Acid-Catalyzed Hydration of Dienes. III. Effects of Ring Strain on Rate, Enthalpy, and Entropy for Hydration of 1,3-Cycloalkadienes

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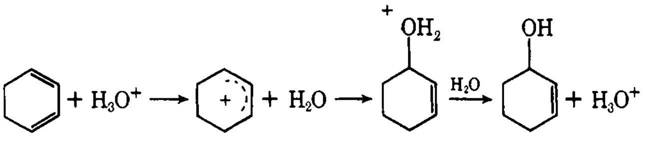
Received June 26, 1975

The effect of ring size on rate and equilibrium of hydration for 1,3-cycloalkadienes (C_5, C_6, C_7, C_8 dienes) in aqueous sulfuric acid is reported. Both rate and equilibrium changes are explained by 1,3-cycloalkadiene conjugative stabilization free energies; maximum estimates are 1.6, 0, 4.5, and 5.4 kcal mol^{-1} for C_5, C_6, C_7, and C_8 dienes, respectively. Maximum conjugative stabilization enthalpy is estimated at 2.5–3.5 kcal mol^{-1} for cyclooctadiene. Entropy changes augment enthalpy changes in rate differences, but compensate for enthalpy changes in equilibrium differences. An approximately linear inverse relationship between strain energy and log (rate of hydration) for olefins hydrating via a conjugated carbonium ion intermediate is reported; simple olefins fall orders of magnitude off the line. The solvent isotope effect for hydration of 1,3-cyclohexadiene is 2.2 (k_{H_2O}/k_{D_2O}). Conclusions reached are as follows. (1) Comparison of kinetic and/or equilibrium data obtained from reactions of alkenes with heats of hydrogenation is of dubious value, since entropy contributions do not necessarily parallel enthalpy contributions to free-energy changes. (2) A value of 3 kcal mol^{-1} seems a good estimate for conjugative stabilization enthalpy for 1,3-cyclooctadiene. The value for 1,3-cyclohexadiene appears near zero. Conjugative stabilization entropy is less certain, but may be comparable in size to enthalpy. (3) All data on olefin hydration may be accommodated by a single mechanism, provided conjugative interactions act to flatten the potential energy surface, giving rise to an "earlier" transition state.

In the first paper of this series[1] the mechanism of hydration of 1,3-cyclohexadiene in aqueous perchloric acid was elucidated. The simplest mechanism consistent with the evidence obtained was analogous to other alkene hydrations: rate-controlling proton transfer from hydronium ion to diene, producing a cyclic allylic carbonium ion which is rapidly attacked by water to produce product, 2-cyclohexenol (Scheme I).

Scheme I



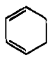
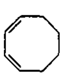
In a recent study on conjugative interactions in cycloalkadienes it was concluded that 1,3-cyclohexadiene is rather different from the C_7 and C_8 analogues: 1,3-cyclohexadiene demonstrates little or no enhanced enthalpic stability attributable to conjugative stabilization arising from a 1,3 π system.[2] The present study compares reactions of 1,3-cycloalkadienes in aqueous sulfuric acid; our intent is to establish the effect of ring strain on rate-controlling proton transfer to olefinic carbon. If in fact there is little or no conjugative interaction in 1,3-cyclohexadiene relative to 1,3-cyclooctadiene or 1,3-cycloheptadiene, then considerable differences in rate should exist; it is important to establish the contribution of enthalpy and entropy to the free-energy difference.

Several previous studies are relevant: most recently it was observed that 1,3-cyclooctadien-2-yl triflate solvolyzes 3×10^3 faster than 1,3-cycloheptadien-2-yl triflate in 50% aqueous ethanol; presumably both reactions proceed via vinyl cationic intermediates.[3] This large difference in rate is not a strain effect per se, however, since cycloocten-1-yl triflate solvolyzes just ten times faster than cyclohepten-1-yl triflate[4] *and* cyclohepten-1-yl triflate solvolyzes at about the same rate as 1,3-cycloheptadien-2-yl triflate. Presumably the large difference of 3×10^3 arises from some allylic cation nature in the transition state of 1,3-cyclooctadien-2-yl triflate solvolysis, made possible by the greater flexibility of the larger eight-membered ring. A number of earlier reports examining the effect of ring strain on solvolysis rates have been reviewed,[5,6] based on pioneering work of Brown.[7] Typically, $C_4 < C_5 > C_6 < C_7 < C_8$, with overall rate changes of a few hundred (e.g., for cycloalkyl tosylates in acetic acid or aqueous ethanol, C_6:C_8 = 1:300).[5]

