d, 6, methyl), 0.99 (m, 2, cyclopropyl); ^{13}C NMR ($CDCl_3$) 27.6, 16.5, 7.7 ppm; precise mass calcd for $C_7B_{10}H_{20}$ 214.2496, found 214.2506.

In addition, 3.7% of **6**, the product of C-H insertion, was found: ^1H NMR (400 MHz, $CDCl_3$) δ 5.43 (m, 1, vinyl), 5.20 (m, 1, vinyl), 2.89 (br s, 1, carborane H), 2.0–3.1 (m, B-H), 2.07 (m, 2, methylene), 1.93 (m, 2, methylene), 6.25 (br, d, 3, methyl); precise mass calcd for $C_7B_{10}H_{20}$ 214.2496, found 214.2498.

Photolyses of Cyclopropanes (4a). Approximately 3 mg of a GC-purified sample of **4b** was dissolved in 500 mL of $CDCl_3$ in an NMR tube. It was photolyzed with a Hanovia lamp for 5.5 h. The solution turned brown. The sample was checked by NMR and GC before and after photolysis. No isomerization to other cyclopropanes was detected. Some of the material decomposed during the photolysis.

Photolysis of Cyclopropane 4b. Approximately 5 mL of a sample predominantly of **4a** was dissolved in 500 mL of benzene-d_6 in an NMR tube. It was photolyzed with a Hanovia lamp for 4 h. The sample was monitored by NMR spectroscopy and flame GC before and after photolysis. No change was found.

Photolysis of Cyclopropanes 2a and 2b. These compounds were dissolved in hexane, degassed, and irradiated with a 450-W Hanovia lamp overnight through Pyrex. Gas chromatographic analysis showed no change.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grants CHE-77-24625, CHE-77-10025, CHE-81-01212) for their generous support of this work. Throughout this work we were ably assisted by the Princeton Spectroscopy Lab and by Mary W. Baum in particular. Our thanks go to them.

Registry No. 1, 77146-03-3; **2a**, 80720-98-5; **2b**, 80779-56-2; **2b′**, 80720-99-6; **2c**, 80779-57-3; **2d**, 80721-00-2; **2e**, 80721-01-3; **2f**, 80721-02-4; **2g**, 80721-03-5; **3**, 80721-04-6; **4a**, 80721-05-7; **4b**, 80779-58-4; **4c**, 80779-59-5; **5**, 80721-06-8; **6**, 80721-07-9; **7**, 75482-33-6; **8**, 80737-44-6; **9**, 17032-21-2; **10**, 16872-10-9; **11**, 20313-28-4; **14**, 71817-60-2; 1-formyl-*o*-carborane, 20394-07-4; 1-formyl-*o*-carborane tosylhydrazone, 80737-45-7; 1-diazomethyl-2-methyl-*o*-carborane, 71823-78-4; 2,3-dimethyl-5-*o*-carboranyl-2-pentene, 80737-46-8; 1-methyl-2-vinyl-*o*-corborane, 23924-82-5; 1-methyl-2-formyl-*o*-carborane, 20669-98-1; 1-methyl-2-formyl-*o*-carborane tosylhydrazone, 80737-47-9; *m*-carborane, 16986-24-6; *o*-carborane, 16872-09-6; *m*-carborane carboxaldehyde diethyl acetal, 80737-48-0; *m*-carborane carboxaldehyde, 20692-76-6; *m*-carborane carboxaldehyde tosylhydrazone, 80737-50-4; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; isobutylene, 115-11-7; trimethylethylene, 513-35-9; tetramethylethylene, 563-79-1; *n*-butane, 106-97-8; methyl iodide, 74-88-4.

Alkene Reactivities in Trifluoroacetic Acid. A Comparison of Norbornene and Protoadamantene in Trifluoroacetic Acid and Aqueous Acid

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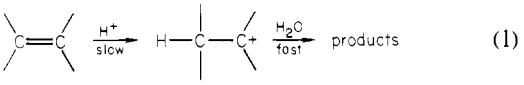
Contribution from the Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada M1C 1A4. *Received October 12, 1981*

Abstract: The kinetics of the reaction of protoadamantene (**1**) and norbornene (**2**) in H_2SO_4, $HClO_4$, and CF_3CO_2H have been measured and the two alkenes are found to have similar relative reactivities, rate dependencies on acidity, solvent isotope effects, and activation parameters, independent of the particular acid. The reactivity of 2-fluoropropene (**7**) in H_2SO_4 has been measured and compared to the reactivity in CF_3CO_2H. A general correlation of the reactivity of alkenes in CF_3CO_2H and in aqueous acids is observed. These results are interpreted in terms of rate-determining proton transfer (the Ad_E2 mechanism) for all of the alkenes in aqueous acids and in CF_3CO_2H. No evidence for the intervention for π complexes as kinetically significant intermediates was obtained. This is contrary to a reported interpretation of the reaction of **1** in CF_3CO_2H.

