The k_Δ values in solvolysis of simple secondary β-arylalkyl systems other than IS-OTs are also correlated well with k_t for the neophyl system. This is true, for example, for the 1-*p*-anisyl-2-propyl OTs[7a,15] and threo-3-phenyl-2-butyl OTs[3,7b,15] systems. The same general picture of competing k_Δ and k_s routes, with little or no leakage between them, and with (k_Δ/k_s) dependent on structure and solvent, applies generally to the simple primary and secondary β-arylalkyl systems.

Quite a different description of the solvolysis of simple primary and secondary β-arylalkyl systems has been evolved by Brown.[9] Since he does not recognize discrete k_Δ and k_s processes, his resulting treatments of rates, phenyl-substituent effects, solvent effects, and stereochemistry are unacceptable.

(15) (a) A. Diaz, unpublished work; (b) S. Winstein, James Flack Norris Award Address, American Chemical Society Meeting, Miami, Fla., April 11, 1967.

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Metal Ion Promoted Hydrolysis of Fluorocarbons

Sir:

The catalytic effect of the hydronium ion on the hydrolysis of a number of fluoro complexes (both cationic and anionic) is well documented.[1] This type of catalysis is also found for the hydrolysis of certain organic fluorides.[2] The theory of hard and soft acid–base behavior interprets this as a specific type of hard acid–hard base interaction. It leads to the anticipation that hard acids other than the hydronium ion should also prove capable of promoting the hydrolysis of suitable fluorocarbons. In particular, the metal cations which are hard acids should show such activity. We have obtained unequivocal experimental proof that this is indeed the case.

Our study has examined the effects of Zr(IV), Th(IV), Ti(IV), Al(III), and Be(II) on the acid hydrolysis of PF_6^-, BF_4^-, $AsF_5(OH)^-$, and benzyl fluoride. Accelerative effects have been general, though dependent upon the media and conditions. Some of the most striking results are found, however, with benzyl fluoride, and these are summarized in Table I.

The data in Table I represent the first quantitative evidence for metal ion catalyzed hydrolytic displacement of fluoride from the C–F linkage.

Table I. Comparison of Half-Lives for the Metal Ion Catalyzed and Uncatalyzed Acid Hydrolysis of Benzyl Fluoride at 25°

Hydrolysis medium	Catalyst	Catalyst Ratio[a]	$t_{1/2}$, min
2 *M* HCl (5% ethanol)	None	. . .	1850
	Th(IV)	10.4	9.0
2 *M* $HClO_4$ (5% ethanol)	None	. . .	1650
	Th(IV)	10.4	7.5
2 *M* HCl (10% acetone)	None	. . .	3000[b]
	Th(IV)	10.4	11
	Zr(IV)	10.4	33.5
	Al(III)	10.3	350
2 *M* $HClO_4$ (10% acetone)	None	. . .	2210
	Th(IV)	9.8	9.1
	Zr(IV)	9.8	28
1 *M* HCl (10% acetone)	Th(IV)	10.3	20.5

[a] Total metal ion concentration/total fluoride. Initial benzyl fluoride was approximately 0.004 *M* in each run. [b] Based on the first 20% of reaction. The first-order plot was nonlinear during later stages of the hydrolysis, presumably from the loss of HF.

For the benzyl fluoride studies the procedure of Swain and Spalding[2a] was used for introduction of the sample, whereby an aliquot of a solution of benzyl fluoride dissolved in a nonaqueous solvent is added to the previously thermostated solution of the other reagents. Our observed rate constant of 1.05×10^{-3} min^{-1} for the reaction in 3 *M* $HClO_4$ with 10% acetone at 25° is in reasonable agreement with their value of 1.19×10^{-3} min^{-1} for the reaction in the same medium at 25.1°. We chose the 2 *M* acid concentration for these initial data so that hydrolysis of the catalyst ions, especially Zr(IV), would be retarded.

The experimental technique used to obtain the rate data consisted of quenching an aliquot of the reaction mixture in an acetate–citrate buffer to give a solution of pH 5.0 followed by the measurement of the potential of an Orion 94-09 fluoride electrode *vs.* sce. The fluoride ion concentration of the resulting solution was then obtained by comparison with standard calibration curves obtained with sodium fluoride solutions obtained under identical conditions of pH, buffer composition, and catalyst concentrations.

