mmol) stirred in dichloromethane (20 mL). After hydrogen evolution ceased (30 min), the solvent was removed at 0.1 mmHg, and the residue was heated at 230 °C. TLC analysis of the distillate revealed one mobile fraction. Chromatography as in the previous experiment yielded **66** (73.8 mg, 41%) identical with the previous sample.

Photolysis of the Sodium Salt of 16. A pentane slurry (200 mL) of the sodium salt of **16** [prepared from **16** (364 mg, 1 mmol), excess sodium hydride, and dichloromethane (20 mL) and then vacuum evaporation] was irradiated 3.5 h with a 450-W Hanovia 679A36 high-pressure mercury arc lamp under nitrogen. Filtration, solvent evaporation, TLC analysis, and chromatography revealed **66** (27.1 mg, 15%) as the only hydrocarbon product.

8-Methylcycloprop[*a*]acenaphthylene (66). An ethereal solution of 1-methylacenaphthylene (**67**; 170 mg, 1.22 mmol) and methylene iodide (2.68 g, 10 mmol) was added to zinc–copper couple [prepared from zinc dust (1.30 g, 20 mmol) and cuprous chloride (200 mg, 2 mmol)]. After the mixture had been refluxed 24 h, the ether solution was washed with 10% sodium thiosulfate and dilute hydrochloric acid, dried, concentrated, and distilled to give **66** (30 mg, 17%) identical with the hydrocarbon from the previous decompositions of **16**.

Pyrolysis of the Sodium Salt of 16 at 750 °C. The sodium salt of **16** [prepared from **16** (750 mg, 2.06 mmol) and sodium hydride in dichloromethane (20 mL)] was dropped gradually (0.05 mm) through a quartz tube at 750 °C. TLC analysis of the condensate revealed one mobile fraction. Chromatography (silica gel/hexane) gave a yellow oil (50.1 mg), a mixture of 1- (**69**), 4- (**70a**), 9- (**70b**), 6- (**70c**) and **7-methylphenalene (70d)**: IR (neat) 3020, 1600, 830, 795 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (s, CH_3), 2.2 (s, CH_3), 2.3 (s, CH_3), 2.5 (s, CH_3), 3.2 (s), 4.0 (br s, benzylic H), 6.0 (m, olefinic H), 6.5 (m, olefinic H), 6.9–7.7 (m, aromatic).

Pyrolysis of 66 at 700 °C. Pure **66** (166.7 mg, 0.92 mmol) was passed through a quartz tube (2.5 cm × 30 cm) at 700 °C (0.4 mm). The dark condensate could not be separated chromatographically. Chromatography of the oily condensate gave a product mixture of **69** and **70a–d** (61.2 mg, 37%) with IR and NMR properties essentially identical with those of the product from pyrolysis of the sodium salt of **16** at 750 °C.

Acenaphthenequinone Ethylene Monoacetal Hydrazone (18). A solution of acenaphthenone ethylene monoacetal (1 g, 4.4 mmol), hydrazine hydrate (5 mL of 95% solution), and methanol (20 mL) was refluxed 3 h, cooled, and filtered. Recrystallization of the precipitate from ethanol yielded **18**: 669 mg (63%); mp 193 °C; NMR ($CDCl_3$) δ 4.46 (m, 4 H, $(CH_2)_2$), 6.0 (br, 2 H, NH_2), 7.3–8.0 (m, 6 H, aromatic).

Anal. Calcd for $C_{14}H_{12}N_2$: C, 69.98; H, 5.03; N, 11.65. Found: C, 69.98; H, 5.10; N, 11.68.

Photolysis of 2-Diazoacenaphthenone Ethylene Acetal (17). A mixture of **18** (240 mg, 1 mmol), activated manganese dioxide (870 mg, 10 mmol), ethyl ether (125 mL), and saturated ethanolic potassium hydroxide (0.15 mL) was stirred for 1 h, filtered, and rotoevaporated to give orange-red crystals of **17**: 215 mg (90%); IR (KBr) 2060 (s, >C=N_2), 1730 cm^{-1} (w, >C=O).

Diazo ketal **17** in ethyl ether (150 mL) was then irradiated under nitrogen in Pyrex for 1 h. After solvent removal, TLC analysis revealed two mobile fractions. Chromatography on silica gel with hexane/benzene (3:1 to 1:1) as the eluent gave (1) 8,9-dihydroacenaphtho[1,2-*b*]-*p*-dioxin [**73**: 80 mg (51%, corrected for **17** recovered); IR (neat) 3040, 1600, 1480, 1320, 1140, 1050, 960, 825, 775 cm^{-1}; NMR ($CDCl_3$) δ 4.26 (s, 5 H, $(CH_2)_2$), 7.26–7.73 (m, 6 H, aromatic); exact mass calcd for $C_{14}H_{10}O_2$ *m/e* 210.060816, found *m/e* 210.068650] and (2) recovered **17**: 57 mg (25%); IR (KBr) 3020, 2900, 1720 (>C=O), 1610, 1210, 1080, 840, 790 cm^{-1}.

Thermolysis of 17 in Benzene. A solution of **17** (220 mg) in dry benzene (20 mL) was refluxed 4 h under argon. Concentration and chromatography as in the previous experiment yielded **73** (58 mg, 30%, corrected for **17** recovered) and **17** (16 mg, 7%). The properties of **73** and **17** are identical with those of the previous experiment.

