Table VI. Summary of Analyses

	calcd, %		found, %	
compd	C	H	C	H
1a	84.42	7.82	84.59	7.85
1b	84.42	7.82	84.08	7.77
1d	84.71	9.35	84.77	9.42
1e	82.24	8.63	82.40	8.62
1f	82.24	8.63	82.10	8.81
2a	84.42	7.82	84.14	7.99
2b	84.42	7.82	84.55	7.47
2c	84.71	9.35	84.98	9.62
2d	84.71	9.35	84.86	9.22
3d[a]	84.71	9.35	84.92	9.13
3d[b]	84.71	9.35	84.69	9.34
2e	82.24	8.63	82.51	8.78
2f	82.24	8.63	82.57	8.84

[a] Higher melting isomer. [b] Lower melting isomer.

(28% yield) of another stereoisomer (a lowering melting isomer) of **3d**. Properties and analyses of the benzocyclobutenols **2a–f** and **3d** are listed in Tables V and VI.

Quantitative Photolyses. Irradiations were done at 25 °C, after degassing the solution in 17 × 120 mm Pyrex tubes by four freeze–thaw cycles below 10^{-2} mmHg, on a merry-go-round apparatus (Riko RH 400-10 W) by 313-nm light which was isolated from a 400-W high-pressure mercury lamp with a K_2CO_3 (1.3%)–K_2CrO_4 (0.13%) filter solution. The benzocyclobutenols produced were analyzed by HPLC. Methyl-2-naphthyl ketone was used as the internal standard. Two parallel runs for quantum yield measurements agreed within experimental error (±10%).

An authentic sample of 1,3-diisopropyl-10,10-dimethylanthrone (**4**) was prepared by extended irradiation (15 h) of a mixture of **2** (X = H) (750 mg) and acetophenone (2.02 g) in benzene (250 mL) under preparative photolysis conditions. After evaporation of the solvent, the residue was separated by column chromatography on silica gel (70 g). Elution with petroleum ether (2400 mL) and then with hexane (1200 mL) afforded successively 40 mg (9% yield) of **4**, acetophenone (1.7 g), and recovered **2** (X = H) (295 mg). The yield of **1** (X = H) was below 1% (by HPLC). Anthrone **4** resisted crystallization even after repeated purification with preparative TLC, but its NMR and IR spectra were close to those of 1-isopropylanthrone prepared by established methods:[21] NMR ($CDCl_3$) δ 8.19 (1 H, d with fine splitting, $J = 7.5$ Hz, $J' = 1.7$ Hz, 8-H), 7.64–7.33 (3 H, m, 5- to 7-H), 7.39 and 7.30 (each peak equals 1 H, d, $J = 1.8$ Hz, 2- and 4-H), 4.41 (1 H, sep, $J = 7$ Hz, 1-$CH(CH_3)_2$), 2.99 (1 H, sep, $J = 7$ Hz, 3-$CH(CH_3)_2$), 1.72 (6 H, s, 10-Me), 1.33 and 1.31 (each peak equals 6 H, d, $J = 7$ Hz, 1- and 3-$CH(CH_3)_2$); IR (neat) 1660 cm^{-1}) (C=O); high-resolution mass spectrum (calcd for $C_{22}H_{26}O$, *m/e* 306.1984), *m/e* 306.1986.

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Registry No. 1a, 84369-66-4; **1b**, 84369-67-5; **1c**, 76893-85-1; **1d**, 84369-68-6; **1e**, 84369-69-7; **1f**, 84369-70-0; **2a**, 84369-71-1; **2b**, 84369-72-2; **2c**, 84369-73-3; **2d**, 84369-74-4; **2e**, 84369-75-5; **2f**, 84369-76-6; *dl*-**3d**, 84369-77-7; *meso*-**3d**, 84369-78-8.

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(21) Ito, Y.; Inada, N.; Matsuura, T., unpublished results.

