Studies of Acid-Base Ion-Molecule Chemistry Using Ion Cyclotron Resonance Techniques and Photoelectron Spectroscopy

Thesis by

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ABSTRACT

Thermochemical properties related to molecular basicity are examined for series of substituted amines and nitriles using ion cyclotron resonance techniques and photoelectron spectroscopy. Proton affinities PA(B), defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, and adiabatic ionization potentials, IP(B), are determined. In previously examined series of bases linear relationships have been established between proton affinities and adiabatic first ionization potentials which correspond to removal of an electron from a lone pair localized at the site of protonation. Nitrile proton affinities are found to be linearly related not to the first CN π ionization potentials but rather to the adiabatic N lone pair σ ionization potentials at higher energy. This relationship provides a useful chemical means for the assignment of bands in photoelectron spectra; specific examples are considered and assigned. Homolytic bond dissociation energies $D(B^+{-}H)$ are obtained using the relation $PA(B) - D(B^+{-}H) = IP(H) - IP(B)$. Systematic effects of substitution on PA(B), $D(B^+{-}H)$, and IP(B) are identified and discussed in terms of the intrinsic factors affecting molecular basicity.

Ion cyclotron resonance techniques are also used to measure relative heterolytic bond dissociation energies $D(R^+{-}Br^-)$ in the gas phase for a series of alkali cations, alkyl carbenium ions, acyl cations, and cyclic halonium ions. $D(R^+{-}Br^-)$ for adamantyl cation is found to be less than for *tert*-butyl cation. A proton affinity for norbornene of $D(B-H^+) = 198.2 \pm 2$ kcal/mol is determined from which $D(R^+-Br^-) = 146.8 \pm 2.3$ kcal/mol is calculated for norbornyl cation, 14 kcal/mol less than for cyclo-pentyl cation. Relative enthalpies of solvation are estimated via appropriate thermochemical cycles by combining the gas phase data with heats of ionization in fluorosulfuric acid. The results show that solvation enthalpies are related to ion size with smaller ions being better solvated. Relative stabilities of cyclic bromonium ions are the same in the gas phase and solution. Stability increases with increasing ring size and in the three-membered rings with methyl substitution. However, solvent has an appreciable effect in attenuating the observed range.

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CHAPTER I

INTRODUCTION

Investigations of the acid-base properties of substances have been an important and continuing part of the science of chemistry from its beginnings. The ideas of Boyle, Arrhenius, Brønsted, Lowry, and Lewis among others have contributed to the qualitative understanding of acid-base concepts.[1] More recently advances have centered on quantitative approaches, and considerable sophistication has developed both in the technology for and correlation of measurements of acid-base behavior.[3]

Association of an acid and a base, reaction 1, may be considered as the simplest possible acid-base process. The energetics of reaction 1 reflect the properties of both the acid A and the base B. Transfer of a reference acid between bases, reaction 2, may be used to provide a measure of relative basicity, and transfer of a reference base between acids, reaction 3, may be used to provide a measure of relative acidity.

$$A + B \rightleftharpoons AB \qquad (1)$$

$$B_1 + AB_2 \rightleftharpoons B_1AB_2 \rightleftharpoons AB_1 + B_2 \qquad (2)$$

$$A_1B + A_2 \rightleftharpoons A_1BA_2 \rightleftharpoons A_1 + A_2B \qquad (3)$$

The advent of ion cyclotron resonance (ICR) techniques has fostered the study of reactions 2 and 3 in the gas phase in cases where A and/or B are ionic species.[3-5] Of particular utility are ion cyclotron double resonance techniques[4] which allow the positive identification of the reactants leading to a given product. The results are useful not only in that they allow the examination of intrinsic (gas phase) factors affecting acid-base properties but also because they may be combined with heats of ionization in solution to yield a quantitative thermodynamic analysis of the energetics of ion solvation.[11-15]

The most widely studied reference acid has been the proton. Proton affinity, PA(B), is defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, equation 4. The homolytic bond dissociation energy $D(B^+{-}H)$ defined by equation 5 is related to PA(B) and the adiabatic ionization potentials IP(H) and IP(B), equation 6, by the thermochemical cycle 7.

$$BH^+ \rightarrow B + H^+ \qquad \Delta H = D(B{-}H^+) \equiv PA(B) \tag{4}$$

$$BH^+ \rightarrow B^{+\cdot} + H\cdot \qquad \Delta H = D(B^+{-}H) \tag{5}$$

$$PA(B) - D(B^+{-}H) = IP(H) - IP(B) \tag{6}$$

$$\begin{tikzcd}
BH^+ \arrow[r, "PA(B)"] \arrow[d, "D(B^+-H)"'] & B + H^+ \\
B^{+\cdot} + H\cdot & B + H\cdot \arrow[l, "IP(B)"'] \arrow[u, "IP(H)"']
\end{tikzcd} \tag{7}$$

Determination of equilibrium constants for proton transfer between two bases, reaction 8, using ICR techniques,[5-11] high pressure mass spectrometry (HPMS),[16] or flowing afterglow (FA)[17, 18]

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+ \qquad \Delta H = PA(B_1) - PA(B_2) \qquad (8)$$

yields accurate (± 0.2 kcal/mol) relative free energies of protonation. Temperature dependence is observed to be slight, confirming the expectation that ΔS for reaction 8 is small and can be accounted for by changes in symmetry numbers.[16] A relative scale of PA(B) has been established by examining reaction 8 for a large number of organic and inorganic bases and calibrated by reference to a variety of species for which absolute values of PA(B) may be derived from appearance potential measurements or ionization potentials of the corresponding free radicals.[7-12, 16, 19] An important test of the validity of this relative scale of proton affinities is the consistency of the results obtained by the various techniques. The range of proton affinity values from below PA(H_2O) to above PA(Et_3N) has been examined both by ICR and HPMS.[7, 12, 16, 19] The results are largely in good agreement. In a few cases particular reactions have been studied by both ICR and FA with good agreement.[9, 18]

The systematic variation of molecular properties related to proton basicity in series of primary, secondary, and tertiary amines,[6, 7, 16] substituted pyridines,[8, 20] and the methyl phosphines[11] has been examined. In particular it has been demonstrated that for homologous series, for example the primary amines, molecular ionization potentials IP(B) and homolytic bond dissociation energies D(B^+–H) are linear functions of PA(B).[6, 7] Stabilization of the conjugate acid BH^+ or radical cation $B^{+\cdot}$ by resonance interactions or hyperconjugation may lead to important exceptions.[7, 10, 11]

Other examples of reactions 2 and 3 have been applied to the investigation of the acid-base properties of molecules. Proton transfer between anions, reaction 2, $A = H^+$, $B = B^-$, has been widely used to examine acidities.[5, 21] Reference acids other than the proton have also been investigated in reaction 2 including Li^+, K^+, and NO^+.[22-25] Comparison of the different scales of basicity afforded by these results is of particular interest.[23] The transfer of a reference base between two acids, reaction 3, $A = R^+$, $B = X^-$, has been used to provide a measure of carbocation stabilities.[26-28] Relative stabilities of alkyl and fluoroalkyl carbenium ions with respect to the reference base F^-[26] and alkali cations, alkyl carbenium ions, acyl cations, and cyclic halonium ions with respect to the reference base Br^-[22, 27] have been studied using ICR techniques. Studies of relative carbenium ion stabilities with respect to the reference base H^- using HPMS have also been reported.[28]

This thesis represents various contributions to the continuing studies outlined above. Some of this work has already appeared in the literature and is not included here, Table I. Chapter II examines the proton affinities and ionization potentials of nitriles. Chapter III examines the effects of alkyl and fluoro substitution on the acid-base properties of amines. And Chapter IV reports studies of carbocation stabilities with respect to the reference base Br^-.

Table I. Bibliography of Published Work Related to this Thesis

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1. Relationship of Nitrogen Lone Pair Interactions to Thermodynamic Parameters Associated with Amine Basicities
   Ralph H. Staley and J. L. Beauchamp
   J. Am. Chem. Soc., **96**, 1604-6 (1974)

2. Nucleophilic Attack on Protonated Oxiranes in the Gas Phase. Identification of the $C_2H_5O^+$ Isomeric Ion Corresponding to Protonated Ethylene Oxide
   Ralph H. Staley, Reed R. Corderman, Michael S. Foster, and J. L. Beauchamp
   J. Am. Chem. Soc., **96**, 1260-61 (1974)

3. Basicities and Ion-Molecule Reactions of the Methylphosphines in the Gas Phase by Ion Cyclotron Resonance Spectroscopy
   Ralph H. Staley and J. L. Beauchamp
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4. Relative Stabilities of Carbonium Ions in the Gas Phase and Solution. A Comparison of Cyclic and Acyclic Alkylcarbonium Ions, Acyl Cations, and Cyclic Halonium Ions
   Robert D. Wieting, Ralph H. Staley, and J. L. Beauchamp
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5. Reactions of Alkali Ions with Organic Molecules in the Gas Phase. Low Energy Pathways for Carbonium Ion Formation and Novel Methods for Generating Alkali Ion Complexes with π- and n-Donor Bases

   Robert D. Wieting, Ralph H. Staley, and J. L. Beauchamp

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6. Equilibrium Studies of Gas Phase Ion-Molecule Reactions. Ion Cyclotron Resonance Results for the Reaction $CO_2H^+ + CH_4 \rightleftharpoons CH_5^+ + CO_2$

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7. Intrinsic Acid-Base Properties of Molecules. Binding Energies of Li^+ to π- and n-Donor Bases

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CHAPTER II

Relationship Between Orbital Ionization Energies and Molecular Properties. Proton Affinities and Photoelectron Spectra of Nitriles

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Abstract: Proton affinities, defined for a base B as the heterolytic bond dissociation energy $D(B-H^+)$ for removing a proton from the conjugate acid BH^+, are determined for a series of nitriles using ion cyclotron resonance techniques. Photoelectron spectra of nitriles are also obtained. In previously examined series of bases, linear relationships have been established between proton affinities and adiabatic first ionization potentials which correspond to removal of an electron from a lone pair localized at the site of protonation. Nitrile proton affinities are found to be linearly related not to the first CN π ionization potentials but rather to the adiabatic N lone pair σ ionization potentials at higher energy. This relationship provides a useful chemical means for the assignment of bands in photoelectron spectra; specific examples are considered and assigned. A linear relationship is also found between nitrile (RCN) and primary amine (RNH_2) proton affinities for a range of substituents R. The results are discussed in terms of the intrinsic factors affecting molecular basicity.

The opportunity to elucidate intrinsic properties related to molecular basicity has been afforded by the recent development of techniques for the study of ion-molecule reactions which allow accurate quantitative determination of molecular binding energies to cationic reference acids in the gas phase.[2-13] While Li^+, K^+, NO^+, and other species are now also being studied,[11-13] the most widely studied reference acid has been the proton.[2-10] Proton affinity, PA(B), is defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, equation 1. The homolytic bond dissociation energy $D(B^+{-}H)$ defined by equation 2 is related to PA(B) and the adiabatic ionization potentials IP(H) and IP(B), equation 3, by the thermochemical cycle 4.

$$BH^+ \rightarrow B + H^+ \qquad \Delta H = D(B{-}H^+) \equiv PA(B) \qquad (1)$$

$$BH^+ \rightarrow B^{+\cdot} + H\cdot \qquad \Delta H = D(B^+{-}H) \qquad (2)$$

$$PA(B) - D(B^+{-}H) = IP(H) - IP(B) \qquad (3)$$

$$\begin{tikzcd}
BH^+ \arrow[r, "PA(B)"] \arrow[d, "D(B^+-H)"'] & B + H^+ \\
B^{+\cdot} + H\cdot & B + H\cdot \arrow[l, "IP(B)"'] \arrow[u, "IP(H)"']
\end{tikzcd} \qquad (4)$$

Determination of equilibrium constants for proton transfer between two bases, reaction 5, using ion cyclotron resonance (ICR) techniques[2-9] or high pressure mass spectroscopy[10]

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+, \quad \Delta H = PA(B_1) - PA(B_2) \qquad (5)$$

yields accurate (± 0.2 kcal/mol) relative free energies of protonation. Temperature dependence is observed to be slight, confirming the expectation that ΔS for reaction 5 is small and can be accounted for by changes in symmetry numbers.[10] A relative scale of PA(B) has been established by examining reaction 5 for a large number of organic and inorganic bases and calibrated by reference to a variety of species for which absolute values of PA(B) may be derived from appearance potential measurements.[9]

The systematic variation of molecular properties related to basicity in series of primary, secondary, and tertiary amines,[2-4, 10] substituted pyridines,[5, 14] and the methyl phosphines[6] has been examined. In particular it has been demonstrated that for homologous series, for example the primary amines, molecular ionization potentials IP(B) and homolytic bond dissociation energies $D(B^+-H)$ are linear functions of PA(B).[3, 4] Stabilization of the conjugate acid BH^+ or radical cation $B^{+\cdot}$ by resonance interactions or hyperconjugation may lead to important exceptions.[4, 7]

In the amine and phosphine series examined to date, the lone pair orbital involved in bond formation to the proton in process 1 corresponds to the lowest ionization potential of the molecule.[4, 6] The present work uses ICR techniques and photoelectron spectroscopy (PES) to examine a series, the nitriles, in which this is not the case, the CN π orbital having the lowest ionization potential.

Experimental

ICR instrumentation and techniques used in these studies have been previously described in detail.[6, 15, 16] Photoelectron spectra were obtained using an instrument built in the Caltech shops employing a 127° electrostatic analyser. Spectra were calibrated using the $^2P_{3/2}$ and $^2P_{1/2}$ lines of an internal argon standard. The capillary discharge lamp was operated at 2 torr of helium for He(I) spectra and at 0.1 torr for He(II) spectra. Both the ICR and PES experiments were conducted at room temperature. Chemicals were used as obtained from readily available commercial sources except for degassing at liquid nitrogen temperature.

Results and Discussion

The gas phase ion chemistry of HCN, MeCN, and various alkyl nitriles has been previously investigated in detail using ICR.[17-19] Electron impact at energies just above the first ionization potential in these systems produces parent ion which reacts to give protonated parent, for example reaction 6. Dimer formation, reaction 7, while

$$CH_3CN^{+\cdot} + CH_3CN \rightarrow CH_3CNH^+ + CH_2CN\cdot \qquad (6)$$

$$MH^+ + M \rightarrow MHM^+ \qquad (7)$$

significant at higher pressures ($> 3 \times 10^{-5}$ torr) was slow at the pressures which were typically used to study reaction 5 (about 3×10^{-6} torr). No other reactions of the protonated parent ions were observed. Proton transfer in mixtures of nitriles with various bases was found to be fast so that equilibrium constants for reaction 5 could be readily measured.

In cyanogen chloride and bromide, the parent ions $XCN^{+\cdot}$ were the predominant ions observed in the 70 eV mass spectrum and react with their respective neutrals to give $X(CN)_2^+$, reaction 8, X = Cl, Br. Similar processes have been observed in the ion chemistry of alkyl halides where, for X = Br, I, formation of dialkyl halonium ions XR_2^+ occurs directly by reaction 9.[20] Double resonance investigation of

$$XCN^{+\cdot} + XCN \rightarrow X(CN)_2^+ + X\cdot \qquad (8)$$

$$RX^{+\cdot} + RX \rightarrow XR_2^+ + X\cdot \qquad (9)$$

the halogen isotopic contributions to the $X(CN)_2^+$ product[20] indicate nearly equal contributions from the ionic and neutral reactants. In studies of the proton transfer reactions of these cyanogen halides in mixtures with other bases, a third gas such as methane was sometimes added to increase the abundance of protonated species.

Mixtures which were examined by ICR for the present work and derived PA values are given in Table I. Proton affinities which appear in Tables I and II for HCN, $CH_2(CN)_2$, Cl_3CCN, $ClCH_2CN$, MeCN, and various reference molecules were available from studies of a large number of organic and inorganic bases, details of which will be published separately.[9]

The proton affinity results reflect changes in polarizability and inductive effects with the substituent group R. Comparison of proton

Table I. Reaction Mixtures Studied and Derived PA(RCN) Values[a]

RCN	Reference Base	PA(B)[b]	$\delta_R \Delta G^\circ$[c]	PA(RCN)[d]
c-C_3H_5CN	HCO_2n-Bu	193.4	0.67 ± 0.2	194.1
i-PrCN	HCO_2Et	192.1	0.95 ± 0.2	193.1
n-BuCN	HCO_2Et	192.1	0.71 ± 0.2	192.8
n-PrCN	HCO_2Et	192.1	0.71 ± 0.2	192.3
n-PrCN	Me_2O	191.4	0.84 ± 0.2	192.2
n-PrCN	EtCN	191.0	1.18 ± 0.2	192.2
EtCN	n-PrCN	192.3	-1.18 ± 0.2	191.1
EtCN	HCO_2Et	192.1	-1.08 ± 0.2	191.0
EtCN	i-PrCHO	191.6	-0.22 ± 0.2	191.4
EtCN	Me_2O	191.4	-0.27 ± 0.2	191.1
EtCN		189.8	0.88 ± 0.2	190.9
EtCN	EtCHO	189.0	1.88 ± 0.2	190.9
$CH_2{=}CHCN$		189.8	-1.20 ± 0.2	188.8
$CH_2{=}CHCN$	EtCHO	189.0	-0.20 ± 0.2	188.8
$CH_2{=}CHCN$	MeCN	188.0	0.76 ± 0.2	188.8
$ClCH_2CH_2CN$	MeCN	188.0	-0.87 ± 0.2	187.1
BrCN	AsH_3	182.0	0.3 ± 0.5	181.5
BrCN	HCO_2H	181.5	-0.3 ± 0.7	180.8
BrCN	F_2CHCH_2OH	179.0	>1.5 ± 0.5	>180.5
ClCN	F_2CHCH_2OH	179.0	-0.5 ± 0.5	178.5
ClCN	HCHO	176.0	>1.5 ± 0.5	177.9

Table I. (Continued)

[a] All data in kcal/mol.

[b] Proton affinities of the reference bases from reference 9: all data is relative to PA(NH_3) = 202.3 ± 2.0 kcal/mol. Relative to NH_3, reported values are estimated to be accurate to ± 1 kcal/mol, with higher accuracy for smaller differences.

[c] Free energy differences for reaction 5 derived from ICR determinations of the equilibrium constant for proton transfer from the reference base to RCN.

[d] Derived from the data of columns 3 and 4 and corrected for changes in ΔS calculated from symmetry number changes for reaction 5.

Table II. Nitrile Proton Affinities, Adiabatic Ionization Potentials, and Homolytic Bond Dissociation Energies[a]

RCN	PA[b]	π IP	σ IP	$\sigma D(B^+-H)$[c]
HCN	175.9	313.9[d]	322.8[d]	185.2
$CH_2(CN)_2$	178.0	292.4[e]	309.2[e] 313.4[e]	173.7[e] 177.8[e]
ClCN	178.5	285.0[f]	318.2[f]	183.2
Cl_3CCN	178.7	- -	320.1[g]	185.2
BrCN	181.2	273.7[f]	312.7[f]	180.3
$ClCH_2CN$	181.9	297.5[g, h]	313.4[g, h]	181.7
$ClCH_2CH_2CN$	187.1	282.5[h]	305.3[h]	178.8
MeCN	188.0	281.3[i]	303.0[i]	177.4
$CH_2{=}CHCN$	188.8	285.0[g]	300.7[g]	175.9
EtCN	191.0	273.3[g, h]	296.3[g, h]	173.8

[a] All data in kcal/mol.

[b] Data from Table I and reference 9.

[c] Calculated using equation 3 and the N lone pair σ ionization potential.

[d] References 26 and 22.

[e] Reference 31, both n^+ and n^- values are given.

[f] References 23 and 30.

[g] Reference 23.

[h] Present work.

[i] Present work and references 22 and 23.

affinities in the nitrile and primary amine series, Figure 1, reveals that the magnitude of these effects are linearly related in the two series but larger for the nitriles.[21] A least squares fit to the data is given by equation 10 with all quantities in kcal/mol.[21]

$$PA(RCN) = 1.3153\ PA(RNH_2) - 90.68 \qquad (10)$$

The photoelectron spectra of several alkyl nitriles are shown in Figure 2. Assignment of the low lying bands in the photoelectron spectra of nitriles has been the subject of several experimental and theoretical papers.[22-31] In MeCN, Figure 2a, the CN π band is clearly separated from the N lone pair σ band allowing this spectrum to be confidently assigned, Table II.[22-24] The photoelectron spectra of EtCN, Figure 2b, and $CH_2{=}CHCN$ have been similarly assigned except that $CH_2{=}CHCN$ has an additional band at 10.91 eV which is associated with ionization of the C=C π bonding electrons.[23, 24] For HCN the CN π and N lone pair σ bands are closer in energy but several detailed analyses have resulted in a convincing assignment.[22, 24-29] While the N lone pair ionization has been unambiguously assigned in ClCN and BrCN, interaction of the CN π orbitals with the halogen π lone pair orbitals is substantial, resulting in two bands which may be associated with ionization of the CN π electrons.[23, 30] The lower of these are given in Table II; the upper bands are at 15.13 and 14.19 eV in ClCN and BrCN, respectively.[23] The spectrum of $CH_2(CN)_2$, which is complicated by interaction of the two equivalent CN groups, has been analyzed by Stafast and Bock.[31]

FIGURE 1

Proton affinities of nitriles, RCN, versus proton affinities of primary amines, RNH_2.

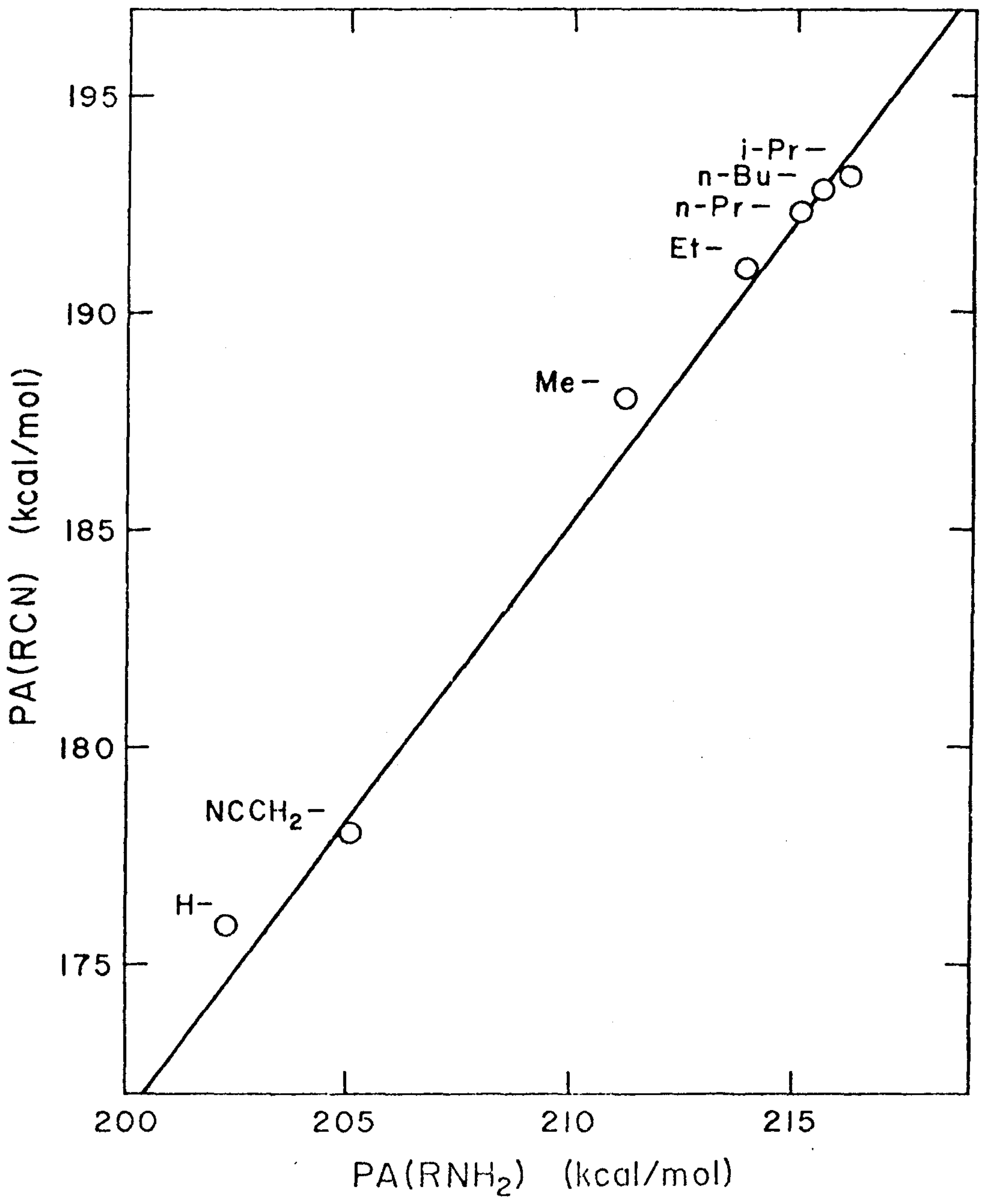
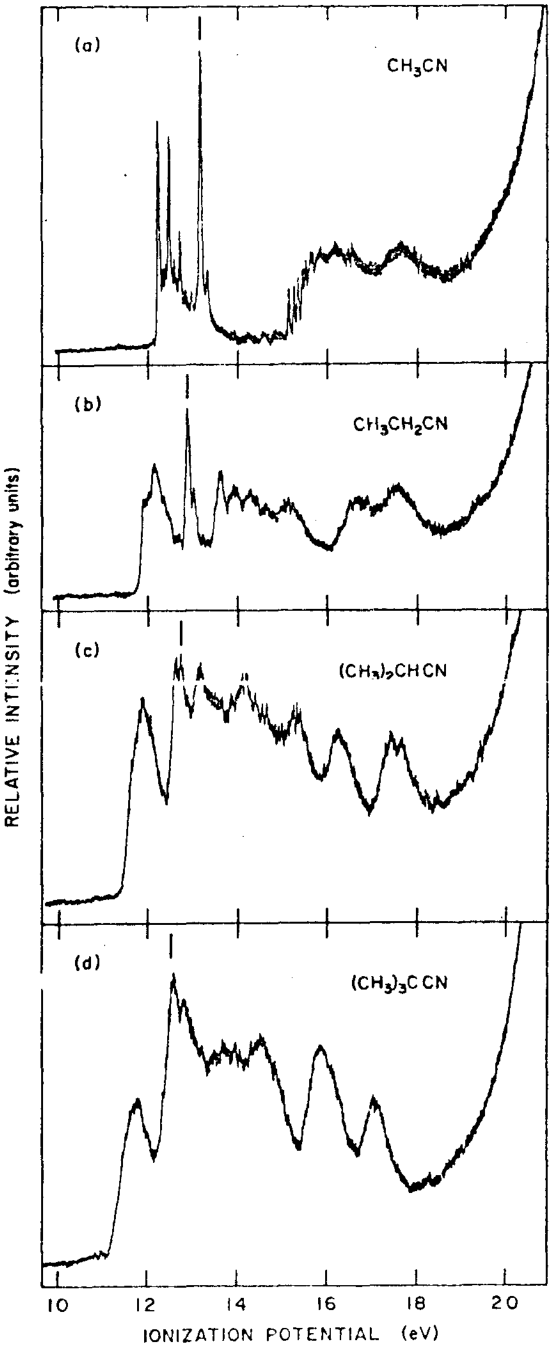

195
190
185
180
175
200
205
210
215
PA(RCN) (kcal/mol)
PA(RNH2) (kcal/mol)
i-Pr–
n-Bu–
n-Pr–
Et–
Me–
NCCH2–
H–

FIGURE 2

He(I) photoelectron spectra of (a) CH_3CN, (b) CH_3CH_2CN, (c) $(CH_3)_2CHCN$, and (d) $(CH_3)_3CCN$. Adiabatic N lone pair σ ionization potentials predicted by equation 11 are indicated by the vertical line above each spectrum.


