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Reactivity of Cyclic and Acyclic Olefinic Hydrocarbons in Acid-Catalyzed Hydration

Willy K. Chwang, Vincent J. Nowlan, and Thomas T. Tidwell*

Contribution from the Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada M1C 1A4.

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Abstract: The rates of hydration of ethylene, propene, 1-hexene, cyclohexene, 1-methylcyclohexene, 1-methylcyclopentene, and norbornene catalyzed by H_2SO_4 and D_2SO_4, and the hydration of cyclohexene catalyzed by $HClO_4$ and $DClO_4$, all at 25 °C, were measured. Ethylene is only a factor of 24 less reactive than *p*-nitrostyrene at $H_0 = -7.37$, but has a very steep slope of log k_{obsd} vs. H_0 of -1.54 so that ethylene rates extrapolated to low acidities appear quite small relative to other alkenes. All of the substrates are interpreted to react by rate-determining protonation on carbon to give the corresponding carbonium ions (the $A_{SE}2$ mechanism). Solvent isotope effects k_{H^+}/k_{D^+} range from 2.82 for propene to 1.06 for cyclohexene, and are only tenuously related to absolute reactivity. Norbornene is 770 times more reactive than cyclohexene, and at least part of this difference is attributed to the unsymmetrical π bond in this molecule endowing it with enhanced nucleophilicity on the exo face.

The steric course of electrophilic additions to cyclic alkenes[1] and the rates of solvolytic reactions of many cycloalkyl esters[2] have been the subject of intense chemical interest. However the effect of structure on the rates of the addition reactions has not been systematically studied; so a unified interpretation of the reactivity of cycloalkyl derivatives has not been possible.

We have recently been successful in the interpretation of the rates of acid-catalyzed hydration of acyclic alkenes in terms of structure effects, particularly σ^+ parameters.[3] It appeared highly desirable to extend this study to the corresponding reactivity of selected cyclic olefinic hydrocarbons. The study of hydration would also be useful for comparison with published studies of trifluoroacetic acid addition to alkenes[4] and stable cations generated from alkenes and other sources.[5]

Of particular interest is ethylene, the parent of the other alkenes. The kinetics of the reaction of ethylene with concentrated sulfuric acid to give ethyl hydrogen sulfate and diethyl sulfate (eq 1)

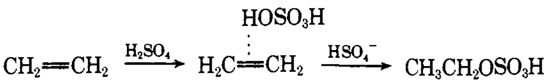
$$CH_2{=}CH_2 + H_2SO_4 \rightleftharpoons CH_3CH_2OSO_3H \rightleftharpoons (CH_3CH_2O)_2SO_2 \qquad (1)$$

have received considerable attention because of their industrial importance. However, this reaction was studied[6] under conditions where high concentrations of the sulfates were present; so the results are not useful for understanding the mechanism of ethylene protonation in aqueous sulfuric acid. It was noted by Purlee and Taft[7] that ethylene reacts with 70% $HClO_4$ at 30 °C at an appreciable rate, but no rate constants were obtained. Apparently the only reported rate constants for the protonation of ethylene in aqueous acid were those of Baliga and Whalley in 0.3–0.63 M HNO_3 at 170–190 °C and 100-bar pressure.[8] In all these cases the conversion of ethylene to products at equilibrium was very high (>95%).[6-8]

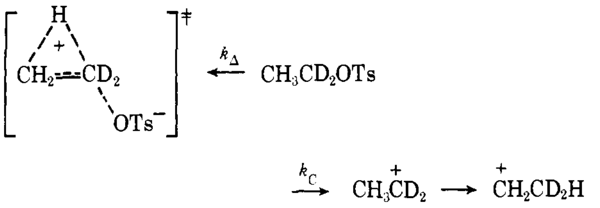
It has been proposed in an excellent recent textbook[9] that isobutene "undoubtedly" hydrates via protonation on carbon to give the *tert*-butyl cation (eq 2)

$$Me_2C{=}CH_2 \xrightarrow{H^+} Me_3C^+ \xrightarrow{H_2O} Me_3COH \qquad (2)$$

but ethylene in 98% H_2SO_4 "almost certainly does *not* involve the primary carbonium ion" but reacts via a π-complex route (eq 3). There is, however, experimental evidence for the $C_2H_5^+$ cation in solutions of $HF\text{-}TaF_5$.[10] Also, although solvolysis of ethyl tosylate in CF_3CO_2H apparently occurs with solvent assistance (the k_S route),[11a,b] reaction of CH_3CD_2OTs in FSO_3H proceeds with some deuterium scrambling in the product.[11c] The latter result suggests either formation of an open ion (k_c process) or hydrogen participation (k_Δ process) (eq 4). A review has favored the latter.[11d] Different theoretical studies favor open[12a-f] or bridged[12g,h] structures for the ethyl cation, while experimental studies in the gas phase show that the hydrogens in $C_2H_5^+$ become randomized, but do not define whether or not the bridged or open structure is more stable.[12i]



