pK_a Studies. The pK_a of acids 16-COOH and 17-COOH was taken by dissolving 0.30 mmol of acid in 50% ethanol (50 mL, 1:1 absolute ethanol-distilled water, v/v) and titrating with 0.05 N aqeuous sodium hydroxide at 29 °C while the pH was measured vs. increments of base added. The pK_a was obtained from the pH at the half-neutralization point. Results are given in Table I.

Kinetic Studies. Standard procedures were followed for the acetolysis studies. Standardized 0.05 M sodium acetate in glacial acetic acid containing 0.3% acetic anhydride was the solvent, with a tosylate concentration of 0.025 M. Aliquots (2 mL) were sealed in ampules and heated to the reaction temperature. The excess sodium acetate was back-titrated in the ampule with standard 0.014 *p*-toluenesulfonic acid in acetic acid with bromophenol blue indicator (yellow to colorless end point). The first-order plots were linear to at least 66% completion. All correlation coefficients were at least 0.993. Results are given in Tables II and III.

Acetolysis Products. Tosylates 16-CH_2OTs and 17-CH_2OTs were studied by dissolution in acetic acid with 2 equiv of anhydrous sodium acetate and refluxing for a number of half-lives. Water was added, and the products were extracted with ether. The combined ether layer were washed with 10% sodium bicarbonate, water, and brine. The resulting solution was dried with anhydrous magnesium sulfate and filtered, and the filtrate was rotary evaporated. The products are shown in Table IV.

For the products of bicyclooctyl tosylate 17-CH_2OTs, gas chromatography (SE-30, 170 °C) showed three possible product peaks in a 6.5:91.4:2.1 ratio. These were collected together (SE-30, 220 °C) and analyzed by NMR, which showed that all major absorptions were in the range δ 1.2-2.4, including the acetate sharp singlet at δ 1.80, indicating that bridgehead acetate **20** was the major product. A very small trace absorption as a singlet at δ 3.80 was interpreted as the carbinyl methylene of unrearranged acetate 17-CH_2OAc. The trace third product, if indeed an acetate, was not determined. Although the alcohol corresponding to rearranged acetate **20** has been reported[26,27] as the hydrolysis product of 17-CH_2OTs, acetate **20** itself is unknown and was therefore analyzed. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.73; H, 10.02.

For the products of tricyclononyl tosylate 16-CH_2OTs, gas chromatography (QF-1, 124 °C) showed four possible product peaks in a 4.0:4.7:8.3:83.0 ratio. The major product was collected and analyzed by NMR as acetate **21**. For a discussion of the 500-MHz NMR spectrum of **21** see the Results and Table V. The 60-MHz ^1H NMR and ^{13}C NMR data of **21** follow: ^1H NMR ($CDCl_3$) δ 1.2-2.9 (m, 11, bridgehead and CH_2), 1.85 (s, 3, CH_3), 0.2-1.0 (m, 4, cyclopropyl); ^{13}C NMR[30] ($CDCl_3$) 169.8 (C=O), 82.7 (CO), 39.5, 30.7, 30.6, 26.9, 26.5, 22.4, 22.2, 19.1, 9.2, 5.7 ppm. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.13.

Acknowledgment. This research was supported in part by the University of Wisconsin—Eau Claire Faculty Research Fund. The NMR instruments used at the University of Chicago were funded in part by the NSF Chemical Instrumentation Program and by NCI via the University of Chicago Cancer Research Center (Grant No. CA-14599).

Registry No. 16 (X = CO_2Et), 65115-95-9; **16** (X = CH_2OTs), 80360-28-7; **16** (X = CH_2OH), 80360-29-8; **16** (X = CO_2H), 65115-96-0; **17** (X = CO_2H), 699-55-8; **17** (X = CH_2OTs), 2346-03-4; **17** (X = CH_2OH), 2574-42-7; **18**, 3725-40-4; **19**, 80360-30-1; **20**, 80360-31-2; **21**, 80360-32-3; cyclopropene, 2781-85-3.

