Benzene as a Selective Chemical Ionization Reagent Gas[†]

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Dilute mixtures of C_6H_6 or C_6D_6 in He provide abundant $[C_6H_6]^{++}$ or $[C_6D_6]^{++}$ ions and small amounts of $[C_6H_7]^+$ or $[C_6D_7]^+$ ions as chemical ionization (CI) reagent ions. The C_6H_6 or C_6D_6 CI spectra of alkylbenzenes and alkylanilines contain predominantly M^{++} ions from reactions of $[C_6H_6]^{++}$ or $[C_6D_6]^{++}$ and small amounts of MH^+ or MD^+ ions from reactions of $[C_6H_7]^+$ or $C_6D_7]^+$. Benzene CI spectra of aliphatic amines contain M^{++} , fragment ions and sample-size-dependent MH^+ ions from sample ion-sample molecules reactions. The C_6D_6 CI spectra of substituted pyridines contain M^{++} and MD^+ ions in different ratios depending on the substituent (which alters the ionization energy of the substituted pyridine), as well as sample-size-dependent MH^+ ions from sample ion-sample molecule reactions. Two mechanisms are observed for the formation of MD^+ ions: proton transfer from $[C_6D_6]^{++}$ or charge transfer from $[C_6D_6]^{++}$ to give M^{++} , followed by deuteron transfer from C_6D_6 to M^{++} . The mechanisms of reactions were established by ion cyclotron resonance (ICR) experiments. Proton transfer from $[C_6H_6]^{++}$ is rapid only for compounds for which proton transfer are exothermic and charge transfer is endothermic. For compounds for which both charge transfer and proton transfer are exothermic, charge transfer is the almost exclusive reaction.

INTRODUCTION

One advantage of chemical ionization (CI) mass spectrometry in qualitative and quantitative analyses is the potential to tailor the chemistry of the reagent-gas system to ionize the sample in a particular manner. A judicious choice of reactant ions will provide selectivity in the types of compounds which will or will not be ionized and, therefore, which will or will not be detected in the analysis. In general, one uses thermochemical criteria for the choice of reactant ions for the analysis of certain classes of compounds: endothermic ionmolecule reactions are expected to have small (or zero) rate constants and consequently to give low (or zero) CI sensitivities for certain classes of compounds; and simple exothermic ion-molecule reactions (like proton, hydride and charge transfer) are expected to have large (and similar) rate constants and hence high CI sensitivities for other classes of compounds.¹

One such low-energy, selective reactant ion is the benzene molecular ion, $[C_6H_6]^{+*}$. Ion-molecule reaction studies indicated that the high-pressure mass spectra of benzene were relatively simple, containing predominantly $[C_6H_6]^{+*}$ and $[(C_6H_6)_2]^{+*}$, whose relative abundances were strongly dependent on the temperature and pressure of benzene.²⁻⁴ The ionization energy of benzene (9.25 eV) is in the middle of the range of ionization energies of alkylbenzenes, olefins and amines;

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and below the ionization energies of alkanes, cycloalkanes and aliphatic alcohols, esters, ethers and ketones.⁵⁻⁷ Consequently, one would expect $[C_6H_6]^+$ to be a selective CI reactant ion, perhaps particularly useful for the identification and quantification of unsaturated compounds in complex mixtures.

Early work in gas chromatography/chemical ionization mass spectrometry (GC/CIMS) showed the selectivity of $[C_6H_6]^{+*}$ for the detection of unsaturated esters in mixtures with saturated esters.⁸ Selectivity among substituted benzene derivatives was related to ionization energies: compounds with ionization energies greater than *IP*(benzene) gave essentially no product ions and compounds with ionization energies below that of benzene gave similar sensitivities and spectra which contained essentially only M⁺⁺ ions.⁸ Fragment ions from $[C_6H_6]^{+*}$ charge transfer were noted with a few compounds (including a surprisingly abundant $[M - H]^+$ ion, 25–35% of M⁺⁺, with toluene) and a small amount of $[M + D]^+$ was reported from the reaction of $[C_6D_6]^{+*}$ with aniline. However, the dominant reaction of $[C_6H_6]^{+*}$ mas simple charge transfer to give M⁺⁺ ions.⁸ Simple charge transfer was reported between $[C_6H_6]^{+*}$ and several aromatic hydrocarbons with rate constants that were approximately constant.^{9,10}

