

Acid-Catalyzed Hydrolysis of Bridged Bi- and Tricyclic Compounds. XXXV. Applications of the Excess Acidity Method to the Hydrolysis of 3-Nortricyclanone at Different Temperatures

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The kinetics of hydrolysis of 3-nortricyclanone was studied using capillary gas chromatography in concentrated aqueous perchloric acid at various temperatures (303–348 K) and acid concentrations (6.1–11.7 M). According to the entropies and enthalpies of activation at different acid concentrations, the mechanism of the reaction is *A*-2, or more precisely *A*-2(carbocation), under all conditions. An excess acidity equation, derived for the *A*-2 mechanism, fits in well with the experimental data. Two of the parameters obtained, namely m^* (0.75 ± 0.02) and m^\ddagger (1.35 ± 0.01 ; one exceptional value, 1.25, excluded), are practically independent of temperature, and two, namely $\text{p}K_{\text{SH}^+}$ (-5.7 – -5.0) and $\log(k_0/K_{\text{SH}^+})$ (-9.0 – -6.2), are reasonably dependent on temperature.

The excess acidity method,¹ an advanced and versatile tool in studying acid-catalyzed reactions in concentrated aqueous acids, has recently been applied to the hydrolysis of several cyclic and bicyclic ethers,^{2–5} alkyl, cycloalkyl and bicycloalkyl phenyl ethers,^{6–10} and bicycloalkyl methyl ethers¹¹ in our laboratory. If the reaction occurs by an *A*-1 mechanism (a carbocation is formed in the unimolecular rate-limiting step), the slope parameter m^\ddagger , characteristic of the transition state, typically varies between 1.3 and 2.3,^{4,6–11} evidently decreasing slightly with increasing temperature.¹² If the reaction occurs by an *A*-2 mechanism (a nucleophile, mostly water, attacks the protonated substrate in the bimolecular rate-limiting step), the slope parameter m^\ddagger typically varies between 1.0 and 1.3.^{2,3,5,6} Thus 1.3 seems to be the limit value common to the *A*-1 and *A*-2 mechanisms. Unfortunately, the kinetics of the probable *A*-2 hydrolyses giving this value were studied only at elevated temperatures (338 or 348 K),^{5,6} and therefore it is not known whether the parameter m^\ddagger increases or decreases (perhaps to 1.0) in the *A*-2 mechanism when the temperature is reduced to room temperature.⁶ This problem is studied in the present work, in the absence of an ether reacting at a suitable rate, with 3-nortricyclanone, the hydrolysis of which has earlier been established to occur by the *A*-2 mechanism.¹³

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Experimental

Preparations. 3-Nortricyclanone was synthesized by the two-phase oxidation of 3-nortricyclanol¹⁴ with dichromic acid.¹⁵ The purity by GC was over 99%. The substrate was identified by GC-FTIR, GC-mass and ¹³C NMR spectra.¹⁶

Kinetic measurements. The rate constants for the disappearance of the substrate were measured by the GC method⁶ using an FFAP capillary column, nitrobenzene as the internal standard and dichloromethane as the extracting solvent. Pseudo-first-order rate constants (k_ψ) were calculated from the slopes of linear ($r = 0.998$ – 0.99999) plots of $\ln S_t$ vs. t ($S_\infty = 0$), where S_t is the ratio of integrals of the substrate and the internal standard at the time t . Each rate constant was measured twice, sometimes even more, and the values were equal at least within 4% (average 1.2%).

Results and discussion

The pseudo-first-order rate constants (k_ψ) for the disappearance of 3-nortricyclanone in aqueous perchloric acid at different temperatures and acid concentrations are given in Table 1. They are in good agreement with those measured earlier.¹³ The activation parameters (Table 2) were calculated from the second-order rate constants

Table 1. Rate constants for the disappearance of 3-nortricyclanone in aqueous perchloric acid at different temperatures and acid concentrations.

$c(\text{HClO}_4)/\text{mol dm}^{-3}$ ^a	X_0^b	a_w^c	$k_\psi/10^{-5} \text{ s}^{-1}$ ^d			
			303.2 K	318.2 K	333.2 K	348.2 K
6.14	2.09	0.447				10.51(5)
6.41	2.25	0.408				13.40(5)
6.95	2.58	0.332				22.6(3)
7.48	2.92	0.261			7.29(3)	37.5(4)
8.05	3.31	0.194			13.3(5)	65.1(5)
8.54	3.67	0.144	0.594(4)	4.10(4)	23.1(3)	109.7(7)
8.93	3.98	0.1103	0.956(7)	6.40(3)	33.8(6)	164.8(14)
9.51	4.44	0.0720	1.922(10)	12.18(8)	63.3(6)	284(3)
9.91	4.78	0.0515	3.07(5)	18.96(12)	95.7(7)	
10.51	5.30	0.0301	5.76(10)	34.6(3)	166.6(20)	
10.95	5.70	0.0194	8.38(17)	50.9(7)	235(9)	
11.26	6.00	0.0140	10.67(20)	60.7(9)		
11.67	6.39	0.0089	13.03(20)	67.3(14)		

^aAt 298.2 K. ^bExcess acidity at 298.2 K.¹⁷ ^cActivity of water at 298.2 K.¹⁸ ^dThe error limits in parentheses are standard deviations.

