in both cases exchange was complete within 3–4 min as indicated by ^1H NMR spectra.

$Nb(O_2CNMe_2)_5 + HNMe_2/^{13}CO_2$ in Toluene-d_8. $HNMe_2$ (ca. 0.12 mmol) and $^{13}CO_2$ (0.28 mmol) were condensed into a solution of NbL_5 (ca. 10 mg, 0.02 mmol) in toluene-d_8 (0.5 ml). ^1H NMR spectra were recorded over the temperature range −25 to 80 °C. At −25 °C, resonances assignable to Nb-L/Nb-L* (δ 2.49) and $[HNMe_2 + {}^{12}CO_2/^{13}CO_2]$ (δ 2.32) were observed which showed $^3J(^{13}C\text{-}H)$ = 3.2 and 3.0 Hz, respectively. At 80 °C broad resonances at δ 2.57 (Nb-L) and 2.37 ppm were observed, $^3J(^{13}C\text{-}H)$ was not visible. See Figure 5 for spectra.

$W(NMe_2)_6$ + MeLi + CO_2. MeLi (1.5 mmol) was added to $W(NMe_2)_6$ (181 mg, 0.40 mmol) in ether (30 ml). After stirring at 25 °C for ca. 5 min, CO_2 (3 mmol) was added. No reaction was observed after 11 h at 25 °C. Additional CO_2 was added (1.3 mmol) and the solution was stirred another 14 h. The solvent was stripped off and the residue was extracted with benzene (15 ml). A ^1H NMR spectrum of the orange benzene solution indicated the presence of *only* $W(NMe_2)_6$.

Preparation of $W_2(O_2{}^{13}CNEt_2)_4Me_2$. This preparation, although similar to that reported for the unlabeled compound,[21] is described because it provides important insight into the mechanism of CO_2 "insertion." $^{13}CO_2$ (1.25 mmol) was condensed into a solution of freshly prepared $W_2(NEt_2)_4Me_2$[21] (187 mg, 0.27 mmol) in hexane (10 ml). The bright red solution was stirred at room temperature for 24 h; no noticeable reaction occurred. $HNEt_2$ (ca. 1 mmol) was condensed into the solution. Immediately upon warming the solution to room temperature, the solution turned from red to yellowish brown and a yellow precipitate formed. The supernatant was decanted via syringe and the yellow precipitate $W_2Me_2(O_2{}^{13}CNEt_2)_4$ was dried in vacuo.

$Ti(N(CD_3)_2)_4 + HNMe_2$. $HNMe_2$ (ca. 0.5 mmol) was condensed into an NMR tube containing TiN'_4 (22 mg, 0.09 mmol) in benzene (0.5 ml). The tube was warmed to 25 °C and ^1H NMR spectra, were taken over a period of 98 h. Amine exchange was complete within ca. 2 h. After 72 h we observed a greenish precipitate. However, the ^1H NMR spectra showed no new resonances.

$Ta(NMe_2)_5 + HN(CD_3)_2$. $HN(CD_3)_2$ (ca. 0.5 mmol) was condensed into an NMR tube containing TaN_5 (15 mg, 0.04 mmol) in benzene (0.5 ml). Amine exchange was complete within ca. 70 min, as shown by the ^1H NMR spectra. Further spectra, taken over 10 days showed no change. The NMR spectra indicate that the compound in solution is probably $Ta(NMe_2)_5(HNMe_2)$: $\delta(NMe_2)$ 3.17; $\delta(HNMe_2)$ 3.19 ppm.[27]

$W(NMe_2)_6 + HN(CD_3)_2$. $HN(CD_3)_2$ (ca. 0.5 mmol) was condensed into an NMR tube containing $W(NMe_2)_6$ (ca. 4 mg, 0.01 mmol) in benzene (0.5 ml). No amine exchange was observed after 48 h at 25 °C.

