

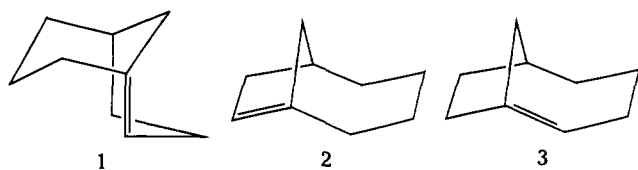
# Kinetics and Mechanism of Hydration of Strained Bridgehead Bicyclic Olefins<sup>1</sup>

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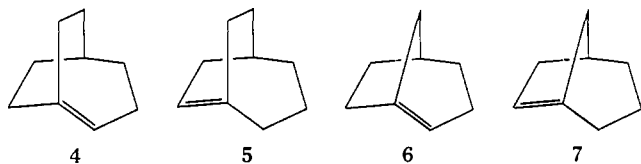
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**Abstract:** Appreciable solvent isotope effects in the normal direction were found for the hydronium ion catalyzed hydration of bicyclo[4.2.1]non-1(8)-ene and bicyclo[3.3.1]non-1-ene ( $k_{\text{H}^+}/k_{\text{D}^+} = 2.1$  and 2.5, respectively), and reaction of the latter substrate also showed general acid catalysis with isotope effects for the general acids in the range 3.6 to 5.8. This is taken to mean that these strained olefins hydrate by the same mechanism as simple unstrained alkenes; rate-determining proton transfer from the catalyst to the substrate is followed by rapid hydration of the ensuing carbonium ion. The transition states in the reactions of the strained substrates, however, are significantly earlier than the very late ones characteristic of the protonation of unstrained olefins, and the present results lead to the estimate that, of the 12 kcal/mol of strain which the bridgehead double bond introduces into bicyclo[3.3.1]non-1-ene, 5 kcal/mol is still left in the protonation transition state whereas only 1.6 kcal/mol exists in the bridgehead cation.

There has been a considerable revival of interest in Bredt's rule<sup>4</sup> of late and, as a result, the limits of stability of bridgehead bicyclic olefins have now been redefined. It has become apparent that the strain in these systems is related less to the total number of atoms in the three bridges ( $S$  number)<sup>5</sup> than to the stability of the trans monocycloalkene which corresponds to that ring of the bicyclic system in which the double bond is found in a trans endocyclic configuration. Thus bicyclo[3.3.1]non-1-ene (**1**),<sup>6</sup> bicyclo[4.2.1]non-1(8)-ene (**2**),<sup>7</sup> and bicyclo[4.2.1]non-1(2)-ene (**3**),<sup>7</sup> which are related to *trans*-cyclooctene, a substance



known for many years as an unstable but isolable compound,<sup>8</sup> have recently been prepared and found to be reasonably stable though quite reactive substances. On the other hand, bicyclo[3.2.2]non-1-ene (**4**),<sup>9</sup> bicyclo[3.2.2]non-1(7)-ene (**5**),<sup>9</sup> bicyclo[3.2.1]oct-1-ene (**6**),<sup>10a</sup> and bicyclo[3.2.1]oct-1(7)-ene (**7**),<sup>10</sup> in all of which the



trans double bond appears in a seven-membered ring, have never been isolated, although there is evidence for their existence as fleeting unstable intermediates; *trans*-cycloheptene is also known only as a reactive transient species.<sup>11</sup>

Inasmuch as the strain energy of the stable bridgehead olefins is appreciable, that of **1** has been estimated as 12 kcal/mol,<sup>12</sup> there is considerable interest in their chemistry and in particular in whether or not they react by the same mechanisms as ordinary, unstrained alkenes. In this paper, we report the results of a study of the acid-catalyzed hydration of **1** and **2**. This reaction in the case of **1** has been shown to go to completion giving the bridgehead alcohol, bicyclo[3.3.1]nonan-1-ol, as the sole product.<sup>6a,b</sup> It seems quite likely that hydration of **2** also goes to completion and gives only the bridgehead alcohol, and these reactions there-

fore represent simple systems especially amenable to detailed kinetic investigation.