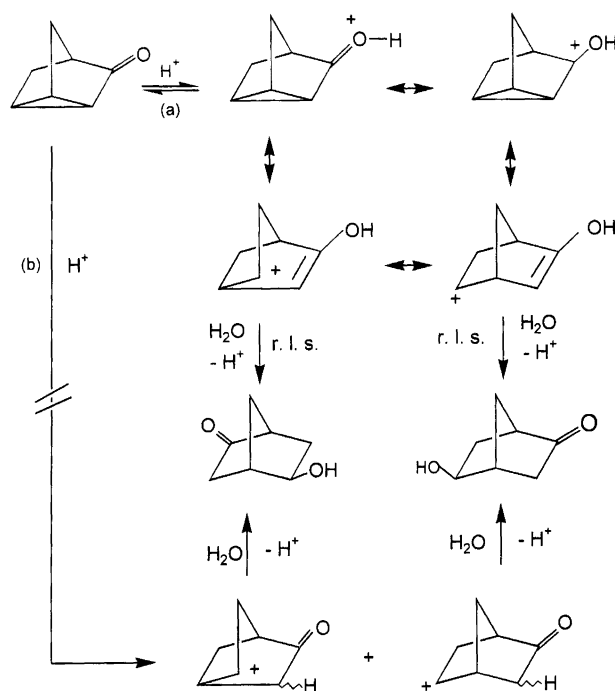
Table 2. The parameters of activation at 298.2 K for the hydrolysis of 3-nortricyclanone in $\text{HClO}_4(\text{aq})$ at different acid concentrations. (The error limits in parentheses are standard deviations.)

$c(\text{HClO}_4)/\text{mol dm}^{-3}$ ^a	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	r^b	N^c
8.01 ^d	102.2(5)	-30.4(13)	0.99998	4
8.54	99.9(5)	-33.3(15)	0.99997	4
8.93	98.3(6)	-35.1(18)	0.99997	4
9.51	95.5(4)	-38.9(11)	0.99998	4
9.91	94.4(7)	-39.1(20)	0.99998	3
10.51	92.3(10)	-41(4)	0.99994	3
10.95	91.5(19)	-41(6)	0.9998	3

^aAt 298.2 K. ^bCorrelation coefficient of the Arrhenius plot. ^cNumber of temperatures in kinetic measurements. ^dLajunen, M. and Yli-Mannila, R. Unpublished results.

$[k_a = k_\psi/c(\text{HClO}_4)]$ measured at the same acid concentration at three temperatures at least. The slight and even reductions of the enthalpy and entropy of activation with increasing acid concentration show no observable change in the reaction mechanism when the conditions become more drastic. The increasing portion of an $A-1$ or Ad_E2 mechanism ($\Delta S^\ddagger > 0$ and ≤ 0 , respectively) and the decreasing portion of the dominating $A-2$ mechanism (see later) should evidently cause an upward bending ΔS^\ddagger vs. $c(\text{HClO}_4)$ plot.¹⁶

The mechanism of hydrolysis was earlier concluded to be mainly $A-2$, i.e. a bimolecular water attack on a bicyclic carbocation formed from the oxygen-protonated substrate (Scheme 1, route a), on the basis of the solvent deuterium isotope effect ($k_H/k_D = 0.621$), the activation parameters, the dependence of rate on acid concentration (at 348 K) and the substituent effects.¹³ Actually the gross reaction is the acid-catalyzed hydration (addition of a water molecule to the cyclopropane ring), which produces dominantly *exo*-5-hydroxy-2-norbornanone.



Scheme 1.

The comparison of the hydration rate constants of 5-substituted 2-norbornenes and of 3-substituted nortricyclanes, however, gave a hint of the minor participation of the Ad_E2 or $A-S_E2$ mechanism, i.e. a rate-determining protonation of C-2 of the cyclopropane ring (Scheme 1, route b) in 1 mol dm⁻³ $\text{HClO}_4(\text{aq})$ at 298 and 348 K.¹³ The portion of this Ad_E2 reaction should evidently increase with increasing acid concentration and decreasing water activity. No such trend can be seen at high acid concentrations (Table 2).