The effect of ring strain appears to be much smaller on electrophilic addition reactions than on solvolysis. This is of course a result of several factors: the limiting SN1 solvolyses just discussed involve changing a reactant state sp^3-hybridized carbon in a ring to a transition state hybridized carbon very nearly sp^2 in nature, whereas electrophilic additions involve changing a reactant state having two sp^2-hybridized carbons in a ring to a transition state having one of these carbons still sp^2 and the other intermediate between sp^2 and sp^3. For electrophilic additions (rate-controlling attack of electrophile) overall rate changes amount to about 10. For example, the acid-catalyzed hydration of 1-methylcyclopentene is about ten times faster than that of 1-methylcyclobutene;[8] 1,2-dihydrofuran is six times faster than 1,2-dihydropyran toward rate-controlling proton transfer (enol ether hydrolysis).[9] The BF_3 or $SnCl_4$ acid-catalyzed addition of acetic acid to cycloalkenes also shows small rate changes, overall about a factor of 2.5 (e.g., cycloheptene and cyclooctene are 2.5 and 2.0 times faster, respectively, than cyclopentene).[10] Although an attempt was made in this latter study to see if the effect was entropic or enthalpic in nature, the small rate changes masked any real differences in thermodynamic characteristics of the reactions. This latter point becomes more significant when it is realized that predicted orders are $C_4 > C_5 < C_6 > C_7 > C_8$, whereas these admittedly fragmented results are $C_4 < C_5 \geq C_6 > C_7 \leq C_8$. The tentative conclusion based on these reports of electrophilic addition reactions is that Brown's model of sp^2 → sp^3 carbon within a ring[7] may be a poor one for reactions of cycloalkenes where at least one carbon within the ring retains sp^2 hybridization. Even accounting for possible "early" transition states, it is reasonable that rate-controlling attack of small electrophiles on cycloalkenes would relieve strain, although the net effect on reaction rate may be different from the case for reactions involving a change in ring carbon hybridization of all sp^3 → one sp^2 (solvolyses) or one sp^2 → all sp^3 (addition to carbonyl).

The results summarized above thus merit further study and we sought to attenuate the strain effect by studying

Table I
Values of k_{obsd} and Equilibrium Ratios ([Product]/[Reactant])[a]

	$10^4 k_{obsd}$, s^{-1}	[2-cycloalkenol] / [1,3-cycloalkadiene]	Temp., °C	$M_{H_2SO_4}$
	7.70	0.80	80	1.05
	2.34	3.43	50	1.05
	8.66	2.46	60	1.05
	25.0	2.65	70	1.05
	60.9 (40.9)[b]	2.56 (1.05)[b]	80	1.05
	311 (153)[b]	4.98 (2.57)[b]	80	2.56
	54.9	12.6	20	5.64
	148	13.7	30	5.64
	359	12.8	40	5.64
	0.140	1.39	80	1.05
	1.22	3.55	60	5.64
	2.90	4.29	70	5.64
	6.15	4.77	80	5.64

[a] Mean values measured at λ_{max} of 1,3-cycloalkadiene; average deviation of measurement $\leq\pm 5\%$. [b] Values in parentheses measured in $D_2SO_4-D_2O$.

rate-controlling electrophilic attack of the hydronium ion on 1,3-cycloalkadienes.

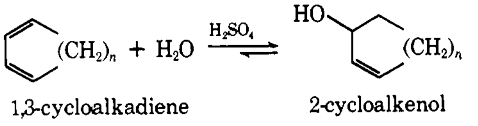
Experimental Section

Substrates were obtained from Aldrich Chemical Co. and were molecularly distilled prior to use. Deuteriosulfuric acid (99% D_2SO_4) and deuterium oxide (99.8%) were from Stohler Isotope Chemicals. Cyclopentadiene was obtained as the dimer and slow distillation of the monomer into ethanol yielded solutions of cyclopentadiene[11] which were stable for days at 0°; a fresh solution was prepared when the absorbance of cyclopentadiene (λ_{max} 238 nm)[12] in the stock solution decreased significantly. The general kinetic procedure is described elsewhere.[13]

Attempts to extend conditions (higher acidities and temperatures) reported in Table I for 1,3-cyclopentadiene and 1,3-cycloheptadiene failed because of the incursion of other, reactions: the kinetics were not pseudo-first-order but gave linear plots when treated as second order in 1,3-cycloalkadiene. Further discussion of these results is deferred to a time when reaction products can be characterized. *All* reaction conditions within Table I exhibited pseudo-first-order kinetics over 8–10 half-lives of reaction time reflecting clear hydration–dehydration; i.e., data reported in Table I are for eq 1.