(a)
CH_3CN
(b)
CH_3CH_2CN
(c)
$(CH_3)_2CHCN$
(d)
$(CH_3)_3CCN$
RELATIVE INTENSITY (arbitrary units)
10
12
14
16
18
20
IONIZATION POTENTIAL (eV)

Lake and Thompson obtained the photoelectron spectra of $ClCH_2CN$ and Cl_3CCN but did not assign the observed bands.[23] Data for the nitrile CN π and N lone pair σ adiabatic ionization potentials and PA(RCN) results are summarized in Table II along with $\sigma D(B^+{-}H)$ values calculated using the N lone pair ionization potentials.[32]

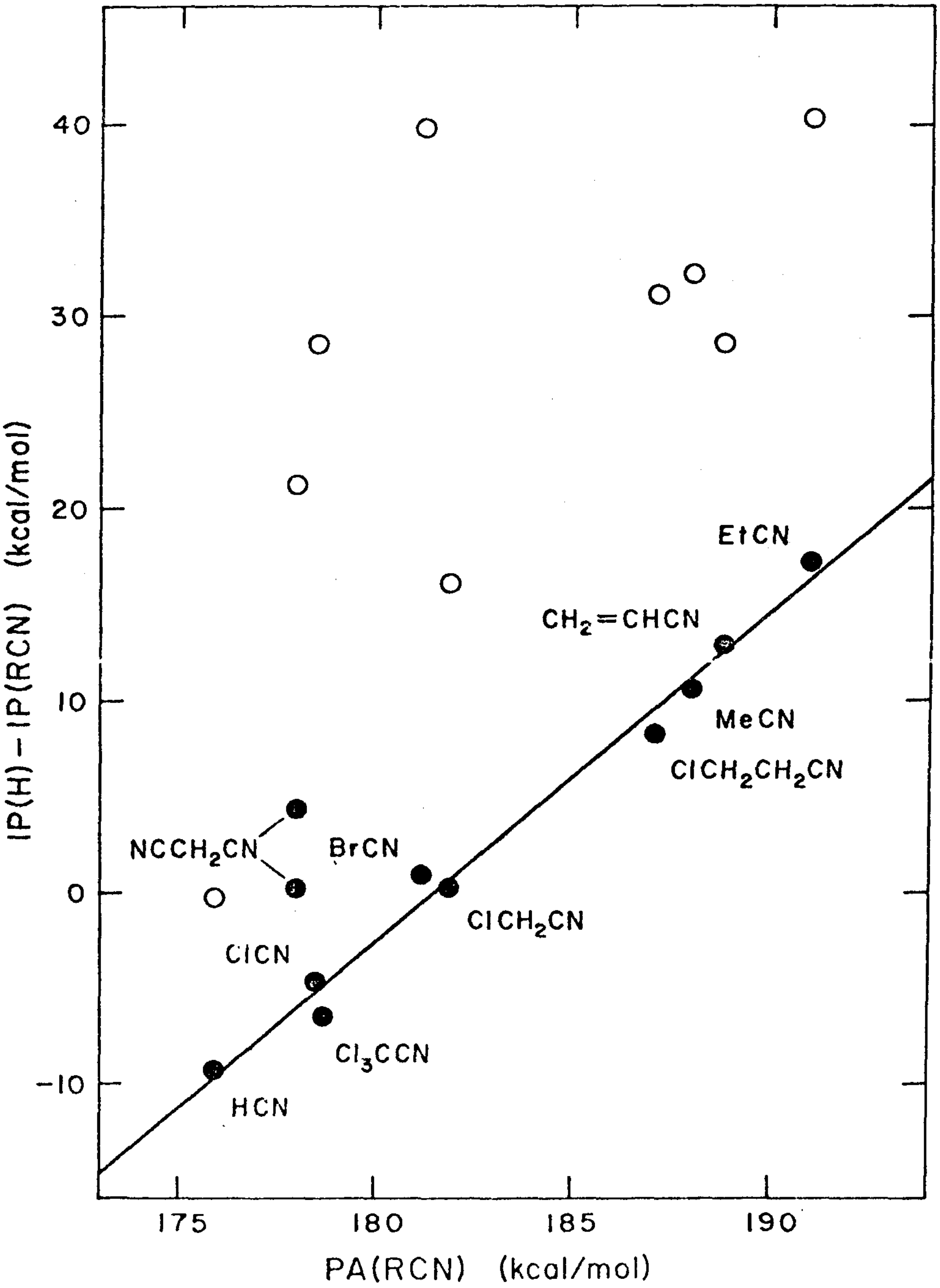
In accordance with equation 3, it is of interest to consider the variation of the quantity IP(H) - IP(RCN) with PA(RCN), Figure 3. It is apparent that CN π ionization potentials are poorly correlated with PA(RCN) values; for N lone pair σ ionization potentials, however, the data fall closely about a straight line. A least squares fit to this data, excluding the points for $CH_2(CN)_2$ which are discussed below, is given by equation 11 with all quantities in kcal/mol.

$$IP(H) - \sigma IP(RCN) = 1.7270\ PA(RCN) - 313.54 \qquad (11)$$

It is reasonable that the N lone pair σ ionization potential but not the CN π ionization potential should be related to PA(RCN). For the protonated species, stabilization of the positive charge is effected by redistribution in the R–C–N–H σ system. Similarly in the σ state of the radical cation, charge stabilization results from electron redistribution in the R–C–N· σ system. The presence of the radical site in the latter case allows for greater charge redistribution by electron donation into the partially filled orbital and accounts for the larger effect of changes in R on ionization potential as compared to proton affinity, equation 11 and Figure 3. It has been suggested that decreasing $D(B^+{-}H)$ in the amine series Me_nNH_{3-n}, n = 0-3, can be

FIGURE 3

The quantity IP(H)−IP(RCN) versus PA(RCN) for adiabatic ○ CN π and ● N lone pair σ ionization potentials for nitriles.


40
30
20
10
0
-10
175
180
185
190
IP(H) - IP(RCN) (kcal/mol)
PA(RCN) (kcal/mol)
EtCN
CH$_2$=CHCN
MeCN
ClCH$_2$CH$_2$CN
NCCH$_2$CN
BrCN
ClCH$_2$CN
ClCN
Cl$_3$CCN
HCN

attributed to the effects of π hyperconjugation[4]; the present series evidences the effects of σ hyperconjugation

$$\mathrm{R{-}C{\equiv}N^{\dot{+}}} \longleftrightarrow \mathrm{R^{+}\ {\cdot}C{\equiv}N{:}} \longleftrightarrow \mathrm{R{\cdot}\ {}^{+}C{\equiv}N{:}}$$

which are also reflected in the dependence of $\sigma D(B^{+}-H)$ on PA(RCN), Table II. In the π state of the radical cation, charge stabilization is affected by different factors, principally, interaction of the CN π orbitals with orbitals of π symmetry in R.

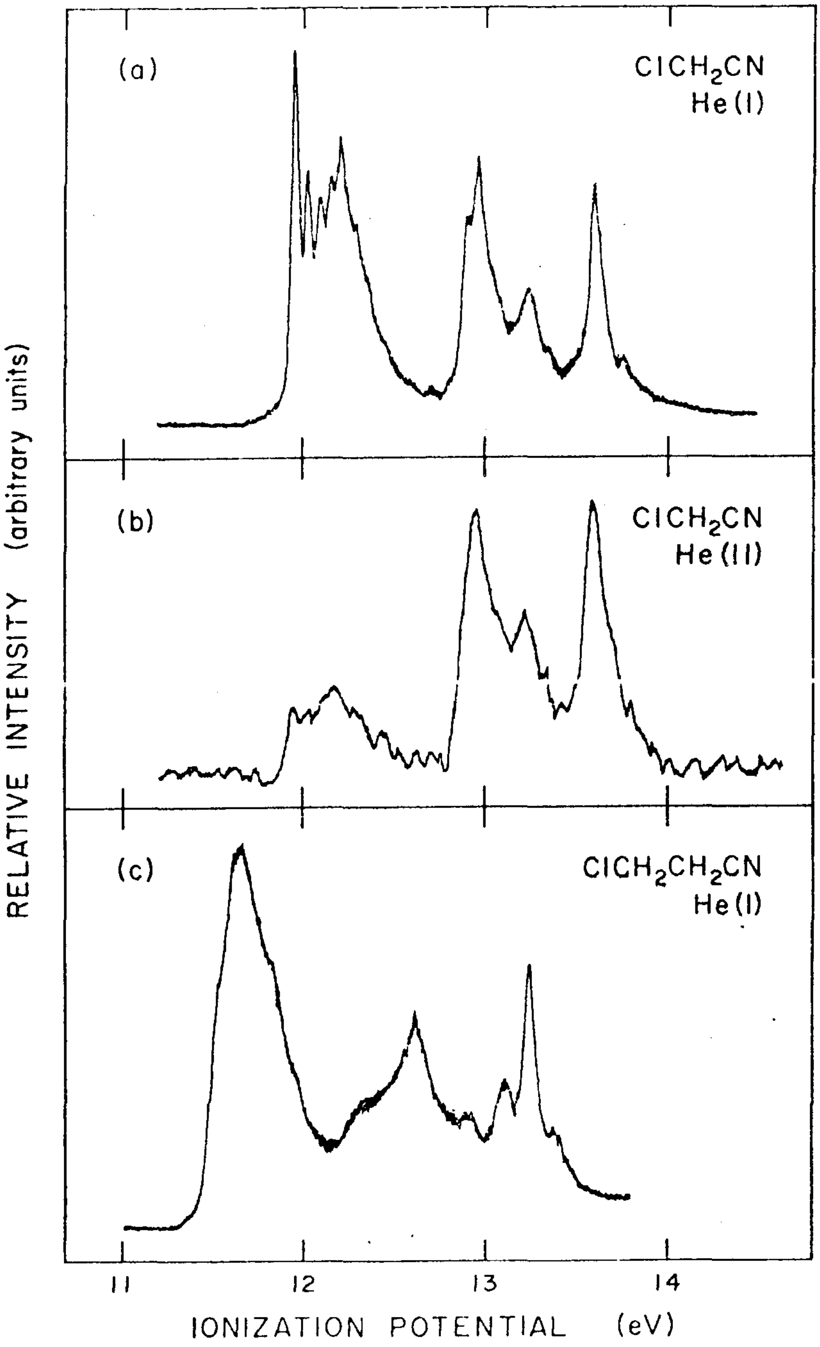
The two data points in Figure 3 for the ionization potentials of the n^{+} and n^{-} combinations of the nitrogen lone pairs of $CH_2(CN)_2$ are clearly an exception to the relationship between σIP(RCN) and PA(RCN) described by equation 11. Previous studies of molecules containing equivalent lone pairs[7] lead to the expectation that this may result from resonance stabilization of the radical cation arising from lone pair interactions. Thru space interactions should be slight since the two nitrogen atoms are separated by about 4 Å.[33] The analysis by Stafast and Bock[31] suggests that both n^{+} and n^{-} orbital energies should be destabilized by thru bond interactions. This is consistent with the present result in which both of the observed ionization potentials are lower than the ionization potential predicted by equation 11. Resonance stabilization of the radical cation, calculated by comparing the n^{+} (lower) ionization potential with the ionization potential predicted by $PA(CH_2(CN)_2)$ = 178.0 kcal/mol and equation 11, amounts to 10.4 kcal/mol, reducing the homolytic bond dissociation energy $\sigma D(B^+-H)$ for $NCCH_2CNH^+$ from an expected 184.1 kcal/mol to 173.7 kcal/mol.

The relationship between N lone pair σ ionization potentials and nitrile proton affinities described by equation 11 provides a useful means for assigning photoelectron spectra. The first three bands in the photoelectron spectrum of $ClCH_2CN$ are shown in Figure 4a.[34] $PA(ClCH_2CN) = 181.9$ kcal/mol and equation 11 predict $\sigma IP(ClCH_2CN) = 13.57$ eV, identifying the strong sharp peak at this energy as the N lone pair ionization. The first band at 11.95 eV may be assigned to the Cl lone pair ionization by noting its reduced intensity in the He(II) spectrum of $ClCH_2CN$, Figure 4b; second row lone pairs are relatively weaker as compared to first row π and σ bands in He(II) spectra.[35] The middle band at 12.90 eV in the $ClCH_2CN$ spectrum can then be assigned to the CN π ionization. The peak at 13.17 eV in this band, a spacing of 2200 cm^{-1}, results from excitation of the C≡N stretching vibration. Assignment of the $ClCH_2CH_2CN$ spectrum, Figure 4c, is similar to that of $ClCH_2CN$, all peaks being shifted to lower ionization potential by about 0.4 eV.[36]

Equation 11 may also be usefully applied to the analysis of spectra which are less well resolved. The photoelectron spectra of a series of alkyl nitriles RCN in which methyl is substituted for hydrogen in CH_3CN appear in Figure 2. As R increases in size, the decreasing ionization potential of the C–C and C–H σ bands obscures the region of the N lone pair, the position of which as predicted by equation 11 is indicated in Figure 2.[37] Similarly, equation 11 and

FIGURE 4

(a) He(I) photoelectron spectrum of $ClCH_2CN$, (b) He(II) photoelectron spectrum of $ClCH_2CN$, and (c) He(I) photoelectron spectrum of $ClCH_2CH_2CN$.


(a)
$ClCH_2CN$
He(I)
(b)
$ClCH_2CN$
He(II)
(c)
$ClCH_2CH_2CN$
He(I)
RELATIVE INTENSITY (arbitrary units)
11
12
13
14
IONIZATION POTENTIAL (eV)

PA(c-C_3H_5CN) = 194.1 kcal/mol predict σIP(c-C_3H_5CN) = 12.66 eV which can be usefully applied in a detailed analysis of the cyclopropyl cyanide spectrum.[38] While relationships of the type given by equation 11 provide useful chemical means for assigning spectra, physical methods such as angular dependent photoelectron spectroscopy[39] might also be usefully applied to further resolve and identify structure in spectra where several bands overlap.

In conclusion, the nitrile results have provided new examples of linear relationships among properties related to molecular basicity. While the slope and intercept of such relationships depend on the nature of the basic site, whether charge is localized in orbitals of π or σ symmetry, and whether the system is closed or open shell, for the results to date the magnitude of substituent effects are proportional in all series, suggesting that a single set of substituent constants might be developed. As additional examples are found, it will be of interest to see whether this proportionality is maintained. The results also point out that caution must be exercised in developing relationships between ionization potentials and molecular properties such as base strength: the correct ionization potential must be chosen and molecules in which the presence of equivalent lone pairs leads to resonance stabilization of the radical cation should be regarded as potential exceptions.

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(36) This spectrum may be complicated by the presence of significant populations of both trans and gauche conformers of $ClCH_2CH_2CN$.

(37) The indicated values for σIP(RCN) are calculated using equation 11 and PA(RCN) data from Table I and reference 9. For t-BuCN, PA(t-BuCN) = 196.3 kcal/mol is estimated using equation 10 and PA($t\text{-}BuNH_2$) = 218.2 kcal/mol from references 4 and 21.

(38) A spectrum of $c\text{-}C_3H_5CN$ appears in reference 22, p. 212.

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CHAPTER III

Effects of Alkyl and Fluoro Substitution on the Heterolytic and Homolytic Bond Dissociation Energies of Protonated Amines

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Received______________

Abstract: Thermochemical properties related to molecular basicity are examined for series of alkyl and fluoro substituted amines using ion cyclotron resonance techniques and photoelectron spectroscopy. Proton affinities, PA(B), defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, and adiabatic first ionization potentials, IP(B), are determined. Homolytic bond dissociation energies $D(B^+-H)$ are obtained using the relation $PA(B) - D(B^+-H) = IP(H) - IP(B)$. Systematic effects of alkyl and fluoro substitution on PA(B) and $D(B^+-H)$ are identified and discussed.

Systematic quantitative evaluation of substituent effects on properties related to molecular basicity has become possible through the recent development of techniques for the study of ion-molecule reactions and for the determination of molecular ionization potentials.[2-11] Ion cyclotron resonance (ICR) techniques[2-10] or high pressure mass spectrometry[11] may be used to measure equilibrium constants for proton transfer between two bases, reaction 1, yielding accurate (± 0.2 kcal/mol) relative free energies of protonation. Temperature dependence is observed to be slight, confirming the expectation that ΔS for reaction 1 is small and can be accounted for by symmetry number changes.[11]

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+ , \qquad \Delta H = PA(B_1) - PA(B_2) \qquad (1)$$

$$BH^+ \rightarrow B + H^+ \qquad \Delta H = D(B{-}H^+) \equiv PA(B) \qquad (2)$$

$$BH^+ \rightarrow B^{+\cdot} + H\cdot \qquad \Delta H = D(B^+{-}H) \qquad (3)$$

$$PA(B) - D(B^+{-}H) = IP(H) - IP(B) \qquad (4)$$

$$\begin{tikzcd} BH^+ \arrow[r, "PA(B)"] \arrow[d, "D(B^+-H)"'] & B + H^+ \\ B^{+\cdot} + H\cdot & B + H\cdot \arrow[l, "IP(B)"'] \arrow[u, "IP(H)"'] \end{tikzcd} \qquad (5)$$

Proton affinity, PA(B), is defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, eq 2. The homolytic bond dissociation energy $D(B^+{-}H)$ defined by eq 3 is related to PA(B) and the adiabatic ionization potentials IP(H) and IP(B), eq 4, by the thermochemical cycle 5. A relative scale of PA(B) has been established by examining reaction 1 for a large number of organic and inorganic bases and calibrated by reference to a variety of species for which absolute values of PA(B) may be derived from appearance potential measurements.[10]

Variation of molecular properties related to basicity in series of primary, secondary, and tertiary amines,[2-4, 11] substituted pyridines,[5, 12] nitriles,[9] and the methyl phosphines[6] has been examined. In particular, it has been demonstrated that for homologous series, for example the primary amines, molecular ionization potentials IP(B) and homolytic bond dissociation energies $D(B^+-H)$ are linear functions of PA(B).[3, 4, 9] Stabilization of the conjugate acid BH^+ or radical cation $B^{\cdot+}$ by resonance interactions or hyperconjugation may lead to important exceptions.[4, 7, 9]

The effects of direct fluoro substitution on nitrogen have been examined in studies of the ion chemistry of NF_3.[13] Fluorine substituent effects on the stabilities of carbenium ions[14] and carbanions[15] and on the acidities of carboxylic acids[16] and alcohols[17] have also been investigated. Theoretical approaches to the understanding of these effects have appeared.[18]

The present work uses ICR techniques and photoelectron spectroscopy (PES) to examine the effects of alkyl and fluoro substitution in series of primary and tertiary amines.

Experimental

ICR instrumentation and techniques used in these studies have been previously described in detail.[6, 18, 19] Photoelectron spectra were obtained using an instrument built in the Caltech shops employing a 127° electrostatic analyzer. Spectra were calibrated using the $^2P_{3/2}$ and $^2P_{1/2}$ lines of an internal argon standard. Both the ICR and PES experiments were conducted at room temperature. The compounds studied were all available from recent investigations of the proton affinities of a large number of organic and inorganic bases.[10] All samples were degassed at liquid nitrogen temperature before use.

Results

Photoelectron spectra of various alkyl and fluoro substituted primary and tertiary amines were obtained and found to have a characteristic first band corresponding to removal of an electron from the nitrogen lone pair orbital, Figure 1. An adiabatic ionization potential was chosen near the beginning of this band for ethyl amine, Figure 2, and in a similar location in each of the other spectra. Adiabatic and vertical ionization potentials for all of the molecules are given in Table I. Relative ionization potentials are estimated to be accurate to ± 0.03 eV. Absolute values are estimated to be somewhat less accurate (± 0.15 eV).

Proton affinities were available from studies of a large number of organic and inorganic bases details of which will be published separately.[10] Relative values for closely spaced proton affinities ($\Delta PA < 3$ kcal/mol) could be measured directly and are estimated to be accurate to ± 0.2 kcal/mol. The cummulative error for relative

FIGURE 1

He(I) photoelectron spectra of (a) $EtNH_2$, (b) $F_2CHCH_2NH_2$, (c) $CF_3(CH_2)_2NH_2$, and (d) $CF_3CH_2NMe_2$.

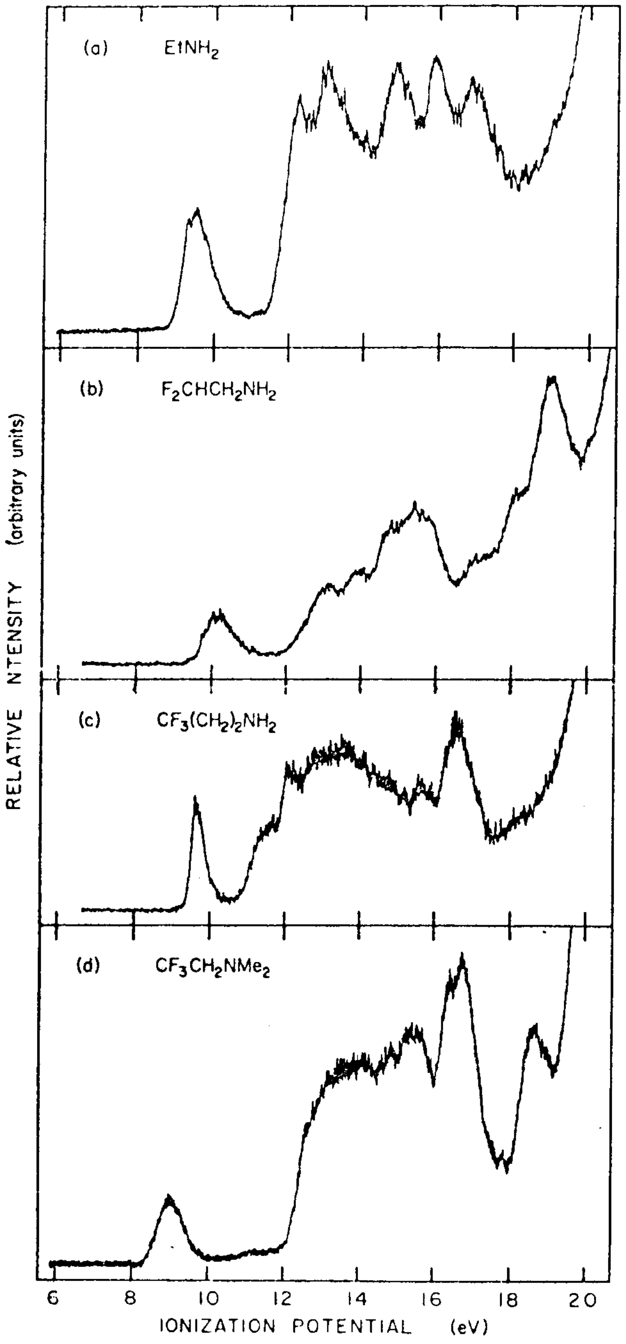

(a) EtNH$_2$
(b) F$_2$CHCH$_2$NH$_2$
(c) CF$_3$(CH$_2$)$_2$NH$_2$
(d) CF$_3$CH$_2$NMe$_2$
RELATIVE INTENSITY (arbitrary units)
6
8
10
12
14
16
18
20
IONIZATION POTENTIAL (eV)

FIGURE 2

He(I) photoelectron spectrum of the first band in $EtNH_2$. The adiabatic first ionization potential is indicated.

