

Acid-catalyzed Hydrolyses of Bridged Bi- and Tricyclic Compounds. XX. The Location of the Transition State in the Hydration of Norbornenes and Nortricyclanes

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The isotopic Brönsted α_i values have been measured for the $A-S_E2$ hydration of 2-methyl-*endo*-5-hydroxy-2-norbornene (1, 0.73 ± 0.03 at 298.2 K), 5-methylene-2-methyl-*endo*-2-hydroxynorbornane (2, 0.91 ± 0.03 at 318.2 K) and 1,6-dimethyl-3-hydroxynortricyclane (3, 0.65 ± 0.02 at 328.2 K). They are similar to those measured earlier for less reactive norbornenes and nortricyclanes with the product-like transition states and do not clearly indicate earlier transition states for the faster proton transfer reactions. The large experimental scattering of the α_i values and the rather narrow rate scale, however, make it difficult to draw conclusions. A comparison of the α_i values with the ordinary Brönsted α values measured earlier in carboxylic acid buffers for the $A-S_E2$ hydration of several unsaturated compounds indicates that the Hammond postulate is probably valid: α or $\alpha_i = -(0.020 \pm 0.006) \log(k_{H^+}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) + (0.67 \pm 0.02)$, if $0.5 \leq \alpha$ or $\alpha_i \leq 1$.

The generally accepted mechanism for the acid-catalyzed hydration of the carbon–carbon double bond and the three-membered carbon ring is the rate-determining proton transfer from a catalytic acid to a substrate followed by the fast water attack on the carbocation ($A-S_E2$ mechanism).^{1–3} The reaction is subject to general acid catalysis, whose observation is usually easy in dilute buffer solutions if the reaction rate is quite great (*e.g.* vinyl ethers).^{1–2} The Brönsted relation (1) indicates the correlation between the second-order rate constant

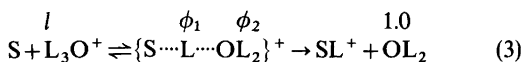
$$k_{HA}/p = G(K_{HA}q/p)^{\alpha} \quad (1)$$

k_{HA} and the dissociation constant of the catalytic acid K_{HA} in different buffer solutions. The constants

q and p are statistical factors and α and G are parameters, which depend on the nature of the reaction and on the conditions but not on the acid used. The exponent of the Brönsted relation, the so-called Brönsted α , is believed to characterize the degree of proton transfer in the transition state ($0 \leq \alpha \leq 1$).^{1–2}

If the reaction is rather slow (*e.g.* simple alkenes and cyclopropanes), the detection of general acid catalysis in buffer solutions is difficult.^{1,2,4,5} In this case measurements can be made in acidic light water–heavy water mixtures, where the kinetic solvent deuterium isotope effect obeys eqn. (2),^{1,2,6,7} when the proton transfer occurs from the lyonium ion L_3O^+ ($L=H$ or D) to a substrate S [eqn. (3)].

$$\frac{k_x}{k_H} = \frac{(1-x+x\phi_1)(1-x+x\phi_2)^2}{(1-x+x\bar{l})^3} F(x) \quad (2)$$



The parameters l , ϕ_1 and ϕ_2 are isotopic fractionation factors for the lyonium ion, the transferring hydrogen and the remaining hydrogens in the transition state, and $F(x)$ is a correction factor (mostly assumed to be unity), which takes into account the transfer energies of the substrate, the lyonium ion and the transition state from H_2O to a H_2O-D_2O mixture of deuterium atom fraction x . The fractionation factor ϕ_2 depends on l according to the exponential eqn. (4),⁶ where α_i (isotopic Brönsted α) characterizes the degree of proton

$$\phi_2 = l^{1-\alpha_i} \quad (4)$$

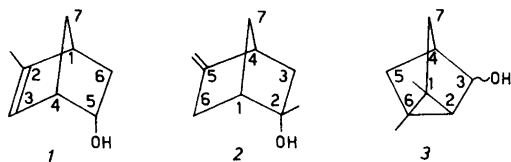
transfer in the transition state ($0 \leq \alpha_i \leq 1$).