Results

The reactions investigated are reversible and at equilibrium the product concentration is generally greater than that of reactant. Pseudo-first-order rate constants were obtained in the traditional manner[1] by following decreasing absorbance at λ_{max} of cycloalkadiene; linear first-order kinetic plots were obtained for 3 half-lives (or longer) of reaction time. Rate constants and equilibrium ratios were calculated using equations below, as described elsewhere.[13]



(1)

1,3-cycloalkadiene 2-cycloalkenol

$$\frac{[\text{2-cycloalkenol}]_e}{[\text{1,3-cycloalkadiene}]_e} = \frac{A_0 - A_e}{A_e} \tag{2}$$

$$k_{obsd} = k_{hyd} + k_{dehyd} \tag{3}$$

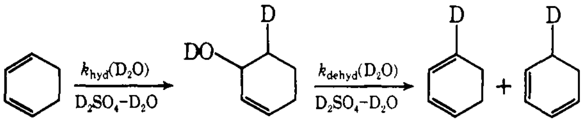
$$\frac{[\text{2-cycloalkenol}]_e}{[\text{1,3-cycloalkadiene}]_e} = \frac{k_{hyd}}{k_{dehyd}} \tag{4}$$

Table II
Solvent Isotope Effects on Hydration of 1,3-Cyclohexadiene in Aqueous Sulfuric Acid

$M_{H_2SO_4}$	$k_{hyd}(H_2O)/k_{hyd}(D_2O)$
1.05	2.1
2.56	2.3

In most instances the equilibrium ratio is considerably greater than unity and therefore k_{hyd} is more precisely defined than k_{dehyd} (i.e., k_{dehyd} is the small difference between the two larger rate constants, k_{obsd} and k_{hyd} in eq 3). As a result, this paper for the most part discusses effects of strain on rate constants for hydration, k_{hyd}.

Solvent Isotope Effect. k_{obsd} was determined in solutions of D_2SO_4 in D_2O. However, exchange of deuterium for hydrogen on the substrate occurs, since acid-catalyzed hydration is reversible to an appreciable extent. To ensure that k_{obsd} (D_2O) was measured prior to exchange becoming important, a computer program was developed[14] similar to the interative type provided by Wiberg.[15] Values of k_{obsd} (D_2O) so obtained were true constants over at least 2 half-lives of reaction time and are listed in Table I in parentheses. Values of A_e calculated by computer program were used to calculate the equilibrium ratio (eq 2). Rate and equilibrium measurements in D_2SO_4–D_2O, then, refer to the following reactions.

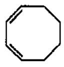


(5)

Ratios $k_{hyd}(H_2O)/k_{hyd}(D_2O)$ reflect both solvation and primary isotope effects,[16,17] whereas $k_{dehyd}(H_2O)/k_{dehyd}(D_2O)$ ratios reflect solvation and secondary isotope effects. The latter ratios cannot be discussed precisely because of their greater inherent error (eq 3 and 4 discussion); however, it is gratifying to note that they fall within 15–20% of unity, which is the magnitude expected for solvation plus secondary isotope effects for this type of reaction.[18] Solvent isotope effects given in Table II can thus be confidently discussed as isotope effects arising from solvation and primary isotope effects on the hydration of 1,3-cyclohexadiene in aqueous sulfuric acid. Regrettably, similar treatment of the data for 1,3-cyclooctadiene failed to yield separable constants: the equilibrium ratio under comparable conditions is much smaller for 1,3-cyclooctadiene, thus k_{dehyd} contributes much more to k_{obsd} (eq 3 and 4) and exchange of deuterium for hydrogen on the substrate becomes important within the first half-life of reaction time in D_2SO_4–D_2O. Qualitatively it can be said that the behavior of 1,3-cyclohexadiene in D_2SO_4–D_2O solutions is paralleled by the other cycloalkadienes studied; however, precise isotope effects could not be obtained in the latter cases and thus the value of $k_{hyd}(H_2O)/k_{hyd}(D_2O) \simeq 2$ for 1,3-cyclohexadiene is taken as typical of this class of alkene. This value is smaller than observed for styrene hydration (ca. 2–5)[18c] and larger than observed for isobutylene hydration (1.4).[19] Presumably the 1,3-cycloalkadienes are intermediate in kinetic basicity between styrenes and isobutylene; i.e., the extent of proton transfer in the transition state is intermediate.

Thermodynamic Parameters. Usual treatment of the dependence of k_{hyd} and equilibrium ratio on temperature affords $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and ΔH, ΔS, respectively.[13] Table III lists values resulting from a least-squares analysis of the data. Medium dependence of these quantities has been described[13] and in this paper comparison is made at the common acidity 5.64 M H_2SO_4. Medium effects can be safely

Table III
Effect of Ring Size on Hydration of 1,3-Cycloalkadienes

	$k_{\text{rel}}{}^a$	$\Delta H\ddagger{}^b$	$\Delta S\ddagger{}^c$	$\left(\frac{[\text{ROH}]_e}{[\text{D}]_e}\right)_{\text{rel}}$	ΔH^e	ΔS^f
	200			1		
	2000	16.5	−12.9	3.2	0	5
	4			1.7		
	1	19.0	−20.6	(.25)	3.5	13