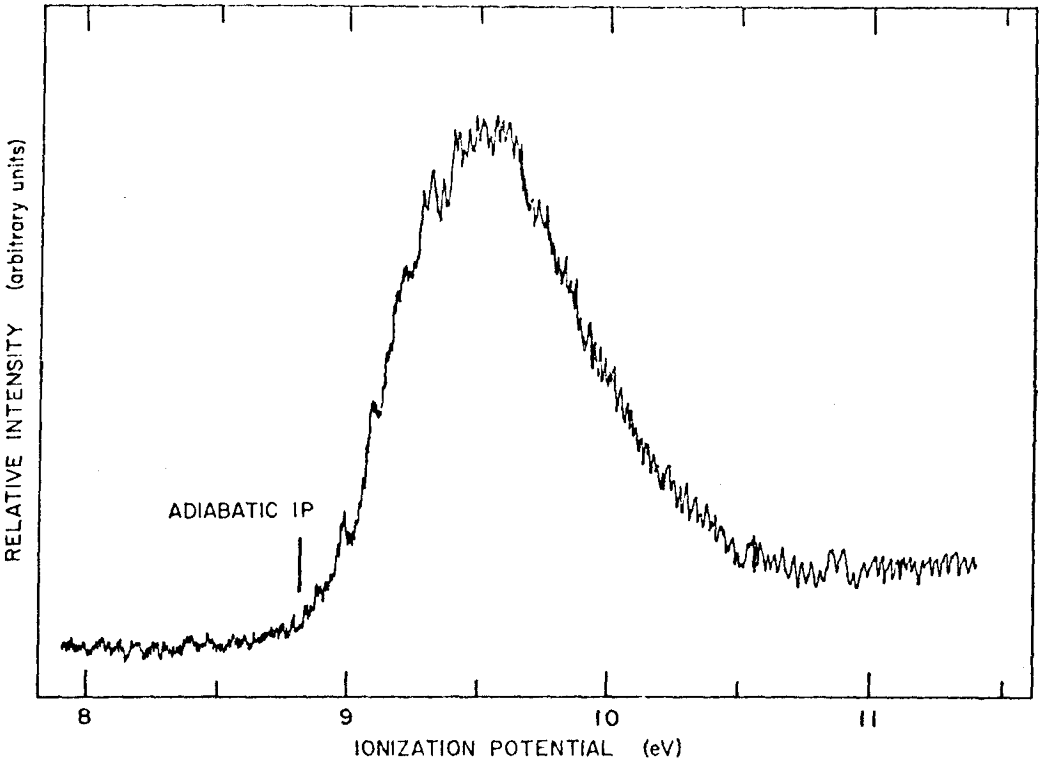

RELATIVE INTENSITY (arbitrary units)
ADIABATIC IP
8
9
10
11
IONIZATION POTENTIAL (eV)

Table I. Adiabatic and Vertical Ionization Potentials for Some Alkyl and Fluoro Substituted Amines[a]

Molecule	aIP[b]	vIP[c]	vIP-aIP
$EtNH_2$	8.80	9.53[d]	0.73
Me_3N	7.87	8.55[d]	0.68
Me_2EtN	7.79	8.47	0.68
$MeEt_2N$	7.63	8.35	0.72
Et_3N	7.42	8.13[d]	0.71
$FCH_2CH_2NH_2$	9.11	9.86	0.75
$F_2CHCH_2NH_2$	9.38	10.15	0.77
$F_3CCH_2NH_2$	9.73	10.46	0.73
$CF_3(CH_2)_2NH_2$	9.31	9.70	0.39
$CF_3(CH_2)_3NH_2$	9.05	9.80	0.75
CF_3NMe_2	9.22	9.99	0.77
$CF_3CH_2NMe_2$	8.26	8.98	0.72

[a] All data in eV measured from photoelectron spectra.

[b] Adiabatic ionization potential.

[c] Vertical ionization potential.

[d] K. Watanabe, T. Nakayama, and J. R. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962), report IP($EtNH_2$) = 8.86 eV, IP(Me_3N) = 7.82 eV, and IP(Et_3N) = 7.50 eV.

values of widely spaced proton affinities is estimated to be less than ± 1.0 kcal/mol. All proton affinity values are relative to PA(NH_3) = 202.3 ± 2.0 kcal/mol.[10] Proton affinities, adiabatic ionization potentials, and homolytic bond dissociation energies calculated using eq 4 are given in Table II for all of the molecules studied.

Discussion

Proton Affinities. Methyl substitution in the series $Et_nMe_{3-n}N$, n = 0-3, and fluoro substitution in the series $F_nCH_{3-n}CH_2NH_2$, n = 0-3, have nearly additive effects on proton affinity, Figure 3, which may be attributed to polarization and inductive factors.[4-6] The incremental effect of methyl substitution, on an α-carbon, in the tertiary amine series $Et_nMe_{3-n}N$, n = 0-3, ~ 2.2 kcal/mol per methyl group, may be compared to ~2.3 kcal/mol per methyl group previously observed in the primary amine series $Me_nCH_{3-n}NH_2$, n = 0-3.[4] In both of these series the effect is slightly nonadditive, 2.5, 2.4, and 2.1 kcal/mol for methyl substitution on the same α-carbon in the primary amine series and 2.4, 2.2, and 2.1 kcal/mol for methyl substitution on different α-carbons in the tertiary amine series. Fluoro substitution has a dramatically larger effect of opposite sign, -4.3 kcal/mol per fluoro substituent on the β-carbon. This effect is also slightly nonadditive with increasing basicity: for the series $F_{3-n}CH_nCH_2NH_2$, n = 0-3, where proton affinity increases with n, the incremental increases are 5.2, 4.0, and 3.8 kcal/mol.

Table II. Proton Affinities, Adiabatic Ionization Potentials and Homolytic Bond Dissociation Energies for Some Alkyl and Fluoro Substituted Amines[a]

Molecule	PA[b]	IP	$D(B^+-H)$[c]
Me_3N	221.5	181.5	89.4
Me_2EtN	223.9	179.6	90.0
$MeEt_2N$	226.1	175.9	88.5
Et_3N	228.2	171.1	85.7
$CH_3CH_2NH_2$	213.3	202.9	102.7
$FCH_2CH_2NH_2$	209.5	210.1	106.0
$F_2CHCH_2NH_2$	205.5	216.3	108.2
$F_3CCH_2NH_2$	200.1	224.4	110.9
$CF_3(CH_2)_2NH_2$	208.2	214.7	109.3
$CF_3(CH_2)_3NH_2$	211.6	208.7	106.7
CF_3NMe_2	193.7	212.6	92.7
$CF_3CH_2NMe_2$	212.4	190.5	89.3

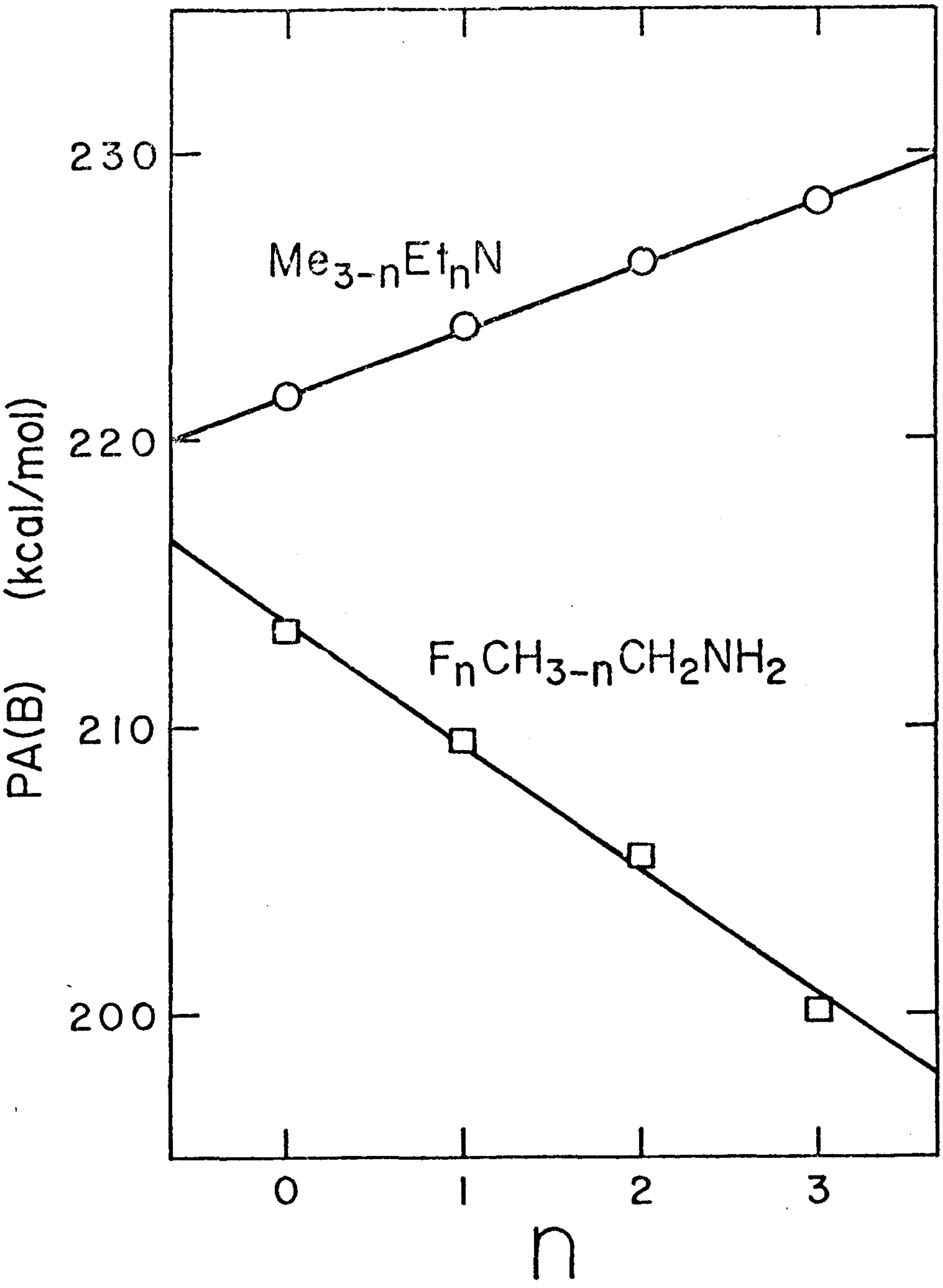
[a] All data in kcal/mol.

[b] Proton affinities relative to $PA(NH_3) = 202.3 \pm 2.0$ kcal/mol, reference 10.

[c] Calculated using eq 4.

FIGURE 3

Variation of proton affinity with successive substitution in the series ○ $Me_{3-n}Et_nN$ and ☐ $F_nCH_{3-n}CH_2NH_2$.


230
220
210
200
PA(B) (kcal/mol)
$Me_{3-n}Et_nN$
$F_nCH_{3-n}CH_2NH_2$
0
1
2
3
n

The total effect in the fluoroethyl amine series, 13.2 kcal/mol, comparing $CH_3CH_2NH_2$ to $CF_3CH_2NH_2$, is matched by a difference of 11.5 kcal/mol for substitution of trifluoromethyl for methyl in the tertiary amines $CH_3CH_2NMe_2$ and $CF_3CH_2NMe_2$. Since polarizability increases in substituting F for H,[21] the marked decrease in proton affinity with CF_3 substitution must be predominantly due to inductive factors. The magnitude of the effect decreases exponentially with the length of the intervening alkyl chain, Figure 4, according to eq 6.[22] A similar exponential decrease with distance is observed

$$\mathrm{PA}[CH_3(CH_2)_nNR_2] - \mathrm{PA}[CF_3(CH_2)_nNR_2] = (27.8\ \mathrm{kcal/mol})\exp(0.69n) \qquad (6)$$

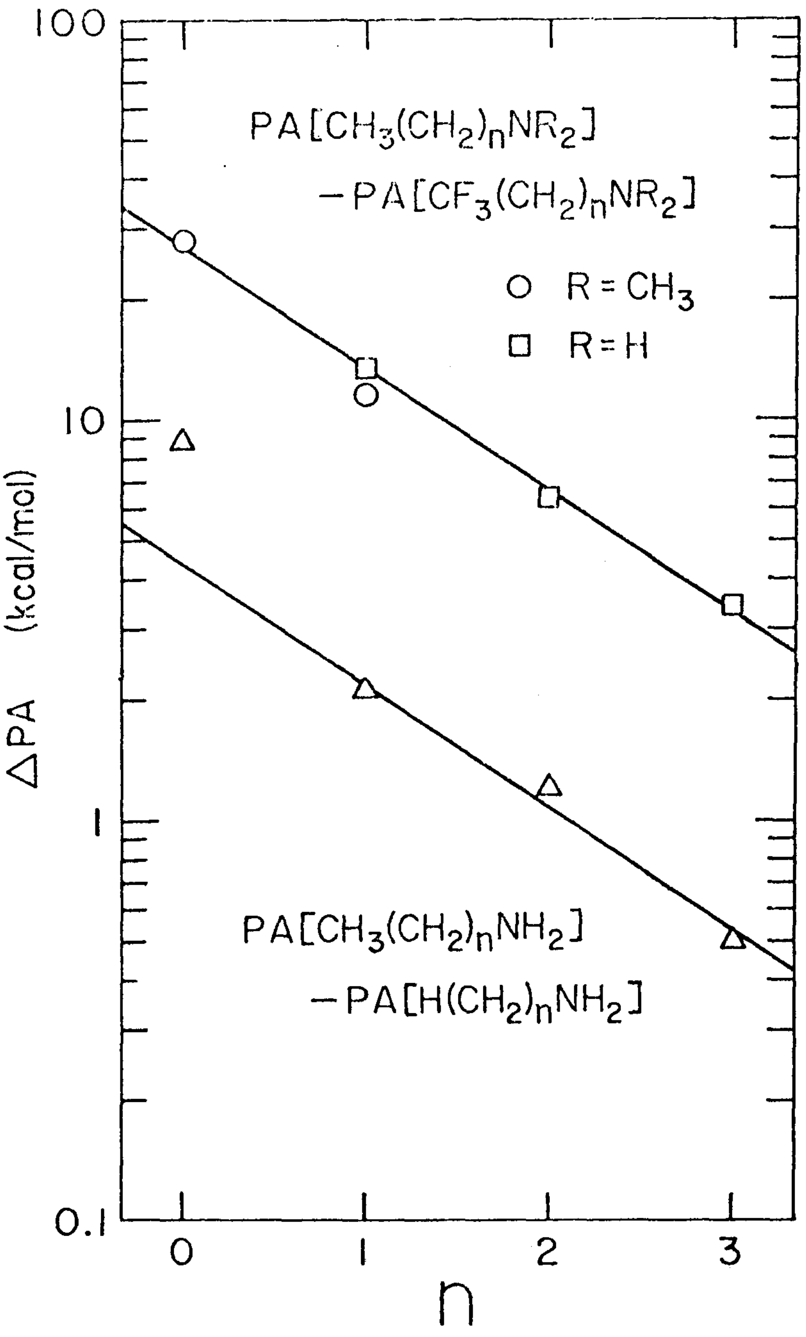
$$\mathrm{PA}[CH_3(CH_2)_nNH_2] - \mathrm{PA}[H(CH_2)_nNH_2] = (5.0\ \mathrm{kcal/mol})\exp(0.69n) \qquad (7)$$

in substituting methyl for hydrogen in the primary amines, Figure 4, eq 7.[22] The difference for $MeNH_2$ and NH_3 is clearly an exception. Whereas the other data in Figure 4, reflect the variation with distance of the inductive effect, the difference for $MeNH_2$ and NH_3 also reflects the effects of polarizability, which for an ion-induced dipole interaction varies with the inverse fourth power of distance.

The size of the effect in substituting F for H on the α-carbon in tertiary amines, 27.8 kcal/mol comparing CF_3NMe_2 to CH_3NMe_2, is comparable to that observed for fluorine substitution in carbonium ions; with respect to the reference base F^-, $CF_3CF_2^+$ is 33 kcal/mol

FIGURE 4

Variation of the proton affinity difference PA$[CH_3(CH_2)_nNR_2]$ - PA$[CF_3(CH_2)_nNR_2]$ with n for ○ R = CH_3 and □ R = H; and △ variation of the proton affinity difference PA$[CH_3(CH_2)_nNH_2]$ - PA$[H(CH_2)_nNH_2]$ with n.


100
10
1
0.1
ΔPA (kcal/mol)
0
1
2
3
n
PA[CH3(CH2)nNR2]
−PA[CF3(CH2)nNR2]
○ R = CH3
□ R = H
PA[CH3(CH2)nNH2]
−PA[H(CH2)nNH2]

less stable than $CH_3CF_2^+$. A similarly large effect is found for fluoro substitution on the α-carbon in carboxylic acids. The acidity of CH_3CO_2H is greater than that of CF_3CO_2H by 25.2 kcal/mol.[16] For fluoro substitution on the β-carbon in alcohols, acidity decreases by 12 kcal/mol in going from CH_3CH_2OH to CF_3CH_2OH.[17] This is similar in magnitude to the differences of 13.5 and 11.5 kcal/mol noted above for β-fluoro substitution in the amines. In its effects on acidities, fluoro substitution stabilizes negative charge whereas in its effects on basicity, it destabilizes positive charge. The similarity of the magnitudes of these effects lends strong support to their interpretation as being largely inductive.

Homolytic Bond Dissociation Energies. Variation of $D(B^+{-}H)$ in the series $Me_{3-n}Et_nN$, $n = 0\text{-}3$, and $F_nCH_{3-n}CH_2NH_2$, $n = 0\text{-}3$, is shown in Figure 5. Methyl substitution in the former decreases $D(B^+{-}H)$, especially for Et_3N, reflecting a smaller stabilizing effect of substitution on BH^+ as compared to $B^{+\cdot}$, Figure 6. This may principally reflect steric crowding in pyramidal BH^+ as compared to planar $B^{+\cdot}$ with increased alkyl substitution.

$D(B^+{-}H)$ systematically increases with fluoro substitution on the β-carbon, Figure 5, indicating that $B^{+\cdot}$ is destabilized more than BH^+, Figure 7. Participation by structures involving hydrogen bonding between N-H and F in pyramidal BH^+ but not planar $B^{+\cdot}$ could account for this result. An alternative explanation might also be offered. Hyperconjugative delocalization of charge

FIGURE 5

Variation of $D(B^+–H)$ with n for the series ○ $F_nCH_{3-n}CH_2NH_2$ and ☐ $Me_{3-n}Et_nN$.

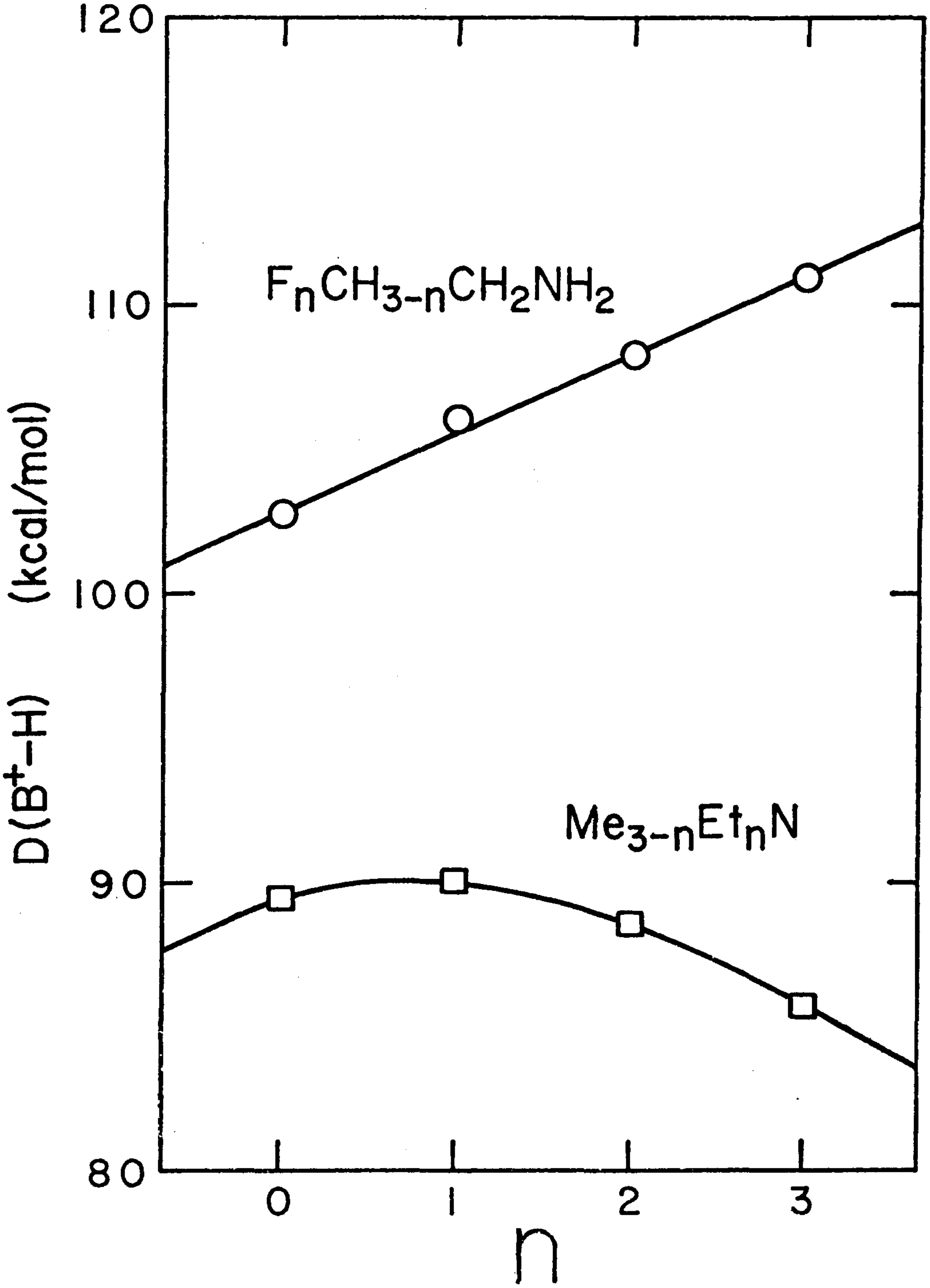

120
110
100
90
80
D(B$^+$-H) (kcal/mol)
0
1
2
3
n
$F_nCH_{3-n}CH_2NH_2$
$Me_{3-n}Et_nN$

FIGURE 6

Changes in relative enthalpies for methyl substituted (top curve, 1) and ethyl substituted (bottom curve, 2) tertiary amines referenced to ΔH_f for the neutral plus a proton (left) in going to the conjugate acid (center) and the radical cation plus a hydrogen atom (right): $PA(B_1) < PA(B_2)$ and $D(B_1^{+}-H) > D(B_2^{+}-H)$. Note that the relative stabilization with substitution is larger for the radical cation $B^{\dot{+}}$ than for the conjugate acid BH^{+}.