Benzene has been used as a CI reagent gas for the detection of polymer pyrolysis products¹¹ and in atmospheric pressure chemical ionization (APCI) of polychlorobiphenyls and polymer decomposition products.^{12,13} Chlorobenzene ions ($[C_6H_5Cl]^{+*}$) have also been used for selective detection and quantification of aromatic hydrocarbons in complex mixtures: only simple charge transfer was reported with these compounds.¹⁴

As indicated above, simple charge transfer to give M^{+} ions is the dominant process which has been

Received 29 May 1990 Accepted 4 July 1990 reported for ion-molecule reactions of $[C_6H_6]^{+\cdot}$; however, a wide variety of classes of compounds has not been investigated. Some of our initial benzene CI experiments with strongly basic compounds showed abundant $[M + H]^+$ ions. An unusual reaction between $[C_6H_6]^{+\cdot}$ and a few alkyl iodides to form arenium ions ($[RC_6H_6]^+$) has been reported previously.^{15,16}

We report here some recent work on the ion chemistry of $[C_6H_6]^+$ as well as some thermochemical consequences and analytical applications of this ion chemistry.

EXPERIMENTAL

The instrumentation used for the GC/CIMS experiments has been discussed recently.¹⁷ The experiments were generally performed with 0.06 Torr of benzene from the manifold and 0.24 Torr of helium from the gas chromatograph at 200 °C. No significant differences in spectra were noted when the benzene was mixed with helium prior to entering the source. Both C_6H_6 (Fisher) and C_6D_6 (Aldrich, 99.5%) were used. Under these conditions the dominant ions were the benzene ions; however, some fragment ions and higher mass ions were observed. Typical ionic distributions at high pressures are shown in Table 1. The larger than isotopic ratio for I(m/z 79)/I(m/z 78) with C_6H_6 and the I(m/z 86)/I(m/z 84) ratio with C_6D_6 indicated the presence of ~8% of $[C_6H_7]^+$ or $[C_6D_7]^+$ among the reactant ions.

The compounds used in this study were obtained from several commercial sources and gave no indications of significant impurities. Approximately 0.50 m solutions in benzene were prepared for the GC/CIMS experiments and the chromatographic conditions and components were adjusted to ensure separation of all of the compounds. Approximately 0.1 μ l samples were injected into the gas chromatograph. Ratios of ionic abundances in these spectra were taken as the ratios of the integrated areas of ion currents across the chromatographic peaks, after appropriate background corrections had been made.

Short-term reproducibilities of the relative areas (several determinations during one day) were $\pm 4-8\%$. Longer-term reproducibilities were 10-15%. There were no systematic variations in relative sensitivities with changes in electron current, multiplier gain or sample size. The ionic distributions for some of the compounds did vary significantly with sample size.

The ion cyclotron resonance (ICR) experiments were performed with an Extrel Fourier transform ICR mass spectrometer (FTMS-2000) at approximately 300 K. Calibration factors for the correction of ionization gauge pressures were taken from the literature or from a correlation between ionization gauge factors and calculated polarizabilities.^{18,19} The two reagents were introduced through different inlet systems and ions were produced by a 5 μ s electron pulse (approximately 10 eV, 10 μ A). Time-dependence studies were performed on some mixtures using sufficiently low-energy electrons to produce only M⁺⁺ ions. In other experiments all ions except those of the desired *m/z* ratio were ejected from