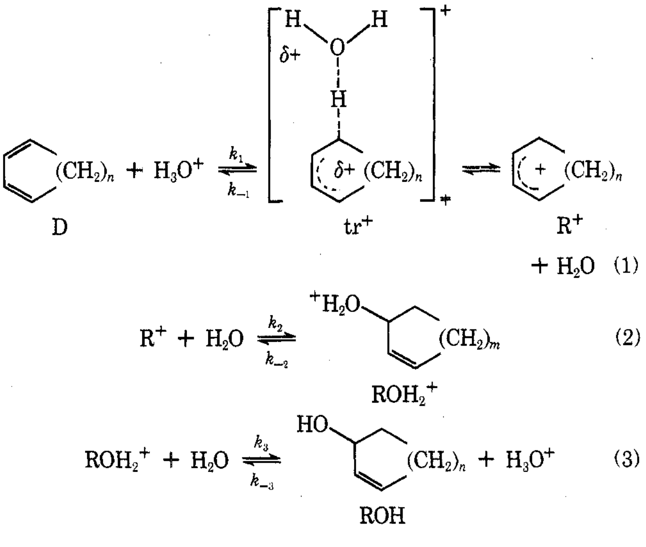
[a] Relative rates of hydration of 1,3-cycloalkadienes at 80° in 1.05 M H_2SO_4. Value for 1,3-cyclooctadiene is from data in ref 13 (extrapolation over 0.8 H_0 units). [b] Enthalpy of activation for hydration of 1,3-cycloalkadienes in 5.64 M H_2SO_4, kcal mol^{-1}. [c] Entropy of activation for hydration of 1,3-cycloalkadienes in 5.64 M H_2SO_4, cal deg^{-1} mol^{-1}. [d] Relative equilibrium ratios (eq 2, text) at 80° in 1.05 M H_2SO_4. Value for 1,3-cyclooctadiene is extrapolated from data in ref 13 in higher acidities; because of the nonlinear relationship between acidity and equilibrium ratio, this value is approximate [$0.25 \leq$ (value) ≤ 1]. [e] Enthalpy of hydration for 1,3-cycloalkadienes in 5.64 M H_2SO_4, kcal mol^{-1}. Calculated from the dependence of equilibrium ratio (eq 2, text) on temperature. [f] Entropy of hydration for 1,3-cycloalkadienes in 5.64 M H_2SO_4, cal deg^{-1} mol^{-1}. Calculated from the dependence of equilibrium ratios (eq 2, text) on temperature.

neglected when comparing thermodynamic data for C_6 and C_8 dienes;[13] the differences seen in Table III are thus due solely to effects of ring size.

Discussion

The mechanism of acid-catalyzed hydration of 1,3-cycloalkadienes is given in Scheme II, based largely on activation parameters, medium dependence, and solvent isotope effect.[1,13] Consistent with a solvent isotope effect of 2.2 (Table II) tr$^+$ is drawn showing significant, but not complete, proton transfer from hydronium ion to diene. The rate of hydration and the equilibrium ratio for hydration according to Scheme II are respectively

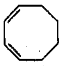
Scheme II



$$k_{\text{hyd}} = k_1 a_{H_3O^+} f_D / f_{tr^+} \tag{6}$$

$$[\text{ROH}]/[\text{D}] = \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}} a_w f_{\text{ROH}} / f_D \tag{7}$$

Table IV
Effect of Ring Size on Strain and Heats of Hydrogenation for 1,3-Cycloalkadienes

	Strain energy^a	$-\Delta H_1{}^b$	$-\Delta H_{\text{total}}{}^c$
	0.8 (4.2)	24.0[21]	49.1[2,21]
	−1.2 (−0.3)	26.5[2,22]	53.6[2]
	1.4 (4.7)	24.1[2]	49.9[2]
	3.8 (5.2)	26.0[2]	49.0[2]

[a] Calculated by the method of ref 2, but anchored on the strain energies of cycloalkanes given by Eliel,[20] kcal mol^{-1}. Values in parentheses are strain energies of respective cycloalkenes, calculated in the same way. [b] Heat of hydrogenation of 1,3-cycloalkadiene to form cycloalkene, kcal mol^{-1}. [c] Heat of hydrogenation of 1,3-cycloalkadiene to form cycloalkane, kcal mol^{-1}. Value for 1,3-cyclopentadiene is corrected for acetic acid solvent effect; i.e., ΔH (given) = ΔH (gas phase) − 1.8, where 1.8 is the difference between the heats of hydrogenation of 1,3-cyclohexadiene in the gas phase and in acetic acid solution.[23]

Equation 7 is actually more complex than written because of significant concentrations of ROH_2^+ in acidities greater than 4–5 M H_2SO_4. This problem is discussed elsewhere[13] and for the present purpose no advantage exists in needlessly complicating eq 7: data to be discussed are in 1 or 5.6 M H_2SO_4, only in the latter case would protonation of ROH be significant, and even so it is almost certain that 2-cycloalkenols are similar in basicity (i.e., pK_a of ROH_2^+ is similar for 2-cyclohexenol and 2-cyclooctenol). Since (a) protonation of ROH is minor (i.e., [ROH] > [ROH_2^+] in acidities of this study) and (b) effects of protonation of ROH are likely to be similar for the 2-cycloalkenols (i.e., pK_a ROH_2^+ is not likely to depend significantly on ring size), equilibrium data will be discussed according to eq 7.

