

lation, 4.63 g (85%) of a mixture of 3-methyl-4-bromobutyl acetate and 2-methyl-4-bromobutyl acetate in a ratio of 2.7:1. The proportions of the isomers were obtained from the integrated intensities of the NMR signals for the methylene protons of the acetate-bearing carbons in the two compounds; ir (CHCl₃) 1730 cm⁻¹; NMR (CCl₄) 0.98 (d, 3 H, CH₃, *J* = 6 Hz), 1.07 (d, 3 H, CH₃, *J* = 7 Hz), 1.5–2.2 (m, 3 H, –CH and CCH₂C), 2.04 (s, 3 H, OCOCH₃), 3.35–3.6 (t, 2 H, CH₂CH₂Br and d, 2 H, –CHCH₂Br), 3.96 (d, 2 H, –CHCH₂O, *J* = 6 Hz), 4.12 ppm (t, 2 H, CH₂CH₂O–, *J* = 7 Hz).

Anal. Calcd for C₇H₁₃BrO₂: C, 40.21; H, 6.27; Br, 38.22. Found: C, 40.31; H, 6.31; Br, 38.16.

Cleavage of 2,5-Dimethyltetrahydrofuran. A mixture of *cis*- and *trans*-2,5-dimethylfuran (2.6 g, 26 mmol) under the standard conditions afforded 5.22 g (88%) of the diastereoisomeric 2-methyl-4-bromopentyl acetates: ir (CHCl₃) 1730 cm⁻¹; NMR (CCl₄) 1.20 (d, 3 H, CH₃CH–O, *J* = 6 Hz), 1.60–1.95 (m, 4 H, CH₂), 1.69 (d, 3 H, CH₃CHBr, *J* = 7 Hz), 2.00 (s, 3 H, CH₃CO₂–), 4.13 (m, 1 H, CHBr), 4.9 ppm (m, 1 H, –CHO).

Anal. Calcd for C₈H₁₅BrO₂: C, 43.07; H, 6.77; Br, 35.82. Found: C, 43.10; H, 6.78; Br, 35.85.

Cleavage of Tetrahydropyran. Application of the usual conditions with the exception of the reaction temperature, 85° in the present case, to tetrahydropyran (2.53 ml, 26 mmol) yielded 3.32 g (50%) of 5-bromopentyl acetate:¹³H NMR (CCl₄) 1.4–1.8 (m, 6 H, CH₂), 2.0 (s, 3 H, OCOCH₃), 3.45 (t, 2 H, CH₂Br, *J* = 6 Hz), 4.08 ppm (t, 2 H, CH₂O, *J* = 7 Hz).

Cleavage of Cyclohexene Oxide. The title compound (2.55 g, 26 mmol) after treatment with magnesium bromide–acetic anhydride and subsequent distillation gave 4.58 g (80%) of *trans*-2-bromocyclohexyl acetate:¹⁴H NMR (CCl₄) 1.15–2 (m, 8 H), 2.05 (s, 3 H), 3.87–4.16 (m, 1 H, CHBr), 4.74–5.0 ppm (m, 1 H, CHOAc).

***cis*-2,5-Dimethyltetrahydrofuran (*cis*-5).** Distillation of commercial 2,5-dimethyltetrahydrofuran at atmospheric pressure through a Nester–Faust annular Teflon spinning band column operating at a reflux ratio of 30:1 afforded *cis*-2,5-dimethyltetrahydrofuran: bp 90–91° (lit.¹⁵ 90–91°); ¹H NMR (CCl₄) 1.15 (d, 3 H, CH₃, *J* = 6 Hz), 1.28–2.24 (m, 4 H, CH₂), 3.81–4.41 (m, 2 H, CH); ¹³C NMR (CDCl₃) 21.60 (CH₃), 33.38 (CH₂), 75.36 ppm (CH). Both GLC analysis on SE-30 silicone rubber and Carbowax 20M and peak height measurements of the ¹³C NMR spectrum of the *cis* compound indicated the presence of no more than 10% of the *trans* isomer *trans*-2,5-dimethyltetrahydrofuran (*trans*-6).