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Registry No. **1**, 2008-77-7; **2**, 81522-34-1; **3**, 81522-35-2; **4**, 66365-89-7; **5**, 81522-36-3; **6**, 81522-37-4; **7**, 13286-14-1; **13**, 79679-93-9; **14**, 81522-38-5; **15**, 81522-39-6; **15** Na, 81522-40-9; **16**, 81522-41-0; **16** Na, 81522-42-1; **17**, 81522-43-2; **18**, 81522-44-3; **22**, 2235-15-6; **22** ethylene ketal, 31445-81-5; **23**, 67-64-1; **25**, 81-84-5; **28**, 81522-45-4; **29**, 81522-46-5; **29** 2,4-dinitrophenylhydrazone, 81522-47-6; **30**, 63169-55-1; **31**, 63169-53-9; **32**, 81522-48-7; **33**, 81522-49-8; **38**, 81522-50-1; **39**, 81522-51-2; **40**, 81522-52-3; **41**, 81522-53-4; **42**, 27544-95-2; **43**, 27544-93-0; **47**, 81522-54-5; **48**, 81522-55-6; **49**, 81522-56-7; **50**, 81522-57-8; **51**, 81522-58-9; **54**, 81522-59-0; **55**, 81522-60-3; **56**, 81522-61-4; **57**, 81522-62-5; **58**, 81522-63-6; **59**, 81522-64-7; **63**, 208-96-8; **66**, 66622-83-1; **67**, 19345-99-4; **69**, 81522-65-8; **70a**, 72814-67-6; **70b**, 72814-49-4; **70c**, 72814-61-0; **70d**, 72814-55-2; **73**, 81626-25-7; benzonitrile, 100-47-0; acrylonitrile, 107-13-1; 5-nitroacenaphthenequinone, 24040-42-4; phenylacetylene, 536-74-3; dimethyl acetylenedicarboxylate, 762-42-5; oxalyl chloride, 79-37-8; anthracene, 120-12-7; aceanthrenequinone, 6373-11-1; methyl acrylate, 96-33-3; 2,2-dimethylacenaphthenone, 18086-43-6; acenaphthenequinone, 82-86-0; 4-methylperinaphthane, 68913-04-2; 6-methylperinaphthane, 81626-26-8.

Addition of Trifluoroacetic Acid to Substituted Styrenes

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The rates of addition of CF_3CO_2H to a series of ring-substituted styrenes ArCH=CH_2 with 100%, 50%, and 20% solutions of the acid in CCl_4 have been measured. The rates of addition of 100% CF_3CO_2H to the isomeric 1-phenylpropenes and the rate of *cis*- to *trans*-stilbene isomerization by this acid are also reported. The rates are correlated with σ^+ parameters of the substituents and with aqueous H_2SO_4-catalyzed hydrations of the same substrates. Deviations from the σ^+ correlation occur with substituents capable of strong hydrogen bonding to the acidic solvents; these deviations are attributed to a decrease in substituent electron-donating ability caused by this interaction. All of the evidence supports a mechanism of rate-determining protonation on carbon (the Ad_E2 mechanism), with no detectable effects from π complexation of the acids with the substrates.

Kinetic measurements of the rates of acid-catalyzed hydration of aryl-substituted styrenes have played a pivotal role in mechanistic studies of protonations of alkenes in general.[1,2] The results on nine different styrene systems

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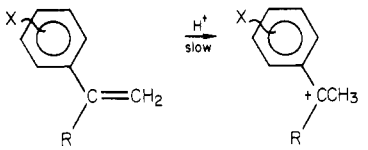
have all been interpreted in terms of rate-limiting protonation on carbon (the Ad_E2 mechanism) to give α-aryl carbonium ions as shown in eq 1. These studies have



(1)

R = *N*-morpholino, HO, EtO, MeO, AcO, $(EtO)_2PO_2$, Me, H, CF_3

frequently provided a diagnostic tool for unraveling mechanistic ambiguities. Thus the good correlation observed when R = $(EtO)_2PO_2$[1f] with the Brown–Hammett σ^+ parameters established the mechanism shown in eq 1 for these derivatives and excluded a role for rate-limiting nucleophilic attack on phosphorous as had been previously postulated. On the other hand, the absence of a correlation with σ^+ constants when R = Me_3SiO helped establish that rate-limiting nucleophilic attack on silicon was important in this series.[1g] The substituent effects also illuminated the mechanistic changeover from $A_{Ac}2$ to Ad_E2 mechanisms for R = OAc.[1h] Rate dependences on substituents X have also been very useful in allowing the dissection of mechanisms for isomerization of *cis*- to *trans*-cinnamic acids (eq 2),[3a] chalcones (eq 3),[3b] and stilbenes (eq 4).[3c]

$$H^+ + cis\text{-}XC_6H_4CH{=}CHCO_2H\ (\mathbf{1}) \rightarrow trans\text{-}\mathbf{1} \quad (2)$$

$$H^+ + cis\text{-}XC_6H_4CH{=}CHCOPh\ (\mathbf{2}) \rightarrow trans\text{-}\mathbf{2} \quad (3)$$

$$H^+ + cis\text{-}XC_6H_4CH{=}CHC_6H_4Y\ (\mathbf{3}) \rightarrow trans\text{-}\mathbf{3} \quad (4)$$