$Ti(N(CD_3)_2)_2(O_2{}^{13}CN(CD_3)_2)_2 + HNMe_2$. $HNMe_2$ (ca. 0.4 mmol) was condensed into an NMR tube containing $TiN_2L'^*_2$ (17 mg, 0.05 mmol) in benzene (0.5 ml). ^1H NMR spectra were taken over a period of 121 h. Exchange of $M\text{-}N(CD_3)_2$ with $HNMe_2$ was complete within 1 h. Exchange of $M\text{-}O_2CN(CD_3)_2$ with $HNMe_2$ was never observed.

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Supplementary Material Available: A listing of data and structural factor amplitudes (22 pages). Ordering information is available on any current masthead page.

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Vinyl Ether Hydrolysis. 7. Isotope Effects on Catalysis by Aqueous Hydrofluoric Acid[1]

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Abstract: Comparison of rates of hydrolysis of three vinyl ethers catalyzed by HF in H_2O and DF in D_2O at 25 °C gives primary isotope effects in the range k_H/k_D = 3.3–3.5. The unexpectedly small size of these effects may be attributed to strong, ω = 1325–1450 cm^{-1}, hydrogenic bending vibrations in the proton transfer transition states of these reactions along with the lack of compensatory bending vibrations in the diatomic proton donor.

Hydrogen fluoride is unique among the hydrohalogen acids in that it remains largely undissociated and therefore diatomic in dilute aqueous solution. It is nevertheless a moderately strong acid, pK_a = 3.17, which makes it an effective proton donor whose catalytic activity can be studied conveniently. This gives it a number of interesting properties,

Table I. Rates of Hydrolysis of Vinyl Ethers in Aqueous (D_2O) Deuteriofluoric Acid Buffers at 25 °C[a]

$10^2[DF]_s$[b]	$10^2[DF]$[c]	$10^4[D^+]$[c]	10^3k_{obsd}, s^{-1}
		Ethyl vinyl ether	
1.97	1.80	5.28	0.639, 0.640, 0.647
3.98	3.48	5.41	0.965, 1.01, 1.01
6.00	5.02	5.46	1.29, 1.30, 1.35
7.94	6.40	5.49	1.55
		$10^3(k_{obsd} - k_{D^+}[D^+])^d = (-0.026 \pm 0.020) + (0.199 \pm 0.005)[DF]$	
		Phenyl isopropenyl ether	
2.87	2.57	5.21	2.87, 2.91
4.80	4.11	5.27	3.80, 3.89, 3.96
5.77	4.84	5.31	4.49, 4.54
7.69	6.20	5.30	5.35, 5.46, 5.58
9.61	7.47	5.30	6.41, 6.43, 6.49
		$10^3(k_{obsd} - k_{D^+}[D^+])^e = (-0.109 \pm 0.075) + (0.730 \pm 0.014)[DF]$	
		Methyl cyclohexenyl ether	
1.94	1.76	5.13	16.3, 16.7, 16.7
3.85	3.37	5.25	22.3, 22.9, 23.8
5.78	4.85	5.28	30.8, 31.5, 32.2
7.71	6.21	5.29	37.3, 37.6, 38.1
9.61	7.47	5.30	41.9, 42.1
		$10^3(k_{obsd} - k_{D^+}[D^+])^f = (1.06 \pm 0.59) + (4.60 \pm 0.12)[DF]$	

[a] $[DF]_s/[NaF]_s = 0.96$; ionic strength maintained at 0.10 M using NaCl. [b] Stoichiometric concentrations. [c] Actual (calculated) concentrations. [d] $k_{D^+} = 0.598$ M^{-1} s^{-1}, ref 8b. [e] $k_{D^+} = 2.02$ M^{-1} s^{-1}, H. L. Chen, Ph.D. thesis, I.I.T., 1968. [f] $k_{D^+} = 14.0$ M^{-1} s^{-1}, D. S. Sagatys, Ph.D. thesis, I.I.T., 1970.

prominent among which are the isotope effects on its proton transfer reactions.