The hydration of alkenes in aqueous acid has been intensively studied for many years, and a consensus has emerged that this process occurs with rate-limiting protonation on carbon (the Ad_E2 mechanism, eq 1).[1,2] Exceptions to this general pattern are certain



(1)

cases where the initial protonation is reversible, so that nucleophilic attack becomes rate limiting,[3] and trimethylsilyl vinyl ethers, in which rate-limiting nucleophilic attack on silicon concerted with protonation has been proposed.[4]

Other acid systems that have been studied include neat trifluoroacetic acid (TFA),[5] TFA in CCl_4,[6] sulfonic acids in acetic acid,[5d,7] and many others, especially hydrogen halides.[8,9] The

(1) Leading references are given in the following: (a) Nowlan, V. J., Jr.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 254–258. (b) Koshy, K. M.; Roy, D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1979**, *101*, 357–363. (c) Csizmadia, V. M.; Koshy, K. M.; Lau, K. C. M.; McClelland, R. A.; Nowlan, V. J.; Tidwell, T. T. *Ibid.* **1979**, *101*, 974–979. (d) Chwang, W. K.; Nowlan, V. J.; Tidwell, T. T. *Ibid.* **1977**, *99*, 7233–7238. (e) Chwang, W. K.; Knittel, P.; Koshy, K. M.; Tidwell, T. T. *Ibid.* **1977**, *99*, 3395–3401.

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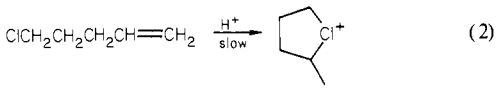
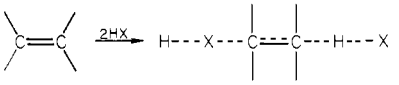
most systematically studied of these systems has been neat TFA,[5] and results in this medium have been interpreted either in terms of rate-limiting protonation (eq 1)[5] or, in certain cases where effective internal nucleophiles were present, as involving concerted protonation and nucleophilic attack (e.g., eq 2).[5b]



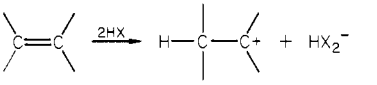
(2)

Roberts[7a] studied the addition of acetic acid to norbornene (**6**), cyclohexene, cyclopentene, and other alkenes catalyzed by CF_3SO_3H and proposed that norbornene undergoes reaction by the Ad_E2 mechanism of rate-limiting proton transfer, but that cyclohexene and cyclopentene reacted by a route involving equilibrium formation of an ion pair, possibly involving a π complex, and that reaction of the ion pair with solvent was rate determining. Other authors[7b] had interpreted the acid-catalyzed addition of acetic acid to cyclohexene as involving the Ad_E2 pathway, and we argued strongly[1d] in favor of this latter interpretation and against any change in mechanism for cyclohexene. The basis for the proposal[7a] of a π complex intermediate in cyclopentene protonation was an isotope effect k_H^+/k_D^+, but we pointed out[1d] that this quantity is often strongly dependent on acid concentration in strong acids and by itself is an unreliable criterion of reaction mechanism. An alternative proposal has been made that the addition of acetic acid to cyclohexene catalyzed by $HClO_4$ involves a concerted anti addition (the Ad_E3 mechanism).[9e]

Additions of HCl and HBr to alkenes have been studied by a variety of authors, and depending upon the particular system, additions that are either first or second order in hydrogen halide were observed.[9] The former process apparently involves rate-limiting proton transfer to give a carbonium ion (the Ad_E2 mechanism). Various possibilities were considered for the Ad_E3 process that is second order in hydrogen halide, including concerted additions (eq 3),[9a-h,k] rate-limiting proton transfer from HX dimers (eq 4),[9b,i] and equilibrium formation of π complexes.[9d,f,h,k] None



(3)