Aromatic Substitution in the Gas Phase. Intramolecular Selectivity of the Reaction of Aniline with Charged Electrophiles

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Abstract: The intramolecular selectivity of the electrophilic reactions of radiolytically formed $C_2H_5^+$, $i\text{-}C_3H_7^+$, $t\text{-}C_4H_9^+$, $(CH_3)_2F^+$, and CH_3CO^+ cations with aniline has been investigated in the gas phase at nearly atmospheric pressure. Under conditions of kinetic control of products, the reactivity of the N atom and of the aromatic ring is comparable, a mixture of ring- and N-substituted products being invariably formed in proportions that depend on the nature of the electrophile. The relative rate of N-substitution increases in the order: $C_2H_5^+ \simeq i\text{-}C_3H_7^+ < (CH_3)_2F^+ < t\text{-}C_4H_9^+ < CH_3CO^+$. The positional selectivity of the gaseous electrophiles, except CH_3CO^+, is characterized by predominant ortho substitution.

Aniline is a typical ambient nucleophile whose reactivity toward gaseous cations has been the subject of numerous recent studies, concerning in particular its preferred protonation site. The combination of various mass spectrometric techniques with theoretical methods[1-12] has led to the accurate determination of the proton affinity (PA) of aniline and to the conclusion that the amine is a nitrogen base in the gas phase as well as in solution. However, the stabilities of the ring- and N-protonated isomers are estimated to be very close, probably within a few kcal mol^{-1}.

These results, and the meager evidence available on ion-molecule reactions of aniline other than proton transfer,[13] bear exclusively on the *thermodynamic* aspects of the problem; e.g.,

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(12) Catalan, J.; Yanez, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 741.

(13) Collisional activation (CA) spectra of the ethylated products formed in the CH_4 chemical ionization (CI) of aniline, [Maquestiau, A.; Van Haverbeke, Y.; Mispreuve, H.; Flammang, R.; Harris, J. A.; Howe, I.; Beynon, J. H. *Org. Mass Spectrom.* **1980**, *15*, 144] suggest a ring-alkylated structure. However, rearrangement of the excited primary ions to more stable isomers may occur in the relatively long time (ca. 10^{-5} s) before structural assay by CA [Dymerski, P. P.; McLafferty, F. W. *J. Am. Chem. Soc.*, **1976**, *98*, 6070].

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the PA values are deduced from mass spectrometric data obtained under equilibrium conditions.

However, the gas-phase reactivity of aniline toward charged electrophiles presents *kinetic* aspects that deserve equally serious consideration in view of their general mechanistic relevance. One of the most interesting questions concerns the evaluation of the intramolecular selectivity of the electrophilic substitution, which reflects the competition of the n- and π-type centers of the ambient nucleophile for the free gaseous cation, unperturbed by the counterion and by a solvation shell.

We have applied to the problem the radiolytic technique previously used for the determination of the substrate and positional selectivity of other gas-phase reactions[14-17] and report in this paper the results concerning a few selected cations, i.e., the $C_2H_5^+$, i-$C_3H_7^+$, t-$C_4H_9^+$, $(CH_3)_2F^+$, and CH_3CO^+ ions.

Experimental Section

Materials. CH_4, C_3H_8, i-C_4H_{10}, CH_3F, CO, and O_2 were research grade gases from Matheson Co. Fluka AG was the source of anhydrous NMe_3 and aniline, and latter being freshly redistilled before use. The substituted aniline and acetophenone standards required for the analysis of the products by GLC were either obtained from Fluka AG or prepared according to established procedures.

Preparation and Irradiation of the Samples. The samples were prepared in 500-mL Pyrex bulbs according to procedures described in details elsewhere.[14] The irradiation was performed at 40 ± 2 °C in a 220 Gammacell from Nuclear Canada Ltd., to a total dose of 1.0 Mrad at a dose rate of 1.0 Mrad h^{-1}. Immediately before the irradiation the sealed Pyrex bulbs were allowed to stand at 40 °C in a thermostatic bath to allow aniline to reach a constant concentration in the gas phase.

