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PROTON TRANSFER TO 2-(4-METHOXYPHENYL)PROPENE

Joel M. Williams, Jr.[1]

University of Minnesota
Minneapolis, Minnesota 55455

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Recently some details of the mechanism of the hydration of $\underline{\alpha}$-methylstyrenes were presented.[2] While the experimental data seem reliable, another treatment of these data appears warranted. Because the reactivity of α-methylstyrenes towards hydration is between those of isobutene[3] and ethyl vinyl ether[4], it is reasonable to expect other related properties to behave likewise. However, the Brønsted alpha ($\alpha = 0.5$) is lower than either the value observed for ethyl vinyl ether (0.66)[5] or that predicted for isobutene (0.9)[6]. Also the isotope effect attributed to the hydronium ion ($k_H/k_D = 3.15$) for 2-(4-methoxyphenyl)propene is approximately equal to that observed for ethyl vinyl ether (3.0)[4,5], but much larger than that for isobutene (1.45)[3]. The more reasonable value of 2.23 for the measured isotope effect (in aqueous $HClO_4$) with this compound was reported earlier[7]. Finally, the isotopic alpha ($\alpha = 0.45$) obtained from the Gross-Butler equation[8] is much too small. The values for ethyl vinyl ether[9] and isobutene[3] are 0.6 and 0.9, respectively. Experimental data on the general acid catalysis, and a dissection of the results previously cited[2] on isotopically mixed solvents are given below.

To obtain a meaningful Brønsted alpha, a homologous series of acids must be used. Germane to this point is the tremendous deviation of the hydronium ion from all known Brønsted plots of carboxylic acids[6]. The observed rates (obtained spectrophotometrically at 257 mμ) for the hydration of 2-(4-methoxyphenyl)propene in water at 48.7° C are given in Table I and Fig. 1. (The equilibrium constant favors alcohol $\geqslant 98\%$, therefore $0.98\ k_{obs} \leqslant k_{forward} \leqslant k_{obs}$). The Brønsted plot clearly shows the deviation of the hydronium ion from the line formed by the carboxylic acids which has a slope of 0.84.

Table I

General Acid-Catalyzed Hydration of 2-(4-Methoxyphenyl)propene at 48.7°

Acid, HA	k_{HA}, $M^{-1}sec^{-1}$	pK_{HA}[a]
$HClO_4$	1.26×10^{-1}	
$NCCH_2CO_2H$	$2.3_6 \times 10^{-3}$	2.45
HCO_2H	$2.6_0 \times 10^{-4}$[b]	3.58
HCO_2H	2.5×10^{-4}[b]	
CH_3CO_2H	3.1×10^{-5}	4.72

(a) Measured in this laboratory: $\mu = 0.3$.
(b) Taken from ref. 2.

The composition of the measured rate in isotopically mixed water using sulfuric acid is quite complex. Significant contribution to the rate is expected from the bisulfate ion[5,6]. Also equations 1 and 2 should be considered. (K_H=0.055* and K_H/K_D=2.2[11].)

$$MSO_4^- + M_2O \xrightleftharpoons{K_x} SO_4^= + \overset{+}{M_3O} \qquad (1)$$

$$K_x = \frac{(1-x + x\ell)^3 K_H}{1-x + x\ell^3 K_H/K_D}$$

$$HSO_4^- + (D)_{M_2O} \xrightleftharpoons{\phi} DSO_4^- + (H)_{M_2O} \qquad (2)$$

$$\phi = K_{HA}^{H_2O}\,\ell^3/K_{DA}^{D_2O} = 0.72$$

Several assumptions are necessary in order to obtain the rate constant for the hydronium ion at each mole fraction of D_2O: (1) $k_{H_3O}/k_{D_3O} = 2.23$ and (2) $k_{HSO_4} = 1.75\ k_{H_3O}$ (this value is obtained from the hydration of styrenes assuming that k_2 for the H_2SO_4-catalyzed reaction is $k_{H_3O} + k_{HSO_4}$ and k_2 for the $HClO_4$ catalyzed reaction is k_{H_3O}).[12] Using these assumptions, the data in reference 1, and equations 1 through 3 (where M is H and/or D and x is the mole fraction of D in the solvent) a value of $k_{HSO_4}/k_{DSO_4} = 4.9$ is obtained which is in fair agreement with the value of 4.2 calculated from equation 4[6], using Brønsted $\alpha = 0.84$ and $(k_H/k_D)_{obs} = 2.23$. The

$$k_x = \frac{k_{obs}^{x} - \Sigma k_{MSO_4}(MSO_4^-)}{(M^+)} \qquad (3)$$

$$(k_H/k_D)_I = \frac{(k_H/k_D)_{obs}}{(k_H/k_D)_{II}} = \frac{(k_H/k_D)_{obs}}{2\alpha_i \log \ell} \qquad (4)$$

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* Calculated from equation 8 of reference 10.