Table 1. Distribution of positive ions in He/benzene*

		Relative al	Relative abundance	
m/z	Formula	С ₆ Н ₆	C ₆ D ₆	
39	C ₃ H ₃	5	_	
42	C ₃ D ₃	_	6	
51	C₄H₃	1		
52	C₄H₄	2	—	
54	C₄D₃	—	1	
56	$C_4 D_4$		3	
77	C ₆ H₅	1		
78	C ₆ H ₆	100	—	
79	¹² C ₅ ¹³ CH ₆ + C ₆ H ₇	15	_	
82	C ₆ D ₅		1	
83	C ₆ D₅H	—	2	
84	C ₆ D ₆	—	100	
85	¹² C ₅ ¹³ CH ₆	—	7	
86	C ₆ D ₇	—	8	
91	C ₇ H ₇	1	_	
98	C ₇ D ₇	—	1	
115	C₂H7	3	—	
116		1	—	
121			1	
122	C ₉ D ₇	_	3	
128	C ₁₀ H ₈	4	—	
129	C ₁₀ H ₉	2	—	
136	C ₁₀ D ₈	_	4	
138	C ₁₀ D ₉	—	2	
154	$C_{12}H_{10}$	1	—	
155	$C_{12}H_{11}$	4		
156	$C_{12}H_{12}$	1	—	
164	$C_{12}D_{10}$	—	1	
166	C ₁₂ D ₁₁		3	
^a Averaç	ge of ten spectra. p(C ₆ H _e	b) or $p(C_6D_6)$	= 0.06 Torr	
p(He) =	0.24 Torr. <i>t</i> = 210 °C.			

the source and time-dependence studies were made on the relative ionic abundances. Other ICR experiments were performed by transferring the ions of the desired m/z ratio from the source to the analyzer region of the FTMS and observing the ionic abundances as functions of time after the addition of a pulse of sample. The kinetic data were analyzed using a simplex non-linear least-squares fitting routine.²⁰

RESULTS AND DISCUSSION

In agreement with previous experiments,⁸⁻¹⁰ rapid charge transfer was observed between $[C_6H_6]^{+*}$ or $[C_6D_6]^{+*}$ and several compounds with ionization energies lower than that of benzene: olefins, alkylbenzenes, polynuclear aromatic hydrocarbons and oxygen- and nitrogen-containing substituted benzenes. Sensitivities for several C_6 to C_{12} alkanes, a few alkylcyclopentanes and alkylcyclohexanes, acetophenone, benzaldehyde and other compounds with ionization energies greater than 9.25 eV were less than 1% of the sensitivity for ethylbenzene. Fast reactions were also observed between $[C_6H_6]^{+*}$ and several amines.

The dominant product ions in the benzene CI spectra of aromatic and olefinic hydrocarbons were M^{+*} ions, as expected. For alkylbenzenes, however, the C₆H₆ CI spectra contained ratios of integrated ion currents, $I([M + 1]^+)/I(M^{+*})$, which were always slightly larger than expected from the isotope ratio and small amounts of $[M + 2]^+$ were observed using C₆D₆. In addition, small amounts of $[C_7H_7]^+$ and higher fragment ions were observed in the high-pressure experiments.

Proton-transfer reactions from $[C_6H_6]^{+*}$ or $[C_6D_6]^{+*}$ to the alkylbenzenes are endothermic with either of the literature values for $PA(C_6H_5)$ and should not occur.^{21,22} No MH⁺ or MD⁺ ions (<1% of the abundance of M^{+*} ions) were detected in ICR experiments from the reactions of $[C_6H_6]^{+*}$ or $[C_6D_6]^{+*}$ with the alkylbenzenes. The MH⁺ and MD⁺ ions in the high-pressure CI spectra probably result from proton (deuteron) transfer reactions from the small amounts of $[C_6H_7]^+$ ($[C_6D_7]^+$) present as reactant ions.

The small amounts of $[C_7H_7]^+$ ions at m/z 91 in these spectra (corrected for the small ion currents at m/z91 in the high-pressure mass spectrum of benzene, itself) decreased to essentially zero with increasing partial pressure of C_6H_6 in the mixtures used for the CI experiments. In addition, ICR experiments on reactions of $[C_6H_6]^{++}$ with alkylbenzenes gave no detectable amounts of $[C_7H_7]^+$ ions (<1% of the abundance of M^{++}). The low-abundance ions at m/z 91 formed in these and in the earlier experiments⁸ probably result from direct electron ionization of the aromatic hydrocarbons.