In a preliminary account of some of the presently described research,[3] we reported that the hydrogen isotope effect on the rate of hydrolysis of ethyl vinyl ether catalyzed by HF is quite small. We attributed this to the absence of bending vibrations in the proton donor, and we showed how this could be used to provide information on the hydrogenic bending vibrations of the proton transfer transition state. We describe that work here in full, and we also present the results of an extension of this study to the hydrolysis of two other vinyl ethers.

Experimental Section

Materials. Ethyl vinyl ether (Aldrich Chemical Co.) was purified by distillation from sodium metal, and phenyl isopropenyl and methyl cyclohexenyl ethers were prepared and purified as described previously.[4] Stock solutions of DF in D_2O were prepared by diluting 48% aqueous HF (Fisher, Reagent Grade) with D_2O (Diaprep, Inc., 99.8%) and then determining exact concentrations by acidimetric titration; at the low acidities employed, the amount of H introduced in this way was negligible. Sodium fluoride-deuterium fluoride buffers were prepared by combining these DF solutions with appropriate amounts of NaF (Mallinckrodt Chemical Works, Certified, dried at 110 °C for 24 h) dissolved in D_2O.

All solutions were prepared and diluted by weight, and polyethylene vessels (beakers with fitted caps or screw cap dropping bottles) were used exclusively for all fluoride solutions. Freshly prepared solutions were used for all kinetic runs.

Kinetics. Rates of hydrolysis were determined spectrally by monitoring the decrease in absorbance due to vinyl ether at 220 nm (ethyl vinyl and methyl cyclohexenyl ethers) or 230 nm (phenyl isopropenyl ether). Measurements were made using a Cary Model 11 Spectrometer with a thermostated cell compartment through which water from a constant temperature bath was circulated. Since HF attacks glass, reactions were conducted in a specially constructed optical cell with sapphire windows and Kel-F body.

Kinetic runs were conducted by allowing buffer solution in this cell to come to temperature equilibrium with the spectrometer cell compartment; a suitable amount of neat vinyl ethyl was then added, and the cell was shaken vigorously and replaced in the cell compartment. A continuous trace of absorbance vs. time was then begun. Data were collected in this way for approximately 4 half-lives, and infinity readings were made after 10 half-lives.

These data conformed to first-order kinetic laws exactly. Rate constants were determined either graphically, as slopes of plots of log $(A - A_\infty)$ vs. time, or by the Guggenheim method[5] with least-squares fitting.

Results

Analysis of the kinetic results, summarized in Table I, is complicated by the fact that hydrogen fluoride in aqueous solution not only dissociates as an acid, (eq 1), but also combines with fluoride ion to form the hydrogen bifluoride anion (eq 2). Each of these reactions occurs to an appreciable extent at the concentrations of DF and F^- used in the present work, and the actual concentration of DF in these solutions is therefore significantly lower than that based upon its stoichiometric amount. However, the equilibrium constants for the reactions of eq 1 and 2 have recently been determined, $K_1 = 3.34 \times 10^{-4}$ and $K_2 = 3.50$,[6] and the actual concentrations of all solution species in the buffers used may therefore by calculated. These calculations, which require the solution of a cubic equation, were done with the aid of a programmable desk calculator, as described for a similar investigation using HF buffers in H_2O solution.[7] The DF and D^+ concentrations so obtained are listed in Table I.

$$DF \rightleftarrows D^+ + F^- \qquad (1)$$

$$DF + F^- \rightleftarrows DF_2^- \qquad (2)$$

Hydrolysis of the vinyl ethers used here is known to be subject to general acid catalysis,[4,8] and each of the three acids present in the buffers employed, DF, D^+, and DF_2^-, might therefore be expected to contribute to the rate of reaction. It has been shown, however, that HF_2^- in H_2O solution is not an effective acid catalyst,[7] and the same would be expected to be true of DF_2^- in D_2O.