In many reactions both the ordinary Brønsted α and the isotopic α_i have been determined and no systematic deviations have been observed between them although single values often differ by 0.1 or even more,^{1,2} possibly at least partly due to an experimental error. In reality α depends to some extent on the character of the catalytic acid (charged or uncharged)⁸ and α_i is very sensitive to experimental scattering.² However, anomalous values have been found for α and explanations have been given to them.^{2,9,10}

Isotopic technique has been used to detect a general acid catalysis in the hydration of substituted norbornenes and nortricyclanes,¹¹⁻¹⁴ since the observations in buffer solutions were uncertain.⁵ The following α_i values were measured: from 0.77 to 0.94 (av. 0.85) for 5-hydroxy-2-norbornenes,¹¹ from (0.49?) 0.59 to 0.79 (av. 0.72) for 5-hydroxy-methyl-2-norbornenes,¹⁴ and from 0.67 to 0.96 (av. 0.83) for 3-hydroxynortricyclanes¹² (possible methyl substituents have not been mentioned, cf. Table 2). The values (0.5?, $0.6 \leq \alpha_i \leq 1$) indicate that the transition state is mostly product-like.

The displacement of a 2- or 3-hydrogen atom by a methyl group increases the hydration rate of 5-hydroxy-2-norbornenes by a factor of 10^4 to 10^5 .^{15,16} Surprisingly, the activation entropies also change in many cases from slightly negative to slightly positive values but the solvent deuterium isotope effects remain normal (k_D/k_H 0.5 to 0.6). In order to see if the hydration mechanism possibly changes from the slow proton transfer (*A-S_E2* mechanism) to a fast pre-equilibrium protonation of the substrate (*A-1* or *A-2* mechanism) or the location of the transition state of the *A-S_E2* mechanism moves toward the initial state (according to the Hammond postulate),¹⁷ the α_i values are determined in this work for 2-methyl-*endo*-5-hydroxy-2-norbornene (1) and 5-methylene-2-methyl-*endo*-2-hydroxynorbornane (2) in H₂O-D₂O mixtures.

The displacement of 1- or 1- and 6-hydrogen(s) by methyl increases the reaction rate by a small factor of 5 to 6 (1-methyl) and 17 (1,6-dimethyl) in the hydration of 3-hydroxynortricyclane.^{12,18} The mean value of α_i does not change markedly due to the 1-methyl substitution [0.85 (1-H)→0.82 (1-Me)]. The effect of the 1,6-dimethyl substitution is studied in this work by measuring α_i for the hydration of 1,6-dimethyl-3-hydroxynortricyclane(3).



EXPERIMENTAL

The syntheses of the substrates (1-3) have been described.^{15,18}

The kinetic measurements were made in 0.1 mol dm⁻³ LCIO₄ (L₂O) solutions by following the disappearance of the substrate by taking samples after proper intervals during 2.5 half-lives, neutralizing them with 1.3 mol dm⁻³ ammonia and analyzing by GLC with cyclohexanol or norcamphor as inert internal standard. First-order kinetics was always observed. The measurements were repeated at least once, often twice or more times. In the cases of 1 and 2 a little isomerization (*e.g.* 2-methyl-5-hydroxy-2-norbornene to 5-methylene-2-hydroxynorbornane) occurred in the gas chromatograph, which decreased the accuracy of the measurements. Isomerization due to the acid-catalyzed dehydration of the alcoholic substrates [R¹OH + H⁺ ⇌ (R¹)⁺ + H₂O ⇌ (R²)⁺ + H₂O ⇌ R²OH + H⁺] was not observed (*cf.* Ref. 15).

RESULTS AND DISCUSSION

The observed solvent deuterium isotope effects for the hydration of the substrates in 0.1 mol dm⁻³ perchloric acid of varying deuterium atom fraction (*x*) are listed in Table 1. The isotope effects k_D/k_H ($k_x = k_H$ when $x=0$ and $k_x = k_D$ when $x=1$) for the bicyclic substrates 1 and 2 are fairly similar to those measured earlier for the same compounds: 0.543 (this work at 298.2 K) and 0.507 (at 293.2 K)¹⁵ for 1 and 0.618 (this work at 318.2 K) and 0.587 (at 303.2 K)¹⁵ for 2. They, as well as the value for 3 (0.513 at 328.2 K), are typical of the rate-determining proton transfer from the lyonium ion to the carbon-carbon double bond or the three-membered carbon ring.¹¹⁻¹⁴

Eqn. (2) fitted the experimental data fairly well. The values 0.69 at 298.2 K and 0.71 at 318.2 and 328.2 K were used for the fractionation factor of the lyonium ion (*l*).¹⁹ The fractionation factor of the hydroxylic hydrogen of the substrates was assumed to remain unchanged in the initial and transition states. *F*(*x*) was approximated to unity. The computed fractionation factors ϕ_1 and ϕ_2 (see eqn. (3)) and the isotopic α_i values [from eqn. (4)]

