Acid-Catalyzed Hydrolysis of Bridged Bi- and Tricyclic Compounds. XXVIII. Evaluation of α-Values for the Protonation of Norbornenes and Nortricyclanes from Solvent Isotope and Acidity Effects and Their Use to Compare the Characters of the Intermediate Carbocations

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α-Values evaluated from solvent deuterium isotope effects and excess acidity correlations have been observed to be very similar in the acid-catalyzed hydrations of both norbornenes (0.77 ± 0.11 and 0.77 ± 0.05, respectively) and nortricyclanes (0.78 ± 0.15 and 0.80 ± 0.03, respectively). By using these, together with reaction constants, the α-values were also estimated for the solvolyses of 2-norbornyl tosylates. They are reasonable (0.88 ± 0.10) if the first-formed carbocations are of similar character in the solvolyses and hydrations, but unreasonable if their characters are different. The estimation method was also applied to some other substrates and their reactions.

The position of the transition state (TS) in reaction (1) is an

$$R \rightleftharpoons [TS] \rightarrow P \qquad (1)$$

important reaction-mechanistic concept, which is often described by symbol α: $0 < \alpha < 0.5$ if TS is reactant-like; $\alpha \approx 0.5$ if TS is symmetric or in the halfway state; and $0.5 < \alpha < 1.0$ if TS is product-like.[1] Originally α was an experimental parameter of the Brønsted catalysis law (2),[2] where k_{HA} is

$$k_{HA} = G(K_{HA})^{\alpha} \qquad (2)$$

an acid-catalyzed rate constant when acid HA (dissociation constant K_{HA}) acts as catalyst, and G is another parameter. According to the principle of Leffler,[3] the parameter α describes the position of the transition state between R and P, because it measures the effect of a substituent of the catalyst acid on the transition state as compared to its effect on the product state. Thus α can be presented by eqn. (3),[1] where δ_R is the effect of substituent R on the activation

$$\alpha = \delta_R \Delta G^{\neq} / \delta_R \Delta G^{\circ} \qquad (3)$$

Gibbs energy ($\Delta G^{\neq}$) and on the standard Gibbs energy of the reaction (ΔG°).

A substitution can also be made in the substrate of the reaction. If the same substituent constants (σ) are used for the comparison of rate constants and equilibrium constants

of the reaction, α can be presented by the aid of reaction constants according to eqn. (4), where ϱ_f is the reaction

$$\alpha = \varrho_f / \varrho_e \qquad (4)$$

constant of the forward reaction, i.e. the slope of log (k_R/k_H) vs. σ_R, and ϱ_e is the reaction constant of the equilibrium between the reactants and products, i.e. the slope of log (K_R/K_H) vs. σ_R.

However, in the cases where the different effects (e.g. inductive and mesomeric) of substituent R develop at different rates, e.g. one lags behind the other, or the distribution of charge is exceptional in the transition state, the α values evaluated from eqns. (3) and (4) may be different from those calculated from the Brønsted catalysis law (2).[1,4] In addition, α depends on the intrinsic energy ($\Delta_i G^{\neq}$) according to the Marcus equation, eqn. (5), which may

$$\alpha = 0.5[1 + (\Delta G^{\circ}/4\Delta_i G^{\neq})] \qquad (5)$$

cause a curvature in the Brønsted plot (log k_{HA} vs. log K_{HA}) and thus a variation of the α-values.[5,6]

The position of the transition state can also be estimated in another way, for instance from quantities which change regularly on going from the reactants to the products. The secondary isotope effect and the activity coefficient of TS are such quantities.[1] These methods of estimation are suit-

able e.g. for acid-catalyzed reactions where the transfer of a hydron occurs from a hydronium ion to a substrate in the rate-limiting stage [eqn. (6)]. Solvent isotope effects can be used for the estimation of the position of TS in this case.