$$CH_2{=}CH_2 \xrightarrow{H_2SO_4} \overset{\overset{HOSO_3H}{\vdots}}{H_2C{=}CH_2} \xrightarrow{HSO_4^-} CH_3CH_2OSO_3H \quad (3)$$



(4)

A recent review of criteria for differentiating bridged and open transition states in addition reactions has appeared[12j] and emphasized the need for further study of hydrations of alkenes. To help resolve the questions regarding hydration of acyclic alkenes and to meet the need for understanding of cycloalkenes we have examined selected examples of each type.

Results

The compounds chosen for study were ethylene (**20**), propene (**19**), 1-hexene (**15**), cyclohexene (**1**), 1-methylcyclohexene (**2**), 1-methylcyclopentene (**3**), and norbornene (**4**) (numbering of the acyclic alkenes is in accord with that used previously[3a]). Rates were followed by observing the disappearance of the ultraviolet end absorption of the alkene and all followed excellent first-order kinetics for at least two half-lives (Table I). For reactions in protiated media the absorbance usually decreased to <5% of the original value, indicating high equilibrium constants for hydration of the alkenes. The equilibrium concentration of cyclohexene determined by the final UV absorbance in 7 M H_2SO_4 beginning from either cyclohexene or cyclohexanol was found to be 9 ± 2%. In 7 M D_2SO_4 the equilibrium absorbance beginning with either cyclohexene or cyclohexanol corresponded to the presence of 6 ± 2% of cyclohexene.

Rates in H_2SO_4 and $HClO_4$ were correlated with the acidity functions H_0 for those media (Table II).[13,14] As we have found before,[3] other acidity functions such as H_R[14a] and H_c[15] are approximately linear in H_0 at the acidities studied and do not give better correlations. Correlation coefficients were 0.998–1.000 in all cases.

The observed rate of a reversible hydration reaction such as that of cyclohexene (eq 5) is related to the rate constants for hydration and dehydration by eq 6. Substituting the value of the equilibrium constant $K_{eq} = k_{hyd}/k_{deh}$ in this expression gives eq 7, which gives eq 8 for the relationship of the observed isotope effect and the isotope effect on the separate steps.

$$H_2O + \text{cyclohexene} \underset{k_{deh}}{\overset{k_{hyd}}{\rightleftharpoons}} \text{cyclohexanol} \quad (5)$$

$$k_{obsd} = k_{hyd} + k_{deh} \quad (6)$$

$$k_{hyd} = k_{obsd}K_{eq}/(1 + K_{eq}) \quad (7)$$

$$k_{hyd}{}^H/k_{hyd}{}^D = k_{obsd}{}^H K_{eq}{}^H(K_{eq}{}^D + 1)/k_{obsd}{}^D K_{eq}{}^D(K_{eq}{}^H + 1) \quad (8)$$

For the cases studied here, where the equilibrium favors the hydrated product to the extent of at least 90%, k_{obsd} is a reasonable approximation to k_{hyd}, and $k_{obsd}{}^H/k_{obsd}{}^D$ is also very close to the isotope effect on the protonation step; so the observed rate constants are taken as the rate constants for protonation.

