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Acid-Catalyzed Hydration of 1-Methylcycloheptene and Methylenecycloheptane. Construction of the Complete Free Energy Profile for Olefin-Alcohol Interconversion in the 1-Methylcycloheptyl System*

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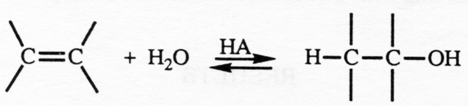
Rates of the reversible hydration of 1-methylcycloheptene (ENDO) to 1-methylcycloheptanol (ROH) and the essentially irreversible hydration of ethylenecycloheptane (EXO) to ROH, plus the position of equilibrium between ENDO and ROH, were determined in concentrated aqueous perchloric acid solution at 25 °C. The results, together with a literature value of the ENDO : : EXO equilibrium ratio, allow dissection of the experimental data into hydronium-ion catalytic coefficients for the following individual processes: ENDO→ROH, $k_{H^+} = 1.02 \times 10^{-3}$ M^{-1} s^{-1}; EXO→ROH, $k_{H^+} = 3.53 \times 10^{-3}$ M^{-1} s^{-1}; ROH→ENDO, $k_{H^+} = 2.17 \times 10^{-5}$ M^{-1} s^{-1}, and ROH→EXO, $k_{H^+} =$ 1.01×10^{-6} M^{-1} s^{-1}. Combination of these results with a previous estimate of the barrier to reaction of tertiary carbocations with water leads to a complete free energy profile for this system.

INTRODUCTION

The acid-catalyzed addition of water to olefins, Eq. (1), is a reversible process



(1)

whose position of equilibrium in dilute aqueous solution at 25 °C usually lies well to the side of alcohol product.[1] The 1-methylcyclooctyl system, however, provides an exception to this generalization in that comparable amounts of alcohol **1**, and olefin **(2)**,

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday

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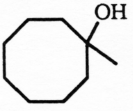
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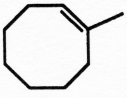
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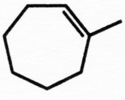
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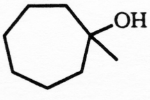
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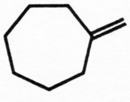
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coexist at equilibrium: K = [alcohol]/[olefin] = 1.27.[2] In order to determine whether this unusual behavior extends to the 1-methylcycloheptyl system, we have now examined the kinetics and product equilibrium composition in the conversion of 1-methylcyclopheptene (**3**), to 1-methylcycloheptanol (**4**), and we have also investigated the hydration of the isomeric olefin, methylenecycloheptane (**5**). This, plus some information from the literature, has allowed us to construct a complete free energy profile for this system.

EXPERIMENTAL

Materials

Methylenecycloheptane was prepared by a Wittig reaction on cycloheptanone using a method reported for cyclohexanone,[3] 1-methylcycloheptene and 1-methylcycloheptanol were best available commercial grades. Samples of these substrates used for quantitative measurements were purified by gas chromatography. Acid solutions were made with distilled water, and concentrations were determined by acidimetric titration.

Measurements

Quantitative measurements were made much as has already been described for the 1-methylcyclooctyl system.[2] Extinction coefficients of the ultraviolet bands of the olefins were determined as slopes of Beer's law plots, and these, coupled with the fact that the alcohol hydration product has negligible absorbance in the region of measurement, were then used to determine olefin-alcohol equilibrium constants from the absorbances of equilibrated solutions of known total substrate concentration. Rate measurements were also made spectrophotometrically, at λ = 200 nm for the interconversion of 1-methylcycloheptene and 1-methylcycloheptanol and at λ = 210 nm for the disappearance of methylenecycloheptane. The extinction coefficient, equilibrium, and slower rate measurements were made with a Cary Model 118C spectrometer and the faster rate measurements were made with a Durrum-Gibson stopped-flow spectrometer; the sample compartments of both instruments were thermostatted, and the temperature of the solutions on which measurements were made was controlled at 25.0±0.02 °C. All of the rate data obeyed the first-order rate law well, and observed first-order rate constants were evaluated by least-squares fitting to linear expressions. Total substrate concentrations were of the order of 10^{-4} M for experiments starting with the alcohol and 10^{-5} M for experiments starting with either olefin.

RESULTS

Extinction Coefficients

The extinction coefficients of the absorption bands of 1-methylcycloheptene and methylenecycloheptane were determined at 2 nm wavelength intervals over the range λ = 196–210 nm. The results are summarized in Table I and are displayed in Figure 1.