***trans*-2,5-Dimethyltetrahydrofuran (*trans*-6).** The higher boiling fraction from spinning band distillation afforded the title compound: bp 91–92° (lit.¹⁵ 92–94°); ¹H NMR (CCl₄) 1.13 (d, 3 H, CH₃, *J* = 6 Hz), 1.28–2.41 (m, 4 H, CH₂), 3.81–4.41 (m, 2 H, CH); ¹³C NMR (CDCl₃) 21.48 (CH₃), 34.31 (CH₂), 74.55 ppm (CH).

Cleavage and Reconstitution of the Isomeric 2,5-Dimethyltetrahydrofurans. Each of the above isomers was subjected to the cleavage conditions described previously. The distilled products were analyzed on a Carbowax 20M column at a programmed temperature rate increase of 2°/min from an initial temperature of 110°. The retention time for *threo*-7 (from *cis*-5) was 10.3 min and that for *erythro*-8 (from *trans*-6) was 11.5 min. Analysis of mixtures of the isomers indicated that 10% of one isomer was detectable in the presence of the other. The bromoacetate *threo*-7 (2.26 g, 10 mmol) was dissolved in 25 ml of ethylene glycol containing 0.7 g of potassium hydroxide. The solution was heated at 60° for 6 hr. Distillation through a Vigreux column at 92° and atmospheric pressure followed by separation of water and drying yielded *cis*-5 (0.44 g, 44%). Gas chromatographic and spectroscopic analysis as described above indicated the presence of 10% or less of the *trans* isomer. Application of the same procedure to *erythro*-8 (2.26 g, 10 mmol) afforded pure *trans*-6 (0.42 g, 42%).

Registry No.—1, 4753-59-7; 2, 96-47-9; 3, 26923-92-2; 4, 26923-93-3; 5, 2144-41-4; 6, 2390-94-5; 7, 56761-56-9; 8, 56761-57-0; tetrahydrofuran, 109-99-9; 3-methyltetrahydrofuran, 13423-15-9; 3-methyl-4-bromobutyl acetate, 56761-58-1; 2-methyl-4-bromobutyl acetate, 56761-59-2; 5-bromopentyl acetate, 15848-22-3; tetrahydropyran, 142-68-7; cyclohexene oxide, 286-20-4; *trans*-2-bromocyclohexyl acetate, 5837-71-8.

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An Unusual Rate Law for Vinyl Ether Hydrolysis. Observation of H₃PO₄ Catalysis at High pH

Gordon Marc Loudon* and Denis E. Ryono

Spencer T. Olin Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853

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An unusual rate law has been observed for hydrolysis of several vinyl ethers in phosphate buffers in the pH range 5.5–7.6. In addition to the expected terms in [H⁺] and [H₂PO₄⁻] alone, a term in [H⁺][H₂PO₄⁻] was also observed. After determination of the p*K'*_a of H₃PO₄ (1.62 ± 0.06) in the 5% dioxane, μ = 1.0 M (KCl), solvent system used for the kinetics, and evaluation from a Brønsted correlation of the contribution expected from H₃PO₄ catalysis, it has been shown that the unusual rate law does not represent a new mechanism, but rather direct observation of H₃PO₄ catalysis at pH values more than four units higher than its p*K'*_a. The consequences of this observation are listed.