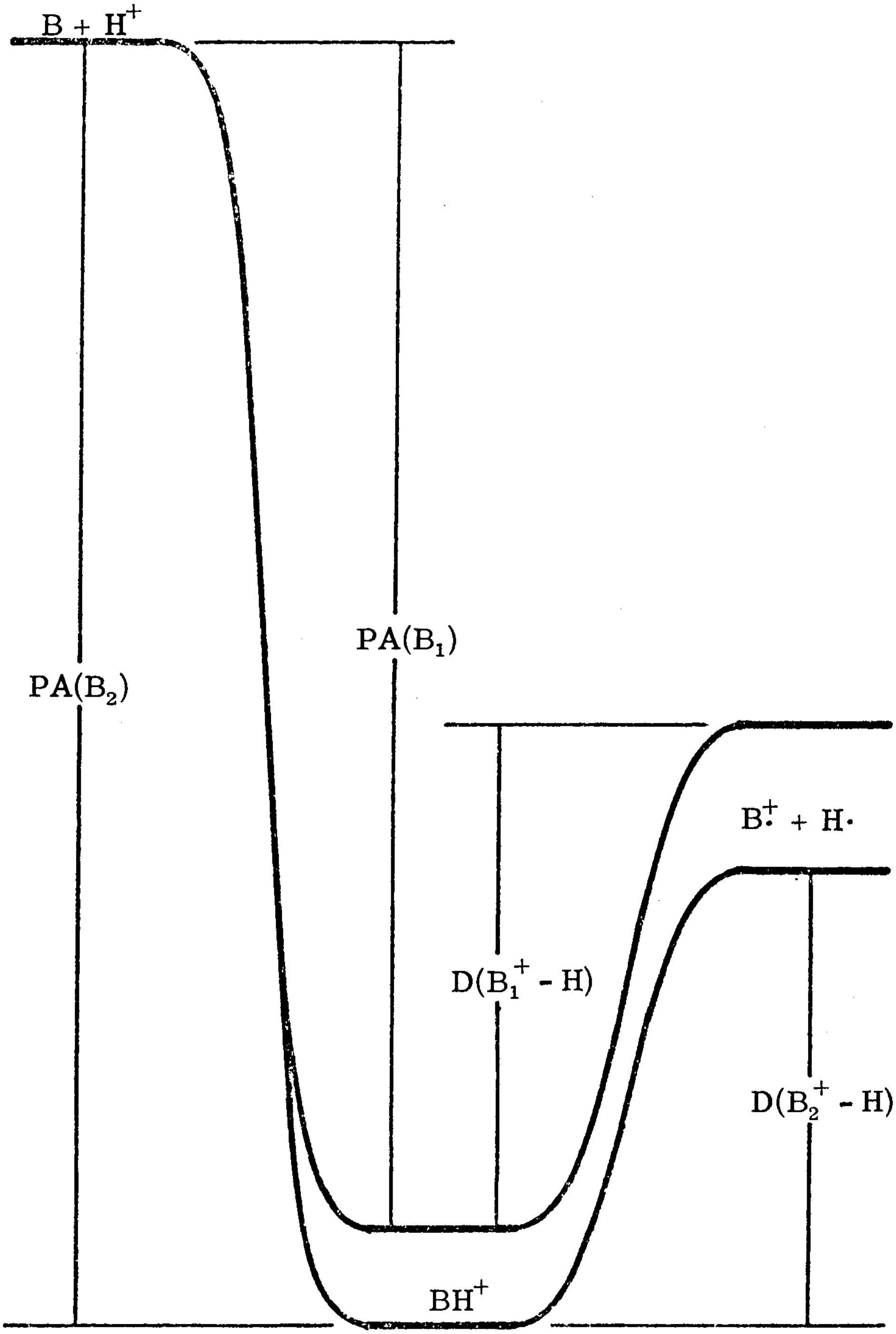
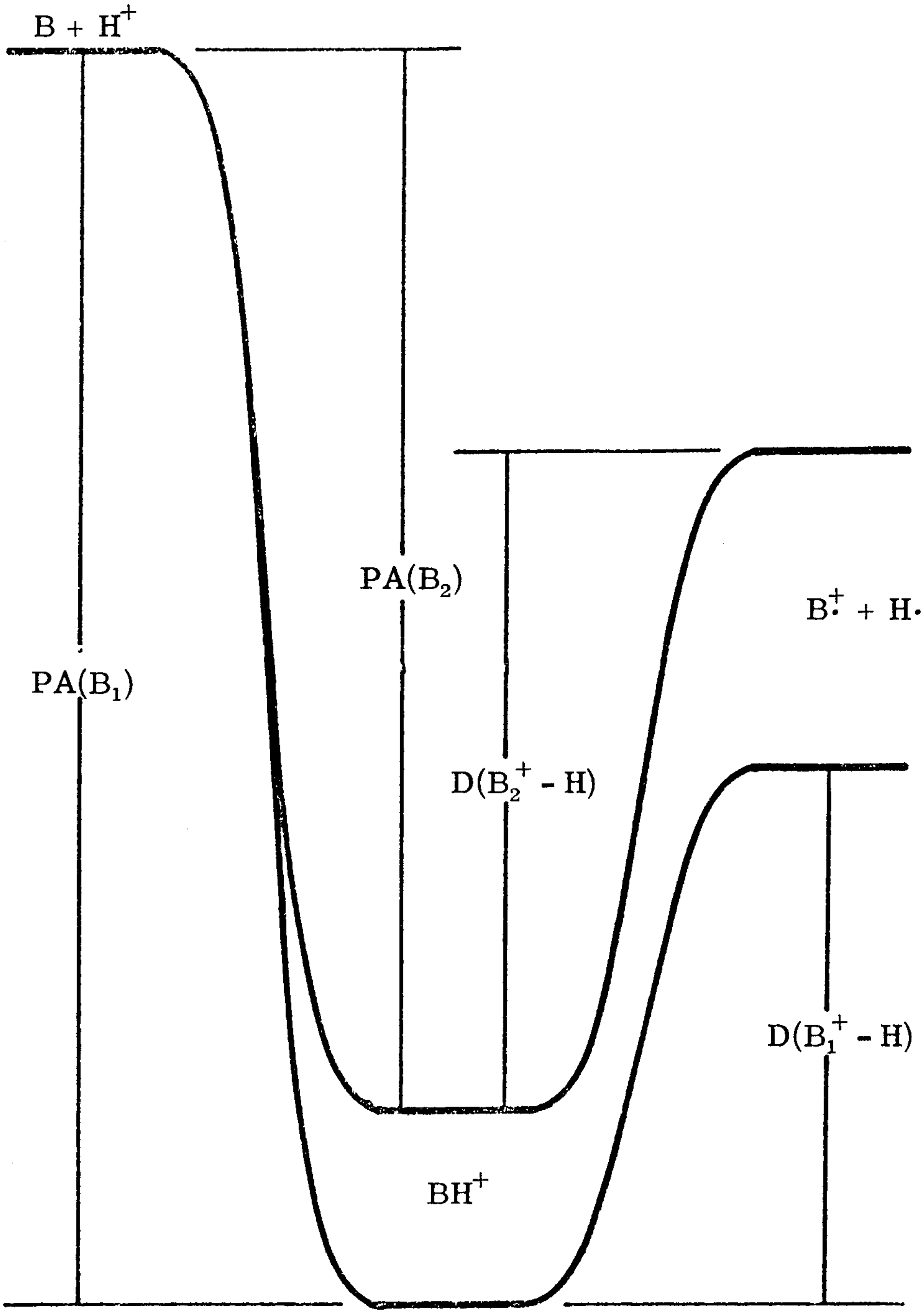
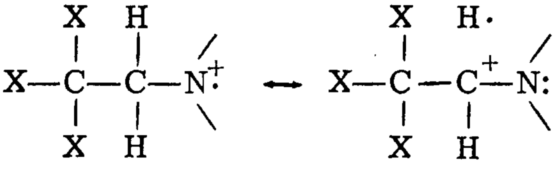

B + H$^+$
PA(B$_2$)
PA(B$_1$)
D(B$_1^+$ - H)
B$^{+\cdot}$ + H·
D(B$_2^+$ - H)
BH$^+$

FIGURE 7

Changes in relative enthalpies for hydrogen substituted (bottom curve, 1) and fluorine substituted (top curve, 2) ethyl amines referenced to ΔH_f for the neutral plus a proton (left) in going to the conjugate acid (center) and the radical cation plus a hydrogen atom (right): $PA(B_1) > PS(B_2)$ and $D(B_1^{+}-H) < D(B_2^{+}-H)$. Note that the relative destabilization with fluorine substitution is greater for the radical cation $B^{\overset{+}{\cdot}}$ than for the conjugate acid BH^{+}.

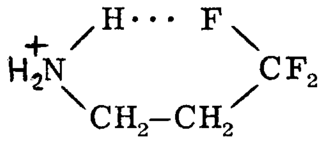

$B + H^+$
$PA(B_1)$
$PA(B_2)$
$D(B_2^+ - H)$
$B^{+\cdot} + H\cdot$
$D(B_1^+ - H)$
BH^+

in the radical cation has been suggested as an important mechanism for charge stabilization in this species.[4] When X=F rather than H,



I II

however, structures such as II are less favored so that the preferential stabilization of the radical cation derived from this mechanism is reduced. For $CF_3(CH_2)_2NH_2$, $D(B^+-H) = 109.3$ kcal/mol is consistent either with this latter argument or with participation by the six member ring structure III. The photoelectron spectrum of



III

$CF_3(CH_2)NH_2$, Figure 1c, shows a significantly narrowed first band compared to the other amines suggesting that the six member ring structure may also contribute significantly to the neutral for this molecule. For $CF_3(CH_2)_3NH_2$ decreased $D(B^+-H) = 106.7$ kcal/mol is consistent with a reduction of the effect due to lengthening of the chain for either model.

$D(B^+-H)$ for CF_3NMe_2 and $CF_3CH_2NMe_2$, 92.7 and 89.3 kcal/mol, respectively, may be compared to $D(B^+-H)$ for CH_3NMe_2 and $CH_3CH_2NMe_2$, 89.4 and 90.0 kcal/mol. CF_3 substitution appears to have little effect on $D(B^+-H)$ in the case of these tertiary amines. The steric factors noted above for the tertiary amine series which tend to decrease $D(B^+-H)$ with substitution may be greater here due to the larger CF_3 group. This could result in the observed cancellation of the expected fluoro substituent effect which would tend to increase $D(B^+-H)$.

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(22) PA[$CH_3(CH_2)_2NH_2$] = 214.5 kcal/mole and PA[$CH_3(CH_2)_3NH_2$] = 215.0 kcal/mol from reference 10.

CHAPTER IV

Carbenium Ion Stabilities in the Gas Phase and Solution. An Ion Cyclotron Resonance Study of Bromide Transfer Reactions Involving Alkali Ions, Alkyl Carbenium Ions, Acyl Cations, and Cyclic Halonium Ions

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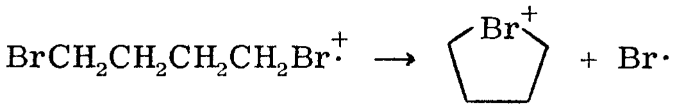
Contribution No. 5163 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received______________

Abstract: Ion cyclotron resonance techniques are used to measure relative heterolytic bond dissociation energies $D(R^+-Br^-)$ in the gas phase for a series of alkali cations, alkyl carbenium ions, acyl cations, and cyclic halonium ions. $D(R^+-Br^-)$ for adamantyl cation is found to be less than for tert-butyl cation. A proton affinity for norbornene of $D(B-H^+) = 198.8 \pm 2$ kcal/mol is determined from which $D(R^+-Br^-) = 146.8 \pm 2.3$ kcal/mol is calculated for norbornyl cation, 14 kcal/mol less than for cyclo-pentyl cation. Relative enthalpies of solvation are estimated via appropriate thermochemical cycles by combining the gas phase data with heats of ionization in fluorosulfuric acid. The results show that solvation enthalpies are related to ion size with smaller ions being better solvated. Relative stabilities of cyclic bromonium ions are the same in the gas phase and solution. Stability increases with increasing ring size and in the three-membered rings with methyl substitution. However, solvent has an appreciable effect in attenuating the observed range.

The quantitative assessment of the energetics of carbenium ion solvation is a difficult problem in organic chemistry. Relatively few stable carbenium ions have been thoroughly studied in aqueous media, where more often these species are invoked as transient intermediates in a wide range of chemical transformations.[2] Only recently has it been possible to devise conditions compatible with the existence of these reactive species for periods of time which permit their study using a variety of spectroscopic techniques.[3-6] With the assurance based on NMR and other spectral data that solution of selected halide precursors in fluorosulfuric acid media leads exclusively to ions of the anticipated structures,[6] calorimetric studies have been carried out leading to the determination of heats of ionization in these solvent systems.[7, 8]

In the gas phase carbenium ions are readily produced by electron impact (EI) ionization of halide precursors, process 1.[9] In the case of dihalides, internal displacement in the parent cation, for example process 2, leads to the production of cyclic halonium ions.[9-11] This is analogous to reaction 3 in which alkyl halide parent

$$RX \xrightarrow{EI} [RX^{+\cdot}]^* + e^- \longrightarrow R^+ + X\cdot + e^- \qquad (1)$$


(2)

$$RX^{+\cdot} + RX \longrightarrow RXR^+ + X\cdot \qquad (3)$$

ions react with neutral alkyl halides to give dialkylhalonium ions.[12]

Ion cyclotron resonance (ICR) techniques, which have been previously described for the reference base F^-, permit the determination of relative gas phase carbenium ion stabilities by examining the preferred direction and equilibrium in reaction 4.[13-15] The reaction proceeds through an intermediate halonium ion complex which is more stable than either reactants or products.[12] The heterolytic bond dissociation energy $D(R^+-X^-)$ as defined by eq 5 ($D(R^+-X^-) \equiv$ halide affinity) is taken as a measure of gas phase stability.

$$R_1^+ + R_2X \rightleftharpoons [R_1XR_2^+]^* \rightleftharpoons R_1X + R_2^+ \tag{4}$$

$$RX \rightarrow R^+ + X^-, \qquad \Delta H = D(R^+-X^-) \tag{5}$$

Alkali cations are also readily produced in the gas phase, by emission from thermionic sources, and may be studied by ICR techniques to provide additional species for the comparison of relative stabilities using reaction 4, $R = Li^+$, Na^+, and K^+.[16, 17]

The present work reports ICR studies of the relative gas phase stabilities with respect to the reference base Br^- of a series of ions R^+ including alkali ions, alkyl carbenium ions, acyl cations, and cyclic halonium ions, and the assessment of the solvation energetics of these ions in fluorosulfuric acid media based on the comparison of the gas phase and solution results.[18]

Experimental

ICR instrumentation and techniques used in these studies have been previously described in detail.[12-14, 16-20] Two instruments were employed: all of the alkali ion results were obtained using a standard Varian V5900 ion cyclotron resonance mass spectrometer equipped with a 9 inch magnet system; other studies utilized an instrument built in the shops at Caltech which incorporates a 15 inch magnet system and is similar in other respects to the Varian spectrometer.

Alkali ions were generated by a thermionic source which was mounted on the trapping electrode inside the source region of the ICR cell, next to the electron emission source. The thermionic source consists of a small (< 1 mm diameter) glass bead containing equal parts of an alkali oxide, SiO_2, and Al_2O_3, on a 7 mil rhenium filament wire.[20] By appropriately biasing the emitter it is possible to confine alkali ions in the trapping well. While the spectrometer was operated in the drift mode for the studies reported herein, we have successfully performed trapped ion experiments by pulsing the bias applied to the thermionic emitter to fill the trapping region with alkali ions at the start of the trapping sequence.[17]

$(CD_3)_2CHBr$ was prepared by reduction of $(CD_3)_2CO$ to $(CD_3)CHOH$ using $LiAlH_4$ in bis(2-ethoxy-ethyl) ether followed by distillation; the $(CD_3)_2CHOH$ was then reacted with PBr_3 at -10°C to give $(CD_3)_2CHBr$ which was purified by distillation. 2, 3-dibromo-2-methylbutane and 2, 3-dibromo-2, 3-dimethylbutane were synthesized by the bromination of the appropriate olefin in CH_2Cl_2 at -10°C. 1-Adamantyl bromide was kindly provided by Professor P. v. R. Schleyer. Other chemicals were obtained from commercial sources.

Samples were examined by mass spectrometric analysis to determine purities; several compounds were further purified by distillation. All samples were degassed at liquid nitrogen temperature before use.

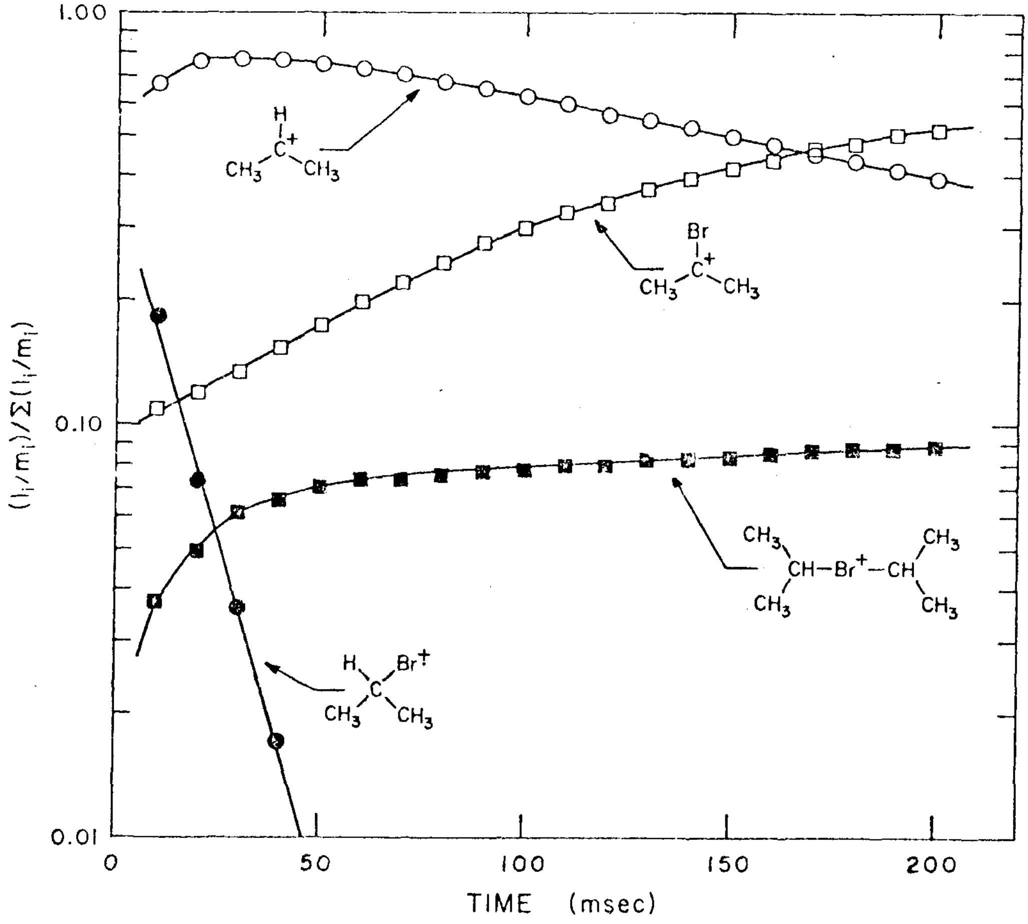
Results

The gas phase ion chemistry of each of the organic bromides, RBr, used in the study of relative stabilities was briefly investigated by examining the variation of ion abundance with pressure and with time and by double resonance experiments.[12-14] The major ion in the mass spectra of these molecules, even at low electron energies, is the fragment R^+.[9-13] While in several systems slow hydride abstraction or condensation reactions with the parent neutral were observed, in mixtures with other neutral bromides, bromide transfer, reaction 4, is fast, allowing the preferred direction of this reaction to be readily ascertained.[12, 13, 18]

Monobromides. The ion chemistry of isopropyl bromide was examined in detail and found to be similar to that of methyl and ethyl bromide which has been previously reported.[12] At 12.0 eV the only species present in the mass spectrum of $(CH_3)_2CHBr$ are the parent ion, $(CH_3)_2CHBr^{+\cdot}$ (m/e 122 and 124) and the isopropyl cation, $(CH_3)_2CH^+$ (m/e 43). Variation of ion abundance with time following a 10 msec., 12.0 eV electron beam pulse is shown in Figure 1. The parent ion reacts to give the isopropyl cation, reaction 6, and

FIGURE 1

Variation of ion abundance with time following a 10 msec, 12.0 eV electron beam pulse in $(CH_3)_2CHBr$ at 2×10^{-6} torr: ● $(CH_3)_2CHBr^{+\cdot}$, ○ $(CH_3)_2CH^+$, □ $(CH_3)_2CBr^+$, ■ $((CH_3)_2CH)_2Br^+$.


1.00
0.10
0.01
0
50
100
150
200
TIME (msec)
$(I_i/m_i)/\Sigma(I_i/m_i)$
$CH_3CHCH_3^+$
$CH_3CBrCH_3^+$
$(CH_3)_2CH-Br^+-CH(CH_3)_2$
$(CH_3)_2CHBr^+$

diisopropyl bromonium ion, reaction 7, with an overall rate constant of 8 × 10^{-10} $cm^3 molecule^{-1} sec^{-1}$. Hydride abstraction by the

$$(CH_3)_2CHBr^{+\cdot} + (CH_3)_2CHBr \xrightarrow{65\%} (CH_3)_2CH^+ + C_3H_7Br_2\cdot \tag{6}$$

$$(CH_3)_2CHBr^{+\cdot} + (CH_3)_2CHBr \xrightarrow{35\%} ((CH_3)_2CH)_2Br^+ + Br\cdot \tag{7}$$

isopropyl cation, reaction 8, proceeds with a rate constant of 0.7 × 10^{-10} $cm^3 molecule^{-1} sec^{-1}$; the product $C_3H_6Br^+$ (m/e 121 and 123) is not observed to undergo further reaction. At higher pressures the isopropyl cation clusters to form the diisopropyl bromonium ion, reaction 9. This accounts for the slow increase of

$$(CH_3)_2CH^+ + (CH_3)_2CHBr \rightarrow C_3H_6Br^+ + C_3H_8 \tag{8}$$

$$(CH_3)_2CH^+ + (CH_3)_2CHBr \rightarrow ((CH_3)_2CH)_2Br^+ \tag{9}$$

$((CH_3)_2CH)_2Br^+$ abundance at long times in Figure 1. In order to identify the site of hydride abstraction in reaction 8, ion-molecule reactions in $(CD_3)_2CHBr$ were examined. Ion abundance and double resonance results show that reaction 10 occurs but not reaction 11, indicating that hydride abstraction is exclusively from the 2 position. Studies of a mixture of $(CD_3)_2CHBr$ and $(CH_3)_3CHBr$ were consistent

$$(CD_3)_2CH^+ + (CD_3)_2CHBr \rightarrow (CD_3)_2CBr^+ + (CD_3)_2CH_2 \tag{10}$$

$$(CD_3)_2CH^+ + (CD_3)_2CHBr \not\rightarrow C_2HD_5Br^+ + (CD_3)_2CHD \tag{11}$$

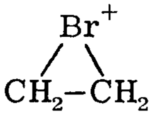
with the previously proposed mechanism for hydride transfer involving participation of a symmetric dialkylhalonium ion intermediate.[12]

In tert-butyl bromide the only ion observed in the mass spectrum at 12.0 eV is the tert-butyl cation, $(CH_3)_3C^+$. The condensation reactions 12-15 occur with an overall rate constant $k = 0.4 \times 10^{-10}$ $cm^3 molecule^{-1} sec^{-1}$. At higher pressures ($> 10^{-4}$ torr) ions of composition $C_9H_{19}^+$, $C_{10}H_{21}^+$, $C_{11}H_{23}^+$, $C_{12}H_{25}^+$, and $C_{13}H_{27}^+$ are also observed.[21]

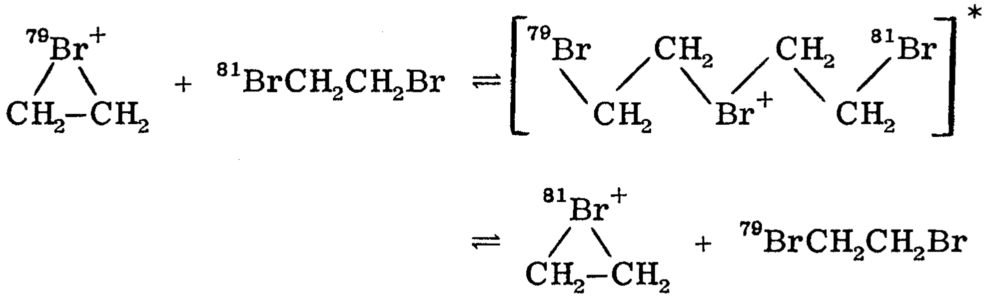
$$(CH_3)_3C^+ + (CH_3)_3CBr \begin{array}{lr} \xrightarrow{45\%} C_5H_{11}^+ + C_3H_7Br & (12) \\ \xrightarrow{33\%} C_6H_{13}^+ + C_2H_5Br & (13) \\ \xrightarrow{12\%} C_7H_{15}^+ + CH_3Br & (14) \\ \xrightarrow{10\%} C_8H_{17}^+ + HBr & (15) \end{array}$$

Norbornyl cation and adamantyl cation are the predominant species in the 16.0 eV mass spectra of exo-2-norbornyl bromide and 1-adamantyl bromide, respectively. At higher pressures or longer delay times, reaction by minor fragment ions increases the abundance of these ions, which are not observed to undergo further reaction. The ion chemistry of 2-bromobutane, cyclopentyl bromide, acetyl bromide and propionyl bromide is similar: R^+ is the predominant ion in the mass spectrum, the abundance of this species increases slightly with pressure or time due to reactions by minor fragments, and no fast bimolecular reactions of this ion are observed with the parent neutral.

