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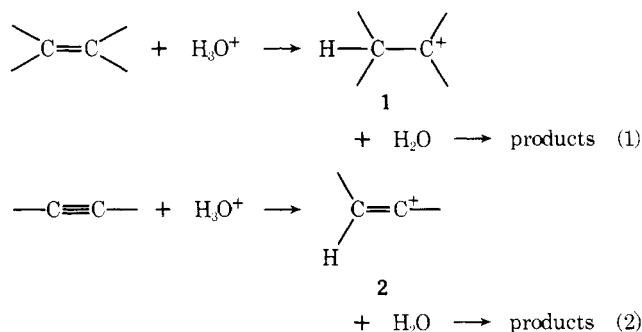
Reactions in Moderately Concentrated Acids. 2.¹ Solvation Effects in the Acid-Catalyzed Hydration of Olefins and Acetylenes

Giorgio Modena, Franco Rivetti, Gianfranco Scorrano, and Umberto Tonellato*

Contribution from the Istituto di Chimica Organica and Centro CNR
Meccanismi di Reazioni Organiche, Università di Padova,
35100 Padova, Italy. Received May 3, 1976

Abstract: Rate data for the hydration of substituted styrenes and phenylacetylenes and of *trans*-3-hexene and 3-hexyne in moderately concentrated aqueous sulfuric acid solutions have been analyzed in terms of the proper linear free energy relationship (for $A_{SE}2$ type mechanisms) discussed in the previous paper. The analysis indicates that the solvation requirements of the transition states of the reaction and hence of the corresponding carbonium ions and vinyl cations are rather modest and closely similar for analogous pairs of olefins and acetylenes. It also appears that the substituent effects within the series of both styrenes and phenylacetylenes increase on going toward more concentrated acid solutions.

Ethylene derivatives undergo hydration in moderately concentrated acids at similar or slower rates than the corresponding acetylene derivatives;² typical $k_{olefin}/k_{acetylene}$ (k_o/k_a) ratios range between 3.6 (1-hexene/1-hexyne, 48.7% H_2SO_4), 0.7 (styrene/phenylacetylene 48.7% H_2SO_4), and 10^{-2} (ethoxyethylene/ethoxyacetylene in aqueous buffers⁵). Clear evidence has been reported,⁶ particularly for styrene⁷ and phenylacetylene⁴ derivatives, that in both cases the hydration mechanism involves a slow proton transfer to the unsaturated reagent (eq 1 and 2) and that the transition states of the reactions closely resemble⁸ the cationic intermediates, carbonium ions **1** and vinyl cations **2**.



The reactivity ratios k_o/k_a observed in hydrations are much lower than those observed for other electrophilic additions,⁹ notably for brominations and chlorinations (10^3 – 10^6 in acetic acid^{3,10}).

The question is then why analogous carbonium ions and vinyl cations (the former are estimated^{2b-d} more stable by 10–20 kcal mol⁻¹ than the latter) are generated with equal or greater ease in hydrations and not in halogen additions. Recently, Yates and co-workers³ turned their attention to the solvent effect on the relative reactivities of olefins and acetylenes and suggested that the low k_o/k_a ratios for acid-catalyzed hydrations could be the result of a much higher solvent stabilization of vinyl cations than that of carbonium ions.

As discussed in the accompanying paper,¹¹ the ϕ_{\pm} value obtained from the analysis of rate data for the hydration reactions through the proper (for A_{SE}2 mechanisms) linear free energy relationship (eq 3) is a measure (eq 4) of the change of the activity coefficient ratio, f_{\pm}/f_S , and hence of the solvation requirements of the transition state.

$$\log k_{\psi} + H_0 = \phi_{\pm}(H_0 + \log [H^+]) + \log k_0 \quad (3)$$

$$\left(\log f_{H^+} - \log \frac{f_{\pm}}{f_S}\right) = (1 - \phi_{\pm}) \left(\log f_{H^+} - \log \frac{f_{BH^+}}{f_B}\right) \quad (4)$$

Therefore, from the ϕ_{\pm} parameters for the hydration of pairs of analogous olefins and acetylenes, we may verify the hypothesis of possible differences in solvation energy between carbonium ions and vinyl cations.