Table IV summarizes literature data relevant to strain in 1,3-cycloalkadienes, based solely on heats of hydrogenation and combustion. Equations 6 and 7 can be related to data in Table III only insofar as enthalpic and entropic contributions to free-energy changes can be separated. Table III summarizes data from the present study which afford such separation. We now wish to discuss effects of n = 1, 2, 3, or 4 (Scheme II) on rates of hydration (eq 6) and hydration equilibrium ratio (eq 7) emphasizing enthalpy (in comparison to Table IV data) and entropy terms.

Strain Effects on Rate. In Table IV, ΔH_1 is a measure of the relative enthalpic strain released on changing from four sp^2-hybridized carbon atoms to two in a carbocyclic ring. Clearly the changes in ΔH_1 with ring size do not parallel changes in relative rate recorded in Table III; strikingly, ΔH_1 is nearly the same (ca. 26 kcal mol^{-1}) for the two dienes differing in rate by $>10^3$. ΔH_{tot} is a measure of the strain released on changing from four sp^2-hybridized carbon atoms to all sp^3 in a carbocyclic ring. The kinetic data do not follow changes in ΔH_{tot} either. Close comparison of ΔH_1 and ΔH_{tot} *vs.* k_{rel} indicate that the greater the heat of hydrogenation, the faster hydration proceeds; i.e., k_{rel} appears to be related to total strain within diene. Strain energies have been calculated several ways for cycloalkanes and cycloalkenes; we have chosen to calculate strain energies for 1,3-cycloalkadienes in a manner consistent with Doering's recent study.[2] Clearly k_{rel} changes with ring size as strain energies do; the greater the strain energy, the *slower*

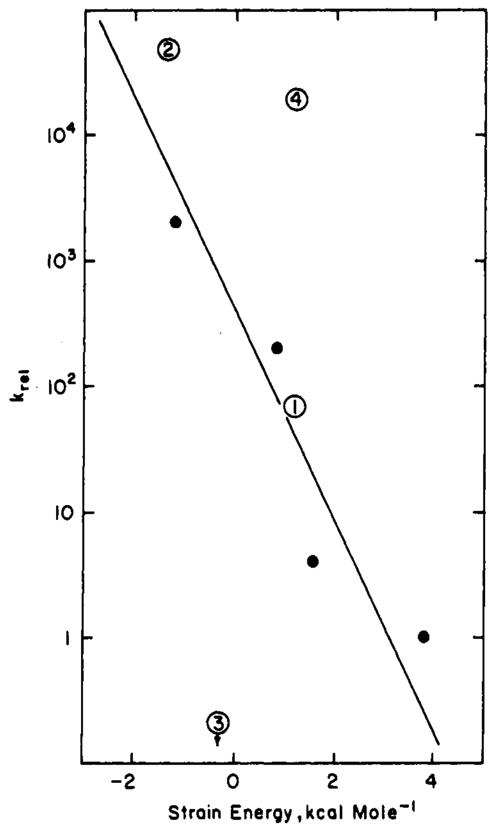


Figure 1. Plot of k_{rel} *vs.* strain energy (Tables III and IV) for 1,3-cycloalkadienes, slope −0.9. Points 1 and 2 are points for styrene[1] and 2-phenylpropene,[1] calculated on the same basis as 1,3-cycloalkadienes (see text), although the heat of hydrogenation[40] on which the strain energy of 2-phenylpropene is based was obtained in a different fashion and that point is not as precisely defined.[23] Point 3 represents the upper limit for cyclohexene hydration.[13] Point 4 is the point for 2,3-dimethyl-2-butene,[1] calculated on the same basis as 1,3-cycloalkadienes (see text) except the total strain was increased by 2 kcal mol^{-1} to help account for strain associated with methyl-methyl interactions in 2,3-dimethylbutane.

