aqueous solution to concentrated acid solution of the general base X and its conjugate acid XH$^+$, or the Hammett aniline indicator B and its conjugate acid BH$^+$ (for which $\varphi_e \equiv 0$). Values of φ_e from ref 4e and 5f are listed in Table XV and are shown to correlate with $-\delta_R \Delta H_{(BH^+)}^{H_2O \rightarrow FSO_3H}$ values. This correlation evidently follows from the greater variation in solvation energies of XH$^+$ than of X (since strictly φ_e values depend upon both XH$^+$ and X) and in approximately proportionally reduced HB(BH$^+$;s) terms in the transfer between water and concentrated H$_2$O–H$_2$SO$_4$ mixtures as compared with the corresponding transfer between water and FSO$_3$H solutions.

Finally, we wish to note that the conclusions reached in this work are further supported by evidence on solvation effects observed recently for excited state BH$^+$ species.[37]

References and Notes

(1) This work has been supported in part by grants from the National Science Foundation (UCI, UP, CIT), the Public Health Service (UCI), the Energy Research and Development Administration (CIT), and CNR (Rome).
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Vinyl Ether Hydrolysis. 10. Methyl α-Cyclopropylvinyl Ether. A Search for a Change in Reaction Mechanism[1]
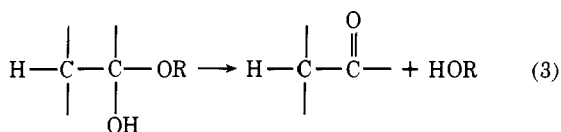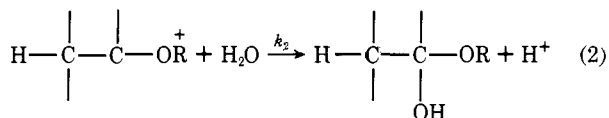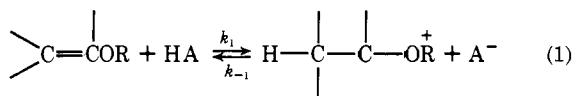
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Abstract: The rate of hydrolysis of methyl α-cyclopropylvinyl ether catalyzed by H$_3$O$^+$, H$_2$O, seven carboxylic acids, six monohydrogen phosphonate anions, two ammonium ions, and biphosphate ion was measured in wholly aqueous solution at 25 °C. These data, the isotope effect on the H$_3$O$^+$ reaction, and a lack of isotopic exchange of the substrate in D$_2$O solution all point to an unchanging rate-determining proton transfer mechanism for this reaction. It is inferred from this constancy of mechanism that the second step of this reaction, hydration of the alkoxycarbonium ion intermediate, is subject to general base catalysis. The combined carboxylic acid and phosphonate anion catalytic coefficients give a curved Brønsted relation from which the Marcus theory parameters $\Delta G_0^{\ddagger} = 6$ kcal/mol and $w^r = 4$ kcal/mol are derived.
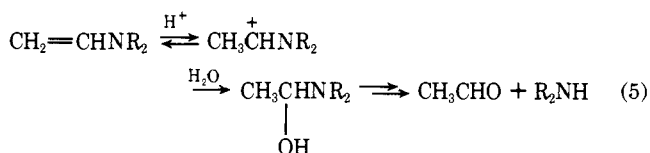
The acid-catalyzed hydrolysis of simple vinyl ethers occurs through electrophilic addition of H$^+$ to a carbon–carbon double bond (eq 1); the alkoxycarbonium ion thus formed then reacts with water to give a hemiacetal or hemiketal interme-

diate (eq 2), which itself undergoes rapid decomposition to alcohol and aldehyde or ketone products (eq 3).