Table 1. Observed and calculated [eqn. (2)] solvent deuterium isotope effects in the hydration of 2-methyl-endo-5-hydroxy-2-norbornene (1), 5-methylene-2-methyl-endo-2-hydroxynorbornane (2) and 1,6-dimethyl-3-hydroxynortricyclane (3) in 0.1 mol dm⁻³ LClO₄ (L=H or D) of deuterium atom fraction *x*. Isotopic fractionation factors ϕ_1 and ϕ_2 [see eqn. (3)] and isotopic α_i values have been calculated from eqns. (2) and (4).

| Substrate (Temp.) | <i>x</i> | <i>k_x/k_H</i> (obs.) | <i>k_x/k_H</i> (calc.) | ϕ_1, ϕ_2 and α_i |
|-------------------|----------------|---|--|---------------------------------|
| 1 (298.2 K) | 0 | 1.000 | 1.000 | |
| | 0.2 | 0.958 | 0.986 | |
| | 0.4 | 0.932 | 0.951 | |
| | 0.5 | 0.923 | 0.922 | $\phi_1 = 0.225(6)$ |
| | 0.6 | 0.869 | 0.883 | $\phi_2 = 0.906(8)$ |
| | 0.7 | 0.849 | 0.832 | $\alpha_i = 0.73(3)$ |
| | 0.8 | 0.788 | 0.764 | |
| | 0.9 | 0.686 | 0.676 | |
| | 1.0 | 0.543 | 0.563 | |
| | 2 (318.2 K) | 0 | 1.000 | 1.000 |
| 0.2 | | 0.958 | 1.002 | |
| 0.4 | | 0.964 | 0.983 | |
| 0.5 | | 0.962 | 0.962 | $\phi_1 = 0.240(6)$ |
| 0.6 | | 0.950 | 0.930 | $\phi_2 = 0.969(8)$ |
| 0.7 | | 0.883 | 0.885 | $\alpha_i = 0.91(3)$ |
| 0.8 | | 0.844 | 0.823 | |
| 0.9 | | 0.737 | 0.739 | |
| 1.0 | | 0.618 | 0.629 | |
| 3 (328.2 K) | | 0 | 1.000 | 1.000 |
| | 0.2 | 0.964 | 0.968 | |
| | 0.4 | 0.923 | 0.917 | $\phi_1 = 0.235(4)$ |
| | 0.6 | 0.819 | 0.835 | $\phi_2 = 0.888(5)$ |
| | 0.7 | 0.787 | 0.779 | $\alpha_i = 0.65(2)$ |
| | 0.8 | 0.717 | 0.710 | |
| | 0.9 | 0.626 | 0.624 | |
| | 1.0 | 0.513 | 0.518 | |

are also given in Table 1 together with the k_x/k_H values calculated from them. The values of ϕ_1 (0.23 to 0.24), ϕ_2 (0.89 to 0.97) and α_i (0.65 to 0.91) are similar to those measured earlier for the hydration of norbornenes and nortricyclanes.^{11,12,14}

The comparison of the α_i values for the substrates 1 and 2 (0.73 and 0.91) with the mean values for much less reactive compounds, 5-hydroxy-2-norbornenes (0.85) and 5-hydroxymethyl-2-norbornenes (0.72), and the comparison of the α_i value for 3 (0.65) with the mean value of the slightly less reactive 3-hydroxynortricyclanes (0.83) do not indicate clearly the movement of the transition state toward the initial state as the Hammond postulate predicts.¹⁷ This may, however, be due to the large experimental error of the α_i values (it is more probable that the error limits are 0.1 or even more, rather than 0.01–0.05 as calculated by the com-

puter) and to the narrow rate scale. The values of ϕ_1 (0.2) and α_i (<1), however, eliminate other possible reaction mechanisms than *A-S_E2* (see above).

It is of interest to compare α_i values presented by us for norbornenes and nortricyclanes, including a similar value measured for the hydration of isobutene (ca. 0.9 by Gold and Kessick or 0.84 as recalculated by Williams and Kreevoy),^{1,20} with the Brønsted α values measured for the rate-determining protonation (*A-S_E2* mechanism) of more reactive unsaturated compounds (vinyl ethers, a vinyl thioether, a bridgehead olefin, azulenes, halomercuro olefins and keten acetals) in carboxylic acid buffers.^{21–28} This comparison is made in Table 2 and Fig. 1 and it more than doubles the rate scale (from 4.8 to 10.6 powers of ten). The interpretation of the data is, however, not easy.

