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Kinetics of Acid-Catalyzed Hydration of 1,3-Butadienes and Vinyl Halides. Correlation of the Reactivity of Vinyl Alkenes and Aryl Alkenes

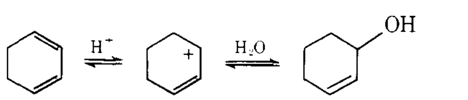
Willy K. Chwang, P. Knittel, K. M. Koshy, and Thomas T. Tidwell*

Contribution from the Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada M1C 1A4. *Received November 18, 1976*

Abstract: Rates of acid-catalyzed hydration were determined for 2-substituted 1,3-butadienes $CH_2{=}CRCH{=}CH_2$ with R = c-Pr, Me, H, and Cl. The rates could be correlated by the previously established equation $\log k_2 = -12.3\Sigma\sigma_p{}^+ - 10.1$ where $\Sigma\sigma_p{}^+$ is the sum of the $\sigma_p{}^+$ substituent constants for the vinyl group and the 2 substituent. The rate derived from literature data for R = EtO also fits the equation. The rate of the vinyl halide 2- bromopropene was also measured and found to be in good agreement with that predicted. The equation $\sigma_p{}^+(XPh) = \sigma_p{}^+(Ph) + 0.2\sigma^+(X)$ was used to derive $\sigma_p{}^+$ constants for substituted aryl groups and literature rates of hydration of 22 substituted styrenes were correlated using these values.

1,3-Dienes are one of the most useful of the functional groups in organic chemistry. The phenomenon of competing 1,2- and 1,4-electrophilic addition to the members of this series has been the object of many investigations.[1] Surprisingly, the kinetics of these reactions have received little attention.[1,2]

The kinetics of acid-catalyzed hydration of 1,3-cycloalkadienes have been found to occur by rate-limiting protonation of a double bond bond (the $A_{SE}2$ mechanism),[3] albeit with some reversal of the reaction so that some diene is present at equilibrium (eq 1). The reactivity of cyclohexadiene was es-


(1)

timated to be about 30 times that of styrene.[3a] The hydration of 1-phenyl-1,3-butadiene has also been found to proceed with rate-determining protonation at C-4, followed by formation of an equilibrium mixture of isomeric alcohols and the diene (eq 2).[4] 2-Ethoxy-1,3-butadiene (**29**) as well as methyl de-

$$\mathrm{PhCH{=}CHCH{=}CH_2} \xrightleftharpoons{\mathrm{H^+}} [\mathrm{PhCH{\cdots}CH{\cdots}CHCH_3}]^+ \xrightleftharpoons{\mathrm{H^+}} \mathrm{PhCH{=}CHCH(OH)CH_3} + \mathrm{PhCH(OH)CH{=}CHCH_3} \quad (2)$$

rivatives of this diene were reported[5a] to undergo $A_{SE}2$ protonation at C-1 in 80% acetone. In this case the reactions proceeded irreversibly to ketonic products (eq 3). Hydration of the 1-ethoxy-1,3-butadienes has also been reported.[5b]

$$\underset{\mathbf{29}}{\mathrm{CH_2{=}C(OEt)CH{=}CH_2}} \xrightarrow{\mathrm{H^+}} \mathrm{CH_3\overset{+}{C}(OEt)CH{=}CH_2} \xrightarrow{\mathrm{H_2O}} \mathrm{CH_3\overset{O}{\overset{\|}{C}}CH{=}CH_2} \quad (3)$$

We have previously had considerable success in the correlation of the rates of the $A_{SE}2$ acid-catalyzed hydration of 1,1-disubstituted alkenes (eq 4) with the sum of the $\sigma_p{}^+$ con-

$$\mathrm{R_1R_2C{=}CH_2} \underset{\text{slow}}{\xrightarrow{\mathrm{H^+}}} \mathrm{R_1R_2\overset{+}{C}CH_3} \underset{\text{fast}}{\xrightarrow{\mathrm{H_2O}}} \mathrm{R_1R_2\overset{OH}{\overset{|}{C}}CH_3} \quad (4)$$

stants for the substituents at C-1 according to

$$\log k_2 = \rho\Sigma\sigma_p{}^+ + C \quad (5)$$

where $\rho = -12.3$ and $C = -10.1$.[6] This correlation included all such alkenes for which rates were known or could be approximated in water at 25 °C, and for which the appropriate $\sigma_p{}^+$ values were available.

2-Substituted 1,3-butadienes should provide an excellent test of the validity of eq 5. The compounds may be classed as 1,1-disubstituted alkenes where one of the substituents is the vinyl group and the other can be varied over a considerable range of substituent types. A reliable $\sigma_p{}^+$ value of -0.16 for the vinyl group has recently become available,[7] so an experimental study of this important class of compounds was an attractive goal.

It also appeared desirable to seek some additional examples of 1-alkenes to further test and extend correlation 5. In particular the two least reactive compounds included in eq 5 were ethylene and styrene, and the results for these compounds were subject to difficulties in interpretation because of experimental uncertainties in the former case and some question as to the $\sigma_p{}^+$ value in the latter.[6] Also rates have not been previously reported for alkenes in which a positive charge is generated adjacent to an electron-withdrawing halogen. Therefore a representative of this class was sought to test the generality of the theory.