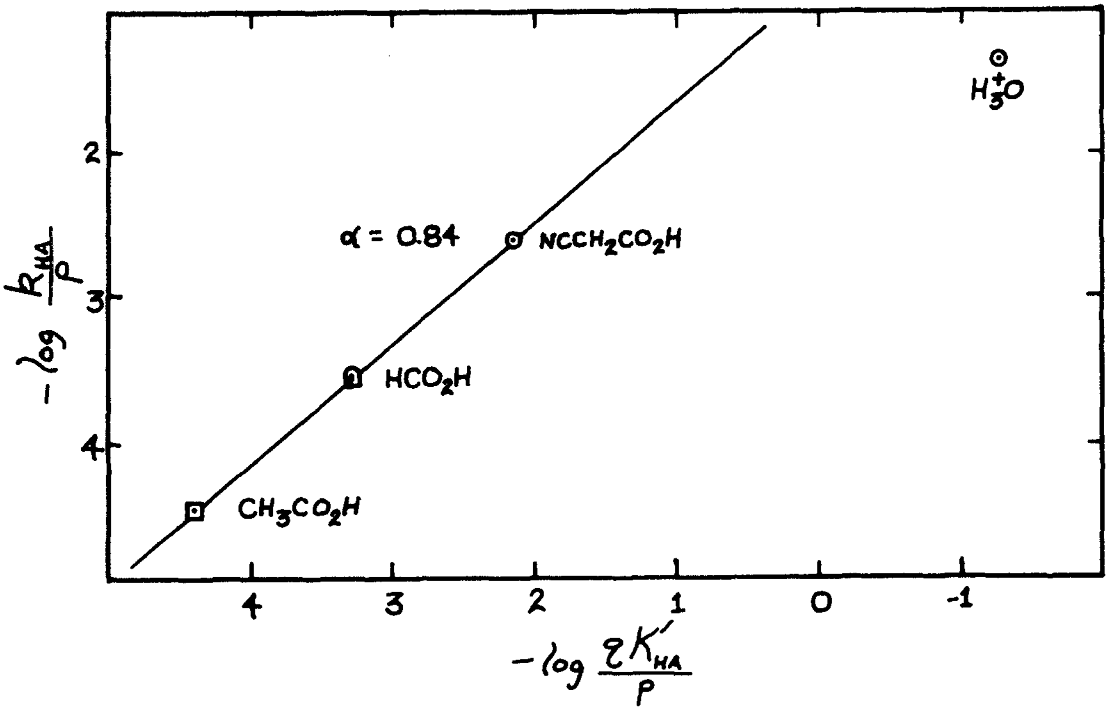

Fig. 1 Brønsted Plot for Hydration of 2-(4-Methoxyphenyl)propene. Circles refer to the present work and squares to reference 1.

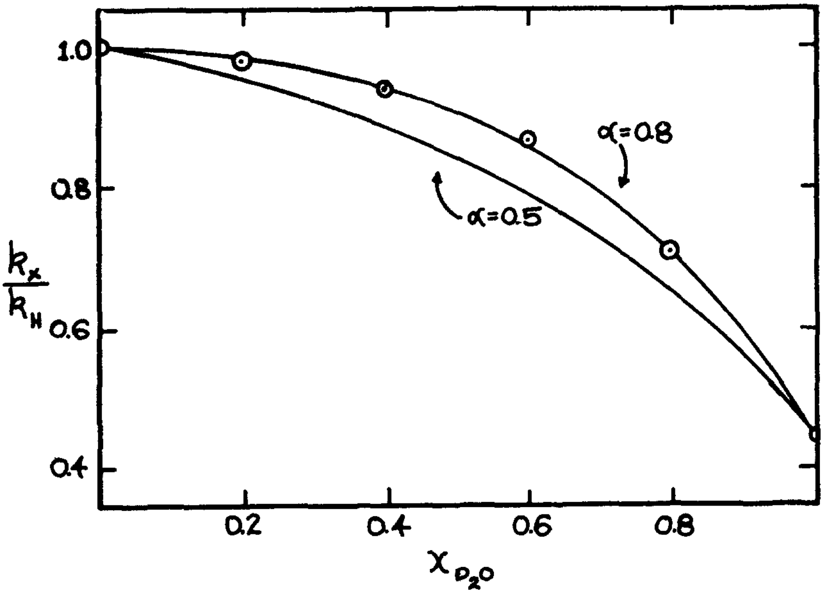

Fig. 2 Variation of Hydronium Ion-Catalyzed Hydration of 2-(4-Methoxyphenyl)propene with Solvent Composition.

values of k_X from equation 3 are plotted in Fig. 2 as k_X/k_H. The calculated ratios using the Gross-Butler equation[8] with $\alpha_i = 0.5$ and $\alpha_i = 0.8$ are given by the solid lines. (Some changes in the various rate constants arise if the k_{HSO_4}/k_{DSO_4} ratio is changed to 4.2, but this has only a small effect on the k_X/k_H ratios: α_i becomes 0.9). The agreements between the calculated and observed ratios is very good considering the assumptions made and possible uncertainties in the experimental data.

The observed ρ for the hydration of aryl substituted α-methylstyenes is -3.2 to -3.3[13,14]. The substituent effect on placing a positive charge next to an aryl group under similar conditions is $\rho = -4.0$.[15] Together these imply that the olefin has acquired a charge of +0.8 and, therefore, that the proton has been transferred to the same degree. This is consistent with the Brønsted and isotopic alpha values above.

Finally, as seen above, the choice of acids is very important when a detailed mechanistic interpretation is sought. Hence, special consideration is required in those reactions involving polybasic acids, such as sulfuric acid.

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