Substituent Effects on the Acid Hydration of Acetylenes

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The rates of hydration in aqueous sulfuric acid of 1-butyne, 2-butyne, 1-hexyne, 1-cyclopropylacetylene, and 1-butene are reported, together with rates in D_2SO_4 for the alkynes plus 3-hexyne. All of the compounds are proposed to react through the Ad_E2 mechanism of rate-limiting protonation on carbon. A general correlation of $\log k_{H^+}(\text{alkyne})/\log k_{H^+}(\text{alkene})$ is observed, whose slope of 1.25 is a quantitative measure of the greater sensitivity to substituent effects of alkynes compared to alkenes in protonation.

The reaction of alkynes with electrophilic reagents, especially protons, has been the subject of continuing interest as described in a number of reviews[1,2] and reports of recent research.[3] A topic of particular interest has been the comparison of the reactivity of particular alkene/alkyne pairs with different electrophiles.[2,4-6]

We have devoted considerable attention to the electrophilic reactions of alkenes, especially to the effect of substituents on reactivity in acid-catalyzed hydrations,[7] including a recent comparative study of the isomers allene and propyne.[8] Therefore, an understanding of the general factors governing the reactivity of alkynes is of interest to us.

The systematic comparison of the effect of substituents on the electrophilic reactivity of alkenes substituted on only one carbon[7] as well as 1,2-disubstituted alkenes[9a] has been quite rewarding as a guide to understanding the details of these processes. It has been particularly en-

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couraging that it is possible to include in the same correlation alkenes with substituted aryl groups ($XC_6H_4CH{=}CH_2$) as well as substituents directly attached to the double bond ($XCH{=}CH_2$). Thus, eq 1 is successful in correlating

$$\log k_{H^+} = -10.5\sum\sigma_p^+ - 8.92 \qquad (1)$$

all the reported hydration rates of alkenes of both types, with the σ_p^+ values being used for the total substituent $X{-}C_6H_4$ and X, respectively. The success of eq 1 is evidence that all these reactions are proceeding through rate-limiting protonation on carbon (the Ad_E2 mechanism, eq 2).

(2)

There have been a number of reports of rates of acid-catalyzed hydration of alkynes, including alkylalkynes,[4a,5] arylalkynes,[4,5,10,11] alkynyl ethers and thioethers,[12] alkynylamines,[13] and ferrocenylacetylene.[14] Rates of addition of trifluoroacetic acid to alkynes have also been reported, and this is a process which apparently is mechanistically very similar to hydration.[4a,6,15]

Heretofore there has been no effort to make a unified interpretation of all the data on alkynes by means of linear free-energy correlations. Also, rate data on several important simple alkynes have not been previously available. We have therefore examined the reactivity of several additional significant alkynes and have carried out a systematic comparison of the reactivities of the alkynes with the structurally related alkenes.

Results

Rates of reaction of 1-butyne, 2-butyne, and cyclopropylacetylene in H_2SO_4 according to eq 3 were measured

$$RC{\equiv}CR' \xrightarrow{H_2SO_4} RC(O)CH_2R' \qquad (3)$$

by UV spectroscopy by observing the appearance of the carbonyl absorption. For 2-butyne the rate of disappearance of the alkyne absorption was also observed and agreed with the product appearance results. Rates for 3-hexyne were reported by Modena et al.,[4a] and from their data we calculate $\log k_{H^+} = -1.14H_0 - 8.25$. Our measured rate in 11.1 M H_2SO_4 ($H_0 = -5.57$) of 1.19×10^{-2} s^{-1} agrees with the value of 1.32×10^{-2} s^{-1} calculated from their data.

In the case of 1-hexyne a gradual increase in the end-point absorpton occurred for both disappearance of the alkyne and appearance of the carbonyl. However, first-order plots were obtained by the Guggenheim method for appearance of the carbonyl absorption. Rates for all five alkynes were also measured in D_2SO_4, and all the data are collected in Tables I and II.

