from the GC collection vessel to the calorimeter ampule which was quickly sealed. The sample weights ranged from 12 to 44 mg.

1-Acetoxybicyclo[3.2.1]octane (2). The addition of 1.0 g of **1** to 7 mL of dry acetic acid was followed by the addition of 20 mL of ether and neutralization with saturated sodium carbonate solution. After drying over magnesium sulfate, the ether was carefully removed through a 24-cm column packed with glass beads. Analysis of the ether distillate indicated that the two impurities had not distilled. The reaction product was analyzed for the amounts of the impurities. In order to obtain a pure sample of **2**, the product was warmed under reduced pressure for 2 h. The material thus obtained was indicated to be pure by GC and was used for the enthalpy of solution measurements.

1,3-Dehydroadamantane (3). The hydrocarbon was prepared as described previously[6] and was stored as an ether solution under oxygen-free nitrogen. It was separated from the solvent using a $^3/_8$ in. × 15 ft 18% Carbowax column at 90 °C, and the hydrocarbon was collected directly into a calorimeter ampule, which was then sealed. The samples were on the order of 20 mg. One ampule was broken in a vial containing dry acetic acid. Analysis of the product indicated only one compound, 1-acetoxyadamantane.

1-Acetoxyadamantane (4). The acetate was prepared by the reaction of 1-hydroxyadamantane with acetic anhydride.[12] After distillation (bp 118 °C at 16-17 mm) it crystallized to give **4**, mp 31-31.5 °C (lit.[11] 33-34 °C). Analysis by GC showed a single product, identical with that obtained from the reaction of **3** with acetic acid.

Calorimetric Studies. The enthalpies of reaction and solution were determined using an LKB 8700 calorimetric system.[13] The calorimeter was checked using the enthalpy of solution of Tris (tris(hydroxymethyl)aminomethane) in 0.100 N hydrochloric acid. The average of seven runs was −7113 ± 5 cal/mol, in good agreement with the accepted value,[14] −7115 ± 8 cal/mol.

In a typical calorimetric run, resistance data were collected during a 5-min foreperiod, a 5-min main period following ampule breaking, and a 5-min afterperiod. The reaction half-lives were less than 30 s. The foreperiod and afterperiod data were separately fitted to the equation

$$R = at^3 + bt^2 + ct + d$$

where t is time using the method of least squares. The root mean square error was on the order of $1\text{-}5 \times 10^{-3}\ \Omega$, which corresponds to about $1\text{-}5 \times 10^{-5}$ deg. The resistance change during the main period was obtained from the least-squares solutions. The resistance correction due to stirring and thermal leakage was calculated by numerical integration of Newton's equation

$$\mathrm{d}T/\mathrm{d}t = a_1 + a_2T + a_3T^2$$

where the last term was added to correct for any nonlinear effects. In terms of resistance this becomes

$$\mathrm{d}R/\mathrm{d}t = R[c_1(\ln R)^2 + c_2 \ln R + c_3]$$

The constants c_1, c_2, and c_3 were determined by fitting the data for both the fore- and afterperiods to the equation. Integration over the main period using these constants gave the temperature correction.

An electrical calibration was carried out for each calorimetric run.

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Hydrolysis of Strained Bridgehead Bicyclic Vinyl Ethers and Sulfides

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Abstract: Rates of hydrolysis of the bridgehead bicyclic vinyl ether 9-oxabicyclo[3.3.1]non-1-ene (**6**) and its vinyl sulfide counterpart 9-thiabicyclo[3.3.1]non-1-ene (**7**), catalyzed by the hydronium ion, were measured in H_2O and in D_2O solution. These data give isotope effects, $k_H/k_D = 2.4$ and 1.9 respectively, which show that these reactions occur by the normal, rate-determining carbon protonation, mechanism. The vinyl ether **6** is less reactive than its olefin analogue, bicyclo[3.3.1]non-1-ene (relative rates $1:{}^1/_{1400}$), as may have been expected for a constrained bicyclic system such as this, where stabilization of the bridgehead carbocation intermediate by conjugation with oxygen is severely impaired. The vinyl sulfide **7**, however, is even less reactive than the vinyl ether (relative rates $1:{}^1/_{140}$); this is a remarkable result in view of the fact that conjugation between the sulfur atom and the cationic center is presumably also strongly inhibited.