Other systems which utilized Brown-Hammett σ^+ correlations to elucidate protonation mechanisms of arylalkenes include the sulfuric acid catalyzed addition of acetic acid to styrenes (eq 5),[4] and the additions of HCl

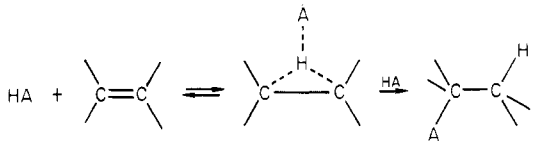
$$XC_6H_4CH{=}CH_2 + H^+ \xrightarrow{HOAc} XC_6H_4CH(OAc)CH_3 \quad (5)$$

$$XC_6H_4CH{=}C{=}CH_2 + HCl \rightarrow XC_6H_4CH{=}CHCH_2Cl \quad (6)$$

$$XC_6H_4CH{=}CHCH{=}CH_2 + HCl \rightarrow XC_6H_4CH{=}CHCHClCH_3 \quad (7)$$

to 1-aryl-1,2-dienes (eq 6)[5a] and 1-aryl-1,3-dienes (eq 7).[5b] Although the authors of ref 4 did not report a correlation of their data with σ^+, we find a satisfactory correlation exists: $\rho^+ = -3.7$, $r = 0.990$.

Recently a report appeared[6] suggesting that the mechanism of trifluoroacetic acid addition to alkenes involved a π-complex mechanism: "These observations point to a mechanism for simple olefins involving π-complex formation followed principally by fully or nearly rate-limiting carbenium ion production, with possible competition from direct product formation or hydride shift." This proposal of a kinetically significant π-complex intermediate, which may be represented as in eq 8,[6] is contrary to the accepted mechanism for not only acid-catalyzed hydration of alkenes[1b] but also trifluoroacetic acid additions.[7]



(8)

The utility of the study of styrene reactivities for the elucidation of protonation reactions has prompted us to study the reactivity of a variety of substituted styrenes with trifluoroacetic acid (TFA). A clarification of the mechanisms of TFA additions is a desirable goal for many reasons, including the large body of experimental data already available for reactions in this medium, the useful properties of this medium (high solubility of many organic substrates, high ionizing power, high acidity, and low nucleophilicity), and the desire to have a unified understanding of protonation reactions in many media. There has also been a report of a nicely complementary study, namely, the reverse $A_{A1}1$ esterification of 1-arylethanols in TFA (eq 9).[8] A recent study from our laboratory dealt

$$ArCHOHCH_3 \xrightarrow{TFA} ArCHCH_3^+ \rightarrow ArCH(O_2CCF_3)CH_3 \quad (9)$$

with the comparison of the reactivity of aliphatic alkenes in trifluoroacetic acid and in aqueous acid,[9] and the current report deals with the reactivity of arylalkenes.

A recent study reports calorimetric measurements of the heats of addition of CF_3CO_2H to alkenes.[10a] This reaction is convenient to study, and the results can be used to derive precise heats of isomerization and heats of hydration of alkenes. In another recent report[10b] an isotope effect, $k(CF_3CO_2H)/k(CF_3CO_2D)$, of 4.33 for addition to *trans*-2-butene at 37 °C has been measured. This result is consistent with rate-limiting proton transfer but not equilibrium protonation followed by a subsequent rate-limiting step. These recent developments provide further impetus to studies designed to clarify the process of trifluoroacetic acid addition.

Results

The kinetics of the reactions of the arylalkenes **17–25**[9] in CF_3CO_2H and in 1:1 and 1:4 (v/v) CF_3CO_2H/CCl_4 were monitored by observing the change in their UV absorption. When 0.5 M MeOH solutions of the substrates were injected into CF_3CO_2H to give 10^{-3} M solutions, good first-

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Table I. Reactivity of Styrenes ($XC_6H_4CH{=}CH_2$) in CF_3CO_2H (TFA)

