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
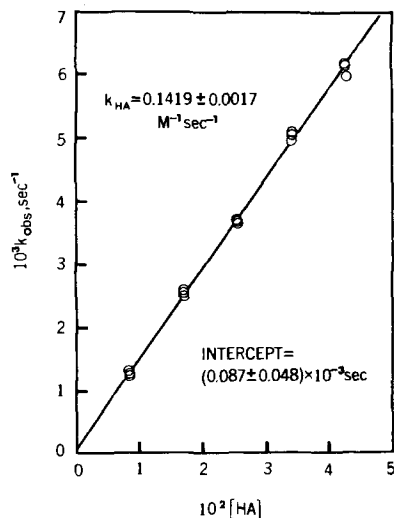
Figure 1. Relationship between buffer acid concentration and rates of hydrolysis of ethyl isopropenyl ether in aqueous $CH_2OHPO_3H^-$/$CH_2OHPO_3^{2-}$ buffers, buffer ratio = 1.07, at 25 °C.
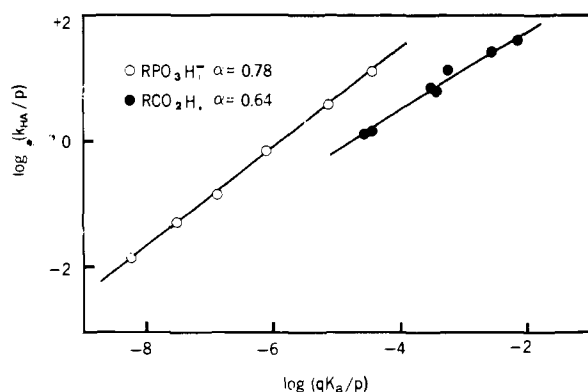

Figure 2. Linear Brønsted relations for the hydrolysis of ethyl isopropenyl ether catalyzed by monohydrogen phosphonate anions and carboxylic acids.

constants were evaluated graphically at slopes of plots of $\ln(A - A_\infty)$ vs. time. The data conformed to the first-order rate law exactly.

Results

Two vinyl ethers and six monohydrogen phosphonate anions were used in this study. For each vinyl ether–phosphonate anion combination, rate measurements were made in a series of buffer solutions of constant buffer ratio but varying buffer concentration (sodium chloride was added as necessary to keep the ionic strength constant). Five different buffer concentrations were generally used, and at each concentration rates were measured at least in duplicate and sometimes as many as four times. These data are summarized in Tables I and II.[7]

General acid catalysis was especially pronounced in these buffer solutions. This is due principally to the appreciable electrostatic acceleration provided by the negative charge of these phosphonate ion general catalysts; in this circumstance, the coefficient k_{HA} of the rate law for this process (eq 1) is

$$k_{obsd} = k_{H^+}[H^+] + k_{HA}[HA] \qquad (1)$$

greater than it would otherwise be, and the term $k_{HA}[HA]$ consequently makes up a larger portion of the total rate. An additional factor contributing to the strength of the general catalysis observed here is the relatively low acid strength of the phosphate ions used ($pK_a = 5-9$).[8]

A typical set of data is shown in Figure 1. The intercept here $(k_{H^+}[H^+])$ is only 1.5% of the total observed rate constant at
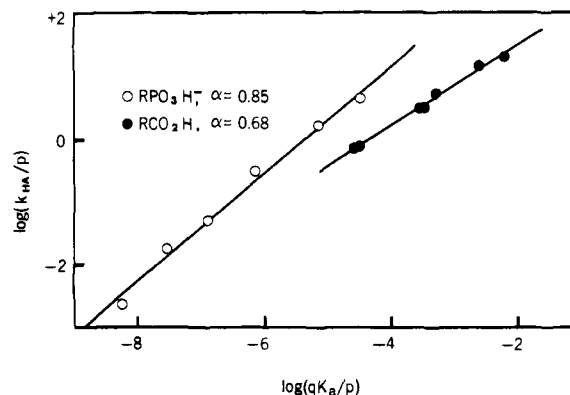

Figure 3. Linear Brønsted relations for the hydrolysis of ethyl cyclopentenyl ether catalyzed by monohydrogen phosphonate anions and carboxylic acids.