In the study of the hydrolysis of vinyl ethers to their corresponding ketones, we^{1,2} and others^{3a} have shown repeatedly that these species undergo hydrolysis by the rate law

$$k_{\psi} = k_H[H^+] + \sum_i k_{HA_i}[HA_i] \quad (1)$$

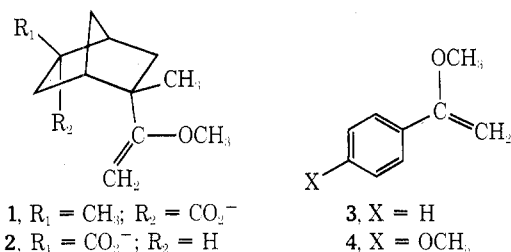
where *k*_ψ is the observed, pseudo-first-order rate constant, and HA_{*i*} is a general acid catalyst. We were therefore rather surprised when, while studying the hydrolysis of compounds 1 and 2 in phosphate buffers,⁴ we observed apparent conformity to the rate law

$$k_{\psi} = k_H[H^+] + k_{H_2PO_4}[H_2PO_4^-] + k_{H_2PO_4,H}[H^+][H_2PO_4^-] \quad (2)$$

The cross term in eq 2 in $[H^+]$ and $[H_2PO_4^-]$ is hitherto unprecedented, and it presented the possibility that an unusual mechanism was operating in these hydrolyses which had previously not been observed. Another explanation of this term in eq 2 is that catalysis by undissociated H_3PO_4 was being observed at pH values *more than four units higher than its pK_a* . In this paper, we demonstrate that the rate law of eq 2 is rigorously followed, and then resolve these two kinetically equivalent possibilities, with the result that one may evaluate H_3PO_4 catalysis in buffers of $H_2PO_4^-$ - HPO_4^{2-} in vinyl ether hydrolysis.

Results

The hydrolysis of all compounds was carried out in either 5% ethanol, 25° (1 and 2), or 5% dioxane, 29.9° (3 and 4), with the ionic strength maintained at 1.0 M with KCl;



excellent pseudo-first-order kinetics were observed. In Table I are summarized the hydrolysis data for these compounds. As we have observed before, plots of the observed pseudo-first-order rate constant, k_{ψ} , vs. total phosphate, $[P_T]$, at a constant pH were strictly linear over the concentration range examined (0.05–0.20 M). Because of the strong buffer catalysis, the intercepts of such plots, which are extrapolated quantities, are a very small fraction of the observed rate constants, and the percent error in these intercepts is therefore quite large. We shall, however, make no use of these intercepts in this work. The slopes of such plots are the quantities of interest here, and they are determined with excellent precision. For a single acid, eq 1 may be rewritten

$$k_{\psi} = k_H[H^+] + k_{HA}f_{HA}[P_T] \quad (3)$$

in which f_{HA} is the fraction of the buffer in the acid form. If \bar{k}_{cat} is the observed slope of the k_{ψ} vs. $[P_T]$ plot, then \bar{k}_{cat} is given by

$$\bar{k}_{cat} = k_{HA}f_{HA} \quad (4)$$

and a plot of \bar{k}_{cat} vs. f_{HA} should be linear through the origin. It is clear from Figure 1 that this behavior is not observed for compounds 1–4 when $HA = H_2PO_4^-$. Although the plots appear to emanate from the origin, evidently significant positive deviations from linearity are observed at $f_{HA} > 0.5$. In contrast, we have previously shown that eq 4 is followed by α -methoxystyrenes when the catalyzing acid is monoprotic.^{1,2} The data in Figure 1 may be fit, however by the equation

$$\bar{k}_{cat} = (k_{H_2PO_4} + k_{H_2PO_4,H}[H^+])f_{HA} \quad (5)$$

with the parameters given in Table II; this equation is equivalent to eq 2. It should be noted that fitting the data in Figure 1 with a simple linear equation gives a severely deteriorated correlation with a substantially negative intercept at $f_{HA} = 0$; such an intercept is physically meaningless since it has been shown that hydrolysis of these vinyl ethers is not accompanied by a salt effect² over the range of buffer concentrations used in this work.