Equilibrium Constants

Exocyclic olefins are generally considerably less stable than their endocyclic isomers, and the ratio at equilibrium for the cycloheptyl system has in fact been deter-

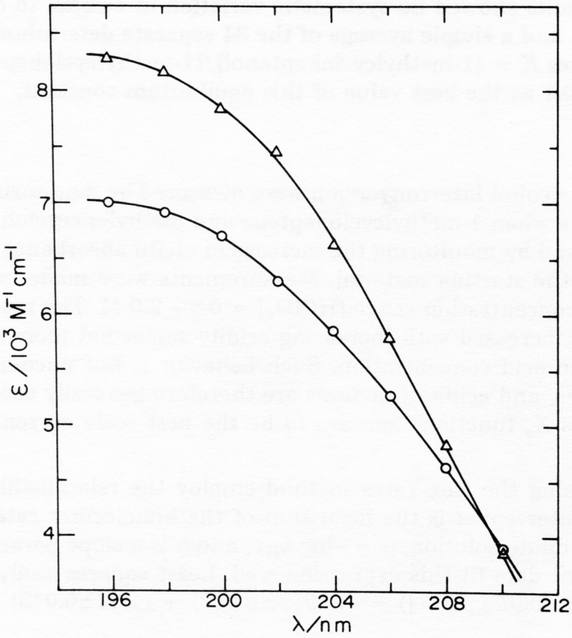


Figure 1. Extinction coefficients for 1-methylcycloheptene (o) and methylenecycloheptane (Δ) in aqueous solution at 25 °C.

TABLE I

Extinction Coefficients for 1-Methylcycloheptene (ENDO) and Methylenecycloheptane (EXO) in Aqueous Solution at 25 °C

λ/nm	$\varepsilon/10^3\ M^{-1}\ cm^{-1}$	
	ENDO	EXO
196	6.99±0.13	8.27±0.08
198	6.91±0.14	8.15±0.08
200	6.71±0.11	7.83±0.07
202	6.30±0.12	7.46±0.14
204	5.86±0.10	6.62±0.07
206	5.27±0.10	5.78±0.07
208	4.62±0.09	4.82±0.07
210	3.89±0.09	3.87±0.06

mined as [1-methylcycloheptene]/[methylenecycloheptane] = 74.[4] There will therefore be little of the exocyclic olefin present at equilibrium in the presently studied olefin hydration reaction, and the equilibrated reaction mixture will consequently consist chiefly of endocyclic olefin and alcohol.

The ratio of alcohol to endocyclic olefin concentrations at equilibrium in aqueous perchloric acid solutions was determined here at 6 different acid concentrations over the range [$HClO_4$] = 0.9–2.0 M; 3–4 replicate measurements were made at each concentration. The results showed no systematic variation of alcohol to olefin ratio with acid concentration, and a simple average of the 34 separate determinations was therefore taken; this gives K = [1-methylcycloheptanol]/[1-methylcycloheptene] = [ROH]/ /[ENDO] = 47.1 ± 0.1 as the best value of this equilibrium constant.

Kinetics

Rates of olefin-alcohol interconversion were measured by monitoring the decreases in olefin absorbance when 1-methylcycloheptene and methylenecycloheptane were the starting materials and by monitoring the increase in olefin absorbance when 1-methylcycloheptanol was the starting material. Measurements were made in perchloric acid solutions over the concentration range $[HClO_4] = 0.3 - 2.0$ M. The reactions were acid catalyzed but rates increased with increasing acidity somewhat more strongly than in direct proportion to acid concentration. Such behavior is not uncommon in concentrated acid solutions, and acidity functions are therefore generally used to analyse the data; the Cox-Yates X_o function[5] appears to be the best scale currently available for this purpose.[6]

Correlations using the Cox-Yates method employ the relationship shown in Eq. (2), in which the intercept a is the logarithm of the bimolecular catalytic coefficient for the reaction in dilute solution, $a = -\log k_{H^+}$, and b is a slope parameter. As Figure 2 shows, the present data fit this expression well. Least squares analysis gave the following relationship: $\log(k_{obs}/[H^+]) = -(2.979 \pm 0.013) + (1.82 \pm 0.013)\, X_o$ for measurements made using the endocyclic olefin, 1-methylcycloheptene, as starting material, $\log(k_{H^+}[H^+]) = -(2.452 \pm 0.010) + (1.59 \pm 0.04)\, X_o$ for those using the exocyclic olefin, methylenecycloheptane, and $\log(k_{obs}/[H^+] = (2.995 \pm 0.020) + (1.80 \pm 0.05)\, X_0$ for those using the alcohol, 1-methylcycloheptanol.

