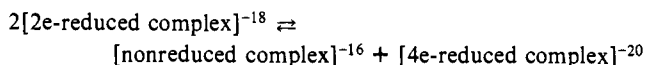ronments (and hence chemical shifts) in a reduced or nonreduced end of the complex are independent of whether the *other* end of the complex is reduced or not. The rate of the concerted exchange is calculable from the line widths.[6,9]

The disproportionation equilibrium constant for

$$2[\text{2e-reduced complex}]^{-18} \rightleftharpoons$$
$$[\text{nonreduced complex}]^{-16} + [\text{4e-reduced complex}]^{-20}$$

was evaluated from peak areas for each species. In the present case both bridged heteropoly portions of the nonreduced complex are identical, and in the 2e-reduced species there is negligible electronic coupling energy between the two portions.[10] No new electronic transition (UV–vis, near-IR) was observed. Therefore the disproportionation equilibrium constant should be 0.25 as statistically dictated,[10] which is (within ±0.01) the experimental value[11] at several different extents of total reduction and several temperatures.

Kinetics. Signals from the P's nearer the $Zn_4O_{16}H_4$ bridge, being somewhat more widely spaced, were used for kinetic analysis. Their $\Delta\nu_{1/2}$'s for nonreduced and 4e-reduced species (1.1 and 1.4 Hz, respectively) were constant, proving intercomplex exchange rates negligible. $\Delta\nu_{1/2}$'s for the 2e-reduced species at five temperatures were the following: 300 K, 12.9 Hz; 310 K, 6.0 Hz; 320 K, 4.2 Hz; 330 K, 2.3 Hz; 340 K, 1.5 Hz. At a given temperature $\Delta\nu_{1/2} = 1/(\pi T_2)$, where T_2 is spin–spin relaxation time, and[9]

$$1/T_{2(2e)} =$$
$$x_{(\text{red})}/T_{2(\text{red})} + x_{(\text{ox})}/T_{2(\text{ox})} + x^2_{(\text{red})}x^2_{(\text{ox})}(2\pi\Delta\nu)^2(\tau_{(\text{red})} + \tau_{(\text{ox})})$$

where $\Delta\nu$ = difference in hertz between the two sharp peaks, $x_{(\text{red})}$ = $x_{(\text{ox})}$ = 0.5 (fractions of reduced and oxidized ends in the 2e-reduced species, and $\tau_{(\text{red})} = \tau_{(\text{ox})}$ = lifetime of an electron in a given heteropoly end.[12] For intramolecular first-order exchange, $k = 1/\tau$. The k's range from 2.0×10^3 s^{-1} at 300 K to 1.8×10^4 s^{-1} at 340 K. Plotting log (k/T) vs. $1/T$ gives a straight line (r = 0.994). Slope and intercept yield enthalpy and entropy of activation, $\Delta H^{\ddagger}$ = 10.4 kcal/mol and $\Delta S^{\ddagger}$ = –8.9 cal/mol K.[13]

Potentialities. Uses for this easy method may be considerable. Rates may be brought within fairly broad appropriate ranges by varying temperature, bridges, bridged groups, substitutions (organic and/or heteropoly), and heteropoly blues, variously reduced by different potentials. Only one electron receptor need be heteropoly, containing only one NMR-active nucleus. Complexes like diamagnetic $[O_{39}W_{11}XCo^{3+}\text{-pyrazine–MR}]^{-n}$ and their blues have been made[1-3] (X = various elements, MR = reducible heteropoly or other complex groups). Exchange rates too slow for line coalescence may be evaluated from line widths,[6] from magnetization transfer experiments, or from T_2 measurements.[12] These interesting mixed-mixed-valence complexes involve one activation energy for through-bridge electron transfer and (an)other(s) for electron hopping within the heteropoly blue portions.

(10) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.
(11) Slow spin–lattice relaxation for P's close to the Zn_4 layer ($T_1 \approx 30$ s) made signals from the other P's ($T_1 \approx 9$ s) more convenient for equilibrium constant calculations.
(12) In case of small line widths, where instrumental contributions to the error could be substantial, a Hahn spin–echo T_2 measurement could provide a superior measurement of τ.
(13) The magnitude of the negative value of the entropy of activation (–8.9 cal/mol K) is consistent with a nonadiabatic character of the intramolecular electron transfer inferred from the fact that the disproportionation constant has the statistical value and from the absence of electronic coupling between the two heteropoly portions of the complex. The electronic factor κ can be estimated,[14] from $\Delta S^{\ddagger} = R \ln \kappa$, to be 1×10^{-2}.
(14) Sutin, N. In *Progress in Inorganic Chemistry*; Vol. 30, Lippard, S. J., Ed.: Wiley-Interscience: New York, 1983; p 479.