Table I
Summary of Hydrolysis Data for Vinyl Ethers 1–4^f

pH	f_{HA}^a	$\bar{k}_{cat},^b M^{-1} \text{ min}^{-1}$	$k_0,^c \text{ min}^{-1}$
Hydrolysis of 1, Phosphate Buffers ^d			
5.49	0.932	10.2 ± 0.9	2.48 ± 0.01
5.78	0.876	10.0 ± 0.1	1.46 ± 0.01
6.08	0.780	8.15 ± 0.44	(7.50 ± 0.66) × 10 ⁻¹
6.30	0.681	6.26 ± 0.16	(5.96 ± 0.20) × 10 ⁻¹
6.44	0.608	5.33 ± 0.61	(4.69 ± 0.78) × 10 ⁻¹
6.63	0.500	4.61 ± 0.19	(2.67 ± 0.19) × 10 ⁻¹
6.83	0.387	3.43 ± 0.26	(1.97 ± 0.28) × 10 ⁻¹
7.05	0.275	2.11 ± 0.34	(1.43 ± 0.13) × 10 ⁻¹
7.37	0.154	1.37 ± 0.06	(5.44 ± 0.49) × 10 ⁻¹
7.70	0.078	0.810 ± 0.048	(2.01 ± 0.34) × 10 ⁻²
Hydrolysis of 2, Phosphate Buffers ^d			
5.37	0.948	7.20 ± 0.60	(3.65 ± 0.80) × 10 ⁻¹
5.43	0.941	7.50 ± 0.06	(2.41 ± 0.05) × 10 ⁻¹
5.59	0.916	6.48 ± 0.06	(1.91 ± 0.05) × 10 ⁻¹
5.76	0.881	5.83 ± 0.04	(1.30 ± 0.05) × 10 ⁻¹
6.06	0.788	4.39 ± 0.16	(9.72 ± 0.24) × 10 ⁻²
6.32	0.671	3.49 ± 0.13	(7.20 ± 0.24) × 10 ⁻²
6.47	0.591	2.86 ± 0.07	(6.36 ± 0.84) × 10 ⁻²
6.65	0.489	2.38 ± 0.02	(4.61 ± 0.27) × 10 ⁻²
6.83	0.387	1.88 ± 0.06	(2.70 ± 0.06) × 10 ⁻²
7.01	0.294	1.42 ± 0.01	(1.87 ± 0.02) × 10 ⁻²
7.32	0.170	0.888 ± 0.006	(5.72 ± 0.99) × 10 ⁻³
7.51	0.119	0.618 ± 0.006	(2.39 ± 0.01) × 10 ⁻³
Hydrolysis of 3, Phosphate Buffers ^e			
5.54	0.900	1.74 ± 0.18	(1.49 ± 1.24) × 10 ⁻²
5.94	0.800	1.30 ± 0.02	(9.30 ± 1.16) × 10 ⁻³
6.24	0.700	1.07 ± 0.07	(5.70 ± 4.81) × 10 ⁻³
6.49	0.600	(9.02 ± 0.48) × 10 ⁻¹	(4.18 ± 2.04) × 10 ⁻³
6.61	0.500	(7.10 ± 0.19) × 10 ⁻¹	(3.60 ± 1.29) × 10 ⁻³
6.82	0.400	(5.14 ± 0.12) × 10 ⁻¹	(2.95 ± 0.81) × 10 ⁻³
7.02	0.300	(3.75 ± 0.14) × 10 ⁻¹	(2.45 ± 0.96) × 10 ⁻³
7.30	0.200	(2.59 ± 0.01) × 10 ⁻¹	(4.03 ± 0.93) × 10 ⁻⁴
7.63	0.100	(1.28 ± 0.01) × 10 ⁻¹	(5.00 ± 9.96) × 10 ⁻⁵
Hydrolysis of 3, Other Buffers ^e			
Acetate,			
4.70	0.500	4.27 ± 0.08	(2.01 ± 0.10) × 10 ⁻¹
Formate,			
3.62	0.500	80.1 ± 4.4	1.72 ± 0.15
Hydrolysis of 4, Phosphate Buffers ^e			
5.54	0.900	20.1 ± 2.8	(3.11 ± 1.93) × 10 ⁻¹
5.94	0.800	17.9 ± 1.0	(1.08 ± 0.66) × 10 ⁻¹
6.24	0.700	14.5 ± 0.7	(7.75 ± 5.18) × 10 ⁻¹
6.49	0.600	12.2 ± 0.2	(6.20 ± 1.30) × 10 ⁻¹
6.61	0.500	9.39 ± 0.36	(4.73 ± 2.44) × 10 ⁻¹
6.82	0.400	7.65 ± 0.11	(2.34 ± 0.78) × 10 ⁻²
7.02	0.300	4.86 ± 0.18	(4.90 ± 1.26) × 10 ⁻²
7.30	0.200	3.39 ± 0.16	(7.09 ± 10.9) × 10 ⁻³
7.63	0.100	1.77 ± 0.03	(5.85 ± 1.94) × 10 ⁻³