The reactivity of vinyl ethers to electrophilic addition is generally very much greater than that of the corresponding olefins. For example, protonation of methyl cyclohexenyl ether (**1**), as determined by its rate of hydrolysis,[3] occurs 1.4×10^5 times faster than protonation of 1-methylcyclohexene (**2**), as measured by its rate of hydration;[4] for the methyl vinyl

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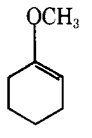
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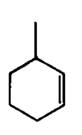
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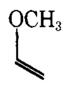
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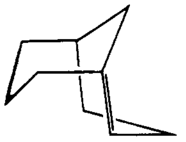
ether-propene pair, **3** and **4**, the corresponding factor is 3.2×10^8.[4,5]

Such a difference is expected on the basis of resonance stabilization of the cationic intermediate formed in vinyl ether hydrolysis, eq 1, which is absent in olefin hydration, and it is

$$CH_2{=}CHOCH_3 \xrightarrow{H^+} CH_3\overset{+}{C}HOCH_3 \leftrightarrow CH_3CH{=}\overset{+}{O}CH_3 \qquad (1)$$

gratifying that when such resonance is inhibited the difference disappears. We reported in a preliminary account of part of this research[6] that the bicyclic bridgehead olefin bicyclo[3.3.1]non-1-ene (**5**) is actually more reactive toward pro-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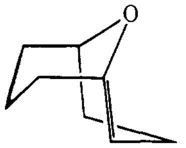
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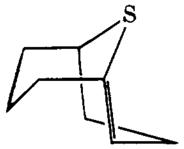
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tonation than is the corresponding vinyl ether, 9-oxabicyclo[3.3.1]non-1-ene (**6**). In **6**, the oxygen atom is held in a configuration which places its bonds in a plane perpendicular to the approximate plane of the carbon-carbon double bond; this oxygen therefore cannot interact effectively with a bridgehead cationic center in a conjugative manner, and resonance stabilization of the kind shown in eq 1 cannot take place without considerable distortion of the bicyclic framework.

In this paper we report our work on the hydrolysis of **6** in full, and we add a description of a companion study on its sulfur analogue, 9-thiabicyclo[3.3.1]non-1-ene (**7**). The latter is of especial interest in connection with current concern over the relative ability of oxygen and sulfur to stabilize an adjacent positive charge.[7]

Experimental Section

Materials. 9-Oxabicyclo[3.3.1]non-1-ene and 9-thiabicyclo[3.3.1]non-1-ene were prepared as described,[6,8] and pure samples for kinetic measurements were obtained by gas chromatography. All other materials were best available commercial grades. Acid solutions were made either from 36% HCl and deionized water, which was purified further by distillation from alkaline permanganate, or from 38% DCl (Merck) and 99.7% D_2O (Merck) used as received; exact concentrations were determined by acidimetric titration.

Kinetics. Rates were determined spectroscopically by following the decrease in the strong low-wavelength UV absorption band of the substrate; for 9-oxabicyclo[3.3.1]non-1-ene observations were made on the long-wavelength shoulder of this band at ca. 210 nm and for 9-thiabicyclo[3.3.1]non-1-ene at the maximum itself, 210 nm. Measurements were made with a Cary 118 C spectrometer whose cell compartment was thermostated at 25.0 ± 0.02 °C. Reactions were begun by adding an appropriate amount of substrate to acid solution contained in a 1-cm quartz cuvette which had been allowed to come to temperature equilibrium with the cell compartment, shaking vigorously, and then replacing the cuvette. For the faster reactions, absorbance was recorded continuously until a stable infinite time reading was achieved; with slower reactions the automatic sample changer accessory of the spectrometer was used to make absorbance readings at convenient time intervals for several runs taking place simultaneously. Rate constants were evaluated as slopes of plots of log $(A - A_\infty)$ vs. time. In all cases the data conformed to the first-order rate law exactly within the precision of the measurement.