$$l \qquad \varphi_a \quad \varphi_b \qquad 1.0$$
$$H_3O^+ + S \rightleftharpoons [H_2O \cdots H \cdots S]^+ \rightarrow H_2O + H-S^+ \qquad (6)$$
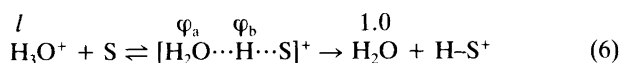
According to the equilibrium theory of isotope effects,[7] the kinetic solvent deuterium isotope effect of reaction (6) in acidic H_2O-D_2O mixtures can be presented by eqn. (7), where l, φ_a and φ_b are isotopic fractionation factors of the exchangeable hydrogens of the hydronium ion and the

$$\frac{k_H}{k_x} = \frac{(1 - x + xl)^3 \, F(x)}{(1 - x + x \, \varphi_a)^2 \, (1 - x + x \, \varphi_b)} \qquad (7)$$

transition state [eqn. (6)], and $F(x)$ is a correction term which takes into account the energies of transfer of the reactants and the transition state from acidic H_2O to an acidic H_2O-D_2O mixture where the deuterium atom fraction is x [$F(x)$ is often approximated to be unity].[8] The secondary isotope effect belongs to the hydrogen atoms which stay in the water molecule that is formed in the dehydronation of the hydronium ion [eqn. (8)], and its regular change can be presented by eqn. (9).[7] (The isotype effect of the hydrogen on transfer does not vary regularly,

$$\left(\frac{k_H}{k_x}\right)_{sec} = \frac{(1 - x + xl)^2}{(1 - x + x \, \varphi_a)^2} \qquad (8)$$

$$\varphi_a = l^{1-\alpha} \qquad (9)$$

but has a maximum value when $\alpha \approx 0.5$).[7] The value of α can be calculated by fitting parameters φ_a and φ_b to the experimental isotope effects in H_2O-D_2O mixtures [eqn. (7)]. However, the α-value becomes more inaccurate as k_H/k_D value approaches unity. Unfortunately the isotope effects close to unity are typical of acid-catalyzed hydrations of many substituted norbornenes and nortricyclanes.[9-12]

In the activity coefficient method, the activity coefficient of TS depends on α according to eqn. (10),[13,14] where α is identical with $m^{\neq}$ in eqn. (11).[15] In the latter equation,

$$y_{TS} = (y_S y_{L_3O^+})^{1-\alpha}(y_{LS^+}y_{L_2O})^\alpha \approx (y_S y_{L_3O^+})^{1-\alpha}(y_{LS^+})^\alpha \qquad (10)$$

$$\log k_\varphi - \log c_{H^+} = m^{\neq}m^*X + \log k_0 \qquad (11)$$

k_φ is an observed rate constant of reaction (6) in an aqueous solution with acid concentration c_{H^+} and excess acidity X. The slope of the linear plot of $\log k_a$ vs. X, where $k_a = k_\varphi/c_{H^+}$, is $m^{\neq}m^*$. Parameter m^* describes the dependence of a ratio of the activity coefficients in the protonation of substrate S upon the corresponding ratio in the protonation of an indicator base [B in eqn. (12)]. Parameter m^* takes a
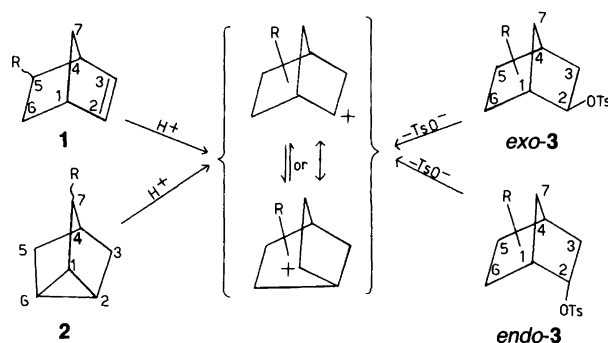
Scheme 1.

constant value of 1.80 ± 0.10 in the formation reactions of carbocations.[16,17]

$$\log (y_S y_{H^+}/y_{SH^+}) = m^* \log (y_B y_{H^+}/y_{BH^+}) = m^*X \qquad (12)$$

The different α-values above, namely, α_B = "Brønsted α" [eqn. (2)]; α_R = "substituent α" [eqns. (3) and (4)]; α_I = "isotopic α" [eqns. (7) and (9)]; and α_A = "excess acidity α" [eqn. (11), $m^{\neq} = \alpha_A$] have been compared earlier and the agreement has generally been good.[1,18] Some exceptions have, however, been found, but they have reasonable explanations.[1,18] A systematic comparison between the values of α_I and α_A have not been made to the author's knowledge, and one may even ask whether they describe the same quantity.