The benzene CI spectra of *tert*-butylbenzene and related compounds contain low abundances of $[M - CH_3]^+$ ions. The abundances of these ions do not approach zero with increasing benzene pressure in the CI experiments as does the abundance of ions at m/z 91. However, single-source ICR experiments on $C_6D_6/tert$ -butylbenzene mixtures using low-energy electrons gave exclusively charge transfer $([M - CH_3]^+ < 1\%$ of the abundance of M^+). The small amounts of $[M - CH_3]^+$ ions in the benzene CI spectra result from dissociative proton-transfer reactions of $[C_6H_7]^+$ ($[C_6D_7]^+$).

The dominant ionic product in the CI mass spectra of *tert*-butylbenzene and related compounds using highenergy protonating agents in the *tert*-butyl ion at m/z 57,^{23,24} and not the $[M - CH_3]^+$ ion, as is observed in the present experiments using the weaker acid, $[C_6H_7]^+$. This striking difference is easily explained, however, from the thermochemistry of the two competing reactions,

$$[C_{6}H_{7}]^{+} + C_{6}H_{5}C(CH_{3})_{3}$$

$$- \bigcup_{c} [C_{6}H_{5}C(CH_{3})_{2}]^{+} + C_{6}H_{6} + CH_{4} \quad (1a)$$

$$- \bigcup_{c} [(CH_{3})_{3}C]^{+} + 2C_{6}H_{6} \quad (1b)$$

Reaction (1a) is 46 kJ mol⁻¹ exothermic and reaction (1b) is 29 kJ mol⁻¹ endothermic.⁷

The high-pressure benzene CI mass spectra of aniline and some ring- and N-substituted anilines (all with ionization energies lower than that of benzene⁵⁻⁷ contain predominantly M^{+*} ions. The sensitivities (or rate constants for charge transfer of $[C_6H_6]^{+*}$) for these compounds are very similar to that for ethylbenzene.

Small amounts of MH^+ (MD^+) (a few per cent of M^{++}) were detected in the high-pressure C_6H_6 (C_6D_6) CI mass spectrum of aniline: amounts which are consistent with proton-transfer reactions from the small

amounts of $[C_6H_7]^+$ ($[C_6D_7]^+$). ICR experiments gave no evidence for proton transfer from $[C_6H_6]^{++}$ to aniline, since replicate time dependence experiments on C_6H_6 /aniline mixtures gave values for the I(m/z 94)/I(m/z 93) ratio which were indistinguishable from that calculated from the normal isotopic abundances and independent of the extent of reaction $(0.070 \pm 0.003 \text{ and} 0.069 \pm 0.010)$. The constancy of the I(m/z 94)/I(m/z 93)ratio in these ICR experiments also shows that $[C_6H_5NH_2]^{++}$ does not react with aniline to give $[C_6H_5NH_3]^+$. Other ICR experiments on C_6D_6 /aniline mixtures also indicated exclusively charge transfer since $[C_6H_5NH_2D]^+/[C_6H_5NH_3]^+ < 0.01$.

These results may be different from the earlier observations of small amounts of protonated aniline in benzene CI mass spectra;⁸ however, they are in agreement with thermochemical expectations. The ionization energy of aniline, 7.69 ± 0.02 eV, is significantly less than the ionization energy of benzene, 9.245 ± 0.005 eV;⁵ hence, the charge-transfer reaction is exothermic and is expected to be rapid. The proton affinity of aniline (877 kJ mol⁻¹)⁷ is either less than the proton affinity of the phenyl radical (887 ± 8 kJ mol⁻¹)²¹ or just slightly larger (870 ± 29 kJ mol⁻¹).²² Therefore, one may reasonably expect predominance of charge transfer over proton transfer.