Analysis of the Products. The irradiated vessels were cooled to the liquid-nitrogen temperature and a measured amount of methanol was added. They were then allowed to come to room temperature, and their walls were carefully washed with the solvent. The dilute solution obtained, containing the products formed in the irradiation, was then used for the GLC analyses by employing a Sigma 1 gas chromatograph from Perkin-Elmer Co., equipped with a FID unit and a Sigma 10 data station. The identity of the products was established from their retention volumes compared to those of authentic samples, and their yields were deduced from the areas of the corresponding elution peaks. The products were also analyzed by GLC-mass spectrometry by using a Model 5982A instrument from Hewlett-Packard Co. connected to a Model 5934A data system, or a ZAB Micromass instrument from VG Co. The identity of the substituted anilines formed was confirmed by comparing their mass spectra with those of authentic specimens. The following columns were used: (i) a 50-m-long, fused quartz capillary column, coated with Carbowax 20M deactivated methyl silicone (SP-2100) fluid, operated at 90 or 150 °C; (ii) a 6-foot-long, 0.25-in. i.d. glass column, packed with 10% Carbowax 20M + 2% KOH on 80–100 mesh Chromosorb W AW, operated at 120–150 °C.

Chemical Ionization Spectra. The aniline mass spectra were recorded by using the instrument in the chemical ionization mode (CI) and by measuring the source pressure with a Bourdon gage. Owing to the many sources of systematic errors and to the lack of an independent calibration based on kinetic data,[18] the nominal pressure readings should be considered exclusively for internal comparison purposes, being reproducible and consistent in the range 0.05–1.0 torr. The CI spectra were recorded with use of highly diluted ($>10^3$:1) gaseous solutions of aniline in the appropriate reactant gas.

Results

Nature and Yields of the Products. The simultaneous formation of ring- and N-substituted anilines occurs in all systems investigated. The ionic character of the substitution process involved is ensured by the presence of an effective radical scavenger (O_2), contained in the gas at concentrations even *higher* than those of aniline, and confirmed by the dramatic decrease of the substitution yields measured in the presence of gaseous bases, such as NH_3 or NMe_3, that are known to intercept the charged electrophiles and/or their precursors.

Owing to the specific purposes of this study and to considerable experimental difficulties,[19] no attempt has been made to measure the *absolute* yields of the substitution processes investigated, which however represent in general major reaction channels. An illustrative example is provided by the competition of aniline and toluene for the i-$C_3H_7^+$ ion, characterized by a ratio of the apparent rate constants of ca. 3:1 in favor of the amine. Since toluene is known to give high yields of cymenes,[20-22] this result, however approximate,[19] suggests that alkylation of the substrate is indeed a major reaction channel of the isopropyl ions in their attack on aniline.

Similar considerations apply to the other electrophiles investigated, with the exception of the t-$C_4H_9^+$ ion, which gives comparatively lower yields of alkylated anilines.

The observation finds a parallel in the trend observed in the chemical ionization (CI) mass spectra of aniline, which allow direct detection of the alkylated adduct ions, $(M + R)^+$, when methane ($R = C_2H_5$), propane ($R = C_3H_7$), and isobutane ($R = C_4H_9$) are used as the reactant gases.

Protonated aniline, $(M + H)^+$, is invariably the most abundant ion in the accessible pressure domain (<1 torr), while the $(M + R)^+/(M + H)^+$ intensity ratio depends on the nature of the reactant gas, its pressure, and the temperature of ion source. Under the same experimental conditions, the relative abundance of the alkylated adduct is *lower* in isobutane than in methane and propane CI spectra. As a typical example, the $(M + C_4H_9)^+/(M + H)^+$ ratio in i-C_4H_{10} at 180 °C under a *nominal* pressure of 0.50 torr is only 0.02, significantly lower than the $(M + C_2H_5)^+/(M + H)^+$ ratio of 0.15 in CH_4 and $(M + C_3H_7)^+/(M + H)^+$ ratio of 0.25 in C_3H_8 at the same pressure.

The CH_3F CI spectra of aniline are also of interest to the present discussion. The most abundant ion is the methylated adduct, $(M + CH_3)^+$, formed from the attack of the $(CH_3)_2F^+$ ions on aniline.

At a *nominal* CH_3F pressure of 0.20 torr, the following relative intensities were recorded: $(M + CH_3)^+ = 1.00$, $(M + H)^+ = 0.23$, $(M + CH_2F)^+ = 0.16$, $(M + (CH_3)_2F)^+ = 0.013$. Increasing the pressure causes a regular decline of the protonation and fluoromethylation channels, illustrated by the relative ionic intensities measured at 0.90 torr; e.g., $(M + CH_3)^+ = 1.00$, $(M + H)^+ = 0.15$, $(M + CH_2F)^+ = 0.06$, and $(M + (CH_3)_2F)^+ = 0.03$.