Dibromides. The principal ion ($> 80\%$ at all electron energies) in the mass spectrum of $BrCH_2CH_2Br$ is $C_2H_4Br^+$ (m/e 107 and 109) corresponding to the cyclic bromonium ion



The relative intensity of this ion is not observed to decrease with increasing pressure or trapping times, suggesting that it is unreactive. However, if the species at m/e 109 is ejected by use of the double resonance oscillator in a time short compared to the time between collisions, Figure 2, then the species at m/e 107 is observed to decay rapidly.[13] This indicates that rapid isotopic exchange is taking place, reaction 16. The measured rate constant (average of



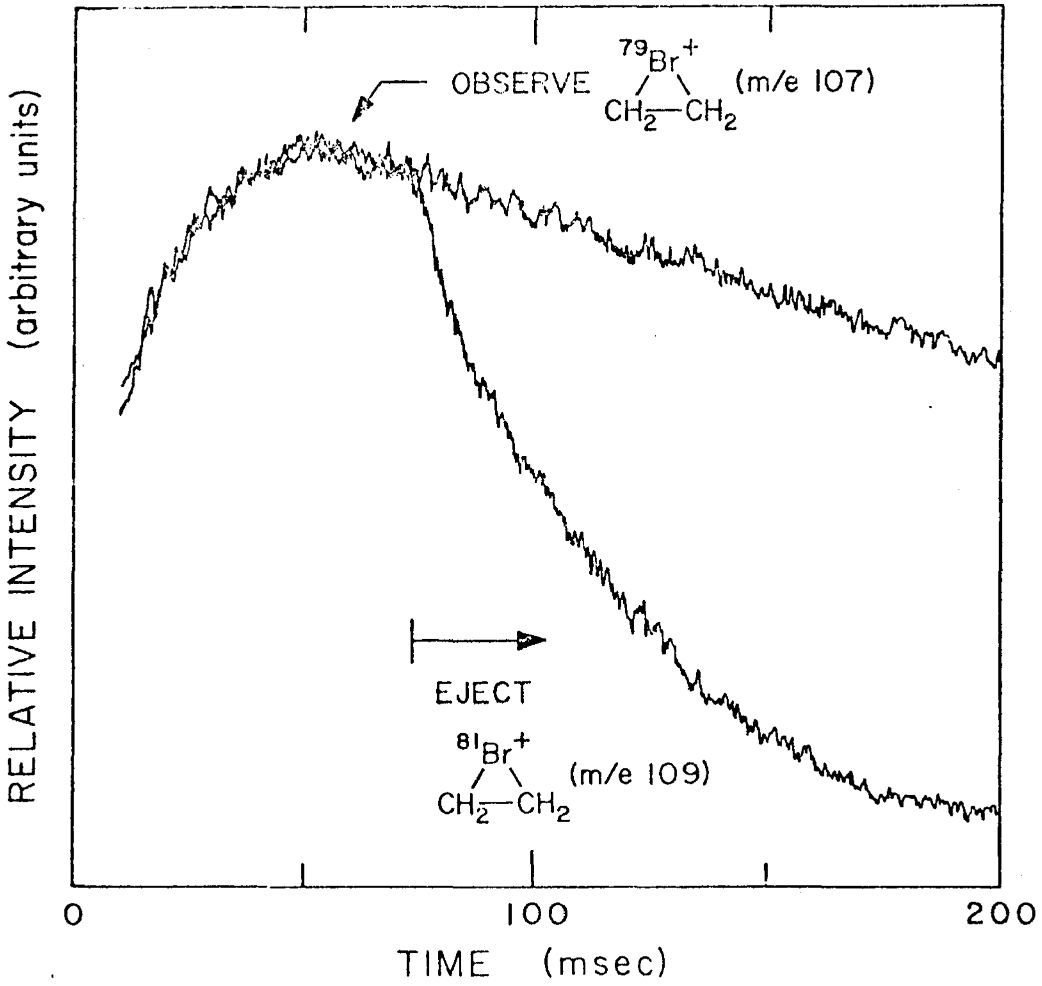
(16)

three determinations) indicates, correcting for statistical factors, an overall rate constant for reaction of 5.2×10^{-10} $cm^3 molecule^{-1} sec^{-1}$. The ion chemistry of other dibromides is similar, the rate constant for thermoneutral bromide exchange decreasing with increasing methyl substitution in the three-member rings. The thermoneutral isotopic exchange reaction was not observed in the five-member-ring bromonium ions.

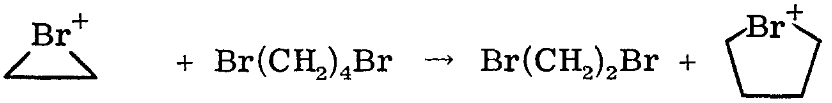
Mixtures. In a binary mixture of organic bromides R_1Br and R_2Br, bromide transfer, reaction 4, provides a measure of the relative stability of the carbonium ions R_1^+ and R_2^+. Examination of

FIGURE 2

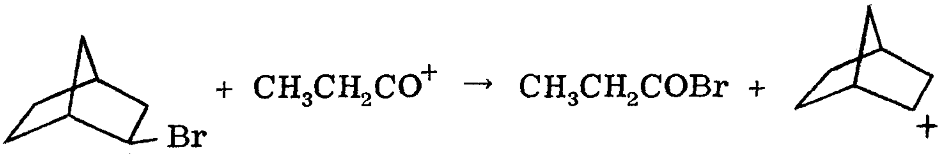
Variation of ion intensity with time following a 10 msec, 16.0 eV electron beam pulse in $BrCH_2CH_2Br$ at 4.0×10^{-6} torr for $C_2H_4\,{}^{79}Br^+$ (m/e 107) with and without continuous ejection of $C_2H_4\,{}^{81}Br^+$ (m/e 109) starting at 75 msec. From the observed first order decay, a rate constant of 1.3×10^{-10} $cm^3 molecule^{-1} sec^{-1}$ is obtained for reaction 16.


OBSERVE $^{79}Br^+$ (m/e 107)
CH_2—CH_2
EJECT
$^{81}Br^+$ (m/e 109)
CH_2—CH_2
RELATIVE INTENSITY (arbitrary units)
0
100
200
TIME (msec)

the trapped ion spectra of these species in such mixtures establishes the preferred direction of reaction. For example, in a mixture of 1, 2-dibromoethane and 1, 4-dibromobutane, reaction 17 proceeds entirely to the right, Figure 3a. In reaction 18, exo-2-norbornyl bromide is observed to transfer Br^- to $CH_3CH_2CO^+$, Figure 3b. The inferred



(17)



(18)

reactions are confirmed by double resonance experiments. For a series of carbonium ions R^+, similar experiments indicate the following order for relative free energies of RBr heterolytic bond cleavage:[22]

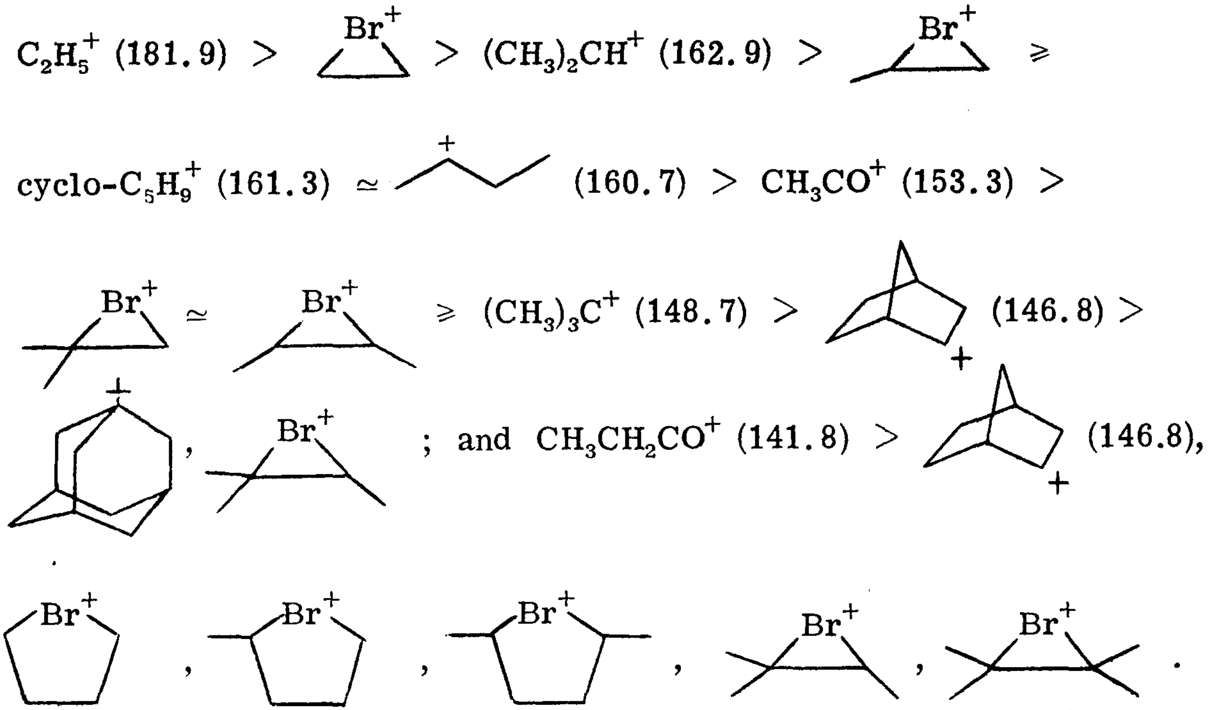
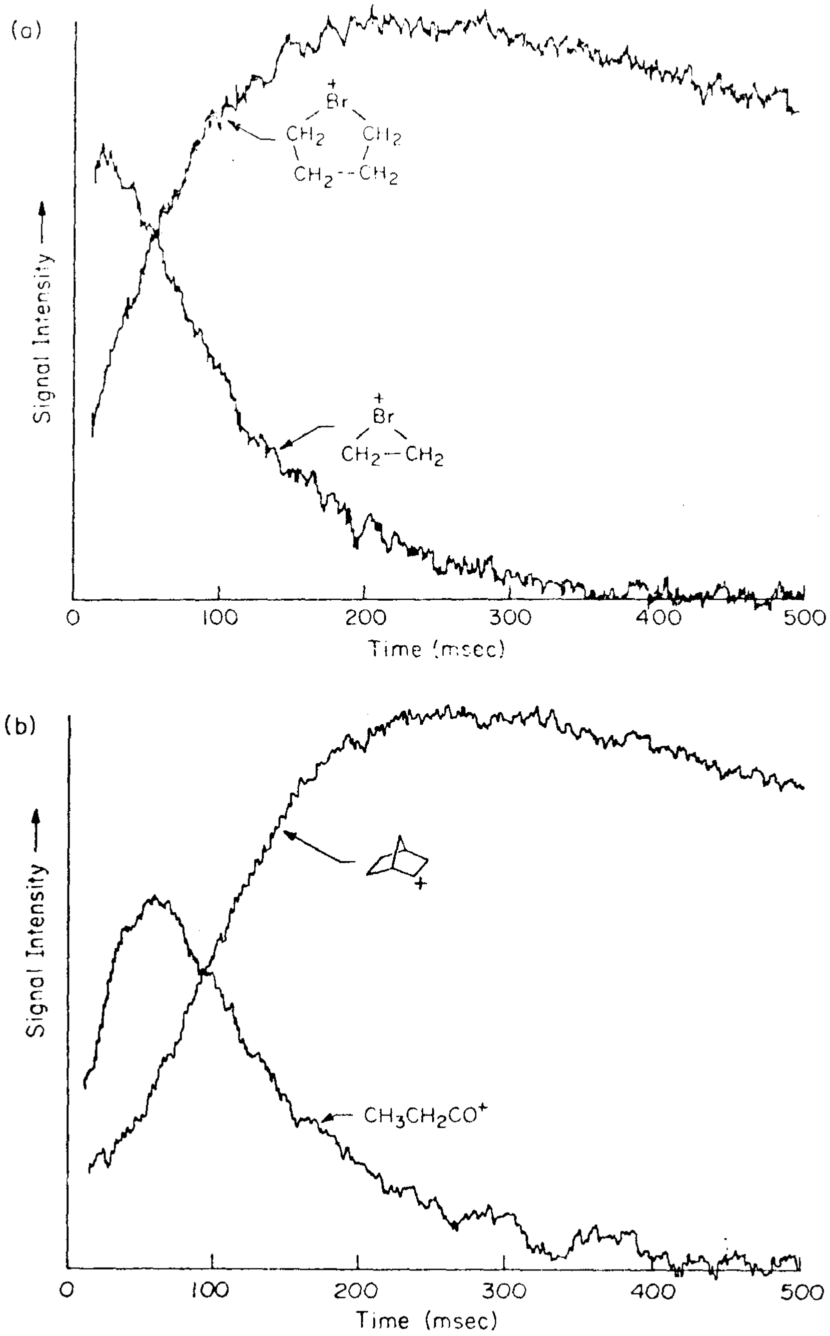


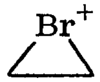
FIGURE 3

Variation of ion intensities with time in two mixtures of bromides. Relative carbonium ion stabilities in the gas phase with respect to Br^- are determined from the direction of Br^- transfer: (a) 6:1 mixture of 1, 2-dibromoethane and 1, 4-dibromobutane at a total pressure of 2×10^{-6} torr: tetramethylene bromonium ion is more stable than ethylene bromonium ion (reaction 17); (b) 7:1 mixture of propionyl bromide and exo-2-norbornyl bromide at a total pressure of 3×10^{-6} torr: norbornyl cation is more stable than propionyl cation (reaction 18). Build up of the displayed species during the first 50 msec is due in part to reaction by fragment ions (not shown) following the initial 10 msec, 16 eV electron beam pulse.

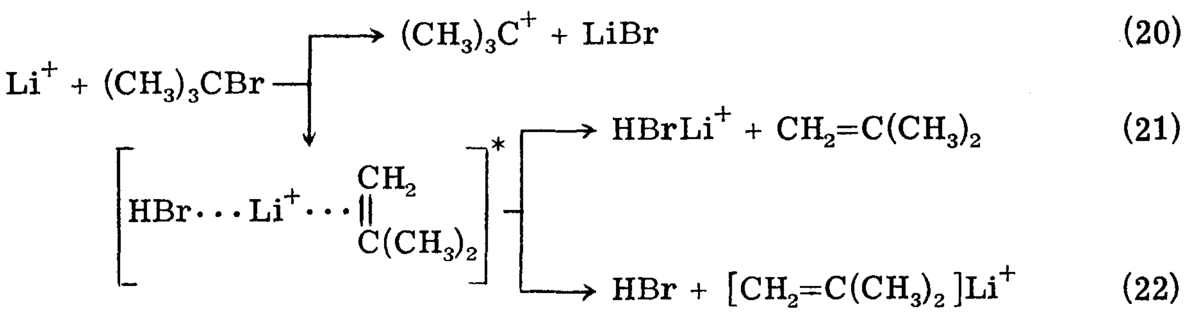

(a)
Signal Intensity
CH2 CH2 CH2--CH2 Br+
Br+ CH2--CH2
0
100
200
300
400
500
Time (msec)
(b)
Signal Intensity
+
CH3CH2CO+
0
100
200
300
400
500
Time (msec)

Estimates of bromide affinities, $D(R^+-Br^-)$, from available thermochemical data considered in detail below are given in parentheses in kcal/mol. Also, in order to investigate the relative stabilities of several isomeric carbenium ions (see below), ion-molecule reactions in a mixture of $(CD_3)_2CHBr$ and $CH_3CHBrCH_2Br$ were examined; reaction 19 was not observed to occur.

$$(CD_3)_2CBr^+ + CH_3CHBrCH_2Br \not\rightarrow (CD_3)_2CBr_2 + \qquad (19)$$



Alkali Ion Reactions. The reactivity of the alkali cations Li^+, Na^+, and K^+ with various organic halides was investigated. Both bromide transfer and elimination reactions were observed. For example, with Li^+ and $(CH_3)_3CBr$, reactions 20-22 were observed. Further studies of the elimination processes 21 and 22 have been reported separately.[16, 17] The bromide transfer reaction 20 is a special case of reaction 4 with $R_1^+ = M^+ = Li^+$ and may be used to infer limits on the relative stability of M^+ and R_2^+ with respect to the reference acid X^-. The observed reactivity of alkali ions with various organic bromides is presented in Table I.



$$Li^+ + (CH_3)_3CBr \rightarrow (CH_3)_3C^+ + LiBr \qquad (20)$$

$$Li^+ + (CH_3)_3CBr \rightarrow \left[HBr \cdots Li^+ \cdots \overset{CH_2}{\underset{C(CH_3)_2}{\|}} \right]^* \rightarrow HBrLi^+ + CH_2{=}C(CH_3)_2 \qquad (21)$$

$$\left[HBr \cdots Li^+ \cdots \overset{CH_2}{\underset{C(CH_3)_2}{\|}} \right]^* \rightarrow HBr + [CH_2{=}C(CH_3)_2]Li^+ \qquad (22)$$

Table I. Reactions Investigated in Mixtures of Organic Bromides with Alkali Ions

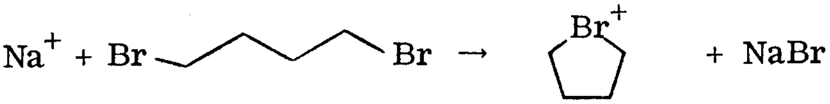
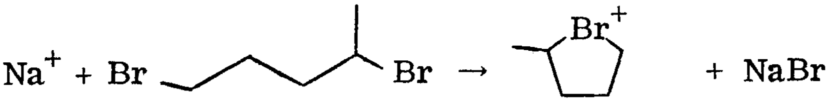
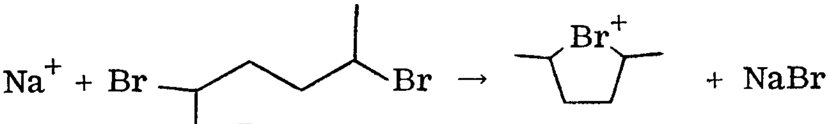
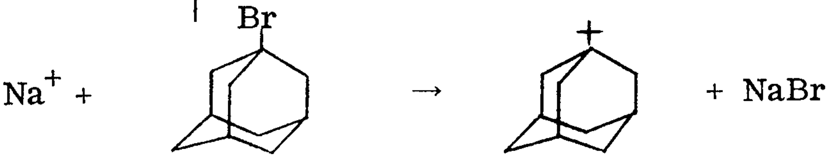
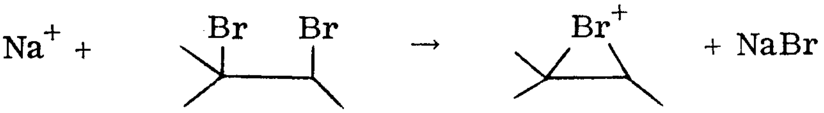
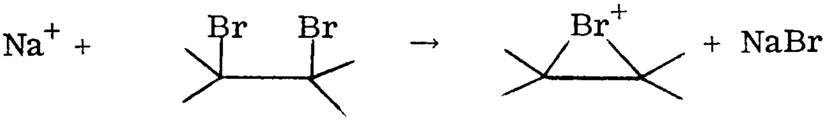
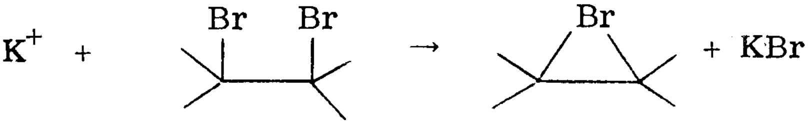
Reaction	Observed Reactivity[a]
$Li^+ + (CH_3)_2CHBr \xrightarrow{<1\%} (CH_3)_2CH^+ + LiBr$	not observed
$\xrightarrow{100\%} [C_3H_6]Li^+ + HBr$	fast
$Li^+ + CH_3COBr \longrightarrow CH_3CO^+ + LiBr$	not observed
$Li^+ + (CH_3)_3CBr \xrightarrow{6\%} (CH_3)_3C^+ + LiBr$	slow
$\xrightarrow{93\%} [C_4H_8]Li^+ + HBr$	fast
$\xrightarrow{1\%} HBrLi^+ + C_4H_8$	slow
$Li^+ + CH_3CH_2COBr \xrightarrow{68\%} CH_3CH_2CO^+ + LiBr$	fast
$\xrightarrow{32\%} [CH_3CHCO]Li^+ + HBr$	fast
	not observed
	not observed
	not observed
	not observed
	not observed
	fast
	not observed

Table I: (Continued)

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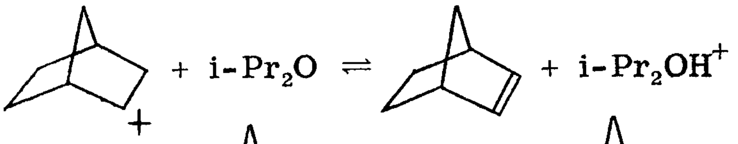
[a] Approximate rate constants have been inferred from observed ion intensities in ICR drift spectra and assigned to one of three ranges: fast, $k \gtrsim 10^{-10}$; slow, $10^{-10} \lesssim k \leq 10^{-12}$; not observed, $k < 10^{-12}$ cm^{3}molecule^{-1}sec^{-1}.

Proton Affinity of Norbornene. Reference values of bromide affinity are required to calibrate the scale of relative bromide affinities established by studies of reaction 4. A reference value for the bromide affinity of norbornyl cation may be calculated from the proton affinity of norbornene. Proton affinity (PA) is defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, equation 23.[23-27] Kaplan, Cross and Prinstein investigated the proton affinity of norbornene and reported a value of 207 kcal/mol.[28] Accurate relative values of proton affinity may be determined by measuring equilibrium constants for proton transfer, reaction 24.[23-27] Proton transfer

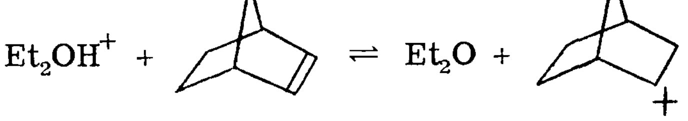
$$BH^+ \rightarrow B + H^+ , \qquad \Delta H = D(B{-}H^+) \equiv PA(B) \tag{23}$$

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+ , \qquad \Delta H = PA(B_1) - PA(B_2) \tag{24}$$

reactions in mixtures of norbornene with various bases were examined. Reaction 25 was observed to proceed entirely to the right ($K > 300$), establishing an upper limit of 203.8 kcal/mol for PA (norbornene). For reaction 26, an equilibrium constant of



(25)

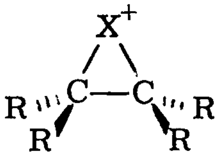


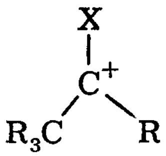
(26)

$K = 2.3 \pm 0.3$ was measured, average of three determinations, from which PA(norbornene) = 198.8 kcal/mol is calculated. All of the quoted values of proton affinity are with respect to PA(NH_3) = 202.3 ± 2.0 kcal/mol which has been established by experiments in which PA(NH_3) is obtained relative to several molecules for which absolute values of proton affinity are known from appearance potential measurements or ionization potentials of the corresponding radicals.[27]

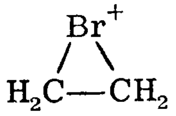
Discussion

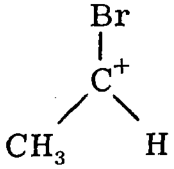
Relative Stabilities of Structural Isomers. The relative stabilities of bridged and open haloalkyl cation isomers, structures I and II, depend on the size and positions of the alkyl substituents, R = H, Me,

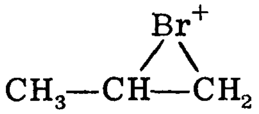

I


II

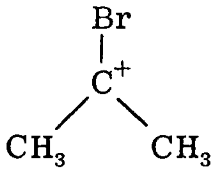
Et, etc., and the particular halogen considered, X = F, Cl, Br.[29, 6] Extrapolation of theoretical results for fluoro- and chloroethyl cations suggests that for the bromoethyl cation, the isomer of structure III is more stable than IV.[29] While cyclic bromo- and iodoalkyl cations, structure I, X = Br, I, have been well characterized in solution by proton and ^{13}C NMR, the existence of the open forms as stable species is questionable.[6]


III


IV



V



VI

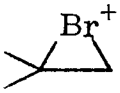
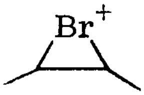
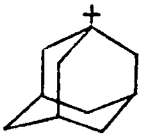
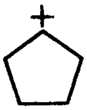
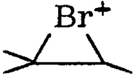
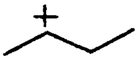
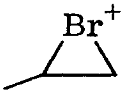
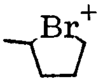
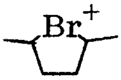
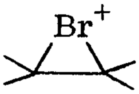
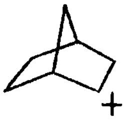
Two isomeric ions of the formula $C_3H_6Br^+$ are encountered in the present work, structures V and VI. In $(CH_3)_2CHBr$ the observed reaction of $(CH_3)_2CH^+$, reaction 8, implies a heat of formation for the product $C_3H_6Br^+$ of $\Delta H_f \leqslant 193.0 \pm 2$ kcal/mol.[30, 31] Since hydride abstraction occurs exclusively from the 2 position, reaction 10, this ion must have structure VI. The observed direction of reaction 8 shows that the carbenium ion center is stabilized by Br substitution, consistent with previous studies which indicate that halogen substitution on carbenium ions is stabilizing when stabilities are defined with respect to the reference base H^-.[12, 13, 32] The $C_3H_6Br^+$ ion formed from 1, 2-dibromopropane is expected to have structure V. From the bromide affinity of this ion (see below) a value of 194.5 ± 2 kcal/mol may be calculated for its heat of formation,[31,33,34] which suggests that this isomer is somewhat less stable than the isomer with structure VI for which $\Delta H_f \leqslant 193.0 \pm 2$ kcal/mol. A direct comparison of the stabilities of these ions with respect to the reference base Br^-, reaction 18, is also consistent with this result: the ion with structure VI does not react with $CH_3CHBrCH_2Br$ to give V. Observation of the reversible bromide exchange reaction for

1, 2-dibromopropane, analogous to reaction 16 in 1, 2-dibromoethane, suggests, however, that the cyclic isomer V retains its structural integrity and does not rearrange to the more stable isomer VI.