X or compd (no.)	temp, °C	k_{obsd}, s^{-1} [a] 100% TFA [k] (log)	1/1 TFA/CCl_4 [l] (log)	1/4 (TFA/CCl_4 [m] (log)	σ^+
p-MeO (17)	25.0			0.112 (−0.95)	−0.78
p-MeS (18)	5.0	6.97×10^{-2}			
	25.0	(0.292) [b] (−0.53)	9.91×10^{-2} (−1.00)	1.82×10^{-2} (−1.74)	−0.54
p-Me (19)	3.7	0.102			
	25.0	(0.453) [b] (−0.34)	2.57×10^{-2} (−1.59)	3.85×10^{-3} (−2.41)	−0.31
p-F (20)	25.0	1.69×10^{-2} (−1.77)	9.57×10^{-4} (−3.02)		−0.07
H (21)	3.7	3.15×10^{-3}			
	5.0	3.30×10^{-3}			
	25.0	1.75×10^{-2} [c] (−1.76)	1.17×10^{-3} [d] (−2.93)	1.36×10^{-4} [e] (−3.87)	0.0
	47.4			6.89×10^{-4}	
	51.9		8.13×10^{-3}		
	63.5		2.22×10^{-2}	1.82×10^{-3}	
p-Br (22)	25.0	2.61×10^{-3} (−2.58)	1.16×10^{-4} (−3.94)	1.98×10^{-5} (−4.70)	0.15
m-Br (23)	25.0	1.74×10^{-4} (−3.76)	8.71×10^{-6} (−5.06)	(1.15×10^{-6}) [f,g] (−5.94)	0.40
	47.4			8.36×10^{-6}	
	69.4			4.59×10^{-5}	
m-Cl (24)	25.0	1.64×10^{-4} (−3.79)	9.15×10^{-6} (−5.04)		0.40
m-CF_3 (25)	25.0	2.40×10^{-5} (−4.62)	(9.19×10^{-7}) [f,h] (−6.04)	(1.58×10^{-7}) [b] (−6.80)	0.52
	51.9		1.50×10^{-5}		
	63.5		4.37×10^{-5}	4.60×10^{-6}	
m-O_2N (26)	25.0	(1.96×10^{-7}) [f,i] (−6.72)	(2.39×10^{-8}) [f,j] (−7.62)		0.67
	67.4	8.95×10^{-6}	1.06×10^{-6}		
	83.5	3.92×10^{-5}	3.80×10^{-6}		
	100.6	1.03×10^{-4}	1.17×10^{-5}		
(*Z*)-$PhCH{=}CHCH_3$ (27)	25.0	8.58×10^{-4} (−3.07)	4.73×10^{-5} (−4.33)		
(*E*)-$PhCH{=}CHCH_3$ (28)	25.0	7.87×10^{-4} (−3.10)	3.28×10^{-5} (−4.48)		
(*Z*)-stilbene (29)	25.0	5.60×10^{-5} (−4.25)			

[a] Average of at least two runs in every case; average deviation ±10%. [b] Estimated by assuming the same activation entropy as styrene in this medium. [c] $\Delta H^* = 12.9$ kcal/mol, $\Delta S^* = -23.4$ eu. [d] $\Delta H^* = 14.3$ kcal/mol, $\Delta S^* = -23.9$ eu. [e] $\Delta H^* = 12.8$ kcal/mol, $\Delta S^* = -33.1$ eu. [f] Calculated from data at other temperatures. [g] $\Delta H^* = 16.2$ kcal/mol, $\Delta S^* = -31.2$ eu. [h] $\Delta H^* = 19.4$ kcal/mol, $\Delta S^* = -21.2$ eu. [i] $\Delta H^* = 17.9$ kcal/mol, $\Delta S^* = -29.1$ eu. [j] $\Delta H^* = 17.5$ kcal/mol, $\Delta S^* = -34.6$ eu. [k] Log $k = -4.82\sigma^+ - 1.93$; $r = 0.996$, omitting 18 and 26. [l] Log $k = -5.08\sigma^+ - 3.15$; $r = 0.993$, omitting 18 and 26. [m] Log $k = -5.39\sigma^+ - 3.96$; $r = 0.996$, omitting 17 and 18.

order kinetics were observed with no evidence of polymerization. A solution of 3-nitrostyrene (26) in CF_3CO_2H prepared in an NMR tube gave a clean spectrum of the styrene at ambient temperature. When the sample was heated, conversion to trifluoroacetate ester could be observed, and this NMR method was used to measure the reaction kinetics. The rates for 17–26 are reported in Table I.

Rate constants for reaction of (*Z*)- and (*E*)-1-phenylpropene (27 and 28, respectively) with 100% CF_3CO_2H were also measured by UV at 25 °C and are given in Table I.

The kinetics of the isomerization of *cis*- to *trans*-stilbene in 100% CF_3CO_2H was observed by UV spectroscopy, and this rate constant is also included in Table I. The UV spectrum of this mixture after about 5 half-lives for reaction corresponded to the distinctive spectrum of the trans isomer, but this then underwent reaction with a first-order rate constant of 9.4×10^{-6} s^{-1} at 25 °C, or about one-sixth the rate of the cis/trans isomerization. However, this process did not give a stable final absorption. Reaction of 1,2-diphenylethanol with CF_3CO_2H gave a rapid conversion to the corresponding trifluoroacetate 31, which was fully characterized. However, on prolonged treatment with CF_3CO_2H, 31 was also unstable. These data suggest that addition of TFA to *trans*-stilbene probably occurs, but other reactions also intervene, so this process was not pursued further.

Direct observation by NMR of the conversion of the styrenes to the corresponding trifluoroacetate esters according to eq 10 could be accomplished for the *m*-CF_3 and

$$XC_6H_4CH{=}CH_2 \longrightarrow XC_6H_4\underset{\underset{O_2CCF_3}{|}}{C}HCH_3 \longleftarrow XC_6H_4\underset{\underset{OH}{|}}{C}HCH_3 \quad (10)$$

m-O_2N derivatives. In the other cases rapid polymerization occurred, and only broad NMR absorptions were visible. However, in the case of the *p*-MeO, *p*-MeS, and *p*-Me substituents and 1,2-diphenylethanol, the clean conversion of the 1-arylethanols to the trifluoroacetate esters was observed by NMR in the reaction media. In particular, the distinctive methine proton of the esters absorbing near δ 5.7–6.2 was readily differentiated from the corresponding signal of the alcohols at δ 4.7–4.8. These esters underwent fairly prompt decomposition, with broadening of all signals, and isolation of the pure esters was not successful.

An authentic sample[11] of $PhCH(O_2CCF_3)CH_3$ was prepared by esterification of the alcohol. When styrene (21) reacted with TFA, the UV spectrum changed to that of this authentic ester.