In addition, the reactions of aniline ions with aniline and with benzene,

$$[C_{6}H_{5}NH_{2}]^{+} + C_{6}H_{5}NH_{2} \rightarrow$$

$$[C_{6}H_{5}NH_{3}]^{+} + [C_{6}H_{5}NH]^{*} (2)$$

$$[C_{6}H_{5}NH_{2}]^{+} + C_{6}H_{6} \rightarrow$$

$$[C_6H_5NH_3]^+ + [C_6H_5]^* \quad (3)$$

are endothermic by approximately 42 and 159 kJ mol⁻¹, respectively, and should not be observed under these conditions.^{7,21}

Similarly, high-pressure C₆H₆ CI mass spectra 4-fluoroaniline of 2-chloroaniline and contain $I(MH^+)/I(M^{+*})$ ratios slightly higher than the expected isotopic values, but consistent with small amounts of proton transfer from the low abundance of $[C_6H_7]^+$ ions. ICR experiments also showed essentially only charge transfer between $[C_6H_6]^+$ and 2-chloroaniline and no subsequent reactions of $[ClC_6H_4NH_2]^+$ with either C_6H_6 or 2-chloroaniline, since the isotopic ratio $I(m/z \ 128)/I(m/z \ 127)$ (m/z $127 = {}^{35}Cl$ isotope of M⁺ for 2-chloroaniline) was independent of the extent of reaction and not significantly different from the calculated isotopic value. This exclusive formation of M⁺⁺ ions in benzene CI is in agreement with expectations from known or estimated thermochemical data on the halogenated anilines: charge transfer is exothermic and proton transfer and other reactions leading to MH⁺ ions are endothermic.

The thermochemistry for the reactions of $[C_6H_6]^+$ with *N*-alkylanilines is somewhat different, as indicated by the example of *N*-methylaniline,

$$[C_{6}H_{6}]^{+} + C_{6}H_{5}NHCH_{3}$$

$$- \int [C_{6}H_{5}NHCH_{3}]^{+} + C_{6}H_{6} \qquad (4a)$$

$$- \int [C_{6}H_{5}NH_{2}CH_{3}]^{+} + [C_{6}H_{5}]^{-} \qquad (4b)$$

The charge transfer reaction is exothermic, as noted for all of the other anilines, $(\Delta H^0 \text{ (Reaction (4a))} = -186 \text{ kJ})$; however, the proton transfer reaction, (4b), unlike proton transfer to aniline or the halogenated anilines, is *exothermic*: $\Delta H^0 \text{ (Reaction 4b)} = -25 \pm 8 \text{ kJ}$ or $-42 \pm 29 \text{ kJ}$, depending on the value chosen for the proton of the phenyl radical.^{7,21,22} Consequently, for *N*-alkylanilines, both proton transfer and charge transfer are exothermic and thermochemically possible. The possible subsequent reactions of M⁺⁺ to give MH⁺,

$$[C_6H_5NHCH_3]^{+} + C_6H_6 \rightarrow$$

$$[C_6H_5NH_2CH_3]^{+} + [C_6H_5]^{-} (5)$$

$$[C_6H_5NHCH_3]^{+} + C_6H_5NHCH_3 \rightarrow$$

$$[C_6H_5NH_2CH_3]^+ + [C_6H_5NCH_3]^{\circ}$$
 (6)

are both endothermic and should not occur.^{7,21,22}

The C_6H_6 CI mass spectra of N-methyl- and Nethylaniline contain almost exclusively M⁺ ions; however, the $I([M + 1]^+)/I(M^{+*})$ ratio was always slightly larger than the expected isotope ratio and the C_6D_6 CI spectra contained small amounts (5–10%) of $[M + 2]^+$ ions. These observations are consistent with proton transfer from small amounts of $[C_6H_7]^+$ or $[C_6D_7]^+$ ions. Reaction of $[C_6D_6]^+$ with Nmethylaniline under ICR conditions indicated that charge transfer was the exclusive process since the ratio of ionic abundances, $I(m/z \ 109)/I(m/z \ 107)$ or $I(MD^+)/I(M^{+*})$, was < 0.01. In addition, the $I(m/z \ 108)/$ $I(m/z \ 107)$ or $I(MH^+)/I(M^{+*})$ ratio was independent of the extent of reaction and not distinguishable from the calculated isotope ratio in ICR experiments on mixtures of C_6H_6 or C_6D_6 with N-methylaniline. Consequently, reactions (4b), (5) and (6) do not occur.