Table I. Rates of Acid-Catalyzed Hydration of Alkynes and Alkenes at 25 °C

compd	$[H_2SO_4]$, M	wt % acid	H_0	k_{obsd}, s^{-1}
$EtC{\equiv}CH$[a]	11.05	68.5	−5.57	9.29×10^{-3}
	10.35	65.4	−5.13	2.78×10^{-3}
	9.83	63.1	−4.82	1.12×10^{-3}
	8.24	55.9	−4.00	7.12×10^{-5}
$MeC{\equiv}CMe$[b]	11.05	68.5	−5.57	9.00×10^{-3}
	10.35	65.4	−5.13	2.01×10^{-3}
	9.52	61.9	−4.69	4.15×10^{-4}
	8.24	55.9	−4.00	4.59×10^{-5}
n-$BuC{\equiv}CH$[c]	11.05	68.5	−5.57	7.48×10^{-3}
	9.52	61.9	−4.69	6.71×10^{-4}
	8.24	55.9	−4.00	1.09×10^{-4}
				10^{-4}
$EtCH{=}CH_2$[d]	9.52	61.9	−4.69	1.44×10^{-2}
	8.24	55.9	−4.00	1.55×10^{-3}
	6.61	47.6	−3.13	7.90×10^{-5}
c-$PrC{\equiv}CH$[e]	4.87	37.4	−2.23	7.34×10^{-2}
	3.98	32.3	−1.87	2.38×10^{-2}
	3.97	31.7	−1.84	2.15×10^{-2}
	3.57	29.0	−1.65	1.29×10^{-2}
	3.24	26.7	−1.50	8.30×10^{-3}
	2.93	24.8	1.39	6.08×10^{-3}

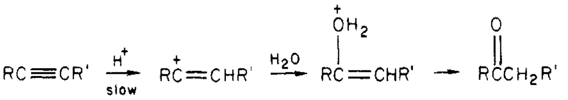
[a] $\log k = -1.356H_0 - 9.540$. [b] $\log k = -1.464H_0 - 10.214$. [c] $\log k = -1.170H_0 - 8.647$. [d] $\log k = -1.450H_0 - 8.632$. [e] $\log k = -1.288H_0 - 4.017$.

Hydration rates for 1-butene had not been previously reported at 25 °C, so these were measured for reference in H_2SO_4 by observing the decrease in alkene absorption and are also included in Table I.[16]

An attempt was made to measure rates of hydration of 1-cyclopropylpropyne (c-$PrC{\equiv}CMe$). The NMR spectrum of the reaction mixture in 5 M H_2SO_4 showed the expected c-$PrCOCH_2CH_3$ as the only significant product, but first-order kinetics for the change of the UV spectrum at either 205 or 255 nm were not observed, and this system was not investigated further.

Discussion

The generally accepted mechanism for hydration of alkynes is the Ad_E2 process involving rate-limiting proton transfer to carbon to give a vinyl cation intermediate, followed by attack of H_2O and rearrangement to the ketone (eq 4). This mechanism has been supported by definitive



$$RC{\equiv}CR' \xrightarrow[\text{slow}]{H^+} \overset{+}{R}C{=}CHR' \xrightarrow{H_2O} R\overset{\overset{+}{O}H_2}{\overset{|}{C}}{=}CHR' \longrightarrow R\overset{\overset{O}{\|}}{C}CH_2R' \qquad (4)$$

chemical evidence in the case of arylalkynes $ArC{\equiv}CH$, whose rates are correlated by the σ^+ parameters of the aryl substituents,[4a,10a,11a] for some alkynes where general-acid catalysis has been observed,[10b,12,13] and for several arylalkynes where solvent isotope effects k_{H^+}/k_{D^+} have been measured.[11-13]

The present results provide evidence that the Ad_E2 mechanism is also applicable to a variety of other alkyne structural types. Thus the rate dependence on acidity measured in terms of slopes of log k vs. H_0 are in the range expected for eq 4, as are the values of k_{H^+}/k_{D^+}. The var-

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(16) The rate constants reported for 1-butene are those for the decrease in the UV absorpion of the alkene. In the event that some alkene is present at equilibrium for the process alkene + H_3O^+ (k_1) $\rightleftharpoons$ (k_{-1}) alcohol the observed rate constant equals $k_1 + k_{-1}$. The hydration of 1-butene at 101.4 °C was found to form 2-butanol to the extent of at least 83% (Manassen, J.; Klein, F. S. *J. Chem. Soc.* **1960**, 4203–13), and addition product is expected to be even more favored at lower temperatures, so the error in the reported rates due to reversibility is small.