Intramolecular Selectivity. The composition of the gaseous systems investigated, the relative yields of the ring- and N-substituted anilines, the apparent $k_{(\text{nitrogen})}/k_{(\text{ring})}$ ratios, and the isomeric composition of the ring-substituted products are given in Table I. The most significant features of the results can be itemized as follows: (i) In no case does substitution occur exclusively at the n-type or at the π-type nucleophilic centers of aniline, a mixture of ring- and N-substituted products being formed from all reactions. Among carbenium ions, $C_2H_5^+$ and i-$C_3H_7^+$ promote predominant ring alkylation, while t-$C_4H_9^+$ displays a marked bias for N-alkylation. Dimethylfluoronium ion methylates at comparable rates the N atom and the ring, and acetylium ion is by far the most selective reagent, leading to predominant (>90%) formation of acetanilide.

(ii) The intramolecular selectivity of the gaseous electrophiles is affected, if to a different extent, by changes in the total pressure and by the presence of a strong base, e.g., trimethylamine. These effects are clearly discernible in the isopropylation, where N-alkylation is enhanced at low pressures and in the presence of

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[19] Owing to the low pressure of aniline at the irradiation temperature and its adsorption onto the glass walls, the *actual* gas-phase concentration of the amine is relatively low, and its measurement is plagued by an unusually high scatter (20–30%), affecting the determination of the *absolute* yields and the results of competition experiments.

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Table I. Intramolecular Selectivity in the Gas-Phase Alkylation and Acetylation of Aniline by Charged Electrophiles

system composition,[a] torr	relative yields of products,[b] %		$k_{\text{nitrogen}}/k_{\text{ring}}$	isomeric composition of $RC_6H_4NH_2$ products,[c] %		
	C_6H_5NHR	$RC_6H_4NH_2$		o-	m-	p-
		Ethylation, R = C_2H_5				
CH_4, 720	22.5 ± 1.2	77.5 ± 1.2	0.29	63	~2	35
CH_4, 720; NMe_3, 3.0	21.9	78.1	0.28	57	*d*	43
CH_4, 200	19.6 ± 2.9	80.4 ± 2.9	0.24	57	~1	42
		Isopropylation, R = i-C_3H_7				
C_3H_8, 720	20.0	80.0	0.25	74	~1	25
C_3H_8, 720; C_6H_5Me, 0.46	21.9	78.1	0.28	76	~1	23
C_3H_8, 720; NMe_3, 10.0	31.5	68.5	0.46	70	*d*	30
C_3H_8, 100	23.7	76.3	0.31	63	~2	35
C_3H_8, 100; NMe_3, 2.0	34.6	65.4	0.53	63	*d*	37
C_3H_8, 30	31.0	69.0	0.45	56	*d*	44
		Tert-Butylation, R = t-C_4H_9				
i-C_4H_{10}, 720	85.9 ± 0.2	14.1 ± 0.2	6.1	84	*d*	16
i-C_4H_{10}, 720; NMe_3, 20.0	86.1	13.9	6.2	69	*d*	31
		Methylation, R = CH_3				
CH_3F, 720	55.0 ± 3.0	45.0 ± 2.9	1.2	76	*d*	24
CH_3F, 720; NMe_3, 7.0	63.2	36.8	1.7	75	*d*	25
CH_3F, 100	46.2	53.8	0.86	72	*d*	28
		Acetylation, R = CH_3CO				
CO, 600; CH_3F, 100	94 ± 1	6 ± 1	15.7	34	*d*	66
CO, 184; CH_3F, 33	90	10	9.0	*e*	*e*	*e*

[a] All systems contained O_2, from 1 to 5 torr depending on the total pressure of the gas, and an amount of aniline slightly above that required to ensure saturation of the gas phase at 40 °C, namely 1.4 torr. [b] Standard deviation 5%, unless otherwise stated. [c] Standard deviation below 10%, except for the meta isomers, formed in traces. [d] Below detection limit, ca. 0.5%. [e] Not determined.

bases, and in acetylation, where a decrease of the CH_3F pressure increases the extent of ring substitution.