Table I. Rates of Hydrolysis of 9-Oxabicyclo[3.3.1]non-1-ene in Aqueous Hydrochloric Acid at 25 °C[a]

10^2[acid], M	10^3k_{obsd}, s^{-1}
	H_2O
10.0	2.33, 2.33
8.0	1.85, 1.84
6.0	1.41, 1.41
4.0	0.981, 0.962
2.0	0.482, 0.489, 0.489
$10^3k_{obsd} = (0.038 \pm 0.010) + (2.28 \pm 0.02) \times 10\,[HCl]$	
	D_2O
10.2	0.985, 0.987, 0.982
8.2	0.793, 0.788, 0.786
4.6	0.447, 0.442, 0.439
2.0	0.202, 0.199, 0.198
$10^3k_{obsd} = (0.0054 \pm 0.0026) + (9.58 \pm 0.04)\,[DCl]$	

[a] Ionic strength held at 0.100 M through the addition of NaCl.

Table II. Rates of Hydrolysis of 9-Thiabicyclo[3.3.1]non-1-ene in Aqueous Hydrochloric Acid at 25 °C

[acid], M	H_0 or D_0[a]	10^3k_{obsd}, s^{-1}
	H_2O	
3.51	−1.27	8.10, 8.11, 7.69
2.93	−1.06	3.85, 4.00
2.34	−0.82	2.26, 2.53
1.17	−0.28	0.416, 0.447
0.936	−0.15	0.262, 0.265, 0.265
0.702	−0.02	0.149, 0.132
$\log k_{obsd} = (-3.782 \pm 0.018) - (1.336 \pm 0.023)H_0$		
	D_2O	
3.38	−1.22	2.87, 2.86
2.91	−1.05	1.93
2.03	−0.69	0.610, 0.604, 0.617
1.35	−0.38	0.246, 0.247
0.675	−0.04	0.077, 0.079, 0.078
$\log k_{obsd} = (-4.068 \pm 0.009) - (1.252 \pm 0.012)D_0$		

[a] E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, **88**, 1177 (1966); D_0 was taken to be equal to H_0 at the same acid concentration [E. Hogfeldt and J. Bigeleisen, *ibid.*, **82**, 15 (1960)].

Hydrolysis of 9-Thiabicyclo[3.3.1]non-1-ene (**7**). One drop of 70% perchloric acid was added to a solution of 25 mg of 9-thiabicyclo[3.3.1]non-1-ene (**7**) in 3 mL of 50% aqueous acetone. The solution was heated under a nitrogen atmosphere on a steam bath for 10 h, cooled, and extracted with 25 mL of ether. The ether was dried over anhydrous sodium sulfate and evaporated on a rotary evaporator to yield a white solid. The infrared spectrum of the white, crystalline solid was identical with that of 9-thiabicyclo[3.3.1]nonan-1-ol (**9**).[8]

Results

Rates of hydrolysis of 9-oxabicyclo[3.3.1]non-1-ene were measured in 0.02–0.10 M hydrochloric acid in both H_2O and D_2O. The data (Table I) show observed first-order rate constants to be proportional to acid concentration, and the reaction is therefore second order overall. Linear least-squares analysis provided relationships between k_{obsd} and acid concentration with essentially zero intercepts (Table I) and gave the following bimolecular rate constants: $k_{H^+} = (2.28 \pm 0.02) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_{D^+} = (9.58 \pm 0.04) \times 10^{-3}\ M^{-1}\ s^{-1}$. These values lead to the isotope effect $k_{H^+}/k_{D^+} = 2.38 \pm 0.02$.