Some additional evidence in support of this conclusion may be obtained from the present work. Combination of the expressions for K_1 and K_2 gives the relationship $[DF_2^-] = K_1K_2[DF]^2/[D^+]$, and, since $[D^+]$ is approximately constant in the buffer series used here (see Table I), $[DF_2^-]$ will vary as the square of [DF] in these solutions. Any reaction through catalysis by DF_2^- would therefore add a quadratic component to the relationship between [DF] and reaction rate. The actual relationships observed, however, are accurately linear—linear

Table II. Isotope Effects on Proton Transfer from Hydrogen Fluoride

Substrate	k_H/k_D[a]
Ethyl vinyl ether	3.51 ± 0.05
Phenyl isopropenyl ether	3.29 ± 0.04
Methyl cyclohexenyl ether	3.32 ± 0.07

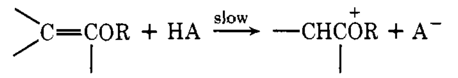
[a] The errors listed are standard deviations of the mean obtained by propagating the experimental scatter in k_{HF} and k_{DF}; they do not include systematic errors.

least-squares analysis of the dependence of $k_{obsd} - k_{D^+}[D^+]$ upon [DF] gives the equations listed in Table I whose correlation coefficients are in the range 0.996–0.998—and catalysis by DF_2^- must therefore be negligible.

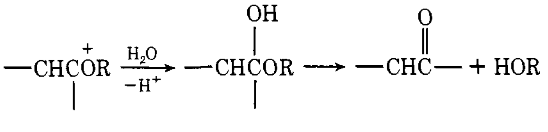
The slopes of these linear relationships provide DF catalytic coefficients, k_{DF}. The latter were also calculated as simple averages of $(k_{obsd} - k_{D^+}[D^+])$, inasmuch as the data for the hydrolysis of these vinyl ethers in H_2O solutions of HF buffers were treated in this way.[7] The two sets of values are in good agreement and produce isotope effects k_{HF}/k_{DF} which never differ by more than 0.2 (the values listed in Table II are based upon the simple average method of calculation of k_{DF}), which is probably a realistic estimate of the reliability of these isotopic effects.

Discussion

It is now well established that the hydrolysis of simple vinyl ethers such as those used here occurs by rate-determining proton transfer from the catalyzing acid to the substrate (eq 3). This is then followed by rapid hydration of the cationic proton transfer product to give a hemiacetal or hemiketal intermediate, which itself decomposes rapidly to the ultimate carbonyl compound and alcohol products (eq 4). An exception to this general mechanism has recently been claimed for a rather unusual vinyl ether,[9] but none of the phenomena upon which this claim is based have been observed for any of the vinyl ethers used here, and the mechanism of their hydrolysis is therefore not in doubt.



$$>C{=}COR + HA \xrightarrow{\text{slow}} -CH\overset{+}{C}OR + A^- \qquad (3)$$



$$-CH\overset{+}{C}OR \xrightarrow[-H^+]{H_2O} -CH\overset{OH}{C}OR \longrightarrow -CH\overset{O}{\overset{\|}{C}}- + HOR \qquad (4)$$

The process to which the presently measured isotope effects refer is thus a particularly simple one-step reaction, proton transfer from HF to a carbon base, and the effects themselves may be viewed quite simply in terms of H–F bond breaking. On this basis, isotope effects considerably larger than the rather small values actually observed, $k_H/k_D = 3.3$–3.5, might have been expected. The HF molecule has an especially strong stretching vibration, $\omega = 3962$ cm^{-1} in the gas phase[10] and 3450 cm^{-1} in aqueous solution,[11] and its isotopically sensitive principal moments of inertia will contribute further to the free-energy difference $G_{HF} - G_{DF}$. In aqueous solution, of course, HF will be hydrogen bonded to the solvent, and its rotations will therefore be replaced by librational motion. The librational frequencies are not known, but a reasonable estimate of their range would be 500–700 cm^{-1}; these limits correspond to partition function ratios in the range $Q_{HF}/Q_{DF} = 0.039\,90$ to $0.033\,25$, which lead to maximum isotope effects of $k_H/k_D = 12.5$ to 15.0. These effects, as well as the maximum value $k_H/k_D = 14.2$ based upon the gas phase ratio $Q_{HF}/Q_{DF} = 0.035\,20$, are some four times greater than the values actually observed.