Rates of hydration of *p*-MeS- (18), *p*-F- (20), and *m*-CF_3-substituted (25) styrenes catalyzed by H_2SO_4 had not previously been reported, so these were measured and are reported in Table II.

Discussion

The interpretation of the effect of substituents on the rate of reaction of CF_3CO_2H with styrenes and the consideration of the mechanism of this process can be usefully based on comparisons of rate constants of TFA addition with the substituent σ^+ parameters[12] and also on comparison of the rates to those of H_2SO_4-catalyzed hydration

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Table II. Reactivity of Styrenes $XC_6H_4CH{=}CH_2$ in Aqueous H_2SO_4 at 25 °C[a]

X	$[H_2SO_4]$, M	wt %	H_0	k_{obsd}, s^{-1}
p-MeS[b]	6.10	44.8	−2.82	6.06×10^{-2}
	5.00	38.3	−2.32	1.05×10^{-2}
	2.96	24.8	−1.36	3.17×10^{-4}
	1.09	10.2	−0.34	3.01×10^{-5}
p-F[c]	8.79	58.5	−4.27	6.09×10^{-2}
	6.10	44.8	−2.82	1.28×10^{-3}
	4.99	38.3	−2.32	2.65×10^{-4}
m-CF_3[d]	12.01	72.3	−6.14	5.15×10^{-2}
	9.66	62.2	−4.73	1.78×10^{-3}
	7.60	52.5	−3.63	8.34×10^{-5}

[a] Duplicate runs in each case; ±5% error. [b] Log $k = -1.34H_0 - 5.10$; $r = 0.995$. [c] Log $k = -1.20H_0 - 6.33$; $r = 0.999$. [d] Log $k = -1.11H_0 - 8.06$; $r = 0.999$.

Table III. Reactivity of Styrenes in Aqueous H_2SO_4 as a Function of Acidity

		log k	
styrene	dk_{obsd}/dH_0	$H_0 = 0$	$H_0 = -2.71$[e-g]
17	−1.27[a]	−4.22	−0.78
18	−1.34[b]	−5.10	−1.47
19	−1.21[a]	−5.47	−2.19
20	−1.20[b]	−6.33	−3.07
21	−1.17[a]	−6.43	−3.26
22	−1.08[a]	−6.70	−3.77
23	−1.11[a]	−7.74	−4.73
24	−1.10[a]	−7.64	−4.66
25	−1.11[b]	−8.06	−5.06
26	−1.16[a]	−9.28	−6.14
28			(−4.21)[c]
29	−1.26[d]	−9.20	−5.78

[a] Reference 1i. [b] This work. [c] Estimated from the rate of 21 and a 21/26 rate ratio of 10 reported by: Yates, K.; Schmid, G. H.; Regulski, T. W.; Garratt, D. G.; Leung, H.-W.; McDonald, R. *J. Am. Chem. Soc.* **1973**, *95*, 106–5. [d] Reference 3c. [e] Log k(100% TFA) = 1.53 log $k(H_2SO_4)$ + 3.12; $r = 0.991$ (omitting 18). [f] Log k(50% TFA) = 1.43 log $k(H_2SO_4)$ + 1.44; $r = 0.994$. [g] Log k(20% TFA) = 1.37 log $k(H_2SO_4)$ − 3.47; $r = 0.993$.

of the same styrenes.[13] The data are collected in Tables I and III.

In Figure 1 log k values for addition of TFA in the various solvent systems are compared to the σ^+ values of the substituent. Linear correlations are apparent as shown, excluding the substituents p-MeO, p-MeS, and m-O_2N, with slopes and correlation coefficients as follows: $\rho^+ = -4.82$, $r = 0.996$ (100% TFA); $\rho^+ = -5.08$, $r = 0.993$ (50% TFA); $\rho^+ = -5.39$, $r = 0.996$ (20% TFA). The causes of the deviations for the p-MeO, p-MeS, and m-O_2N substituents are considered in more detail below.

In Figure 2 log k values for the TFA additions are compared to log k for hydration of the same substrates catalyzed by H_2SO_4.[13] Respective slopes and correlation coefficients, respectively, in the different media are as follows: 1.53, 0.991 (100%, TFA); 1.43, 0.994 (50% TFA); 1.37, 0.993 (20% TFA). Only the point for the p-MeS derivative in 100% TFA was not included in the correlation.

Figures 1 and 2 show that there are direct relationships between the rates of reaction of styrenes in CF_3CO_2H and both the σ^+ parameters and the rates in H_2SO_4. Dependence of log k on σ^+ is diagnostic of rate-limiting carbonium ion formation, so this result provides strong evidence that this is the mechanism followed. Similarly the close

(13) The H_2SO_4 rates are calculated at $H_0 = -2.71$, which is the H_0 for 100% CF_3CO_2H: Spitzer, U. A.; Toone, T. W.; Stewart, R. *Can. J. Chem.* **1976**, *54*, 440–7.