$$\log(k_{obs}/[H^+]) = a + b\, X_o \tag{2}$$

The first and third of these relationships, those for the endocyclic olefin and the alcohol, differ by less than their combined experimental uncertainties. This is the expected behavior for two substances evolving toward a common equilibrium mixture, for in this circumstances specific rates of approach to equilibrium are the same sum of forward plus reverse rate constants for reactions initiated with either of the equilibrating substances. The second of the present relationships, on the other hand, is different from the other two, again as expected for a substance not present to any significant extent in the equilibrium mixture of the other two materials. The kinetic behavior of all three substances combined thus reinforces the conclusion reached above that equilibrium in the present system involves chiefly only alcohol and the endocylic olefin. It follows then that hydration of the exocyclic olefin is an essentially irreversible process.

This reasoning allows the kinetic data for endocyclic olefin and alcohol to be combined into a single relationship, $\log(k_{obs}/[H^+]) = -(2.982 \pm 0.013) + (1.80 \pm 0.03)\, X_o$. The intercept in this expression corresponds to the hydronium catalytic coefficient $k_{H^+} = (1.04 \pm 0.03) \mathrm{x} 10^{-3}\ M^{-1}\ s^{-1}$, which of course is equal to the sum of catalytic coefficients for the forward (hydration) reaction $(k_{H^+})_f$, and the reverse (dehydration) reaction $(k_{H^+})_r$, as depicted schematically in Eq. (3). Since the equilibrium constant $K = 47$,

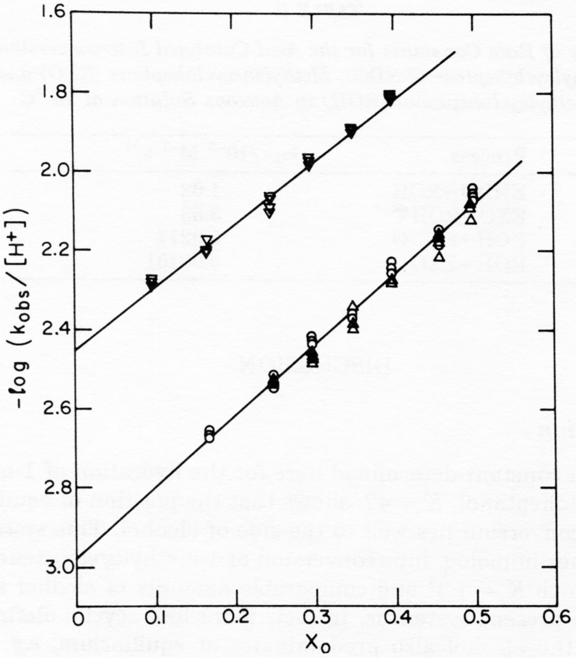


Figure 2. Acidity function correlations for olefin-alcohol interconversion in aqueous perchloric acid solution at 25 °C starting with 1-methylcycloheptene (o), methylenecycloheptane (∇), and 1-methylcycloheptanol (Δ).

$$\mathrm{ENDO} + H_2O + H^+ \underset{(k_{H^+})_r}{\overset{(k_{H^+})_f}{\rightleftharpoons}} \mathrm{ROH} + H^+ \qquad (3)$$

determined here for this reaction is equal to the ratio of the forward to reverse rate constants $K = (k_{H^+})_f/(k_{H^+})_r$, the rate and equilibrium results may be combined to obtain individual values of forward and reverse rate constants. This produces the catalytic coefficients $(k_{H^+})_f = (1.02 \pm 0.03) \times 10^{-3}$ M^{-1} s^{-1} and $(k_{H^+})_r = (2.17 \pm 0.07) \times 10^{-5}$ M^{-1} s^{-1}.

The intercept of the X_o correlation for hydration of the exocyclic olefin gives $k_{H^+} = (3.53 \pm 0.08) \times 10^{-3}$ M^{-1} s^{-1} as the hydronium-ion catalytic coefficient for this reaction. Although this process is essentially irreversible, a rate constant for the reverse reaction may nevertheless be calculated from the hydration rate constant plus an estimate of the equilibrium constant for the process made by combining the equilibrium constant for endocyclic olefin-alcohol interconversion determined here, $K = 47$, with the literature value of the endocyclic-exocyclic olefin ratio, 74.[4] The result, $K =$ $= 3500$, then gives $k_{H^+} = (1.01 \pm 0.03) \times 10^{-6}$ M^{-1} s^{-1} for dehydration of the alcohol to endocyclic olefin.