Table II. Solvent Isotope Effects in Acid-Catalyzed Hydration of Alkynes at 25 °C

alkyne	$[D_2SO_4]$, M	wt % acid	D_0[a]	$k[H_2SO_4]$, s^{-1} [b]	$k_{obsd}[D_2SO_4]$, s^{-1}	k_{H^+}/k_{D^+}
EtC≡CEt	11.20	67.1	5.72	1.96×10^{-2} [c]	1.24×10^{-2}	1.58
	9.53	59.7	4.68	1.27×10^{-3} [c]	8.64×10^{-4}	1.47
MeC≡CMe	11.20	67.1	5.72	1.44×10^{-2}	1.02×10^{-2}	1.42
	9.53	59.7	4.68	4.34×10^{-4}	5.44×10^{-4}	0.797
n-BuC≡CH	11.20	67.1	5.72	1.11×10^{-2}	6.57×10^{-3}	1.69
	9.53	59.7	4.68	6.74×10^{-4}	6.07×10^{-4}	1.11
EtC≡CH	11.20	67.1	5.72	1.64×10^{-2}	7.80×10^{-3}	2.10
	9.53	59.7	4.68	6.40×10^{-4}	4.13×10^{-4}	1.55
c-PrC≡CH	3.90	29.6	1.85	2.32×10^{-2}	7.22×10^{-3}	3.22
	2.84	22.6	1.34	5.11×10^{-3}	1.98×10^{-3}	2.58

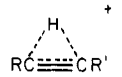
[a] Obtained from: Wyatt, P. A. H. *J. Chem. Soc. B* **1970**, 1570. [b] Calculated from the relation $\log k = \gamma H_0 + \epsilon$ by using $H_0 = D_0$. [c] See footnote *h* of Table III.

Table III. Comparative Reactivity of Alkynes, RC≡CR′, and Alkenes (*Z*)-RCH=CHR′, in Acid-Catalyzed Hydration at 25 °C

		k_{H^+}, M^{-1} s^{-1}		$\log k_{H^+}$				
R	R′	alkyne	alkene[k]	alkyne	alkene	k_{alkyne}/k_{alkene}	pt no.	σ_p^+ (R)
Me	H	0.674×10^{-11} [a]	0.238×10^{-8}	−11.17	−8.62	0.0028	1	−0.31
Et	H	0.258×10^{-9} [b]	0.233×10^{-8} [b]	−9.54	−8.63	0.12	2	−0.30
n-Bu	H	0.225×10^{-8} [b]	0.432×10^{-8}	−8.65	−8.36	0.52	3_1	−0.30
c-Pr	H	0.961×10^{-4} [b]	0.254×10^{-3}	−3.91	−3.60	0.38	4	−0.47
p-Anis	H	0.376×10^{-3} [c]	0.645×10^{-4}	−3.42	−4.19	5.8	5	−0.34
p-Tol	H	0.50×10^{-5} [c]	0.249×10^{-5}	−5.30	−5.60	2.0	6	−0.24
m-Tol	H	(0.57×10^{-6})[d]	0.977×10^{-5}	−6.24	−6.01	0.058	7	−0.20
Ph	H	0.30×10^{-6} [c]	0.326×10^{-6}	−6.52	−6.49	0.92	8	−0.18
p-BrC_6H_4	H	(0.66×10^{-7})[d]	0.200×10^{-6}	−7.18	−6.70	0.33	9	−0.15
p-ClC_6H_4	H	0.17×10^{-6} [c]	0.104×10^{-6}	−6.80	−6.98	0.81	10	−0.16
m-BrC_6H_4	H	(0.54×10^{-8})[d]	0.182×10^{-7}	8.27	−7.74	0.30	11	−0.10
m-ClC_6H_4	H	(0.63×10^{-8})[d]	0.229×10^{-7}	−8.20	−7.64	0.28	12	−0.10
EtO	H	329[e]	1.76	2.52	0.25	136	13	−0.83
MeO	H	77.7[e]	0.762	1.89	−0.12	102	14	−0.78
MeS	H	0.21[f]	0.108×10^{-1}	−0.68	−1.97	19	15	−0.60[o]
(Ets)								
Ph	Me	0.720×10^{-8} [g]	1.08×10^{-8} [l]	−8.14	−7.97	6.7	16	
Me	Me	6.11×10^{-11} [b]	0.448×10^{-8}	-10.21	−8.35	0.014	17	
Et	Et	5.68×10^{-9} [h]	0.127×10^{-7}	−8.25	−7.90	0.45	18	
piperidinyl	Ph	3.5×10^{7} [i]	1.2×10^{4} [m]	7.54	4.08	2.9×10^3	19	
p-Anis	CO_2H	4.13×10^{-6} [j]	4.44×10^{-7} [p]	−5.38	−6.35	9.3	20	
Ph	CO_2H	2.44×10^{-9} [j]	1.40×10^{-10} [p,q]	−8.61	−9.85	17	21	
p-ClC_6H_4	CO_2H	8.41×10^{-10} [j]	2.48×10^{-11} [p,r]	−9.08	−10.61	34	22	
EtO	Me	2.99[n]	0.159	0.48	−0.80	19	23	