Bromide Affinities. Reference values of bromide affinity to calibrate the scale of relative bromide affinities established by studies of reaction 4 are available from several sources. Heats of formation for a number of alkyl carbenium ions are available from the work of Lossing who has measured ionization potentials for the corresponding radicals.[30, 35] Heats of formation for the acyl cations CH_3CO^+ and $CH_3CH_2CO^+$ are available from appearance potential measurements.[36,37] All of these values may be combined with values for the heats of formation for the corresponding neutral bromides[31] and $\Delta H_f(Br^-) = -52.3$ kcal/mol[33, 34] to give bromide affinities, Table II. Bromide affinity values for the alkali ions Li^+, Na^+, and K^+ are also available in the literature, Table II.[34] The experimental results from studies of reaction 4 are all consistent with these values.

From the measured proton affinity of norbornene PA(norbornene) = 198.8 ± 2 kcal/mol, the reported heat of hydrogenation of norbornene to norbornane of 33.13 ± 0.21 kcal/mol,[38] and the difference in heats of formation of norbornane and exo-2-norbornylbromide of $\Delta\Delta H_f = -2.4 \pm 1$ kcal/mol estimated from group heats,[31] a bromide affinity for norbornyl cation of 146.8 ± 2.3 kcal/mol is calculated. While consistent with other results, this value is higher than $D(CH_3CH_2CO^+-Br^-) = 141.8$ kcal/mol in contradiction to the observed result, reaction 18 and Figure 3b, that

Table II. Heterolytic $R^+–X^-$ Bond Dissociation Energies

R^+	$D(R^+–Br^-)^a$	R^+	$D(R^+–Br^-)^a$
CH_3^+	217.7 ± 2[b, c]		146.8 ± 2
$C_2H_5^+$	181.9 ± 2[b, c]		146.4 ± 2
	169.9 ± 8	$CH_3CH_2CO^+$	141.8 ± 3[b, h]
	162.9 ± 2[b, c]		134.9 ± 7
	161.3 ± 2[b, d]		132.0 ± 7
	160.7 ± 2[b, c]		130.6 ± 7
	159.6 ± 2		130.6 ± 7
CH_3CO^+	153.3 ± 2[b, e]		130.6 ± 7
Li^+	148.7 ± 3[f]	Na^+	127.9 ± 1[f]
$(CH_3)_3C^+$	148.7 ± 2[b, c]		117.8 ± 7
	146.8 ± 2[f]	K^+	113.7 ± 1[f]

[a] All data in kcal/mol. [b] References 31, 33, and 34. [c] Reference 30. [d] Reference 35. [e] Reference 36. [f] References 33 and 34. [g] Present work and references 28 and 38, see text. [h] Reference 37.

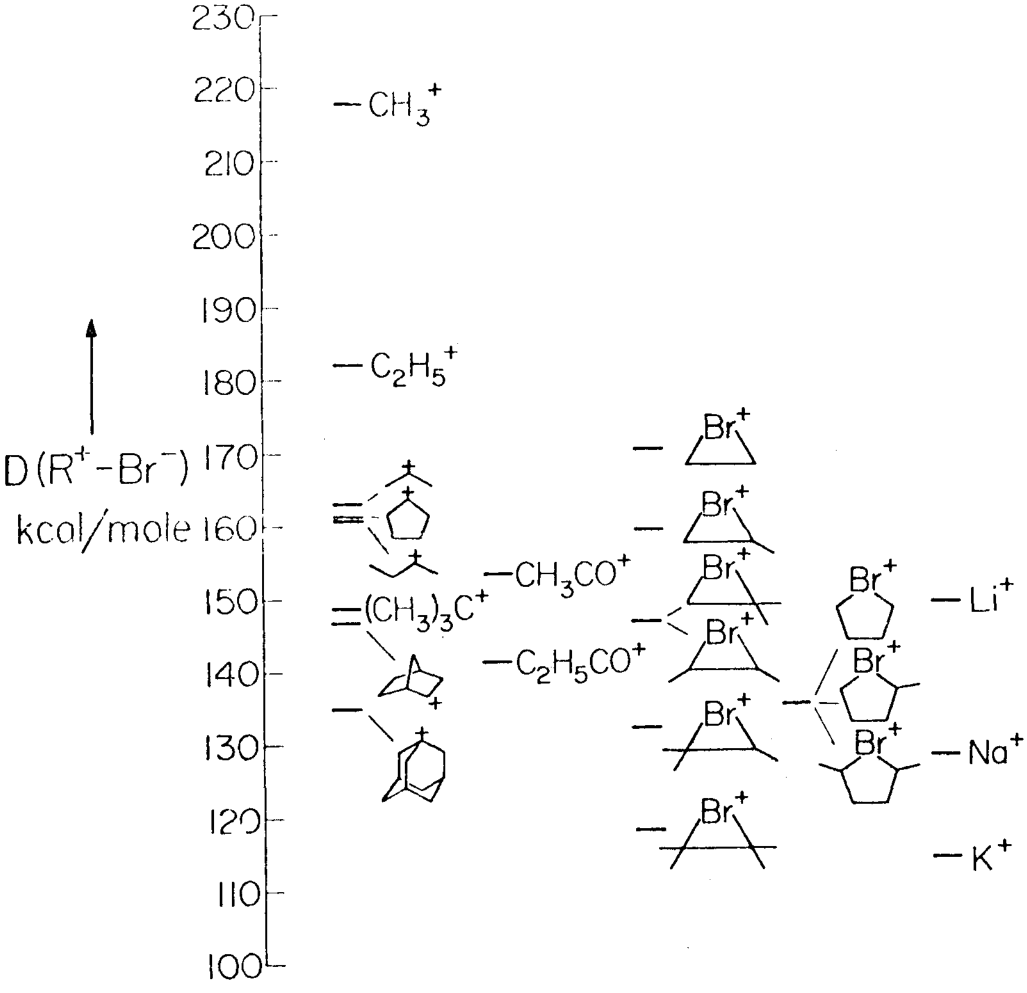
norbornyl cation is more stable than propionyl cation with respect to the reference base Br^-. This conclusion assumes that the free energy result can be compared to the calculated enthalpies since symmetry number changes or ring formation are not involved in reaction 18.[23-27] It would be of great interest to resolve this contradiction. In particular $\Delta H_f(CH_3CH_2CO^+) = 143.5$ kcal/mol[37] should be reexamined.[39]

The relative order of free energies for process 4 established by the observed bromide transfer reactions may be combined with the results from the alkali ion studies and the calculated values for $D(R^+-Br^-)$ for the reference compounds to obtain bromide affinities for all of the compounds studied, Table II, Figure 4. Enthalpies of bromide transfer are estimated from the relative free energies by making the appropriate corrections for entropy changes. It is expected that with the exception of symmetry number changes,[23-27] ΔS will be small for processes such as reaction 15 but cannot be ignored in processes such as reaction 14 where entropies of cyclization are large. Estimates of this effect indicate that the bromide affinities for the three, four, and five membered ring bromonium ions would respectively decrease by 2.9, 3.6, and 4.3 kcal/mol relative to alkali ions, alkyl carbenium ions, and acyl cations.[40]

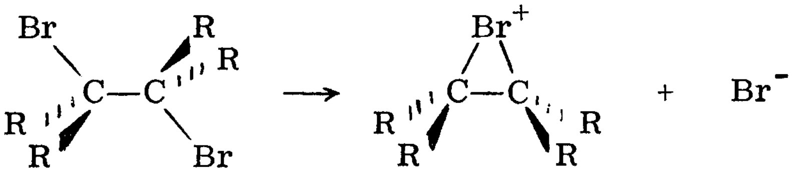
The effect of methyl substitution in the three-member-ring bromonium ion series is systematic and constant, about 13 kcal/mol per methyl group. The stabilizing effect of methyl substitution in this series is nearly as large as is found in methyl substitution of

FIGURE 4

Gas phase bromide affinities of alkyl carbenium ions, acyl cations, cyclic bromonium ions, and alkali cations.


230
220
210
200
190
180
170
160
150
140
130
120
110
100
D(R+-Br−)
kcal/mole
CH3+
C2H5+
(CH3)3C+
CH3CO+
C2H5CO+
Br+
Br+
Br+
Br+
Br+
Br+
Br+
Br+
Br+
Li+
Na+
K+

carbenium ions where from ethyl to isopropyl carbenium ions $D(R^+-Br^-)$ decreases by 19.0 kcal/mol and from isopropyl to tert-butyl 14.2 kcal/mol. Comparable results are also found in the effects of methyl substitution on proton affinity in the phosphine and arsine series (13.4 and 12.3 kcal/mol per methyl, respectively).[24, 41] However, while in these series the effect is smaller for larger members of the series, no decrease with size is apparent in the bromonium ion series. This may in part be due to the increased effect of steric factors which destabilize the neutral relative to the ion, process 27, in the bromonium ion series as H is replaced by



(27)

methyl. The five-member-ring tetramethylene bromonium ion is about 16 kcal/mol more stable than the isomeric dimethylethylene bromonium ion, reflecting reduced ring strain in the larger ring.[42]

Also of particular interest is the result for adamantyl cation, which is found to be more stable than tert-butyl cation. This indicates that the strain energy due to the nonplanarity of the carbonium ion center in the 1-adamantyl carbenium ion relative to the tert-butyl carbenium ion is smaller than the stabilization afforded by the interaction of the charge with the added hydrocarbon framework.[43] It would be of interest to refine the measurement of the heat of formation for adamantyl cation to better quantify this difference.

Solvation Energetics. The thermochemical cycle 28 where

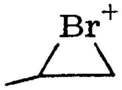
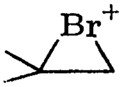
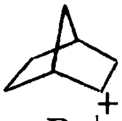
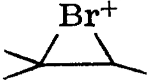
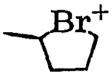
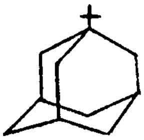
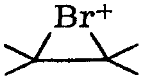
$$\begin{tikzcd}
RBr(g) \arrow[r, "\Delta H_i(g)"] \arrow[d, "\Delta H_s(RBr)"'] & R^+(g) \arrow[d, "\Delta H_s(R^+)"'] & + & Br^-(g) \arrow[d, "\Delta H_s(Br^-)"'] \\
RBr(\ell) \arrow[r, "\Delta H_i(\ell)"] & R^+(\ell) & + & Br^-(g)
\end{tikzcd} \tag{28}$$

g and ℓ designate the gas and liquid phases and subscripts i and s designate ionization and solution processes, respectively, may be employed to obtain heats of solvation of R^+, $\Delta H_s(R^+)$, if the other quantities are known.[44] Values for $\Delta H_i(g)$ are available from the present work. Relative heats of ionization in solution $\Delta H_i(\ell)$ are available for a number of the ions examined in this study from calorimetrically determined heats of solution of RX in HSO_3F solution, Table III.[7, 8, 45-48] Observed relative heats of formation, ΔH_{obsd}, may be used to calculate relative values for $\Delta H_i(\ell)$ in HSO_3F by correcting ΔH_{obsd} for the heat of vaporization (or sublimation) of RX, equation 29. Only relative heats of ionization $\Delta H_i(\ell)_{rel}$ may be obtained since the heats of formation of Br^- and

$$\Delta H_i(\ell)_{rel} = \Delta H_{obsd} - \Delta H_{vap} \tag{29}$$

Cl^- in HSO_3F solution are not known. $\Delta H_i(\ell)_{rel}$ from chloride precursors are converted to values for ionization of RBr by reference to the value for $R^+ = (CH_3)_3C^+$. Estimated relative enthalpies of solution of R^+ in HSO_3F, Table IV, may be calculated using the data

Table III. Relative Heats of Ionization in HSO_3F Solution[a]

Ion	$\Delta\bar{H}_{S,\,CCl_4}$	ΔH_{obsd}	ΔH_{vap}[b]	$\Delta H_i(\ell)_{rel}$[c]
Bromide Precursors[d] $RBr \rightarrow R^+ + Br^-$				
	0.2	+1.0	9.9	- 8.9
	0.1	- 3.3 ± 0.5	9.8	-13.1
	0.0	- 8.4 ± 0.9	10.6	-19.0
$(CH_3)_3C^+$	0.1	-14.5 ± 2.0	7.4	-21.9
	2.2	-13	11.0	-24.0
	-0.3	-13.4 ± 0.9	11.5	-24.9
	0.3	-13.8 ± 1.9	13.0	-26.8
	3.8	-14.3 ± 0.2	18.3[c]	-32.6
	2.4	-22.9 ± 4.0	15.8	-38.7
Chloride Precursors[f] $RC\ell \rightarrow R^+ + C\ell^-$				
$(CH_3)_3C^+$	0.2	- 6.7 ± 0.2	6.9	-13.6
CH_3CO^+	1.0	-21.2 ± 0.2	7.2	-28.4
$C_2H_5CO^+$	0.8	-19.4 ± 0.3	8.3	-27.7

---

[a] All data in kcal/mol.

[b] Data from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970; or estimated from boiling point data.

Table III. (Continued)

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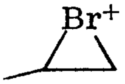
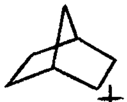
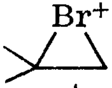
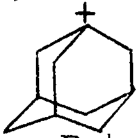
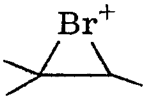
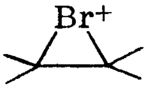
[c] Calculated using equation 29.

[d] Data from references 8, 45, and 46.

[e] The heat of sublimation of adamantyl bromide (a solid at room temperature) used in the cycle was estimated using data from P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, J. Am. Chem. Soc., **92**, 2377 (1970), as described in A. Bondi, J. Chem. Eng. Data, **8**, 371 (1963).

[f] Data from reference 7.

Table IV. Estimated Relative Enthalpies of Solution of R^+ in HSO_3F[a]

R^+	$\Delta H_i(g)$[b]	$\Delta H_i(\ell)$[c]	ΔH_s[d] $(R^+ + Br^-)$	$\delta_R \Delta H_s$ (R^+)
CH_3CO^+	153.3 ± 2	-36.7 ± 3	-189.0 ± 3	-19
	169.9 ± 8	-8.9	-178.6 ± 8	-8
$CH_3CH_2CO^+$	141.8 ± 3	-36.0 ± 5	-177.0 ± 6	-7
	159.6 ± 2	-13.1 ± 0.5	-172.6 ± 1	-2
$(CH_3)_3C^+$	148.7 ± 2	-21.9 ± 2	-170.5 ± 2	0
	146.8 ± 2	-24.0[f]	-168.6 ± 3[f]	2[f]
	146.8 ± 2	-19.0 ± 0.9	-165.8 ± 2	5
	134.9 ± 7	-32.6 ± 0.2	-163.7 ± 7[h]	7
	130.6 ± 7	-26.8 ± 2	-157.1 ± 7	13
	132.0 ± 7	-24.9 ± 0.9	-157.2 ± 7	13
	117.8 ± 7	-38.7 ± 4	-154.1 ± 8	16

[a] All data in kcal/mol at 298 K.

[b] Data from Table II.

[c] Data from Table III.

[d] Calculated using equation 30.

[e] Heats of solvation of R^+ relative to that of $(CH_3)_3C^+$.

[f] See footnote 47.

from Tables II and III and equation 30, which is derived from the thermochemical cycle 28. It is apparent from these data that

$$\Delta H_s(R^+) + \Delta H_s(Br^-) = -\Delta H_i(g) + \Delta H_i(\ell) + \Delta H_s(RBr) \qquad (30)$$

solvation enthalpies are related to ion size; smaller ions are better solvated. A direct comparison of $D(R^+{-}Br^-)$ in the gas phase and solution is also revealing. The relative bromide affinities of cyclic bromonium ions are the same in the gas phase and solution. Stability increases with increasing ring size and, in the three-membered rings, methyl substitution. However, solvent has an appreciable effect in attenuating the observed range.

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(47) Recent experiments suggest that the heat of ionization of norbornyl bromide in solution relative to *tert*-butyl bromide may be somewhat reduced (E. M. Arnett, private communication). This would also reduce the heat of solvation of the norbornyl cation relative to $(CH_3)_3C^+$, Table III.

PROPOSITIONS

PROPOSITION I

Use of Valence Band ESCA Intensities to Determine Lone Pair s Character in Ammonia and the Methylamines

The general nature of photoelectron spectroscopy (PES) has been discussed in the introduction to Part One of this report with respect to the use of the He(I) resonance line (21.2168 eV) as a source of ionizing radiation. This spectroscopy can also be conducted using various other sources of monochromatic radiation. Specifically of interest here is the use of the $MgK\alpha_{1,2}$ x-ray line source (1253.6 eV). Photoelectron spectroscopy using this source (or the $AlK\alpha_{1,2}$ line at 1486.6 eV) has usually been referred to as ESCA[1-4] or XPS (X-ray Photoelectron Spectroscopy). K. Siegbahn and his co-workers have been largely responsible for the development of the ESCA technique.[1,2] They and others[3,4] have made extensive use of ESCA for studying the physical and chemical properties of solids. With solid samples, however, this spectroscopy is limited by the mean free path of the primary photoelectrons to the study of a thin surface layer of the sample. Mean escape depths for the primary photoelectrons have been estimated to be typically on the order of 10 Å.[5] Also, with nonconducting solid samples a considerable problem arises as to how to obtain a meaningful calibration of the binding energy scale. Removal of electrons from the surface layer by primary and secondary ionization processes results in charging of upwards of several volts at the surface. In some studies internal standards can be successfully employed.

But the comparison of line positions in different samples generally requires the use of external standards. Several types of external calibration standards have been employed but to date none has been found to give wholly satisfactory results.[6]

Siegbahn[2] and others[7] have also made some use of ESCA for studying gases. Gas samples require that differential pumping be provided between the sample region and the analyser since a clear path is needed for the electrons and low pressures are needed for operation of the analyser. The somewhat elaborate sample region facilities required for the study of gas samples have been included in only a few existing ESCA instruments. The calibration of the binding energy scale with gas samples, however, is quite easy. A second gas of known spectrum is mixed with the sample, and line positions are measured with respect to a line in its spectrum of known ionization potential.

Some use has been made in PES of relative band intensities. Lohr and Robin[8] discovered that computed cross sections were nearly constant for ionization from all of the pi electron molecular orbitals in a variety of planar hydrocarbons. And, Eland[9] has made some use of this observation in assigning hydrocarbon photoelectron spectra. Robin, Kuebler, and Brundle[10] have noted that compared to cross sections for 2s and 2p electrons, the relative cross sections of 3s and 3p electrons are drastically reduced when going from He(I) to He(II) radiation. They have made some use of this 'He(II) intensity effect" in distinguishing phosphorous and chlorine lone pair orbitals from overlapping pi orbitals. Price, Potts, and Streets[11] and Gelius[12] have discussed the theory of relative line intensities in PES and presented a number of experimentally obtained values for relative intensity ratios. In general, it may be concluded that while the relative intensities obtained using a single light source are not particularly informative and in fact may even be misleading,[4] relative intensity information obtained by comparing spectra obtained using light sources of different energy can be most useful for the assignment of bands.

Gelius[12] extended his previous work[2] on relative intensities and that of Lohr and Robin[8] to obtain quantitative values for the relative intensities of 2s and 2p electrons in the first row elements for $MgK\alpha_{1,2}$ radiation (Table I). He also showed that both experimental evidence and theoretical considerations support the idea that if a molecular orbital is expressed as the sum of atomic orbitals

$$\psi_j = \sum c_{ij} \phi_i , \tag{1}$$

its relative intensity in ESCA spectra is given by the sum

$$I_j = \sum |c_{ij}|^2 I_i \tag{2}$$

where the I_i's are the relative intensities for ionization of the atomic orbitals ϕ_i. It will be noted that the 2s/2p ratios for the first row elements C, N, O, and F (Table I) are large, about 11, and within the uncertainty of the present figures, about ±2, approximately constant, the tending to increase slightly for lower atomic numbers. Gelius

Table I

Relative intensities in the ESCA ($MgK\alpha_{1,2}$) spectra of some of the first row elements[a]

Element	2s/2s (C)	2s/2p
C	1	13
N	1.2	11
O	1.4	8.8
F	2.0	10
Ne	–	8.7

[a] Reference 12.

successfully applied this model to the molecular orbital intensities in the ESCA spectra of benzene, furan, thiophene, CF_4, SF_6, C_3O_2 and N_2. The model may also be applied for the assignment of orbitals. In the spectra of H_2O and CH_3OH, for example,[2] the b and a″ orbitals, respectively, from which s character is excluded by symmetry, may be readily identified by their low relative intensity.

Another application to which this model may be put is the measurement of s character of orbitals. This may lead to particularly interesting results if applied to the measurement of s character in lone pair orbitals for a series of related molecules. It is proposed to use the relative ESCA band intensity to measure the s character of the lone pair orbital in ammonia and the methyl amines: $(CH_3)_nNH_{3-n}$, $n = 0, 1, 2, 3$.

The dipole moments of ammonia and the methylamines are given in Table I. Hudson[14] suggests that the greater moment of ammonia with respect to trimethylamine may be due to the more polar N–H bonds augmenting the lone pair moment. Change of the lone pair moment is not considered. Parry[13] notes that this implies electron withdrawal by the methyl groups as compared to hydrogen, contrary to the usual inductive effect. Examination of the lone pair ionization potentials for this series (Table II) suggests that the usual inductive effect may indeed be operating. There is a marked decrease in ionization potential from ammonia to trimethylamine implying that the lone pair is destabilized by electron release from the methyl groups.

Table II

Dipole moments (D), lone pair ionization potentials (kcal/mole), N1s ionization potentials (kcal/mole) and proton affinities (kcal/mole) for ammonia and the methylamines

	μ^a	IP(ℓp)	IP(1s)^d	PA^e
NH_3	1.47	235.0^b	9196.0	207.0
CH_3NH_2	1.28	206.8^c	9184.5	216.3
$(CH_3)_2NH$	1.03	190.0^c	9179.9	222.4
$(CH_3)N$	0.612	180.3^c	9174.3	226.6

[a] Reference 13.

[b] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, Molecular Photoelectron Spectroscopy, Wiley-Interscience, New York, 1970.

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Parry proposed a "polarization model" to explain the observed change in dipole moment. He suggests that substitution produces a large change in the lone pair moment. The change in bond moment from N-H to N-CH_3 is small compared to the lone pair moment change. The latter dominates and results in a smaller total dipole moment. In the polarization model the substitution of an alkyl group for a hydrogen on nitrogen is seen to result in a loosening of the lone pair charge cloud and a concurrent distortion of the electrons toward carbon. As a result the lone pair will be more nearly centered on nitrogen. The lone pair becomes more polarizable, less tightly bound, and assumes more pure s character.

This view is supported by structural data, Table III. The H-N-H angle is slightly decreased from ammonia to methylamine consistent with slightly more p character in the methylamine bonds. It is also noted that the N-H and N-CH_3 bond distances are constant thruout the series implying that these bond moments remain constant. This assumption allows the calculation of the difference in these bond moments with the result that the N-CH_3 moment is greater by 0.09 D. The structural data also establishes a relation between the remaining unknowns: the values of the lone pair and the N-H moments (Figure 1). This quantitatively relates the size of the lone pair moment to the degree of methyl substitution.

