Acid-Catalyzed Hydration of α-Cyano and α-Trifluoromethyl Vinyl Ethers. Additivity of Strongly Activating and Strongly Deactivating Substituent Effects

Annette D. Allen, Fereidoon Shahidi, and Thomas T. Tidwell*

Contribution from the Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada M1C 1A4. Received July 27, 1981. Revised Manuscript Received November 2, 1981

Abstract: The reactivities of 1-cyano-1-ethoxyethene (1) and 1-(trifluoromethyl)-1-ethoxypentene (2) in aqueous H_2SO_4 and D_2SO_4 have been measured. The kinetics and products establish the mechanism of these reactions as rate-limiting protonation on the double bond. The observed rates are predicted with surprising accuracy by the previously introduced correlation log $k_{H^+} = -10.5 \sum \sigma_p^+ - 8.92$.

Recently the quantitative study of the effects of strongly electron-withdrawing substituents on solvolytic reactions leading to electron-deficient intermediates has been actively pursued. Substituents that have been experimentally studied include CF_3,[1,2] CN,[3] $C=O$,[4] and CHOTs.[5] Theoretical studies of the effects of these groups have also appeared.[6]

An interesting aspect of these previous investigations has been the finding that the influence of the α-cyano group on a developing carbonium ion center appears to be variable. In studies of solvolysis kinetics of systems containing a relatively strong stabilizing substituent such as homoallyl H/CN rate ratios of approximately 10^6 have been observed,[3b,e] whereas in situations where only alkyl substituents are present the H/CN ratio ratio[3] is near 10^3.

The explanation advanced[3,6] for this behavior is that variable resonance electron donation by cyano can occur (eq 1) and that

$$\underset{}{>}\overset{+}{C}-C\equiv N \longleftrightarrow \underset{}{>}C=C=\overset{+}{N} \qquad (1)$$
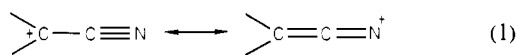
this effect is most significant when the electron demand at the carbonium ion center is high. The possibility of the interaction shown in (1) has been supported by the theoretical studies[6] and by the ^{15}N chemical shift[7] of Ph_2CCN^+.

In one of these theoretical studies it was found that CN was a π acceptor when attached to a π-donating group and a π-donor when attached to an electron-deficient center.[6e] In a calculation by Paddon-Row, Houk, and Tidwell[6c] it was predicted that although CN would be less destabilizing than CF_3 in the ion XCH_2^+ because of π donation by CN, the effect of these substituents in $HOCHX^+$ would be equally destabilizing. We have now undertaken an experimental test of this prediction.

The protonation of alkenes is well suited for the quantitative testing of the ability of substituents to affect the rates of carbonium ion forming reactions. It has already been shown[8a] that the correlation of the reaction in eq 2 by our eq 3[8b] fits the data for

$R_1 = Ar$ and $R_2 = CF_3$. Therefore this reaction has been chosen for an examination of the CN and CF_3 groups paired with the highly electron-donating EtO group.

$$\underset{}{>}C=C\overset{R_1}{\underset{R_2}{}} \quad \xrightarrow{H^+} \quad H-\overset{|}{\underset{|}{C}}-\overset{+}{C}\overset{R_1}{\underset{R_2}{}} \qquad (2)$$
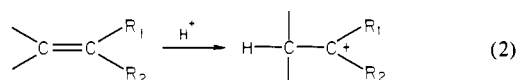
$$\log k_{H^+} = -10.5 \sum \sigma_p^+ - 8.92 \qquad (3)$$

Results and Discussion

The rates of reaction of $CH_2=C(CN)OEt$ (1)[9a] and n-$PrCH=C(CF_3)OEt$ (2)[9b] in sulfuric acid solutions were measured by observing the disappearance of the alkene chromophores in the UV and are reported in Table I. The reaction products were found to be acetic acid from 1 and 1,1,1-trifluoro-2-hexanone from 2.