## Experimental Section

**Materials.** Bicyclo[3.3.1]non-1-ene and bicyclo[4.2.1]non-1(8)-ene were prepared as described,<sup>6b,7</sup> and pure samples for kinetic measurement were obtained by vapor phase chromatography. All other materials were best available commercial grades. Aqueous solutions were made from either deionized H<sub>2</sub>O, which was purified further by distillation from alkaline permanganate, or from 99.7% D<sub>2</sub>O (Merck) used as received. Buffer solutions were prepared by mixing aqueous acids, whose concentrations had been determined by direct titration, with appropriate amounts of standardized aqueous sodium hydroxide.

**Kinetics.** Rates were measured spectroscopically by following the decrease in the strong absorption band of the olefins located at approximately 200 nm. Measurements were generally made on the shoulder of this band in the region 210–220 nm using spectrometers (Cary 11 and Cary 15) whose cell compartments were thermostated at 25.0 ± 0.1°. Reactions were initiated by adding an appropriate (small) amount of olefin suspended in absolute ethanol (both substrates are only sparingly soluble in this solvent) to the acid or buffer solution contained in a 1-cm quartz cuvette which had been allowed to come to temperature equilibrium with the spectrometer cell compartment; the reaction mixture was then shaken thoroughly and placed back into the cell compartment, and a continuous recording of absorbance as a function of time was begun. Measurement was continued for 3–4 half-lives. End points were either recorded after 10–12 half-times or, when this was impractical, rate constants were obtained by the method of Guggenheim<sup>13</sup> and/or Swinbourne.<sup>14</sup> In all cases, the data conformed to the first-order rate law exactly within the precision of the measurement over the entire course of the reaction.

## Results

**Bicyclo[4.2.1]non-1(8)-ene (2).** This substance gave conventional rates of hydration in dilute aqueous strong acid, and measurements were therefore made in H<sub>2</sub>O and D<sub>2</sub>O solutions of perchloric acid. The data (Table I)<sup>15</sup> show that this reaction is first order in substrate and first order in acid and is therefore second order overall. Least-squares analysis of the dependence of observed first-order rate constants upon acid concentration gave relationships with zero intercepts in both cases:  $k_{\text{obsd}} = -0.00019 \pm 0.00012 + (0.278 \pm 0.002)[\text{H}^+]$  and  $k_{\text{obsd}} = -0.00005 \pm 0.00009 + (0.135 \pm 0.001)[\text{D}^+]$ . These results provide the solvent isotope effect  $k_{\text{H}^+}/k_{\text{D}^+} = 2.06 \pm 0.02$ . These data are summarized in Table II.

**Bicyclo[3.3.1]non-1-ene (1).** Hydration of this olefin

**Table II.** Summary of Rate Constants for the Hydration of Bicyclic Olefins at 25°

Catalyst	pK <sub>a</sub>		k, M <sup>-1</sup> sec <sup>-1</sup>		k <sub>H</sub> /k <sub>D</sub>
	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	
H <sub>3</sub> O <sup>+</sup>	Bicyclo[4.2.1]non-1-ene				
	-1.74	-1.74	0.278	0.135	2.06 ± 0.02
CNCH <sub>2</sub> -CO <sub>2</sub> H	Bicyclo[3.3.1]non-1-ene				
	2.47 <sup>a</sup>	2.94 <sup>b</sup>	0.462	0.129	3.6 ± 0.2
ClCH <sub>2</sub> -CO <sub>2</sub> H	2.87 <sup>c</sup>	3.33 <sup>b,d</sup>	0.516	0.0964	5.4 ± 0.3
CH <sub>3</sub> OCH <sub>2</sub> -CO <sub>2</sub> H	3.57 <sup>e</sup>		0.136		
HCO <sub>2</sub> H	3.75 <sup>f</sup>	4.21 <sup>b,g</sup>	0.104	0.0179	5.8 ± 0.4
HOCH <sub>2</sub> -CO <sub>2</sub> H	3.83 <sup>h</sup>	4.37	0.0906	0.0160	5.7 ± 0.4
CH <sub>3</sub> CO <sub>2</sub> H	4.76 <sup>i</sup>	5.31 <sup>j</sup>	0.0176	0.00394	4.5 ± 0.2
CH <sub>3</sub> CH <sub>2</sub> -CO <sub>2</sub> H	4.88 <sup>k</sup>		0.163		
H <sub>3</sub> O <sup>+</sup>	-1.74	-1.74	31.4	12.4	2.53 ± 0.05