In very nearly all examples of this reaction, the carbon protonation step is rate determining, i.e. in these cases, reversal

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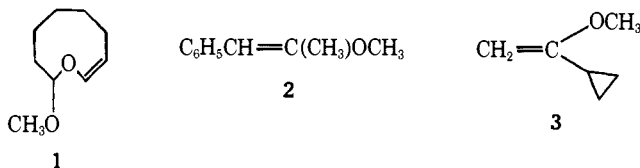$$\text{C}{=}\text{COR} + \text{HA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{H}{-}\text{C}{-}\text{C}{-}\overset{+}{\text{OR}} + \text{A}^- \qquad (1)$$

$$\text{H}{-}\text{C}{-}\text{C}{-}\overset{+}{\text{OR}} + \text{H}_2\text{O} \xrightarrow{k_2} \text{H}{-}\text{C}{-}\text{C}{-}\text{OR} + \text{H}^+ \qquad (2)$$

with OH below.

$$\text{H}{-}\text{C}{-}\text{C}{-}\text{OR} \rightarrow \text{H}{-}\text{C}{-}\overset{\text{O}}{\overset{\|}{\text{C}}}{-} + \text{HOR} \qquad (3)$$

with OH below.

of this step is more difficult than alkoxycarbonium ion hydration: $k_{-1}[\text{A}^-] < k_2[\text{H}_2\text{O}]$. But the margin by which this inequality holds cannot be very great. In the closely related hydration of simple olefins such as isobutene (eq 4), for ex-

$$\text{CH}_2{=}\text{C}\begin{smallmatrix}\text{CH}_3\\\text{CH}_3\end{smallmatrix} \overset{\text{H}^+}{\rightleftharpoons} \text{CH}_3\overset{+}{\text{C}}\begin{smallmatrix}\text{CH}_3\\\text{CH}_3\end{smallmatrix} \overset{\text{H}_2\text{O}}{\rightleftharpoons} \text{CH}_3\text{C}\begin{smallmatrix}\text{CH}_3\\|\\\text{OH}\\|\\\text{CH}_3\end{smallmatrix}{-}\text{OH} \qquad (4)$$

$$\text{CH}_2{=}\text{CHNR}_2 \overset{\text{H}^+}{\rightleftharpoons} \text{CH}_3\overset{+}{\text{CHNR}_2}$$

$$\xrightarrow{\text{H}_2\text{O}} \text{CH}_3\underset{\overset{|}{\text{OH}}}{\text{CHNR}_2} \longrightarrow \text{CH}_3\text{CHO} + \text{R}_2\text{NH} \qquad (5)$$
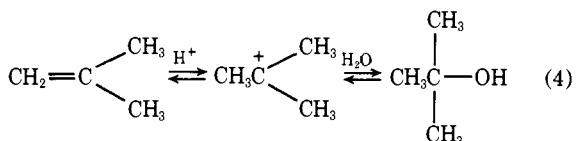
ample, the carbonium ion intermediates hydrate only one to two orders of magnitude more rapidly than they revert to starting materials,[2] and in the hydration of enamines (eq 5), rapidly reversible carbon protonation followed by rate-determining hydration is not uncommon.[3] Even with vinyl ethers the condition $k_{-1}[\text{A}^-] > k_2[\text{H}_2\text{O}]$ has been achieved; there is evidence that the somewhat unusual vinyl ether 2-methoxy-2,3,4,5,6,7-hexahydrooxonin (**1**) undergoes hydrolysis

(structure 1) $\text{C}_6\text{H}_5\text{CH}{=}\text{C}(\text{CH}_3)\text{OCH}_3$ $\text{CH}_2{=}\text{C}\begin{smallmatrix}\text{OCH}_3\end{smallmatrix}$ (cyclopropyl)

1   **2**   **3**

by the conventional rate-determining proton transfer mechanism in dilute strong acid solutions, but in acetic acid buffers, where acetate ion serves as an additional and more powerful proton acceptor, protonation becomes rapid and reversible and hydration is slow.[4]