The rate of hydrolysis increases rather steeply with

increasing acid concentration (Table 1). This effect can be considered quantitatively with the excess acidity theory,¹ which offers eqn. (1)

$$\log k_{\psi} - \log c_{\text{H}^+} - \log a_{\text{w}} - \log [c_{\text{s}}/(c_{\text{s}} + c_{\text{SH}^+})] \\ = m^{\ddagger} m^* X_0 + \log(k_0/K_{\text{SH}^+}) \quad (1)$$

for the A-2 mechanism. In the equation, X_0 represents the excess acidity¹⁷ and a_{w} the activity of water¹⁸ in the perchloric acid solution of acid concentration c_{H^+} , while m^{\ddagger} and m^* are slope parameters, the former being indicative of the transition state and the latter the site of proton attack. K_{SH^+} stands for the thermodynamic dissociation constant of the protonated substrate, c_{s} and c_{SH^+} are the concentrations of the unprotonated and protonated substrate, while k_0 is the medium-independent rate constant of the rate-limiting stage (r.l.s.) of the reaction (Scheme 1). Equation (1) is linear [the left side vs. X_0 is a straight line with slope $m^{\ddagger} m^*$ and intercept $\log(k_0/K_{\text{SH}^+})$]. Evaluation of the parameters is, however, easier with the nonlinear equation [eqn. (2)]

$$\log k_{\psi} - \log c_{\text{H}^+} - \log a_{\text{w}} \\ = m^{\ddagger} m^* X_0 - \log [1 + (c_{\text{H}^+}/K_{\text{SH}^+}) 10^{m^* X_0}] \\ + \log(k_0/K_{\text{SH}^+}) \quad (2)$$

in which the correction term, $-\log[c_{\text{s}}/(c_{\text{s}} + c_{\text{SH}^+})]$, of eqn. (1) has been changed to an exponential form by the aid of eqn. (3):

$$\log(c_{\text{SH}^+}/c_{\text{s}}) - \log c_{\text{H}^+} = m^* X_0 + \text{p}K_{\text{SH}^+} \quad (3)$$

The parameters of eqn. (2), namely, m^{\ddagger} , m^* , K_{SH^+} and k_0 [or $\log(k_0/K_{\text{SH}^+})$], can be evaluated by the method of a nonlinear least-squares minimization by fitting the experimental values (Table 1) of $\log k_{\psi} - \log c_{\text{H}^+} - \log a_{\text{w}}$ vs. c_{H^+} [$=c(\text{HClO}_4)$] and X_0 (c_{H^+} , X_0 and a_{w} have been corrected for temperature).^{1,19} The iterated best values of the parameters at four temperatures are given in Table 3.

The $\text{p}K_{\text{SH}^+}$ values (Table 3), which indicate the basicity of 3-nortricyclanone in aqueous perchloric acid, increase with rising temperature. This trend is in agreement with the approximation made by Cox *et al.*²⁰ that the $\text{p}K_{\text{SH}^+}$

Table 3. Parameters of the excess acidity equation [eqn. (2)] at different temperatures for the hydrolysis of 3-nortricyclanone in $\text{HClO}_4(\text{aq})$. (The error limits in parentheses are standard deviations.)

T/K	m^*	$\text{p}K_{\text{SH}^+}$	m^{\ddagger}	$\log(k_0/K_{\text{SH}^+})$
303.2	0.75(2)	-5.71(8)	1.35(3)	-8.97(6)
318.2	0.74(2)	-5.33(5)	1.35(2)	-7.91(5)
333.2	0.75(1)	-5.15(13)	1.34(3)	-7.09(4)
348.2	0.78(2)	-5.01(17)	1.25(2)	-6.18(3)
348.2 ^a	0.77(1)	— ^b	1.23(1)	-6.11(1)

^aEvaluated from the combined rate constants of Ref. 13 (3.0–7.0 M HClO_4) and of this work (6.1–9.5 M HClO_4).

^bUncertain owing to the good linearity ($r=0.9998$) of the plot $\log k_{\psi} - \log c_{\text{H}^+} - \log a_{\text{w}}$ vs. X_0 in this case.

values follow eqn. (4):

$$\text{p}K_{\text{SH}^+}(T_2) = (T_1/T_2) \text{p}K_{\text{SH}^+}(T_1) \quad (4)$$

in the case of proton transfer reactions (the equation is based on the assumption that $\Delta S^{\ddagger} \approx 0$ and thus $\Delta G^{\ddagger} \approx \Delta H^{\ddagger}$ for these processes).

