

The  $k_{\Delta}$  values in solvolysis of simple secondary  $\beta$ -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<sup>7a,15</sup> and threo-3-phenyl-2-butyl OTs<sup>8,7b,15</sup> systems. The same general picture of competing  $k_{\Delta}$  and  $k_s$  routes, with little or no leakage between them, and with  $(k_{\Delta}/k_s)$  dependent on structure and solvent, applies generally to the simple primary and secondary  $\beta$ -arylalkyl systems.

Quite a different description of the solvolysis of simple primary and secondary  $\beta$ -arylalkyl systems has been evolved by Brown.<sup>9</sup> Since he does not recognize discrete  $k_{\Delta}$  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(15) (a) A. Diaz, unpublished work; (b) S. Winstein, James Flack Norris Award Address, American Chemical Society Meeting, Miami, Fla., April 11, 1967.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.<sup>1</sup> This type of catalysis is also found for the hydrolysis of certain organic fluorides.<sup>2</sup> 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  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{AsF}_5(\text{OH})^-$ , 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.

For the benzyl fluoride studies the procedure of Swain and Spalding<sup>2a</sup> 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  $1.05 \times 10^{-3} \text{ min}^{-1}$  for the reaction in 3 *M*  $\text{HClO}_4$  with 10% acetone at 25° is in reasonable agreement with their value of  $1.19 \times 10^{-3} \text{ min}^{-1}$  for the reaction in the same medium

(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).

**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 <sup>a</sup>	$t_{1/2}$ , min
2 <i>M</i> HCl (5% ethanol)	None	...	1850
	Th(IV)	10.4	9.0
2 <i>M</i> $\text{HClO}_4$ (5% ethanol)	None	...	1650
	Th(IV)	10.4	7.5
2 <i>M</i> HCl (10% acetone)	None	...	3000 <sup>b</sup>
	Th(IV)	10.4	11
	Zr(IV)	10.4	33.5
2 <i>M</i> $\text{HClO}_4$ (10% acetone)	Al(III)	10.3	350
	None	...	2210
	Th(IV)	9.8	9.1
1 <i>M</i> HCl (10% acetone)	Zr(IV)	9.8	28
	Th(IV)	10.3	20.5

<sup>a</sup> Total metal ion concentration/total fluoride. Initial benzyl fluoride was approximately 0.004 *M* in each run. <sup>b</sup> 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.

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.<sup>2a</sup> Recovery of fluoride upon complete hydrolysis has typically amounted to 97% of theoretical for  $\text{C}_7\text{H}_7\text{F}$ . 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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### Mass Spectrometric Evidence for the Gaseous AIOCN Molecule

Sir:

In connection with the investigation of the vapor components over the aluminum nitride-graphite system,<sup>1,2</sup> a molecule containing one atom each of

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

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