There is also available in the literature a large body of data

Table I. Rates of Acid-Catalyzed Hydration of 1,3-Butadienes $CH_2{=}CRCH{=}CH_2$ in H_2O at 25 °C

R	$[H_2SO_4]$, M	% H_2SO_4	H_0	H_R	k_{obsd}, s^{-1}	Log k_{obsd}[a]
H	10.57[b]	66.3[c]	−5.27	−10.55	8.29×10^{-2}	−1.081
(**28**)	9.25[b]	60.5[c]	−4.52	−9.05	7.61×10^{-3}	−2.119
	8.10[b]	55.1[c]	−3.92	−7.72	1.684×10^{-3}	−2.773
	6.85[d]	48.7[b]	−3.27	−6.38	2.85×10^{-4}	−3.545
Cl	12.35[d]	73.5[b]	−6.33	−12.40	3.70×10^{-2}	−1.431
(**27**)	10.57[b]	66.3[c]	−5.27	−10.55	3.20×10^{-3}	−2.495
	9.81[d]	63.0[b]	−4.82	−9.68	1.54×10^{-3}	−2.814
	9.25[b]	60.5[c]	−4.52	−9.05	3.53×10^{-4}	−3.452
	8.10[b]	55.1[c]	−3.92	−7.72	1.044×10^{-4}	−3.981
	6.85[d]	48.7[b]	−3.27	−6.38	4.29×10^{-5}	−4.367
Me	4.84[d]	37.2[b]	−2.21	−4.35	1.38×10^{-2}	−1.860
(**26**)	4.33[b]	33.9[c]	−1.98	−3.82	6.27×10^{-3}	−2.203
	3.85[b]	30.8[c]	−1.78	−3.36	3.68×10^{-3}	−2.434
	2.37[d]	20.4[c]	−1.03	−1.98	5.48×19^{-4}	−3.261
c-Pr	1.00[d]	9.24[b]	−0.32		3.05×10^{-2}	−1.515
(**24**)	0.80[d]	7.48[b]	−0.18		1.99×10^{-2}	−1.702
	0.50[d]	4.75[b]	0.07		1.08×10^{-2}	−1.965
	0.30[d]	2.88[b]	0.34		5.84×10^{-3}	−2.234
	0.10[d]	0.973[b]	0.87		1.65×10^{-3}	−2.784

[a] Rates were correlated by the equation $\log k_{obsd} = \gamma H_0 + \epsilon$ as follows (values of γ, ϵ, and correlation coefficient, respectively): **28** (−1.22, −7.56, and 0.999), **27** (−1.00, −7.76, and 0.992), **26** (−1.16, −4.48, and 0.998), and **24** (−1.04, −1.88, and 0.999). Correlation by the equation $\log k_{obsd} = \gamma H_R + \epsilon$ gave the respective values: **28** (−0.58, −7.29, and 0.998), **27** (−0.50, −7.75, and 0.989), and **26** (−0.59, −4.42, and 1.000). [b] Interpolated from molarity vs. percentage tables. [c] Determined by density measurements. [d] Determined by titration.

on the hydration reactivity of styrenes substituted in the aryl ring (eq 6).[8-13] These reactivities have been found to be correlated rather well by the σ^+ substituent constants, and it appeared desirable to develop a theory which could accommodate the reactivities of the alkenes with the substituents directly attached to the double bond (eq 4) and those in which the substituent was removed from the double bond by the aryl ring.

$$ArCR{=}CH_2 \xrightarrow{H^+} ArC^+RCH_3 \qquad (6)$$

Results

2-Cyclopropyl-1,3-butadiene (**24**,[14] dienes are numbered in sequence with those of the previous paper[6]) was prepared by addition of vinylmagnesium bromide[15] to cyclopropyl methyl ketone and dehydration of the resulting carbinol[16] (eq 7). 2-Phenyl-1,3-butadiene (**25**)[17] was obtained from the corresponding reactions of acetophenone. 2-Methyl- (**26**) and 2-chloro-1,3-butadiene (**27**) as well as 1,3-butadiene (**28**) itself were available commercially.

$$RC(=O)CH_3 \xrightarrow[2.\ H_2O]{1.\ CH_2=CHMgBr} CH_3C(OH)RCH{=}CH_2 \quad \mathbf{1},\ R = \text{c-Pr}$$

$$\xrightarrow[250\ ^\circ C]{MgSO_4} CH_2{=}CRCH{=}CH_2 \qquad (7)$$

24, R = c-Pr
25, R = Ph

The kinetics of the acid-catalyzed hydration of **24–28** were obtained by monitoring the decrease in the strong ultraviolet absorption of these dienes at their maxima between 219 and 229 nm. Good first-order kinetics were observed for **26–28** and are reported in Table I. In the case of the phenyl derivative **25**, the solutions became turbid and reliable rate constants were not obtained. Plots of log k for **26–28** vs. H_0 or H_R were linear; coefficients for the equation $\log k = \gamma H + \epsilon$ are given in Table I. Kinetic isotope effects were also obtained and are listed in Table II. The initial absorbance for **26–28** decreased by more than 90% during these reactions. Less than 20% methyl vinyl ketone was present in the product from **27** as shown by the UV spectra.

Table II. Solvent Isotope Effects in the Hydration of 1,3-Butadienes $CH_2{=}CRCH{=}CH_2$ at 25 °C

R	Acid	k_{obsd}, s^{-1}	k_{H^+}/k_{D^+}
H	7.62 M D_2SO_4	4.49×10^{-4}	1.8
	7.62 M H_2SO_4[a]	8.15×10^{-4}	
Me	4.57 M D_2SO_4	5.24×10^{-3}	1.8
	4.57 M H_2SO_4[a]	9.28×10^{-3}	
Cl	11.26 M D_2SO_4	5.63×10^{-4}	1.4
	11.26 M H_2SO_4[a]	7.90×10^{-3}	
c-Pr	4.25 M D_2SO_4	3.97×10^{-3}	1.2
	4.25 M H_2SO_4[a]	4.66×10^{-3}	
	0.763 M D_2SO_4	1.75×10^{-2}	1.1
	0.763 M H_2SO_4[a]	1.93×10^{-2}	

[a] Interpolated from the plot of log k_{obsd} vs. H_0.

For **24** in dilute acids the initial absorbance decreased by about 40% of the initial value and then increased until reaching a constant value that was about 80% of the original value (Figure 1). The beginning portion of the decrease followed first-order kinetics when calculated by the Swinbourne[18] method. Similarly, the subsequent increase in absorbance also followed first-order kinetics. In 0.3 M H_2SO_4 the rate constants were k_{obsd} (decrease) = $5.84 \times 10^{-3}\ s^{-1}$ and k_{obsd} (increase) = $8.05 \times 10^{-4}\ s^{-1}$. When the alcohol **1**, the expected product of the hydration, was subjected to the reaction conditions, the absorbance increased paralleling the increasing absorbance with the diene **24** as the starting material and eventually reached a comparable final absorbance. In much more concentrated acid these events were followed by a further first-order decrease in the absorbance. The rate constants for these processes are presented in Tables I–III.