(iii) As to the positional selectivity of the ring substitution, the NH_2 group of aniline displays a powerful ortho/para orienting effect, all the reactions investigated yielding but traces of the meta isomer, frequently falling below detection limits. A bias for ortho orientations is apparent in isopropylation, methylation by $(CH_3)_2F^+$ ions, and tert-butylation, as shown by ortho:2para ratios above unity. The high proportion of the ortho isomer formed in *tert*-butylation is particularly significant, in view of the large steric requirements of the bulky cation.[23] Among the reagents investigated, only the CH_3CO^+ ion promotes predominant para substitution, characterized by a ortho:2para ratio well below unity.

Discussion

The Charged Reagent. All electrophiles have been obtained from the irradiation of suitable gaseous systems, in accordance with processes well established by extensive mass spectrometric and radiolytic studies. Thus, ethyl ions ($H_f° = 219$ kcal mol^{-1})[24] are formed[25] via the sequence

$$CH_4 \rightsquigarrow CH_3^+ + H + e \qquad (1)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad (2)$$

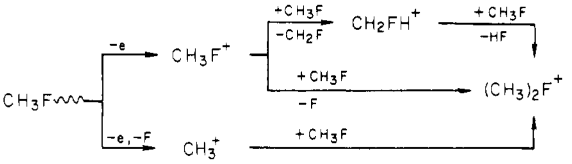
Isopropyl ions ($H_f° = 192$ kcal mol^{-1})[24] are obtained[26] from the radiolysis of propane, either directly

$$C_3H_8 \rightarrow i\text{-}C_3H_7^+ + H + e \qquad (3)$$

or via exothermic hydride ion abstraction from C_3H_8 by fragment ions, e.g.,

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + i\text{-}C_3H_7^+ \qquad (4)$$

Entirely analogous processes lead to the formation of *tert*-butyl ions ($H_f° = 164$ kcal mol^{-1})[24] from the radiolysis of isobutane, while irradiation of CH_3F yields $(CH_3)_2F^+$ ions ($H_f° = 161$ kcal mol^{-1}),[27] according to the reaction network[28]



(5)

Irradiation of CO/CH_3F mixtures yields gaseous acetylium ions ($H_f° = 156$ kcal mol^{-1})[29] via methylation of carbon monoxide by reactive fluorinated cations[30]

$$(CH_3)_2F^+ + CO \rightarrow CH_3F + CH_3CO^+ \qquad (6)$$

$$CH_3FH^+ + CO \rightarrow HF + CH_3CO^+ \qquad (7)$$

The charged electrophiles undergo a large number of unreactive collisions with the molecules of the bulk constituent(s) of the gas before a reactive encounter with aniline can occur. It is reasonable to assume that any ions produced in an excited state from their exothermic formation processes are collisionally deactivated and react with aniline essentially as thermal species.

The Substitution Process. The essential features of the attack of gaseous electrophiles E^+ on aniline, useful for a discussion of its intramolecular selectivity, can be outlined as follows. Two major reaction channels are allowed, i.e., proton transfer

$$E^+ + C_6H_5NH_2 \rightarrow C_6H_5NH_3^+ + A \qquad (8)$$

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(23) Even unsolvated, free t-$C_4H_9^+$ ions in the dilute gas state fail to alkylate toluene in the ortho positions [Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1973**, *95*, 5851].

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(27) Calculated from (a) the $H_f°$ value of CH_3F from Cox and Pilcher (Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970) and (b) its methyl cation affinity (cf: Beauchamp, J. L.; Holtz, D.; Woodgate, S. D.; Patt, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 2798).

(28) Speranza, M.; Pepe, N.; Cipollini, R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1179 and references therein.

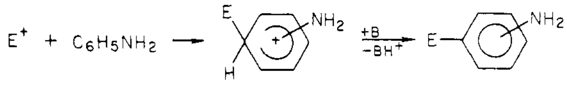
(29) Calculated from the $H_f°$ value of CH_2CO taken from ref 27a and its PA, taken from ref 24.