Parry applies the polarization model to the interpretation of base strengths in the amine series. The increase in base strength from ammonia to methylamine is seen to result from the loosening

Table III

STRUCTURAL PARAMETERS FOR METHYLAMINES

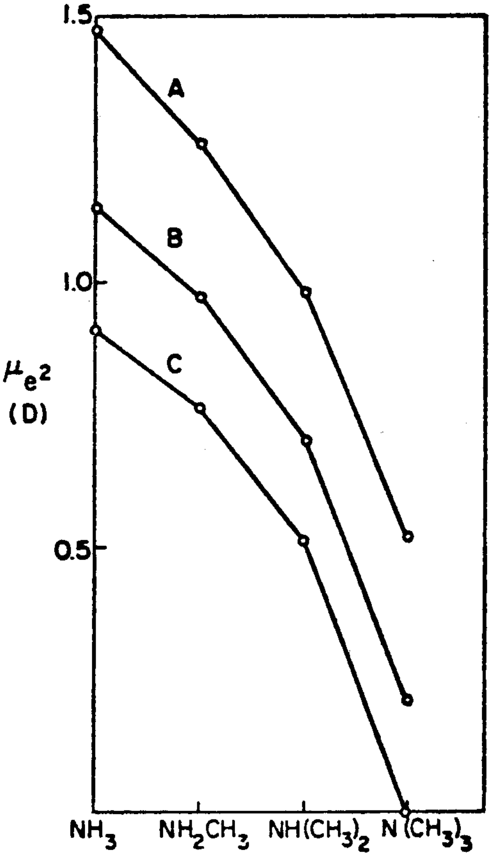
Amine property	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
N–H distance	1.012 ± 0.004 A	1.011 A (3)	1.011 A[a]	
N–C distance	. . .	1.474 A (3)	1.474 A[a]	1.472 ± 0.008 A (4)
H–N–H angle	107° (2)	105.9° (3)	. . .	. . .
H–N–C angle	. . .	112.0° (3)	112°[a]	. . .
C–N–C angle	. . .	. . .	109°[a]	108.7 ± 1.0 (4)
ϵ	. . .	3.5°	. . .	. . .
μ_{total}	1.47 (2)	μ_a = 0.304 (3) μ_c = 1.247 (3) μ_T = 1.283 (3)	μ_T = 1.03 (16)	0.612 ± 0.003 (4)
β	119.5°	128.7°	130.1°	. . .
Quadrupole coupling constant	−4.08 Mc	−4.5 to −4.9 Mc (Z comp)	. . .	−5.47 Mc

[a] Interpolated from values for methyl- and trimethylamine.

Figure 1

Lone pair moments for several assumed values of the N–H dipole moment; from reference 13.

	N–H moment	N–CH_3 moment
A	0	0.09
B	0.30	0.39
C	0.50	0.59


1.5
1.0
0.5
μ_{e^2} (D)
A
B
C
NH$_3$
NH$_2$CH$_3$
NH(CH$_3$)$_2$
N(CH$_3$)$_3$

effect of methyl substitution. The more polarizable, less tightly bound lone pair is more easily distorted to bond a proton. The decrease in lone pair dipole moment works in the opposite direction however. Parry, citing data for base strengths in solution, erroneously concludes that this second effect dominates for the last two members of the series explaining the decrease in base strength from dimethylamine to trimethylamine. However, it is now known that the anomalous decrease in base strength for dimethylamine and trimethylamine is due to solvation effects.[15] In the gas phase (Table II) basicity or proton affinity monotonically increases thruout the series. Therefore the increase in polarizability may be seen to dominate the change in dipole moment thruout the series. However the cancelling effect of the change in dipole moment may be responsible for the relatively smaller methyl substituent effect on basicity in the amines with respect to the phosphines (see Part Two of this report).

The decrease in ionization potential for the lone pair orbital (Table II) has already been cited. In terms of the polarization model, it is seen to reflect the loosening of the binding of the lone pair electrons with methyl substitution. Gas phase ionization potentials for the N1s electrons are available from ESCA spectra (Table II). The decrease in binding energy with methyl substitution which is observed may be interpreted as a greater localization of charge about the nitrogen core. Simple electronegativity and CNDO calculations which were made in interpreting these spectra incorrectly predict that ionization potential should increase with methyl substitution.[7]

These calculations erroneously assign all of the lone pair charge density to the nitrogen. The observed shifts in ionization potential may be taken to support the conclusion of the polarization model that the lone pair electrons are increasingly centered on the nitrogen with increasing methyl substitution.

A central point of the polarization model description of the electronic structure of the amines is that the lone pair shifts inward and develops greater s character with methyl substitution. This point could be directly tested by examination of the relative intensity of the lone pair band in the ESCA spectra of ammonia and the methyl amines. Low resolution He(I) photoelectron spectra establish that the lone pair band is separated from the second band by at least 3 electron volts for all members of the series. This is sufficient to permit resolution of this band in the ESCA spectra. Intensity calibration of the spectra could be achieved by reference to core level intensities. The 13:1 2s/2p intensity ratio should result in a dramatic increase in the relative intensity of this lone pair band if the predictions of the polarization model of substantial increase in s character are true. A quantitative measure of the s character could be obtained and compared to the predicted lone pair moment variation (Figure 1).

Further applications of the 2s/2p intensity ratio are possible. For example, considerable difficulty has been found in work on the He(I) PES of carbonyls in determining band assignments for lone pair and carbonyl pi orbitals. Determination of the s character of these bands by examination of their relative intensities in ESCA spectra should prove useful in their assignment.

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PROPOSITION II

Hydrogen-Exchange Studies of Conformational Changes in Hemoglobin

The hydrogens of alcohol, amine and amide groups in small molecules undergo rapid exchange with solvent hydrogens in water solution. The half-times for these reactions are typically less than a second and are pH dependent. In acidic or basic media specific catalysis by hydronium or hydroxide ions results in higher exchange rates.

In macromolecules the exchange rate for hydrogens of a given group may be substantially altered from the rate for that group in small molecules. In proteins, for example, the exchange of labile hydrogens of groups at the surface of the molecule will be greatly accelerated by general catalysis by nearby acidic or basic side chain groups. Also, many of the potentially exchangeable hydrogens of the molecule will be located in the interior, hydrogen bonded, and involved in various forms of secondary structure; these hydrogens will exchange slowly if at all. Half-times for exchange of minutes, hours, and even days have been observed.[1]

The effect of structure on exchange rate in macromolecules may be examined in terms of the various levels of structure which occur: primary, secondary, tertiary and quarternary. For proteins the effects of primary structure (the sequence of amino acid residues in the protein molecule) has been examined in several studies.[2-4] Nuclear magnetic resonance studies of H-D exchange in small molecule peptide derivatives have established the effects of neighboring peptide groups on the exchange rate of main chain amide hydrogens.[4] H-T exchange studies on homopolypeptides[3] confirm these results and establish the size of the isotope effects involved. Molday, Englander and Kallen[4] have used the rates obtained from these studies to predict the exchange curve for oxidized ribonuclease, a heteropolypeptide of known primary structure which exists in solution as a random coil. Excellent agreement is obtained between the predicted and observed curves (Figure 1).

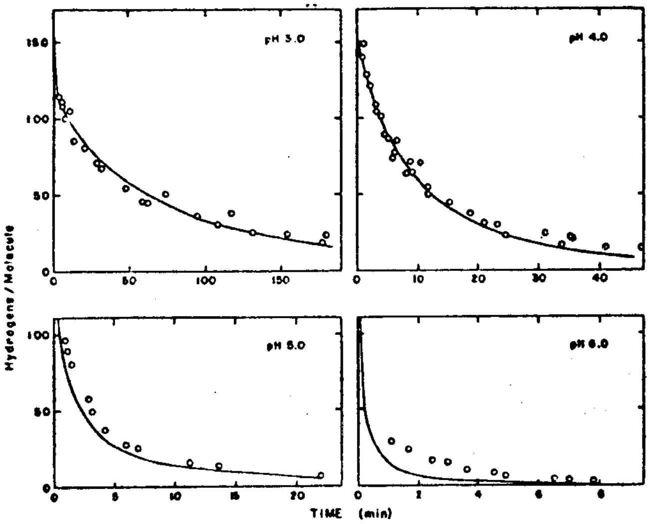
The exchange behavior of a number of macromolecules in their native state has been examined and interpreted in terms of their secondary and quarternary structure.[1] The effects of secondary structure (local structure of the peptide chain: α-helix, etc.) has been examined by studying the H-T-exchange of various model peptides.[3] Englander[2] studied the exchange behavior of native ribonuclease and interpreted the results in terms of the tertiary structure (three dimensional structure of the peptide chain in the molecule) of this protein.

Recently the hydrogen exchange technique has been extended to the study of quarternary structure (arrangement of subunits in a protein) and conformational change. Examination of the exchange behavior of immunoglobin G showed blocking of the attachment site of the antibody in the presence of antigen.[5] These studies also revealed that antigen

Figure 1

T-H exchange data for oxidized ribonuclease at 0°C and various pH. Solid lines represent exchange curves predicted for oxidized ribonuclease taking into account effect of neighboring side chains on peptide hydrogen exchange rates as determined from model peptides, reference 4.

18


pH 3.0
pH 4.0
pH 5.0
pH 6.0
Hydrogens / Molecule
150
100
50
0
0
50
100
150
0
10
20
30
40
100
50
0
0
5
10
15
20
0
2
4
6
8
TIME (min)

binding results in the faster exchange of several hydrogens. These hydrogens were interpreted to be located in the interior of the molecule near the hinge site. Binding of antigen causes an opening of the Y-structure at the hinge and exposure of these hydrogens resulting in their more rapid exchange.

Various techniques have been used to measure hydrogen-exchange rates in macromolecules. In the most common procedure exchange sites are labeled by exposure of the macromolecule to solution containing high concentrations of tritium as TOH. The macromolecule is allowed to "react" with this solution for some period, t_1, under conditions of fixed pH and temperature. During this period a number of tritium atoms will exchange onto the molecule. If this exchange reaction is not allowed to reach equilibrium, the more rapidly exchanging sites are preferentially labeled. After the exchange-on period the macromolecule is transferred to a solution having a low, ideally negligible, tritium concentration.

This transfer is accomplished either by passing the protein thru a sephadex column or by rapid dialysis. On the sephadex column the TOH and other small solution molecules penetrate the sephadex beads and are thus delayed in their passage down the column compared to the macromolecules which are excluded by their large size from the beads. Reduction in tritium levels in the solution volume containing the macromolecule by factors of 10^6 to 10^7 can be achieved with a single passage thru a column requiring less than a minute. In the rapid dialysis technique, a small volume (1 ml) of the solution containing the macromolecule and tritium is placed inside a dialysis bag permeable to the small solution molecules but not the macromolecule. In order to maximize the surface to volume ratio, the bag is stretched between clamps at the ends so that it becomes flat. The bag is spun in a cylinder containing a large volume (1000 ml) of fresh (tritium free) solution. Dilution of the solution tritium into the total solution volume occurs rapidly. After a minute or so of spinning the bag is transferred to another cylinder containing fresh solution. Reductions in tritium levels in the solution volume containing the macromolecule by factors of 10^6 to 10^7 can be achieved in a few minutes.

After transfer of the macromolecule to the new solution has been accomplished, the tritium present will be that which has been carried by the macromolecule. Tritium atoms will exchange off of the macromolecule at the exchange rates for the various sites at which they are bound. After a second period of time, t_2, has elapsed, the macromolecule is again transferred to fresh solution. The concentration of macromolecule is then determined by absorption spectroscopy and the amount of tritium present measured by scintillation counting techniques. The ratio of count rate to concentration is a measure of the fraction of tritium still carried by the macromolecule after time t_2. An exchange-out curve is obtained by plotting the number of tritium atom still carried per molecule as a function of the time t_2.

Exchange-out curves for various exchange in times, t_1, may be obtained. A total exchange curve is usually first obtained, however, for $t_1 \rightarrow \infty$. Exchange-in is carried out under conditions favorable to reasonably rapid exchange at all exchange sites. Equilibrium can usually be achieved within a few hours at high pH and temperature, typically pH 9 and 38°C.

If a macromolecule contains n exchangeable hydrogens exchanging with rate constants K_m (pH,T) which are functions of pH and temperature, the average number of sites exchanged after time t will be given by

$$N = \sum_{m=1}^{n} (1 - e^{-k_m t}). \tag{1}$$

If exchange-in for a period t_1 is followed by exchange-out for a period t_2, the average number of hydrogens carried is given by

$$N = \sum_{m=1}^{n} (1 - e^{-k_m t_1}) e^{-k'_m t_2} \tag{2}$$

where the prime indicates that the exchange-out conditions may be different from the exchange-in conditions resulting in a different rate constant for the site. The total exchange curve is described by

$$N_T = \sum_{m=1}^{n} e^{-k_m t_2}. \tag{3}$$

In principle the experimental curves can be analysed to give all of the individual rate constants K_m (pH, T). In practice groups of hydrogens on the molecule are found to exchange at very similar rates which show the same pH and temperature dependence. The rates for these classes can frequently be obtained from the data without elaborate analysis.

The sizes and rate constants for the rate classes of a given macromolecule can be analyzed in terms of its structure. For macromolecules whose structure is known by x-ray diffraction the members of the rate classes may be identified with specific exchangeable hydrogens in the structure. The exchange rates at the various sites are sensitive to the state of the macromolecule and are affected by such factors as solution pH and salt concentration. Specifically they are sensitive to changes in the macromolecule's structure which may occur because of interactions with other macromolecules or substrates. Such interactions can be investigated in two ways. The exchange curves can be obtained for macromolecules with and without the presence of interactions, i. e., for each of the structural states involved. Changes in the various rate classes can be related to the structure via the established corespondence of the rate classes to structural features. Or, the interacting species may be introduced at some point in the exchange curve and its effect on the subsequent exchange, including the possible sudden release of hydrogens whose rate constants have been greatly increased, examined. Again the changes may be related to structure via analysis of the rate class affected.

Hydrogen-exchange thus provides a tool for the examination of structural changes in macromolecules. Other techniques including electron paramagnetic resonance and nuclear magnetic resonance have been used to study structural changes in macromolecules. These involve the introduction of spin or nmr labels into the molecule which are sensitive to changes in their local environment. Compared to hydrogen-exchange these techniques have the advantage that the label is contained in a single well-defined site. But they have the disadvantage that the introduction of the label may alter the structure and behavior of the molecule. The label used in hydrogen-exchange, amounting to the presence of an occasional tritium atom in place of a hydrogen, is much less likely to affect the molecular structure or behavior. With the availability of x-ray structures for the molecules under study, it may even be possible to quite specifically relate the hydrogen exchange results to structural changes in the molecule.

It is proposed to use hydrogen exchange to study the conformational changes in hemoglobin which take place with oxygen uptake.

Hemoglobin is a globular protein consisting of four subunits of about 18000 molecular weight, two identical α-chains and two identical β-chains. Each subunit contains an iron atom capable of reversibly binding an O_2 molecule. Equilibrium studies of oxygen binding indicate that the binding constant for oxygen at one of the four binding sites of the hemoglobin molecule is larger if oxygens are already bound at the other sites. Kinetic evidence shows that oxygen binding on the α- and β-chains is not equivalent.[6]

The structures of both oxy- and deoxy-hemoglobin have been determined by x-ray diffraction studies.[7-9] The structures are not equivalent, there being changes both in the secondary and quarternary structure of the molecule. These structural changes are thought to be important in determining the cooperativity which is demonstrated in oxygen binding. The remaining questions regarding the role of structural change in oxygen binding on hemoglobin are: what are the intermediate structures which occur when only one, two, or three oxygen molecules are bound to the molecule? And, what is the mechanism by which structural change is effected to transmit the information that oxygen is bound at another site and by which the binding constant at a site is altered?

Electron spin resonance has been used to study these questions.[10, 11] Asakura[11] was able to introduce the nitroxide spin label 2, 2, 5, 5-tetramethyl-3-aminopyrrolidine-1-oxyl on one of the propionic acid groups without causing a measurable change in the optical or oxygen binding properties of the molecule. The moderately immobilized spin label showed sensitivity to oxygen binding on the molecule. A nonlinear relation between fractional EPR change and fractional saturation with oxygen was observed and attributed to non-equivalent interaction between hemoglobin subunits.

Nuclear magnetic resonance has also been used to study these questions. Huestis and Raftery[12-15] were able to introduce covalently bound 3, 3, 3-trifluoroacetonyl groups on the β-chain cystein residues at position 93. This had a small effect on oxygen binding properties. They have been able to show that with this ligand present the α-chains show greater oxygen affinity than the β-chains in the early stages of binding.

Hydrogen-exchange studies on myoglobin, a globular protein very similar to the hemoglobin subunits, have already been conducted and interpreted in terms of the myoglobin structure which is also known by x-ray diffraction.[16] The hydrogen-exchange curves for both oxy- and deoxy-hemoglobin should be examined and interpreted in terms of both the previous myoglobin studies and the known structures of oxy- and deoxy-hemoglobin.

Several types of experiments could be conducted to examine the role of structural change on oxygen binding in hemoglobin. The hydrogen-exchange curves for partially oxygenated hemoglobin could be examined. These could be used to determine at what stage of oxygenation differences in the hydrogen-exchange curves between oxy- and deoxy-hemoglobin occur. This question could also be examined by the introduction of oxygen at various times in the exchange-out curves.

Another type of experiment could be conducted which would be directed at determining differences in oxygen binding by the α- and β-chains. α- or β-subunits could be labeled with tritium separately (only one labeled) and then mixed with the other subunit to assemble the hemoglobin molecule. Differences in the exchange-out behavior on introduction of oxygen could be interpreted to establish preferential oxygen binding by α- or β-subunits at various degrees of fractional oxygenation. These experiments would also yield information about conformational changes in subunits not binding oxygen when oxygen is bound to another subunit.

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PROPOSITION III

A Practical Instrument for Photoelectron–Photoion Coincidence Spectroscopy

Photoelectron-photoion coincidence spectroscopy (PPCS) has recently become technically feasiable as a result of advances in the performance of electron energy analysers and electron and ion counting devices. It has the potential to greatly enlarge the range of experimental information which can be obtained in the study of photoionization events and their related chemistry.

PPCS will permit the investigation of various chemically interesting features which are observed in photoelectron spectra. Principle among these are predissociated ionizations. As described in Part One of this report and in greater detail by Miasek,[1] ionization of a molecule to an unbound electronic state of its ion results in dissociation with release of excess kinetic energy. If the molecule is larger than diatomic, then some of the excess energy released may be contained in the internal energy of the fragments. PPCS permits the identification of the photoelectron band associated with a given dissociative process. This is accomplished by scanning the photoelectron coincident with the appearance of the fragment ion. Also, the partitioning of the excess energy into translational and internal modes can be determined as a function of the excess energy. This is accomplished by time-of-flight analysis of the ion fragments (or possibly, more directly, by employing energy as well as mass analysis of the ions). Eland[2-4] has already made use of PPCS to study the predissociative ionization of CH_2Cl_2, O_2, and CO_2.

Another application of PPCS is for the preparation of ground electronic state ions with known amounts of vibrational excitation. When sufficient vibrational energy is present, fragmentation of the molecular ion may take place. The experiment is conducted by observing the relative intensities of the various fragment ions produced in coincidence with photoelectrons of a given energy. The results may be interpreted in terms of the quasiequilibrium theory of unimolecular decomposition. Stockbauer[5] has recently made use of PPCS to study the decomposition of methane and ethane molecular ions as a function of internal energy.

A third application to which PPCS could be put is to obtain the photoelectron spectrum of a single molecular species in mixtures. This would be particularly useful for obtaining the spectra of chemically reactive species which would be difficult to produce in pure form. For example, the study of free radicals in beam sources as described in Part One of this report would be greatly facilitated by the availability of a way to positively identify the species of interest with the various spectral features observed. The experiment would be conducted by scanning the photoelectron spectrum coincident with the molecular (or possibly fragment) ions of the species of interest. Experiments involving this application have not been reported to date.

Finally, PPCS could in principle be used to study the ion-molecule reactions of ions in excited electronic or vibrational states.

However, this would require that times for radiative dexitation be long compared to reaction times and that the mean free path for collisions be short in comparison to the dimensions of the apparatus. For the study of vibrationally excited species, this means that the pressure of the neutral species be in the range of several torr. This introduces several experimental problems. Other techniques may be more suited to conducting experiments of this type.

Several types of instruments have been employed to date to conduct photoelectron-photoion coincidence experiments. All have been constructed as modifications to existing photoelectron or photoionization mass spectrometers Brehm and von Puttkamer[6-8] combined a 60° magnetic mass spectrometer (existing as part of a photoionization mass spectrometer) with an einsel lens--retarding grid photoelectron spectrometer capable of 13 mV resolution. They obtained a coincidence rate of about 3 counts/second at an electron energy resolution of 100 mV. Danby and Eland[2-4] added a time-of-flight mass spectrometer to an existing parallel plate photoelectron spectrometer. They obtained a coincidence rate of about 6 counts/second at a resolution of 150 mV. And, Stockbauer[5] modified an existing photoionization mass spectrometer by addition of a zero energy electron detector which consisted of a drift tube electron energy analyser followed by a 127° cylindrical electrostatic analyser. Coincidence rates of up to 16 counts/second were obtained.

Eland[2] considered the basic principles and theory of PPCS. The rate of true coincidences, C, is given by

$$C = N g_e f_e f_i \tag{1}$$

where N is the total ionization rate, g_e is the fraction of photoelectrons falling within the acceptance energy of the electron analyser, and f_e and f_i are the efficiencies for counting electrons and ions respectively. The time required for counting a photoelectron is on the order of 100 nanoseconds. During this time the ion produced in this ionization event will have traveled only a short distance, on the order of 10^{-2} cm even if external fields of up to a few volts/cm are applied. Thus, the detection of a photoelectron may be used to gate the ion detection channel after a suitable delay to obtain the coincidence feature of the experiment. If the gate is open for a period τ for each photoelectron detected, then the observed coincidence rate will be

$$C' = \left(1 + \frac{N\tau}{f_i}\right) C = \left(1 + \frac{\tau C}{g_e f_e f_i^2}\right) C . \tag{2}$$

The masses of ions and magnitudes of voltages which can be employed put a practical lower limit on τ of a few microseconds.

It is desirable of course for C to be as large as possible so that the experiment can be conducted quickly. If this is to be possible without creating a large background of false coincidences (noise), the noise factor $1/g_e f_e f_i^2$ must be as small as possible. Ion collection efficiencies, f_i, approaching one can be achieved if careful attention is given to the design of the source region and ion extracting electrodes. Stockbauer[5] obtains an efficiency of 0.1, and Eland an efficiency of 0.35. Since the noise factor is proportional to the inverse <u>square</u> of

f_i, the gains which might be achieved may justify giving more attention to the design of the ion optics. The factor g_e is determined by the substance under study and the resolution which is acceptable in a given experiment. To date it has been necessary to limit the experiments undertaken so that g_e would be larger than about 10^{-2}. The electron collection efficiencies in the apparatus of Eland and that of Stockbauer were small, about 10^{-5} and 10^{-4}, respectively. These values leave considerable room for improvement and are largely responsible for the low coincidence rates which were obtained.

The three instruments for PPCS described above have been put to rather limited uses largely because of the low counting rates which were obtained, only about 10 counts/second. Several aspects of their designs, however, are subject to significant improvement. Such improvement, if it would result in the attainment of counting rates on the order of 10^3 counts/second for resolutions of about 100 mV, would allow the application of PPCS to much larger (and chemically more interesting) molecules. The potential rewards, if those improvements can be realized, include substantial gains in our understanding of the structures of various chemically unstable species and their corresponding molecular ions, the partitioning of excess energy into translational and internal modes in predissociative ionizations, and the dependence of decomposition rates for various routes of ion fragmentation as a function of internal energy. In each of these areas experiment currently lags behind theory in contributing to our understanding of the phenomenon involved. The development of PPCS to the state where it becomes a practical experiment to conduct on a variety of chemically interesting species would thus represent a significant advance in experimental science. Therefore, it is proposed to design and construct a practical instrument for photoelectron-photoion coincidence spectroscopy.

Noise factors for the three instruments described above are all about 10^6 for a resolution of about 100 mV and for a value of g_i of about 10^{-1}. The single factor contributing most to this large noise factor is the electron counting efficiency f_e. It should be possible to improve significantly on the present values of 10^{-4} to 10^{-5}. Since there is an approximately inverse relationship between sensitivity and resolution, it is important to determine the necessary resolution at the outset. Note that the analysers described above are all capable of operation at resolutions of better than 20 mV. If a resolution of 100 mV is deemed satisfactory (no better has yet been attained in coincidence experiments), it is possible to design an analyser having a collection efficiency of better than 10^{-2}.

Turner [9] has published the design of a medium resolution photoelectron spectrometer of high sensitivity. A 127° cylindrical electrostatic analyser of small radius, 2 cm, is used. The small dimensions of the apparatus obviate the need for magnetic field compensation and lead to the increased sensitivity. However, a resolution of 50 mV is still obtained. The spectrum is swept by applying a retarding voltage between the scattering chamber and the analyser. An analysis energy of 0.4 eV is employed.