The rate of hydration of 2-ethoxy-1,3-butadiene (**29**) was calculated from the reported[5a] rate in 80% acetone at 22 °C. A conversion factor $k_2(H_2O)/k_2(80\%\ \text{dioxane})$ of 22.9 has been found,[19] and the rate in 80% dioxane at 25 °C may be approximated as the reported rate in 80% acetone,[5a] inasmuch as the Y values of these solvents are almost identical.[20] The rate

Table III. Rates of Reaction of 3-Cyclopropylbuten-3-ol (**1**) and 3-Methylhexa-1,3-dien-6-ol (**3**) in Aqueous Acid at 25 °C

Reactant	$[H_2SO_4]$, M	% H_2SO_4	H_0	k_{obsd}, s^{-1}	Log k_{obsd}
1[a]	1.00[b]	9.24[c]	−0.32	4.95×10^{-3}	−2.306
	0.80[b]	7.48[c]	−0.18	3.75×10^{-3}	−2.426
	0.50[b]	4.75[c]	0.07	1.86×10^{-3}	−2.730
	0.30[b]	2.88[c]	0.34	8.55×10^{-4}	−3.068
	0.10[b]	0.97[c]	0.87	2.85×10^{-4}	−3.545
3[e]	4.33[b]	33.9[c]	−1.98	1.66×10^{-3}	−2.781
	3.85[b]	30.8[c]	−1.78	1.10×10^{-3}	−2.959
	2.98[c]	24.8[d]	−1.38	3.99×10^{-4}	−3.399

[a] k_{obsd} 0.254 M D_2SO_4 1.36×10^{-3} s^{-1}, k 0.254 M H_2SO_4 7.77×10^{-4} s^{-1} (calcd), $k_{H^+}/k_{D^+} = 0.57$. k_{obsd} 0.763 M D_2SO_4 6.60×10^{-3} s^{-1}, k 0.763 M H_2SO_4 3.26×10^{-3} s^{-1} (calcd), $k_{H^+}/k_{D^+} = 0.49$. Rates monitored at 229 nm. Correlated by the equation $\log k_{obsd} = -1.06H_0 - 2.65$, correlation coefficient 0.998. For **1** $k_2 = k_{obsd}\ (0.1\ M)/h_0 = 2.11 \times 10^{-3}\ M^{-1}\ s^{-1}$. [b] Determined by titration. [c] Interpolated from molarity vs. percentage tables. [d] Determined by density. [e] k_{obsd} 4.20 M D_2SO_4 7.28×10^{-4} s^{-1}, k 4.20 M H_2SO_4 (calcd) 1.55×10^{-3} s^{-1}, $k_{H^+}/k_{D^+} = 2.1$. Rates monitored at 229 nm. Correlated by the equation $\log k_{obsd} = -1.04H_0 - 4.83$, correlation coefficient 0.999. At $H_0 = 0.0$, $k_2 = 0.148 \times 10^{-4}\ M^{-1}\ s^{-1}$.

Table IV. Rates of Acid-Catalyzed Hydration of 2-Bromopropene in H_2O at 25 °C

$[H_2SO_4]$, M[a]	% H_2SO_4[b]	H_0	H_R	k_{obsd},[c,d] s^{-1}	Log k_{obsd}
12.09	72.5	−6.18	−12.18	6.42×10^{-3}	−2.192
11.22	69.0	−5.65	−11.26	2.16×10^{-3}	−2.666
10.57	66.3	−5.27	−10.55	9.81×10^{-4}	−3.008
9.81	63.0	−4.82	−9.68	5.04×10^{-4}	−3.298
9.10	59.8	−4.44	−8.87	1.47×10^{-4}	−3.833
8.67	57.8	−4.19	−8.38	8.26×10^{-5}	−4.083

[a] Interpolated from molarity vs. percentage tables. [b] Determined by density measurements. [c] Values of the coefficients of the equation $\log k_{obsd} = \gamma H + \epsilon$ are for H_0 −0.94, −7.96, and 0.995 (correlation coefficient); and for H_R −0.49, −8.10, and 0.996. [d] k_{obsd} 10.45 M D_2SO_4 5.02×10^{-4} s^{-1}; k_{calcd} 10.45 M H_2SO_4 7.80×10^{-4} s^{-1}; $k_{H^+}/k_{D^+} = 1.55$.

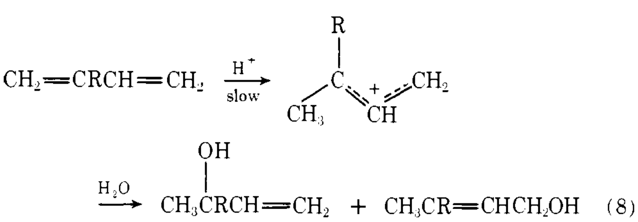
constant calculated on the basis of this assumption is 6.0 $M^{-1}\ s^{-1}$.

The rates of hydration of 2-bromopropene (**30**) were monitored by observing the disappearance of the absorption of this compound on the shoulder at 217 nm for 75% reaction. The rates are reported in Table IV. The ultraviolet spectrum of the product corresponded to that of acetone, λ_{max} 262 nm.