## Inhibition of the Hydrolysis of p-(Dimethylamino)benzoyl Fluoride by Potassium Fluoride[1]

Byeong Doo Song and William P. Jencks*

Contribution No. 1612
*Graduate Department of Biochemistry, Brandeis University
Waltham, Massachusetts 02254*

Received February 9, 1987

Previous reports[2-4] of the rate-enhancing effect of electron-donating substituents on the solvolysis of substituted benzoyl halides and the large sensitivity to solvent ionizing power (in highly polar solvents) of the solvolysis of acid halides with electron-donating substituents suggest that these reactions occur through acylium ion like transition states. For the hydrolysis of 2,4,6-trimethylbenzoyl chloride, a significant inhibition by tetra-*n*-butylammonium chloride was observed in 99% acetonitrile,[3] but little inhibition by chloride ion was observed in 95% acetone,[5] even though ρ is –3.9 for the hydrolysis of 4-substituted 2,6-dimethylbenzoyl chlorides in 99% acetonitrile[3] and in 89.1% acetone.[4]

We report here inhibition of the hydrolysis of p-(dimethylamino)benzoyl fluoride in water by added potassium fluoride at constant ionic strength, which is expected for a common ion effect in a monomolecular solvolysis (eq 1). Figure 1 shows 50% inhibition by 2.0 M potassium fluoride of the hydrolysis of p-(dimethylamino)benzoyl fluoride[6] (1) and the theoretical curves for the observed rate constants, obtained from eq 2 with $k_1 = 3.5 \times 10^{-3}$ s^{-1} (3.3×10^{-3} s^{-1} in D$_2$O) and $k_{-1}/k_h = 0.6$ M^{-1}, based on the reaction scheme of eq 1.
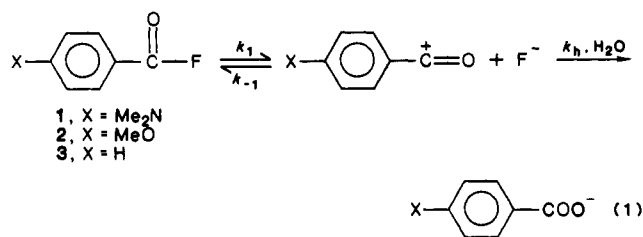
$$k_c = k_1 k_h/(k_{-1}[\text{F}^-] + k_h) = k_1/\{(k_{-1}/k_h)[\text{F}^-] + 1\} \quad (2)$$

In contrast, for p-anisoyl (2)[6] and benzoyl (3) fluorides, 1.0 M potassium fluoride *increases* the hydrolysis rate by 7.7- and 6.6-fold, respectively. The solvent deuterium isotope effect is $k_{\text{HOH}}/k_{\text{DOD}} = 1.1$ for 1 and 2.3 ± 0.2 for 2 and for 3 in the presence and in the absence of 1.0 M potassium fluoride.[7] This rate increase and the solvent isotope effect in the presence of fluoride ion for 2 and 3 suggest that fluoride ion and solvent both act as general base catalysts for nucleophilic attack of water on these acid fluorides.

