Acid-Catalyzed Hydrolysis of Oxetane

Martti Lajunen* and Juha-Matti Koskinen

Department of Chemistry, University of Turku, FIN-20500 Turku, Finland

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Hydrolysis of oxetane was restudied in aqueous perchloric acid solutions. The rate constants, activation entropy and solvent deuterium isotope effect are in agreement with the literature data, but the $\log(k_{\psi}/\mathrm{s}^{-1})$ vs. H_0 acidity function plot is curved, and not linear as reported earlier. The kinetic excess acidity method gives the reasonable p K_{SH^+} value of -2.75 ± 0.19 at 283 K, and the m^{\neq} parameter is 1.03 ± 0.01 , which is in accord only with an A-2 hydrolysis mechanism. An early transition-state probably rationalizes the exceptional isotope effect found $(k_{\mathrm{H}}/k_{\mathrm{D}}=0.39\pm0.02)$.

The hydrolysis of simple epoxides (oxiranes) and oxetanes in acidic, neutral and basic aqueous solutions has been studied fairly extensively. 1-6 Oxirane was observed to react clearly faster than oxetane under all conditions, and the acid-catalyzed hydrolyses were found to be the fastest of the three different reactions. 2c,5c The results of the studies were, however, contradictory with regard to the participation of water in the acid-catalyzed opening of the ring, i.e. whether the mechanism is A-1 without water participation in the transition state (1) or A-2 with water participation (2).

Recently acid-catalyzed hydrolysis of 1,4-epoxycyclohexanes or 7-oxabicyclo[2.2.1]heptanes was reported. 7-9 The kinetic parameters and the products were also contradictory in these cases with regard to the A-1 and A-2 mechanisms. Therefore oxetane has been reinvestigated in the present work, owing to its convenient hydrolysis rates in rather concentrated aqueous acids.

Experimental

Material. Oxetane was purified by distillation from a commercial product (Aldrich, tech., 96%). The purity was > 99.5% (by GC) and the ¹H and ¹³C NMR spectra were in agreement with the published data. ^{10,11}

Kinetic measurements. The disappearance of oxetane (ca. 0.025 mol dm⁻³) in aqueous perchloric acid was followed by GC using cyclopentanone as internal standard. Twelve samples were taken after equal intervals during ca. three half-lives, extracted with chloroform and analyzed on a Perkin Elmer AutoSystem gas chromatograph equipped

with an FFAP capillary column. The ratios (S_t) of integrals of the substrate and the internal standard peaks were used to calculate the pseudo first-order rate constants from the linear plot $\ln S_t = -k_{\psi}t + \ln S_0$ $(S_{\infty} = 0)$. The rate constant under each condition was measured two or more times, and the values were equal at least within 5% (av. 1.4%).

Product analysis. Oxetane (0.5 cm³) was stirred with 50 cm³ of 1.0 mol dm⁻³ HClO₄(aq) in a tightly stoppered bottle at room temperature for 2 h (over 10 half-lives). The solution was extracted 20 times with 10 cm³ portions of chloroform. The organic phases were combined, dried over K₂CO₃ (fast) and Na₂SO₄ and concentrated by distillation of the solvent, and the rest was analyzed by GC (FFAP capillary column) and by GC/FT-IR (Hewlett-Packard 5890 Series II gas chromatograph and 6030 Galaxy infrared spectrometer). 1,2-Propanediol (E. Merck AG) and 1,3-propanediol (BDH) were used for identification of the products, and the latter diol was submitted to a similar hydrolysis experiment as oxetane.

^{*} To whom correspondence should be addressed.

Table 1. Disappearance rate constants of oxetane in aqueous perchloric acid at different temperatures and acid concentrations as well as the activation parameters and solvent deuterium isotope effect at 298.2 K and parameters for several log k_{ψ} vs. acidity function plots at 283.2 K.

T/K	c(HClO ₄)/mol dm ^{-3 a}	X ₀ ^b	$k_{\psi}/10^{-4} \mathrm{s}^{-1}$
283.2	1.006		3.02(3)
293.2	1.004		10.47(9)
298.2	1.002		18.87(12)°
303.2	1.000		33.6(3)
313.2	0.997		98.2(9)
298.2	0.101		1.19(3)
298.2	0.101		3.02(5) ^d
283.2	0.511	0.160	1.158(6)
283.2	0.760	0.226	1.961(9)
283.2	1.006	0.288	3.02(3)
283.2	1.501	0.408	5.72(4)
283.2	1.989	0.520	9.52(7)
283.2	2.484	0.646	15.64(10)
283.2	3.003	0.795	26.9(12)
283.2	3.469	0.947	39.8(14)
283.2	4.034	1.154	64.3(8)