Discussion

In order to compare rates obtained at different acidities we have extrapolated the log k_{obsd} vs. H_0 plots to $H_0 = 0$ and defined k_2 values at that point as k_{obsd}/h_0 ($-\log h_0 = H_0$). Within the limits of utility of acidity functions,[21] we believe that this is a reasonable way to derive rate constants for structure–reactivity correlations.[22]

Mechanism of Hydration. The linear dependence of log k on H_0, the kinetic isotope effects, and the 90% or greater decrease in absorption during the reaction indicate that **26–28** are all reacting by the $A_{SE}2$ path of rate-limiting alkene protonation followed by addition of water to the allylic carbonium ion (eq 8). These reactions are analogous to other electrophilic



(8)

26, R = Me
27, R = Cl
28, R = H

additions of these dienes. For example, addition of concentrated HCl to **28** was reported[23a] to give a 65/35 ratio of

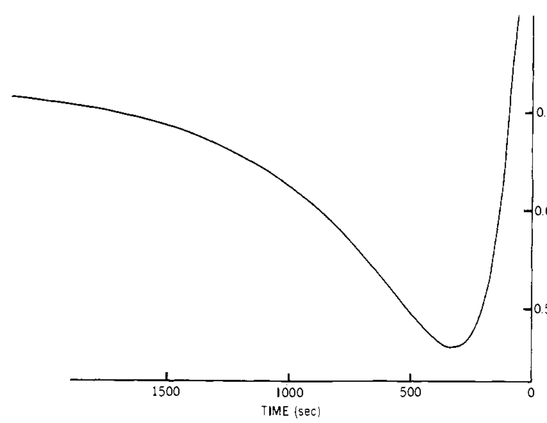


Figure 1. Reaction of CH_2=C(c-Pr)CH=CH_2 (**24**) in 0.50 M H_2SO_4.

CH_3CH=$CHCH_2Cl$ and $CH_3CHClCH$=CH_2, whereas bromination gave equal amounts of (*E*)-$BrCH_2CH$=$CHCH_2Br$ and $BrCH_2CHBrCH$=CH_2.[23b] The equilibrium mixture contained more than 90% of the 1,4-dibromo isomer under these conditions.[23b] Addition of HCl to isoprene (**26**) gave >96% Me_2CClCH=CH_2,[23c] which hydrolyzes to give mainly Me_2COHCH=CH_2.[24] Addition of halogens to chloroprene (**27**) proceeded by 1,4-addition to give $HalCH_2CCl$=$CHCH_2Hal$,[25a] and addition of HCl gave CH_3CCl=$CHCH_2Cl$, which could be hydrolyzed in 75% yield to CH_3CCl=$CHCH_2OH$.[25b] There was some evidence for formation of methyl vinyl ketone in this hydrolysis, resulting from hydration of the chlorine bearing carbon.[25b] Our measurement of the UV spectrum of the product of hydration of **27** confirms that methyl vinyl ketone can only be present in small amounts.

The hydration of **24** may be discussed in terms of Scheme I. The initial decrease in absorbance corresponds to the pro-

Table V. Correlation of the Rates of Acid-Catalyzed Hydration of Alkenes $R_1R_2C{=}CH_2$ at 25 °C

No.	R_1	R_2	$\Sigma\sigma_p^+$ [a]	k_2, $M^{-1}\ s^{-1}$ [b]	Log k_2
24	c-Pr	$CH{=}CH_2$	−0.63	0.122×10^{-1} [c]	−1.91
26	Me	$CH{=}CH_2$	−0.47	0.319×10^{-4}	−4.50
27	Cl	$CH{=}CH_2$	−0.05	0.201×10^{-7}	−7.70
28	H	$CH{=}CH_2$	−0.16	0.396×10^{-7}	−7.40
29	EtO	$CH{=}CH_2$	−0.88	6.0[d]	0.78
30	Me	Br	−0.16	0.110×10^{-7}	−7.96

[a] The values of σ_p^+ used (ref 6) are −0.47 (c-Pr), −0.31 (Me), 0.11 (Cl), −0.72 (EtO), −0.16 (vinyl), and 0.15 (Br). The value for c-Pr is slightly revised from that used previously (see footnote *a*, Table VII, ref 19). [b] Derived by extrapolation plots of log k_{obsd} vs. H_0 to H_0 = 0.0. [c] Derived from k_{obsd} (0.1 M H_2SO_4)/h_0. [d] Calculated from data in ref 5a; see text.

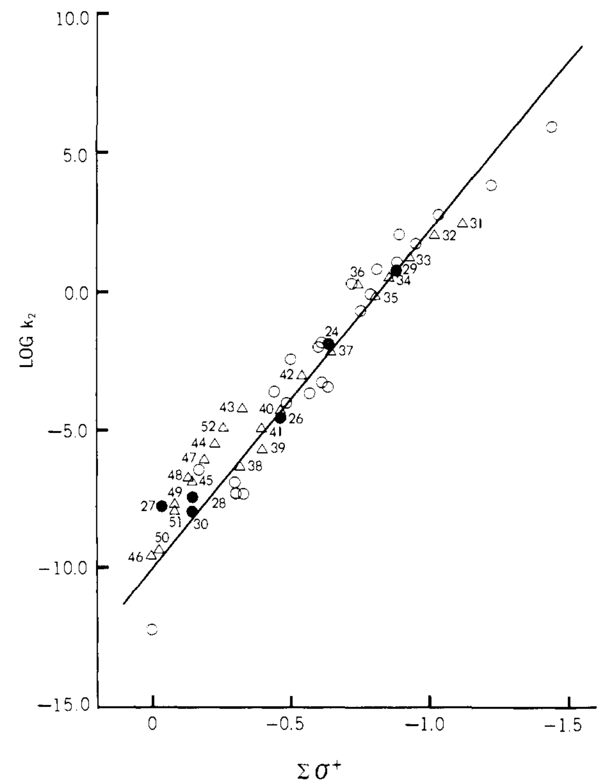
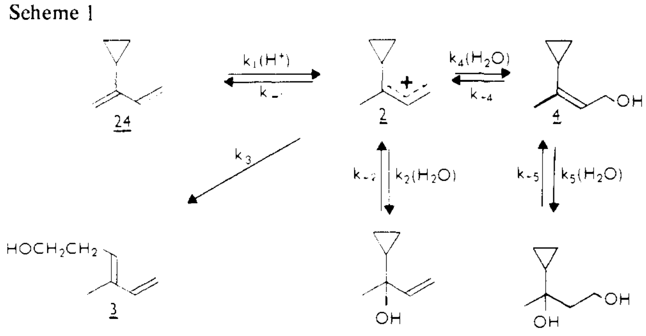


Figure 2. Hydration of 1,3-butadienes (●), 2-bromopropene (●), and substituted styrenes (△).