The position of the transition state in the acid-catalyzed hydrations of norbornenes (1) and nortricyclanes (2), which are started by the slow protonation of the carbon double bond or the cyclopropane ring, respectively, producing a 2-norbornyl cation (Scheme 1), has been of interest in our laboratory.[9-12] The hydration rates have earlier been measured in acidic H_2O-D_2O mixtures and the α_I-values have been calculated and published.[9g] In the present paper, the α_A values are calculated from eqn. (11) by using rate constants measured earlier[9-12] in aqueous perchloric acid solutions of varying concentration, and they are compared with the α_I-values. An effort is also made to estimate an α-value for the solvolyses of 2-norbornyl tosylates (3), which also produce the 2-norbornyl cation as an intermediate (Scheme 1).

Results and discussion

The values of α_I and α_A calculated from eqns. (7), (9) and (11) for the protonation of 14 norbornenes are presented in Table 1, together with the rate constants of hydration in an appropriate standard state: 1.00 mol dm^{-3} aqueous $HClO_4$ at 298.2 K. The corresponding values for eight nortricyclanes are listed in Table 2. The slow proton transfer mechanism [$A-S_E2$ or Ad_E2, eqn. (6)] has earlier been confirmed by substituent effects, entropies of activation, solvent deuterium isotope effects and/or general acid

Table 1. Isotopic α_I- and excess acidity α_A-values for the acid-catalyzed hydrations of substituted norbornenes under different conditions, and rate constants under standard conditions (1 mol dm^{-3} HClO$_4$ at 298.2 K).

Substituent	T/K	c(HClO$_4$)/M	α_I	α_A[a]	k_q/s^{-1}	Ref.
2-CH$_3$-endo-5-OH	298.2	0.1	0.73(3)		2.6×10^{-2}	9g
H	298.2	0.8–4		0.79(4)	1.1×10^{-4}	9e
2-CH$_3$-5-oxo	298.2	1–5		0.78(3)	1.2×10^{-5}	9d
endo-5-CH$_2$OH	348.2	0.1	0.79(2)		1.2×10^{-5}	9c
5-CH$_3$-endo-5-CH$_2$OH	348.2	0.1	0.49(1)?		1.1×10^{-5}	9c
exo-5-CH$_2$OH	348.2	0.1	0.59(2)		8.9×10^{-6}	9c
5-CH$_3$-exo-5-CH$_2$OH	348.2	0.1	0.79(1)		8.5×10^{-6}	9c
endo-5-OH	348.2	0.1	0.94(1)		1.1×10^{-6}	9a,b
exo-5-OH	348.2	0.1	0.77(5)		5.7×10^{-7}	9a,b
endo-5-NO$_2$	348.2	2–6		0.68(2)	4.5×10^{-8}	9h
exo-5-NO$_2$	348.2	1–6		0.78(2)	1.2×10^{-8}	9h
endo-5-CN	348.2	1–5		0.80(2)	2.1×10^{-8}	9f
exo-5-CN	348.2	1–5		0.80(2)	2.7×10^{-8}	9f
4-CH$_3$-5-oxo	348.2	2–5		0.73(2)	1.5×10^{-9}	9d

[a] X-values employed are X_0-values from Ref. 16. The correlation coefficients of log k_a vs. X_0 varied between 0.996 and 0.9995.

catalysis. The substrates which are hydrolyzed by other mechanisms, e.g. A-1 or A-2, have been eliminated.[9–12]

The protonation of the carbon double bond takes place from the *exo* side in the case of norbornenes; thus a substituent at C(5) has no marked steric effect.[10] If the substituent at C(5) is strongly electronegative (e.g. CN or NO$_2$), the proton attacks C(3) almost entirely. If the substituent is not strongly electronegative (e.g. CH$_3$, CH$_2$OH or OH) or is strongly electronegative but has a hyperconjugative (frangomeric) effect (e.g. oxo), the protonation occurs at both C(2) and C(3). A methyl substituent at one olefinic carbon causes the proton attack entirely upon another olefinic carbon.[19] The protonation of nortricyclanes substituted at C(7) mostly takes place at the C(2)–C(6) edge of the cyclopropane ring, i.e. opposite to the substituent.[12,20]