Table I. Rates of Hydration of Alkenes in Aqueous Acid at 25 °C

Alkene	$[H_2SO_4]$, M[a]	H_0[b]	k_{obsd}, s^{-1}
Ethylene (**20**)	15.56	−8.26	7.79×10^{-3}
	14.89	−7.85	1.75×10^{-3}
	14.29	−7.48	4.10×10^{-4}
	13.68	−7.12	1.38×10^{-4}
	13.20	−6.84	5.02×10^{-5}
	13.66[c]		4.81×10^{-5}
Propene (**19**)	9.35	−4.58	5.62×10^{-3}
	8.25	−3.99	8.56×10^{-4}
	7.47	−3.57	2.21×10^{-4}
	8.77[c]		7.42×10^{-4}
1-Hexene (**15**)	8.65	−4.18	4.25×10^{-3}
	8.10	−3.92	1.61×10^{-3}
	7.86	−3.78	1.05×10^{-3}
	6,85[d]	−3.25	1.94×10^{-4}
	8.20[c]		1.16×10^{-3}
Cyclohexene (**1**)	8.65	−4.18	1.12×10^{-2}
	8.10	−3.92	4.08×10^{-3}
	7.81	−3.77	2.56×10^{-3}
	6.85	−3.25	6.03×10^{-4}
	6.48	−3.02	3.04×10^{-4}
	5.90	−2.69	1.31×10^{-4}
	8.18[c]		4.77×10^{-3}
	7.28[c]		1.11×10^{-3}
	6.33[c]		2.27×10^{-4}
	8.15[e]		1.87×10^{-2}
	7.20[e]		1.89×10^{-3}
	5.55[e]		6.56×10^{-5}
	7.11[f]	−3.57	2.14×10^{-3}
	6.67[f]	−3.32	6.92×10^{-4}
	6.22[f]	−3.02	2.41×10^{-4}
	5.77[f]	−2.72	9.12×10^{-5}
	5.37[f]	−2.51	4.30×10^{-5}
1-Methylcyclohexene (**2**)	2.44	−1.09	6.38×10^{-3}
	1.95	−0.82	3.11×10^{-3}
	1.00	−0.28	6.50×10^{-4}
	0.80	−0.11	4.21×10^{-4}
	0.60	0.05	2.72×10^{-4}
	0.40	0.24	1.53×10^{-4}
	1.98[c]		2.77×10^{-3}
1-Methylcyclopentene (**3**)	2.44	−1.09	1.92×10^{-2}
	1.95	−0.82	9.96×10^{-3}
	1.46	−0.53	4.12×10^{-3}
	1.00	−0.28	1.96×10^{-3}
	0.60	0.05	8.26×10^{-4}
	0.40	0.24	4.51×10^{-4}
	1.98[c]		8.04×10^{-3}
Norbornene (**4**)	4.11	−1.90	9.26×10^{-3}
	3.87	−1.79	5.58×10^{-3}
	3.42	−1.59	3.14×10^{-3}
	2.90	−1.33	1.54×10^{-3}
	2.44	−1.09	8.04×10^{-4}
	1.95	−0.82	3.76×10^{-4}
	3.70[c]		2.10×10^{-3}

[a] Acid concentrations measured by titration and converted to percentages using standard tables. [b] Acidity function derived from percentage acid using values of ref 13. [c] In D_2SO_4. [d] Rate in 48.7% H_2SO_4 reported by K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973). [e] In $DClO_4$. [f] In $HClO_4$.

Table II. Correlation of Reactivities of Alkenes with H_o of H_2SO_4

Alkene	γ^a	ϵ^a	k_2, $M^{-1}\ s^{-1}$ [b]	k_{H^+}/k_{D^+} [c]
20	−1.54	−14.83	0.146×10^{-14}	2.62
19	−1.39	−8.62	0.238×10^{-8}	2.82
15	−1.43	−8.36	0.432×10^{-8}	1.68
1	−1.28	−7.35	0.443×10^{-7}	1.06[d]
1[e]	−1.57	−8.32	0.476×10^{-8}	[f]
2	−1.22	−3.52	0.305×10^{-3}	1.16
3	−1.23	−3.04	0.915×10^{-3}	1.23
4	−1.25	−4.47	0.341×10^{-4}	2.13

[a] From $\log k_{obsd} = \gamma H_o + \epsilon$. [b] k_{obsd}/h_o at $H_o = 0.0$. [c] $k_{obsd} \cdot [H_2SO_4]/k_{obsd}[D_2SO_4]$ at the concentrations measured for D_2SO_4 from Table I using interpolated rates in H_2SO_4 of the same molarity. [d] The same isotope effect was found in 8.18, 7.28, and 6.33 M acids. [e] $HClO_4$. [f] The ratio of $k_{obsd}[HClO_4]/k_{obsd}[DClO_4]$ was 1.82, 1.34, and 0.87 in 8.15, 7.20, and 5.55 M acids, respectively. These values may not correspond to actual solvent isotope effects; see text.