A commercial sample of benzyl fluoride (Columbia Organic Chemicals, Co., Inc., Columbia, S. C.) has been used without further purification due to the reported tendency of benzyl fluoride to decompose *via* polymerization upon distillation except under special conditions.[2a] Recovery of fluoride upon complete hydrolysis has typically amounted to 97% of theoretical for C_7H_7F. Catalyzed hydrolyses, all of which have been conducted with pseudo-first-order concentrations of catalyst, have produced first-order plots which are somewhat nonlinear with respect to unhydrolyzed benzyl fluoride. This problem appears to arise from the amount and kind of organic solvent used and is being investigated further.

The results here suggest strongly that the hard and soft acid–base theory may well provide a valuable guide in the development of metal-catalyzed substitution processes on saturated carbon.

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(1) See, for example: (a) M. Anbar and S. Guttman, *J. Phys. Chem.*, **64**, 1896 (1960); (b) S. C. Chan, *J. Chem. Soc.*, 2375 (1964); (c) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956); (d) A. E. Gebala and M. M. Jones, *J. Inorg. Nucl. Chem.*, **31**, 771 (1969); (e) L. N. Devonshire and H. H. Rowley, *Inorg. Chem.*, **1**, 680 (1962).

(2) (a) C. G. Swain and R. E. T. Spalding, *J. Am. Chem. Soc.*, **82**, 6104 (1960); (b) N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1677 (1952); (c) C. W. L. Bevan and R. F. Hudson, *ibid.*, 2187 (1953).

Mass Spectrometric Evidence for the Gaseous AlOCN Molecule

Sir:

In connection with the investigation of the vapor components over the aluminum nitride–graphite system,[1,2] a molecule containing one atom each of

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(1) K. A. Gingerich, *Naturwissenschaften*, **54**, 646 (1967).

(2) K. A. Gingerich, submitted for publication.

Table I. Partial Pressures Over AlN(s)–Graphite System

	Pressure, atm				
Temp, K°	Al	N_2	AlCN	Al_2O	AlOCN
1879	1.21×10^{-4}	5.13×10^{-5}	1.81×10^{-6}	9.18×10^{-8}	2.83×10^{-8}
1900	1.98×10^{-4}	6.91×10^{-5}	2.76×10^{-6}	1.31×10^{-7}	3.37×10^{-8}
1935	2.45×10^{-4}	1.15×10^{-4}	4.98×10^{-6}	1.96×10^{-7}	4.39×10^{-8}

Table II. Enthalpies of Reactions Involving the AlOCN Molecule over the Aluminum Nitride–Graphite System

Reaction	Temp, K°	$-R \ln K_p$	$-\Delta[(G°_T - H°_{298})/T]$, cal deg^{-1} mol^{-1}	$\Delta H°_{298}$, kcal mol^{-1}
$Al_2O(g) + N_2(g) + 2C(graph.) = AlOCN(g) + AlCN(g)$	1879	8.98	(15.0)	45
	1900	9.10	(15.0)	46
	1935	9.23	(15.0)	47
$Al_2O(g) + 0.5N_2(g) + C(graph.) = AlOCN(g) + Al(g)$	1879	10.45	(20.6)	58
	1900	10.13	(20.6)	58
	1935	10.49	(20.6)	60
$Al_2O(g) + AlCN(g) = AlOCN(g) + 2Al(g)$	1879	11.91	(26.1)	71
	1900	11.16	(26.1)	71
	1935	11.76	(26.1)	73

aluminum, oxygen, carbon, and nitrogen could be identified. This molecule may be aluminum cyanate (AlOCN), aluminum isocyanate (AlNCO), oxoaluminum cyanide (OAlCN), aluminum fulminate (AlCNO), or another possible isomer containing these four atoms. No gaseous metal cyanates, oxocyanides, or their isomers have previously been reported. An evaluation of the atomization energy and heat of formation of the AlOCN molecule, as it will be referred to, is presented here.