The rate constants for each of the olefin-alcohol interconversions determined in this way are summarized in Table 2.

TABLE II

Summary of Rate Constants for the Acid-Catalyzed Interconversion of 1-Methylcycloheptene (ENDO), Methylenecycloheptane (EXO) and 1-Methylcycloheptanol (ROH) in Aqueous Solution at 25 °C

Process	$k_{H^+}/10^{-3}\ M^{-1}\ s^{-1}$
ENDO→ROH	1.02
EXO→ROH	3.53
ROH→ENDO	0.0217
ROH→EXO	0.00101

DISCUSSION

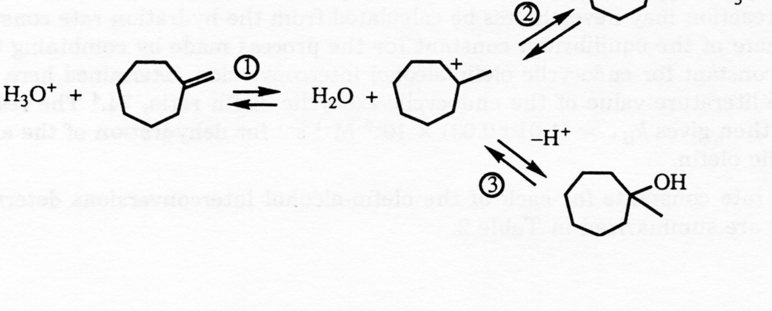
Equilibrium Position

The equilibrium constant determined here for the hydration of 1-methylcycloheptene to 1-methylcycloheptanol, $K = 47$, shows that the position of equilibrium for this olefin-alcohol interconversion lies well to the side of alcohol. This system is therefore unlike the next higher homolog, interconversion of 1-methylcyclooctene and 1-methylcyclooctanol, for which $K = 1.3$[2] and comparable amounts of alcohol and olefin exist at equilibrium. The present system is, in fact, more like acyclic olefin-alcohol interconversions where the alcohol also predominates at equilibrium, *e.g.* $K = 8000$ for isobutene/*t*-butyl alcohol,[7] or $K = 200$ for 2-methyl-2-butene/2-methyl-2-butanol.[8] The present system also resembles its cyclopentyl homolog, inasmuch as $K = 60$ for 1-methylcyclopentene/1-methylcyclopentanol.[9]

The position of equilibrium giving comparable amounts of olefin and alcohol in the 1-methylcyclooctyl system thus appears to be unusual. It is interesting that this unusual behavior extends to cyclooctene itself, where $K = 1.8$ for hydration of this olefin to cycloocatnol;[10] that suggests that the phenomenon is due to some property, probably conformational, of the eight-membered ring.

Energies

The acid-catalyzed hydration of olefins and dehydration of alcohols is commonly believed to occur through a carbocationic intermediate; use of such a mechanism in the present case then leads to the reaction scheme shown in Eq. (4).



(4)

The relative free energies of the various substances shown in this scheme may be evaluated in the following way. The equilibrium constant, $K = 47$, determined here puts the endocyclic olefin 2.3 kcal mol^{-1} above the alcohol, and the endocyclic-exocyclic olefin ratio reported for this system, [ENDO]/[EXO] = 74,[4] puts the exocyclic olefin 2.5 kcal mol^{-1} above the endocyclic one. These differences are shown in the diagram of Figure 3 on a scale which sets the free energy of the alcohol at zero.

The energy levels of the transition states in this reaction scheme may be deduced from the rate constants determined here, plus the fact that the essentially non-reversible conversion of the exocyclic olefin to a mixture of alcohol and endocyclic olefin occurred with good first-order kinetics for the entire course of reaction investigated (90% completion). This first-order behavior requires the alcohol plus olefin products of the reaction to be formed directly in equilibrium proportions. If this were not so, deviations from first-order behavior would have been observed as the exocyclic olefin first gave a nonequilibrium mixture of alcohol plus endocyclic olefin and this mixture then equilibrated; such biphasic kinetics were in fact observed for the corresponding reaction in the 1-methylcyclooctyl system.[2] This requirement means that the difference in free energy between the two transition states leading from the carbocationic intermediate to alcohol and to endocyclic olefin, labelled 3 and 2 in Eq. (4), must be the same as the difference in free energy between the alcohol and this olefin, $\Delta G = 2.3$ kcal mol^{-1}, and that puts the transition state leading to olefin, 2, above that leading