Discussion

The first-order kinetics, the dependence of rates on acidity, and the solvent isotope effects are consistent with all of the alkenes studied undergoing rate-determining $A_{SE}2$ protonation. The decrease in the ultraviolet absorption in protiated media indicate that the alkenes undergo addition to the extent of at least 90% at equilibrium. Alkyl sulfates are probably formed to some extent in the more concentrated solutions.[6b] The corresponding alcohols have been isolated from acid-catalyzed hydration reactions of ethylene,[8] norbornene,[16] cyclohexene,[17] and 1-methylcyclopentene.[18] The addition of acetic acid to cyclopentene and cyclohexene has been found to give 96 and 93% formation of addition product at equilibrium, respectively.[19] This parallels the 90% formation of cyclohexanol from cyclohexene.

The acidity dependences of the rates of the linear alkenes are extremely steep, and the magnitude of the slope −1.54 for ethylene (**20**) is the largest of which we are aware for an alkene protonation, and this olefin is also the least reactive for which rates have been reported. However, there is some overlap in the acidities at which the rates of ethylene and *p*-nitrostyrene (**46**)[20] were measured.

In the range of experimental observations at $H_o = -7{,}37$ ethylene is less reactive than **46** by a factor of only 24. The calculated value of $\Sigma\sigma^+_p$ for **46** is −0.02[3b] as compared to 0,0 for ethylene. Our previously introduced[3] correlation (eq 9)

$$\log k_2 = \rho\Sigma\sigma^+_p + C \tag{9}$$

of the rates of hydration of acyclic alkenes by the $A_{SE}2$ mechanism predicts that **46** will be modestly more reactive than ethylene. This mechanism has been clearly established for **46**, and the accuracy of the prediction of eq 9 of the similar rates for ethylene and **46** supports the $A_{SE}2$ mechanism for both. For this mechanism the ethylene rate should be divided by a statistical factor of 2 to account for the two equivalent sites for protonation. When the rates are extrapolated to $H_o = 0$, the rate of ethylene decreases relative to **46** by a factor of 10^4 because of its much stronger dependence of rate on acidity, as shown in Figure 1. This exaggerated difference at $H_o = 0$ makes comparisons at this acidity of limited utility, but the closeness of the rates within the range of experimental observation, predicted for the $A_{SE}2$ mechanism, supports this pathway for both compounds.

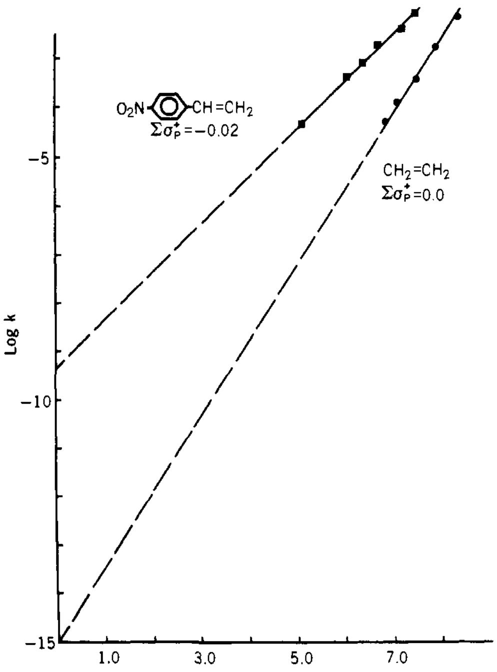


Figure 1. Dependence of rates of hydration of ethylene (**20**) and *p*-nitrostyrene (**46**) on acidity.

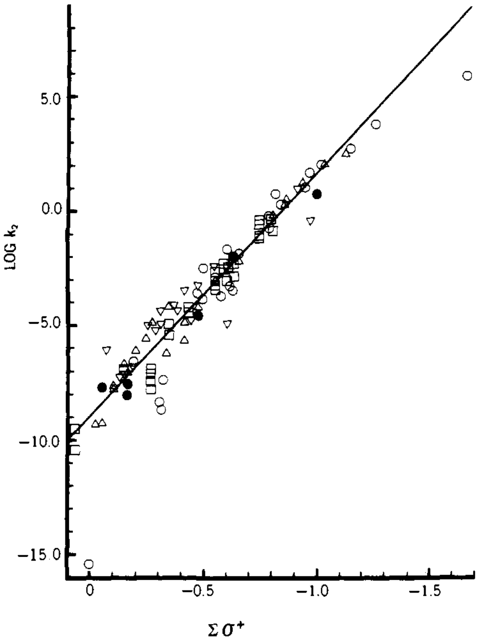


Figure 2. Correlation of the reactivity of alkenes with substituent parameters: ○, original group of 1,1-disubstituted alkenes; ●, 1,3-butadienes and 2-bromopropene; △, substituted styrenes; ▽, vinyl esters; □, 1,2-disubstituted alkenes.