[a] Reference 8. [b] This work. [c] References 4a and 10b. [d] Derived from the data of ref 10a. [e] Reference 12a. [f] Reference 12b. [g] Reference 11b. [h] Reference 4a; $\log k = -1.14H_0 - 8.25$. [i] Reference 13. [j] Reference 11a. [k] Alkene rates taken from ref 7 and 9 except as noted. [l] Calculated from the *k*(PhC≡CMe)/*k*(PhCH=CHMe) ratio of 0.67 reported in ref 5. [m] Reference 17. [n] Reference 12c. [o] A revised value of −0.54 for σ_p^+ for the MeS substituent derived from *p*-nitrobenzoate solvolysis has appeared (Brown, H. C.; Gunda Rao, C.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 7663). The older value derived from chloride solvolysis is used here, consistent with our previous practice. [p] Rate of *Z* to *E* isomerization. [q] Derived from calculated rates at 45 and 70 °C of 1.27×10^{-9} and 1.40×10^{-8} M^{-1} s^{-1} ($H_0 = 0$), respectively. [r] Derived from calculated rates at 45 and 90 °C of 5.21×10^{-10} and 1.46×10^{-7} M^{-1} s^{-1} ($H_0 = 0$), respectively.

iations of this latter ratio with acidity are consistent with previous experience,[7,11] although the causes of the trends are not clear. An alternative mechanism involving formation of a proton-bridged intermediate or rate-limiting transition state (I) is quite unlikely on the basis of theoretical calculations,[17] which indicate that bridging is not favored in protonation of substituted alkynes. The effects of substituents on reactivity, as discussed below, also are inconsistent with a significant role for such an intermediate.



I

As already mentioned the study of the effect of substituents on the reactivity of alkenes has been completely consistent with the Ad_E2 path (eq 2). Consideration of the mechanism proposed for alkyne protonation (eq 4) suggests that similar structure–reactivity behavior should be observed for alkenes and alkynes. The data for comparison are assembled in Table III, which includes all substrates for which comparable second-order rate constants for hydration are available. The correlation of $\log k_{H^+}$ for alkynes vs. alkenes is shown in Figure 1. Overall, a reasonable correlation is observed, including all the points, with a slope of 1.25 and a correlation coefficient of 0.979. This result is consistent with the proposal of a common Ad_E2 mechanism for all the alkenes and alkynes alike.