It is of interest to inquire whether a similar change in rate-determining step could be induced in other vinyl ethers by making suitable structural modifications; whether, for example, incorporating the double bond in an extended conjugated system would reduce the activation energy for deprotonation to the point where proton transfer could be made reversible. We found in previous work[5] that introducing a phenyl group into the β position, as in β-methoxy-β-methylstyrene (**2**), did not accomplish this purpose, possibly because this also reduced the reactivity of the system markedly and made the protonation transition state productlike, which robbed it of double-bond character. We have now extended that study to a more reactive substrate in which the double bond is conjugated with a cyclopropyl group, methyl α-cyclopropylvinyl ether (**3**). Placing the substituent in the α position in this way has in fact produced the most reactive vinyl ether we have yet encountered, and this has enabled us to extend our search for a mechanistic change down to its very limit, to conditions where

A^- in the quantity $k_{-1}[\text{A}^-]$ is hydroxide ion, the strongest base available in dilute aqueous solution, and the protonation step therefore stands the best chance of being reversible.

Experimental Section

Materials. Methyl α-cyclopropylvinyl ether was prepared from cyclopropyl methyl dimethyl ketal, which in turn was obtained by treating cyclopropyl methyl ketone with trimethyl orthoformate and a trace of p-toluenesulfonic acid in methanol solution. This ketal split off methanol readily, and the vinyl ether could be prepared simply by refluxing ketal through a fractional distillation column packed with a spiral of platinum wire and collecting alcohol as it formed. Both ketal and vinyl ether were purified by distillation: ketal bp 130 °C (760 mm) and vinyl ether bp 78 °C (760 mm); samples used for kinetic determinations were purified further by gas chromatography. Both substances gave satisfactory carbon and hydrogen analyses and had NMR and IR spectra consistent with their structures.

Phosphonic acids were samples prepared before for pK_a determinations.[6] All other materials were best available commercial grades. Solutions were prepared using deionized water purified further by distillation from alkaline permanganate; D_2O solutions were prepared using D_2O (Merck Sharp and Dohme) as received.

Kinetics. Rates of reaction were measured spectroscopically by monitoring either the decrease in vinyl absorption at 200–215 nm or the increase in absorption due to methyl cyclopropyl ketone at 260 nm. Measurements were made using a Cary Model 118C spectrometer for slow runs and a Durrum-Gibson stopped-flow machine for fast reactions; the cell compartment of the Cary spectrometer was thermostated at 25.0 ± 0.05 °C and the Durrum-Gibson machine was also operated at 25.0 °C.

Absorbance readings were continued for 4–5 half-lives, and infinite-time measurements were taken after 10–12 half-lives. The data so obtained were found to follow the first-order rate law exactly. Rate constants were evaluated graphically, either as slopes or plots of log $(A - A_\infty)$ vs. time, or in the case of very slow reactions, by the Guggenheim[7] or Swinbourne methods.[8]

Results

First-order rate constants for the hydrolysis of methyl α-cyclopropylvinyl ether in dilute H_2O and D_2O solutions of hydrochloric acid (Table S1)[9] proved to be accurately first order in acid over a sixfold variation in acid concentration in both solvents. Second-order rate constants were therefore calculated by linear least-squares analysis as the gradients of observed first-order rate constants upon acid concentration; this treatment gave zero intercepts, which means that catalysis by solvent was negligible under these conditions, in keeping with the very slow rates of reaction actually measured for H_2O and D_2O species (Table S2). These second-order rate constants give the isotope effect $k_{\text{H}_3\text{O}^+}/k_{\text{D}_3\text{O}^+} = 4.51 \pm 0.05$.

Rates of water reaction were measured in H_2O and D_2O solutions containing hydroxide ion introduced to suppress catalysis by hydrogen ions. These data (Table S2)[9] give the isotope effect $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 4.0 \pm 1.1$.