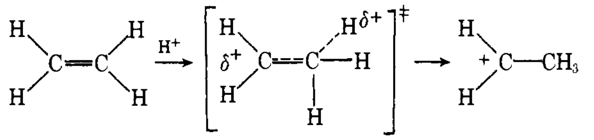
A revised version of the correlation of eq 9 is shown in Figure 2, The points shown are those for all the alkenes for which we have been able to obtain rates for reaction in dilute acid or for which the rates can be readily approximated or extrapolated at $H_o = 0$ and for which reliable σ^+_p constants for the substituents are available,[21] Significant changes in the data used include revised values of σ^+_p for the ethoxy[22a] and cyclopropyl groups,[22b] and a revised k_2 value for styrene (**22**).[23] In Figure 2 the least-squares correlation line includes all the points; $\rho = -10.5$, $C = -8.92$, correlation coefficient (r) 0.938. The correlation coefficient is rather low because of the unrealistically low extrapolated rate constants for ethylene (**20**), propene (**19**), and 1-hexene (**15**), as well as some other rates of low reliability which were included. A selected set of the 29 best data points gives $\rho = -10.7$, $C = -8.96$, and $r = 0.980$.[25] Thus the selected points defined the same correlation line as the complete set but with a correlation coefficient significantly improved over that for all the points, or that originally published.[3a]

Table III. Rates of Acid-Catalyzed Hydration of Alkenes at 25 °C

Alkene	k_2, $M^{-1}\ s^{-1}$	k_{rel}	k_{H^+}/k_{D^+}
$Me_2C{=}CH_2$	0.371×10^{-3} [a]	1.0	1.45[b]
$Me_2C{=}CHMe$	0.214×10^{-3} [c]	0.58	1.22[d]
Methylenecyclobutane	0.223×10^{-3} [e]	0.60	
1-Methylcyclobutene	0.74×10^{-4} [e]	0.2	
1-Methylcyclopentene	0.915×10^{-3} [f]	2.5	0.93,[d] 1.23[f]
1-Methylcyclohexene	$0,305 \times 10^{-3}$ [f]	0.82	1.16[f]
1,3-Cyclohexadiene[g]	0.70×10^{-5}	1.8×10^{-2}	2.2, 1.2[h]
Bicyclo[3.3.1]non-1-ene	31.4[i]	8.5×10^{4}	2.5
Bicyclo[4.2.1]non-1[8]-ene	0.278[i]	7.5×10^{2}	2.1
exo-5-Hydroxynorbornene	0.429×10^{-6} [j]	1.2×10^{-3}	1.53
endo-5-hydroxynorbornene	0.985×10^{-6} [j]	2.7×10^{-3}	1.87
Cyclohexene	0.443×10^{-7} [f]	1.2×10^{-4}	1.06
Norbornene	0.341×10^{-4} [f]	9.2×10^{-2}	2.13
1-Hexene	0.432×10^{-8} [f]	1.2×10^{-5}	1.68
Propene	0.238×10^{-8} [f]	6.4×10^{-6}	2.82
Ethylene	0.146×10^{-14} [f]	3.9×10^{-12}	2.62
$PhCH{=}CHPh$ (*E*)	0.354×10^{-10} [k]	9.5×10^{-8}	2.6
$PhCH{=}CH_2$	0.240×10^{-6} [l]	6.5×10^{-4}	2.3

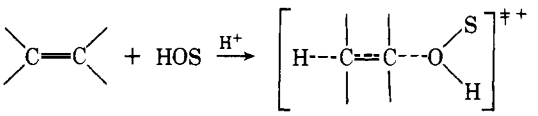
[a] H. J. Lucas and W. F. Eberz, *J. Am. Chem. Soc.*, **56,** 460 (1934). [b] V. Gold and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965). [c] H. J. Lucas and Y.-P. Liu, *J. Am. Chem. Soc.*, **56,** 2138 (1934). [d] E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78,** 5807 (1956). [e] Rates relative to isobutene in 0.973 M HNO_3[18] have been converted to k_2 values by multiplying by the rate given for isobutene. The values calculated in this way for 1-methylcyclopentene ($8.50 \times 10^{-4}\ M^{-1}\ s^{-1}$) and 2-methylbutene ($2.49 \times 10^{-4}\ M^{-1}\ s^{-1}$) agree well with the measured values. [f] This work. [g] J. L. Jensen and D. J. Carré, *J. Org. Chem.*, **36,** 3180 (1971). Rates were run at 40 °C. The rate at 25 °C was approximated by multiplying the rate constant for styrene at 25 °C by the 1,3-cyclohexadiene/styrene ratio of 29 at 40 °C to give the value listed. [h] Values are reported of 2.1 and 2.3 for 1.05 and 2.56 M sulfuric acid at 80 °C, respectively: J. L. Jensen and V. Uaprasert, *J. Org. Chem.*, **41,** 649 (1976). A value of 1.2 was found for 1.05 M $HClO_4$ at 40 °C.[g] [i] Y. Chiang, A. J. Kresge, and J. R. Wiseman, *J. Am. Chem. Soc.*, **98,** 1564 (1976). [j] Reference 16b. The isotope effects were measured at 75 °C. [k] D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Am. Chem. Soc.*, **90,** 4635 (1968). [l] Reference 23.