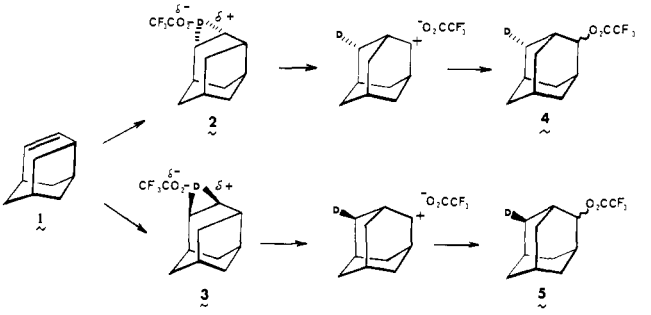


(4)

of the references cited claimed definitive evidence for the intervention of π complexes as kinetically significant intermediates. The fact that HCl and HBr are very weakly dissociated in these media and their tendency to self-associate no doubt contribute to this variety of mechanistic behavior. A critical discussion of HCl additions to alkenes has appeared.[9l]

Thus in the prevailing interpretation, acid-catalyzed hydrations and CF_3CO_2H additions proceed by analogous mechanisms. The trifluoroacetic acid medium has the useful features that it is a better solvent than aqueous acid for most organic substrates and furthermore has much lower nucleophilicity than aqueous media.

Scheme I



Very recently, however, a report by Nordlander and co-workers has appeared[10] on the reactivity of protoadamantene (**1**) in TFA. On the basis of kinetic, regiochemical, and stereochemical data, they proposed that **1** reacts via the π complexes **2** and **3** and that rearrangements of these complexes to the observed products **4** and **5** determine both the observed rates and the product stereochemistry, Scheme I. These authors also suggested that this mechanism might apply to the TFA additions, which had been extensively studied by Peterson et al.: "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".[5a-c] Peterson et al.[5a-c] had not presented an analysis of the possible role of π complexes in these reactions.

Because of our experience in the study of the mechanisms of acid-catalyzed hydrations of alkenes, including polycyclic structures such as norbornene,[1a,d] we were quite interested in these results and conclusions. The involvement of π complexes in the reactions of **1** as proposed[10] differs from the prevailing views for reactions in aqueous acids,[1,2] trifluoroacetic acid,[5] and sulfonic acids in acetic acid,[7] and it appeared desirable to examine this substrate in more detail. The rationale of the present study has been to compare the reactivity of protoadamantene (**1**) to that of norbornene (**6**) in both TFA and aqueous acid. The products

6

of TFA addition to **6** have already been carefully examined,[11] and the additional kinetic measurements reported herein allow an extensive comparison between these two alkenes. Furthermore, the reactivities of norbornene (**6**) in aqueous sulfuric acid,[1a,d] perchloric acid,[12] TFA,[11] acetic acid catalyzed by sulfuric acid,[5d] and acetic acid catalyzed by CF_3SO_3H[7a] have all been interpreted by a diverse group of investigators in terms of rate-limiting protonation (the Ad_E2 mechanism); so the reactivity of this compound provides a useful standard of comparison for protoadamantene (**1**).

A recent report of the measurement of heats of addition of TFA to the five *n*-hexenes renders an understanding of the mechanism of these reactions even more significant.[12b]

Results

The rates of hydration of protoadamantene (**1**) and norbornene (**6**) in various aqueous acids were measured by monitoring the disappearance of the UV absorption and are reported in Table I. The reactivities of these cycloalkenes are compared in Table II as to slopes of log k vs. H_0 in $HClO_4$ and H_2SO_4, solvent isotope effects, and activation parameters.

The reactivities of norbornene (**6**) and cyclohexene (**10**) in TFA were measured at −9.8 °C by the gas chromatographic method[5a-c] and are also recorded in Table I.

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(9) (a) Pasto, D. J.; Gadberry, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 1469–1473. (b) Pasto, D. J.; Meyer, G. R.; Lepeska, B. *Ibid.* **1974**, *96*, 1858–1866. (c) Fahey, R. C.; Monahan, M. W.; McPherson, C. A. *Ibid.* **1970**, *92*, 2810–2816. (d) Fahey, R. C.; Monahan, M. W. *Ibid.* **1970**, *92*, 2816–2820. (e) Fahey, R. C.; McPherson, C. A.; Smith, R. A. *Ibid.* **1974**, *96*, 4534–4542. (f) Fahey, R. C.; McPherson, C. A. *Ibid.* **1971**, *93*, 2445–2553. (g) Fahey, R. C.; McPherson, C. A. *Ibid.* **1969**, *91*, 3854–3859. (h) Hammond, G. S.; Collins, C. H. *Ibid.* **1960**, *82*, 4323–4327. (i) Pocker, Y.; Stevens, K. D. *Ibid*, **1969**, *91*, 4205–4210. (j) Staab, H. A.; Wittig, C. M.; Naab, P. *Chem. Ber.* **1978**, *111*, 2965–2981. (k) Naab, P.; Staab, H. A. *Ibid.* **1978**, *111*, 2982–2996. (l) Brown, H. C.; Liu, K.-T. *J. Am. Chem. Soc.* **1975**, *97*, 600–610.