(1) Supported in part by grants from the National Institutes of Health (GM 20888) and the National Science Foundation (PCM 8117816).
(2) (a) Hudson, R. F.; Wardill, J. E. *J. Chem. Soc.* **1950**, 1729. (b) Crunden, E. W.; Hudson, R. F. *J. Chem. Soc.* **1956**, 501. (c) Beguin, C. C.; Coulombeau, C.; Hamman, S. *J. Chem. Res., Synop.* **1977**, 178. (d) Bentley, T. W.; Harris, H. C. *J. Chem. Soc., Perkin Trans. 2* **1986**, 619.
(3) Bender, M. L.; Chen, M. C. *J. Am. Chem. Soc.* **1963**, *85*, 30.
(4) Ugi, I.; Beck, F. *Chem. Ber.* **1961**, *94*, 1839.
(5) Hudson, R. F.; Moss, G. *J. Chem. Soc.* **1964**, 2982.
(6) Prepared according to *Organic Syntheses*; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Collect. Vol. 5, p 66. p-(Dimethylamino)benzoyl chloride, the precursor of the corresponding acid fluoride, was prepared according to: Harada, N.; Chen, S. L.; Nakanishi, K. *J. Am. Chem. Soc.* **1975**, *97*, 5345.
(7) The reaction was followed spectrophotometrically at 25 °C, ionic strength = 1.0, maintained with potassium chloride, and wavelength = 330 nm for 1, 275 nm for 2, and 240 nm for 3. The stock solution of potassium fluoride of ≈pH 6.0 was prepared by addition of 2.96 N HCl (2.5 mL) to 4.0 M KF (200 mL); no buffer was added for the reaction. The hydrolysis of 1 is independent of the concentration of potassium phosphate, 50% dianion, up to 1.0 M. For 2 and 3, the same rate constant was observed in the absence of buffer and extrapolated to zero concentration of potassium phosphate, 50% dianion.
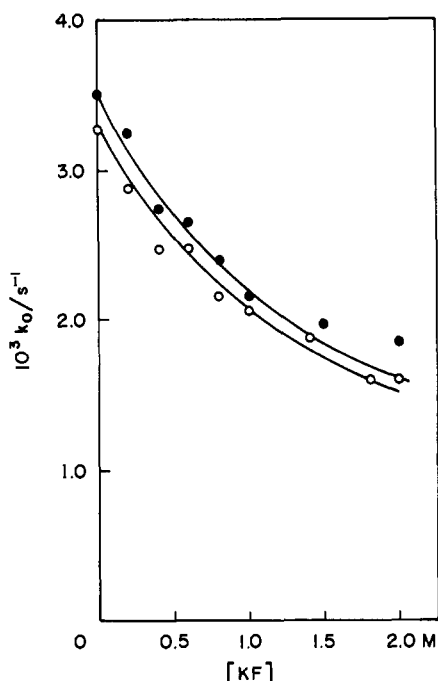
Figure 1. Dependence on potassium fluoride concentration of the hydrolysis of *p*-(dimethylamino)benzoyl fluoride in H_2O (●) and in D_2O (○) at 25 °C with ionic strength = 2.0 maintained with potassium chloride. The solid lines are calculated from eq 2.

Table I. Effects of Salts and Organic Solvents on the Hydrolysis of *p*-(Dimethylamino)benzoyl Fluoride[a]

salt/solvent	concn, M	ionic strength	$10^3 k_o$, s^{-1}
no salt	0	0	3.5
$NaClO_4$	1.0	1.0	4.6[b]
NaCl	1.0	1.0	4.5[b]
KCl	1.0	1.0	3.9[b]
NaBr	1.0	1.0	4.6[b]
$NaNO_3$	1.0	1.0	4.0[b]
Na_2SO_4	0.33	1.0	3.8[b]
	0.6	1.8	3.8[b]
	1.0	3.0	3.9[b]
KH_2PO_4/K_2HPO_4(1:9)	0.36	1.0	3.9
	1.0	2.8	4.7
NaF	0.9	0.9	2.9
KF	1.0	1.0	2.5
HCOONa	1.0	1.0	4.2[c]
CF_3COONa	1.0	1.0	3.1[c]
CH_3COONa	1.0	1.0	3.0[c]
EtCOONa	1.0	1.0	2.5[c]
MeOH	1.0	0.02	2.8[b]
	1.0	1.0[e]	3.5[b]
CF_3CH_2OH	1.0	0.01	2.9[d]
	1.0	1.0[e]	3.0[d]
CH_3CH_2OH	1.0	0.02	2.5[b]
	1.0	1.0[e]	2.2[b]
CH_3CN	1.0	0.02	2.9[b]
	1.0	1.0[e]	2.3[b]
CH_3CONH_2	1.0	0.02	2.1[b]
	1.0	1.0[e]	2.3[b]

[a] At 25 °C. [b] In the presence of 0.01 M potassium phosphate, 50% dianion. [c] At ≈pH 6.5. [d] In the presence of 0.01 M sodium acetate, 90% base. [e] Ionic strength was maintained with NaCl.