Kinetic parameters for 1 and 2, specifically the slopes of plots of log k_{obsd} vs. the acidity function H_0 and kinetic isotope effects k_{H^+}/k_{D^+} are reported in Table I and are consistent with those which have been observed for a large number of other vinyl ethers which have been examined in aqueous acid.[10] In general the mechanisms of hydrolyses of vinyl ethers have been assigned to the Ad-E2 pathway of rate-limiting protonation on carbon, with the only exceptions being 9-methoxyoxacyclonon-2-ene (3)[11a] in
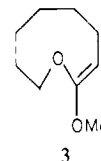
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which the initial protonation becomes reversible, and vinyl trimethylsilyl ethers,[11b] in which nucleophilic attack on silicon is involved in the rate-limiting step. The closest analogs to 1 and 2 which have been previously examined are the (E)- and (Z)-2-cyanovinyl ethyl ethers (NCCH=CHOEt),[10b] which were studied at acidities ($H_0 = -2.62$ to -4.30) comparable to those of 1 and 2 and which gave slopes of log k vs. H_0 of -0.95 and -0.96 for the Z- and E isomers, respectively, comparable to the values -0.94 and -0.89 for 1 and 2, respectively. The solvent isotope effects

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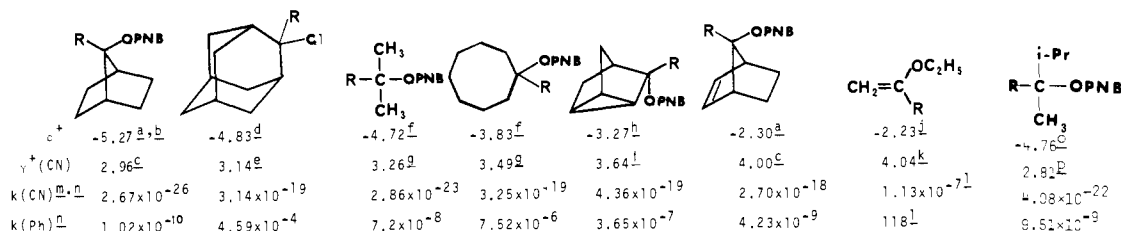
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Hydration of Cyano and Trifluoromethyl Vinyl Ethers

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Table I. Reactivity of Alkenes in Aqueous Sulfuric Acid at 25 °C

alkene	[H₂SO₄],^{c} M	wt %^{d}	H_0	k_{obsd}^{e}	[D₂SO₄],^{c} M	wt %^{d}	D_0^{f}	k_{obsd}^{e}	k_{H^+}/k_{D^+}^{g}
CH₂=C(CN)OEt^a	10.81	68.0	-5.50	1.61×10^{-2}	10.63	64.9	-5.41	2.48×10^{-3}	5.44
1	9.17	60.7	-4.54	2.22×10^{-2}	10.18	63.2	-5.14	1.59×10^{-3}	4.73
	8.16	55.5	-3.96	5.68×10^{-4}	9.07	58.3	-4.51	4.53×10^{-4}	4.25
	6.61	47.6	-3.13	9.94×10^{-5}	7.25	49.0	-3.49	5.63×10^{-5}	3.77
n-PrCH=C(CF₃)OEt^b	12.87	75.5	-6.64	1.17×10^{-2}	13.17	76.6	-7.18	4.92×10^{-3}	6.12
2	12.09	72.5	-6.18	3.32×10^{-3}	10.63	64.9	-5.41	1.55×10^{-4}	5.08
	10.92	67.9	-5.48	7.24×10^{-4}	10.48	64.4	-5.32	1.56×10^{-4}	4.20
	9.70	62.6	-4.77	2.33×10^{-4}	10.23	64.1	-5.28	1.34×10^{-4}	4.50
	8.90	58.5	-4.27	7.56×10^{-5}					

^{a} $\log k_{obsd} = -0.939H_0 - 6.95$. ^{b} $\log k_{obsd} = -0.894H_0 - 7.94$. ^{c} Determined by titration. ^{d} Determined by weighing and titration. ^{e} Rate constants were obtained in duplicate (±5%) by monitoring the decrease in UV absorption at 217 nm (1) or 205 nm (2). ^{f} D_0 values obtained from: Wyatt, P. A. H. *J. Chem. Soc. B* 1970, 1570. ^{g} Isotope effects were determined by calculating k_{H^+} at the H_0 equal to the D_0 at which k_{D^+} was measured.

	c^+	$\gamma^+(CN)$	$k(CN)^{m,n}$	$k(Ph)^o$
	$-5.27^{a,b}$	2.96^c	2.67×10^{-26}	1.02×10^{-10}
	-4.83^d	3.14^e	3.14×10^{-19}	4.59×10^{-4}
	-4.72^f	3.26^g	2.86×10^{-23}	7.2×10^{-8}
	-3.83^f	3.49^g	3.25×10^{-19}	7.52×10^{-6}
	-3.27^h	3.64^i	4.36×10^{-19}	3.65×10^{-7}
	-2.30^a	4.00^c	2.70×10^{-18}	4.23×10^{-9}
	-2.23^i	4.04^k	1.13×10^{-7}^{l}	118^l
	-4.76^c / 2.82^p		4.08×10^{-22}	9.51×10^{-9}