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Table I. Reactivity of Alkenes in Acid

alkene	acid	T, °C	[HA], M	H_0	k_{obsd}, s^{-1} [d]
protoadamantene (1)	$HClO_4$	52.4	2.92	−1.35	2.38×10^{-2}
		52.4	2.01	−0.805	5.99×10^{-4}
		52.4	0.500	−0.0600	5.40×10^{-5}
	$HClO_4$	52.5	3.91		8.78×10^{-3}
		37.7	3.91		1.86×10^{-3}
		24.9	3.91	−1.76	3.92×10^{-4}
	H_2SO_4[a]	25.0	6.08	−2.78	1.46×10^{-2}
			4.92	−2.25	2.42×10^{-3}
			4.14	−1.91	7.31×10^{-4}
			3.43	−1.59	3.91×10^{-4}
	D_2SO_4	24.9	5.26	−2.32[f]	1.64×10^{-3}
			2.88	−1.34[f]	8.43×10^{-5}
norbornene (6)	$HClO_4$	52.5	2.92	−1.35	2.10×10^{-2}
			2.01	−0.805	6.50×10^{-3}
		52.5	0.1006		6.29×10^{-5}
			0.0202[e]		1.52×10^{-5}
	$HClO_4$	38.7	2.92		6.37×10^{-3}
		38.7	2.01		1.605×10^{-3}
		24.6	2.92		1.055×10^{-3}
		24.6	2.01		2.75×10^{-4}
	H_2SO_4[b]	25.0	6.08	−2.78	5.68×10^{-2}
			4.92	−2.25	2.06×10^{-2}
			4.14	−1.91	8.10×10^{-3}
			3.43	−1.59	3.11×10^{-3}
			1.65	−0.66	2.42×10^{-4}
	D_2SO_4	24.9	2.88	−1.34[f]	6.82×10^{-4}
	TFA	−9.8			6.80×10^{-2}
cyclohexene (10)	TFA	−9.8			6.34×10^{-6}
2-fluoropropene (7)	H_2SO_4[c]	25.0	8.79	−4.27	3.91×10^{-2}
			7.57	−3.65	7.59×10^{-3}
			6.12	−2.83	1.16×10^{-3}
			4.99	−2.32	2.72×10^{-4}
	D_2SO_4	25.0	7.89	−3.79[f]	4.66×10^{-3}[g]
			7.25	−3.48[f]	2.06×10^{-3}[h]

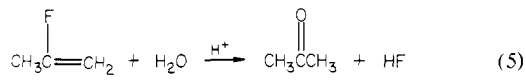
[a] $\log k_{obsd} = -1.35H_0 - 5.633$; $k_{H^+} = 0.233 \times 10^{-5}$ M^{-1} s^{-1}. [b] $\log k_{obsd} = -1.17H_0 - 4.365$; $k_{H^+} = 0.432 \times 10^{-4}$ M^{-1} s^{-1} (includes six additional acidities reported in ref 1d). [c] $\log k_{obsd} = -1.08H_0 - 6.050$; $k_{H^+} = 0.892 \times 10^{-6}$ M^{-1} s^{-1}. [d] Reported rates are averages of at least two runs, maximum deviation ±5%. [e] Ionic strength adjusted to 0.1 (NaCl). [f] D_0. Isotope effect calculated at $H_0 = D_0$. [g] $k_{H^+}/k_{D^+} = 2.37$. [h] $k_{H^+}/k_{D^+} = 2.48$.

Table II. Summary of Comparative Reactivities of Protoadamantene (1) and Norbornene (6)

cycloalkene	acid	$d \log k_{obsd}/dH_0$	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}(cyclohexene)	k_{H^+}/k_{D^+}	k_{rel}[(norbornene)/(protoadamantene)]
1	$HClO_4$	−1.28[a]	21.1	−3.3	140[j]		
	H_2SO_4	−1.35[b]			52,[l] 90[k]	1.93,[c] 1.79[d]	
	TFA				410[b]		
6	$HClO_4$	−1.05[e]	20.1[f]	−4.6[f]	2.3×10^{4}[l]		19[l]
			21.2[g]	−3.4[g]			
	H_2SO_4	−1.17[h]			770[l]	2.36,[d] 2.13[i]	17[l]
	TFA				1.1×10^{4}[m]		26[n]
cyclohexene	$HClO_4$	−1.57[i]					
	H_2SO_4	−1.28[i]				1.06[i]	

[a] 52.4 °C. [b] 25 °C. [c] 5.26 M D_2SO_4. [d] 2.88 M D_2SO_4. [e] At 52.5 °C. [f] 2.92 M $HClO_4$. [g] 2.01 M $HClO_4$. [h] From rates at 11 different acidities, this work and ref 1d. [i] Reference 1d. [j] 3.91 M $HClO_4$, 25 °C. [k] In 4.92 M H_2SO_4. [l] At $H_0 = 0$. [m] At −9.8 °C. [n] Derived from the reactivities relative to cyclohexene of **2** (at −9.8 °C) and **1** (at 25 °C).

