would be expected to contribute more to the EFG than the imbalance in the p electrons. Thus the formation of a stronger metal–ligand π bond with the sixth ligand in $[Ru(CN)_5X]^{-n}$ should result in a positive EFG, and a weaker π bond should result in a negative EFG. The EFG for $K_2[Ru(CN)_5NO]$ would be expected to be positive and that for $K_4[Ru(CN)_5NO_2]$ would be expected to be negative. The EFG for the analogous $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ has been found to be positive.[9] Additional studies will need to be made to actually determine the sign of the V_{zz} element of the EFG tensor in these complexes.

While the trend in the quadrupole splittings for these ruthenium complexes is the same as that reported for the analogous iron complexes, the splitting parameters are much smaller, *e.g.*, ΔE for $K_2[Fe(CN)_5NO]\cdot 2H_2O$ is 1.72 mm/sec and ΔE for $Na_4[Fe(CN)_5NO]$ is 0.89 mm/sec. Another striking difference between the Mössbauer spectra for the two sets of compounds is the asymmetric quadrupole split spectra for the ruthenium complexes. Since the samples were analyzed as polycrystalline samples, the asymmetry could be a consequence of the Goldanskii effect.[10] Additional studies are being carried out on the correlation of these asymmetric spectra with the sign of the EFG.

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Nucleophilic Displacement Reactions in the Gas Phase

Sir:

In recent publications we have utilized ion cyclotron resonance spectroscopy (icr) to examine the gas-phase ion chemistry and thermochemical properties of organic molecules.[1–6] Not surprisingly, analogies to processes common to solution chemistry have been found. For example, we recently reported the gas-phase ionic dehydration of aliphatic alcohols, a reaction which has the character of an acid-catalyzed *elimination* process.[1–3] We report here the factors governing the occurrence of another gas-phase ionic process which has the character of a *nucleophilic displacement* reaction.

As part of our continuing program of determining proton affinities (basicities) in the gas phase,[4–6] we had occasion to examine a 1:3.5 mixture of CH_3F and HCl. The results obtained at low electron energy (14.9 eV) are illustrated in Figure 1. At low pressures the parent ions $HCl\cdot^+$ and $CH_3F\cdot^+$ are the major species present. With increasing pressure both ions react to form the protonated species H_2Cl^+ and CH_3FH^+. Careful examination of the pressure dependence of these latter two species in conjunction with ion cyclotron double-resonance experiments indicate the proton affinity of CH_3F to be greater than HCl. At the highest pressures employed both CH_3FH^+ and H_2Cl^+ are observed to decrease and disappear, reacting to generate $(CH_3)_2F^+$ and CH_3ClH^+. The formation of protonated methyl chloride is especially intriguing and indicates the occurrence of the nucleophilic displacement reaction[7]

$$HCl + CH_3FH^+ \longrightarrow CH_3ClH^+ + HF \qquad (1)$$

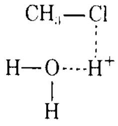
Double-resonance experiments indicate that CH_3FH^+ and ions such as H_2Cl^+, $HCl\cdot^+$, and $CH_3F\cdot^+$, which form CH_3FH^+, are the ionic precursors to CH_3ClH^+.[10] The second-order rate constant associated with reaction 1 was determined to be 3.1 ± 0.3 × 10^{-10} cm^3 molecule^{-1} sec^{-1} (2 × 10^{11} M^{-1} sec^{-1}).

To test the generality of the nucleophilic displacement process mixtures of H_2O with CH_3Cl and C_2H_5Cl were investigated. While reaction 3 is observed, reaction 2 does not occur. The reason for this difference

$$CH_3ClH^+ + H_2O \not\longrightarrow CH_3OH_2^+ + HCl \qquad (2)$$

$$C_2H_5ClH^+ + H_2O \longrightarrow C_2H_5OH_2^+ + HCl \qquad (3)$$

follows directly from a consideration of the probable reaction mechanism. A reasonable representation of the intimate reaction complex for processes 2 and 3 in which the labile proton is shared between the two polar reactants is illustrated by I and II. The proton affinity



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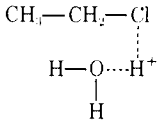