Rates of hydrolysis of 9-thiabicyclo[3.3.1]non-1-ene were also measured in hydrochloric acid solutions in H_2O and D_2O. This substrate, however, was much less reactive than its oxygen analogue, and moderately concentrated rather than dilute acids had to be used. As is typical of reactions of this kind in such solutions, observed rate constants increased somewhat more rapidly than acid concentrations (Table II), but the data could

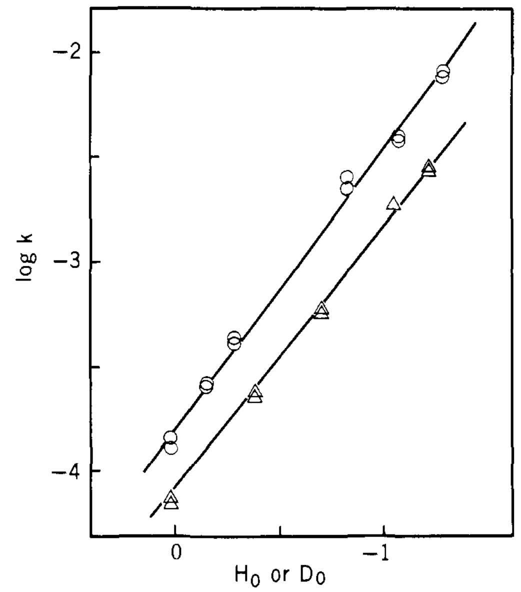
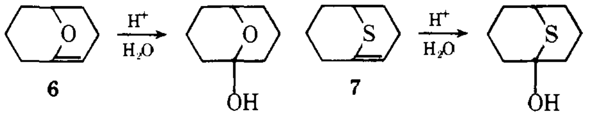


Figure 1. Acidity dependence of observed first-order rate constants for the hydrolysis of 9-thiabicyclo[3.3.1]non-1-ene; circles, HCl in H_2O; triangles, DCl in D_2O.

be correlated well using the H_0 acidity function. Plots of log k_{obsd} vs. H_0 or D_0 were accurately linear (Figure 1) with slopes of the order of 1.3. Linear least-squares analysis of the data gave relationships (Table II) from which the following bimolecular rate constants (values of k_{obsd} at H_0 = 0.00) were obtained: $k_{H^+} = (1.65 \pm 0.07) \times 10^{-4}\ M^{-1}\ s^{-1}$ and $k_{D^+} = (8.55 \pm 0.17) \times 10^{-5}\ M^{-1}\ s^{-1}$. These give the isotope effect $k_{H^+}/k_{D^+} = 1.93 \pm 0.09$.

Discussion

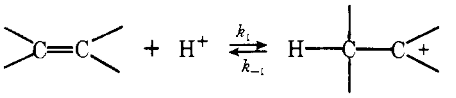
Isotope Effects and Reaction Mechanism. The hydration of 9-oxabicyclo[3.3.1]non-1-ene (**6**) has been shown to give the bridgehead alcohol (**8**), which in this case is also a stable hemiketal;[6] similarily, the hydration of 9-thiabicyclo[3.3.1]non-1-ene (**7**) gives 9-thiabicyclo[3.3.1]nonan-1-ol (**9**) (eq 2).



(2)

6 **8** **7** **9**

Reactions such as these are known to proceed in two stages: (1) protonation of the carbon-carbon double bond (eq 3) is followed by (2) hydration of the ensuing carbonium ion (eq 4).



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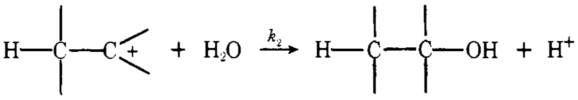


(4)

Protonation is generally rate determining, i.e., k_{-1} is usually less than $k_2[H_2O]$ and protonation is therefore not reversible. This is especially likely to be the case here, for reversal of step 1 would regenerate a highly strained olefinic system: the strain energy of the parent hydrocarbon, bicyclo[3.3.1]non-1-ene (**5**), has been estimated as 12 kcal/mol.[9]