For further comparison with reactivities in TFA, rates of hydrolysis of 2-fluoropropene (**7**) in aqueous sulfuric acid were measured as reported in Table I. The UV spectrum of the product was identical with that of acetone, consistent with reaction 5.



$$CH_3\overset{F}{\overset{|}{C}}{=}CH_2 + H_2O \xrightarrow{H^+} CH_3\overset{O}{\overset{\|}{C}}CH_3 + HF \qquad (5)$$

7

Discussion

The data summarized in Table II are particularly notable for the consistent pattern of behavior displayed not only for both **1** and **6** when the reactivity of each is considered for aqueous $HClO_4$, aqueous H_2SO_4, and TFA but also when **1** is compared to **6**. Specifically the slopes of the log k_{obsd} vs. H_0 plots are in the range considered diagnostic of the Ad_E2 mechanism, as are the values of the activation parameters and the solvent isotope effects k_{H^+}/k_{D^+}.[1,2] While any one of these criteria in itself should not be considered definitive, taken together they uniformly support this path, which as already discussed has been generally accepted for **6**. On the basis of the present results this path can also be considered firmly established for **1** in the aqueous acids as well.

For the reactions in TFA the norbornene/protoadamantene rate ratio is 26, as compared to the values of 19 for $HClO_4$ and 17 for H_2SO_4. The close similarity of these ratios is good evidence that similar mechanisms are followed for both substrates in all three acids. If there was an acceleration of the rate of protoadamantene in TFA due to a change in mechanism to a process where rearrangement of a π complex became rate limiting, then there should be a change in the **6**/**1** rate ratio. As discussed above, the evidence favors the Ad_E2 path for **1** and **6** in aqueous acids and for **6** in TFA. The consistency of the **6**/**1** rate ratio thus is strong evidence for this mechanism for **1** in TFA as well.

Table III. Comparative Reactivity of Alkenes in CF_3CO_2H and Aqueous Acids at $H_0 = -2.71$ at 25 °C

alkene	k(TFA),[a] s^{-1}	log k(TFA)	log $k(H_2SO_4)$[b]
protoadamantene (1)	5.27×10^{-2}[c]	−1.28	−1.97
norbornene (6)	1.4[d]	0.15	−1.19
2-fluoropropene (7)	3.40×10^{-3}	−2.47	−3.12
propene (8)	4.81×10^{-5}	−4.32	−4.85
2-bromopropene (9)	3.95×10^{-6}	−5.40	−5.41
cyclohexene (10)	1.29×10^{-4}[c]	−3.89	−3.88
1-butene (11)	8.06×10^{-5}	−4.09	−4.70[f]
1-hexene (12)	1.10×10^{-4}[e]	−3.96	−4.48
(Z)-3-hexene (13)	2.0×10^{-4}[e]	−3.70	−4.19[g]
(E)-3-hexene (14)	1.3×10^{-4}[e]	−3.89	−4.23[g]
cyclooctene (15)	1.05×10^{-3}[e]	−2.98	−3.12[h]
bicyclooctene (16)	3.22×10^{-3}[i]	−2.49	−3.60[i]

[a] Reference 5 unless noted. [b] Reference 1, or this work, unless noted. [c] Reference 10. [d] Extrapolated from the observed rate at −9.8 °C with use of reactivity relative to cyclohexene, this work. [e] Estimated from data at 35 °C. [f] Allen, A. D.; Chiang, Y.; Kresge, A. J.; Tidwell, T. T. *J. Org. Chem.* **1982**, *47*, 775-779. [g] Chwang, W. K.; Tidwell, T. T. *J. Org. Chem.* 1978, *43*, 1904-1908. [h] In $HClO_4$ at $H_0 = -2.71$, derived from the relation $k_{obsd} = -1.36H_0 - 6.82$ (Kresge, A. J., unpublished results privately communicated). [i] Reference 14.