The relative sensitivities for benzene CI with several substituted pyridines are approximately the same, but different ionic products are observed, depending on the substituent, and therefore, on the ionization energy of the compound. For some halogenated pyridines, for which proton transfer is exothermic and charge transfer is endothermic, only proton transfer is observed. For these compounds (see Table 2) M^{+*} ions are present at less than 0.5% of the abundance of MH⁺ ions.

For other substituted pyridines for which both proton transfer and charge transfer are exothermic, both M⁺ and MH⁺ ions are observed. However, M⁺ ions are the dominant product and the $I(MH^+)/I(M^{+*})$ ratios increase with increasing sample size across a chromatographic peak in the C₆H₆ CI spectra. Both MH^+ and MD^+ ions are observed in the C_6D_6 CI spectra. The $I(MH^+)/I(M^{+*})$ ratio increases with increasing sample size across the chromatographic peak in the C_6D_6 CI spectra, and the $I(MD^+)/I(MH^+)$ $+ M^{+}$ ratio is independent of sample size, but increases with increasing C_6D_6 pressure. ICR experiments (Fig. 1) confirmed the sequence of reactions with three substituted pyridines (P): 2-methylpyridine (2picoline); 2-methoxypyridine; and 2,6-dimethylpyridine (2,6-lutidine).

$$[C_6 D_6]^{+} + \to P^{+} + C_6 D_6 \tag{7}$$

$$P^{+} + [C_6H_6] + C_6D_6 \to PD^+[C_6D_5]^{-}$$
 (8a)

$$P^{+} + P \rightarrow PH^{+}(P - H)$$
] (8b)

Table 2. Charge transfer vs. proton transfer

	Heat of reaction (kJ)*		Relative	
Compound	СТ	PT	reaction rate	
C₅H₅NH₂	-151	+8	PT/CT < 0.01	
C ₆ H ₅ NHCH ₃	-184	-25	PT/CT < 0.01	
2-CH ₃ C ₅ H ₄ N	-21	-59	PT/CT < 0.01	
2-CH₃OC₅H₄N	-50	-46	PT/CT < 0.01	
2,5-(CH ₃) ₂ C ₅ H ₃ N	-38	-67	PT/CT < 0.01	
4-CIC ₅ H ₄ N	+59 (+25) ^b	-25	CT/PT < 0.01	
3-BrC₅H₄N	+50	-13	CT/PT < 0.01	
2-BrC₅H₄N	+42	-13	CT/PT < 0.01	
n-C ₄ H ₉ NH ₂	- 79	-33	PT/CT < 0.02	
t-C ₄ H ₉ NH ₂	-92	-42	PT/CT < 0.02	
2-CIC₅H₄N	+42 (-25)	-13	CT/PT < 0.01	
3-CIC₅H₄N	+13 (-13)	-13	CT/PT < 0.01	
		⊢≁₩⁺⁺⊣	C ₆ H ₆ (CT	
	[C ₆ H ₆]' + M	L ⊳ MH⁺	+ [C ₆ H ₅]' (PT	

^a Heat of formation data taken from Refs 5, 6, 7 and 30.

^b Values in parentheses taken from Ref. 7 and are considered as inaccurate or inapplicable.

The ICR experiments shown in Fig. 1 give no indications of any significant amounts of direct proton transfer from $[C_6D_6]^+$ to 2-methylpyridine and similar experiments give no evidence of direct proton transfer to 2-methoxypyridine or to 2,6-dimethylpyridine. The $I(MH^+)/I(MD^+)$ ratios are independent of the extent of reaction and the $I(MH^+)/I(M^{+*})$ and $I(MD^+)/I(M^{+*})$ ratios extrapolate essentially to zero at zero time as one expects from the consecutive reactions presented above.

