has been a polyatomic molecule. In such systems, effects of transition-state bending motion are obscured by counter-balancing effects of the initial-state bending vibrations. Very recently, however, it has been demonstrated that hydrogen fluoride, a diatomic molecule with no bending vibrational modes, behaves as a normal proton donor in aqueous solution and that rates of proton transfer from this acid to ethyl vinyl ether can be evaluated easily and accurately.[4] We have therefore determined the isotope effect on this reaction by measuring its rate in D_2O solution.

Hydrogen fluoride undergoes two equilibrium reactions in aqueous solution, ionization as an acid (eq 1) and association with fluoride ion to form hydrogen bifluoride (eq 2). The latter, however, is not catalytically active in the hydrolysis of ethyl vinyl ether,[4] and the rate law for this reaction therefore consists only of terms in hydrogen fluoride and hydronium ion (eq 3). Unfortunately, it is not possible, as it was for

$$\mathrm{DF} + \mathrm{D_2O} \overset{k_1}{\rightleftarrows} \mathrm{D_3O^+} + \mathrm{F^-} \tag{1}$$

$$\mathrm{DF} + \mathrm{F^-} \overset{k_2}{\rightleftarrows} \mathrm{DF_2^-} \tag{2}$$

$$-\mathrm{d}[\mathrm{S}]/[\mathrm{S}]\mathrm{d}t = k_{\mathrm{D_3O^+}}[\mathrm{D_3O^+}] + k_{\mathrm{DF}}[\mathrm{DF}] \tag{3}$$

H_2O solution,[4] to evaluate the relative contributions of these two terms by straightforward calculation of solution compositions, for the necessary equilibrium constants, K_1 and K_2, are not known for D_2O solution. We therefore used an indicator method employing 2,4-dichloroaniline, which is known to measure H_3O^+ concentration in H_2O solutions of hydrogen fluoride accurately,[4] to determine D_3O^+ concentrations. These indicator data also provided a rough estimate of K_2 which enabled us to make allowance for the small (*ca.* 2%) change in DF concentration produced by the reaction of eq 2 over that effected by the ionization according to eq 1. Using the known value of $k_{\mathrm{D_3O^+}}$,[5] we could then evaluate k_{DF} as $(2.01 \pm 0.02) \times 10^{-2}$ M^{-1} sec^{-1} at 24.9°. Combined with k_{HF},[4] this gives 3.35 ± 0.05 as the isotope effect on proton transfer from hydrogen fluoride to ethyl vinyl ether.

This isotope effect is very small; it is less than one-quarter of the value estimated for uncompensated loss of the (very large) stretching vibration of hydrogen fluoride. It seems unlikely that very much of this lowering can be due to a "symmetrical" stretching vibration in the transition state whose frequency is sensitive to the mass of the hydrogen being transferred. The value of Brønsted's α for this reaction[6] as well as solvent isotope effects in H_2O–D_2O mixtures[5] and more directly measured secondary isotope effects[6] all point to a transition state in which this hydrogen is held with approximately equal force by the two bases between which it is moving. This reasoning is supported by the fact that the isotope effect for this reaction catalyzed by the hydronium ion has a near-maximum value[3b] and that for catalysis by formic acid is also large.[5] It is reasonable to conclude, therefore, that the presently measured isotope effect is as small as it is largely because the absence of initial-state bending vibrations leaves the effect of bending motion in the transition state uncompensated.

If all of this decrease in isotope effect is assigned to transition-state bending vibrations, and if it is further assumed that protium and deuterium frequencies are related in the simple way $\nu_{\mathrm{H}} = \nu_{\mathrm{D}}\sqrt{2}$, a frequency of approximately 1100 cm^{-1} can be calculated for the two degenerate transition-state bending modes. This value is in remarkably good agreement with that (1080 cm^{-1}) calculated from a simple electrostatic model for proton transfer,[7] and it also falls in the range estimated for transition states by analogy with stable molecules.[2b] A frequency of 1100 cm^{-1}, moreover, is not very different from that of hydrogenic bending vibrations in many molecules; this suggests that transition-state and initial-state bending frequencies might in general be quite well matched, and this would account for the success in predicting maximum values of isotope effects enjoyed by the commonly used approximation which takes into consideration only the stretching vibration of the initial state.