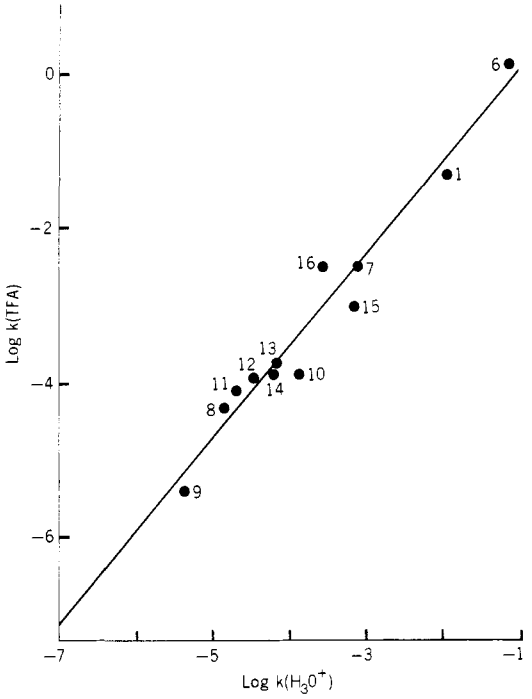


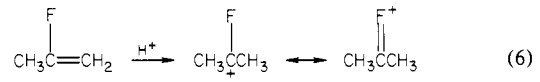
Figure 1. Comparative reactivities of alkenes in CF_3CO_2H and aqueous H_2SO_4.

A wider perspective on the reactivity of alkenes in aqueous acid and in TFA can be obtained by a linear free-energy comparison of the reactivities of all of the alkenes that have been studied in both media. In order to provide another useful point for this correlation, we have measured the rate of reaction of 2-fluoropropene (**7**) in aqueous acid. This substrate is known to have a greatly enhanced reactivity relative to that of propene (**8**) or 2-bromopropene (**9**) in TFA ($k_{rel} = 71/1/0.082$),[5c] and this same behavior is observed in aqueous acid ($k_{rel}(H_0 = -2.71) = 54/1/0.28$).[1] This acidity was chosen as the standard for comparison because this is the value of H_0 for pure TFA,[13] and so the rates are being compared at constant acidity. Furthermore this acidity is near the midpoint of the various acidities at which rates on the alkenes were actually experimentally determined.

(13) Spitzer, U. A.; Toone, T. W.; Stewart, R. *Can. J. Chem.* **1976**, *54*, 440-447.

Comparative data for alkene reactions[14] are collected in Table III and are plotted in Figure 1. A good correlation is observed, log k(TFA) = 1.20 log $k(H_3O^+)$ + 1.27, $r = 0.976$.[15] The point **1** for protoadamantene fits the plot, which provides strong evidence that the reactivities of alkenes in general and protoadamantene in particular follow the same mechanisms in aqueous acid and in TFA. Since the Ad_E2 mechanism is firmly established for the reactions in aqueous acid, this is further evidence that the same mechanism applies in TFA as well as for the rest of these alkenes.

2-Fluoropropene (**7**) is a particularly apt substrate for testing for the mechanism of protonation. Despite its high electronegativity, fluorine is predicted[1] to be a net activator in the Ad_E2 mechanism (eq 6) because of its ability to donate electrons by



7 (6)

resonance as manifested in its σ_p^+ parameter of −0.07.[16] As noted above the experimental result is that **7** is significantly activated relative to propene (**8**).[17] This resonance-electron donation by fluorine would be expected to be ineffective in a π-complex mechanism so that the fit of this point in Figure 1 is strong evidence against this latter process.

cis-Cyclooctene is another good candidate to use in testing for the intervention of rate-limiting processes besides proton transfer, as the propensity of the cyclooctyl cation for cross-ring hydride transfer[18] and even formation of a stable hydrido-bridged cation[18a]

(14) Reactivity data on bicyclooctene (**16**) are also included. The H_3O^+

16

rate for this compound was derived from the experimentally determined relation, log $k = -1.21H_0 - 6.78$ in 20% EtOH-80% aqueous H_2SO_4 at 25 °C (W. K. Chwang, unpublished results), and a factor of 0.78 for converting rates in this medium to rates in aqueous H_2SO_4 at $H_0 = -2.71$ (footnote *g*, Table III). The rate in TFA at 25 °C was determined from the rate relative to cyclohexene of 25 at 20 °C given in ref 5d.