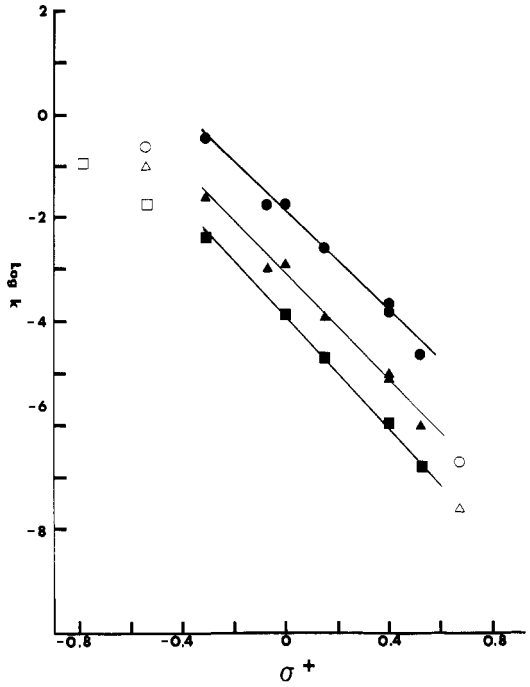


Figure 1. Correlation of rates of addition of CF_3CO_2H to styrenes $XC_6H_4CH{=}CH_2$ with σ_x^+ in 100% (●), 50% (▲), and 20% (■) (v/v) CF_3CO_2H in CCl_4 at 25 °C (open characters not included in the linear correlations shown).

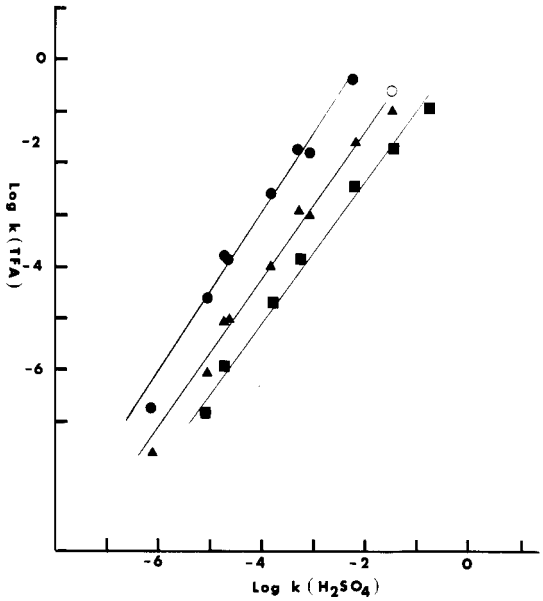
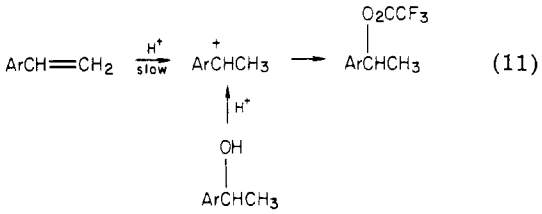


Figure 2. Rates of addition of CF_3CO_2H to styrenes $XC_6H_4CH{=}CH_2$ in 100% (●), 50% (▲), and 20% (■) (v/v) CF_3CO_2H in CCl_4 compared to rates of hydration in aqueous H_2SO_4, $H_0 = -2.71$ at 25 °C (open character not included in the linear correlations shown).

correspondence of the rates of TFA addition and the H_2SO_4-catalyzed hydrations argues strongly for a similarity in mechanism for both processes and since the Ad_E2 pathway is generally supported for the latter process it is indicated for the former as well.

The product studies indicate that addition of TFA to the styrenes occurs in dilute solutions, although for the more reactive styrenes polymerization is dominant in more concentrated solutions, and the products are relatively unstable as well. Gillen, Knipe, and Watts[8] showed that 1-phenylethanols substituted with m- or p-O_2N, m- or p-Cl, and p-Me groups all reacted with TFA to give the corresponding esters, and we have directly observed formation

of the esters from the p-MeO, p-MeS, and p-Me alcohols and the m-O_2N- and m-CF_3-substituted styrenes. The addition of TFA to styrene in an 0.8 M solution in CCl_4 has also been reported.[14] Thus the kinetic and product studies taken together provide strong evidence that the styrenes undergo rate-limiting protonation by CF_3CO_2H to give intermediate carbonium ions which can also be generated from the corresponding alcohols and that these ions form trifluoroacetate esters (eq 11) which are, however, not always stable to the reaction conditions.



(11)

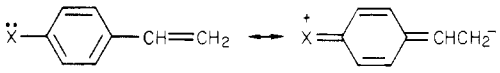
While it appears unequivocal that rate-limiting protonation of the styrenes by TFA occurs, it is also clear that certain deviations from the correlations occur. Specifically the p-MeO, p-MeS, p-F, and m-O_2N styrenes are all less reactive than expected from the rate correlations with σ^+. Significantly, all of these substituents are capable of hydrogen bonding with the acidic solvent, and such an interaction would be expected to make these substituents less electron donating than would be indicated by their σ^+ constants, which are derived from solvolysis in aqueous acetone.[12]

This phenomenon has been previously reported by several authors. Thus it was found that ^{13}C chemical shifts of the ring carbons of substituted benzenes could be correlated with the σ^+ constants of the substituents, and the chemical shifts in turn could be used to predict σ^+ constants.[15,16] Much more positive σ^+ values were found for p-O_2N and p-MeO groups in TFA by this method, and this result was attributed[15] to the ability of this solvent to hydrogen bond to these substituents.