We feel that a definite decision can be made on the mechanism of ethylene protonation in favor of the $A_{SE}2$ route of attack at carbon (eq 10) as opposed to the π-complex route (eq 3).[9] Solvent molecules (water and sulfuric acid) which are strongly bound to the electrophilic proton and loosely associated with the substrate and the intermediate cation are not included in eq 10 as their exact constitution cannot be specified with certainty, Such solvent will certainly play a role, but we believe a specific interaction as in the π complex of eq 3 can be excluded, If formation of a transition state resembling the open ion (eq 10) was energetically unfavorable relative to the complex, then this stabilization of the π complex relative to the open ion ought to be evidenced by a deviation for ethylene above the correlation line expected for the $A_{SE}2$ route. However, the comparison within the range of experimental observation (Figure 1) shows that ethylene has the reactivity relative to *p*-nitrostyrene expected for a common mechanism of protonation, namely the $A_{SE}2$ route leading to an open ion. There is no evidence for enhancement of the ethylene rate by formation of a bridged ion within the range of observation or in rates extrapolated to lower acidity. Additional evidence for the open ethyl cation as the intermediate in ethylene protonation comes from the activation parameters, including volumes of activation, compiled by Baliga and Whalley[8] for ethylene, propene, and isobutene. The similar values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ and a monotonic decrease in $\Delta H^{\ddagger}$ with methyl substitution observed suggest that these compounds react by a common mechanism.


(10)

It may be argued that the transition state for ethylene protonation is that of the $A_{SE}2$ route but that the intermediate is the π complex. However, it is usually assumed that the transition state resembles the first intermediate and a contrary conclusion would require some independent confirmation. Another view of ethylene protonation is that the first step involves formation of an initial π complex (eq 3),[5a] but that this rearranges to an open ethyl cation,[5a,d] However, as discussed above our results do not support the intervention of a π complex in the rate-determining step.

Still another possibility is concerted protonation and addition of solvent (H_2O or H_2SO_4, eq 11), Solvent assistance is known to be important in solvolysis of secondary and primary alkyl esters,[26] and intramolecular neighboring-group participation is known to accelerate certain alkene protonations in trifluoroacetic acid.[4b] While our data can be consistently interpreted in terms of the $A_{SE}2$ mechanism (eq 10), the possibility of solvent participation cannot be excluded, Such solvent assistance might have been expected to show up in the activation parameters,[8] but such data must always be interpreted cautiously. Further information regarding the nucleophilic properties of these strong acid solutions may help to resolve this point,


(11)

Reactivity of Cycloalkenes. For ease of comparison the rates of the pertinent alkenes for which suitable kinetic data are available in the literature are given in Table III together with those examined in this study.

One striking feature of the comparative data is the close correspondence of the rates of reaction of 1-methylcyclohexene and 2-methyl-2-butene. This result indicates that the former compound reacts as a normal alkene with no special features arising from its cyclic structure.

Despite the attention devoted to the study of the reactivity of norbornyl derivatives,[5b,27] there is a dearth of information available on the kinetics of generation of norbornyl cations by protonation, although the relative reactivities of norbornene and 7,7-dimethylnorbornene toward a variety of reagents have been examined.[28] According to the data in Table III norbornene is more reactive than cyclohexene by a factor of 770. This high reactivity of norbornene is probably not due only to ground-state strain in the molecule, as some strained alkenes do not show such enhanced rates. Norbornene is strained by an estimated 22.8 kcal/mol, but this is only 4 kcal/mol more than the strain in norbornane.[29] The strain in 1-methylcyclobutene is ~28 kcal/mol, ~2 kcal more than the strain of methylcyclobutane,[29] but, although 2-methylcyclobutene is more strained than norbornene, it not only shows no rate enhancement but is less reactive than 1-methylcyclohexene. Thus it does not appear that strained alkenes will necessarily show a reduction in strain on attaining the transition state for protonation that would cause enhanced reactivity, and that in norbornene in particular some other factor may be operative.