Table 2. Values of ordinary Brönsted α in carboxylic acid buffers and of isotopic α_i in 0.1 mol dm⁻³ LClO₄ (L=H or D), and rate constants (k_{H^+}) in 1.0 mol dm⁻³ aqueous perchloric acid at 298.2 K (unless otherwise marked) for rate-determining proton transfer reactions.

| Substrate | No. | α | α_i | $k_{H^+}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | Ref. |
|--|-----|-------------------|-----------------------|---|---------------|
| 2-Methyl- <i>endo</i> -5-hydroxy-2-norbornene | 1 | | 0.73(3) | 2.6×10^{-2} | 15, this work |
| 5-Methylene-2-methyl- <i>endo</i> -2-hydroxynorbornane | 2 | | 0.91(3) ^a | 4.1×10^{-3} | 15, this work |
| 1,6-Dimethyl-3-hydroxynortri-cyclane | 3 | | 0.65(2) ^b | 4.7×10^{-5} | 18, this work |
| <i>exo</i> -5-Hydroxy-2-norbornene | 4 | | 0.77(5) ^c | 4.3×10^{-7} | 11, 30 |
| <i>endo</i> -5-Hydroxy-2-norbornene | 5 | | 0.94(1) ^c | 9.9×10^{-7} | 11, 30 |
| <i>exo</i> -5-Hydroxymethyl-2-norbornene | 6 | | 0.59(2) ^c | 8.9×10^{-6} | 14 |
| <i>endo</i> -5-Hydroxymethyl-2-norbornene | 7 | | 0.79(2) ^c | 1.23×10^{-5} | 14 |
| 5-Methyl- <i>exo</i> -5-hydroxymethyl-2-norbornene | 8 | | 0.79(1) ^c | 8.5×10^{-6} | 14 |
| 5-Methyl- <i>endo</i> -5-hydroxymethyl-2-norbornene | 9 | | 0.49(1)? ^c | 1.07×10^{-5} | 14 |
| 3-Hydroxynortri-cyclane | 10 | | 0.85(2) ^c | 2.8×10^{-6} | 12, 30 |
| 1-Methyl- <i>cis</i> -3-hydroxynortri-cyclane | 11 | | 0.96(3) ^c | 1.27×10^{-5} | 12 |
| 1-Methyl- <i>trans</i> -3-hydroxynortri-cyclane | 12 | | 0.67(3) ^c | 1.67×10^{-5} | 12 |
| Isobutene | 13 | | 0.84 ^d | 6.4×10^{-4e} | 1, 20 |
| Phenyl vinyl ether | 14 | 0.84(5) | | 7.2×10^{-3e} | 21 |
| Ethyl vinyl ether | 15 | 0.70(3) | | 3.9 ^e | 21 |
| Phenyl isopropenyl ether | 16 | 0.61(3) | | 13.2 ^e | 21 |
| Methyl cyclohexenyl ether | 17 | 0.66(3) | | 93 ^e | 21 |
| Ethyl cyclohexenyl ether | 18 | 0.58(3) | | 176 ^e | 21 |
| Ethyl cyclopentenyl ether | 19 | 0.63(3) | | 1.00×10^{3e} | 21 |
| Ethyl isopropenyl ether | 20 | 0.64(4) | | 1.27×10^{3e} | 21 |
| Methyl- α -cyclopropyl vinyl ether | 21 | 0.67(3) | | 1.65×10^{4e} | 22 |
| β -Methoxy- <i>trans</i> - β -methyl styrene | 22 | 0.70(3) | | 3.7 ^e | 23 |
| 3-Methoxyindene | 23 | 0.64(5) | | 127 ^e | 24 |
| Bicyclo[3.3.1]non-1-ene | 24 | 0.67(5) | | 69 ^e | 25 |
| Methyl vinyl sulfide | 25 | 0.73 ^f | | $4.6 \times 10^{-2e,g}$ | 26, 27 |
| Azulene | 26 | 0.61(7) | | 0.40 ^{e,g} | 28 |
| Quiaiazulene | 27 | 0.54(3) | | 13.4 ^{e,g} | 28 |
| Allyl mercuric iodide | 28 | 0.67(2) | | 3.1×10^{-2e} | 1, 9 |
| Isobutenyl mercuric bromide | 29 | 0.69(4) | | 5.3×10^{-2e} | 1, 9 |
| 2,2-Dichloromethylene-1,3-dioxolan | 30 | 0.49 | | 230 ^e | 1, 9 |
| Cyanoketen dimethyl acetal | 31 | 0.62 | | 53 ^e | 1, 9 |

^a 318.2 K. ^b 328.2 K. ^c 348.2 K. ^d In 0.442 mol dm⁻³ LClO₄. ^e An H_0 correction has been made, i.e. the second-order rate constants in dilute acid ($[H^+] \leq 0.1 \text{ mol dm}^{-3}$) have been multiplied by 2.2. ^f 323.2 K. ^g In aq. HCl.