Results

We have measured the rate of hydration of phenylacetylene and its *p*-chloro, *p*-methyl, and *p*-methoxy derivatives in aqueous sulfuric acid solutions by following the disappearance of the substrate and/or the appearance of the corresponding acetophenone derivative.^{4,12} The rates of hydration of *trans*-3-hexene and 3-hexyne have been measured for H₂SO₄ solutions containing 2% methanol by monitoring the disappearance of the substrate. Methanol has here been added to increase the otherwise too low solubility of the substrate. The observed rate constants are in Table I; see paragraph at end of paper regarding supplementary material.

The rates of hydration of phenylacetylenes have been compared to those of styrenes reported by Coussemant and co-workers¹³ for H₂SO₄ solutions containing 1% methanol or ethanol. Such a limited amount of added alcohol is no cause of concern since we have proven that the hydration rate of styrene in 39.2 and 48.5% H₂SO₄ with and without 1% added methanol was identical within the experimental error.

Table II shows the slope and intercept parameters resulting from the application of eq 3 to the kinetic data of Table I as well as to those reported for styrene derivatives using recent¹⁴ H_0 values.

The activity coefficients of styrene and phenylacetylene have been measured by the distribution method.¹⁵ The following values ($\log f_S$) were obtained for styrene and phenylacetylene at the H₂SO₄ (%) concentrations indicated in parentheses: 0.15, 0.12 (9.92); 0.29, 0.29 (19.95); 0.39, 0.37 (29.98); and 0.45, 0.43 (40.00). In the range of acidity explored both substrates are mildly salted out at a similar extent (within the experimental error, 5–6%), the behavior closely resembling that of benzene.¹⁶

In complementary experiments we have also measured the rate of addition of trifluoroacetic acid (TFA) to both styrene and phenylacetylene in carbon tetrachloride (0.80 M at 25 °C), by an NMR technique. The second-order rate constants (M⁻¹ s⁻¹) are $3.6 \pm 0.1 \times 10^{-6}$ for styrene and $4.6 \pm 0.2 \times 10^{-6}$ for phenylacetylene and the primary product was in both cases the expected 1:1 adduct.

Table II. Correlation with Acidity (eq 3) of the Rates of Hydration of Olefins and Acetylenes^a

Substrates	ϕ_{\pm}^b	$-\log k_0^b$	n^c
XC ₆ H ₄ C≡CH			
X = <i>p</i> -OMe	-0.67 ± 0.08	3.67 ± 0.03	8
<i>p</i> -Me	-0.58 ± 0.05	5.25 ± 0.06	5
H	-0.44 ± 0.05	6.55 ± 0.10	7
<i>p</i> -Cl	-0.29 ± 0.04	6.85 ± 0.11	6
XC ₆ H ₄ CH=CH ₂ ^d			
X = <i>p</i> -OMe	-0.54 ± 0.03	4.38 ± 0.03	9
<i>p</i> -Me	-0.34 ± 0.03	5.50 ± 0.04	7
<i>m</i> -Me	-0.22 ± 0.08	6.10 ± 0.17	5
H	-0.31 ± 0.04	6.60 ± 0.06	7
<i>p</i> -Cl	-0.28 ± 0.03	6.95 ± 0.10	6
<i>p</i> -Br	-0.20 ± 0.08	6.80 ± 0.18	5
<i>m</i> -Cl	-0.11 ± 0.06	7.56 ± 0.12	7
<i>m</i> -Br	-0.13 ± 0.07	7.69 ± 0.24	5
<i>m</i> -NO ₂	-0.05 ± 0.01	8.67 ± 0.06	8
EtC≡CEt ^e	-0.25 ± 0.04	8.30 ± 0.06	10
<i>trans</i> -EtCH=CH ^e	-0.34 ± 0.02	7.55 ± 0.08	5

^a In aqueous H₂SO₄ at 25 °C. ^b ϕ_{\pm} and $\log k_0$ are the slope and intercept (with the standard deviation calculated from least-squares analysis) of the plot ($\log k_{\psi} + H_0$) vs. ($H_0 + \log [H^+]$); see eq 3. ^c Number of points. ^d 1% methanol or ethanol added. ^e 2% methanol added.