Separate values of σ^+ for substituents in aqueous H_2SO_4 have been derived from equilibrium constants for arylmethyl cation formation,[17] and these values are also more positive for p-MeO and p-F than those obtained from cumyl chloride solvolysis.[12] Also, in a study of TFA additions to 4-aryl-1-butenes the rates of the methoxy and other derivatives were interpreted as being diminished due to hydrogen bonding of the substituent to the solvent which diminished the electron-donating ability of the substituents.[18a] Proton NMR shifts of substituted alkanes in TFA were also ascribed to hydrogen bonding.[18b] Similarly, in a study of the influence of solvents on substituent-induced ^{19}F chemical shifts, large effects were attributed to hydrogen bonds of CF_3CO_2H to MeO, MeS, and O_2N groups but not F itself.[18c] A correlation of the rates of Beckmann rearrangement of acetophenone oximes in 98.2% H_2SO_4 also showed negative deviations for MeO, F, and NO_2 substituents, and in the case of the NO_2 substituents these deviations were attributed to hydrogen bonding of the substituents to the solvent.[18d] Finally, a lower than expected solvolysis rate for 2-anisylethyl tosylate in acetic acid was attributed to hydrogen bonding of the solvent to the methoxy group.[18e]

Thus there are several independent lines of evidence that indicate that the σ^+ values derived from rates in aqueous acetone are not completely suitable for correlation of rate measurements in acidic media. This is confirmed by the much better correlations which are obtained when the rates of styrene protonations in TFA solutions are compared to rates in aqueous H_2SO_4 (Figure 2). All of the substituents are included in these correlations, with the one exception being p-MeS in 100% TFA. These results offer strong confirmation that the deviations for the p-MeO, p-MeS, and m-O_2N substituents are caused by hydrogen bonding of the substituents to the acidic solvent and that the effects are similar in H_2SO_4 and CF_3CO_2H. The fact that the points for these three substituents still deviate somewhat below the TFA–H_2SO_4 correlation suggests that the former medium may form somewhat stronger hydrogen bonds.

A quite different effect which may be considered as a cause for the deviations in the correlations of log k with σ^+ for the H_2SO_4-catalyzed reactions would be the existence of selective ground-state stabilization in certain styrenes that is not present in the corresponding cumyl chlorides. Specifically extended conjugation between resonance electron donating substituents and the vinyl group could occur as shown in eq 12, and if this interaction



(12)

caused a significant lowering of the ground-state energy, then deviations in the direction of lower than anticipated reactivity could occur.

Calculations of the effects of para substituents on the stability of styrene (STO-3G minimal basis set with fixed geometries) showed that electron-donating and electron-withdrawing substituents all stabilized the molecule.[16] However, there is no firm evidence for a significant role for the effect shown in eq 12 on the kinetics, so we prefer to interpret the deviations in the rates of the styrene protonations as due to an increase in substituent electron-withdrawing power caused by hydrogen bonding.

The reactivities of the styrenes in TFA and in aqueous H_2SO_4 could be used to define specific σ^+ parameters for use in acidic solvents, but as these should be continuously variable for the range of possible solvents, it appears preferable to utilize the existing solvolytic parameters,[12] with due consideration of the factors that cause them to vary.

It is also striking that there is little variation of ρ^+ for styrene protonations even though the solvent varies from 100% to 20% CF_3CO_2H in CCl_4. However, it may be noted that other ρ^+ values are not strongly solvent dependent. The the ρ^+ for cumyl chloride solvolysis is −4.43 in 2-propanol and −4.82 in methanol.[19] Also the dielectric constant of CF_3CO_2H (ϵ = 8.22)[13] is low, so that large changes in this parameter are not expected to occur when this solvent is diluted with CCl_4.

The comparison of rates in TFA with those in aqueous H_2SO_4 also permits the inclusion in the comparison of substrates such as the 1-phenylpropenes and stilbene in addition to the aryl-substituted styrenes shown in Figure 2. All of these substrates can also be included in the

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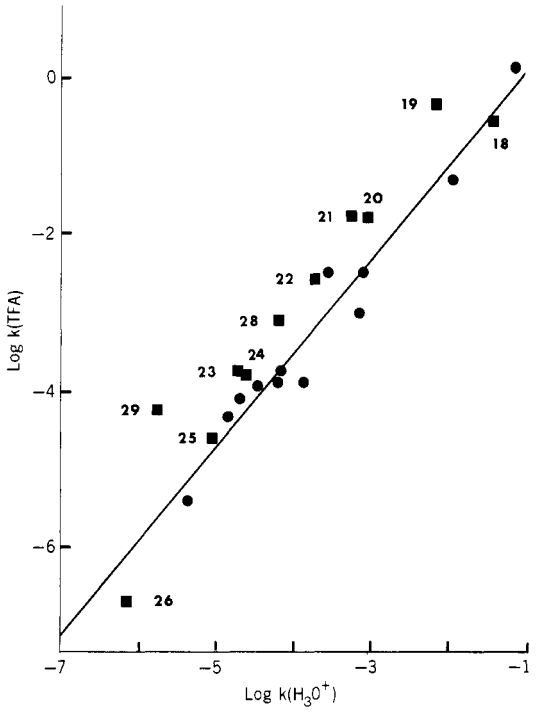

Figure 3. Rates of addition of 100% CF_3CO_2H to alkenes (■, styrenes; ●, aliphatic alkenes) compared to rates of hydration in aqueous H_2SO_4, $H_0 = -2.71$, at 25 °C.

comparison with the aliphatic substrates in these same two media, as previously presented (Figure 3).[9] The subset of points **19–26** give a slightly steeper slope than the previously defined line, but it is not certain if this effect is chemically significant. It is clear that there is a definite correspondence between the reactions of all the substrates in the two acids. This confirms our earlier conclusion[9] that there is a direct similarity in mechanism in these media and that the addition of CF_3CO_2H proceeds by rate-limiting protonation on carbon (eq 11) with no detectable kinetic consequences of any prior π complexation.