(15) The greater sensitivity of the rates in TFA compared to aqueous acid at $H_0 = -2.71$ is striking, but the cause of this behavior is not certain. Sulfuric acid of $H_0 = -2.71$ is 5.93 M (43.7%). The H_R function of 100% CF_3CO_2H is −11.30, which corresponds to 11.22 M (69.0%) H_2SO_4. The slope of log k(TFA) vs. log $k(H_3O^+)$ is 1.26 at this acidity, but the correlation is poorer. Our general experience has been that H_R functions are no better than H_0 for correlating alkene reactivities. Furthermore the absolute rates of particular substrates are similar at $H_0 = -2.71$ and are quite different at $H_R = -11.30$, which exceeds the acidity at which rates were actually measured for all of the alkenes included here except **9**. These findings reinforce our belief that H_0 is the best acidity function for the correlation of alkene protonations. Further confirmation that H_0 is the acidity function of choice is the correspondence of the maximum in k_{obsd} for the reaction of TFA with 1-hexene near 4% H_2O content (ref 5a), which corresponds to the maximum in the magnitude of H_0 in TFA-H_2O mixtures at 97% (by wt) TFA (ref 13). No such maximum occurs for H_R.

A referee has pointed out the value of the quantitative correlation between rates in these two media for the interpretation of solvent effects on rates for alkene additions. In this regard it may be noted that the nucleophilicites of TFA and aqueous H_2SO_4 at $H_0 = -2.71$ should be drastically different. The N_{OTs} values of TFA and pure H_2O are −5.56 and −0.44, respectively [quoted in Brown (Brown, H. C.; Ravindranathan, M.; Chloupek, F. J.; Rothberg, I. *J. Am. Chem. Soc.* **1978**, *100*, 3143-3149)], and the activity coefficient of H_2O changes very little between pure H_2O ($a_w = 1.0$) and 43.7% H_2SO_4 ($a_w = 0.56$). (Giauque, W. F.; Hornung, E. W.; Kinzler, J. E.; Rubin, T. R. *J. Am. Chem. Soc.* **1960**, *82*, 62-70; Cox, R. *Ibid.* **1974**, *96*, 1059-1063). Thus the nucleophilicity of aqueous H_2SO_4 at $H_0 = -2.71$ is expected to be enormously greater than that of pure TFA, and the correspondence between the rates in the two media suggests there is no significant nucleophilic process involved in the rate-limiting step in either medium.

(16) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979-4987.

(17) Prediction of k_{H^+} for **7** from our published[1] relation log $k_{H^+} = -10.5 \sum\sigma_p^+ - 8.92$ gives a value of 1.2×10^{-5} s^{-1} as compared to the value observed here of 8.9×10^{-7} s^{-1}. The agreement within a factor of 13 fits the normal limits of this correlation.

(18) (a) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1979**, *101*, 3240-3243. (b) Nordlander, J. E.; Owour, P. O.; Cabral, D. J.; Haky, J. E. *Ibid.* **1982**, *104*, 201. (c) Schneider, H.-J.; Heiske, D. *Ibid.* **1981**, *103*, 3501-3505.

is well documented. However the point **15** for this compound fits the correlation reasonably well, and this excludes the possibility of any change in mechanism between H_3O^+ and TFA addition in this case.

The reactivity of substituted styrenes with TFA is also under study. These results,[19] to be presented shortly, also fit the plot in Figure 1.

The origin of the high reactivity observed for **1** and **6** deserves consideration, as the 408-fold greater reactivity of **1** relative to cyclohexene was one of the principal arguments advanced for a change in mechanism for this compound.[10] We previously suggested that the origin of high reactivity in norbornene is due to enhanced nucleophilicity of the double bond, which is "unsymmetrically" distorted".[1a,d] This reactivity factor was first proposed by Fukui et al.,[20a] who described it as "nonequivalent orbital extension". This high reactivity of norbornene was considered in detail by Huisgen, Allinger, and co-workers,[20b] who did not reach a final judgement on the origin of the behavior but entitled the unknown the "X-factor". The concept pioneered by Fukui has received support by many authors,[20] who have termed it "orbital distortion",[20c] "non-planar π-systems",[20d,e] "twisted π-systems",[20g] "uneven distribution of π-electrons",[20f] and "nonplanar alkenes".[20h] In protoadamantene the double bond is also unsymmetrically disposed in the molecule, and the molecule is quite strained (Nordlander et al. cite[10] the fact that protoadamantane is 11.22 kcal/mol less stable than adamantane). The observed rate of reaction of **1** appears to us to be plausibly consistent with Ad_E2 protonation, with acceleration arising from orbital distortion. Furthermore, **1** is distorted in such a way that the four lobes of the two p orbitals are all nonequivalent. This effect could explain the fact that electrophilic attack by H^+ or Hg^{2+} on protoadamantene displays a very strong positional selectivity and only modest directional selectivity. Confirmation of this proposal must however await quantitative study.