The measurements were made at a temperature between 298.2 and 358.2 K but mostly at 348.2 K.[9–12] The α-values cannot be seen to be dependent on the temperature (Tables 1 and 2; the acid concentrations and excess acidities[16] were corrected to the real temperatures).[15] Likewise, they seem to be independent of the rate constants under the standard conditions. Thus the mean values of α are appropriate for comparison when the effect of experimental scatter can be relieved.

The mean values of α_I, 0.73 ± 0.15 (or 0.77 ± 0.11 if a clearly exceptional value of 0.49 is excluded), and of α_A, 0.77 ± 0.05, for the protonation of norbornenes are surprisingly equal, as are also the corresponding values for nortricyclanes: $\alpha_I = 0.78 \pm 0.15$ and $\alpha_A = 0.80 \pm 0.03$ (the error limits are standard deviations). On the basis of them it seems evident that the values of α_I and α_A measure the same quantity, but their independence of the reaction rate measured under standard conditions hints that they are characteristic of the type of substrates and reactions and that the substituents generally have no marked effect on the position of the transition state. The excess acidity val-

ues of α are within the much narrower limits than the isotopic α-values, which is probably due to the sensivity of the latter values to experimental scatter. Therefore the excess acidity method is more suitable for the slow hydration reactions whose solvent deuterium effects are small.

The α_A-values are particularly similar (0.79 ± 0.01) for such norbornenes whose protonation only involves participation of the 1,6- and/or 4,5-bond(s). The α_A-value is, however, clearly smaller in two cases, namely, the hydrations of 4-methyl-5-oxo- (0.73) and endo-5-nitro-2-norbornenes (0.68), where a frangomeric effect and neighbouring-group participation, respectively, are probable.[9d,h,10,21] These may operate at a different rate than the inductive effects of the substituents. More investigations are needed to solve this problem.

It would be of interest to compare the evaluated α-values in Tables 1 and 2 with the α_B- and/or α_R-values estimated for the same substrates. To the author's knowledge, the Bröndsted α-values have not been measured for the hydrations of norbornenes and nortricyclanes (a general acid catalysis was found in the hydration of *exo*- and *endo*-5-hydroxynorbornenes in phosphoric acid – dihydrogen phosphate buffers, but the α_B-values, ca. 0.6, obtained when only two catalyst acids were comployed, are very rough).[9b,22] The α_R-values are also unknown. If, however, eqn. (4) is written for two reactions, say A and B, and one equation is divided by another, ratio (13) is obtained. The

$$\alpha(A)/\alpha(B) = [\varrho_f(A)/\varrho_f(B)][\varrho_c(B)/\varrho_c(A)] \tag{13}$$

ratio of the ϱ_c-values is difficult, if not impossible, to determine in the case of formation reactions of carbocations [P = a carbocation in eqn. (1)]. If it is, however, assumed that the reaction constants, the ϱ_c's in eqn. (13), are approximately equal, the approximation (14) is obtained. The as-

$$\alpha(A)/\alpha(B) \approx \varrho_f(A)/\varrho_f(B) \tag{14}$$

Table 2. Isotopic α_I- and excess acidity α_A-values for the acid-catalyzed hydrations of substituted nortricyclanes under different conditions, and rate constants under standard conditions (1 mol dm^{-3} HClO$_4$ at 298.2 K).

Substituent	T/K	c(HClO$_4$)/M	α_I	$\alpha_A{}^a$	k_q/s^{-1}	Ref.
H	298.2	0.5–3		0.83(5)	8.6×10^{-4}	9e
2,6-(CH$_3$)$_2$-7-OH	328.2	0.1	0.65(2)		4.7×10^{-5}	9g, 11b
2-CH$_3$-trans-7-OH	348.2	0.1	0.67(3)		1.7×10^{-5}	11a
2-CH$_3$-cis-7-OH	348.2	0.1	0.96(3)		1.3×10^{-5}	11a
7-OH	348.2	0.1	0.85(2)		2.8×10^{-6}	9a, 11a
7-COCH$_3$	318.2	1–5		0.79(4)	1.3×10^{-6}	11c
7-CN	348.2	1–5		0.80(2)	3.7×10^{-8}	9f
7-NO$_2$	358.2	1–6		0.76(2)	5.5×10^{-9}	9h

^{a}X-values employed are X_0-values from Ref. 16. The correlation coefficients of log k_a vs. X_0 varied between 0.990 and 0.9990.

sumption demands that the substrates and products of reactions A and B must be of the same type and the substituents must be situated at the same positions.