In summary, the addition of CF_3CO_2H to substituted styrenes is found to occur by slow protonation on carbon (the Ad_E2 mechanism) in pure acid as well as in 20% and 50% solutions of acid in CCl_4. A direct correspondence between CF_3CO_2H additions and H_2SO_4-catalyzed hydration is observed, and compounds bearing substituents capable of hydrogen bonding to the acidic medium are found to react at rates lower than predicted on the basis of σ^+ parameters for these groups derived from solvolytic behavior.

Experimental Section

Trifluoroacetic acid (Aldrich) was distilled immediately before use. Trifluoroacetic anhydride has a significant UV absorption in the region in which the styrenes absorb and so was not used for drying purposes. Styrenes **17**, **19–24**, and **26–30** were obtained from commercial sources. 4-$MeSC_6H_4CH{=}CH_2$ (**18**)[20] and *m*-$CF_3C_6H_4CH{=}CH_2$ (**25**)[21] were prepared by P_2O_5 dehydration of the 1-arylethanols.

Except for **26**, the kinetics of TFA addition were measured by observing the decrease in the styrene absorption by UV spectroscopy with a Cary 210 instrument with a thermostated cell compartment. Wavelengths of observation were at 258 nm except for **17** (257 nm), **18** (280 nm), and **22** (290 nm). These were not always the absorption maxima because of interference from solvent absorption. For kinetic measurements on **26** a 0.3 M solution of TFA was sealed in an NMR tube and immersed in the constant-temperature bath. At intervals the tube was withdrawn, the vinyl and methine absorptions were integrated, and the sample was replaced in the bath. Time intervals between readings were 0.5–3 h, depending upon the temperature.

Rates in H_2SO_4 were measured for 2×10^{-4} M solutions at the absorption maxima of **18** (280 nm) and **20** (244 nm) and at 258 nm for **25** (not a maximum).

For product studies the esters $PhCH(O_2CCF_3)CH_3$,[11] $PhCH(O_2CCF_3)CH_2CH_3$, and $PhCH(O_2CCF_3)CH_2Ph$ were prepared by treatment of the corresponding alcohols with trifluoroacetic anhydride and pyridine.[11] The latter ester after vacuum distillation (15 mm, 100 °C) gave the following: NMR (CCl_4) δ 3.2 (m, 2, diastereotopic CH_2), 6.00 (q, 1, CHO), 7.2 (m, 10, aromatic). Anal. Calcd for $C_{16}H_{13}F_3O_2$ (mol wt 294.27): C, 65.31; H, 4.45. Found (Galbraith): C, 65.43; H, 4.56.

Esters $XC_6H_4CH(O_2CCF_3)CH_3$ were generated by treatment of **25**, **26**, and 1-arylethanols with CF_3CO_2H in CCl_4 and characterized by their NMR spectra which showed doublets (J = 7 Hz) due to the CH_3 at δ 1.30–1.40 and the methine proton as a quartet (J = 7 Hz) at δ 6.06 (*p*-MeO, 7% TFA), 5.99 (*p*-MeS, 10% TFA), 6.06 (*p*-Me, 50% TFA), 6.22 (*m*-CF_3, 100% TFA), 6.11 (*m*-O_2N, 50% TFA), and 5.88 (H, CCl_4, prepared as above[11]). The esters with *p*-MeO, *p*-MeS, and *p*-Me decomposed on prolonged standing in solution. Dilution of the solution with water followed by ether extraction, $NaHCO_3$ washing, drying, and evaporation gave the isolated trifluoroacetate ester for *p*-MeS as further characterized by the sharp carbonyl bond in the IR at 1700 cm^{-1} (CCl_4). However, this ester decomposed on attempted distillation.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. M.R. was a recipient of an NSERC summer undergraduate fellowship, 1981.

Registry No. **17**, 637-69-4; **18**, 18760-11-7; **19**, 622-97-9; **20**, 405-99-2; **21**, 100-42-5; **22**, 2039-82-9; **23**, 2039-86-3; **24**, 2039-85-2; **25**, 402-24-4; **26**, 586-39-0; **27**, 766-90-5; **28**, 873-66-5; **29**, 645-49-8; CF_3CO_2H, 76-05-1; $PhCH(O_2CCF_3)CH_2Ph$, 82638-97-9; *p*-$MeOC_6H_4CH(O_2CCF_3)CH_3$, 82638-98-0; *p*-$MeSC_6H_4CH(O_2CCF_3)CH_3$, 82638-99-1; *p*-$MeC_6H_4CH(O_2CCF_3)CH_3$, 82639-00-7; *m*-$CF_3C_6H_4CH(O_2CCF_3)CH_3$, 82639-01-8; *m*-$O_2NC_6H_4CH(O_2CCF_3)CH_3$, 82639-02-9; $C_6H_5CH(O_2CF_3)CH_3$, 1524-12-5.

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