Electrophilic additions of HCl, acetic acid, and trifluoroacetic acid to norbornene proceed with substantial formation of unrearranged product.[30] Therefore it appears that σ bridging to form the nonclassical norbornyl cation does not occur in these reactions and cannot explain the high reactivity of norbornene. A factor that could contribute to the decreased activation energy is that norbornene is puckered unsymmetrically, and it is plausible that the p orbitals of the double bond are correspondingly unsymmetrically distorted so that the lobes of the orbitals on the exo face are enlarged and contain excess electron density (Figure 3). Thus the rate of electrophilic attack on the exo face would be enhanced over that of either the endo face or over a symmetrical, undistorted alkene because the electron distribution of the molecule already resembles that of the transition state for exo attack. This argument has received theoretical justification in the work of Fukui.[31]

The rate of hydration of norbornene in aqueous $HClO_4$ has been recently measured using a gas chromatographic method.[16b] The rate constant in $HClO_4$ at 25 °C was reported as 1.10×10^{-4} M^{-1} s^{-1} as compared to our extrapolated value in H_2SO_4 of 0.341×10^{-4} M^{-1} s^{-1}. The minor difference in the rates arises partly from the different dependence of the rates on the acidity function H_0; the slope vs. log k_{obsd} is -1.11 in the former case and -1.25 in the latter. The basic agreement between the rates measured in different acids and using different techniques is a gratifying confirmation of the validity of the experimental results.

There has also been a recent report of the reactivities of cycloalkenes in the trifluoromethanesulfonic acid catalyzed addition of acetic acid.[19] Relative rates for cyclohexene, cyclopentene, and norbornene were found to be 1:1:600 at 45 °C. This pattern of reactivity parallels very closely that we have found for hydration. However, the acetic acid additions were proposed to involve ion-pair intermediates and formation of π complexes.[19] Furthermore the rate-determining step in the cyclopentene and cyclohexene reactions was proposed to be a conversion of a protonated olefin–trifluoromethanesulfonate intimate ion pair to an acetic acid solvent separated ion pair, whereas for norbornene the rate-determining step was proposed to be rearrangement of a π complex of a σ-bonded ion as in the proposal of Taft.[32] The principal reason that different mechanisms were proposed[19] for norbornene and cyclopentene was the difference in solvent isotope effects: $(k_{H^+}/k_{D^+}) = 0.75$ for cyclopentene, 1.6 for norbornene.

We believe that the consistency of the relative rates in water and in acetic acid argues that the same rate-determining step pertains in each medium. The role of ion pairs should be much more important in acetic acid than in water, but evidently these do not affect the relative rates. As discussed above we have been able to consistently interpret the reactivities of acyclic alkenes in terms of structural effects on the $A_{SE}2$ mechanism, and the reactivities of the cyclic alkenes are readily explicable on the same basis. In particular the relative reactivities of the alkenes in Table III follow the order expected for proton transfer to form carbonium ions. As shown in Table III there is a considerable variation in solvent isotope effects, but the fact that these isotope effects are consistently low both in water and in acetic acid for cyclopentene and cyclohexene, and their much more reactive 1-methyl analogues, and for 2-methyl-2-butene argues strongly against a change in mechanism giving rise to the observed effects. Rather it appears that structural factors of a not fully understood type are responsible, as discussed below.

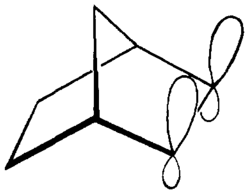


Figure 3.

