from the attachment of Et[+] to aniline has allowed Cooks and co-workers[3] to identify a *non-covalent* adduct, characterized as a weakly bound $C_6H_5NH_2 \cdot Et^+$ complex, regarded by the authors as a proton-bound dimer of aniline and ethylene.[20] The mass, properties, and stability (lifetime exceeding 10^{-6} s) of the observed adduct correspond to those expected for a species such as **5** (R, X = H), which differs from a conventional proton-bound dimer exclusively in the additional stabilization of the Et[+] cation arising from its electrostatic interaction with the π system.

Conclusion

The radiolytic and CI results suggest that attack of a purely alkylating cation, such as Me_2F^+, is characterized by an appre-

ciable kinetic bias for the N atom of anilines. The correlation between the apparent k_N/k_{ring} ratio and the absolute yields suggests that the N atom is also kinetically preferred by gaseous carbenium ions such as Et[+] and *i*-Pr[+], which, however, react predominantly as Brønsted acids, protonating the amino group.

As to positional selectivity, aside from the usual orienting effects of substituents, the alkylation of anilines displays a typical feature of gas-phase aromatic substitution, namely the enhanced reactivity of the ring positions ortho to an n-type substituent. The effect is traced to the increased local concentration of the electrophile caused by the preliminary formation of an electrostatic adduct with the anilines,[4a,b] in agreement with independent evidence from CID spectrometry.[3]

(20) A $[C_6H_5NH_2 \cdot Me_2F]^+$ adduct (of unknown structure) has been observed in the MeF CI spectrum of aniline, ref. 2.

Transient Absorption and Two-Step Laser Excitation Fluorescence Studies of Photoisomerization in 2-(2-Hydroxyphenyl)benzoxazole and 2-(2-Hydroxyphenyl)benzothiazole

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Abstract: The transient absorption spectra of 3-methylpentane solutions of 2-(2-hydroxyphenyl)benzoxazole (HBO) and -thiazole (HBT) exhibit transient absorption bands at 390–450 and 420–480 nm, respectively. The absorption band of HBO shows a single exponential decay (τ = 260 ns), while that of HBT shows a double exponential decay (τ = 9.4 and 53.3 μs) at room temperature. Both absorption bands may be attributable to their respective ground-state phototautomers generated by the intramolecular excited-state proton transfer and the fluorescence relaxation in HBO and HBT. The two-step laser excitation (TSLE) fluorescence spectra of the direct excitation of their transient absorption bands are identical with the large Stokes-shifted fluorescence spectra (λ_{max} 490 nm for HBO and 515 nm for HBT). The decay kinetics of the ground-state phototautomers by the transient absorption and the TSLE fluorescence variable delay technique suggest that there are two phototautomers in the ground state of HBT and only one phototautomer for HBO. Two types of ground-state phototautomers in HBT were tentatively ascribed to planar and twisted conformers about the C_1–C_7 bond between two aromatic moieties.

Recently we have investigated the reaction kinetics and dynamics of the proton transfer and isomerization in the ground and excited states of several hydrogen-bonding systems by the time-resolved fluorescence and transient absorption spectra and by the two-step laser excitation (TSLE) fluorescence, which has been developed by us as one of recent advances of laser spectroscopy.[1–4] The first laser excitation of the intra- and intermolecular hydrogen-bonding system induces the excited-state proton transfer followed by the fluorescent or nonfluorescent relaxation to the ground-state phototautomer. The second laser excitation of the

transient absorption band due to this ground-state phototautomer within the lifetime affords the two-step laser excitation fluorescence spectra and lifetime which should be identical with those of the ordinary fluorescence. Recently our investigations of the transient absorption and the TSLE fluorescence including the variable delay technique have revealed the intervention of the unexpectedly long-lived ground-state intermediate (phototautomer) in the excited-state isomerization and relaxation of 3-hydroxyflavone and 3-hydroxychromone in nonpolar solvents.[4,5] Recently, in the methanol solution of 7-hydroxyflavone (7-HF), two phototautomers have been suggested to be involved both in the ground and excited states by time-resolved TSLE fluorescence spectra and

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