 $0.75 \\ 0.75 \\ 0.5 \\ 0.25 \\ 0.25 \\ 0.05 \\ 0.05 \\ 0.1 \\ 0.15 \\ 0.25 \\ 0.25 \\ 0.25 \\ 0.25 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.3 \\ 0.25 \\ 0.3 \\ 0.3 \\ 0.25 \\ 0.3 \\$

Figure 1. ICR kinetic plots for a $C_6 D_6/2$ -methylpyridine mixture. $p(C_6 D_6) = 3 \times 10^{-7}$ Torr; $p(CH_3 C_5 H_4 N) = 3 \times 10^{-7}$ Torr; $T \sim 300$ K. All ions except $[C_6 D_6]^{++}$ ejected from the source and ionic distributions monitored as functions of time. Normalized to 1.00 at each time. ¹³C isotopes included in calculations of total ion current, but not for the individual ions in the figure. Relative intensities at m/z 94 and 95 corrected for ¹³C isotopes.

$$[C_6D_6]^{++} + CH_3C_5H_4N \rightarrow [CH_3C_5H_4N]^{++} + C_6D_6$$
 (a)

$$[CH_{3}C_{5}H_{4}N]^{+} + CH_{3}C_{5}H_{4}N \rightarrow [CH_{3}C_{5}H_{4}NH]^{+} + [C_{6}H_{6}]^{-} (b)$$

$$[CH_{3}C_{5}H_{4}N]^{+} + C_{6}D_{6} \rightarrow [CH_{3}C_{5}H_{4}ND]^{+} + [C_{6}D_{5}]^{-} (c)$$

 $k_a = 3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_b = 1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_c = 0.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Alkylpyridines can be distinguished from isomeric alkylanilines by the presence of abundant MH^+ (MD) ions in the C_6H_6 (C_6D_6) CI mass spectra of the alkylpyridines.

Figure 2 shows typical C₆H₆ CI spectra of two alkylamines. For these and other alkylamines the abundances of MH⁺ ions, as percentages of the total sample ionization, increased with increasing sample size across a chromatographic peak. These observations indicated that the MH⁺ ions were formed by sample ion-sample molecule reactions. The C₆D₆ CI spectra of these amines also contained MH⁺ ions whose abundances increased with increasing sample size across a chromatographic peak, indicating sample ion-sample molecule reactions. Small amounts of MD⁺ ions are also observed which result mostly from proton transfer from the small amounts of $C_6 D_7$]⁺ ions present in the highpressure benzene spectrum. Although both charge transfer and proton transfer are exothermic, charge transfer is the dominant process.

Additional ICR experiments showed that the reactions with *tert*-butylamine are the following:

$$[C_{6}H_{6}]^{+} + t - C_{4}H_{9}NH_{2} \rightarrow$$

$$[(CH_{3})_{2}C = NH_{2}]^{+} + CH_{3}^{*} + C_{6}H_{6} \quad (9)$$

$$[(CH_{3})_{2}C = NH_{2}]^{+} + t - C_{4}H_{9}NH_{2} \rightarrow$$

 $[t-C_4H_9NH_3]^+ + (CH_3)_2C=NH$ (10)

The rate constant for direct proton transfer from $[C_6H_6]^{+}$ to $t-C_4H_9NH_2$ is less than 2% of the rate constant for charge transfer. The presence of $[t-C_4H_9NH_3]^+$ in ICR and high-pressure CI experiments indicates that the rate constant for reaction (10) is relatively large, of the order of 10^{-10} cm³ molecule⁻¹ s⁻¹. This observation is inconsistent with the current values⁷ for $PA((CH_3)_2C=NH) = 925$ kJ mol⁻¹ and $PA(t-C_4H_6NH_2) = 924$ kJ mol⁻¹, but is in agreement with the earlier observation that reaction (10) does occur.²⁵



Figure 2. C_6H_6 CI mass spectra of butylamines. (a) $t-C_4H_9NH_2$; (b) $n-C_4H_9NH_2$.

The dissociative charge-transfer reaction, (9), is expected to be rapid because $AP([CH_3)_2C=NH_2]^+$, $t-C_4H_9NH_2) = 8.89 \text{ eV}.^{26}$ The absence of M⁺⁺ ions indicates that the excited ions produced by charge transfer decompose too rapidly to be stabilized by collisions, even at the pressures of the CI experiments.