Figure 1. Cyano substituent effects on reactivity: a, Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* 1970, *92*, 2549–51 (*p*-nitrobenzoates in 70% dioxane); b, ref 15b; c, ref 3b; d, Tanida, H.; Tsushima, T. *J. Am. Chem. Soc.* 1970, *92*, 3397–403 (chlorides in 90% acetone); e, ref 3c; f, Brown, H. C.; Ravindranathan, M.; Peters, E. N.; Gunda Rao, C.; Rho, M. M. *Ibid.* 1977, *99*, 5373–8 (*p*-nitrobenzoates in 80% acetone); g, ref 3a; h, Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* 1975, *97*, 1927–9 (*p*-nitrobenzoates in 80% acetone); i, ref *3e*; j, Chiang, Y.; Chwang, W. K.; Kresge, A. J.; Robinson, L. H.; Sagatys, D. S.; Young, C. I. *Can. J. Chem.* 1978, *56*, 456–60 (vinyl ether protonation in aqueous acid); k, this work; l, k_{H^+} (M⁻¹ s⁻¹); m, conversion factors used include k(OPNB, 70% dioxane) = $(1.59 \times 10^{-10})k$(OTs, HOAc) from a, k(OTs, HOAc) = $(3.9 \times 10^{-3})k$(OTs, TFE) from : Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1976, *98*, 7667–76, k(OPNB, 80% acetone) = $(3.27 \times 10^{-11})k$(OTs, HOAc) from ref 15b, k(Cl, 90% acetone) = $(5.58 \times 10^{-8})k$(OTs, HOAc) from ref 15 b [these factors led to the new relations k(OPNB, 70% dioxane) = $(6.2 \times 10^{-13})k$(OTs, TFE), k(OPNB, 80% acetone) = $(1.28 \times 10^{-13})k$(OTs, TFE), and k(Cl, 90% acetone) = $(2.18 \times 10^{-10})k$(OTs, TFE)]; n, s⁻¹, 25 °C; o, Brown, H. C.; Peters, E. N.; Ravindranathan, M. *J. Am. Chem. soc.* 1977, *99*, 505–9; p, ref 3d.

for **1** and **2** are dependent upon the acidity but are always much greater than 1.0, and this behavior is convincing evidence for the Ad-E2 mechanism.[10a] These kinetic results and the observed products permit the assignment of the Ad-E2 path for **1** and **2**, as shown in eq 4 and 5. The formation of **4** as the precursor to acetic acid from **1** is consistent with the known reactivity of the postulated intermediate **4** in aqueous acid.[12,13]

$$CH_2\!=\!C \begin{array}{c} CN \\ OEt \end{array} \xrightarrow[slow]{H^+} CH_3C^+ \begin{array}{c} CN \\ OEt \end{array} \xrightarrow[fast]{H_2O} [CH_3CCN] \xrightarrow{H_2O} CH_3CO_2H \quad (4)$$

1 , **4**

$$n\text{-}PrCH\!=\!C \begin{array}{c} CF_3 \\ OEt \end{array} \xrightarrow[slow]{H^+} n\text{-}PrCH_2C^+ \begin{array}{c} CF_3 \\ OEt \end{array} \xrightarrow[fast]{H_2O} n\text{-}BuCCF_3 \quad (5)$$

2
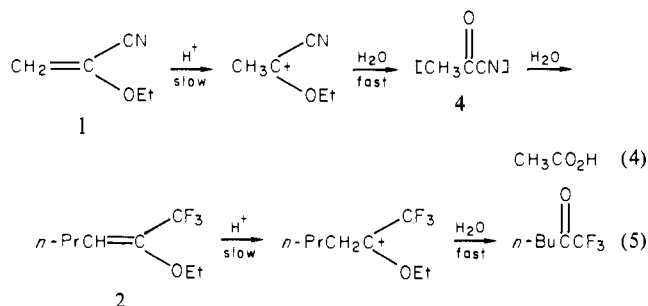
The k_{H^+} values predicted[14] for **1** and **2** by eq 3 are 7.33×10^{-8}