^a Equation 3. ^b Equation 4. ^c $k_0 = k_H[H^+]$; eq 1, 2, or 3. The values of k_0 are generally of very low precision, especially at the higher pH values. This fact is due to the very strong buffer catalysis, which means that k_0 , an extrapolated number, is a very small percent of the values of k_{ψ} actually observed, whereas the error in k_0 is of the same order as the errors in k_{ψ} . ^d 25°, 5% ethanol, $\mu = 1.0 M$ (KCl). ^e 29.9°, 5% dioxane, $\mu = 1.0 M$ (KCl). ^f In each case, the parameters \bar{k}_{cat} and k_0 (see note c) were determined by a plot of k_{ψ} vs. $[P_T]$ at constant pH, varying the value of $[P_T]$ from 0.05 to 0.20 M. The concentrations of the individual buffer species $H_2PO_4^-$ and HPO_4^{2-} can be calculated from the mass action law and the pK_a' of $H_2PO_4^-$.

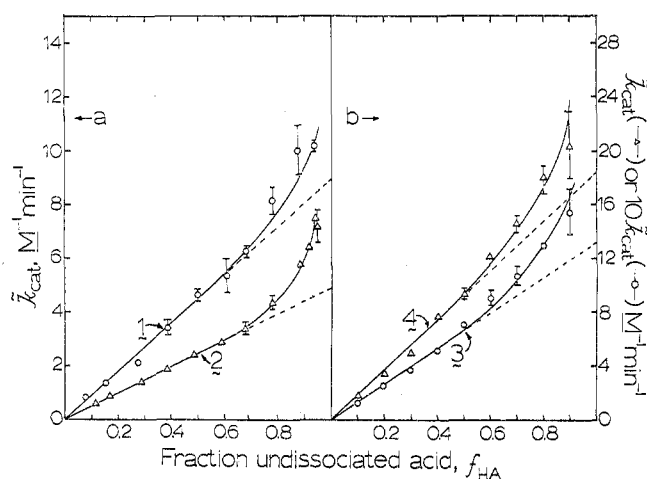


Figure 1. Slopes of buffer plots (eq 5) plotted vs. the fraction of the buffer in the H_2PO_4^- form. The points are experimental, and the lines are calculated from eq 5 and the parameters in Table II. The parameters were determined by a weighted, nonlinear least-squares fit of the points using eq 5.