Discussion

Medium Effects. The ϕ_{\pm} values obtained for the hydration of the five pairs of analogous olefins and acetylenes listed in Table II are closely similar and mostly identical within the estimated error. Therefore, for each pair considered, the changes in the activity coefficient ratios, f_{\pm}/f_S (see eq 4), with changing acidity of the medium are equal. Moreover, it has been verified for styrene and phenylacetylene that the corresponding changes of the substrate activity coefficients, f_S , are identical and rather modest as expected for neutral species.¹⁵ Hence, one must conclude that the solvation requirements of the transition states for the hydration of analogous olefins and acetylenes are virtually the same.

Further support to the above main conclusion is given by the observation that the k_o/k_a ratio for styrene and phenylacetylene, which lies between 0.60 and 0.75 in the range of aqueous sulfuric acid actually explored, is still ca. 0.8 in the addition¹⁷ of TFA in a quite different medium such as carbon tetrachloride. Similarly, the k_o/k_a ratios for the pairs *trans*-3-hexene/3-hexyne and 1-hexene/1-hexyne³ are ca. 9.0 and 3.6 in 48% H₂SO₄ at 25 °C and 2.6 and 5.2 in the addition of TFA (in TFA at 60 °C¹⁸), respectively.

Such insensitivity of the relative rate factors to solvent effects is not entirely surprising since carbon cations are not strongly solvated by specific interactions with water. The ϕ_c slope parameters¹¹ for equilibria involving diarylmethyl and triaryl carbonium ions as acidic terms are in the range -0.7 to -1.6 and the estimated¹⁸ free energy of transfer of carbonium ions of various structures from gas phase to water is very small.

Substituent Effects. In the series of both styrenes and phenylacetylenes the slope parameters (see Table II) decrease steadily on going from electron-withdrawing to electron-donating substituted terms. By substituting the correlation of eq 3 for the k_{ψ} s into the Hammett $\rho\sigma^+$ correlation, $\rho = (\log k_{\psi}^s - \log k_{\psi}^u)/\sigma^+$, one obtains

$$\rho = \rho_0 + \frac{\phi_{\pm}^s - \phi_{\pm}^u}{\sigma^+} (H_0 + \log [H^+]) \quad (5)$$

where the superscripts s and u refer to substituted and unsubstituted terms and $\rho_0 = (\log k_0^s - \log k_0^u)/\sigma^+$ is the reaction constant at infinite acid dilution. For styrenes eq 5 be-

comes $\rho = -3.0 (\pm 0.1) + 0.3 (\pm 0.08) (H_0 + \log [H^+])$ using²⁰ σ^+ . For phenylacetylenes a numerical definition of eq 5 is prevented by the few terms considered, although both ρ_0 and $(\phi_{\pm}^s - \phi_{\pm}^u)/\sigma^+$ are apparently larger (close to -3.5 and 0.35 , respectively) than in the case of styrenes. Although less precise than desirable, these values are a measure of the rate of increase of the negative ρ value with increasing acid concentration and serve as a warning against comparing ρ values as a mechanistic tool for acid-catalyzed reaction without taking into account their acidity dependence.

The sensitivity of the ϕ_{\pm} parameters to substituent effects may somehow reflect a different position of the transition states of the variously substituted terms along the reaction coordinate. However available evidence in terms of Brønsted α values⁴ and of solvent isotope effects⁸ accords with the idea that the proton is largely transferred to the substrate in the transition states and therefore the effect of substituents should not be very important in this respect. Very likely the main factor involved is the degree of charge dispersal into the transition state structure: the more fully delocalized the lower the ϕ_{\pm} slope parameters. Such trend is also manifest in the ϕ_c parameters of acid–base equilibria involving substituted aryl ketones²¹ and triphenylcarbinols²² as bases, and it may be somehow related to the fact that the ρ values for rate and equilibria of organic reactions are magnified²³ by factors as large as 10 on going from water to gas phase.