The isotope effects found here, $k_{H^+}/k_{D^+} = 2.4$ for the hydration of 9-oxabicyclo[3.3.1]non-1-ene and $k_{H^+}/k_{D^+} = 1.9$ for the hydration of 9-thiabicyclo[3.3.1]non-1-ene, provide conclusive evidence that protonation is in fact rate determining. If this step were rapidly reversible and hydration were rate determining, these isotope effects would have been inverse, i.e., $k_{H^+}/k_{D^+} < 1.00$. Rate-determining proton transfer to carbon, on the other hand, generally gives $k_{H^+}/k_{D^+} > 1.00$. The presently observed isotope effects, moreover, are in good agreement with values expected from a correlation recently found between isotope effects and reaction rate for the hydrolysis of a large group of vinyl ethers which are known to react through rate-determining proton transfer to carbon:[10] this correlation predicts $k_{H^+}/k_{D^+} = 2.2$ for 9-oxabicyclo[3.3.1]non-1-ene (found 2.4 and $k_{H^+}/k_{D^+} = 1.5$ for 9-thiabicyclo[3.3.1]non-1-ene (found 1.9).

Table III. Comparison of Reactivities in the 9-X-Bicyclo[3.3.1]non-1-ene System

	X = CH_2	O	S
rel rates of hydration[a]	1.00	7.3×10^{-3} (1/1400)	5.3×10^{-6} (1/190,000)
rel rates of solvolysis of saturated bridgehead chlorides[b]	1.00	0.32 (1/3.1)	0.011 (1/93)

[a] Data for X = CH_2 from ref 12; remainder, this work. [b] Reference 17.

It may be seen in Figure 1, as well as from the relationships between rate constants and acidity function given in Table II, that the hydration of 9-thiabicyclo[3.3.1]non-1-ene has a slightly but significantly steeper acidity dependence in H_2O than in D_2O. This causes the isotope effect k_{H^+}/k_{D^+} to increase with increasing acidity and reaction velocity. Such an increase is consistent with the isotope effect correlation mentioned above, and its approximate magnitude agrees with that expected from the correlation as well; for example, the correlation predicts that the value of k_{H^+}/k_{D^+} at $H_0 = -1.00$ should be 1.28 times that at $H_0 = 0.00$ whereas the measurements give a ratio of 1.21.

This change in isotope effect implies that the structure of the transition state in the hydration of 9-thiabicyclo[3.3.1]non-1-ene changes with changing acidity. In particular it suggests that, although the transition state is still fairly product-like in all of the solutions investigated here, increasing acidity does move it in a reactant-like direction. Changes in transition-state structure deduced from isotope-effect variations such as this have been reported before in systems where reactivity changes were effected by varying the composition of a water-organic solvent reaction medium,[11] but to our knowledge this is the first instance of the effect produced by changing the concentration of the acid component of a wholly aqueous water-inorganic acid mixture.

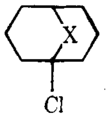
Relative Reactivities. The present results, when combined with the specific rate of hydration of bicyclo[3.3.1]non-1-ene,[12] show the vinyl ether in this series to be 1400 times less reactive to protonation than the parent olefin and the sulfide to be 140 times less reactive than the vinyl ether (Table III). As pointed out in the introduction to this paper, and also in a preliminary account of this research,[6] vinyl ethers generally protonate much more readily than do the corresponding olefins. The present reversal of this general trend is a consequence of steric constraints within the bicyclic system to which these substrates belong. Similar inversions of reactivity have been found before in other constrained systems, and there as here they are understandable as the result of steric inhibition of the normally dominant cation-stabilizing resonance effect of oxygen, which allows the usually hidden cation-destabilizing polar effect of this atom to come into prominence.[13]

The further reduction in reactivity produced by substituting sulfur for oxygen in this series is considerably more difficult to understand. Classically, divalent sulfur is considered to have a weaker cation-stabilizing resonance effect than oxygen, and to have a weaker cation-destabilizing polar effect as well.[14]

Recent calculations[7a] support this view in part: they predict the weaker polar effect for sulfur and in fact they find the polar effect of sulfur to be mildly cation stabilizing. But they disagree with the classical picture in that they give sulfur a stronger cation-stabilizing resonance effect than oxygen. The fact that the vinyl ether and the vinyl sulfide in the present series are both less reactive than the corresponding olefin shows that resonance effects are of minor importance here, and this difference between classical and modern views is therefore of no consequence in the present application. On both accounts, therefore, substituting sulfur for oxygen should stabilize the adjacent cationic center produced by protonation of the carbon-carbon double bond, and this should be reflected in a rate increase rather than the decrease actually observed.