(30) Speranza, M.; Sparapani, C. *J. Am. Chem. Soc.* **1980**, *102*, 3120 and references cited therein.

where A denotes the conjugate base of E^+, and addition, either to the n-type center

$$E^+ + C_6H_5NH_2 \rightarrow \underset{\text{I}}{C_6H_5NH_2^+\text{-}E} \xrightarrow[-BH^+]{+B} C_6H_5NH\text{-}E \qquad (9a)$$

or to the π-type centers of aniline



(9b)

II

Proton transfer is exothermic from all E^+ reagents, with the possible exception of $(CH_3)_2F^+$, the $\Delta H°$ value of the reaction being ca. −48 kcal mol^{-1} from $C_2H_5^+$, ca. −27 kcal mol^{-1} from $i\text{-}C_3H_7^+$, and ca. −15 kcal mol^{-1} from $t\text{-}C_4H_9^+$ and CH_3CO^+.[24]

The lack of thermochemical data prevents in most cases similar calculations for the addition processes, which are undoubtedly highly exothermic, as shown by the $\Delta H°$ value of process 9a, −83 kcal mol^{-1} for the ethyl ion, −67 kcal mol^{-1} for the dimethylfluoronium ion, and $\leq$−50 kcal mol^{-1} for the acetylium ion.[31]

Proton transfer (eq 8) predominates at low pressures, as shown by the abundance of the $(M + 1)^+$ ion in the CI spectra of aniline recorded at pressures below 1 torr, using CH_4, of C_3H_8, and $i\text{-}C_4H_{10}$ reactant gases.

However, increasing the pressure in the ion source causes a significant increase of the abundance of $(M + E)^+$ adduct ions, and extrapolation of the trend to the much higher pressures typical of the radiolytic experiments suggests that processes 9a and 9b should become indeed quite significant, consistent with the yields of substituted anilines formed in most systems.

Intermediates I and II, excited by the exothermicity of their formation processes, can undergo fragmentation and/or isomerization, occurrence of the latter process being suggested by the changes in the composition of the products caused by a substantial decrease of the pressure in the irradiated systems.

However, taking into account the efficiency of collisional stabilization typical of gaseous environments at nearly atmospheric pressure and the evidence[14] concerning the extent of isomerization of comparably excited aromatic ions, it is reasonable to assume that the composition of products from the experiments carried out at the highest pressures reflects the population of isomeric intermediates I and II formed in the kinetically significant step of the substitution.

So that this central assumption can be verified, control experiments were carried out involving the irradiation of gaseous systems at atmospheric pressure, containing H_2 (D_2) as the bulk component, in the presence of small concentrations of *N*-isopropylaniline. In these systems, intermediate I can be expected to be formed in a highly excited state, owing to the large exothermicity,[24] 110 kcal mol^{-1}, of the proton transfer process,

$$H_3^+ + C_6H_5\text{-}NH\text{-}i\text{-}C_3H_7 \rightarrow H_2 + C_6H_5\text{-}NH_2^+\text{-}i\text{-}C_3H_7 \qquad (10)$$

yet no detectable formation of cumidines could be observed.

This result speaks against appreciable intramolecular isomerization of I into II in systems at atmospheric pressure, at least as far as isopropylated adducts are concerned.

Evidence against the occurrence of the inverse process, i.e., the II $\rightarrow$ I isomerization, is provided by a mass spectrometric study on the structure of the $(M + C_2H_5)^+$ adduct formed in the CH_4 CI of aniline.[13] In this investigation collisionally induced dissociation (CID) and mass analyzed ion kinetic energy spectrometry (MIKES) have been used to characterize the adducts as the ring-substituted isomers (II), consistent with the results of the present study. If one considers the high excitation level of the adduct from ethylation, the most exothermic among processes (eq 9), and the comparatively low pressures prevailing in the mass spectrometric experiments, the retention of structure II after the considerable time lag (10^{-5} s) before CID and MIKES structural assay shows that isomerization into ions I does not occur at any significant rate.