Scheme I

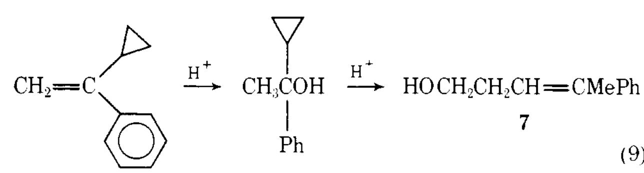


tonation of **24** to carbonium ion **2** which partitions between hydration to **1, 3,** and **4.** The initial large drop in absorbance indicates that $k_2 + k_4 > k_3$. Both **1** and **4** are known to undergo carbon skeleton rearrangement to that of **3** on treatment with HBr,[16] and, for comparison, the solvolysis rate ratio $k(Me_2C{=}CHCH_2Cl)/k(Me_2CClCH{=}CH_2)$ was estimated as 0.2.[26] Apparently $k_2 \gg k_4$, judging from the 96% 1,2-addition of HCl to isoprene (**26**).[23c] The change in the UV absorption indicates that **1** is rather quickly converted to **3** in dilute acid, and **3** is then converted to a nonconjugated product, presumably diol, in stronger acid.

The observed rate constant beginning with either **24** or **1** would be $k_{obsd} = k_{hyd} + k_{deh}$ if the further formation of **3** and **4** did not occur. As an approximation k_{obsd} is taken equal to k_1 in Table I and in the correlation of the rates, because the initial sharp decrease in absorbance indicates that $k_{hyd} > k_{deh}$. Similarly the formation of **24** during the conversion of **1** to **3** is evidently minor so the rate constant for the disappearance of **1** may be taken as $k_2k_3(k_2 + k_3)^{-1}$ (Table III). The solvent isotope effect for **24** is lower than expected for k_1, presumably because of the reversible steps. This phenomenon is under further study.

The absorption maximum of **3** has been reported[16] as 230 nm, almost exactly that which we observe for **24** (229 nm). It would be anticipated that **3** would be 2–10 times less reactive in hydration than isoprene (**26**) based on the rate effects observed for β-alkyl substituents in other alkene hydrations.[19] The rate data for **3** are given in Table III, and the rate of hydration of **3** at $H_0 = 0$ is a factor of 0.5 times that of **26.** The excellent agreement with the anticipated result provides confirmation of the validity of Scheme I.

The cyclopropylcarbinyl carbonium ion ring opening in Scheme I is of a type elucidated by Julia, and has been documented for the reaction of **1** with HBr.[16] We also observed completely analogous behavior in our previous work[6] with the structurally related α-cyclopropylstyrene (**5**), which underwent initial hydration to **6**, but this product was converted in a slower step to the ring-opened alcohol **7** (eq 9). The *Z* configuration



5 **6** **7** (9)

was assigned to **7,** and by analogy the same configuration for **3** is indicated in Scheme I. Ring openings have been reported in other electrophilic additions to vinylcyclopropanes.[27]

The acidity dependence of the rates, isotope effects, and UV spectra also indicate that hydration of 2-bromopropene (**30**) proceeds by the $A_{SE}2$ mechanism, with eventual formation of acetone (eq 10).

$$\underset{\mathbf{30}}{CH_2{=}CBrCH_3} \xrightarrow[\text{slow}]{H^+} CH_3\overset{\overset{\large Br}{|}}{\underset{+}{C}}CH_3 \xrightarrow{H_2O} CH_3\overset{\overset{\large O}{\|}}{C}CH_3 \qquad (10)$$

Correlation of the Rates. The data to test the correlation of **24** and **26–30** by eq 5 are tabulated in Table V, and the points are added to the original correlation line in Figure 2. In general it may be noted that the new points fit very well on the previous plot, and the agreement of the dienes is better than was the case with the original points that determined the line. This success of the correlation to predict the reactivity of these new types of alkenes is an impressive achievement and gives added confidence to the correctness of the reasoning behind it. Also this result adds further strong support to the proposed reaction mechanisms for hydration of the dienes (eq 8) and 2-bromopropene (eq 10).

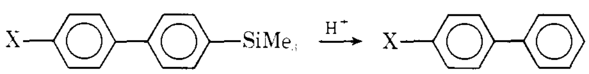
The successful correlation of **27** and **30**, with electron-withdrawing halogen substituents, is particularly impressive. These are the first rates reported for $A_{SE}2$ reactions generating carbonium ion centers adjacent to electron-withdrawing substituents.

Equation 5 may also be used to predict that chloroprene (**27**) undergoes initial protonation at C-1. The sum of the σ_p^+ constants for chloro and vinyl, appropriate for prediction of protonation at C-1, is −0.05. The σ_p^+ constant for the α-chlorovinyl group, appropriate for C-4 attack, may be approximated as that for vinyl plus the amount (0.30) by which an α-chloro changes the σ_p^+ of methyl, giving a net value of 0.14.

In order to incorporate the data for substituted styrenes into our general correlation of rates it is necessary to derive substituent constants for aryl groups as discrete substituents. We have chosen to assume that the combined effect of the aryl group is the sum of the effect of the phenyl group, unperturbed by the substituent, plus the effect of the substituent, attenuated by a transmission coefficient τ for transmission through the aryl ring (eq 11).[28]

$$\sigma_p^+(\mathrm{PhX}) = \sigma_p^+(\mathrm{Ph}) + \tau\sigma^+(\mathrm{X}) \qquad (11)$$

The value of the transmission coefficient τ in eq 11 is available independently from two different sources. Inukai[29] measured the rates of solvolysis of cumyl chlorides substituted in the para position by substituted aryl groups. When the log k/k_0 values of these solvolyses are plotted against log k/k_0 values for cumyl chloride solvolyses for the same substituent in each series a satisfactory straight line of slope 0.20, correlation coefficient 0.982, is obtained (Figure 3). It may be noted that Inukai[29] interpreted the same plot as being curved but in our view within the limits of the experimental uncertainty the line is straight. Similarly Eaborn and co-workers[30] measured the rates of protodesilylation of para-substituted biphenylyl trimethylsilanes (eq 12). The plot of log $k(p\text{-ArPhSiMe}_3)$ vs.



(12)

log $k(\mathrm{ArSiMe_3})$ is linear with a slope of 0.22. Therefore we have adopted the value of 0.2 for the transmission coefficient τ in eq 11.