hydration proceeds. In fact, considering reasonable errors in values of ΔH used to calculate strain energies (± 0.5 kcal mol^{-1} overall), the correlation is surprisingly linear with slope of −0.9 (Figure 1). The significance of this correlation is somewhat clouded by the uncertainty and interrelativity of strain energies; however, the correlation is real. Use of strain energies calculated by the single conformation increment provided by Schleyer[24] gives a plot at least as linear, but of slope −1.3. An interesting observation deserves mention. We have measured the hydration of styrene and 1,3-cyclohexadiene under comparable conditions in aqueous perchloric acid:[1] assuming the rate *difference* between these two compounds to be the same in 2.57 M $HClO_4$ at 50° as in 1.05 M H_2SO_4 at 80° (a reasonable assumption since $\Delta H^\ddagger$ values are nearly equal[1] and *differences* in $\Delta H^\ddagger$ do not seem to be very dependent on acidity[13]), styrene plots equally well on the line of Figure 1 as the cycloalkadienes. The strain energy for styrene (1.2) was calculated based on strain = 0 for ethylbenzene and heat of hydrogenation 28.6.[28] Similar calculations–extrapolations for 2,3-dimethylbutene and cyclohexene hydration gave points many orders of magnitude off the line in Figure 1. It is probably *not* coincidence that reactions proceeding via conjugated carbonium ions plot on the line and others do not. Data are much too scarce to allow more than just a report of this intriguing observation.

It is interesting that the rate order observed for hydration of 1,3-cycloalkadienes ($C_5 < C_6 > C_7 > C_8$) is exactly the same as for additions to cycloalkanones;[7] however, this order would not have been predicted based on consideration of strain energies and/or heats of hydrogenation using reasoning advanced in earlier studies.[6–8] That is, the fastest reacting diene ought to be the one undergoing the most favorable change in strain energy: using cycloalkadiene → cycloalkene as a model, column 1 of Table IV predicts the order $C_6 \geq C_8 > C_7 \sim C_5$. Thus our observed correlation between 1,3-cycloalkadiene strain energy and rate of hydration requires further analysis: it appears formally that tr$^+$ is more highly strained than diene, by an amount nearly proportional to the diene strain energy. The correlation may result from the following: (1) both rate and strain may be related to a common variable (e.g., conjugative interaction); (2) ring strain is enthalpic, entropy changes may override enthalpy giving rise to observed rate order; (3) a fortuitous interrelating of several factors (e.g., 1 and 2), which may themselves not be independent of each other, giving rise to what is in fact an artifact; (4) the model cycloalkadiene → cycloalkene may be inappropriate (certainly 2-methyl-1,3-cycloalkadiene → 3-methylenecycloalkene would be a useful model, but data are unavailable).

The term ring strain as applied to hydration of 1,3-cycloalkadienes is a composite of angle strain, eclipsing, and crowding interactions, part or all of which may be offset by conjugative interactions of the π system. These quantities have been amply defined by others,[2,24,25] but the present study affords a new and sensitive probe into their interrelationships. Supporting the importance of conjugative interaction (or lack of it in C_5 and C_6 cycloalkadienes) is that the rate difference we observe (overall $>10^3$) is at least an order of magnitude greater than that observed in other studies, *except* for a recent solvolysis study where conjugative stabilization was evident for C_8 ring dienyl cation but not for C_7.[3] In fact, other studies involving electrophilic attack on cycloalkenes[8–10] exhibited rate differences (overall) of <10. We see no other way to explain rate-controlling proton transfer to 1,3-cyclohexadiene being 2×10^3 faster than 1,3-cyclooctadiene except by invoking large differences in conjugative stabilization of the dienes.

It was observed above that our rate order parallels Brown's but that the order would not have been predicted based on similar consideration of strain energies and/or heats of hydrogenation. The reason lies in the overriding importance of the conjugative effect, both in reactant *and* transition states. Our discussion must be moderated by the rather ill-defined nature of the transition state, although for hydration of alkenes it is known to resemble a carbonium ion[1,13,18,19] (that is, tr$^+$ in Scheme II has considerable C–H bond formation and associated positive charge on carbon). The relative rates in Table III can be explained by differences in conjugative interaction in reactant states, augmented or moderated by associated changes in angle and/or eclipsing strain on going from diene to tr$^+$. Conjugative interaction in tr$^+$ is assumed to be comparable for C_5–C_8, and cycloalkenes are assumed to be good models for angle and/or eclipsing strain in tr$^+$ (column 1, Table III). Thus the summary below.

1,3-Cyclohexadiene: conjugative interaction is minimal (or nonexistent)[2] in diene; angle and eclipsing strain may be eased somewhat in tr$^+$.

1,3-Cyclopentadiene: conjugative interaction is minimal in diene; angle and/or eclipsing strain may be increased in tr$^+$.

1,3-Cycloheptadiene and 1,3-cyclooctadiene: considerable conjugative interaction ($C_8 > C_7$), angle and/or eclipsing strain is probably eased in tr$^+$.