These estimates, of course, are maximum isotope effects on H–F bond breaking, i.e., complete initial state effects unopposed by any transition state isotopic differences. Primary hydrogen isotope effects may differ from maximum values calculated in this way for a number of reasons, one of which is related to the symmetry of the process: as the bases between which the proton is moving in a proton transfer reaction become dissimilar in strength, and the process becomes increasingly exo- or endothermic, k_H/k_D diminishes. It was originally thought that this effect was due to an increase in the isotopic sensitivity of the symmetrical stretching vibration of the transition state as the system moved away from thermoneutrality,[12] but this view has recently been questioned and the phenomenon has been ascribed to proton tunnelling.[13] Whatever its origin, this variation in isotope effect magnitude is correlated reasonably well by Marcus rate theory,[14] and the theory may be used to estimate the isotope effect diminution for the present case. The relevant relationship is given in the following equation:

$$\ln (k_H/k_D) = 4\alpha(1 - \alpha) \ln (k_H/k_D)_{max} \qquad (5)$$

where α is the exponent of the Bronsted relation for the process under examination.[15] Bronsted exponents for the hydrolysis of the three vinyl ethers studied here range from 0.62 to 0.70,[4] and use of the average value $\alpha = 0.65$ leads to the prediction that the dissymmetry of these reactions has reduced the isotope effect by only 13%. With 3.4 as the average observed isotope effect, this gives an "observed" maximum effect of $k_H/k_D = 3.4/1.18 = 3.8$.

The sizable discrepancy between this and the maximum effects calculated above using initial state partition function ratios points to a further, much more appreciable isotopic difference in the transition states of these reactions. No significant contribution to this difference will be made by transition state masses and moments of inertia, and the symmetrical stretching vibration of the transition state has already been taken into account, either by estimating its influence to be a 13% lowering of k_H/k_D, or by presuming it to be isotopically insensitive whereupon the 13% becomes a difference in tunnel effects. That leaves only the two hydrogenic bending vibrations of the transition state as the source of the requisite free-energy difference.

The frequencies of these transition state bending vibrations may be estimated using the relationship $k_H/k_D = 3.8 = (Q_H^{\ddagger}/Q_D^{\ddagger})/(Q_{HF}/Q_{DF})$. Then, assuming that these vibrations are doubly degenerate and anticipating that their frequencies will be high, $Q_H^{\ddagger}/Q_D^{\ddagger} = \exp[(\omega_D - \omega_H)hc/kT]$. With $\omega_H = \omega_D\sqrt{2}$, the values of Q_{HF}/Q_{DF} for HF in solution given above lead to $\omega_H = 1325$–1455 cm^{-1}, and the gas phase value provides $\omega_H = 1415$ cm^{-1}. These results are consistent with the predictions of a simple electrostatic model for proton transfer, which gives $\omega_H = 1080$ cm^{-1},[16] and also with more sophisticated calculations which produce values in the range 800–1050 cm^{-1}.[17] It is significant, too, that the frequency of the bending vibration of the HF_2^- ion, a frequently used model for the proton transfer transition state, is 1206 cm^{-1} in aqueous solution.[18]

Small isotope effects attributable to the absence of bending vibrations in a diatomic reactant have also been found in the homolytic reaction of HBr with a series of organic free radicals.[19] It seems likely as well that the inverse isotope effect observed in the addition of HBr to cyclopentene[20] owes its unusual magnitude to the same cause.

