

blet attributable in both cyclic and noncyclic cases to the F bound to the phosphorus of the ligand disappears and the doublet characteristic of $[\text{PF}_6]^-$ appears clearly at low temperature. The low temperature ^{31}P spectrum also shows the septet characteristic of $[\text{PF}_6]^-$. The ^{31}P chemical shift values further show a significant trend in the series shown in Chart I. The ^{31}P δ values relative to H_3PO_4 are -138 , -182 , -264 , and -294 ppm, respectively. Comparable values for the noncyclic ligand series are -153 , -192 , -264 , and -308 ppm. Increasingly negative values indicate that the phosphorus is becoming more deshielded, and more acidic through each series. In all cases this increased acidity shows up as more facile exchange of fluoride between the PF_6^- ion and the phosphorus of the cation. For cation **2** and $[\text{PF}_6]^-$ the fluoride doublet of $[\text{PF}_6]^-$ collapses at about -60°C , indicating rapid exchange of fluoride between $[\text{PF}_6]^-$ and cation **2**. In contrast the ^{19}F doublet of the $[\text{PF}_6]^-$ associated with the simple, noncoordinated cyclic cation **1** shows no collapse up to above 60°C . Corresponding temperatures for the noncyclic case are -72 and 10°C . In studying this phenomenon of fluoride lability, purity of the system is extremely important. Small traces of base have dramatic effects in raising collapse temperatures.⁷

Amidofluorophosphine metal carbonyls involving Ni, Pt, P, Cr, W, Mn, Co, Cu, and Ag, have been prepared.^{7,8} Most react with PF_5 to generate $[\text{PF}_6]^-$ and the corresponding cationic carbonyl complex.

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A Donor-Acceptor Structure for the Acetyl Chloride-Aluminum Chloride Complex in Methylene Chloride from Aluminum-27 Nuclear Magnetic Resonance

Sir:

Although the Friedel-Crafts reaction is a familiar one,¹⁻³ the structure of the 1:1 complex between acetyl chloride and aluminum chloride in solvents relevant to usual synthetic practice is not well defined. An ion-pair structure for the solid was determined by x-ray diffraction⁴ after many conflicting solid-state IR studies had been reported.^{4,5} The ^1H , ^{19}F , and ^{13}C NMR studies of Olah and coworkers⁶ on acetyl halides and Lewis acids indicate that either the ion-pair or donor-acceptor form may be present, depending on the solvent system. The donor-acceptor form is indicated for the 1:1 acetyl chloride-aluminum chloride complex in 1,2-dichloroethane from the

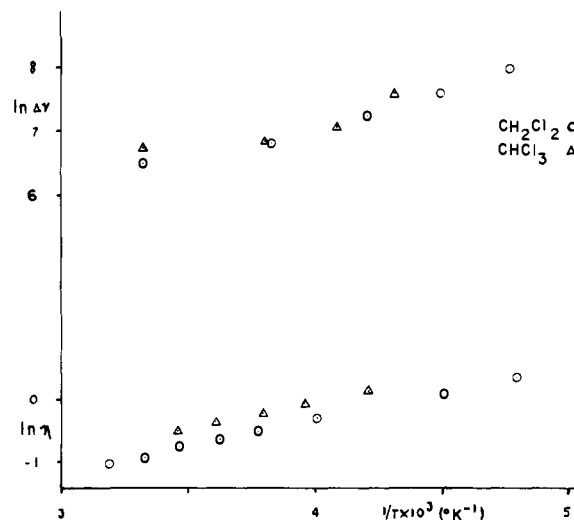


Figure 1. Logarithmic plot of aluminum-27 line widths, $\Delta\nu$, for the 1:1 acetyl chloride-aluminum chloride complex and solvent viscosities,¹⁵ η , vs. reciprocal temperature. Concentrations are 1.4 M for methylene chloride, 0.118 M for chloroform.