Kresge²¹ concluded from the values for the vinyl ethers 14–20 (numbering in Table 2) that the α values depend, although slightly, on the rates of the reactions: the slope for α vs. $\log [k_{HA}/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})]$ at $\text{p}K_{HA}=4$ is -0.036 ± 0.010 . However, if an exceptional point for less reactive phenyl vinyl ether (14) is omitted, the slope is reduced to

-0.013 ± 0.016 . Very recently Johnson interpreted the same data together with some others (14 to 27 excluding 24) so that the slope is really zero and he used this result as evidence against the reactivity–selectivity principle.²⁹

If we use the α values for the reactive substrates 14 to 31 in Table 2, we get eqn. (5) (the broken line in

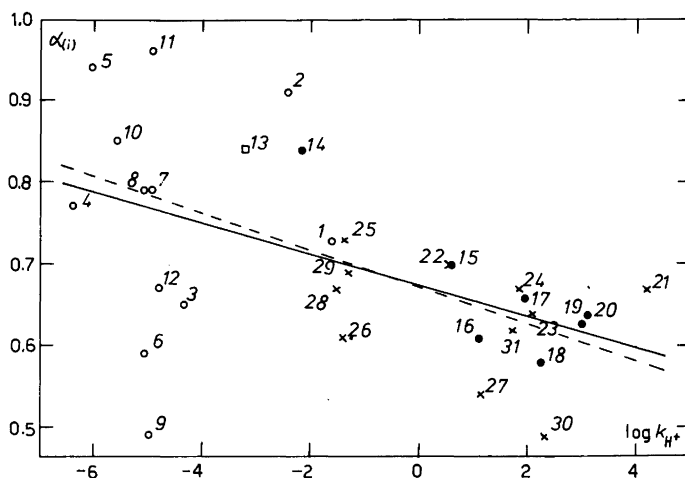


Fig. 1. Values of Brønsted α in carboxylic acid buffers and of isotopic α_i in 0.1 mol dm⁻³ LClO₄ vs. log ($k_{H^+}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) (k_{H^+} in 1 mol dm⁻³ mineral acid at 298.2 K) for rate-determining proton transfer reactions. (The numbering, see Table 2. Symbols: ○, norbornenes and nortricyclanes; □, isobutene; ●, original values for vinyl ethers by Kresge; ×, other values for vinyl ethers, a vinyl thioether, a bridgehead olefin, azulenes, halomercuro olefins and keten acetals. —, compounds 1 to 31; ---, compounds 14 to 31.)

$$\alpha = -(0.023 \pm 0.009) \log (k_{H^+}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) + (0.67 \pm 0.02) \quad (5)$$

Fig. 1), and if we use the α and α_i values for all the substrates in Table 2, we get equation (6) (the full line in Fig. 1). The rate constant k_{H^+} in eqns. (5) and (6) refers to the value in 1 mol dm⁻³ aqueous

$$\alpha \text{ or } \alpha_i = -(0.020 \pm 0.006) \log (k_{H^+}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) + (0.67 \pm 0.02) \quad (6)$$

mineral acid at 298.2 K. The equations are very similar and indicate, in our opinion, a slight but probably significant dependence of α or α_i on the rate of the slow proton transfer when $0.5 \leq \alpha$ or $\alpha_i \leq 1$. (Perhaps a slightly nonlinear relationship between the α or α_i values and the log k_{H^+} values would be more truthful but it has not been applied owing to the large experimental scattering of the data.)

The calculated difference between the α_i value of the most reactive norbornene [1, α_i (calc.)=0.70 (obs. 0.73)] and the least reactive norbornene [4, α_i (calc.)=0.80 (obs. 0.77)] is hardly larger than the experimental error, but the difference between the mean values of the less reactive compounds 1 to 13 ($\bar{\alpha}_i = 0.77 \pm 0.04$; 0.75 ± 0.05 for the bicyclic compounds and 0.78 ± 0.07 for the tricyclic compounds)

and the more reactive compounds 14 to 31 ($\bar{\alpha} = 0.65 \pm 0.02$) is evident, if we take into account the great number of the data. This result agrees with the Hammond postulate.¹⁷

According to Bell² and Kresge²¹ there might be a difference (0.1 or even more) between the α values measured in carboxylic acid buffers and the α_i values determined in strong mineral acids. The two equations [(5) and (6)], however, imply that the difference is not significant, which is in agreement with the opinion of Williams and Kreevoy.¹

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