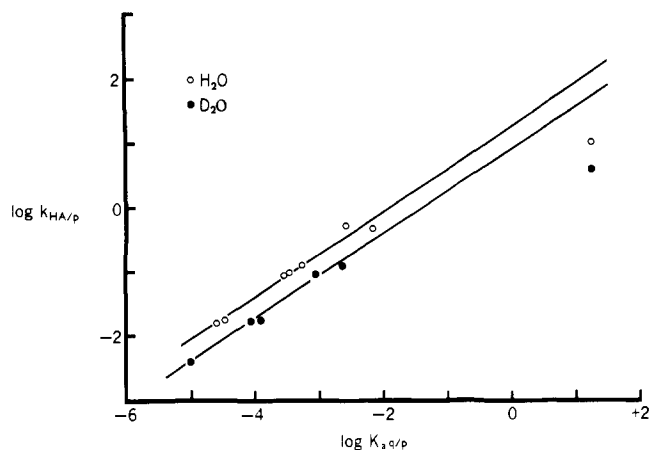
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proved to be too rapid to allow accurate rate determinations in dilute strong acid without recourse to fast reaction techniques. Measurements were therefore conducted in carboxylic acid buffer solutions. Marked general acid catalysis was observed in all cases, and carboxylic acid catalytic coefficients as well as specific rates of reaction catalyzed by the hydronium ion could therefore be determined.

Series of runs were done in buffer solution of a given acid at constant stoichiometric buffer ratio but varying buffer acid concentrations. The data so obtained (Table III)<sup>15</sup> were corrected to constant hydronium ion concentration wherever necessary by the method outlined previously.<sup>16</sup> Bimolecular rate constants were determined by linear least-squares analysis of the relationship between first-order rate constants and buffer acid concentration; the slopes of these relationships afforded carboxylic acid catalytic coefficients and the intercepts, when divided by the (calculated) hydronium ion concentrations of the buffer solutions, provided bimolecular rate constants for catalysis by the hydronium ion.

Measurements were made in H<sub>2</sub>O using seven different buffer acids; these gave hydronium ion catalytic coefficients ranging from 30.0 to 32.3 M<sup>-1</sup> sec<sup>-1</sup> and an average value of k<sub>H+</sub> = 31.4 ± 0.04 M<sup>-1</sup> sec<sup>-1</sup>. In D<sub>2</sub>O, five carboxylic acids were used, giving hydronium ion catalytic coefficients in the range 12.0 to 13.0 M<sup>-1</sup> sec<sup>-1</sup> for an average value of k<sub>D+</sub> = 12.4 ± 0.2 M<sup>-1</sup> sec<sup>-1</sup>. The isotope effects which these measurements provide, as well as the catalytic coefficients themselves, are summarized in Table II.