Table III. Summary of Catalytic Coefficients for the Hydrolysis of Ethyl Isopropenyl and Ethyl Cyclopentenyl Ethers in Aqueous Solution at 25 °C

Acid	$pK_a{}^a$	k_{HA}, M^{-1} s^{-1} Ethyl isopropenyl ether	Ethyl cyclopentenyl ether
$CCl_3PO_3H^-$	4.93	12.2	4.40
$CHCl_2PO_3H^-$	5.60	3.70	1.61
$CH_2ClPO_3H^-$	6.59	0.689	0.305
$CH_2OHPO_3H^-$	7.36	0.142	0.0526
$CH_3PO_3H^-$	8.00	0.0522	0.0180
$(CH_3)_3CPO_3H^-$	8.71	0.0135	0.00240

^{a} Reference 6.

the highest buffer concentration (0.04 M), and it rises to no more than 7% of the total rate at the lowest buffer concentration (0.009 M). As a consequence, the general acid catalytic coefficient can be determined with unusually good precision; in this example the uncertainty (standard deviation) in k_{HA} is only 1.2% of its value. These buffers are therefore especially good systems with which to detect general acid catalysis in marginal cases.

On the other hand, since only a small fraction of the rate constants measured in these buffers is due to catalysis by the hydronium ion, hydronium ion catalytic coefficients are correspondingly unreliable. That provided by the intercept of Figure 1, for example, is 639 ± 350 M^{-1} s^{-1}, which, though consistent with the value measured directly in perchloric acid solutions, 579 ± 11 M^{-1} s^{-1},[5] has a 55% uncertainty.

Bimolecular rate constants for the hydrolysis of both substrates by each of the phosphonate anions were obtained by least-squares analysis of plots such as that shown in Figure 1. With some of the stronger acids at the rather low buffer concentrations used, hydrogen ion concentrations did not remain strictly constant along the buffer series, and observed rate constants were therefore corrected as described previously.[2,5] Concentration dissociation constants needed for this purpose were calculated from published pK_a values[6] and activity coefficients based upon the formula $\log f = -0.5Z^2I^{1/2}/(1 + I^{1/2}) + 0.1I$. The results obtained are summarized in Table III.

Discussion

Figures 2 and 3, in which the catalytic coefficients determined here for vinyl ether hydrolysis catalyzed by monohydrogen phosphonate anions are displayed as Brønsted relations, show that these negatively charged acids do give good linear correlations. These figures also contain the Brønsted relations
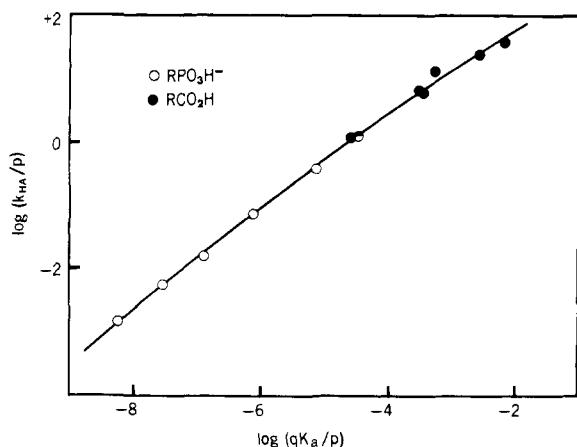
Figure 4. Curved Brønsted relation for the hydrolysis of ethyl isopropenyl ether based upon carboxylic acid and (transposed) phosphonate anion data.
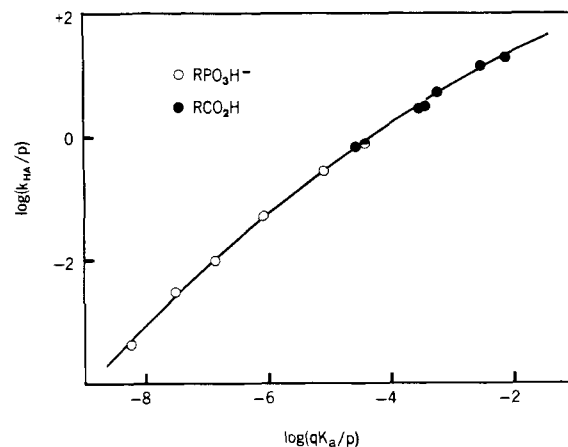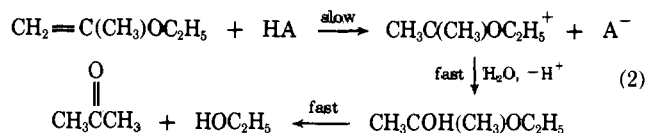

Figure 5. Curved Brønsted relation for the hydrolysis of ethyl cyclopentenyl ether based upon carboxylic acid and (transposed) phosphonate anion data.

obtained previously[5] for these two reactions catalyzed by neutral carboxylic acids, and comparison of the two correlations shows that in both cases the negatively charged acids are considerably better catalysts than neutral acids of the same acid strength.