The standard conditions chosen for the comparison are k_{H^+} values (M^{-1} s^{-1}) at 25 °C. For the less reactive substrates, large extrapolations to $H_0 = 0$ are required for this comparison. For alkenes with significantly different slopes of $\log k_{H^+}$ vs. H_0, this can lead to distortions of the relative reactivities, and this is in part responsible for the apparent low reactivities of propyne and 2-butyne (points 1 and 17). Examination of the data for 2-butyne and 1-hexyne, which have similar reactivities at the acidities at which the rates

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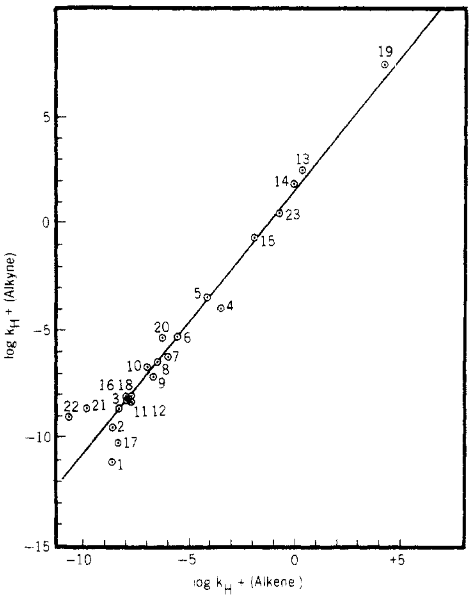


Figure 1. Comparison of k_{H^+} of alkynes with k_{H^+} of alkenes.

were measured, reveals that changes in relative rates of factors of 10^2 can appear in the extrapolated k_{H^+} values.

The alkenes for points **21** and **22** (cinnamic acids, ArCH=CHCO$_2$H) required extrapolations in temperature which exaggerate the low reactivity of these substrates relative to **20**.[18] Fortuitiously the deviations of **1** and **17** from the line tend to cancel those of **21** and **22** so that these computational artifacts have little effect on the slope. Point **19** for the piperidinyl (c-C$_5$H$_{10}$N–) substituent required a rather drastic correction to the same β substituent,[19] but this point also rather fortuitously falls close to the correlation line.

A moderate deviation for point **4** (*c*-PrC≡CH/*c*-PrCH=CH$_2$) from the line is noticeable. Unfortunately *c*-PrC≡CCH$_3$ did not give useable kinetics so the effort to test for the generality of the cyclopropyl deviation was not successful. A theoretical study[20a] of substituent effects on vinyl cations hints that this low reactivity of *c*-PrC≡CH may be typical. Thus for the *c*-Pr/Ph comparison cyclopropyl is calculated to be relatively poorer in donating electrons to a vinyl cation than to an ethyl cation.[20] This parallels the experimental result but does not provide an explanation as to the cause of this effect. As was pointed out,[20] the calculations ignore solvation effects and so can only be applied with extreme caution to the interpretation of the solution-phase results.

The fact that the slope of the plot of log *k*(alkyne)/log *k*(alkene) is 1.25 gives quantitative expression to the qualitative observation[4a] the alkyne reactivities are more responsive to substituent stabilization than are alkenes. This effect was not detected in the aforementioned theoretical study of substituent effects on vinyl cations,[20a] where the statement was made "for the groups examined here, substituent effects are inherently similar for alkenyl and for alkyl cations. The proton affinities of substituted acetylenes and olefins are comparable...".

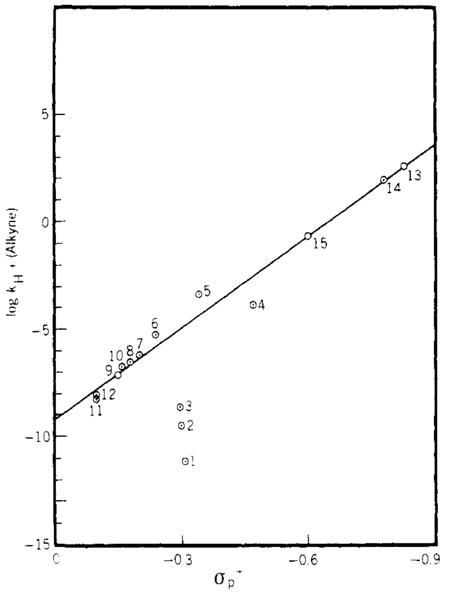
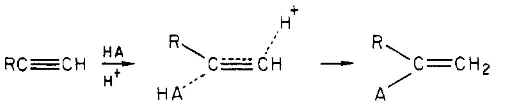


Figure 2. Correlation of k_{H^+} for alkynes RC≡CH with σ_p^+(R).