By the same reasoning, the increasingly larger negative ρ values for phenylacetylenes than styrenes with increasing acid concentrations is likely to be the result of a more effective conjugative interaction of the positive carbon with the aromatic ring in vinyl cations than in carbonium ions due to a shorter $C_{sp}-C_{Ar}$ than $C_{sp^2}-C_{Ar}$ bond.^{2b-d} In fact, the k_o/k_a ratios decrease from ca. 0.7 to 0.1 and 0.01 on going from phenyl to *p*-methoxyphenyl and to ethoxy 1-substituted ethylenes and acetylenes.

Conclusions

The treatment here applied to the rates of hydration of olefins and acetylenes allows a satisfactory definition of the medium effects and a safe appreciation of even subtle differences in behavior among the various substrates.

Indeed, we may conclude that solvation is not the factor capable of equalizing the ease of formation of carbonium ions **1** and vinyl cations **2** by protonation of analogous olefins and acetylenes at least in the case of the substrates here examined. The difference in stability between **1** and **2** must be compensated for by other factors such as the greater strength of the “double” than that of the “triple” bond being broken in the addition.^{2b-d}

The high k_o/k_a ratios in halogen additions are then to be explained. Although several factors may be involved, a major role is likely to be played by the different stabilities and properties of the bridged structures²⁴ in the transition states of the halogenation of alkenes and alkynes.

Experimental Section

Materials. Phenylacetylene, styrene, *trans*-3-hexene, and 3-hexyne were commercial products purified by fractional distillation under reduced pressure. *p*-Chlorophenylacetylene, mp 45 °C (lit.²⁵ 43–44 °C), *p*-methylphenylacetylene, bp 79–81 °C (30 mm) (lit.²⁶ 79–82 °C (31–33 mm)), and *p*-methoxyphenylacetylene, mp 27–28 °C (lit.²⁷ 29 °C), were prepared by literature methods and purified by standard procedures.

Kinetics. The acid concentration of each solution was determined in duplicate or triplicate by density measurements or by titration. The kinetic solutions of phenylacetylenes were typically prepared by dissolving the approximate weight of substrate into 50 mL of the proper deaerated acid solutions under vigorous stirring for 15 s to 3 min. After standing for a short time the solution was then transferred by aid of a pipet into the cuvette and the changes in absorbance monitored. The

solutions thus obtained were $1\text{--}3 \times 10^{-5}$ M as measured from the absorbance of the acetophenone derivative⁴ at the end of the reaction.

The kinetic solutions of *trans*-3-hexene and 3-hexyne were obtained by adding 0.200 mL of a methanol (0.04 M) solution of the substrate into 10 mL of the acid solution with stirring. Absorbance changes of the resulting solution were measured at 195 nm.

The addition of trifluoroacetic acid to phenylacetylene and to styrene was followed for equimolar (0.80 M) solutions of acid and substrate in carbon tetrachloride. Changes in the integral ratios of the proper NMR signals of reactants and products were recorded after convenient interval times. In the case of phenylacetylene the only detectable product up to 15–20% conversion was the 1-phenylvinyl trifluoroacetate from its IR spectrum;²⁸ NMR δ 5.26 and 5.62 (two d, $J = 2.8$ Hz) and 7.4–7.5 (m). As the reaction proceeded further, acetophenone (NMR δ 2.70 (s), 7.4–7.5 (m), and 7.9–8.1 (d)) was also observed, presumably deriving from slow decomposition of the vinyl trifluoroacetate.²⁹ In the case of styrene, the only product observed was the 1-phenylethyl trifluoroacetate, from its IR³⁰ spectrum: NMR δ 1.66 (d, $J = 6.2$ Hz), 6.03 (q, $J = 6.1$ Hz).