Table II
Parameters of Equation 5 for Hydrolysis of
Vinyl Ethers 1-4

Compd ^a	$k_{\text{H}_2\text{PO}_4}, \text{M}^{-1} \text{min}^{-1}$	$k_{\text{H}_2\text{PO}_4, \text{H}^+}, \text{M}^{-1} \text{min}^{-1}$
1	$(1.44 \pm 0.06) \times 10^{-1}$	$(1.14 \pm 0.17) \times 10^4$
2	$(7.58 \pm 0.20) \times 10^{-2}$	$(1.57 \pm 0.08) \times 10^4$
3	1.33 ± 0.04	$(2.53 \pm 0.47) \times 10^5$
4	18.6 ± 0.6	$(2.62 \pm 1.00) \times 10^6$

^a 1 and 2 in 5% ethanol, $\mu = 1.0 \text{ M}$ (KCl); 3 and 4 in 5% dioxane, $\mu = 1.0 \text{ M}$ (KCl).

To evaluate the possible contribution of catalysis by H_3PO_4 it was necessary to determine its operational pK'_a in the solvent systems used here. Whereas operational pK'_a values may be determined for weak acids by half-neutralization, this procedure is not satisfactory for stronger acids because of "buffer failure".³ For H_3PO_4 , we used a variant of the Ostwald dilution procedure, as follows, to determine the pK'_a of H_3PO_4 in the 5% dioxane, $\mu = 1.0 \text{ M}$ (KCl), system. When an acid HA is present in solution at M_0 mol/l. stoichiometric concentration, the mass action law becomes

$$K'_a = \left(\frac{x^2}{M_0 - x} \right) \left(\frac{\gamma_{\text{H}}\gamma_{\text{A}}}{\gamma_{\text{HA}}} \right) \quad (6)$$

where x/M_0 is the degree of dissociation of the acid, and γ_i is the activity coefficient of species i referred to 1 M infinitely dilute solution in the 5% dioxane, $\mu = 1.0 \text{ M}$ solvent system used for the kinetics. In logarithmic form, recognizing that $x = [\text{H}^+]$, we have

$$\text{p}[\text{H}^+] = \text{pK}'_a/2 - \frac{1}{2} \log (M_0 - [\text{H}^+]) + \frac{1}{2} \log \frac{(\gamma_{\text{H}}\gamma_{\text{A}})}{\gamma_{\text{HA}}} \quad (7)$$

We have previously determined the relationship in this solvent system between pH meter reading and $\text{p}[\text{H}^+]$, namely, that the two are by coincidence equal;¹ thus, we have a method for determining $[\text{H}^+]$. A plot of pH vs. $-\log (M_0 - [\text{H}^+])$ should have slope 0.5 and intercept $\frac{1}{2}\text{pK}'_a + \frac{1}{2}\log (\gamma_{\text{H}}\gamma_{\text{A}}/\gamma_{\text{HA}})$. If we assume that HA makes a small perturbation in the nature of the medium (e.g., the change in ionic strength over the entire range of H_3PO_4 concentration used was found to be about 4%), then the activity coefficient term may be ignored. The linearity and slope of a plot of the data according to eq 7 are tests of this assumption, or of the less restrictive but operationally equivalent assump-

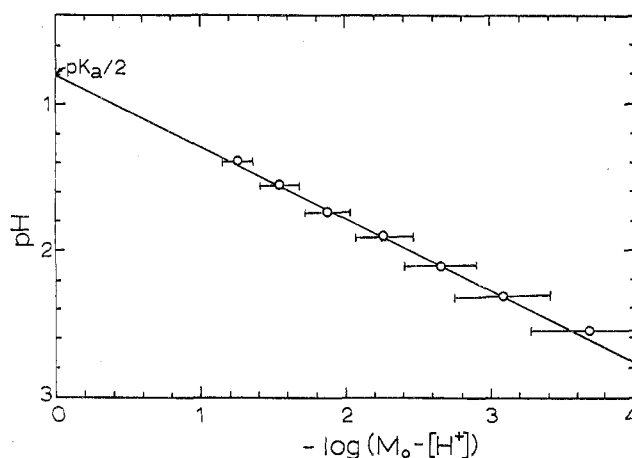


Figure 2. Dilution plot for determination of the pK'_a of H_3PO_4 in 5% dioxane, $\mu = 1.0 \text{ M}$ (KCl). The error bars are standard deviations in $\log (M_0 - [\text{H}^+])$, assuming a constant data. error of 0.03 in pH. The line is calculated for a slope of 0.49 and intercept of $\text{pK}'_a/2 = 0.81$, determined by a weighted least-squares fit of the data.