The values of the substituent constants obtained by eq 11 should agree with those calculated directly from the p-arylcumyl chloride solvolyses, as was done by Inukai.[29] Our calculated values do agree with small deviations of 0.01–0.04 σ^+ units. Equation 11 has the advantage that it may be used to calculate σ_p^+ values for many aryl groups for which the rates of solvolysis of the corresponding p-arylcumyl chloride are not available.[31]

The values of the calculated substituent constants for the aryl groups and the corresponding rate constants for their hydration are given in Table VI, and the fit of the points (triangles) to the correlation line is shown in Figure 2. The rates of 22 different compounds available from the literature are accounted for in a very satisfactory fashion.

In summary eq 5 has been subjected to a stringent test with two classes of compounds, 1,3-butadienes and vinyl halides, for which rates were not heretofore available. The success in correlating the results lends more authority to the use of the equation, and also establishes the reaction mechanisms of these important compounds. In addition, derivation of σ^+ constants

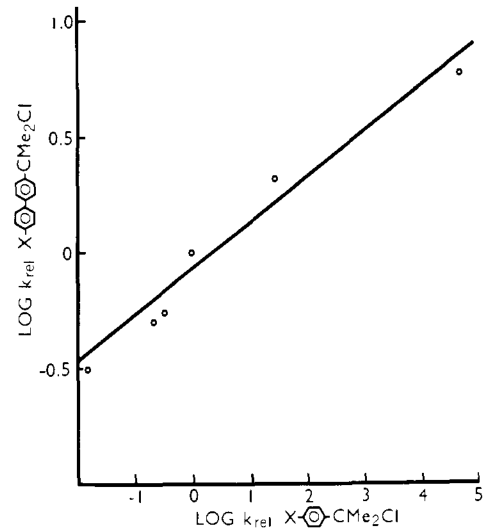


Figure 3. Solvolysis of cumyl chlorides and p-arylcumyl chlorides.

for aryl groups allows a test of the applicability of eq 5 to substituted styrenes, and these compounds are found to fit the general theory.

The most conspicuous deviation from the correlation is the point for ethylene, at $\sigma_p^+ = 0$. The rate constant for this compound at 25 °C was extrapolated[6] from 170–190 °C and we have little confidence in the validity of this extrapolation. We are attempting to measure the rate of this important compound at 25 °C, and also to redetermine some of the σ_p^+ values. When these results are available the correlation of eq 5 will be reevaluated.

Experimental Section

^{1}H NMR spectra were run using a Varian T-60 instrument in carbon tetrachloride solutions with tetramethylsilane as an internal standard. Vapor phase chromatographic (VPC) analyses and separations were carried out using a Varian-Aerograph Model 920 instrument with the columns specified.

1,3-Butadiene (28) was obtained from Matheson Coleman and Bell. **2-Methyl-1,3-butadiene (26)** was obtained from Eastman and was distilled twice, bp 34–35 °C. **2-Chloro-1,3-butadiene (27)** was obtained from Polysciences Co. as a 50% solution in xylene and was purified immediately before use by two fractional distillations through a metal helix packed column, bp 59.8 °C. **2-Bromopropene (30)** was obtained from Aldrich.

2-Phenyl-1,3-butadiene (25)[17] was obtained by first preparing vinylmagnesium bromide[15,17] by the slow addition of vinyl bromide (Aldrich, 53.0 g, 0.50 mol) dissolved in an equal weight of THF (distilled from $LiAlH_4$) to a vigorously stirred mixture of 12.0 g (0.50 mol) of Mg in 100 mL of dry THF in a flame-dried apparatus. After the reaction was initiated the vinyl bromide was added at a rate to maintain a pot temperature of 50 °C. After completion of the addition the flask was heated to 80 °C for 30 min and then cooled to 0 °C with continued stirring. Acetophenone (58.0 g, 0.48 mol) dissolved in dry THF was added dropwise and after warming to room temperature the mixture was allowed to stand overnight. The solution was then hydrolyzed with saturated NH_4Cl, extracted with ether, dried, and distilled at 12 Torr to give a mixture of 3-phenyl-3-hydroxybutene, **25**, and acetophenone. The mixture was dehydrated[14] by dropwise addition to anhydrous $MgSO_4$ heated to 250 °C with continuous distillation of the product at 12 Torr into a flask cooled to 0 °C. The diene **25** was collected from the mixture by VPC (20% 3 m × 10 mm OV-17 column on Chromosorb W at 200 °C, He 60 mL/min, retention time 5 min) and was isolated in 10% overall yield: NMR (CCl_4) δ 5.0–5.4 (m, 4, 4 vinyl H), 6.4–6.9 (m, 1, vinyl H), and 7.30 (s, 5, Ph).

2-Cyclopropyl-1,3-butadiene (24)[14] was prepared by the same procedure described for **25** using 27.5 g of methyl cyclopropyl ketone (Aldrich). Dehydration of the crude carbinol[16] mixture was carried out at 250 °C with distillation of the product at atmospheric pressure. The diene **24** was collected in 10% yield using a 1.5 m × 10 mm 40%