Rates of reaction were also determined in buffer solutions of carboxylic acids ($\text{RCO}_2\text{H}/\text{RCO}_2^-$), monohydrogen phosphonate anions ($\text{RPO}_3\text{H}^-/\text{RPO}_3^{2-}$), and ammonium cations ($\text{RNH}_3^+/\text{RNH}_2$). Measurements were carried out in series of solutions of constant buffer ratio, and therefore constant hydrogen ion concentration, but varying buffer concentration; ionic strengths were kept constant (at 0.10 M) by adding inert electrolyte (NaCl). In all cases, observed first-order rate constants were found to be accurately proportional to buffer acid concentration. A typical example is shown in Figure 1, and all of the data are summarized in Table S3.[9]

The rate law which applies in a situation such as this is given by

$$k_{\text{obsd}} = k_{\text{H}^+}[\text{H}^+] + k_{\text{HA}}[\text{HA}] \qquad (6)$$

Since $[\text{H}^+]$ is constant along a series of buffer solutions, values of k_{HA} can be obtained as gradients of k_{obsd} upon $[\text{HA}]$. Best

Table I. Summary of Rate Constants for the Hydrolysis of Methyl α-Cyclopropylvinyl Ether in Aqueous Solution at 25 °C

Acid	pK_a	k, $M^{-1} s^{-1}$
H_3O^+	−1.74	7490
CH_2CNCO_2H	2.47[a]	711
CH_2ClCO_2H	2.87[b]	400
$CH_3OCH_2CO_2H$	3.57[c]	128
HCO_2H	3.75[d]	111
$HOCH_2CO_2H$	3.83[e]	67.0
CH_3CO_2H	4.76[f]	20.0
$CH_3CH_2CO_2H$	4.88[g]	18.4
$CCl_3PO_3H^-$	4.93[h]	167
$CHCl_2PO_3H^-$	5.60[h]	66.3
$CH_2ClPO_3H^-$	6.59[h]	11.6
$HOCH_2PO_3H^-$	7.36[h]	2.72
$CH_3PO_3H^-$	8.00[h]	1.38
$(CH_3)_3CPO_3H^-$	8.71[h]	0.224
$H_2PO_4^-$	7.20[i]	5.39
$(HOCH_2CH_2)_3NH^+$	7.76[j]	0.0240
$(HOCH_2)_3CNH_3^+$	8.07[k]	0.008 61
H_2O	15.74	2.2×10^{-7}

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values of k_{HA} were obtained by least-squares analysis; these are summarized in Table I.

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 to constant hydrogen ion concentration as described previously.[5,10] The concentration dissociation constants needed for this purpose were obtained from published pK_a values[6,11] using activity coefficients recommended by Bates[12] or calculated by the formula $\log f = -0.5Z^2 I^{1/2}/(1 + I^{1/2}) + BI$ with $B = 0.1$ for univalent ions and $B = 0.4$ for divalent species.

As eq 6 shows, values of k_{H^+} may also be obtained from these measurements in buffer solutions by dividing the least-squares intercepts by hydrogen ion concentrations. This was done using hydrogen ion concentrations calculated as described above. However, the intercepts were generally quite small, especially in the case of monohydrogen phosphonate buffers where an electrostatic effect operated to make k_{HA} greater than it would be otherwise,[10a,13] and values of k_{H^+} obtained in this way were subject to considerable uncertainty. Nevertheless, agreement between these results, $k_{H^+} = (6.4 \pm 1.9) \times 10^3$ $M^{-1} s^{-1}$ (average of all buffers), and the value measured directly in strong acid solutions, $k_{H^+} = (7.49 \pm 0.06) \times 10^3$ $M^{-1} s^{-1}$, is good.

Some measurements were also made of the rate of hydrolysis of cyclopropyl methyl dimethyl ketal. These experiments were done in tris(hydroxymethyl)methylamine buffers at two different buffer ratios (Table S4).[9] No catalysis by undissociated acid was observed in either case, and the two series of solutions gave nicely consistent values of k_{H^+}; the best (average) value is $k_{H^+} = (3.35 \pm 0.05) \times 10^4$ $M^{-1} s^{-1}$.