This difference is easily understood in terms of the mechanism of this reaction. Much evidence, chief among which is the observation of general acid catalysis[2,5,9] and the presence of large kinetic isotope effects,[1,9a,10] points to a general reaction scheme for vinyl ether hydrolysis in which slow proton transfer from the catalyzing acid to the substrate is followed by rapid hydration of the ensuing carbonium ion and hydrolysis of the hemiketal intermediate (eq 2).[11] The rate-determining tran-

$$CH_2\!\!=\!\!C(CH_3)OC_2H_5 + HA \xrightarrow{\text{slow}} CH_3C(CH_3)OC_2H_5^+ + A^-$$

$$\underset{\substack{\shortparallel \\ O}}{} \qquad\qquad \text{fast} \downarrow H_2O, -H^+ \qquad (2)$$

$$CH_3CCH_3 + HOC_2H_5 \xleftarrow{\text{fast}} CH_3COH(CH_3)OC_2H_5$$

sition state for this reaction is therefore a species in which the subtrate is taking on positive charge. This charge will undergo Coulombic interaction with any charge present initially on the catalyst; if the catalyst is negatively charged, this interaction will be attractive and energy lowering, and if the catalyst is positive, the interaction will be repulsive and energy raising. Thus, the transition state for proton transfer from negatively charged acids will be more stable than that for transfer from neutral ones, and the negatively charged acids will be the better catalysts. The converse will hold true for positively charged acids. There is, of course, also a Coulombic interaction between the initial charge on the catalyst and the negative charge being generated there in the transition state, but that interaction is also present in the final state of the process, i.e. in the conjugate base of the catalyzing acid; it therefore does not lead to deviations from rate-equilibrium correlations such as the Brønsted relation.

The electrostatic acceleration shown by these negatively charged phosphonate anions is greater than the deceleration observed previously for a group of positively charged amino acids.[2] The magnitudes of the present accelerations depend somewhat on where the comparison is made, but, if it is based upon trichloromethyl phosphate ion and acetic acid, two acids with nearly identical values of log (qK_a/p), rate constant ratios of 9.3 and 5.8 are found for the hydrolysis of ethyl isopropenyl ether and ethyl cyclopentenyl ether, respectively. The positively charged amino acids, on the other hand, never show a deceleration much more than a factor of two.

This difference is consistent with the fact that the negative

charge in the present group of phosphonate anions is considerably closer to the acidic proton (and therefore also to the positive charge generated on the substrate in the transition state) than is the positive charge to the acidic proton in the set of positively charged amino acids. In flexible systems such as these, moreover, the electrostatic attraction of an energy-lowering and rate-accelerating interaction will draw the charges together and thus enhance the acceleration, whereas the repulsive interaction operating in a rate-retarding situation will increase the intercharge distance and reduce the deceleration.

There is another, perhaps less expected difference between the positively and negatively charged catalyst series. The positive acids were found to give a Brønsted relation closely parallel to that based upon a series of neutral carboxylic acids: the slopes of the two correlations are $\alpha = 0.64 \pm 0.04$ and $\alpha = 0.70 \pm 0.03$ for the charged and neutral acids, respectively.[2] However, as Figures 2 and 3 show, the present set of negatively charged catalysts gives consistently steeper Brønsted relations than do the neutral carboxylic acids: for ethyl isopropenyl ether the α values are 0.78 ± 0.01 and 0.64 ± 0.04 and for ethyl cyclopentenyl ether they are 0.85 ± 0.04 and 0.63 ± 0.03.