Inhibition by fluoride ion is not a specific salt effect on the hydrolysis of **1**, on the basis of the following observations: Among the 13 salts examined (Table I), only NaF, KF, and some RCOONa inhibit, even though F^-, $RCOO^-$, HPO_4^{2-}, and SO_4^{2-} have similar properties,[8] including their basicity and their effect on the OH vibration frequency, ^1H chemical shift, reorientation

(8) (a) Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*; Wiley: New York, 1975; pp 174–209. (b) Collins, K. D.; Washabaugh, M. W. *Q. Rev. Biophys.* **1985**, *18*, 323–422.

time, and self-diffusion coefficient of water. The $HCOO^-$ ion does not inhibit; the inhibition by CF_3COO^-, CH_3COO^-, and $CH_3CH_2COO^-$ ions may be attributed to a medium effect of the nonpolar group because large rate decreases are caused by 1.0 M CH_3CN, CH_3CONH_2, CF_3CH_2OH, MeOH, and EtOH (Table I). Therefore, there is specific inhibition by fluoride ion.

The entropies of activation for hydrolysis in water are −12.3 eu for methyl chloride and −26.2 eu for methyl fluoride.[9] The large sensitivity to nonpolar organic cosolvents (Table I) and the entropies of activation for the hydrolysis of methyl halides suggest that fluoride ion requires strong solvation in the transition state for solvolysis. The entropy of activation for the hydrolysis of **1**, −12 eu, calculated from rate constants at five different temperatures between 10 and 45 °C, could be accounted for mainly by solvation of the leaving fluoride ion. The entropy of activation due only to the molecularity of the transition state could be zero or positive, which is consistent with a monomolecular mechanism.

The rate constants for hydrolysis are $10^4 k_o$ = 39 s^{-1} for **1**, 2.6 s^{-1} for **2**, and 18 s^{-1} for **3**.[7] The negative ρ value for **1** and **2**, the effects of fluoride ion, and the solvent isotope effects show that **1** behaves differently than **2** and **3**. The hydrolysis of **1** exhibits the characteristics that are expected for hydrolysis through an acylium ion mechanism (eq 1).

(9) Robertson, R. E *Prog. Phys. Org. Chem.* **1967**, *4*, 213–280.
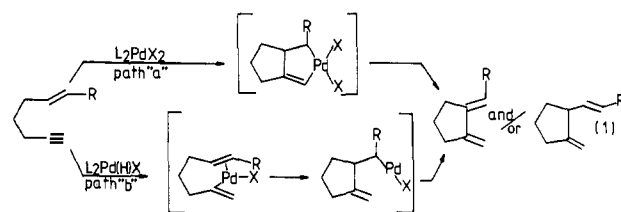
A Reductive Cyclization of 1,6- and 1,7-Enynes

Barry M. Trost* and Frode Rise

*McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706*

Intramolecular carbametalation reactions of enynes and diynes appear to be highly promising approaches for cyclization under extremely mild conditions.[1–4] A palladium-based method has the advantage of being truly catalytic and offering the prospect of controlling the regioisomeric nature of the product (i.e., a 1,3- or 1,4-diene) as in eq 1 depending largely upon the olefin sub-

stituent R.[5] As illustrated in eq 1, two mechanisms appear to

(1) Intramolecular carbalkylation–carbonylation using stoichiometric cobalt complexes has become known as the Pauson–Khand reaction. See: Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977. Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. Billington, D. C.; Pauson, P. L. *Organometallics* **1982**, *1*, 1560. Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851.

(2) For stoichiometric titanium-mediated reductive cyclizations, see: Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422. This method is reported to fail with terminal acetylenes.

(3) For a stoichiometric zirconium-mediated reductive cyclization, see: Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(4) For Pd- and Rh-catalyzed cyclizations of dienes, see: Grigg, R.; Malone, J. F.; Mitchell, T. R. B.; Ramasubbu, A.; Scott, R. M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1745. In the Pd reactions, use of HCl in refluxing chloroform is required. The same group has reported cyclizations of vinyl bromides onto olefins by using Pd catalysts. See: Grigg, R.; Stevenson, P.; Worakun, T. *Chem. Commun.* **1984**, 1073.