The greater reactivity of norbornene relative to cyclohexene is analogous to the reactivity of *endo*-dicyclopentadiene, in which the norbornenyl moiety undergoes selective hydration.[36] It has recently been reported[37] that in CF_3CO_2H addition the bicyclo[2.2.2]oct-2-ene to cyclohexene rate ratio is 24. However, from studies of hydration in 20% EtOH we find these compounds to have very similar reactivities.[38]

Isotope effects on the alkene hydrations are presented (Table II) as rate ratios in H_2SO_4 and D_2SO_4 at equal molarities. This is a reasonable comparison as it has been found that the acidity functions of these acids are essentially identical in all but very dilute acids and above 97% acid.[33] The agreement of the scales is particularly close when comparisons are made at constant molarity.[33b] The isotope effect in sulfuric acid for cyclohexene is invariant with acidity, but comparisons at the same molarity of perchloric acid show a variation from 0.87 in 5.55 M acid to 1.82 in 8.15 M acid (footnote *f*, Table II). Isotope effects sometimes,[34] but not always,[24b] increase moderately with increasing acidity, but this increase of more than 100% is remarkable. However, an acidity function for $DClO_4$ has not been reported,[39] and it is quite possible that the changes in the isotope effect represent changes in the medium. Therefore further discussion of this unusual effect must be deferred. It is interesting to note, however, that the reported isotope effects for 1,3-cyclohexadiene (Table III) in sulfuric and perchloric acids differ by 90%, but it is not known in this case if the perchloric acid isotope effect varies with concentration. Coussemant and co-workers[24b] found a similar solvent isotope effect for *p*-chloro-α-methylstyrene in perchloric and sulfuric acids at a single concentration.

There is only a tenuous relation (Table III) between the reactivities of the alkenes and their solvent isotope effects in sulfuric acid. It is commonly argued that variations in isotope effects with reactivity arising from changes in structure correspond to changes in the degree of proton transfer at the transition state.[35] In particular a maximum isotope effect is suggested for the case in which the proton is half transferred, and lower isotope effects are proposed for the cases where the extent of proton transfer is slight or nearly complete. However, our results emphasize that these arguments can be treacherous. On multidimensional reaction hypersurfaces the connection between reactivity and degree of proton transfer is by no means clear. Even for compounds with the apparent structural similarity of cyclohexene and norbornene the reaction surfaces are apparently quite different. Thus the assignment of transition-state structure by isotope effect–reactivity correlations should be done with extreme prudence.

Experimental Section

Deuterated acids were obtained from Merck Sharpe & Dohme and were diluted with D_2O from the same source. Concentrations of the resulting solutions were measured by titration.

Solutions of the gaseous substrates dissolved in sulfuric acid were prepared by bubbling the alkenes into the solvent contained in the cells for the ultraviolet spectrometer and then capping the cells so that no gas spaces remained. Other solutions were prepared by injecting about 5 μL of 0.3-0.9 M solutions of the alkenes in dry methanol into 1-cm cells containing 3 mL of the appropriate acid and shaking the resulting $0.5\text{-}1.5 \times 10^{-3}$ M solutions. Runs in $DClO_4$ were carried out using 0.5×10^{-3} M alkene in 1-cm small-volume cells containing 1 mL of acid. Rates were monitored by observing the decrease in the end absorption of the alkenes in the ultraviolet. Ethylene (**20**) and propene (**19**) were monitored at 186 and 189 nm, respectively, using a Cary 16 spectrophotometer swept with N_2. The other alkenes were observed using a Cary 118 spectrophotometer at wavelengths (nm) of 198 (**15**), 200 (**1**), 202 (**2**), 202 (**3**), and 200 (**4**). Reported rates are the average of at least two runs which agreed within ±5%.

Equilibration experiments with cyclohexene were carried out by setting the spectrophotometer at 202.5 nm at which wavelength cyclohexene had an extinction coefficient of 172 in water. Solutions of cyclohexene and cyclohexanol in 7 M H_2SO_4 were allowed to reach constant absorbance at this wavelength, and the final absorbance corresponded to 10 ± 1% cyclohexene beginning with cyclohexene and 8 ± 1% beginning with cyclohexanol. When D_2SO_4 was used the final absorbance beginning with cyclohexene or cyclohexanol corresponded to 6 ± 2% cyclohexene.

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(22) (a) A value of −0.83 has been determined by solvolysis of *p*-ethoxycumyl *p*-nitrobenzoate (K. M. Koshy, unpublished results); (b) the average value derived from published *p*-cyclopropylcumyl chloride solvolyses is −0.47 (footnote *a*, Table 7, ref 3d).

(23) An average of $2.40 \times 10^{-7}\ M^{-1}\ s^{-1}$ is obtained from the values of 1.09×10^{-7} and $3.72 \times 10^{-7}\ M^{-1}\ s^{-1}$ derived by extrapolation of $H_0 = 0$ of the observed rates in $HClO_4$[20] and H_2SO_4,[24] respectively.

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