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PROTONATION OF 1-ARYL-3,3,3-TRIFLUOROPROPYNES

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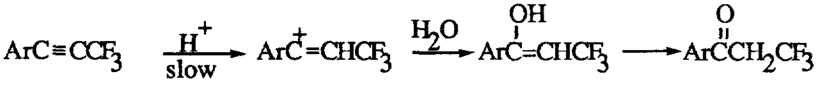
Abstract. 1-Aryl-3,3,3-trifluoropropynes (**1**) react in aqueous acid with $\rho^+ = -6.5$, and the gas phase basicity of $4\text{-}CH_3C_6H_4C{\equiv}CCF_3$ is 7.8 kcal/mol less favorable than that of $4\text{-}CH_3C_6H_4C{\equiv}CH$, showing high electron demand and major destabilization in $Ar\overset{+}{C}{=}CHCF_3$.

Protonation of arylalkynes in solution[2] and in the gas phase[3] has been of wide interest, and we have undertaken a study of the effect of the β-CF_3 substituent on formation of vinyl carbocations in this reaction, as illustrated in Eq. 1 for hydration in aqueous acid.



$$\underset{\mathbf{1}}{ArC{\equiv}CCF_3} \xrightarrow[\text{slow}]{H^+} \underset{\mathbf{2}}{Ar\overset{+}{C}{=}CHCF_3} \xrightarrow{H_2O} Ar\overset{OH}{\overset{|}{C}}{=}CHCF_3 \longrightarrow \underset{\mathbf{3}}{Ar\overset{O}{\overset{\|}{C}}CH_2CF_3} \qquad \text{(Eq. 1)}$$

Despite the strong electron withdrawing power of the CF_3 group it has proved possible to generate a variety of carbocations with α-CF_3 substituents.[4a,b] The destabilization of these carbocations by the α-CF_3 group results in large rate decellerations for their formation by factors of 10^6 in many systems, but there are only a few studies of the effects of more remote CF_3 groups.[4]

Rates of hydration of $ArC{\equiv}CCF_3$[5] catalyzed by H_2SO_4 according to Eq. 1 were measured by UV spectroscopy and gave excellent correlations with the acidity function

H_o, as reported in Table I. These reactivities cover a very large range of reactivity (10^8), and the correlation of the rates with the electrophilic substituent parameter σ^+ (Fig. I) gave a ρ^+ value of -6.51 ($r = 0.964$). The deviation of the 4-CH_3O derivative below the correlation line and the resulting mediocre correlation coefficient **r** is likely due to hydrogen-bonding of the acidic solvent to the substituent, a phenomenon observed previously.[6]

Fig. I. Correlation of Protonation Reactivity of **1** with σ^+

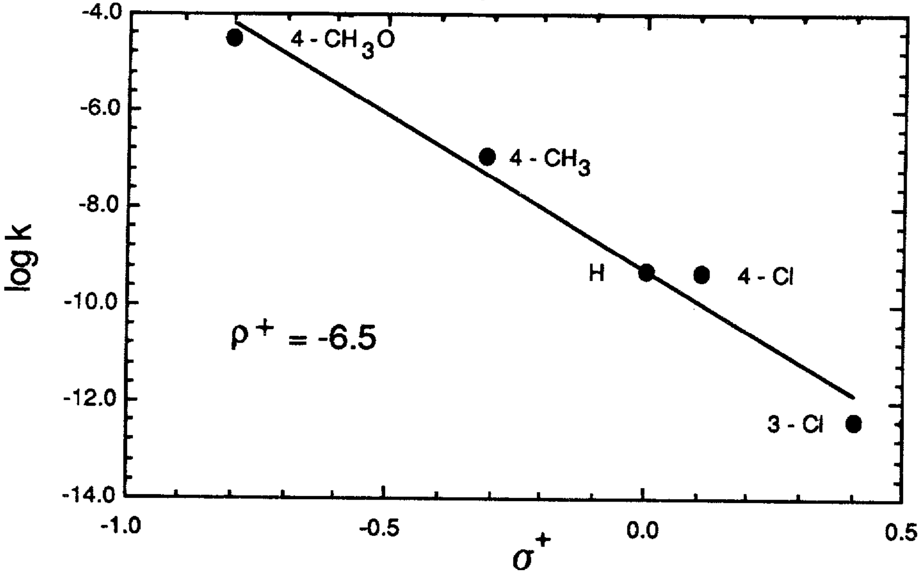


Table I. Hydration of $XC_6H_4C{\equiv}CCF_3$ with H_2SO_4 at 25°C

X	Slope[a]	log k_{H^+}[b]	k_{H^+}($M^{-1}s^{-1}$)	$\frac{k_{H^+}(ArC{\equiv}CH)^c}{k_{H^+}(ArC{\equiv}CCF_3)}$
4-CH_3O	-1.12	-4.60	0.251×10^{-4}	15
4-CH_3	-1.11	-7.00	1.00×10^{-7}	50
H	-1.21	-9.33	0.468×10^{-9}	650
4-Cl	-1.15	-9.38	0.417×10^{-9}	410
3-Cl	-1.38	-12.39	0.407×10^{-12}	1.5×10^4

[a] d k_{obs}/d H_o [b] intercept of d k_{obs}/d H_o [c] ref. 2a,c

The magnitude of ρ^+ is much greater than those of -3.8[2c] and -3.5[2d] observed for solution phase hydration of ArC≡CH and indicates strong electron demand in the transition state. The positive deviation of the point for the 4-Cl derivative suggests an enhanced electronic donation from this group.

The rate ratios k_{H^+}(ArC≡CH)/k_{H^+}($ArC≡CCF_3$) (Table I) decrease with stronger donor power of the aryl substituent and indicate that strong aryl donors overcome much of the transition state destabilization due to the CF_3. Other studies of β-substituent effects on alkyne protonation show complex behavior.[2a,7] Thus a CH_3 group at the position of protonation has a variable effect, as $PhC≡CCH_3$ is less reactive than PhC≡CH by factors of 247[a] to 28,[7d] but $CH_3C≡CCH_3$ is more reactive than $CH_3C≡CH$.[2a] The acid-catalyzed hydration of phenylpropiolic acids $ArC≡CCO_2H$ to $ArCOCH_2CO_2H$[7b] and of ArC≡CCOPh[7c] to $ArCOCH_2COPh$ gave ρ^+ values of -4.77 and -4.21, respectively, and k_{H^+} for $PhC≡CCF_3$ is 18 and 42 times greater than those for $PhC≡CCO_2H$ and PhC≡CCOPh, respectively. These effects are under further study.

Measurement of the gas phase basicity of $4\text{-}CH_3C_6H_4C≡CCF_3$ (Eq. 2)[8] gives a GB value of 189 kcal mol^{-1}, which is 7.8 kcal mol^{-1} less than that of $4\text{-}CH_3C_6H_4C≡CH$[3a] (GB = $-\Delta G°$). Thus the CF_3 group is having a strong destabilizing effect on the stability of this carbocation in the gas phase which is far greater than suggested by the rate difference of only a factor of 50 for these substrates in solution (Table I). Studies to further elucidate the fascinating behavior of these compounds are underway.

$$4\text{-}CH_3C_6H_4C{\equiv}CCF_3 \quad +H^+ \rightleftharpoons 4\text{-}CH_3C_6H_4\overset{+}{C}{=}CHCF_3 \qquad (2)$$

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(8) Measured as previously described[3a] using a Nicolet FT-MS 1000 spectrometer of the "Servizio FT-MS, Area di Ricerca del CNR di Roma".

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