Discussion

Reaction Mechanism. The isotope effect on the hydrolysis of methyl α-cyclopropylvinyl ether in hydrochloric acid solu-
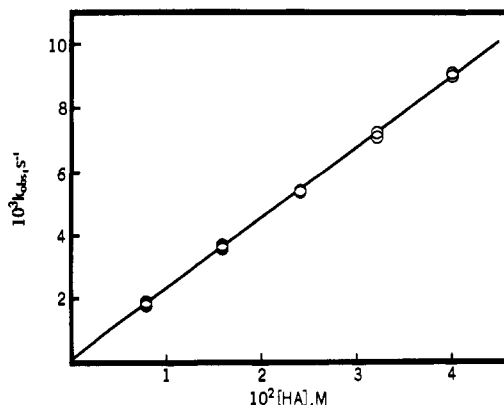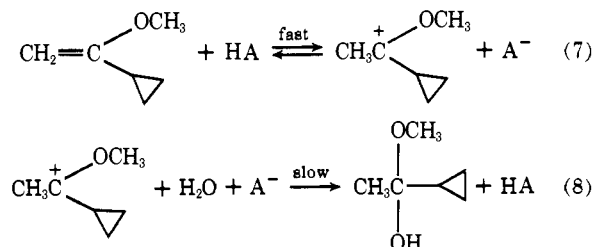

Figure 1. Relationship between buffer acid concentration and rate of hydrolysis of methyl α-cyclopropylvinyl ether in aqueous $(CH_3)_3$-$CPO_3H^-/(CH_3)_3CPO_3^{2-}$ buffer solutions at 25 °C; buffer ratio 2.00 and ionic strength 0.100 M.

tions is $k_{H_3O^+}/k_{D_3O^+} = 4.5$. This is an unusually large isotopic rate ratio for proton transfer from the hydronium ion; it is, in fact, some 20% greater than the maximum, $k_{H_3O^+}/k_{D_3O^+} = 3.7$, predicted by a correlation of isotope effects on the hydrolysis of a large number of other vinyl ethers.[1] It would seem safe to conclude, therefore, that proton transfer is fully rate determining in this reaction under these conditions, i.e., that the conventional mechanism for vinyl ether hydrolysis is operating, and that a modest tunnel effect may even be augmenting the isotope effect.

In less strongly acidic media, on the other hand, the reaction mechanism could be different. The basic species present in such solutions might promote deprotonation of the alkoxycarbonium ion reaction intermediate (eq 1) while having little effect on the subsequent hydration reaction (eq 2); this would foster the condition $k_{-1}[A^-] > k_2[H_2O]$ and lead to an unconventional, reversible proton transfer mechanism. In this circumstance the reaction would no longer show general acid catalysis, and it was, in fact, partly on the basis of just such a switch from general acid to specific hydrogen ion catalysis that the unconventional mechanism was assigned to the hydrolysis of 2-methoxy-2,3,4,5,6,7-hexahydrooxonin.[4] But no such change in mechanism can be occurring in the presentation reaction, for strong general acid catalysis was observed in all of the buffer solutions examined, even, as Figure 1 indicates, down to solutions of the weakest acid used, $(CH_3)_3CPO_3H^-$, whose pK_a is 8.7.

There is still another possible mechanism, however, which would show general acid catalysis; this is rapidly reversible protonation (eq 7) followed by general base assisted hydration (eq 8). But the overall general acid catalytic coefficients for this scheme would necessarily be lower than those for the first proton transfer step (eq 7); otherwise the second step (eq 8)

$$CH_2{=}C\overset{OCH_3}{\diagdown}\ +\ HA\ \underset{}{\overset{fast}{\rightleftharpoons}}\ CH_3\overset{+}{C}\overset{OCH_3}{\diagdown}\ +\ A^- \quad (7)$$