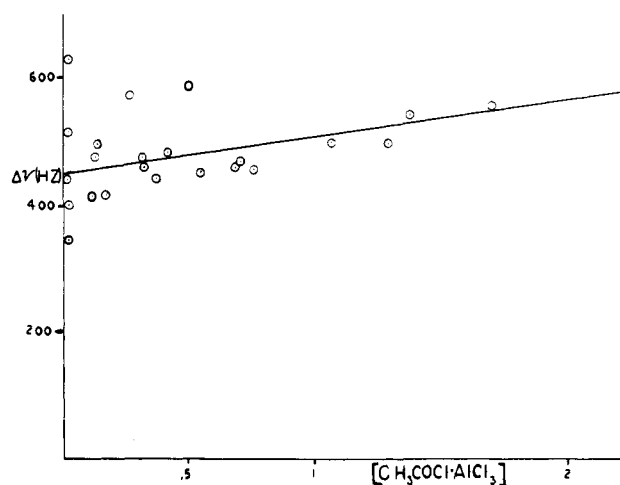


Figure 2. Aluminum-27 line widths, $\Delta\nu$, for the 1:1 acetyl chloride-aluminum chloride complex in methylene chloride vs. concentration. Temperature is 28°C .

^1H NMR spectrum.^{6a} The ^{27}Al NMR spectrum of this 1:1 complex has not been reported to our knowledge, although the ^{27}Al NMR parameters for aluminum chloride in acetyl chloride have been interpreted⁷ to favor an ion-pair structure.

The ^{27}Al and ^1H NMR results reported here demonstrate that the 1:1 complex between acetyl chloride and aluminum chloride has a donor-acceptor structure in methylene chloride solution; only a minor fraction, if any at all, is present as the ion-pair form. Our conclusions come from two aspects of this study: the temperature and concentration dependence of the ^{27}Al NMR spectra of the 1:1 complex; the products shown by ^{27}Al and ^1H NMR to be formed on addition of halide ion to acetyl chloride-aluminum chloride and to acetyl bromide-aluminum chloride complexes.

^{27}Al FT NMR spectra (at 15.636 MHz) of the 1:1 complex⁸ showed the following features: the line width, greater than that of tetrachloroaluminate by at least two orders of magnitude, showed a slight temperature and concentration dependence (Figure 1, 2); the chemical shift, 92.4 ppm,⁹ did not change over a temperature range of -60 to 40°C and over a concentration range of 10^{-3} to 2 M. The large line width and the chemical shift show that the complex does not exist as separated ion pairs in methylene chloride.¹⁰ The temperature dependence of the ^{27}Al line width can be accounted for by vis-

cosity effects, similar to those observed in ^{27}Al spectra of aluminum alkyl derivatives.¹¹ The concentration dependence can also be attributed to viscosity effects and, in any case, would imply that no more than 10% of the 1:1 complex is present as separated ion pairs at low concentrations (10^{-3} M or greater). The concentration and temperature dependence of the ^1H NMR spectra of the 1:1 complex, which will be reported in detail elsewhere,¹² are consistent with this interpretation also.

Excess tetraethylammonium bromide (TEABr) added to a methylene chloride solution of the 1:1 complex gave, immediately after preparation, a three-line ^{27}Al spectrum: chemical shifts, 92.1, 97.5, and 101.4 ppm; line widths, 25, 25, and 15 Hz; relative intensities, 0.4, 1, and 1. These lines can be assigned to the ions dibromodichloroaluminate, bromotrichloroaluminate, and tetrachloroaluminate,¹³ respectively. The ^1H NMR spectrum for the bromide addition showed lines for both acetyl chloride (δ 2.62) and acetyl bromide (2.76) with relative intensities of 1:2. Immediately after excess TEABr was added to a methylene chloride solution of tetraethylammonium tetrachloroaluminate, no change was observed in the narrow line at 102.4 ppm assigned to tetrachloroaluminate ion. In this latter experiment, the bromotrichloroaluminate line at 97.5 ppm did not appear until 1 week after the addition of bromide; the dibromodichloroaluminate line was not observed. The same ^{27}Al spectrum appeared 1 week after addition of bromide to the 1:1 complex.¹⁴ Addition of TEACl to the 1:1 complex, acetyl bromide-aluminum chloride, gave spectra like that for the addition of TEABr to the 1:1 complex, acetyl chloride-aluminum chloride. These results suggest that the 1:1 complex is not *exclusively* an ion pair, where halide would add at the carboxonium carbon of the acylium ion, rather than to the tetrachloroaluminate. We note also that our results show that rapid exchange of halide between tetrahaloaluminate and acetyl halide does not occur in the absence of complex.