In summary, the detailed comparison of the reactivities of protoadamantene (**1**) and norbornene (**6**) in both aqueous acid and TFA shows a consistency in the behavior of the two alkenes that strongly indicates the same reaction mechanism holds for both. It is generally agreed that norbornene reacts by the Ad_E2 mechanism of rate-limiting protonation on carbon, and this pathway is indicated for protoadamantene as well. A good linear free-energy correlation of available rate data for alkenes in TFA with rates in aqueous acids is observed, including **1**, **6**, and 2-fluoropropene. This result also supports the Ad_E2 mechanism in the entire series. The high reactivities of **1** and **6** relative to models such as cyclohexene can be attributed to orbital distortion.

No evidence attributable to the intervention of a π complex as a kinetically significant intermediate has been observed, although the occurrence of such a species as a shallow minimum early on the reaction coordinate cannot be excluded. Differentiation of such a species from the ground state of the alkene interacting with the hydrogen-bonding solvent is a subtle problem beyond the scope of our investigations.

A detailed consideration of the arguments presented[10] in favor of the π-complex mechanism is too lengthy to present here but is available in the supplementary material.

Experimental Section

A sample of protoadamantene was generously provided by Professor J. E. Nordlander. 2-Fluoropropene was obtained from PCR, Inc.

Kinetic studies in aqueous acid were carried out by continuous observation of the decrease in the alkene end absorption at 202 nm for **1**, 207 nm for **6**, and 200 nm for **7** with Cary 118 and 210 UV spectrophotometers with thermostated cell compartments. For **7** the increase in carbonyl absorption by the product acetone at 255 nm was also observed and gave good agreement with the rates obtained by the decrease in alkene absorption. A stock solution of **1** in EtOH was prepared by diluting a saturated solution of unknown concentration 10-fold with EtOH and injecting 15-μL aliquots into the acid solution in 1-cm UV cells. These were observed at an absorbance range of 0–0.2. Reactions of **6** were initiated by injecting 10 μL of a 0.23 M solution in MeOH into 3 mL of acid solution in the UV cell. Solutions of **7** were prepared by bubbling **7** into the acid solution contained in the UV cell.

For rates in TFA **6** (0.33 g, 3.5×10^{-3} mol) was dissolved in 0.54 mL of *tert*-butylbenzene (dried over Na ribbon) in a stoppered 25-mL volumetric flask. This solution was placed in a constant-temperature bath at −9.8 °C, and after 30 min, 20.8 g (0.18 mol) of TFA (preequilibrated at −9.8 °C) was added. Eight samples of approximately 1.5 mL were withdrawn from the solution at approximately 6-s intervals by use of pipets that had been stored over dry ice. The sample frozen in the pipet was injected into 150-mL portions of ice water. Each product mixture was extracted with ether (3 × 40 mL), washed with saturated $NaHCO_3$ (100 mL), dried, and concentrated by distillation. Each mixture was analyzed for the ester by GLC (20% OV 17, Chrom W 45/60, 3 m × 10 mm) with use of *tert*-butylbenzene as internal standard. The areas were calculated by multiplying the height by the width at half height. The average of two runs gave the rate constant 6.80×10^{-2} s^{-1}. Rates for cyclohexene were measured by a similar procedure.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. Special thanks are due to Professor J. E. Nordlander for donation of the sample of **1** and many informative discussions including a frank exchange of views concerning the reactivity of **1** in TFA.

Registry No. **1**, 19026-94-9; **6**, 498-66-8; **7**, 1184-60-7; **8**, 115-07-1; **10**, 110-83-8; **11**, 106-98-9; **12**, 592-41-6; **13**, 7642-09-3; **14**, 13269-52-8; *cis*-**15**, 931-87-3; **16**, 931-64-6.

Supplementary Material Available: A detailed consideration of the arguments presented in favor of the π-complex mechanism (11 pages). Ordering information is given on any current masthead page.

(19) Allen, A. D.; Rosenbaum, M.; Seto, N. O. L.; Tidwell, T. T., submitted for publication.

(20) (a) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054–4061. (b) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *Ibid.* **1980**, *102*, 3951–3953. (c) Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703–1708. (d) Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1980**, *21*, 4445–4448. (e) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H. A.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095–2096. (f) Fujikura, Y.; Inamtoto, Y.; Takaishi, N.; Ikeda, H.; Aigami, K. *J. Chem. Soc.*, Perkin *Trans. 2* **1976**, 2133–2137. (g) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891–1900. (h) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *Ibid.* **1981**, *103*, 2436–2438. (i) Giddings, M. R.; Hudec, J. *Can. J. Chem.* **1981**, *59*, 459–467.