These data were also used to construct Bronsted relations. The results (Figure 1), based upon carboxylic acid catalytic coefficients only, are H<sub>2</sub>O: log (k<sub>HA</sub>/p) = 1.28 ± 0.17 + (0.67 ± 0.05) log (qK<sub>a</sub>/p) and D<sub>2</sub>O: log (k<sub>DA</sub>/p) = 0.92 ± 0.14 + (0.67 ± 0.04) log (qK<sub>a</sub>/p); the statistical factors p and q were assigned values of 1 and 2, respectively. In each case, the hydronium catalytic coefficients fall short of these Bronsted relations by about an order of magnitude;



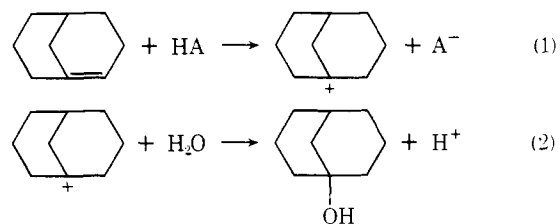
**Figure 1.** Bronsted plots for the hydration of bicyclo[3.3.1]non-1-ene catalyzed by carboxylic acids: (O) data obtained in H<sub>2</sub>O and (●) D<sub>2</sub>O. Hydronium ion points are shown but were not used in obtaining the indicated correlation lines.

the actual deviations, using p = 3 and q = 1 for H<sub>3</sub>O<sup>+</sup>, are H<sub>2</sub>O: 12X and D<sub>2</sub>O: 14X. A Bronsted relation was also constructed from the H<sub>2</sub>O data using only those five carboxylic acids with which measurements had been made in D<sub>2</sub>O. The result, log (k<sub>HA</sub>/p) = 1.25 ± 0.25 + (0.66 ± 0.08) log (qK<sub>a</sub>/p) was hardly different from that obtained using all of the data, and the hydronium ion deviation was exactly the same (12X).

## Discussion

**Reaction Mechanism.** Both of the hydration reactions investigated here show strong positive solvent isotope effects for the hydronium ion catalyzed processes. The values obtained, k<sub>H</sub>/k<sub>D</sub> = 2.5 for **1** and 2.1 for **2**, lie in the range observed for the addition of water to the carbon-carbon double bond in vinyl ethers,<sup>17</sup> and that suggests that the present reaction, just as is the case in vinyl ether hydration,<sup>18</sup> occurs through rate-determining proton transfer from the catalyzing acid to the substrate. This view is reinforced by the fact that the carboxylic acid catalysts used in the hydration of **1** show large primary isotope effects as well (see Table II).

Reactions which proceed by rate-determining proton transfer must show general acid catalysis, and it is therefore significant that this form of catalysis was found in the present study. Thus, all of the evidence taken together points to a simple two-stage mechanism for the hydration of strained bridgehead olefins such as bicyclo[3.3.1]non-1-ene: (1) slow protonation of the double bond at the atom away from the bridgehead position (eq 1) followed by (2) rapid hydration of the carbonium ion thus formed (eq 2). This is



completely analogous to the mechanism now known to apply to the hydration of simple unstrained olefins,<sup>19</sup> and these strained systems may thus be seen to react normally.

**Transition State Structure.** Having established that the hydration of both strained and unstrained olefins proceeds via rate-determining proton transfer, it is of interest to inquire further whether the transition states of the two reac-

tions are similar in structure and, in particular, whether there is any difference in the degree of proton transfer at the two transition states.

Simple unstrained olefins are thought to have quite late protonation transition states in which proton transfer is very nearly complete. This view is based upon the small isotope effects which these reactions show, viz.,  $k_{H^+}/k_{D^+} = 1.5$  for isobutene,<sup>20</sup> and is reinforced by studies using  $H_2O$ - $D_2O$  mixtures. The latter provide an isotopic exponent  $\alpha_i$  which is believed to be a direct measure of the extent of proton transfer; for the hydration of isobutene,  $\alpha_i = 0.9$ ,<sup>20</sup> which implies that proton transfer is 90% complete. Some additional support comes from the difficulty of detecting general acid catalysis in these reactions;<sup>19</sup> this implies a large Bronsted exponent, and Bronsted exponents are also thought to be measures of proton transfer at transition states.

Protonation of the strained olefins investigated here, on the other hand, shows larger isotope effects:  $k_{H^+}/k_{D^+} = 2.1$  and 2.5. General acid catalysis, moreover, is easily detected, and the Bronsted exponent is not particularly large:  $\alpha = 0.67$ . This implies that the transition states in these reactions occur somewhat earlier along the reaction coordinate and that proton transfer is not as far advanced as it is in the case of simple olefins.