It is significant that the frequencies of the transition state bending vibrations provided by the presently measured isotope effects, 1325–1450 cm^{-1}, are similar to those of C–H bending vibrations in many stable molecules. This suggests that, insofar as the present results are typical, initial state and transition state bending vibrations may in general be quite well matched, and that the single frequency approximation, which ignores bending vibrations, may often provide valid estimates of isotope effect magnitude on hydrogen transfer reactions in polyatomic systems.

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Vinyl Ether Hydrolysis. 8. Electrostatic Effects Produced by Negatively Charged Catalysts[1a]

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Abstract: A group of simple alkyl monohydrogen phosphonate anions, RPO_3H^-, were found to be better catalysts for the hydrolysis of ethyl isopropenyl and cyclopentenyl ethers than neutral carboxylic acids of the same pK_a by about one order of magnitude in specific rate; this effect is attributed to an energy-lowering electrostatic interaction in the transition states of these reactions. These phosphonate ion catalyzed hydrolyses give good Brønsted relations which appear to be linear but whose slopes are greater than those of correlations based upon catalysis by the (stronger) carboxylic acids; this suggests that these seemingly linear correlations are straight-line segments of an overall curved Brønsted relation. Analysis of the combined data according to simple Marcus theory leads to small intrinsic barriers and large work terms.

We reported recently that charged catalysts produce electrostatic effects on the rate of vinyl ether hydrolysis which can be understood in terms of Coulombic interactions in the transition states of these reactions.[2] In that study, we examined both positively and negatively charged acid catalysts. The positive species formed a structurally similar set; all gave negative deviations from a Brønsted relation based upon neutral acids, i.e., were poorer catalysts, and the set as a whole gave a good Brønsted relation of its own. The negatively charged catalysts, on the other hand, showed no discernible correlation, but they were fewer in number and of widely different structural types.

We have now extended this study to a set of structurally homogeneous negatively charged catalysts, a group of monohydrogen phosphonate anions: RPO_3H^-. The behavior of these substances complements that of the positively charged acids: all negative species are better catalysts than neutral acids of the same pK_a, and the group as a whole gives a good Brønsted correlation of its own. But there is also an important difference between the two charge types: whereas the slopes of the Brønsted relations based upon the neutral and positively charged catalysts are nearly identical, those of the correlations using the negatively charged acids are significantly different. This difference in behavior may be understood in terms of curved Brønsted relations, and analysis of the curvature provided by a suitable combination of all of the data using simple Marcus theory[3] leads to the interesting conclusion that the intrinsic barriers for these reactions are rather small and the work terms are correspondingly large.

Experimental Section

Materials. Ethyl isopropenyl ether was prepared by decarboxylation of β-ethoxycrotonic acid, obtained by saponification of the corresponding ethyl ester, which in turn was made by oxygen ethylation of ethyl acetoacetate.[4] Ethyl cyclopentenyl ether was prepared by eliminating ethanol from cyclopentanone diethyl ketal, itself obtained by treating cyclopentanone with triethyl orthoformate,[5] and the phosphonic acids were samples used before in a recent determination of their pK_a values.[6]

All other reagents were best available commercial grades. Solutions were prepared using distilled, CO_2-free water.

Kinetics. Rates of vinyl ether hydrolysis were measured spectrally by monitoring the decrease in absorption at 220–225 nm. Measurements were made using Cary Model 14 or 118C spectrometers whose cell compartments were thermostated at 25.0 ± 0.02 °C. One-centimeter quartz cuvettes containing about 3 ml of buffer solution were allowed to come to thermal equilibrium with these cell compartments and reactions were then initiated by injecting 5 μl of a methanol solution of vinyl ether, at a concentration (usually 20%) which would give a convenient initial absorbance reading, and shaking the cuvette vigorously to ensure complete mixing.

Absorbance was recorded continuously for 3–4 half-lives, and infinity readings were taken after at least 10 half-lives. First-order rate