II

(basicity) of H_2O (164 kcal/mol)[4] lies between the proton affinity of CH_3Cl (160 kcal/mol)[8] and that of C_2H_5Cl (167 kcal/mol).[8] Thus, in I the proton is transferred to H_2O, destroying the nucleophilicity of water and inhibiting the displacement reaction. As a result reaction 2 does not occur, even though it is calculated to be exothermic. Instead, the simple proton-transfer reaction 4 is observed. In II however,

$$CH_3ClH^+ + H_2O \longrightarrow H_3O^+ + CH_3Cl \qquad (4)$$

the proton remains bound to chlorine and HCl is displaced by H_2O. It appears that gas-phase displacement reactions occur provided two criteria are met: (1) *the reaction is exothermic* (a general requirement for ion–molecule reactions);[11–14] and (2)

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[7] It is to be noted that $(CH_3)_2F^+$ also forms by a nucleophilic displacement process: $CH_3FH^+ + CH_3F \rightarrow (CH_3)_2F^+ + HF$. All of the dialkylhalonium ions can be similarly generated in the gas phase[8] and have recently been generated in solution, isolated, and characterized.[9]

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[10] Some CH_3ClH^+ may be generated directly from H_2Cl^+ in the reaction $H_2Cl^+ + CH_3F \rightarrow CH_3ClH^+ + HF$.

Table I. Proton and Methyl Cation Affinities in the Gas Phase[a]

	NH_3	CO	H_2S	CH_2O	HI	H_2O	HBr	HCl	Zn	Cd	N_2	Hg	HF	CH_4
MCA[b]	111	82	79	74[e]	67	66	56	51	45[h]	45[h]	42[f]	38[h]	36	26
PA[c]	207	143	170	165	145	164	141	140			116		137[g]	126
Δ[d]	96	61	91	91	78	98	85	89			74		101	100

[a] Thermochemical values are in kcal/mol and unless noted otherwise are derived from J. L. Franklin and J. G. Dillard; H. M. Rosenstock, J. T. Herron, and K. Draxl; and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969; unpublished results of our laboratory; M. A. Haney, and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969). [b] Methyl cation affinity—defined in text. [c] Proton affinity—defined in ref 4. [d] Δ = PA − MCA. [e] A. G. Harrison, A. S. Blair, and B. G. Keyes, Abstracts, 18th Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, Calif., 1970, p E3. [f] B. G. Gowenlock and J. R. Majer, as reported in Z. Prásil and W. Forst, *J. Amer. Chem. Soc.*, **90**, 3344 (1968). [g] Authors' estimate. [h] G. Distefano and V. H. Dibeler, *Int. J. Mass. Spectrom. Ion Phys.*, **4**, 59 (1970).

proton transfer from the protonated substrate to the nucleophile is endothermic.

The labile proton involved in reactions 1 and 3 need not initially be bound to substrate. For the ethyl chloride–water mixture, besides reaction 3, reaction 5 also occurs. Thus, the labile proton can initially be bound to the nucleophile with proton transfer occurring as the first step in the formation of the reaction complex (structure II).

$$H_3O^+ + C_2H_5Cl \longrightarrow C_2H_5OH_2^+ + HCl \qquad (5)$$

The apparently general nucleophilic displacement reaction illustrated by reactions 1 and 3 has several interesting implications. From proton affinity and other thermochemical data, one can predict the orders in which various nucleophiles will displace one another in methyl-substituted species (reaction 6). A useful

$$N + CH_3M^+ \longrightarrow CH_3N^+ + M \qquad (6)$$

thermochemical quantity to employ in the description of these processes is the methyl cation affinity, defined as the negative of the enthalpy change for attaching a methyl cation as depicted in the general process

$$M + CH_3^+ \longrightarrow MCH_3^+ \qquad (7)$$

Available data (Table I) indicate that the following will be the order in which nucleophilic displacements occur (decreasing methyl cation affinity): $NH_3 > CO > H_2S > CH_2O > HI > H_2O > HBr > HCl > N_2 > HF$.