This conclusion is consistent with the fact that the strained olefins studied here are considerably more reactive than simple unstrained alkenes. The principal effect of this strain must be to raise the energy of the initial state of the protonation reaction without affecting very much that of its cationic product, and thereby to make the process less endothermic. This change, according to reasoning such as that embodied in the Hammond postulate,<sup>21</sup> should make the transition state less product-like and thus decrease the extent of proton transfer.

It is interesting that this change to an earlier transition state is in the same direction as that brought about by introducing cation stabilizing groups at one end of the carbon-carbon double bond, as in vinyl ethers. The structural change there also serves to make the reaction less endothermic, but it does so by stabilizing the final state without affecting very much the initial state of the reaction, which is opposite to the mode of action of the strain in the systems investigated here. It is gratifying that either kind of change, raising the initial state energy or lowering the final state energy, produces the same effect, for this demonstrates that it is the energy difference between reactants and products and not the absolute values of the individual energies which controls transition state structure. That, of course, is consistent with theoretical considerations, such as those embodied for example in Marcus rate theory.<sup>22</sup>

**Strain Energies.** It is of interest to obtain a quantitative estimate of the rate acceleration provided by the strain in the systems investigated here. Since the double bond in both **1** and **2** is substituted with three alkyl groups, a suitable unstrained reference olefin would be 2-methyl-2-butene. Unfortunately, the rate of hydration of this substance seems not to have been measured in dilute acid, but it is reported to be 0.67 times as reactive as isobutene in 1 M  $HNO_3$ .<sup>23</sup> That, when combined with the specific rate for isobutene,<sup>24</sup> gives  $k_{H^+} = 2.5 \times 10^{-4} M^{-1} sec^{-1}$  for the hydration of 2-methyl-2-butene at 25°. The rate acceleration in the case of bicyclo[3.3.1]non-1-ene is then  $(3.1 \times 10^1)/(2.5 \times 10^{-4}) = 1.24 \times 10^5$  and that for bicyclo[4.2.1]non-1(8)-ene is  $(2.8 \times 10^{-1})/(2.5 \times 10^{-4}) = 1.12 \times 10^3$ .

It is significant that the free energy difference which corresponds to the rate acceleration in the case of bicyclo[3.3.1]non-1-ene, 7 kcal/mol, is considerably less than the

12 kcal/mol determined to be the strain energy produced by introducing the double bond at the bridgehead in this molecule.<sup>12</sup> This implies that considerable strain is still present in the protonation transition state, which is, of course, to be expected if proton transfer is only partly complete, i.e., if the transition state still bears some resemblance to the initial state.

It is also significant that the ratio of the rate acceleration to the total strain energy,  $7/12 = 0.58$ , is somewhat less than the Bronsted exponent for this reaction,  $\alpha = 0.67$ . This implies either that Bronsted exponents and strain energy do not measure progress along the reaction coordinate in the same way, or that some strain remains in the reaction product. Since this product is a bridgehead carbonium ion which cannot assume a completely planar configuration, the latter alternative is not at all unlikely. In fact, if the view is adopted that the Bronsted exponent for this reaction is indeed a measure of the fractional reduction in strain energy accomplished at the transition state, the strain left in the carbonium ion may be calculated as  $12 - (7/0.67) = 1.6$  kcal/mol. This result is in creditable agreement with a theoretical calculation showing this carbonium ion to be strained 3 kcal/mol relative to the parent hydrocarbon,<sup>25</sup> and it is consistent also with the modest (60–100 $\times$ ) solvolysis rate differences observed between bicyclo[3.3.1]nonyl halides and corresponding *tert*-butyl derivatives.<sup>26</sup>

**Supplementary Material Available:** Tables I and III, hydration rates (six pages). Ordering information is given on any current masthead page.

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