Precedent for 1,3-cyclopentadiene conjugative interaction is lacking; the factor of 10 observed ($C_5 < C_6$) could be due either to increased strain in tr$^+$ or to slightly greater conjugative interaction in C_5 diene than C_6. If the latter is true, the order of conjugative stabilization in 1,3-cycloalkadienes is $C_8 > C_7 > C_5 > C_6$. Assuming (a) zero conjugative stabilization for 1,3-cyclohexadiene[2] and (b) that differences in rate observed reflect differences *primarily* in conjugative interaction in dienes, produces the following maximum estimates of conjugative stabilization in 1,3-cycloalkadienes: 1,3-cyclopentadiene, 1.6 kcal mol^{-1}; 1,3-cyclohexadiene, 0 kcal mol^{-1}; 1,3-cycloheptadiene, 4.5 kcal mol^{-1}; 1,3-cyclooctadiene, 5.4 kcal mol^{-1}. These values, of course, are free energies of conjugative stabilization and may be greater or lesser than those calculated from enthalpy measurements, depending on entropy contributions. For 1,3-cyclooctadiene,[2] conjugative stabilization enthalpy has been estimated as about equal to that for 1,3-butadiene,[26] 3.6 kcal mol^{-1}. From Table III, the enthalpy estimate is 2.5 kcal mol^{-1}, in good agreement considering assumptions built into our calculation of conjugative stabilization energies.

Of considerable interest is the finding that only about *half* of the rate difference lies in the enthalpy term. The preceding discussion correlated free-energy differences (or relative rates) with known enthalpy differences because of the common effect of conjugative stabilization. Now, however, it has been demonstrated that enthalpy accounts for slightly less than half the free-energy difference. This means that relative rate data will not correlate with strain effects *unless* entropy changes parallel enthalpy changes (or happen to be negligible). The entropy of activation for hydration of 1,3-cyclohexadiene (−12.9 eu) is typical for olefin hydration, considering medium effects;[13] entropy of activation for a variety of olefins appears rather insensitive to relative changes in tr$^+$ (e.g., extent of proton transfer).[1] The entropy of activation for hydration of 1,3-cyclooctadiene thus appears "too negative" by about 8 eu. Knowing that (a) 1,3-cyclohexadiene is more nearly planar[27–29] than 1,3-cyclooctadiene,[2,30] (b) $\Delta S^\ddagger$ is relatively insensitive to changes in tr$^+$ arising from reasonably small differences in degree of proton transfer,[1] it can be concluded that the 8 eu arises from a transition state more nearly planar about sp^2-hybridized carbons than is the 1,3-cycloalkadiene (which is consistent with the inverse correlation of rate with strain). Thus, relative to 1,3-cyclohexadiene, 1,3-cyclooctadiene has greater conjugative stability (by ~4–5 kcal mol^{-1}), π–π dihedral bond[30] angle of ~30° (~15° for 1,3-cyclohexadiene),[28] and overall "loses" 8 eu on → tr$^+$. It is rather clear that 1,3-cyclohexadiene must be a much less flexible molecule than 1,3-cyclooctadiene, otherwise it (C_6) would achieve the conformation allowing significant π–π interaction, calling for ~30° π–π dihedral bond angle such as found in 1,3-cyclooctadiene. While the size (8 eu) seems rather large to be attributed solely to such an effect, our experimental error (±1–2 eu) does not justify further elaboration.

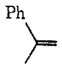
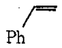
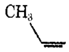
Strain Effects on Equilibrium. Enthalpic data in Table IV do not explain or correlate with the experimentally observed order of the equilibrium ratios in Table III. This is because of near cancellation of ΔH changes by ΔS. For example, the 3.5 kcal mol^{-1} enthalpy barrier for 1,3-cyclooctadiene relative to 1,3-cyclohexadiene is nearly cancelled by 2.8 kcal mol^{-1} (at 80°) entropy contribution. Presumably the other dienes exhibit comparable (but not equal) effects. The 3.5 kcal mol^{-1} enthalpy difference is close to the 3.6 kcal mol^{-1} conjugative stabilization enthalpy estimated earlier.[2] *However,* equilibrium ratios do not reflect this large difference because of compensating entropy contributions to free-energy differences. Differences in ΔH are thus explained totally on the basis of relative conjugative stabilization of 1,3-cycloalkadiene relative to 2-cycloalkenol.

Entropy differences (ΔS) between hydration of 1,3-cyclohexadiene and 1,3-cyclooctadiene probably reflect greater C_8 ring flexibility for diene → ene relative to C_6. Unfortunately, free-energy (and thus ΔS) data are not available from hydrogenation studies of 1,3-cycloalkadiene → cycloalkene; however, it is known that ΔS changes contribute significantly to free energies of hydrogenation.[31]

Though acyclic diene hydration would be of interest, our data indicate that studies of conjugated diene hydration are only possible insofar as mechanistic implications are possible from studies of 2-alkenol dehydration. That is, 1,3-cyclohexadiene is favorably hydrated because of lack of conjugative stabilization of diene, and 1,3-cyclooctadiene is hydrated measurably (but less than C_6) largely because of the large inherent strain[2] in the diene which partially compensates for conjugative stabilization.