The determination of methyl cation affinities is of great thermochemical interest and has far-reaching consequences for the general theory of acids and bases beyond simply predicting the order of nucleophilic displacements. Pearson[15] has recently espoused an empirical theory of hard and soft acids and bases (HSAB) which, at least qualitatively, serves to rationalize large areas of chemical reactivity. The experimental determination of methyl cation affinities by icr will allow more quantitative assignments of "hardness" and "softness." For example, toward a given neutral M, a quantitative measure of the difference in the behavior of the soft acid, CH_3^+, from that of the hard acid, H^+, is simply the difference in the methyl cation and proton affinities of M (Table I). As an obvious extension, quantitative thermodynamic affinities can in principle be determined by icr for other acids such as CF_3^+, CH_3CO^+, CH_3Hg^+, and Li^+.

The present findings have important implications for many other studies dealing with ionization phenomena. For example, species such as NH_3, H_2S, H_2O, and CH_4 are frequently utilized as ionic scavengers or ionization agents in photolysis,[16] radiolysis,[17,18] or chemical ionization experiments.[19,20] Clearly, in understanding the chemical activity of these additives, it is necessary to recognize the possible occurrence of processes such as generalized in reaction 6.

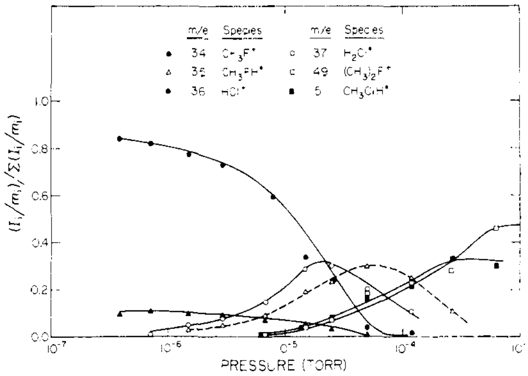

Figure 1. Variation of ion densities (reported as normalized mass corrected single resonance intensities) with pressure for the major ionic species present in a 1:3.5 mixture of CH_3F and HCl at 14.9 eV.

We are engaged in experimentally verifying the predicted order of nucleophilic displacements for a wide variety of attacking and leaving groups. For example, N_2 and CO, as predicted in Table I, have been observed to displace HF from CH_3FH^+ forming $CH_3N_2^+$ and CH_3CO^+, respectively. In addition an investigation of the spatial relationships of reactants during the displacement process employing bridgehead substituents in rigid bicyclic structures has commenced.

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(22) Alfred P. Sloan Foundation Fellow, 1968–1970.
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Absorption Spectra and Kinetics of the Intermediate Produced from the Decay of Azide Radicals

Sir:

Azide ions in aqueous solution undergo a one-electron oxidation mechanism on reaction with hydroxyl radicals

$$N_3^- + OH \longrightarrow N_3\cdot + OH^- \qquad (1)$$

This reaction has been studied by generating OH radicals in the pulse radiolysis of aqueous solutions, in the presence of 1 atm of nitrous oxide to convert >98% of e_{aq}^- to OH radicals. Single pulses of 2.3-MeV electrons and 30-nsec duration were used; all experimental details have been described.[1] Figure 1 shows the transient absorption spectrum obtained immediately after the pulse—this band has a λ_{max} at 278 nm, and is assigned to the $N_3\cdot$ radical. An identical spectrum has recently been obtained,[2] and similarly identified, in the flash photolysis of N_3^- ions in its CTTS band

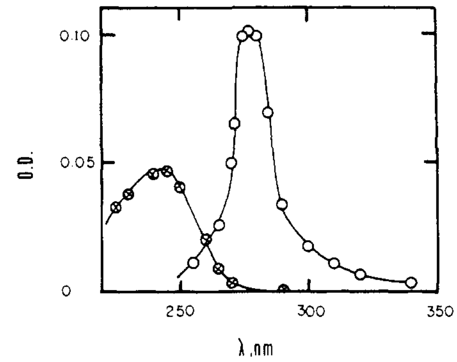

Figure 1. Transient absorption spectra produced from the reaction of OH radicals with 1 m*M* N_3^- ions in aqueous solution at pH 9.2. OD measured at 0.1 μsec (○) and 10 μsec (⊗) after a 30-nsec single pulse of electrons, total dose 4 krads. Identical spectra observed in the presence of 0.1 *M* NaCl and in 10 m *M* NaN_3.