The estimation method [eqn. (14)] can be tested by using the average α-values evaluated for the hydrations of nor-bornenes (1) and nortricyclanes (2), together with the reaction constants measured for the same reactions[10,12] and for the solvolyses of analogously substituted 2-norbornyl tosylates (3).[23] All the reactions produce a 2-norbornyl cation (Scheme 1). The best α-value is 0.77 for the hydration of norbornenes and 0.79 for the hydration of nortricyclanes. The reaction constants are collected in Table 3. They are medium-dependent;[24] thus similar types of solvents are appropriate for the reactions. The protonation of a 5-substituted norbornene (1) can occur either at C(2), when the same cation is produced as in the solvolysis of the similarly 6-substituted norbornyl tosylate (3), or at C(3), when the cation is the same as is formed in the solvolysis of the similarly 5-substituted 2-norbornyl tosylate (3). The sub-

stituent and the leaving group may be at the exo or endo position. The protonation of 7-substituted nortricyclanes (2) mostly takes place at the C(2)–C(6) bond, and the cation is thus the same as is formed in the solvolysis of syn- and anti-7-substituted 2-norbornyl tosylates (3). The α-values estimated for the solvolyses of norbornyl tosylates by using eqn. (14) are also listed in Table 3.

The error limits of the obtained α(solv.)-values are large, but two groups of values can, however, be separated: a group of exo solvolysis – norbornene protonation with α(solv.) $= 0.88 \pm 0.10$, and a group of endo solvolysis – norbornene protonation and exo and endo solvolysis – nortricyclane protonation with α(solv.) $= 0.46 \pm 0.07$. The former value is identical with (a) the value (0.89 $\pm$ 0.05), measured by Arnett et al.[25] for the slope of the Gibbs energy of activation of S_N1 ethanolysis of several alkyl chlorides versus their enthalpy of ionization in a superacid (SbF$_5$–SO$_2$ClF), and (b) the average degree of charge separation in the transition state (0.87 $\pm$ 0.05) estimated by

Table 3. Reaction constants for the protonation of the carbon double bond of 5-substituted norbornenes[10] and of the cyclopropane ring of 7-substituted nortricyclanes[12] and for the solvolysis of analogously substituted 2-norbornyl tosylates,[23] and α(solv.)-values estimated [eqn. (14)] from them.

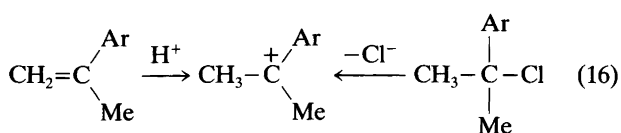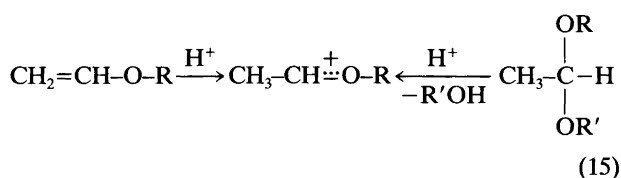| Position of OTs	Position of protonation	Position of substituent	ϱ(prot.)	ϱ(solv.)	α(solv.)^a
exo-2	C(2)	exo-6	−1.56	−2.00	0.99
exo-2	C(2)	endo-6	−1.56	−1.75	0.86
exo-2	C(3)	exo-5	−0.92	−0.96	0.80
exo-2	C(3)	endo-5	−0.92	−	−
					av. 0.88(10)
endo-2	C(2)	exo-6	−1.56	−0.78	0.39
endo-2	C(2)	endo-6	−1.56	−0.94	0.46
endo-2	C(3)	exo-5	−0.92	−0.54	0.45
endo-2	C(3)	endo-5	−0.92	−	−
					av. 0.46(7)
exo-2	C(2)–C(6)	anti-7	−1.30	−0.96	0.58
endo-2	C(2)–C(6)	anti-7	−1.30	−0.72	0.44
					av. 0.46(7)

$^a\alpha$(prot.) $= 0.77$ for norbornenes and 0.79 for nortricyclanes. They are the mean values of the α_I and α_A-values in Tables 1 and 2.