Mechanistic Implications. Table V lists some intriguing relative rate data: replacing hydrogen by phenyl increases the rate of hydration by about the same amount as replacement by methyl (e.g., α-methylstyrene rate ~ isobutylene rate). Propenes and styrenes hydrate via carbonium ions and the reactions are subject to considerable substituent effects, ρ_m[33] ~ ρ_+[18] ~ ρ_*[34] = −(3–4). However, it has long been known that in limiting SN1 solvolyses, the rate enhancement of phenyl is comparable to *two* methyl groups.[35] This means that *phenyl* activates an alkyl halide much more than methyl toward a reaction proceeding via a carbonium ion, while *methyl* activates an alkene slightly more than phenyl toward a reaction proceeding via a carbonium ion. This rate effect is largely enthalpic (Table V) and is easily attributable to conjugative stabilization of the reactant state. The rate difference translates to about 5 kcal mol^{-1} at 25°,[36] which represents the maximum conjugative stabilization free energy for phenyl with an ethylenic group. In general terms, the similar reactivity of propene and styrene are probably not so much due to a less than expected stabilization of the transition state by phenyl (e.g., "early transition state") as to a conjugative stabilization of the reactant state. *However,* a simple application of the Hammond postulate[37] would lead to the conclusion that

Table V
Relative Rates of Hydration of Selected Alkenes[a]

Alkene	k_{rel}	$\Delta H^\ddagger$	Ref
	3×10^3	20.0	1
	1.3×10^3		32
	8×10^2	19.9	1, 32
	30	22.8	1
	1	24.2	1
	10^{-1}		32

[a] Rates from data in ref 33 normalized to conditions of ref 1, using mutually listed data for styrene and α-methylstyrene: 2.5 M $HClO_4$ and 30°.

the transition states for styrene hydrations occur comparable (e.g., α-methylstyrene) to or later (e.g., styrene) than for isobutylene and tetramethylethylene hydrations. This is contradictory to observed solvent isotope effects and general catalysis experiments: $k_{H_2O}/k_{D_2O} = 1.4$ for isobutylene hydration,[19] $k_{H_2O}/k_{D_2O} = 2–4$ for styrene hydrations[18] and general acid catalysis is easily observable for hydration of styrenes ($\alpha \simeq 0.8$),[18] but not for isobutylene[19,38] or tetramethylethylene. Thus the Hammond postulate suggests an earlier transition state for isobutylene and tetramethylethylene hydrations, whereas experimental data show that the reverse must be true. That is, both the low solvent isotope effect ($k_{H_2O}/k_{D_2O} = 1.4$) and the lack of observation of general catalysis ($\alpha = 0.85$, based on experiments in H_2O–D_2O mixtures)[19] indicate that proton transfer is nearly complete in the transition state for hydration of aliphatic alkenes. *However*, the above simple application of the Hammond postulate ignores a very basic assumption implicit in the postulate: not only must the reactant and intermediate states be considerably different in energy (certainly true for olefin hydration), *but* the general *shape* of the energy surface must not change. There are three ways in which the data for alkene hydration can be accommodated based on the two-dimensional energy surface describing proton transfer from acid, HA, to alkene. (1) The reactant state energy well may be broadened for aliphatic alkenes relative to conjugated alkenes. (2) The carbonium ion state energy well may be broadened for conjugated alkenes relative to aliphatic alkenes. (3) The shapes of the energy wells may be similar, but the energy maximum for conjugated alkenes may be truncated relative to that for aliphatic alkenes. Perhaps this rather complex situation is best viewed as resulting from the greater polarizability of conjugated π systems, resulting in a gradual flattening of the potential energy surface as the proton is in the intermediate stages of transfer. Thus contributions from 1 and 2 may be important, but perhaps the end result appears much as 3.

Thus the major role played by conjugative stabilization in diene hydration justifies differences in potential energy surfaces for simple alkene hydration and hydration of conjugated alkenes. This in turn accommodates all evidence accumulated to date on alkene hydration.

Acknowledgments. Financial support by the California State University at Long Beach Research Foundation is gratefully acknowledged. J.L.J. thanks California State University, Long Beach, for granting a sabbatical leave during 1974–1975, and the Graduate Department of Biochemistry at Brandeis University for providing opportunity to write the manuscript. Particular thanks is expressed to Professor W. P. Jencks for professional support and encouragement.

Registry No.—1,3-Cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 1,3-cyclooctadiene, 1700-10-3; 2-cyclopentenol, 3212-60-0; 2-cyclohexenol, 822-67-3; 2-cycloheptenol, 4096-38-2; 2-cyclooctenol, 3212-75-7.

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