$$N_3^-\cdot H_2O \xrightarrow{h\nu} N_3\cdot + e_{aq}^-$$

Based on $G(OH) = 5.6$, the extinction coefficient of $N_3\cdot$ is found to be ϵ_{278} 2.3×10^3 M^{-1} cm^{-1}. The azide radical decays by a second-order process with $2k = 9 \pm 1 \times 10^9$ M^{-1} sec^{-1}, in excellent agreement with the value 9.2×10^9 M^{-1} sec^{-1} obtained from flash photolysis work.[2] The rate constant $k(OH + N_3^-) = 1.2 \times 10^{10}$ M^{-1} sec^{-1} was obtained, based on kinetic competition with the benzoate ion, and taking[3] $k(OH + PhCOO^-) = 6 \times 10^9$ M^{-1} sec^{-1}.

Azides resemble halides and in many respects react like pseudohalides. They do not, however, appear to produce N_6^- radicals

$$N_3\cdot + N_3^- \rightleftharpoons N_6\cdot^-$$

similar to $Cl_2\cdot^-$, $Br_2\cdot^-$, and $I_2\cdot^-$ radicals. The absorption maximum, the decay rate, and the extinction coefficient of the 278-nm band were found to be independent of $[N_3^-]$ in the range 0.4–10 m*M*. The decay kinetics at 280 nm were found to be independent of the ionic strength of the solution (up to 0.2 *M* Na_2SO_4), indicating the absence of a charge on the radical. Finally, in the presence of 0.1 *M* Cl^- ions the $N_3\cdot$ band was unchanged, suggesting the absence of the complex $N_3\cdot + Cl^- \rightleftharpoons N_3Cl\cdot^-$.

Concomitant with the second-order decay of the $N_3\cdot$ radical is the formation of another intermediate with λ_{max} at 242 nm; see Figure 1. This new species X is produced by a second-order process with $2k = 6.2 \times 10^6$ ϵ_{242} M^{-1} sec^{-1}

$$2N_3\cdot \longrightarrow X \qquad (2)$$

Assuming this mechanism, ϵ_{242} is 2.1×10^3 M^{-1} cm^{-1}, and the rate of formation of X is $2k = 1.3 \times 10^{10}$ M^{-1} sec^{-1}, in good agreement with the rate of decay of $N_3\cdot$ radicals at 278 nm.

The intermediate X decays by a first-order process to give nitrogen

$$X \longrightarrow 3N_2 \qquad (3)$$

with $k_3 = 3.6 \times 10^3$ sec^{-1}, *i.e.*, $\tau_{1/2}$ of ~200 μsec. In support of reactions 2 and 3, the yield of N_2 in this system was determined, since in earlier work[4] complicated factors involving the reaction of e_{aq}^- were not eliminated. ^{60}Co γ irradiation of 10^{-2} *M* NaN_3, pH 8.5, saturated with N_2O gave a $G(N_2) = 11.0 \pm 0.4$, $G(H_2) = 0.33$, and $G(O_2) = 0.37$. Assuming $G(OH) = G(e_{aq}^-) = 2.8$, $G(H) = 0.6$, $G(H_2) = 0.45$, and $G(H_2O_2) = 0.72$, a $G(N_2) = 11.8 \pm 0.4$ can be expected, based on reactions 1–3. The formation of O_2 and the slightly lower yield of N_2 observed could be due to

$$H + N_3^- \longrightarrow N_2 + NH^- \text{ (or } NH_2) \qquad (4)$$

$$NH^- + H_2O_2 \longrightarrow NH_3 + O_2^- \qquad (5)$$

$$O_2^- + O_2 \xrightarrow{2H_2O} H_2O_2 + O_2 + 2OH^- \qquad (6)$$

$$N_3\cdot + H_2O_2 \longrightarrow \text{products} \qquad (7)$$

where $k_4 = 7.3 \times 10^9$ M^{-1} sec^{-1} (ref 5). Under the above experimental conditions, the reaction of $N_3\cdot$ with H_2O_2 plays only a minor part.

It is interesting to speculate on the nature and structure of the intermediate X. The azide ion[6] is linear and symmetrical, and since removal of an electron from the nonbonding orbital is expected to have almost no effect on the bond lengths, vibration frequencies, and force constants, $N_3\cdot$ can be said to resemble closely N_3^-. Dimerization of N_3 is not forbidden by spin-conservation rules and, thermochemically, is highly

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