Similar ICR experiments confirm that the dominant reactions with *n*-butylamine are the following:

$$[C_{6}D_{6}]^{++} + n - C_{4}H_{9}NH_{2} \rightarrow n - C_{4}H_{9}NH_{2}]^{++} + C_{6}D_{6} \quad (11)$$
$$[n - C_{4}H_{9}NH_{2}]^{++} + n - C_{4}H_{9}NH_{2} \rightarrow [n - C_{4}H_{9}NH_{3}]^{+} + [C_{4}H_{10}N]^{+} \quad (12)$$

Both high-pressure benzene CI and ICR experiments indicate that dissociative charge transfer occurs,

$$[C_{6}H_{6}]^{+} + n \cdot C_{4}H_{9}NH_{2} \rightarrow$$
$$[CH_{2}=NH_{2}]^{+} + [C_{3}H_{7}]^{*} + C_{6}H_{6} \quad (13)$$

However, using current heat of formation data, the dissociative charge-transfer reaction, (13), is *endothermic* by 33 kJ if $[n-C_3H_7]^*$ is formed and by 21 kJ if $[s-C_3H_7]^*$ is formed.^{7,21,26} No other experiments give indications of significant amounts of reactions of excited benzene ions. The relatively abundant MH⁺ ions indicate that the rate constant for reaction (12) is large, in agreement with previous kinetic data on ion-molecule reactions in amines.²⁷

The isomers, sec-butylamine and isobutylamine, are easily distinguished from each other and from the two previously discussed butylamines. The benzene CI mass spectra for sec-butylamine contain 44. m/z $[CH_3CH=NH_2]^+$, as the base peak, a very low abundance M⁺, and variable amounts of MH⁺. The benzene CI mass spectra for isobutylamine contain m/z = 30, $[CH_2 = NH_2]^+$, as the base peak, an abundant M⁺, and variable amounts of MH⁺. Benzene CI may be as useful as low-voltage electron ionization for the identification and characterization of aliphatic amines.28

The data of Table 2 show a striking variation in the ratio of charge transfer to proton transfer for the reactions of $[C_6H_6]^+$ with several compounds: exothermic proton transfer is observed only if charge transfer is endothermic. For six of the first ten compounds in this list and for eight other compounds (not in this list²⁹) for which both proton transfer and charge transfer are exothermic, charge transfer is the almost exclusive reaction. This dominance of charge transfer is not sensitive to the relative exothermicities of the two processes, as indicated by a comparison of the pyridines and butylamines. This observation was unexpected to us, since the relative sensitivities in benzene CI for proton transfer to the halogenated pyridines are approximately twothirds of the relative sensitivity for charge transfer to ethylbenzene.

Two compounds in Table 2 are apparently exceptions to this observation. Several replicate ICR and highpressure CI experiments were performed with 2- and 3chloropyridine to verify that charge transfer was the almost exclusive reaction. The high-pressure CI experiments gave only trace amounts of M^{++} , $I(M^{++})/I(MH^{+}) < 0.005$. The ICR experiments also showed only deuteron transfer and no detectable charge transfer between $[C_6D_6]^{+*}$ and 2- and 3-chloropyridine, with a $I(M^{+*})/I(MD^{+})$ ratio of less than 0.01. The reaction sequence of rapid charge transfer followed by rapid deuteron transfer, which is shown in Fig. 1 for a $C_6D_6/2$ -methylpyridine mixture, does not occur. The charge-transfer reactions between the molecular ions of 2-chloropyridine or 3-chloropyridine with neutral C_6D_6 were very fast.

The recently estimated low values for the ionization energies of $2-\text{ClC}_5\text{H}_4\text{N}$ and $3-\text{ClC}_5\text{H}_4\text{N}$ of 9.00 eV and 9.10 eV, respectively, were obtained from the onsets of the photoelectron bands.^{7,30} However, the vertical ionization energies (or at least the maxima in the first

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photoelectron band) are 9.24 eV for benzene, 9.69 for 2-ClC₅H₄N and 9.38 for 3-ClC₅H₄N.³¹ Either these threshold values for ionization energies (and hence heats of formation of the ions) are incorrect or the vertical ionization energies are more important than the threshold values in determining the charge-transfer rate constants.

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