(12) Hibbert, F.; Satchell, D. P. N. *J. Chem. Soc. B* 1967, 755–7.
(13) Conversion of **1** in H₂SO₄ to CH₂=C(CO₂H)OEt has been claimed by: Movsum-Zade, E. M.; Mamedov, M. G.; Nuriev, F. L.; Shikhiev, I. A. *Zh. Org. Khim.* 1977, *13*, 1828–30. Under the conditions they report we find that **1** gives only acetic acid. The acid hydrolysis of CH₂=C(OEt)CHO has recently been reported by Keiko et al. (Keiko, N. A.; Musorina, T. N.; Frolov, Yu. L.; Shulanova, A. M.; Chuvashov, Yu. A.; Voronkov, M. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1981, 1993–6).
(14) The rates were calculated by our usual procedure at $H_0 = 0$ using σ_p^+ constants of 0.66 (CN), 0.61 (CF₃), and -0.83 (EtO). The *n*-propyl group is expected to have only a minor effect on the reactivity of **2**, as it is known that effects of β-alkyl substituents on the rates of protonation of alkenes according to eq 2 are small but variable, with values of k_{unsub}/k_{sub} ranging from 11 to 0.51 (Knittel, P.; Tidwell, T. T. *J. Am. Chem. Soc.* 1977, *99*, 3408–14). The rate of the unknown CH₂=C(CF₃)OEt is presumably related to that of **2** by a similar factor, so that there is an uncertainty of this magnitude in the rate for **2** calculated by eq 3.

and 2.45×10^{-7} M⁻¹ s⁻¹, whereas the observed values are 1.13×10^{-7} and 1.14×10^{-8} M⁻¹ s⁻¹, respectively. If these points and included in the correlation of eq 3 based on 29 selected points previously reported,[8b] the correlation coefficient for the complete set improves, with errors for **1** and **2** of 0.40 and -1.14, respectively, as compared to the standard deviation of 0.83. Thus the fit of points **1** and **2** to the correlation compares favorably with that of the points used to define the correlation. This illustrates the predictive value of this equation and strongly supports the mechanisms of eq 4 and 5.

It is worthy of further note that whereas the predicted rate ratio **1**/**2** is 0.30, the observed value is 10. Thus the cyano compound is modestly more reactive than the CF₃ derivative, whereas the reverse is predicted. This raises the question of whether or not there is still some residual resonance electron donation by CN relative to that predicted from the σ_p^+ constants or whether the deviations are simply beyond the predictive powers of eq 3. A definitive answer to this question cannot be given, but there is an independent method available for quantitatively assessing the electron-donating abilities of substituents in situations of variable electron demand. This is the γ^+ treatment in which the ability of a substituent to influence the rate of formation of a carbonium ion **5** is assessed by fitting the rate effect of the α substituent on

$$R\!-\!C^+ \qquad Ar\!-\!C^+$$

5 , **6**
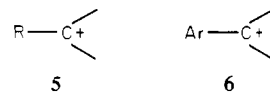
formation of the cation **5** to the correlation of the effect of aryl groups on formation of the cations **6**.[15] Thus the γ^+ constant

(15) (a) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* 1967, *89*, 2304–16. (b) Peters, E. N. *Ibid.* 1976, *98*, 5627–32. (c) Peters, E. N. *J. Org. Chem.* 1977, *42*, 1419–24. (d) McManus, S. P.; Harris, J. M. *Ibid.* 1977, *42*, 1424–9.
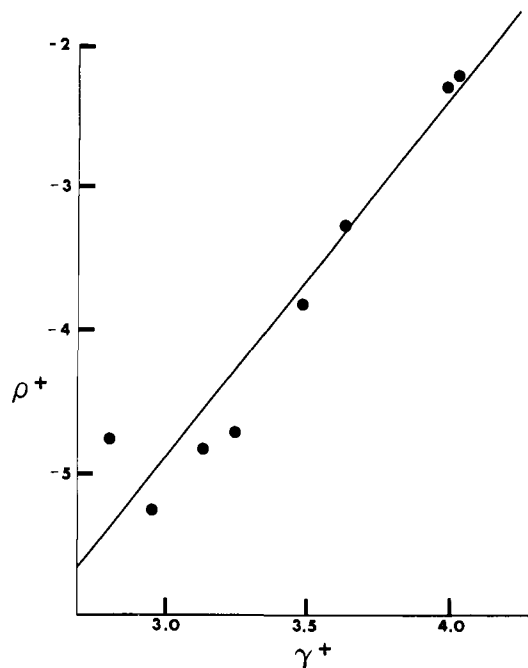
Figure 2. Correlation of γ^+ with ρ^+ for cyano substituted derivatives.

for Ar = Ph is defined as 0.0. Calculated γ^+ values for CN in various situations from available data are shown in Figure 1 and are compared to ρ^+ values as a measure of electron demand in these systems.