Activity Coefficients Measurements. Activity coefficients for phenylacetylene and styrene were determined by the distribution method using a double extraction technique.³¹ Three milliliters of a 1.8×10^{-2} M solution of the substrate in cyclohexane was stirred mechanically with 25 mL of water or sulfuric acid solutions for 3 min in a thermostated (25 ± 0.1 °C) separatory funnel. After 30 s of standing, the aqueous layer was separated and 10 mL of it was shaken with 10 mL of cyclohexane for 1 min. Two milliliters of the organic layer was pipetted in the UV cell and the absorbance spectrum recorded in the region 236–246 nm (phenylacetylene) and 243–248 nm (styrene). The activity coefficients were obtained from the ratio of the absorbance recorded for water and the given acid solutions. Reproducible data within the estimated error ($\pm 5\text{--}6\%$) were obtained using a 8×10^{-2} M cyclohexane solution and different shaking periods (2–6 min) in the first extraction.

Supplementary Material Available: Rates of hydration of acetylene derivatives (Table I) (2 pages). Ordering information is given on any current masthead page.

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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

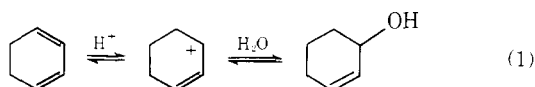
Willy K. Chwang, P. Knittel, K. M. Koshy, and Thomas T. Tidwell*

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

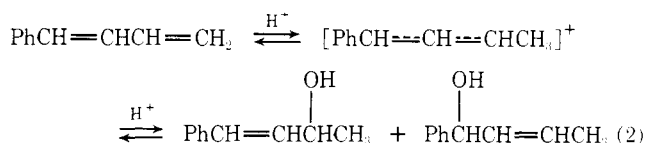
Abstract: Rates of acid-catalyzed hydration were determined for 2-substituted 1,3-butadienes $\text{CH}_2=\text{CRCH}=\text{CH}_2$ with $\text{R} = \text{c-Pr}$, Me , H , and Cl . The rates could be correlated by the previously established equation $\log k_2 = -12.3\Sigma\sigma_p^+ - 10.1$ where $\Sigma\sigma_p^+$ is the sum of the σ_p^+ substituent constants for the vinyl group and the 2 substituent. The rate derived from literature data for $\text{R} = \text{EtO}$ 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 $\sigma_p^+(\text{XPh}) = \sigma_p^+(\text{Ph}) + 0.2\sigma^+(\text{X})$ was used to derive σ_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}

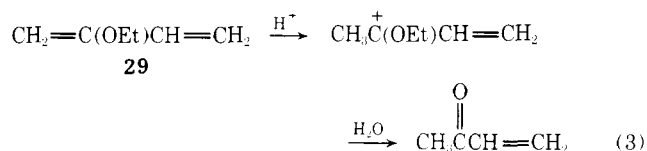
The kinetics of acid-catalyzed hydration of 1,3-cycloalkadienes have been found to occur by rate-limiting protonation of a double bond (the $\text{A}_{\text{SE}2}$ mechanism),³ albeit with some reversal of the reaction so that some diene is present at equilibrium (eq 1). The reactivity of cyclohexadiene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



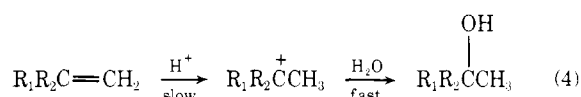
timated to be about 30 times that of styrene.^{3a} The hydration of 1-phenyl-1,3-butadiene has also been found to proceed with rate-determining protonation at C-4, followed by formation of an equilibrium mixture of isomeric alcohols and the diene (eq 2).⁴ 2-Ethoxy-1,3-butadiene (**29**) as well as methyl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



derivatives of this diene were reported^{5a} to undergo $\text{A}_{\text{SE}2}$ 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}



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



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 σ_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 σ_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 σ_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