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A Sign Inversion in the Geminal Phosphorus–Fluorine Coupling Constant

Sir:

It is now well established that the P–C–H coupling constant undergoes a sign change when a phosphine is quaternized or enters into complex formation.[1] By contrast it has been considered hitherto that the P–C–F coupling constant is unlikely to be subject to a sign inversion.[1c,2] It is the purpose of this communication to present some evidence to the contrary. As such this appears to be the first report of a sign change in a coupling constant involving phosphorus and fluorine.

The crucial point in our argument is illustrated in Figure 1. Irradiation of the lowest field line of the F(3) resonance of $CF_2{=}CFPCl_2$ causes lines 3 and 7 of the F(2) resonance (Figure 1b) to split into doublets, thus indicating that the P–C–F coupling is opposite in sign to the *cis*-P–C–C–F coupling. However, in $CF_2{=}CFPF_2$ irradiation of the lowest field line of the F(3) resonance causes perturbations in triplets 1 and 5

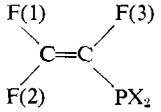

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Figure 1. (a) ^{19}F nmr spectrum of F(2) of $CF_2{=}CFPCl_2$ phase detected undecoupled. (b) ^{19}F nmr spectrum of F(2) of $CF_2{=}CFPCl_2$ with lowest field line of F(3) irradiated at 5012 Hz. (c) ^{19}F nmr spectrum of F(2) of $CF_2{=}CFPF_2$ phase detected undecoupled. (d) ^{19}F nmr spectrum of F(2) of $CF_2{=}CFPF_2$ with lowest field line of F(3) irradiated at 5479 Hz.

of the F(2) resonance (Figure 1d) which indicates that the P-C-F and *cis*-P-C-C-F couplings are of the same sign. The signs of the other couplings, which were also obtained by "tickling" experiments,[3] are presented in Table I. Since the directly bonded P-F coupling constant is not anticipated to be other than negative[2,4] on the basis of its substantial magnitude, the signs for the P-C-F, *cis*-P-C-C-F, and *trans*-P-C-C-F couplings in $CF_2{=}CFPF_2$ can be considered absolute positive. If the *cis*- and *trans*-P-C-C-F couplings are also positive in $CF_2{=}CFPCl_2$, then J_{PCF} is negative in this compound. The possibility that the *cis*- and *trans*-P-C-C-F couplings are negative in $CF_2{=}CFPCl_2$ is considered much less likely, not only because this would require a change of sign for two couplings, but also because the change in $J_{cis\text{-}PCCF}$ would be quite large (~155 Hz). In some respects the above result is similar to the ^{13}C-C-^{1}H coupling in aldehydes where increasing the electronegativity of the tetrahedral carbon atom substituents leads to an increase in J_{CCH}.[5]

Table I. The Signs and Magnitudes of the Nmr Coupling Constants of CF_2—$CFPCl_2$ and CF_2—$CFPF_2$

Compound	Coupling	Sign	Magnitude, Hz
$CF_2{=}CFPCl_2$	A[a] F-C-F	±	39.1
	cis-F-C-C-F	±	32.0
	trans-F-C-C-F	∓	123.4
	B[a] P-C-F	−	17.2
	cis-P-C-C-F	+	85.7
	trans-P-C-C-F	+	7.3
$CF_2{=}CFPF_2$	A[a] F-C-F	±	42.5
	cis-F-C-C-F	±	31.0
	trans-F-C-C-F	∓	123.5
	F-P-C-F	±	11.1
	cis-F-P-C-C-F	±	2.9
	trans-F-P-C-C-F	±	13.2
	B[a] P-F	−	1202
	P-C-F	+	20.9
	cis-P-C-C-F	+	69.6
	trans-P-C-C-F	+	4.8

[a] Relative signs indeterminate between groups A and B.

Another point of interest concerns the observation that the *cis*-P-C-C-F coupling is larger than the *trans*-P-C-C-F coupling. This forms an interesting contrast to the corresponding P-C-C-H couplings in vinylphosphines.[6] The diminution of J_{PCF} as the carbon atom hybridization changes from sp^3 to sp^2 is also the obverse of the trend observed with the corresponding P-C-H coupling. The observation that the *trans*-F-C-C-F coupling is opposite in sign to the *cis*-F-C-C-F and F-C-F couplings is consonant with the results of previous work on trifluoroethylene derivatives.[7,8]

The above results have prompted a more general study of the pattern of relative signs in a variety of perfluorovinyl-substituted compounds.

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