The proposed design makes maximum use of the benefits of reduction in size and adds several features to further improve sensitivity while maintaining a resolution of better than 100 mV. A conventional He(I) resonance lamp would be used as a source (S, Figure 1) with the sample gas introduced as a beam (B). To further improve sensitivity over Turner's design, a 180° spherical electrostatic analyser of small radius (2 cm) would be employed to give focusing in both the horizontal and vertical. A chenneltron electron multiplier (ED) would provide a low noise detector for the electrons. A quadropole mass spectrometer (Q) would be used along with another channeltron electron multiplier to provide analysis and counting of the ions. When combined with conventional source plates, these components should result in an improvement of the noise factor to about 10^4 to 10^5.

Significant further improvement can be made by employing einsel lenses[10] in the regions between the source and the analysers. Substantial loss of electron collecting efficiency normally results from the defocusing which occurs between the source and electron energy analyser entrance due to the retarding voltage which is applied in this region. It has been noted (see Part One of this report) that the herzog lens at the analyser entrance of a conventional photoelectron spectrometer may be adjusted to significantly increase the signal intensity with only a slight loss of resolution. This lens is normally adjusted to the cylinder center potential to reduce fringing fields at the entrance for best resolution. When its potential is adjusted

Figure 1

PPCS components.

B -- Beam source

S -- He(I) resonance lamp source exit

EL -- Electron lenses

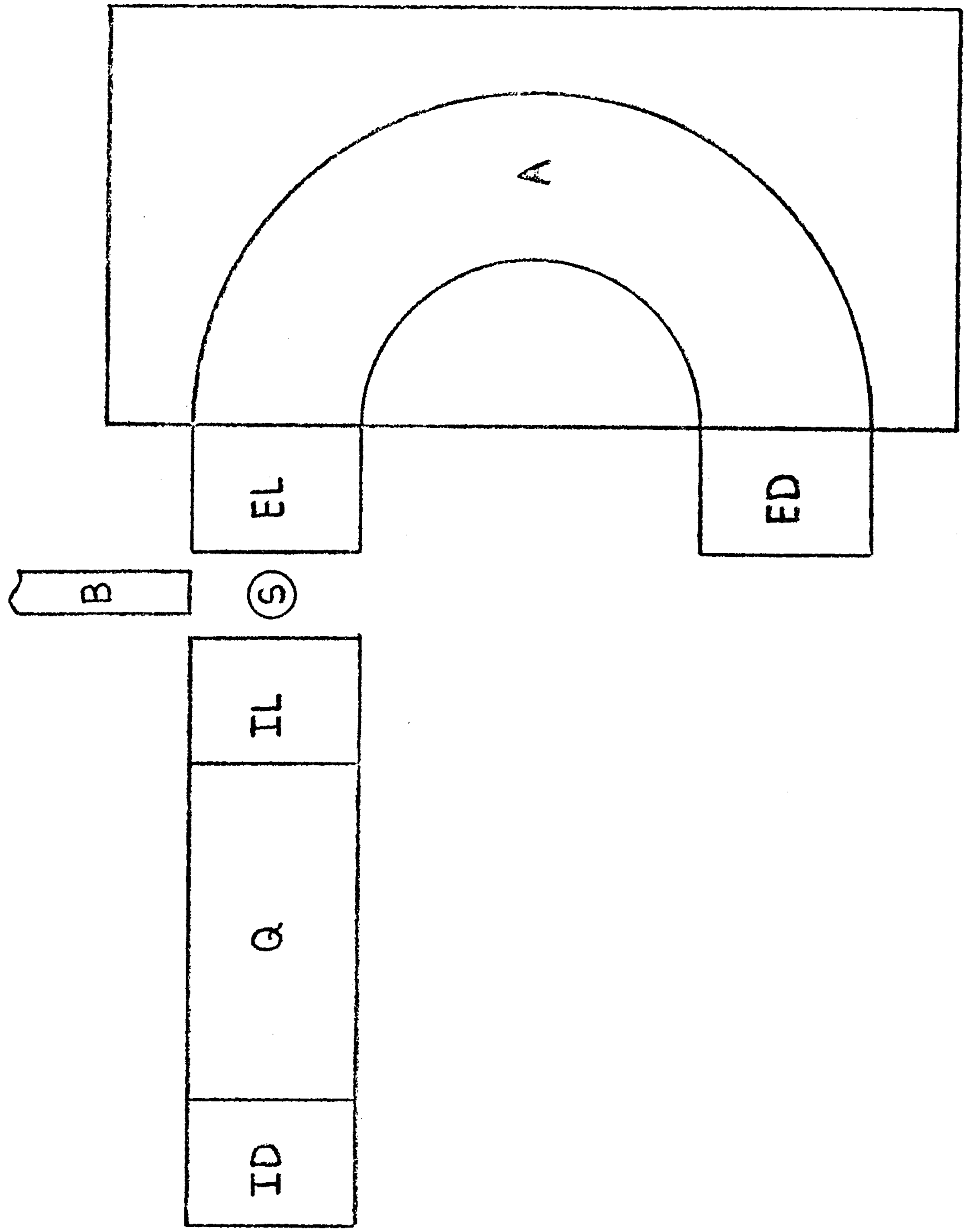
A -- Electron analyser, spherical type

ED -- Electron detector

IL -- Ion lenses

Q -- Quadropole mass spectrometer

ID -- Ion detector


A
EL
ED
B
S
IL
Q
ID

significantly above or below this potential, it acts as a focusing lens and partially compensates for the defocusing due to the retarding voltage.

Focusing lenses have not previously been used in the entrance optics of photoelectron spectrometers. Presumably it has been thought that they would have an adverse effect on resolution. It appears that this view has been over-cautious. It should be possible to design an einsel lens system which will very substantially increase the electron collecting efficiency while causing only a small decrease in resolution.

Such a design is indicated in Figure 2. The elements P1 and P3 are shorted and maintained at the sphere center potential. P4 and P6 are shorted and are at a potential such that the electron deceleration occurs between elements P4 and P3. The center elements P2 and P5 are adjusted significantly above or below the potentials of their neighboring elements to provide focusing. A single einsel lens consisting of elements P7, P8 and P9 is provided for focusing of the ions.

The electron collecting efficiency of this source and analyser should be better than 10^{-2}. The ion collecting efficiency could approach unity. In operation, detection of a photoelectron would be used to trigger a change in the source potentials to make P7 negative with respect to P6 drawing the ion into the mass spectrometer. The gate time (τ) need only be on the order of a few microseconds and could be applied after some delay to permit the investigation of decay times in

Figure 2

The source region.

B -- Beam source

S -- Ionization region

A -- Electron analyser

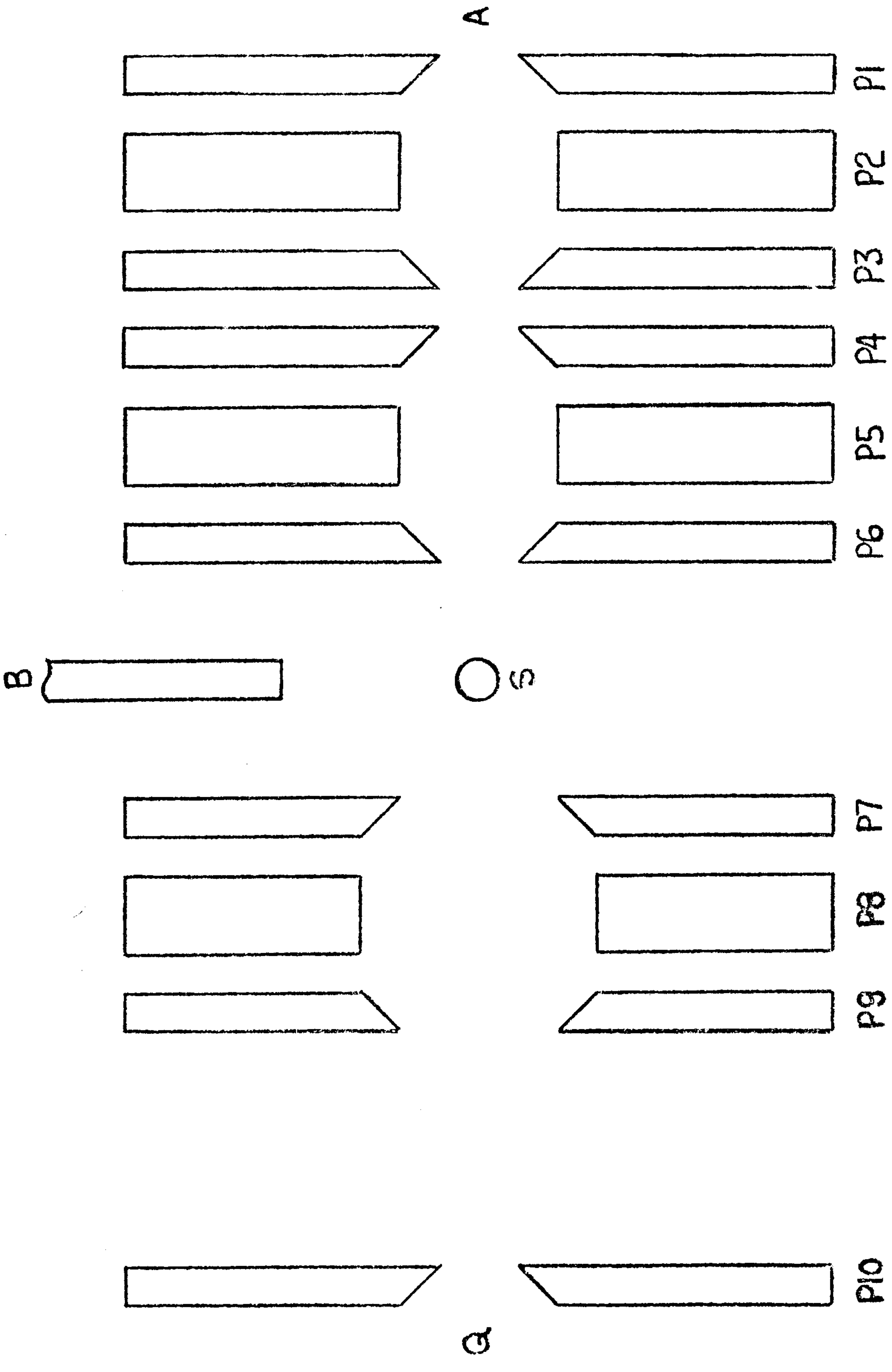
Q -- Quadropole mass spectrometer

P1, P2, P3 -- Post-deceleration electron einsel lens

P4, P5, P5 -- Pre-deceleration electron einsel lens

P7, P8, P9 -- Ion einsel lens

P10 -- Quadropole entrance aperture


A
P1
P2
P3
P4
P5
P6
B
S
P7
P8
P9
P10
Q

unimolecular ion decompositions. Time of flight analysis of the fragment ions in predissociated ionizations would allow the determination of their kinetic energy distributions.

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PROPOSITION IV

Separation of ^{235}U and ^{238}U by Freeze-Fry Chemistry

Freeze-fry chemistry,[1] involving a co-condensation on a cold surface of high temperature species such as metal atoms along with organic substrate molecules, has recently been undergoing rapid development as a novel synthetic technique for the preparation of metal complexes.[1-15] At sufficiently low temperatures in inert matrices, metal atoms may be isolated in the substrate matrix. Spectra under these conditions will be similar to those in the gas phase.[9] If an appropriate reactant is present in the "inert" matrix, however, reaction may be photochemically induced.[3, 10] By selectively exciting only atoms of a particular isotopic species, this may be used to achieve isotope separation. It is proposed to use these techniques to separate ^{235}U and ^{238}U.

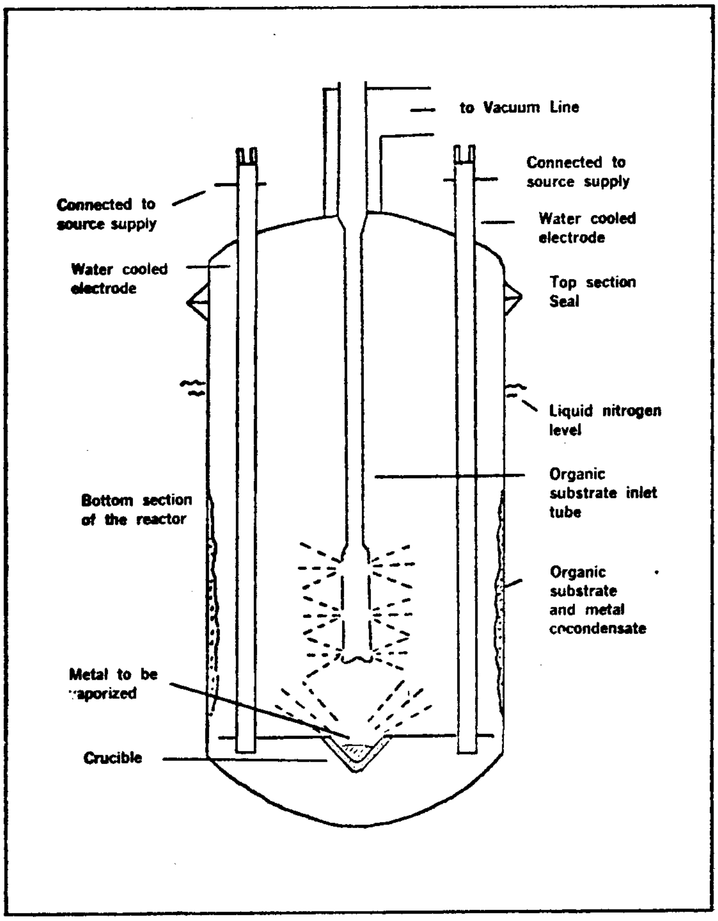
The development by Skell of a carbon vapor reactor[16, 17] for the synthesis of very reactive organic species has been followed by similar approaches in the area of organometallic chemistry.[1-15] Timms has recently reviewed metal atom techniques.[12] A number of papers reporting work using metal atom techniques, including several[1-11] based on the proceedings of a symposium "Metal Atoms in Chemical Synthesis," have appeared in the literature.[1-15] Applications to date have concentrated on synthesis of low valent transition metal complexes and other novel species, many of which are inaccessible by conventional synthetic routes.

The design of an apparatus for laboratory scale batch synthesis using metal atom techniques illustrated in Figure 1 is typical of several which have been used in these studies.[1, 2, 11-13] A two section glass vacuum chamber, the lower half of which may be immersed in liquid nitrogen, is connected to a vacuum system employing diffusion pumps. An organic substrate inlet tube is provided in the center of the chamber. Below this a resistively heated crucible is mounted on water cooled electrodes which connect through the top. An apparatus of similar design is now commercially available.[18] During operation organic substrate and metal atoms co-condense on the side walls of the chamber. Subsequent treatments may include warming and introduction of additional reactants.[1-5, 11-15] Following reaction, the products are removed by vacuum techniques if they are volatile; or the chamber may be opened and the products recovered by extraction from the residue on the walls.

Metal evaporation and vacuum technology are well developed and provide the possibility of considerable flexibility in equipment design.[5-7, 19] A variety of resistively heated metal atom sources have been used in thin film production. Electron beam and inductively heated sources as well as sputtering sources are also commonly used. The conditions and technology for the evaporation of most metals, including uranium,[11] are well-known.[2, 5, 6, 12] Similar techniques are familiar in high temperature chemistry.[20] Recently, evaporation techniques employing high power lasers have also been developed.[7] Scale up of these processes for either batch

Figure 1

Apparatus for condensing metal atoms with volatile compounds.


to Vacuum Line
Connected to source supply
Connected to source supply
Water cooled electrode
Water cooled electrode
Top section Seal
Liquid nitrogen level
Organic substrate inlet tube
Bottom section of the reactor
Organic substrate and metal cocondensate
Metal to be vaporized
Crucible

or continuous production operations is feasible. Much of the necessary technology is already in use, for example, in industrial metal cladding plants.[5]

Matrix isolation techniques for spectroscopic study of reactive species in inert matrices have been extensively developed.[9,21] Part of the proposed work would involve use of these techniques to examine the spectra of uranium atoms both at very low temperatures $< 10°K$ in inert matrices such as argon and also under other matrix conditions which would be developed as the study progressed. Gas phase spectra of uranium are available and would be helpful in the assignment and analysis of matrix spectra.[22] In the gas phase a typical shift between spectral lines arising from ^{235}U and ^{238}U atoms is $0.5\ cm^{-1}$.[22] Matrix conditions under which this resolution could be maintained would be necessary to allow selective excitation of a single isotopic species. Investigations of the dependence of resolution on matrix composition and temperature would be undertaken.

Metallic uranium is a very reactive substance.[22-26] Moreover, the heat of formation of uranium atoms in the gas phase is 125 kcal/mol.[23] Identification of suitable inert matrix materials would therefore probably require some investigation. Sheline and Slater[11] have studied uranium atom reactions with CO in an argon matrix. Polyhalohydrocarbons which have been successfully used with other metals should also be considered.[1-5, 11-15] The chemistry of uranium has been very extensively studied[22-26] but may not provide much guidance for the discovery of an appropriate photochemically induced reaction. Initial studies would require a trial and error approach. Spectroscopic, vacuum, and conventional wet chemistry techniques would be used for the identification and separation of reaction products.

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PROPOSITION V

Some Novel Analytical Approaches to Elucidating the Structure of Coal

The chemical structure of coal is not well understood.[1] This situation is particularly unfortunate since the rapidly expanding use of coal as a source of energy and chemicals demands increasingly more sophisticated chemical manipulation of this organic rock.[2] Economically and energetically cheap methods for liquification and gasification are needed to facilitate handling and transport.[3] Purification procedures must be developed to remove sulfur and ash forming minerals.[4] And, preferably at the same time, degradation methods should maximize the recovery and production of organic starting materials needed in a large variety of chemical industries.[5]

What is coal? It is a porous solid composed mostly of carbon but containing several percent H, O, N, S and a number of lesser impurities. Interestingly a significant gaseous component, mostly CH_4, is originally present but is usually not recovered in mining. Approaches to a more detailed chemical understanding have generally involved application of some degradation procedure followed by analysis of the resulting small molecules and further degradation of the remaining bulk.[1, 5-10] Reconstruction of the original structure from the fragments produced by these methods is difficult and of questionable validity. Consistent results for such important parameters as the ratio of aromatic to aliphatic carbon[1, 5-10] and of organic to inorganic sulfur[11] have not been obtained. Nonetheless various models of the original structure have been proposed, Figure 1.[1] A more detailed and accurate understanding of the distribution and functionality of H, O, N, and S atoms, of acidic and basic sites and of the three dimensional structure of the carbon lattice would, however, be helpful in the design of improved degradation procedures.

Spectroscopic as well as chemical means have been employed to attempt to understand coal structure. Analysis by IR and NMR techniques would be most desirable. While direct approaches to the study of bulk coal have not been successful, IR spectra can be obtained on pulverized samples.[12] Recently, application of ^{13}C NMR and IR techniques to the products of relatively gentle digestion procedures has been reported.[13] Continued efforts along these lines may be expected to substantially increase our understanding of the molecular structure of coal.

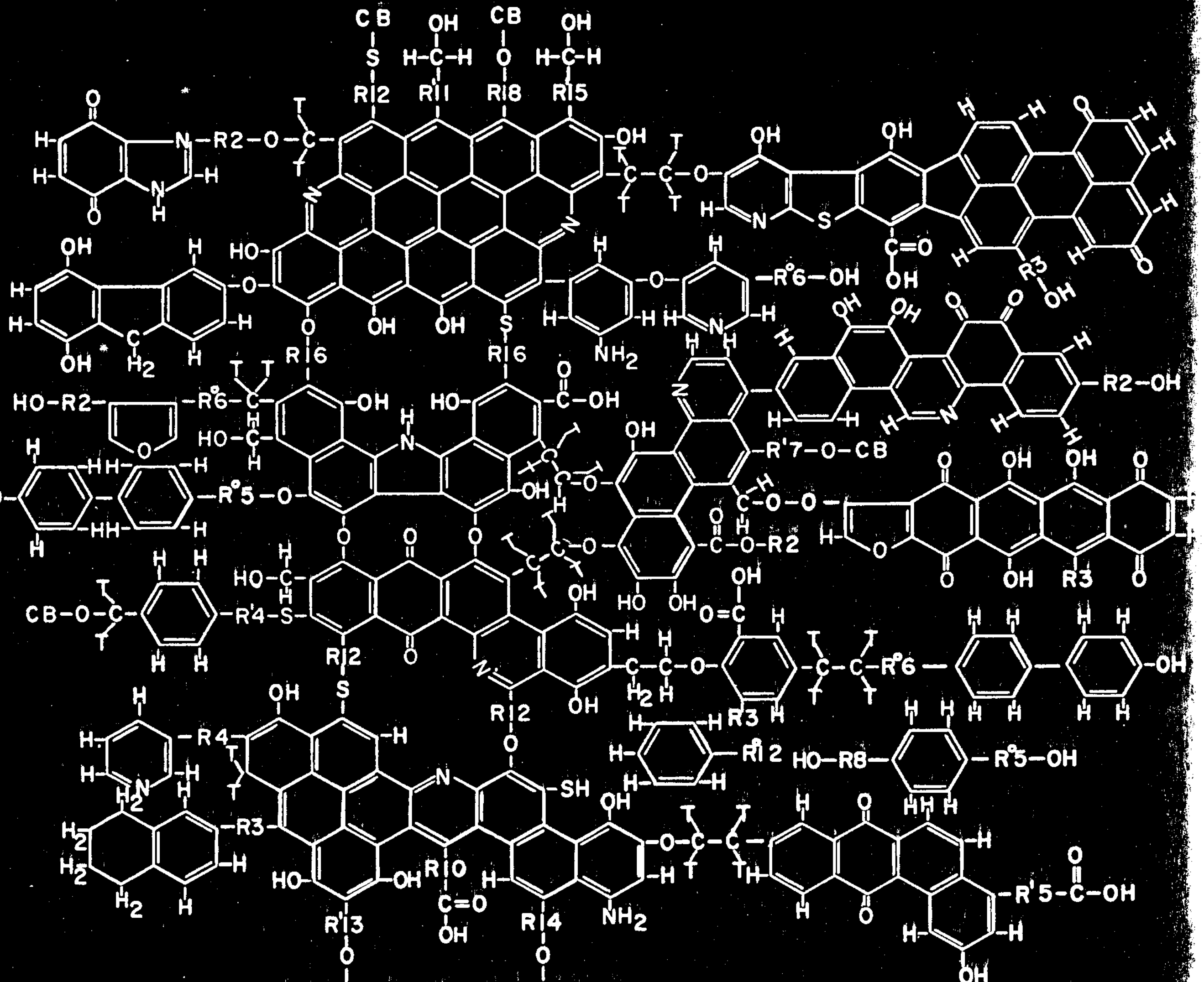
Techniques for the direct study of the molecular properties of bulk coal are also needed. Several recently developed spectroscopies have the potential for being usefully applied to this problem. It is proposed to use x-ray photoelectron spectroscopy (XPS)[14] and photoacoustic spectroscopy[15] for the direct study of the molecular properties of bulk coal.

XPS has been the subject of several recent reviews.[15] The XPS spectrum of coal should reveal C, O, N, S, and the minor

Figure 1

Typical cross-bonded structure for high volatile coals.

A NEW CHEMICAL STRUCTURE FOR COAL



CROSS BONDING TO MORE HETEROCYCLIC GROUPS

Typical Cross-bonded Structure for High Volatile Coals

R°N	**Alicyclic rings of N carbons**
RN	**Alkyl side chain of N carbons**
R'N	**Unsaturated alkyl side chain of N carbon**
CB	**Cross-bonding by O or S to new heterocyclic groups with side chains**
T	**Tetrahedral 3-dimensional C-C bonds, C-O bonds, and C-S bonds**

impurities in a distribution of chemical environments. Information about molecular structure may be obtained by comparison of these spectra with those of model aromatic and aliphatic compounds containing appropriate functional groups.

Photoacoustic spectroscopy[16] has also been recently reviewed. This technique might be usefully applied throughout the spectral range but especially in the infrared using laser sources. Results may be expected to resemble previously observed IR spectra of powdered coal although a detailed comparison may show significant differences.

It is further proposed that the changes induced by nondestructive chemical treatment of coal with acidic and basic reagents be investigated by XPS and photoacoustic spectroscopy.[16, 17] Acidic species such as BX_3, BR_3, AlX_3, and AlR_3 will bind to π- and n-donor basic sites in coal on exposure. Similarly, acidic sites could be investigated by treatment with appropriate bases. Changes in the XPS and photoacoustic spectra should reflect the local environment of the binding sites. Spectral features of both coal and the bound reagents would be studied. Various of the effects produced by altering, for example, the alkyl groups in a BR_3 reagent should provide powerful tools for probing the molecular framework of the binding sites. Information about the distribution and relative reactivity of sites could be obtained by sequential treatment with reagents having distinguishable spectral features. Comparison with results for model compounds would be an important part of this work.

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