Abraham[26] for the S_N1 solvolysis of t-butyl chloride in water, water–methanol mixtures and alcohols from different solvent effects.

The excellent agreement must be, at least partly, fortuitous. The α(solv.)-value (0.46) estimated for the latter group is, on the contrary, exceptionally small and is not in agreement with the expected product-like character of the transition state in the carbocation formation reactions.[25-27]

A reasonable explanation for the different α(solv.)-values is the character of the first-formed intermediate, which has a strong effect on the product-like transition state [eqn. (3)]. There is a σ-participation in both the reactions of the *exo* solvolysis – norbornene protonation group,[10,23,28] thus their reaction constants and α-values are in harmony, but in the *endo* solvolysis the first-formed carbocation (or at least the transition state) has a classical character;[23,28] thus its values disagree with those of the protonation of norbornene. The protonation of nortricyclanes produces directly an edge-protonated nortricyclyl cation,[12] which is different from both the nonclassical and classical 2-norbornyl cations; thus the values estimated for the corresponding solvolysis of 7-substituted 2-norbornyl tosylates are unreasonable in the cases of both *exo* and *endo* solvolysis. The estimation is, however, very rough, especially in the case of 7-substituted nortricyclanes, because the protonation does not occur entirely at the C(2)–C(6) bond, but also at the other cyclopropane ring bonds,[20] and, besides, the values of reaction constants are not known for the solvolyses of *syn*-7-substituted 2-norbornyl tosylates,[29] although corresponding products are formed in the hydration of 7-substituted nortricyclanes. The first-formed different intermediate cations are rapidly transformed into the nonclassical 2-norbornyl cations, which yield the products.[28]

An applicability of eqn. (14) to other types of substrates and their reactions can be easily tested in the case of two pairs: vinyl ether hydrolysis–acetal hydrolysis [both in aqueous acids, eqn. (15)] and α-methylstyrene hydration (in aqueous H_2SO_4)–t-cumyl chloride hydrolysis [in 90% aqueous acetone, eqn. (16)]. In the former case, ϱ(acetal)/

$$CH_2=CH-O-R \xrightarrow{H^+} CH_3-CH\overset{+}{\cdots}O-R \underset{-R'OH}{\overset{H^+}{\longleftarrow}} CH_3-\overset{\overset{\displaystyle OR}{|}}{\underset{\underset{\displaystyle OR'}{|}}{C}}-H$$

$$(15)$$

$$CH_2=C\overset{\displaystyle Ar}{\underset{\displaystyle Me}{\diagup}} \xrightarrow{H^+} CH_3-\overset{+}{C}\overset{\displaystyle Ar}{\underset{\displaystyle Me}{\diagup}} \overset{-Cl^-}{\longleftarrow} CH_3-\overset{\overset{\displaystyle Ar}{|}}{\underset{\underset{\displaystyle Me}{|}}{C}}-Cl \quad (16)$$

ϱ(vinyl ether) = 1.7^{30} and α_1(vinyl ether) = 0.58 ± 0.07,[1,31] thus α(acetal) $\approx 0.98 \pm 0.12$. In the latter case, ϱ^+(t-cumyl

chloride)/ϱ^+(styrene) = 1.6^{32} and α_1(styrene) = 0.59 $\pm$ 0.09,[33] thus α(t-cumyl chloride) $\approx 0.94 \pm 0.14$. The estimated α-values are approximate but in agreement with the late transition state, which seems reasonable.[25,26,34] Thus the first-formed intermediate oxocarbenium ions are of the same character in reaction pair (15), as are also the carbocations in reaction pair (16), and their reaction constants and α-values are in harmony.

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