The intercept parameter, $\log(k_0/K_{\text{SH}^+})$, which is the logarithm of the second-order rate constant (k_a) of the hydrolysis in aqueous perchloric acid with $X_0=0$, i.e. in the ideal 1 mol dm^{-3} acid (practically pure water), obeys the Arrhenius equation fairly well ($r=0.9994$) at different temperatures, giving activation parameters at 298 K, $\Delta H^{\ddagger} = 121 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = -16 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$, which, as expected, follows the increasing trend with decreasing acid concentration (see above and Table 2).

The value of m^* (0.75 ± 0.02) does not practically depend on temperature, which accords with the former studies.^{12,20,21} This parameter is characteristic of the site of protonation and is clearly different from the value (1.00 ± 0.01) measured for the protonation of many ether oxygen atoms,^{2–12} but in agreement with those (0.64 ± 0.10) measured earlier for the protonation of the carbonyl group in aqueous sulfuric acid.^{20–22}

The value of m^{\ddagger} , the slope parameter which depends on the character of the transition state, remains constant (1.35 ± 0.01) at the three lowest temperatures (303–333 K), in accordance with the statement by Cox *et al.*,²⁰ but is exceptionally slightly smaller (1.25) at 348 K. Because the last case may be due to experimental scatter, the experimental data used in the iterations at this temperature were enlarged using those measured earlier by Lajunen and Wiksten.¹³ The parameters evaluated from these 13 data points (3.0–9.5 M HClO_4), instead of 8 (6.1–9.5 M HClO_4), are also given in Table 3. The new excess acidity parameters are in good agreement with the other values in Table 3, but the m^{\ddagger} parameter, 1.23, remains practically equal to that obtained from the 8 data points. We did not find any explanation for this small value. The m^{\ddagger} values at the four temperatures, however, clearly show that the parameter does not become 1.0 at room temperature in the hydrolysis of 3-nortricyclanone. One reason for these perhaps slightly high values for the A-2 hydrolysis (such values have also been found earlier)^{5,6,20,22} may be the carbocation character of the transition state of the rate-limiting stage (r.l.s. in Scheme 1, route a) in this special case, when the mechanism is actually A-2(carbocation) with a feature typical of the A-1 mechanism, for which $m^{\ddagger} > 1$.^{1,4,7–12}

The excess acidity method was also applied to the hydrolysis of 3-nortricyclanone by assuming an A-1 or $\text{Ad}_{\text{E}2}$ mechanism.^{8,23} The m^{\ddagger} values were, however, unreasonable: 0.97–1.09 (± 0.05) in the former case, for which typically $m^{\ddagger} > 1$,^{1,4,7–12} and 0.37 ± 0.02 in the latter case, when the proton transfer from the hydroxonium ion to the cyclopropane ring of the substrate (Scheme 1, route b) should be at an early stage in the transition state, which is very improbable in the protonation of nortricyclanes.^{16,24} The excellent linearity ($r=$

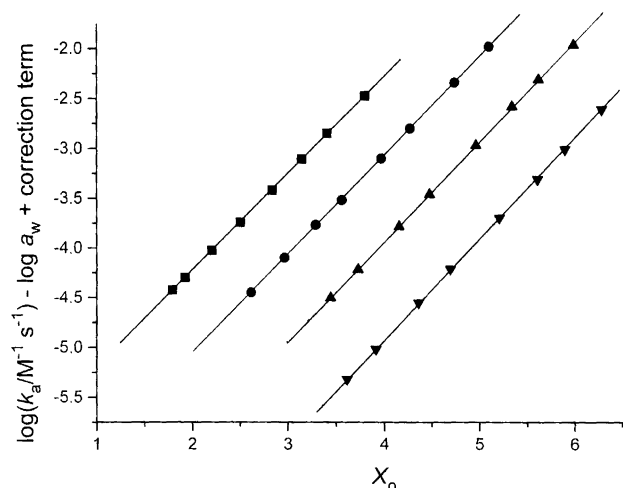


Fig. 1. Excess acidity plots for the hydrolysis of 3-nortri-cyclanone in $\text{HClO}_4(\text{aq})$ at different temperatures: ∇ , 303.2; \blacktriangle , 318.2; \bullet , 333.2 and \blacksquare , 348.2 K. $k_a = k_\psi / c(\text{HClO}_4)$. The straight lines have been calculated using eqn. (1) with the correction term, $-\log[c_S / (c_S + c_{\text{SH}^+})]$, calculated by eqn. (3) from parameters m^* and $\text{p}K_{\text{SH}^+}$ in Table 3.

0.99995–0.99998) of the excess acidity plots at the four temperatures in the case of the *A*-2 mechanism [eqn. (1); the correction term was calculated from the parameters in Table 3 by the aid of eqn. (3)] also shows (Fig. 1) that there is no change of mechanism, e.g. from *A*-2 to *Ad*_E2, with increasing acid concentration (see above).

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