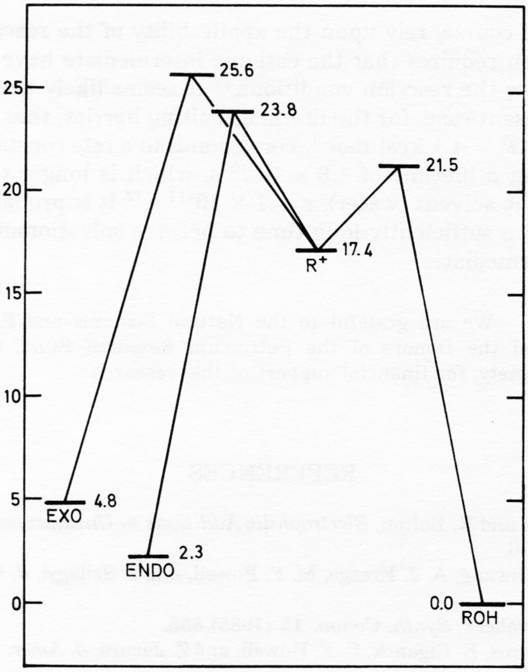


Figure 3. Free energy diagram for the interconversion of methylenecycloheptane (EXO), 1-methylcycloheptene (ENDO), and 1-methylcycloheptanol (ROH) *via* the 1-methylcycloheptyl cation (R^+) in 1.00 M aqueous perchloric acid solution at 25°.

to alcohol, 3. The rate-determining step for interconversion of alcohol and endocyclic olefin must then be reaction of the cationic intermediate to give olefin, and the height of the transition state for this step may therefore be evaluated directly from the rate constant for this reaction, $k_{H^+} = 2.17 \times 10^{-5}$ $M^{-1}s^{-1}$. This argument also fixes the other transition state in this process, that for formation of the cationic intermediate from alcohol, 3, at 2.3 kcal mol^{-1} below the rate-determining one.

The other overall reaction in this system, formation of the exocyclic olefin from alcohol, is slower then formation of the endocyclic olefin. Its rate-determining step must then also be conversion of the cationic intermediate to olefin, for if it were not, its rate-determining transition state would have to be formation of the intermediate from alcohol, and that would make this process faster than formation of the endocyclic olefin. The height of the transition state for formation of exocyclic olefin from the cationic intermediate, 1, may therefore also be evaluated directly from the rate constant for conversion of alcohol to this olefin, $k_{H^+} = 1.01 \pm 10^{-6}$ M^{-1} s^{-1}. The transition state energy levels produced by these arguments are shown in Figure 3.

No direct information is available concerning the free energy level of the cationic intermediate. However, the free energy of activation for reaction of a tertiary carbocation, such as the present one, with water has been estimated to be $\Delta G^{\ddagger} = 4.1$ kcal mol^{-1}, [2] and use of that value fixes the free energy of the present cation relative to its hydration transition state and thus also relative to the other species in the reaction scheme.

These results, of course, rely upon the applicability of the reaction mechanism of Eq. (4), which in turn requires that the cationic intermediate have a sufficiently long lifetime to exist under the reaction conditions.[11] It seems likely that this requirement is fulfilled in the present case, for the lifetime-limiting barrier, that for reaction of the cation with water, $\Delta G^{\ddagger} = 4.1$ kcal mol^{-1}, corresponds to a rate constant of 6.2×10^{9} s^{-1}. This gives this cation a lifetime of 1.6×10^{-10} s, which is longer than the rotational correlation time of the solvent (water), $\tau = 1 \times 10^{-11}$ s.[12] It is probable, therefore, that this cation exists for a sufficiently long time to become solvationally equilibrated and is thus a viable intermediate.

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SAŽETAK

Kiselo katalizirana hidratacija 1-metilcikloheptena i metilencikloheptana. Konstrukcija kompletnog profila slobodne energije za interkonverziju olefina u alkohol u 1-metilcikloheptilnom sustavu

Y. Chiang, A. J. Kresge, P. A. Obraztsov i J. B. Tobin

Određene su brzine hidratacije naslovnih spojeva u koncentriranoj vodenoj perklornoj kiselini pri 25 °C. Iz kinetičkih podataka izračunati su i katalitički koeficijenti za reakciju hidratacije i dehidratacije za obje reakcije. Kombinacijom tih rezultata s literaturnim podacima za srodne sustave konstruiran je profil slobodne energije za razmatrane reakcije.