tion that variations in the various activity coefficients are self-compensating. This is, of course, the advantage of using a high ionic strength medium: contributions of buffer components at low concentration cause only a negligible change in the nature of the solvent. Figure 2 is a dilution plot constructed from eq 7; the slope is 0.49 ± 0.01 , at the theoretical prediction; the intercept of 0.81 ± 0.03 translates into a pK'_a of 1.62 ± 0.06 for H_3PO_4 in the 5% dioxane solvent system.

Discussion

It is clear from Figure 1 that the observation of the rate law of eq 2 for vinyl ether hydrolysis, first observed for 1 and 2, is not unique to a particular structure, and is probably general for this reaction. The curves presented in Figure 1, which were adequately reproduced by eq 2 or 5, may equally well be represented by eq 8.

$$k_{\psi} = k_{\text{H}}[\text{H}^+] + k_{\text{H}_2\text{PO}_4}[\text{H}_2\text{PO}_4^-] + k_{\text{H}_3\text{PO}_4}[\text{H}_3\text{PO}_4] \quad (8)$$

The equivalency between the two expressions is given by the relation

$$k_{\text{H}_2\text{PO}_4, \text{H}} K'_{\text{H}_3\text{PO}_4} = k_{\text{H}_3\text{PO}_4} \quad (9)$$

in which $K'_{\text{H}_3\text{PO}_4}$ is the dissociation constant of H_3PO_4 determined above. In deciding between the two kinetically equivalent alternatives of eq 2 and 8, we were required to have a reasonable estimate of what to expect for catalysis by H_3PO_4 . A direct measurement of $k_{\text{H}_3\text{PO}_4}$ is precluded by the fact that the observed rate constants at pH values such that $[\text{H}_3\text{PO}_4]$ would be present in measurable concentration would be immeasurably fast (ca. 10^3 min^{-1}) by the method used here. A Brønsted α determined for α -methoxystyrene hydrolysis is 0.62 (acetate and formate buffers); this value differs from that previously given^{1,2} because the previous value of 0.46 was based on the difference between acetate and phosphate; in fact, H_2PO_4^- catalysis is faster by nearly a factor of 10 than that predicted from Brønsted plots of carboxylate buffers, in accord with Kresge's³ and our^{1,4} observation of positive electrostatic assistance of vinyl ether hydrolysis by negatively charged acids. Kresge and coworkers⁵ have found that the hydrolysis of ethyl cyclopentenyl ether and ethyl isopropenyl ether, two vinyl ethers only slightly less reactive than α -methoxystyrene, shows $\alpha = 0.63 \pm 0.03$ and 0.64 ± 0.04 , respectively, for catalysis by carboxylic acids, in excellent agreement with

the value of 0.62 found above. Extrapolation of the Brønsted correlation (with statistical corrections) to the pK'_a of H_3PO_4 , determined as discussed in the Results section, gives an expected value for $k_{H_3PO_4}$ of $1.07 \times 10^3 M^{-1} \text{ min}^{-1}$; the observed value (Table II, eq 9) is $6.25 \times 10^3 M^{-1} \text{ min}^{-1}$, a factor of 5.8 larger than predicted. Since it has been shown by direct measurement of $k_{H_3PO_4}$ for ethyl vinyl ether that this catalytic constant lies about 0.5 log unit (a factor of 3) above the Brønsted prediction based on carboxylate buffers, our observed $k_{H_3PO_4}$ is thus within a factor of 2 of the expected value. The significance of the remaining difference is questionable in view of the assumptions and approximations made in this and other³ work. The calculated values of $k_{H_3PO_4}$ for 1, 2, and 4 show similar agreement with observed values when we assume that the pK'_a of H_3PO_4 in the 5% ethanol, $\mu = 1.0 M$ (KCl) system is the same as that in the dioxane system. This last assumption is quite reasonable, since a number of acids of diverse types show such an identity in pK'_a in the two solvents.