These data show a regular increase in γ^+ with ρ^+ (Figure 2, $\rho^+ = 2.50\gamma^+ - 12.4$, $r = 0.960$). Thus the destabilizing effect of CN is enhanced as the carbonium ion becomes more stable. This result is consistent with the other information available[3,6] on the effect of the CN group, and the fact that the quantitative fit is only fair is not surprising in view of the very different types of substrates being compared. Values of γ^+ show some dispersion even for substituents expected to have a constant interaction mechanism such as hydrogen and methyl.

There are not yet many data available to allow derivation of γ^+ values for CF_3. From the present results, the value calculated for vinyl ether protonation is 4.49, as compared to values of 3.69 from solvolysis of $PhC(CF_3)CH_3OTs$[1c] and 3.00 for CF_3CMe_2OTf.[1b] The latter system, however, reacts by rate-limiting elimination and **2** is only an approximate model for the vinyl ether correlation, so clearly more systems must be studied to properly analyze this substituent. The other studies of the CF_3 substituent lead to the expectation that this group will have a relatively constant substituent effect.

The tentative conclusion from Figure 2 is that the α-CN substituent has a continuously variable electronic effect depending

upon cation stability. It will be interesting to see if this trend is confirmed by further studies.

The vinyl ethers **1** and **2** are the least reactive ever studied, with **1** being less reactive than the isomeric (E)-NCCH=CHOEt, which heretofore had the lowest reported value for k_{H^+} at $H_0 = 0$,[10b] by a factor of 20. The α-cyano vinyl ether **1** is unique among cyano-substituted substrates in being less reactive than the β isomer in contrast to the results for sulfonate solvolysis. For the latter systems reported so far[3c,d] the α isomers are more reactive by factors of 10^2–10^4, a result attributed to resonance electron donation in these isomers. In **1** the requirement for such stabilization has been suppressed by the strong electron donation of the ethoxy group.

In summary the utility of eq 3 for predicting the rates of alkene protonations has been confirmed again, and this relation has been shown to be applicable to situations where both strongly donating and strongly electron-withdrawing substituents are present. The resonance electron-donating effect of cyano appears to be directly related to the electron demand at a developing carbonium ion center, as measured by the magnitude of the ρ^+ value.

Experimental Section

1-Cyano-1-ethoxyethene (**1**) was prepared by the reported method[9a] with the modification that the precursor 1-ethoxy-1,2-dibromoethane was prepared by the addition of Br_2 to ethyl vinyl ether (Aldrich): NMR (**1**, $CDCl_3$) δ 1.35 (t, 3, J = 7 Hz, CH_3), 3.86 (q, 2, J = 7 Hz, OCH_2), 4.95 (q, 4, CH_2=). 1-(Trifluoromethyl)-1-ethoxypentene (**2**) was prepared by the reported method.[9b] The alkene stereochemistry has not been assigned.[9b]

Kinetics for **1** were monitored by injecting 1.5 μL of a 0.1 M solution of **1** in CH_3CN into 1.2 mL of acid solution in a 1-cm path length UV cell to give a 1.2×10^{-4} M solution and then observing the decrease in the alkene maximum at 217 nm using an absorbance range of 0–1. For **2** 5 μL of a 0.2 M solution in MeOH was injected into 3 mL of acid to give a 3×10^{-4} M solution and the decrease in the alkene end absorption at 205 nm using an absorbance range of 0–0.1 was then observed with a Cary 118 spectrophotometer.

For a product study 0.32 g (3.3 mmol) of **1** was heated 3 h at 100 °C in a solution of 0.8 mL of H_2O and 0.8 g of concentrated H_2SO_4. The sulfuric acid was neutralized with $(NH_4)_2CO_3$ and the solution repeatedly extracted with ether. Evaporation of the ether extract gave acetic acid as the only detectable product as identified by NMR and formation of the cyclohexylamine salt.

Reaction of **2** (0.6 g, 3.3 mol) in 9 M H_2SO_4 for 48 h at 25 °C followed by ether extraction and washing with cold 5% KOH gave CF_3CO-n-Bu as the only observable product by comparison with an authentic sample.[16]

(16) Dishart, K. T.; Levine, R. *J. Am. Chem. Soc.* **1956**, *78*, 2268–70.