$$CH_3\overset{+}{C}\overset{OCH_3}{\diagdown}\ +\ H_2O\ +\ A^-\ \overset{slow}{\longrightarrow}\ CH_3\overset{OCH_3}{\underset{OH}{\overset{|}{\underset{|}{C}}}}{-}{\diagdown}\ +\ HA \quad (8)$$

could not be rate determining. This would either produce a break, i.e., a change to lower slope, in a plot such as that of Figure 1 at the point where the mechanism changed from rate-determining proton addition to that of eq 7 and 8; or, if the mechanistic change had already taken place at buffer base
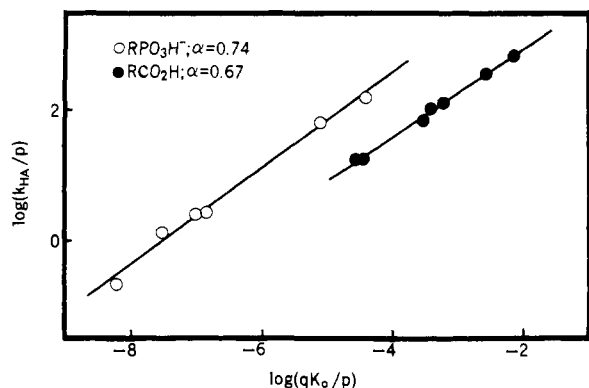
Figure 2. Separate linear Brønsted relations for the hydrolysis of methyl α-cyclopropylvinyl ether catalyzed by carboxylic acids and by monohydrogen phosphonate anions.

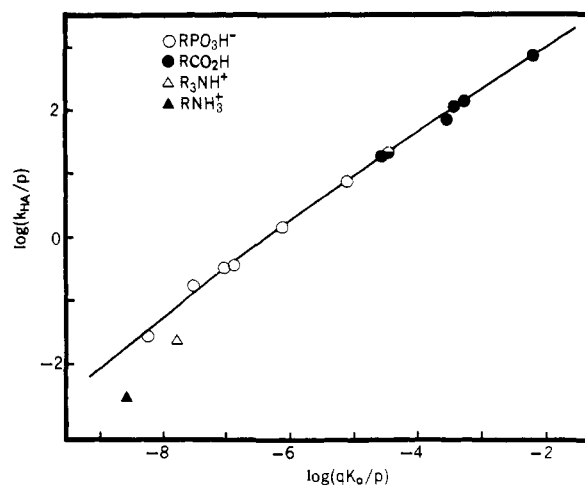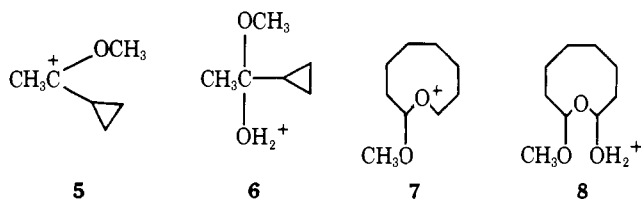
Figure 3. Curved Brønsted relation based upon combined data for the hydrolysis of methyl α-cyclopropylvinyl ether catalyzed by carboxylic acids and monohydrogen phosphonate anions.

concentrations below the lowest used in such a plot, the intercept obtained would give a value of k_{H^+} greater than that measured in strong acid solutions. All of the buffer solutions investigated here gave accurately linear buffer plots with no break, and in all cases the intercepts produced values of k_{H^+} in good agreement with the strong acid measurements, e.g., from the data of Figure 1 $k_{H^+} = (5.4 \pm 2.5) \times 10^3 \, M^{-1} \, s^{-1}$ whereas for HCl solutions $k_{H^+} = (7.49 \pm 0.06) \times 10^3 \, M^{-1} s^{-1}$. Thus, this third mechanism can be safely ruled out.