Table VI. Rates of Hydration at 25 °C of Styrenes $ArCR{=}CH_2$ in Aqueous Acid

No.	Ar	σ_p^{+a}	R	σ_p^+	$\Sigma\sigma_p^+$	k_2, $M^{-1}\ s^{-1}$	Log k_2	Ref
31	*p*-Anis	−0.34	OMe	−0.78	−1.12	3.83×10^2	2.58	*b*
32	*p*-Tol	−0.24	OMe	−0.78	−1.02	1.26×10^2	2.10	*b*
33	*p*-BrPh	−0.15	OMe	−0.78	−0.93	1.95×10^1	1.29	*b*
34	*p*-MeO_2CPh	−0.08	OMe	−0.78	−0.86	3.38	0.53	*b*
35	*p*-O_2NPh	−0.02	OMe	−0.78	−0.80	0.794	−0.10	*b*
36	*p*-O_2NPh	−0.02	OEt	−0.72	−0.74	1.98	0.30	*c*
37	*p*-Anis	−0.34	Me	−0.31	−0.65	8.0×10^{-3}	−2.10	*d,e*
38	*p*-O_2NPh	−0.02	Me	−0.31	−0.33	5.5×10^{-7}	−6.26	*f*
39	*p*-HO_2CPh	−0.10	Me	−0.31	−0.41	2.5×10^{-6}	−5.60	*g*
40	*p*-ClPh	−0.16	Me	−0.31	−0.47	6.1×10^{-5}	−4.21	*g*
41	*m*-ClPh	−0.10	Me	−0.31	−0.41	1.4×10^{-5}	−4.85	*g*
42	*p*-Tol	−0.24	Me	−0.31	−0.55	1.1×10^{-3}	−2.96	*g*
43	*p*-Anis	−0.34	H	0	−0.34	6.45×10^{-5}	−4.19	*h*
44	*p*-Tol	−0.24	H	0	−0.24	2.49×10^{-6}	−5.60	*h*
45	*p*-ClPh	−0.16	H	0	−0.16	1.04×10^{-7}	−6.98	*h*
46	*p*-O_2NPh	−0.02	H	0	−0.02	4.93×10^{-10}	−9.31	*i*
47	*m*-MePh	−0.20	H	0	−0.20	9.77×10^{-5}	−6.01	*j*
48	*p*-BrPh	−0.15	H	0	−0.15	0.200×10^{-6}	−6.70	*j*
49	*m*-ClPh	−0.10	H	0	−0.10	0.229×10^{-7}	−7.64	*j*
50	*m*-O_2NPh	−0.05	H	0	−0.05	0.525×10^{-9}	−9.28	*j*
51	*m*-BrPh	−0.10	H	0	−0.10	0.182×10^{-7}	−7.74	*j*
52	*p*-c-PrPh	−0.27	H	0	−0.27	0.147×10^{-4}	−4.83	*k*

[a] Calculated from the formula $\sigma_p^+(XPh) = 0.2\sigma^+(X) + \sigma_p^+(Ph)$. [b] Rates for **31-35** obtained under different conditions (ref 11) were adjusted using a relative rate factor for a common substrate. Rates at 29.9 °C in 5% dioxane were approximated to 25 °C in pure H_2O by the factor 54.5/175 where 54.5 and 175 $M^{-1}\ s^{-1}$ are the rate constants for $PhCOMe{=}CH_2$ reported at 25 °C in *c* and 29.9 °C in ref 11, respectively. The validity of these conversions is confirmed by the fact that when the rate of **36** is multiplied by the MeO/EtO rate factor of 0.39 (footnote *i*, Table IV, ref 19) the resulting rate constant of 0.77 $M^{-1}\ s^{-1}$ is in excellent agreement with that reported for **35**. [c] Reference 10. [d] Average of the value $9.0 \times 10^{-3}\ M^{-1}\ s^{-1}$ from *e* and the value of $7.0 \times 10^{-3}\ M^{-1}\ s^{-1}$ calculated from ref 8 using the h_0 value of 0.129 for the experimental determination in 0.102 M $HClO_4$. [e] k_2 from ref 9 calculated by dividing k_{obsd} by the value of h_0 of 0.79 for the experimental determination in 4.8% H_2SO_4. [f] Reference 9; data at higher acidities extrapolated to $H_0 = 0$. [g] Reference 9; data not available to extrapolate to $H_0 = 0$ so k_{obsd} for the experimental determination in 20.2% H_2SO_4 divided by the h_0 value of 11 for that acidity. [h] Average of values extrapolated to $H_0 = 0$ from ref 8 and 12. Respective k_2 ($M^{-1}\ s^{-1}$) values follow: **43**, 6.90 and 6.0×10^{-5}; **44**, 1.59 and 3.39×10^{-6}; and **45**, 0.418 and 1.66×10^{-7}. [i] Reference 8, extrapolated to $H_0 = 0.0$. [j] Reference 12, extrapolated to $H_0 = 0.0$. [k] Reported $k_{obsd} = 7.04 \times 10^{-4}\ s^{-1}$ (L. B. Jones and S. S. Eng, *Tetrahedron Lett.*, 1431 (1968)) in 3.83 M $HClO_4$ (31.7%), $H_0 = -1.68$ (K. Yates and H. Wai, *J. Am. Chem. Soc.*, **86**, 5408 (1964)), $h_0 = 48$, $k_2 = 1.47 \times 10^{-5}$.

$AgNO_3$-ethylene glycol column[32] at 50 °C, He 60 mL/min, retention time 10 min: NMR (CCl_4) δ 0.4–1.0 (m, 4, CH_2CH_2), 1.2–1.7 (m, 1, CH of c-Pr), 4.9–6.7 (m, 5, vinyl H).

Kinetics. Acid solutions were prepared by diluting concentrated H_2SO_4 with distilled water. Acid strengths were determined either by measurements of densities or by titration with standard NaOH. Deuterated acid solutions were prepared by dilution of concentrated D_2SO_4 (Aldrich) with D_2O.

Kinetic measurements were made using Cary 14 or 118 instruments. Sufficient diene was dissolved in 95% EtOH (gaseous 1,3-butadiene was bubbled in until a sufficient quantity dissolved) to give about 10^{-2} M solutions and 5–10 μL of the solution was injected into 1 cm UV cells containing 3 mL of acid solution thermally equilibrated in the spectrometer. After thorough shaking the decrease in absorbance was observed as a function of time. The initial absorbances near 0.8 decreased to less than 0.1 at 10 half-lives. Rate constants were calculated from the expression $k_1t = \ln (A_0 - A)/(A_0 - A_\infty)$ and gave good first-order kinetics over 75% reaction. Reactions were monitored at the UV maximum of each diene: **24**, 229; **25**, 222; **26**, 225; **27**, 220; and **28**, 219 nm.

In the case of 2-phenyl-1,3-butadiene (**25**) turbidity developed in the solution during one reaction, even when the initial diene concentration was reduced by 90%. The absorbance increased for several minutes after mixing, then decreased, and on longer reaction times increased somewhat and then decreased again. Good first-order kinetics could not be derived for any portion of the reaction so further study of this compound was deferred.