Since the temperature and concentration dependence of the 1:1 complex ^{27}Al spectra can be accounted for by viscosity effects, one can conclude that an equilibrium between separated and "tight" ion pairs or between "tight" ion pairs and donor-acceptor favors one form almost exclusively.¹⁶ Since the halide addition results eliminate the ion pair as this predominant form, we can conclude that the donor-acceptor is the principal species in methylene chloride. Additional evidence for a donor-acceptor structure is the close similarity of the ^{27}Al NMR parameters for the 1:1 acetyl chloride-aluminum chloride complex and the 1:1 complex between 3,3-dimethyl-2-butanone (pinacolone) and aluminum chloride. This latter complex, which must necessarily have a donor-acceptor structure, gives a single ^{27}Al line at 92.8 ppm, with line width 296 Hz.¹²

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- The 1:1 complex was prepared by addition of acetyl chloride to an equimolar amount of aluminum chloride (as a suspension of AlCl_3 in methylene chloride); the product gave IR and ^1H NMR (in D_2O) spectra similar to those reported in ref 4e.
- Chemical shifts are relative to an external hexaquoaluminum standard; downfield shifts are positive. An external, water proton field-frequency lock was used. The hexaquoaluminum line was monitored (before and after the accumulation of free induction decays) to ensure that shift or resolution changes were negligible. Field homogeneity limited line widths were of the order of 10 Hz for the 10-mm nonspinning samples. The "true" line width for tetrachloroaluminate ions (as tetraethylammonium tetrachloroaluminate) in methylene chloride was ~ 3.9 Hz at 28°C , as determined by a Carr-Purcell, Meiboom-Gill pulse sequence.
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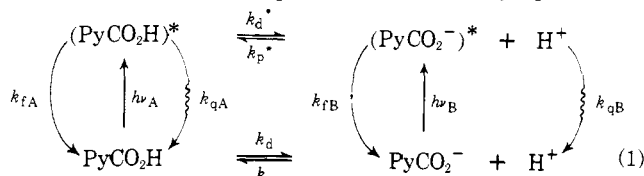
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Ultrafast Excited-State Proton Transfer in Reversed Micelles

Sir:

Charge and proton relay through hydrogen bonds have been proposed to contribute to the catalytic efficiency of enzymes.¹⁻³ Proton inventory, taken by measuring kinetic isotope effects in mixtures of protium and deuterium oxides, has provided evidence for the coupled motions of protons.⁴ An additional factor in enhancing reaction rates is the reduction in dimensionality.⁵⁻⁸ Determinations of proton transfer or translocation rates would yield direct information on the processes involved. Experimental difficulties have precluded to date the kinetic investigations of ultrafast proton-transfer rates at enzyme-active sites. Reversed micelles^{9,10} have been used in the present work to mimic enzyme active sites. Taking advantage of nanosecond time resolved fluorescence, the present communication reports, we believe, the fastest proton transfer is far observed in a solution.

Ground- and excited-state protonation of pyrene-1-carboxylic acid, PyCO_2H ,¹¹ was investigated in water and in 0.10 M dodecylammonium propionate (DAP)¹² entrapped 0.55 M water in benzene.¹⁴ The equilibria is described by eq 1¹⁶ where



k_p , k_p^* and k_d , k_d^* are rate constants for ground- and the first singlet excited-state protonation and deprotonation; K_a and K_a^* are the corresponding ground- and excited-state equilibrium constants ($K_a = k_d/k_p$, $K_a^* = k_d^*/k_p^*$); k_{fA} and k_{fB} are rate constants for the fluorescence decay of the acid and base; and k_{qA} and k_{qB} represent all competing deactivation processes. The ground-state dissociation constant of PyCO_2H was found to be identical in bulk and surfactant entrapped water