These arguments show that carbon protonation of methyl α-cyclopropylvinyl ether is not reversible in aqueous solution even in the presence of moderately basic proton acceptors such as monophosphonate dianions, RPO_3^{2-}. It is of interest to extend this search for reversibility to the most basic proton acceptor available in aqueous solution, the hydroxide ion. The great reactivity of methyl α-cyclopropylvinyl ether makes such experiments practical in this case, i.e., rates of reaction in hydroxide ion solution where water molecules are the proton donors are not so slow as to preclude measurements in these media. Even here, however, protonation is not reversible. This is indicated most clearly by the fact that methyl α-cyclopropylvinyl ether recovered from a D_2O solution containing 0.01 M NaOD shows no evidence of deuterium incorporation: even after 2 half-lives the ratio of P to P + 1 peak intensities in the mass spectrum of unreacted vinyl ether is the same within experimental uncertainty (±1%) as that of pure starting material. This result is consistent with the sizable isotope effect, $k_{H_2O}/k_{D_2O} = 4 \pm 1$, observed under these conditions, although the possible presence of solvent and secondary effects makes the unambiguous interpretation of this isotope effect rather difficult.

Additional evidence that carbon protonation in the present system is not reversible comes from the hydrolysis of the related substance, methyl cyclopropyl ketone dimethyl ketal (**4**). The hydrolysis of simple ketals of this kind is known to occur by rate-determining formation of alkoxycarbonium ion intermediates through a mechanism (eq 9) which requires specific hydrogen ion catalysis;[14] as the data of Table S4 show, hydrolysis of **4** does give this form of catalysis. The alkoxycarbonium ion produced in this reaction is identical with that given by carbon protonation of methyl α-cyclopropylvinyl ether, and, if this carbon protonation reaction were reversible, then vinyl ether would be formed in the course of the ketal hydrolysis reaction. But no vinyl ether could be detected in ketal hydrolysis reaction mixtures,[15] and rates of product (ketone) formation, moreover, were accurately first order with no sign of the induction period which would have appeared had significant amounts of vinyl ether been generated.

This total lack of evidence for reversible carbon protonation in the hydrolysis of methyl α-cyclopropylvinyl ether covers an

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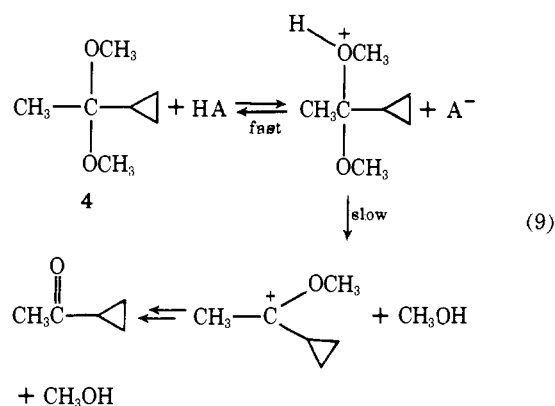
unusually wide range of reaction conditions, from acidic hydrochloric acid to basic sodium hydroxide solutions, and it spans a variation in bimolecular rate constant for proton transfer to the substrate of 3×10^{10}. The corresponding change in rate of the hypothetical reverse reaction, calculated from the relationship $k_{-1} = k_1 K_{SH}/K_{HA}$ in which K_{SH} and K_{HA} are the acidity constants of the protonated substrate and the proton donor, respectively, is 1.4×10^{-7}. It was argued at the beginning of this paper that deprotonation and hydration of alkoxycarbonium ion reaction intermediates in vinyl ether hydrolysis occur at rates which are not very different, i.e., that, although $k_{-1}[A^-]$ is less than $k_2[H_2O]$, the two quantities are nevertheless roughly comparable, and the lack of a mechanistic change over so large a variation in $k_{-1}[A^-]$ therefore suggests that $k_2[H_2O]$ is changing as well. This implies that the hydration reaction is a base-catalyzed process. General base catalysis of cation hydration reactions has been observed directly in other systems,[16] and the phenomenon is believed to be rather widespread.[16b]