This difference could be the result of Brønsted plot curvature. The pK_a ranges covered by the neutral and positively charged acids are nearly the same, 2.5 to 4.9 and 1.8 to 4.0, respectively, and these catalysts would therefore provide linear segments of an overall curved correlation which have nearly the same slope. The phosphonate anions used here, on the other hand, are significantly weaker acids, $pK_a = 4.9$ to 8.7, and their linear segment of the curved correlation might therefore have a different slope. Any such difference should be in the direction observed, i.e. a steeper slope for the phosphonate anions, since, being weaker acids, they will have later transition states in which proton transfer is farther advanced.[13] Some additional support for this hypothesis comes from our previous work in which neutral and positively charged carboxylic acids were compared:[2] although the Brønsted relations there were nearly parallel and it is questionable whether their exponents are significantly different ($\alpha = 0.64 \pm 0.04$ and 0.70 ± 0.03), the difference is at least in the expected direction.[14]

Figures 4 and 5 show that respectable curved Brønsted relations can in fact be obtained from suitable combinations of the data for neutral and negatively charged catalysts for both of the presently investigated reactions. In these correlations, the phosphonate anion points were simply transposed downward by an amount equal to the acceleration shown by trichloromethyl phosphonate anion over acetic acid, i.e., the rate constants for these two catalysts of nearly identical acid

strength were set equal to one another. The combined data were then fitted by least-squares analysis to a quadratic expression in log (qK_a/p), and the lines indicated in the figures were obtained.

It is possible to relate the coefficients of such quadratic expressions to certain fundamental parameters by which proton transfer reactions may be characterized according to Marcus rate theory.[3] This treatment when applied to the data for the hydrolysis of ethyl isopropenyl ether gives an intrinsic barrier $\Delta G^{\ddagger}_0 = 4.0 \pm 1.2$ kcal/mol ($\Delta G^{\ddagger}_0$ is the free energy of activation for that member, in the present case hypothetical, of the series for whose reaction $\Delta G^\circ = 0$; it is therefore the purely kinetic component of the reaction barrier[3,16]) and a work term $w^r = 9.1 \pm 1.7$ kcal/mol. (w^r is the energy required to bring the reactants together and to form them into a reaction complex.) For ethyl cyclopentenyl ether, the results are $\Delta G^{\ddagger}_0 = 2.1 \pm 0.3$ kcal/mol and $w^r = 13.5 \pm 0.4$ kcal/mol.

These values imply that relatively little of the considerable barrier which these moderately slow reactions experience comes from the actual proton transfer step itself; much of the energy required for reaction is expended in bringing the catalyst and substrate together, performing whatever desolvation is required, and then positioning the two reactants so that proton transfer may take place. Interesting as these results are, however, their significance can be questioned inasmuch as they are based upon a rather arbitrary combination of data for two different types of acid catalyst.

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Ionization of Group 6 and 7 Protonic Acids in Dimethyl Sulfoxide

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Abstract: Enthalpies of deprotonation, ΔH_D, by K^+DMSYL^- in Me_2SO are reported for 21 alcohols, seven thiols, selenophenol, and the hydrogen halides. Evidence is presented supporting the notion that alkoxide ions interact strongly with counterions and with unionized alcohol. Thiols behave quite differently. By means of a previously reported correlation between ΔH_D and pK_a in Me_2SO, the pK_a's of all compounds discussed here are estimated and compared with scattered literature estimates of acidity. An excellent linear correlation of ΔH_D with Taft's σ^* values is found and shown to be dominated by solvation effects rather than structural effects on intrinsic acidity. The effect of variation of the central atom on the acidity of their hydrides is discussed for group 6 and 7 acids in the gas phase, Me_2SO, and H_2O. Finally, enthalpies of solvation for halide ions from the gas phase to Me_2SO are calculated and compared with published values for solvation in water.

Introduction

The hydrides of group 6 and of the halogens are of such fundamental importance to chemistry that they are considered in the most elementary textbooks. Their organic derivatives—the alcohols, mercaptans and alkyl halides—comprise a considerable fraction of the most useful reactants and intermediates for synthesis, industry, and living systems. Hydroxide, alkoxide, mercaptide, and halide ions are the prototype nucleophiles for mechanistic and synthetic chemistry. Therefore, it would be hard to exaggerate the significance of the Bronsted acid-base pairs of groups 6 or 7. It would be impossible to give a brief outline of their many crucial roles.

In sharp contrast to the importance of these acids and their anions is the dearth of information on their relative propensities to undergo the simplest (and perhaps only) reaction which they have in common—proton transfer.

The ionization of carboxylic acids and phenols to give resonance-stabilized anions has been a large and fertile area of solution thermodynamics for nearly a century[1-5] since their protolysis is readily studied in aqueous solution within the normal pH scale. However, most aliphatic alcohols are too weak and the hydrogen halides are too strong for convenient study under these conditions, and the few reliable studies of their acid strengths[6-9] have employed nonaqueous media or