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(22) The ideal conditions for rate comparisons are solutions of dilute acid in which the k_{obsd} values are directly dependent on $[H^+]$. However, the rates of many of the less reactive compounds are too low to be measured accurately under such conditions and are instead measured in stronger acids. Plots of log k_{obsd} vs. the acidity functions H_0 or H_R[21] have given reasonable straight lines, but the slopes of these plots are usually not unity. As a result conversion of the k_{obsd} values to k_2 by use of the relation $k_2 = k_{obsd}/h$ (−log $h = H$) gives different values of k_2 for different values of H. Extrapolations of k_{obsd} to lower values of acidity and then calculation of k_{obsd}/h still makes k_2 a function of the particular value of acidity chosen for the extrapolation. The extrapolation of the k_{obsd} vs. H plots can also introduce errors, either if the linear relation between the two is not exact within the experimentally observed range or if it changes outside the observed range. Plots of log k vs. H should have slopes of −1.0 at low acidities where the pH and H scales merge, but at higher acidities the magnitudes of these slopes usually are different from unity. In cases where the rates cannot be measured reliably at low acidity it cannot be determined where the scales merge, and the value of H to which k_{obsd} is extrapolated to determine k_2 is therefore rather arbitrary. Fortunately the values obtained by extrapolations to the region $H_0 = -1$ to $+1$ do not differ greatly. For example, k_2 values for ten substituted styrenes calculated by this method are larger for the higher acidity by factors of between 1.4 and 3.6.[12] These differences are significant but are small over the total range of substrate reactivity examined. The relationship between the acidity functions H_0 and H_R has been examined (A. J. Kresge, H. J. Chen, and Y. Chiang, *J. Chem. Soc., Chem. Commun.*, 969 (1972)) for hydrochloric and perchloric acids. It was found that in decreasingly acidic solutions down to values of about −1.0 these functions were linearly related, but that the relationship between the acidity functions was then curved to a value of about 1.0, at which point the functions each became equal to pH. Because of the extensive curvature at lower acidities it was concluded that linear extrapolations from higher acidities could not safely be carried beyond $H = 0$. The H_0 scale for sulfuric acid was also found to be almost equivalent to the pH scale at a value of about 1.0.

We have elected to use $H_0 = 0.0$ as a reasonable point of extrapolation based on its nearness to the region where the H_0 scale merges with pH, and its closer proximity to the range of experimental observations than some lower acidity. Because we have found little to choose between the use of H_0 or H_R functions we have based our extrapolations on the former. In those cases where the variation of the rate with acidity has not been determined we have used the relation $k_2 = k_{obsd}/h_0$ for the particular acidity studied. There is some inconsistency in k_2 values obtained this way; in particular the adoption of H_R as the standard for extrapolation, or a different acid strength as the point of extrapolation, would give different values of k_2. However, these variations are usually small compared to the overall range of reactivity examined, and the rates are very useful for comparative purposes, especially when the log k_{obsd} vs. H_0 slopes are near unity.

The most severe problem is with relatively unreactive compounds that have steep slopes of log k_{obsd} vs. H_0. The long extrapolations with a strong dependence of rate on acidity can cause large changes in rates relative to compounds with more gentle slopes. In the present series 1,3-butadiene (**28**) has a steeper slope than the other compounds, and the ratio k(**28**)/k(**27**) decreases from 26 at $H_0 = -5.27$ to 2.0 at $H_0 = 0$. This is the only extreme divergence in this group but illustrates that care is needed in the interpretation of small rate differences.

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Acid-Catalyzed Hydrolysis of Vinyl Phosphates and Vinyl Acetates. The Substituent Effects of Diethyl Phosphoryloxy and Acetoxy Groups

Sonia Y. Attia,[1a] James P. Berry,[1b] K. M. Koshy, Y.-K. Leung,[1a] E. P. Lyznicki, Jr., V. J. Nowlan, Kiyotaka Oyama, and Thomas T. Tidwell*

Contribution from the Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada M1C 1A4, and Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.

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Abstract: The rates of hydration of diethyl α-substituted vinyl phosphates ($(EtO)_2PO_2CR{=}CH_2$, R = H, Me, c-Pr, and EtO) and α-substituted vinyl acetates ($AcOCR{=}CH_2$, R = c-Pr and EtO) in aqueous acid at 25 °C have been determined. The rates, solvent isotope effects, isotopic labeling studies, and acidity dependence of the rates are consistent with the $A_{SE}2$ mechanism of rate-determining protonation on carbon. Electrophilic substituent parameters (σ_p^+) have been determined for the groups diethyl phosphoryloxy and acetoxy as −0.13 and −0.06, respectively. Use of these substituent parameters allows the correlation of the rates of these vinyl esters by the equation $\log k_2 = \rho\Sigma\sigma_p^+ + C$. In addition the rates of 11 other vinyl esters available in the literature can also be included in the correlation.

Vinyl phosphates and vinyl acetates are two of the most important classes of alkenes. Vinyl phosphates are critical intermediates in a variety of metabolic pathways, and also are widely used as insecticides. Vinyl acetates are important synthetic intermediates and are extensively used in the preparation of polymers.

The hydrolysis mechanisms of vinyl phosphates and vinyl acetates have been established in some detail. By a variety of mechanistic criteria vinyl phosphates of the type $RC(OPO_3Et_2){=}CH_2$ have been shown to react in acid by the $A_{SE}2$ mechanism of rate-determining protonation of the double bond followed by addition of water with C–O bond cleavage (eq 1).[2-6] Vinyl acetates react through the same mechanism when

$$RC(OPO_3Et_2){=}CH_2 \xrightarrow[\text{slow}]{H^+} R\overset{+}{C}(OPO_3Et_2)CH_3$$

$$\xrightarrow{H_2O} RC(\overset{+}{O}H_2)(OPO_3Et_2)CH_3 \longrightarrow R\overset{O}{\overset{\|}{C}}CH_3 + (EtO)_2PO_2H \quad (1)$$

the group R is electron donating, but when R is electron withdrawing react by the normal $A_{AC}2$ mechanism of ester hydrolysis (eq 2).[7,8]