A plot of log k_{H^+} vs. σ_p^+ for the substituents on the monosubstituted alkynes is shown in Figure 2. The line shown (slope −14.1, r = 0.989) is drawn by omitting points **1**–**3** for the three monoalkylalkynes which deviate significantly. Just as in the case of the corresponding correlation of alkenes, the deviation of these points is at least partly due to the very high rate dependence of **1**–**3** on acidity, which results in very low values of k_{H^+} which are obtained after extrapolation to H_0 = 0. The cause of this steep dependence of rate on acidity remains a question of interest. It does not arise from nucleophilic solvent participation in the rate limiting step (the Ad$_E$3 mechanism, eq 5) because the solvent nucleophilicity is decreasing rapidly in the stronger acids. Selective ground-state destabilization of these substrates would explain the trends, and there is evidence that other small molecules such as ethylene and propene are "salted out" in concentrated HClO$_4$ solutions, but comparative data for larger alkenes and alkynes are not available, and this remains a topic for further study. Better solvation of the smaller cations from **1**–**3** in the more acidic media is another possible cause of this behavior.



(5)

The slope of −14.1 of the log k_{H^+} vs. σ_p^+ correlation is significantly greater in magnitude than that of −10.5 for the alkenes. This is another manifestation of the greater sensitivity of the alkyne reactivities to the substituent effects already noted. The value of −14.1/−10.5 (=1.34) is equivalent to the slope of log *k*(alkyne/log *k*(alkene) (1.25), and the slight difference between these quantities is due to the different data sets used.

It has been proposed that the greater sensitivity of the alkynes to substituents arises from the shorter bond to the substituent from the sp-hybridized carbon of the developing ion,[4a,11] and this simple explanation appears adequate to account for the major trend in the comparison.

In summary, these results establish that a reasonable correlation exists between rates of alkene and alkyne hydrations, with a slope of 1.25 which quantitatively expresses the greater sensitivity of alkynes to substituent stabilization. The reaction mechanisms of the two classes

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(18) (a) Noyce, D. S.; King, P. A.; Kirby, F. B.; Reed, W. L. *J. Am. Chem. Soc.* **1962**, *84*, 1632–5. (b) Noyce, D. S.; Avarbock, H. S. *Ibid.* **1962**, *84*, 1644–6.

(19) Point 19 required a rough estimate for the rate of 1-(piperidinyl)-2-phenylethene based on the published rate for 2-methyl-1-(piperidinyl)-propene (Stamhuis, E. J.; Maas, W. *J. Org. Chem.* **1965**, *30*, 2156–60) of 1.4 × 10^5 M^{-1} s^{-1} divided by a conversion factor of 12, based on the estimated β-rate retarding factors of 30 for Me$_2$ and 360 for Ph.[9a]

(20) (a) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* **1977**, *42*, 3004–11. (b) Wolf, J. F.; Harch, P. G.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 2902–4.

(21) Purlee, E. L.; Taft, R. W., Jr. *J. Am. Chem. Soc.* **1956**, *78*, 5811–2.

of compounds are similar, and their response to changes in reaction conditions follow comparable trends.

Experimental Section

Cyclopropylacetylene[22] and 1-cyclopropylpropyne[23] were prepared by a didehydrohalogenation procedure.[22] Rates were monitored by UV spectroscopy with Cary 118 and 210 instruments by observation of the decrease of the alkyne or alkene absorption or the increase of the product carbonyl absorption. Gaseous reactants were bubbled into the acid solutions contained in 1-cm UV cells until approximately 3×10^{-3} M solutions were obtained. For liquid substrates, 30 μL of 0.3 M solutions dissolved in MeOH were injected into 3 mL of acid solutions to give 3×10^{-3} M concentrations. The wavelengths of observation were 256 (1- and 2-butyne), 201 (1-butene), 260 (1-hexyne), 202 (3-hexyne), and 218 or 255 nm (1-cyclopropylacetylene). All rates listed are the average of at least two runs (reproducibility ±5%). The absorbance change was generally 0.1 unit.