In the hydrolysis of 2-methoxy-2,3,4,5,6,7-hexahydrooxonin a change in reaction mechanism does take place, and this suggests that cation hydration here may not be subject to general base catalysis. This difference in behavior from methyl α-cyclopropylvinyl ether can be understood in terms of the different stabilities of the two alkoxycarbonium ions involved. The ion generated from methyl α-cyclopropylvinyl ether (**5**) benefits greatly from the powerful electron-donating effect of an adjacent cyclopropyl group, and its energy may well be less than that of the protonated hemiketal, **6**, derived from it by non-base-catalyzed hydration; general base catalysis of the hydration reaction would then avoid an unfavorable interme-

OCH₃

CH₃C⁺—OCH₃ ▽

CH₃C—◁ with OCH₃ and OH₂⁺

$\quad$ 5 $\qquad$ 6 $\qquad$ 7 $\qquad$ 8

diate (6) and provide a favorable low-energy reaction path. On the other hand, the ion obtained from 2-methoxy-2,3,4,5,6,7-hexahydrooxonin (7) is destablized by a nearby methoxy group. This might put its energy above that of the corresponding protonated hemiacetal, 8, which would make this substance a favorable rather than an unfavorable intermediate and remove the need for general base catalysis.[17]

Brønsted Relation. The rate constants determined here for the hydrolysis of methyl α-cyclopropylvinyl ether catalyzed by carboxylic acids and by monohydrogen phosphonate anions give separate Brønsted relations displaced vertically by about an order of magnitude, with the negatively charged ions better catalysts than neutral acids of the same pK_a (Figure 2). This behavior has been observed before in other vinyl ether hydrolysis reactions,[13] and the phenomenon can be understood in terms of electrostatic effects which operate in the transition states of these reactions.[10b]

These two Brønsted relations also have somewhat different slopes: $\alpha = 0.67 \pm 0.03$ for the carboxylic acids and $\alpha = 0.74 \pm 0.03$ for the phosphonate ions. We have argued before[13] that this is because these correlations are linear segments of more extended curved relations, and we have shown how this curvature may be demonstrated by moving each of the phosphonate ion points down by an amount equal to the difference between log k_{HA} for $CCl_3PO_3H^-$ and that for CH_3CO_2H, two acids with nearly identical values of log (qK_a/p). The result of such treatment in the present case is shown in Figure 3.

The line connecting the points in this figure was obtained by quadratic least-squares analysis of the combined data. It is possible, with the aid of Marcus rate theory,[18] to transform the coefficients of quadratic expressions obtained in this way into certain fundamental parameters which are useful for characterizing proton transfer reactions. When this is done in the present case, the intrinsic barrier $\Delta G_0^{\ddagger} = 6.1 \pm 2.7$ kcal/mol and the work term $w^r = 4.1 \pm 3.9$ kcal/mol are obtained. These results suggest that in this reaction comparable amounts of energy must be spent to bring the reactants together and form them into a reaction complex (w^r) and to transfer the proton from donor to acceptor within this complex ($\Delta G_0^{\ddagger}$). This is somewhat different from the outcome of correlations of this type for other vinyl ether hydrolyses[13] and of a correlation of isotope effects in vinyl ether hydrolysis[1] where w^r was found to be considerably greater than $\Delta G_0^{\ddagger}$, but the uncertainty of the presently determined values is rather large and

the difference between these and previous results may not be significant.

It is noteworthy that biphosphate ion fits the Brønsted relation for monohydrogen phosphonate ions, in keeping with its hydroxyphosphonate ion structure ($HOPO_3H^-$); this datum was therefore used both in the linear correlation shown in Figure 2 and in the curved relation given in Figure 3. The data for the ammonium ions, on the other hand, fall below even the curved relation (see Figure 3); it is likely that these deviations are due at least in part to electrostatic effects operating in the transition states of these reactions.[10b] The hydrogen ion and water points miss the correlations by rather wide margins, as is not unusual for solvent and solvent-derived species.

References and Notes

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