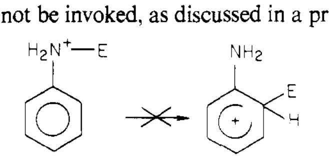
Nitrogen vs. Ring Competition. Evaluation of the intramolecular selectivity of charged electrophiles in their gas-phase attack on aniline was the major object of this study. The results show in the first place that the reactivity of the two nucleophilic centers of aniline, the N atom and the aromatic nucleus, must be comparable since a mixture of N- and ring-substituted products is formed in all cases. In a sense, this finding represents the kinetic counterpart of the comparable thermodynamic stability of the ring and N-protonated isomers of aniline in the dilute gas state.

The $k_{\text{Nitrogen}}:k_{\text{ring}}$ ratio typical of the different electrophiles increases in the order $C_2H_5^+ \simeq i\text{-}C_3H_7^+ < (CH_3)_2F^+ < t\text{-}C_4H_9^+ < CH_3CO^+$. Such a reactivity scale is not unexpected in the light of current generalizations. If one is willing to adopt the language of the HSAB theory, the situation is aptly described by the statement that the relative extent of N substitution increases according to the *hardness* of the gaseous acids, which is known to follow the order $C_2H_5^+ < i\text{-}C_3H_7^+ < t\text{-}C_4H_9^+ < CH_3CO^+$. In fact, soft acids can be expected to bind preferentially to the softest basic center of aniline, i.e., the aromatic ring, while hard acids bind preferentially to the hardest basic site in the aniline molecule, i.e., the N atom.

From the standpoint of the ring vs. N competition, the CH_3CO^+ ion is the most selective among the reagents studied, giving only ca. 6% of ring substitution. In general, reactions of charged electrophiles with aniline display a sharper discrimination between the n-type substituent and the ring than with other ambient aromatics, as shown by the *higher* proportions of ring-substituted products from the attack of $i\text{-}C_3H_7^+$ and CH_3CO^+ ions on phenol and anisole in systems at atmospheric pressure.[32,33]

Positional Selectivity. When the analysis is restricted to the ring positions, the present study shows that aniline undergoes almost exclusively ortho–para substitution by all reagents investigated, giving negligible, or barely detectable ($\leq$2%) yields of the meta isomers. Again, orientation is more selective than in comparably activated aromatics, as indicated by the lower yields of meta-substituted products from isopropylation, acetylation, and methylation of aniline than of phenol and anisole under comparable conditions.[33-35]

In analogy with the behavior of various substrates containing other n-type substituents, such as phenol, anisole, and chlorobenzene, aniline undergoes a high extent of ortho substitution, except by the CH_3CO^+ ion. While some kind of participation of the n-type center is apparently involved, the intramolecular isomerization of the anilinium ion I to the ortho-substituted arenium ion II cannot be invoked, as discussed in a previous section.[36]



(11)

II

A more reasonable explanation can be found assuming that, *in addition to the direct attack* on the ortho positions, ring substitution can occur following the preliminary formation of a sort of gaseous "chelate", as originally suggested by Attinà and Giacomello[37] to account for the orientation prevailing in the gas-phase

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[31] Calculated from the PA of methylaniline[24] and ethylaniline (cf.: Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504). The PA of acetanilide was estimated to be $\simeq$210 kcal mol^{-1}; the PA of acetamide was taken from Walder et al. (Walder, R.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.*, **1980**, *36*, 85). The data concerning neutral species were taken from ref 27a.

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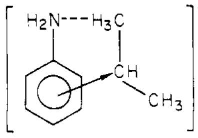
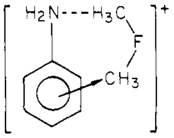
(36) Intramolecular isomerization involving the transfer of E^+ from I to the ortho position of another molecule of aniline is also very unlikely on account of the high extent of ortho substitution still prevailing in systems containing an excess (up to 20:1) of NMe_3 over aniline. In these systems, because of the competitive alkylation and protonation of Me_3N, the absolute yields of alkylanilines were dramatically lowered.

isopropylation of chlorobenzene. The "chelate" is characterized by the electrostatic interaction of the cation with both the n electrons of the substituent and the π system of the ring, e.g.,



III



IV

Such electrostatic complexes can be conceivably formed by $C_2H_5^+$, i-$C_3H_7^+$, t-$C_4H_9^+$, CH_3CO^+, and even by $(CH_3)_2F^+$, which is probably characterized by a planar structure similar to that of a carbenium ion.[28]

While the "chelates" III formed by carbenium ions cannot be distinguished on the grounds of their m/e ratios from the anilinium ions I or the arenium ions II, it is tempting to assign the "chelate" structure IV to the $(M + (CH_3)_2F^+)$ ion actually observed, if with low abundances, in the CH_3F CI spectra of aniline.