Formation of ketones from the alkynes according to eq 4 was confirmed by the UV spectra of the products.

Acid molarities were measured by titration of measured volumes. Weight percentages were obtained by titration of weighed samples, and these were used to obtain H_0 and D_0 values.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. EtC≡CH, 107-00-6; MeC≡CMe, 503-17-3; n-BuC≡CH, 693-02-7; EtCH=CH$_2$, 106-98-9; c-PrC≡CH, 6746-94-7; EtC≡CEt, 928-49-4.

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[22] Schoberth, W.; Hanack, M. *Synthesis* **1972**, 703.

[23] Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1941–52.

Electronic Effect of Substituted Methyl Groups (CH_2X). Carbon-13 and Fluorine-19 Nuclear Magnetic Resonance Study of Some Benzobicyclo[2.2.2]octen-1-yl Derivatives

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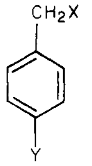
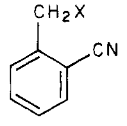
A number of 1-substituted (X) 4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalenes (**6**), as well as most of their corresponding 6- and 7-fluoro derivatives (**7** and **8**, respectively), have been synthesized and their ^{13}C and ^{19}F NMR spectra have been recorded. The most important feature of these new stereochemically well-defined model benzylic systems is that the CX bond is constrained to the nodal plane of the adjacent aromatic π system; hence, the electronic effect of substituted methyl groups can be assessed in the absence of hyperconjugative interactions involving the CX bond. Linear multiple regression analysis of the ^{13}C SCS of the remote carbon centers in **6** (C6 and C7) and the corresponding ^{19}F SCS of **7** and **8** have been carried out to assess their dependency on substituent parameters (σ_I and $\sigma_R{}^0$). Although the correlations of the former parameters are only fair, the latter parameters provide good to excellent correlations and, moreover, indicate a significant resonance interaction by the substituent (X). The implications of this result with respect to discordant observations concerning the electronic effect of CH_2X groups in $C_6H_5CH_2X$ systems is discussed.

There is continued interest in the nature of the electronic effect of substituted methyl groups (CH_2X).[1-5] One particular aspect concerns whether or not the conjugative component of the electronic effect of these groups in the neutral ground state is dependent on the resonance capability of the substituent (X). According to the results of multiparameter correlative analyses of ^{13}C[3,6] and ^{19}F[3,7] substituent chemical shifts (SCS; sensitive monitors of π electron effects at remote centers of substituted arene ring systems) as well as infrared frequency shift (ν_{CN} mode)[4] data for the para position of α-substituted toluenes **1–3**, the electronic effect of CH_2X groups relative to the methyl substituent (X = H) is predominantly, if not exclusively, determined by the polar nature of the substituent (σ_I effect). The resonance contribution ($\sigma_R{}^0$ effect) has been interpreted as being statistically insignificant.[3]



1, Y = H
2, Y = F
3, Y = CN



4

XCH_2CN
5

In contrast, a similar analysis of the cyano frequency shifts (ν_{CN}) of α-substituted *o*-toluonitriles (**4**)[8] and α-substituted acetonitriles (**5**)[4] suggests, besides a polar contribution, a significant dependency of the CH_2X electronic effect on the resonance capability of the substituent (X). The origin of the resonance effect was attributed to orbitals on the substituent (X) interacting with the C–H or C–CN σ bonds.[4] Moreover, it was suggested that since this effect can only be significant through space to a nearby probe, the observation of the phenomenon in system **4** but not in **3** is understandable.

We believe the aforementioned apparent discordant experimental observations concerning the electronic effect

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[1] Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.*, **1977**, *99*, 5901 and references cited therein.

[2] Pross, A.; Radom, L. *Aust. J. Chem.* **1980**, *33*, 241 and references cited therein.

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