The mass spectrometric measurements were performed under the same conditions under which the Al_2N molecule was studied.[2] The instrument used and the treatment of the data have been described elsewhere.[3] The sample consisted of gold and powdered aluminum nitride that was placed inside a graphite effusion cell. The AlOCN molecule was identified by its m/e ratio of 69, its ionization efficiency curve, its appearance potential of 6.8 ± 0.5 eV, and its intensity distribution in the molecular beam. The oxygen impurity in the sample used also caused the formation of gaseous Al_2O. In Table I the partial pressures of some simultaneously observed molecules are given. The values for AlOCN have been corrected for a small contribution of ^{69}Ga. The measurements were performed with 15-eV electrons with the exception of N_2^+ for which 30-eV electron were used. No indication of any fragment contribution to the signal at m/e 69 could be found. The complete mass spectrum observed will appear elsewhere.[2]

In Table II the results of an evaluation of the enthalpies of several homogeneous and heterogeneous reactions by the third law method are given. Under the assumption that equilibrium conditions prevailed for all reactions evaluated, a heat of atomization of 472 kcal mol^{-1} is obtained for the AlOCN molecule from the average enthalphy of either of the reactions evaluated.

The auxiliary data used for the calculation of the heat of atomization are 170.9 ± 0.45 kcal mol^{-1} for the heat of sublimation, $\Delta H_s°_{298}$, of carbon;[4] 226.0 ± 2.0 kcal mol^{-1} for the dissociation energy, $D°_{298}$, of N_2;[4] 247 ± 7 kcal mol^{-1} for the heat of atomization, $D°_{298}$, of Al_2O;[4] and 297 ± 5 kcal mol^{-1} for the heat of atomization, $D°_{298}$, of AlCN. The latter was determined from third law evaluations of the reactions $AlCN(g) = Al(g) + 0.5N_2(g) + C(graph.)$, and $2AlCN(g) + Au(g) = Al(g) + N_2(g) + AlAu(g) + 2C(graph.)$, using the vapor pressures in Table I, and from additional experimental data.[5] The free energy functions for the reactants and products other than AlCN and AlOCN were taken from the JANAF tables;[4] those for AlCN and AlOCN were estimated by analogy with similar molecules such as SiC_2, NaCN, and HNCO.[4] The $-(G°_{1900} - H°_{298})/T$ values used are 70.68 and 82.65 eu for AlCN(g) and AlOCN(g), respectively. The relative ionization cross sections were based on Mann's[6] values.[3]

Evaluations of reactions involving solid AlN as a reactant indicated a comparatively small deviation from equilibrium conditions due to the low vaporization coefficient of AlN(s).[7,8] For the reactions of the molecules AlOCN and AlCN, which did not involve AlN(s) as a reactant, equilibrium was essentially achieved in the present investigation.

The uncertainty of the enthalpies for the reactions given in Table II is estimated as ±5 kcal mol^{-1}. Considering in addition the uncertainties in the values of the auxiliary thermochemical data used for the calculation of the atomization energy of AlOCN, the latter is 472 ± 15 kcal mol^{-1}. This value, together with the appropriate JANAF auxiliary data,[4] yields a standard heat of formation, $\Delta H_f°_{298} = -51.5 \pm 15$ kcal mol^{-1}, for the thermodynamically most stable isomer of the AlOCN molecule.[9]

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(3) K. A. Gingerich, *J. Chem. Phys.*, **49**, 14 (1968).

(4) "JANAF Thermochemical Tables," D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1965, and quarterly supplements.

(5) K. A. Gingerich, to be published.

(6) J. B. Mann, *J. Chem. Phys.*, **46**, 1546 (1967).

(7) L. H. Dreger, V. V. Dadape, and J. L. Margrave, *J. Phys. Chem.*, **66**, 1556 (1962).

(8) D. L. Hildenbrand and W. F. Hall, *ibid.*, **67**, 888 (1963).

(9) The mass spectrometric experiments for this work have been performed at the Columbus Laboratories of the Battelle Memorial Institute. Their evaluation and interpretation have been supported by the Research Council of Texas A & M University.

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