The electrostatic "chelate" can evolve into different ionic species, i.e., protonated aniline, the N-substituted ion I, or the arenium ion II, whose relative proportions depend on the nature, the structure, and the charge distribution of the electrophile involved. Thus, the "assisted" ring-substitution mechanism can be expected to contribute little to ortho acetylation, since CH_3CO^+ would tend to bind preferentially to the hard N base of aniline. Consequently, the relatively low proportions of ortho-acetylated isomers from aniline, as well as from phenol and anisole,[32,34] are likely to reflect essentially the rate of the *direct* attack on the ortho positions of the ring.

Conclusion

It is customary to close the discussion of any given gas-phase aromatic substitution with a comparison involving the corresponding reaction occurring in solution. Such comparison is difficult in the present case because of the meagerness of data on the reactivity of aniline in substitution processes occurring in solution, whose study is complicated by the basic properties of the amine. In fact, the electrophilic species behaving as Brønsted or Lewis acids interact with the amino group, changing the very nature of the substrate and preventing the kinetic study of the free amine.[37] As a consequence, most of the data from solution-chemistry experiments refer to *derivatives* of aniline, such as *N,N*-dimethylaniline or acetanilide, whose reactivity is of course entirely different from that of the free amine.

In conclusion, perhaps is not unwarranted to claim that the results of this gas-phase study provide the first data on the intramolecular selectivity of the electrophilic attack on *free* aniline, irrespective of the reaction environment, at least as far as substitution by electrophilic carbon is concerned.

Acknowledgment. The authors acknowledge the financial support from Italian National Research Council (CNR), the experimental help of C. Sparapani and A. DiMarzio, and the useful discussions with P. Giacomello.

Registry No. C_6H_5Me, 108-88-3; NMe_3, 75-50-3; $C_2H_5^+$, 14936-94-8; i-$C_3H_7^+$, 19252-53-0; t-C_4Hg^+, 14804-25-2; CH_3CO^+, 15762-07-9; Me_2F^+, 64710-12-9; CH_4, 74-82-8; C_3H_8, 74-98-6; i-C_4H_{10}, 75-28-5; CH_3F, 593-53-3; CO, 630-08-0; O_2, 7782-44-7; aniline, 62-53-3.

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Infrared Laser Induced Heterogeneous Reactions: 2-Propanol with Cupric Oxide

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Abstract: The heterogeneous decomposition of 2-propanol vapor in the presence of CuO solid has been induced by infrared laser radiation. The reaction produces both acetone by dehydrogenation and propene by dehydration. Yields and branching ratios are quite sensitive to experimental variables. Experiments have been carried out in one of two basic configurations: either the CuO surface is parallel to the laser beam as it passes through the cell or the CuO surface is perpendicular to and intercepts the laser beam. Reaction occurs in both geometries although much more readily in the latter. Branching ratios from 0.02 to 6.0 have been observed.

Introduction

Infrared multiphoton absorption by polyatomic molecules to induce chemical reactions has been demonstrated to be a fairly general phenomenon.[1] In a typical experiment, a gas-phase sample at relatively low pressure is placed in the beam path of an infrared laser and excited to some high vibrational level of the electronic ground state. If sufficient energy has been deposited in the sample, chemical reaction can occur. It is possible to exert some control over the reactivity of the sample by controlling irradiation variables. Choices for these parameters, like laser power or frequency, in turn control which components of a complex mixture absorb radiation and the number of photons they absorb.[2] Nevertheless, the resulting homogeneous decomposition usually leads to products predominantly via the lowest energy reaction pathway of the absorbing species.[3]

In principle, the chemical versatility of this activation method could be substantially enhanced through the use of heterogeneous gas/solid reaction channels.[4–6] This added variable, a catalytic

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