It might be argued that the observed reactivity order is the result of diminished strain in 9-thiabicyclo[3.3.1]non-1-ene. This substance and its oxygen analogue belong to a bicyclic system which is strained because it possesses a trans double bond contained in an eight-membered carbocyclic ring. The system is therefore related to *trans*-cyclooctene, but it is significantly more strained than *trans*-cyclooctene inasmuch as the strain energy of the parent hydrocarbon, bicyclo[3.3.1]non-1-ene, has been estimated as 12 kcal/mol[9] whereas that of *trans*-cyclooctene is only 9 kcal/mol.[15] This additional strain may be attributed to the added constraint imposed by the single atom carbon bridge. As such, it should be approximately the same in bicyclo[3.3.1]non-1-ene and in 9-oxabicyclo[3.3.1]non-1-ene, but it might be somewhat less in 9-thiabicyclo[3.3.1]non-1-ene: since carbon-sulfur bonds are significantly longer than either carbon-carbon or carbon-oxygen bonds, 1.82 Å vs. 1.54 and 1.43 Å, respectively,[16] the single-atom bridge in 9-thiabicyclo[3.3.1]non-1-ene will be longer than that in either of the other two substances and the constraint it imposes on the system should therefore be less severe. The consequent reduction in strain energy would then diminish the strain-relief acceleration given to the hydrolysis of 9-thiabicyclo[3.3.1]non-1-ene and that would lower its rate of reaction.

This explanation, however, is inconsistent with data on the solvolysis of the related bridgehead bicyclic chlorides, 1-chloro-9-oxabicyclo[3.3.1]nonane (**10**) and 1-chloro-9-thiabicyclo[3.3.1]nonane (**11**).[17] These reactions produce the same cationic intermediates as are formed in the protonation of the analogous vinyl ether and vinyl sulfide, but the chlorides are not particularly strained and their solvolysis is not accelerated by strain relief; yet substitution of sulfur for oxygen here produces a rate retardation just as in the protonation reaction (Table III).



10, X = O
11, X = S

In acyclic systems, where resonance is not inhibited as it is in the present series, early evidence put oxygen ahead of sulfur in ability to facilitate reactions where positive charge is generated on an adjacent carbon atom, and this was commonly ascribed to oxygen's more powerful conjugative effect.[18] It is now known, however, that the oxygen vs. sulfur rate ratios in such reactions can vary over a wide range. For example, in the gas phase, α-thio carbocations are consistently formed in preference to α-oxo carbocations.[7b,19] Even in solution, systems have been found where sulfur is better than oxygen,[7c,20] and a recent survey lists k_O/k_S ratios from 440 to 0.08.[7c] The upper limit of this range can be extended to nearly 20 000 by adding rates of acid-catalyzed hydrolysis of *tert*-butyl ethynyl sulfide,[21] and, if carbocation-destroying reactions are included, the lower limit can be stretched to 0.0002 by including the rates of reaction with water of 1-methoxy- and 1-methylthio-1,1-dianisylmethyl cations.[22] In view of this wide diversity of behavior, it is surprising that the oxygen vs. sulfur rate ratio for a simple acyclic analogue of the constrained bicyclic system investigated here is only a factor of 4 different from the ratio for the constrained series: for the acid-catalyzed hydrolysis of methyl vinyl ether and methyl vinyl sulfide, $k_S/k_O = 0.03$,[23] whereas for the hydrolysis of **6** and **7**, $k_S/k_O = 0.007$. This reluctance of the rate ratio to change significantly when much of the resonance effect is turned off is quite remarkable indeed.

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