Several conclusions result from this work. (1) Kresge's caution,^{3,6} that one should construct Brønsted plots from the same type of catalysts, is further underscored. (2) H_3PO_4 is confirmed to be an unusually active catalyst in vinyl ether hydrolysis, and probably in similar reactions as well. (3) Catalytic constants determined for components of polyprotic acids should be based on an exploration of the full range of pH covered by the buffer, because (4) strong acids, even if present in miniscule amounts, may have detectable catalytic activity. (5) In favorable cases such as this, catalytic constants for the stronger acids in a polyprotic array may be evaluated without direct measurement at pH values at which the strong acid dominates, at which the reaction under consideration may be too fast to measure, and at which buffer failure leads to troublesome complications in measuring buffer catalysis. (6) Finally, effects similar to those observed here might be anticipated for poly-

basic amines in reactions during which negative charge is present in the rate-determining step.

Experimental Section

The synthesis of all compounds, product analyses, and kinetic methods have been previously described.^{1,4}

To determine the pK'_a of H_3PO_4 , standard 0.1 M phosphoric acid was established by potentiometric titration with standard KOH. Known molarities, M_0 , of H_3PO_4 were formulated in the 5% dioxane, $\mu = 1.0 M$ (KCl) solvent system, and the pH was determined on a Radiometer Model 26 instrument using a combination electrode standardized at several pH values. The hydrogen ion concentration was determined from the pH meter reading (see Results section for a justification of this procedure) and a dilution plot, Figure 2, constructed according to eq 7. A weighted, linear least-squares analysis⁷ was carried out to obtain the parameters of fit.

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The Oxidation of Terminal Olefins to Methyl Ketones by Jones Reagent Is Catalyzed by Mercury(II)¹

Harold R. Rogers, Joseph X. McDermott,² and George M. Whitesides*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The oxidation of terminal olefins by Jones reagent in the presence of a catalytic quantity of mercury(II) affords good yields (>70%) of the corresponding methyl ketones. Similar oxidations of 1,2-disubstituted olefins gives fair (20–70%) yields; in the case of unsymmetrically substituted olefins, mixtures of ketones are produced.

The Wacker process for oxidation of olefins to ketones has three mechanistically distinct parts:³ first, activation of the olefinic double bond toward nucleophilic attack by coordination with Pd(II) and addition of a hydroxide moiety to this electrophilic double bond; second, conversion of the resulting 2-hydroxyethylpalladium(II) compound to ketone and a (formally) Pd(0) atom by a series of palladium(II) hydride addition-eliminations involving vinylic alcohol intermediates; third, reoxidation of the palladium(0) to palladium(II) by copper(II). Wacker oxidation is an extremely useful and general reaction. It is, nonetheless, worthwhile to try to develop procedures for oxidizing olefins that use as catalysts metals less expensive than palladium, and which involve reactions (and possibly generate

products) different from those of the Wacker oxidation. Mercury(II) is an obvious candidate for the catalyst for new oxidation reactions: it resembles palladium(II) in its ability to activate olefins for nucleophilic attack,⁴ but differs in that decomposition of the oxymercuration products normally generates cations by loss of mercury(0) rather than olefins by loss of mercury hydride.⁵ Unfortunately, neither we nor others⁶ have been able to discover a satisfactory solution to the principal problem in developing a mercury(II)-catalyzed analog of the Wacker oxidation: viz., an efficient regeneration of mercury(II) from mercury(0). In the absence of a solution to this problem, there are, however, ways of involving mercury(II) in catalytic oxidation of olefins other than in a direct analog of a Wacker oxidation.