Kinetic parameters

$$\begin{split} \Delta H^{\neq} &= 83.4(2) \text{ kJ mol}^{-1} \\ \Delta S^{\neq} &= -17.4(7) \text{ J K}^{-1} \text{ mol}^{-1} \\ k_{\text{H}}/k_{\text{D}} &= 0.389(17) \\ \log(k_{\text{W}}/\text{s}^{-1}) &= -0.95(3)H_{\text{O}} - 3.84(3); \ r &= -0.996^{\,g} \\ \log(k_{\text{a}}/\text{M}^{-1} \text{ s}^{-1}) &= 0.87(2)X_{\text{O}} - 3.78(1); \ r &= 0.998^{\,f} \\ \log(k_{\text{a}}/\text{M}^{-1} \text{ s}^{-1}) &- \log a_{\text{w}} &= 1.01(2)X_{\text{O}} - 3.80(1); \ r &= 0.9991^{\,g} \\ \log(k_{\text{a}}/\text{M}^{-1} \text{ s}^{-1}) &- \log[c_{\text{S}}/(c_{\text{S}} + c_{\text{SH}}^{+})] &= 0.914(15)X_{\text{O}} - 3.787(10); \ r &= 0.9991^{\,f, \, h} \\ \log(k_{\text{a}}/\text{M}^{-1} \text{ s}^{-1}) &- \log[c_{\text{S}}/(c_{\text{S}} + c_{\text{SH}}^{+})] &- \log a_{\text{w}} &= 1.046(12)X_{\text{O}} - 3.807(8); \ r &= 0.9995^{\,g, \, h} \end{split}$$

Results and discussion

The disappearance rate constants of oxetane were measured in aqueous perchloric acid solutions at different temperatures and acid concentrations as well as in deuterioperchloric acid. The rate constants, activation parameters, solvent deuterium isotope effect and the parameters for several plots of $\log k_{\psi}$ vs. an acidity function are listed in Table 1.

The present rate constants are in fair agreement with those reported earlier, 1b,5c as are the activation entropy 1b,5d and the solvent deuterium isotope effect. $^{+2c,12}$ A clear difference can, however, be found in the plot of log k_{ψ} vs. the H_0 acidity function; this was earlier observed to be strictly linear with slope -1.00, 2c but the present plot (Fig. 1) is clearly curved. Therefore, the excess acidity method is applied here. 13

According to the kinetic excess acidity method,¹³ the rate constant of the unimolecular acid-catalyzed hydrolysis (A-1 mechanism) should follow eqn. (1) and that of the corresponding bimolecular hydrolysis (A-2 mechanism) eqn. (2),

$$\log k_{\psi} - \log c_{\mathrm{H}^{+}} - \log[c_{\mathrm{S}}/(c_{\mathrm{S}} + c_{\mathrm{SH}^{+}})] = m^{\neq} m^{*} X_{0} + \log(k_{0}/K_{\mathrm{SH}^{+}})$$
(1)

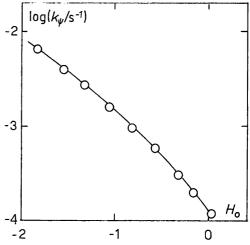


Fig. 1. $\log(k_{\psi}/\mathrm{s}^{-1})$ vs. $H_{\rm O}$ plot for the hydrolysis of oxetane in HClO₄(aq) at 283.2 K. The $H_{\rm O}$ values are at 298 K. ¹⁴

^aTemperature corrected. ^bExcess acidity, ¹⁵ temperature corrected. ¹³ ^cCalculated from the activation parameters. ^dMeasured in DCIO₄(D₂O). ^eCurved; H_0 values at 298.2 K. ¹⁴ $f_{k_a} = k_{\psi}/c_{H^+}$; slightly curved. ^gThe activity of water, a_{w} , at 298.2 K. ¹⁴ ^hThe correction term was calculated [eqn. (3)] by using the m^* value of 1.01 and the p K_{SH^+} value of -2.75 (see text).

 $k_{\rm H}/k_{\rm D} = 0.38(2)$ in 0.1 M and 0.39(2) in 1.0 M LClO₄ (L₂O) (L = H or D) at 298.2 K.¹²

$$\log k_{\psi} - \log c_{\text{H}^{+}} - \log[c_{\text{S}}/(c_{\text{S}} + c_{\text{SH}^{+}})] - \log a_{\text{w}}$$

$$= m^{\neq} m^{*} X_{0} + \log(k_{0}/K_{\text{SH}^{+}})$$
(2)

if the substrate (S) is partially protonated in the aqueous acid with concentration $c_{\rm H}$, activity of water $a_{\rm w}$, ¹⁴ and excess acidity X_0 . ¹⁵ If the substrate is essentially unprotonated within the acid concentrations employed, the correction term $\log[c_{\rm S}/(c_{\rm S}+c_{\rm SH}^{\perp})]$ can be totally eliminated. The slope parameters $m^{\neq}m^*$ of eqns. (1) and (2) with values 0.87 and 1.01, respectively (Table 1), were calculated in this way, but the plots were slightly curved. Therefore it is necessary to estimate the value of the correction term $\log[c_{\rm S}/(c_{\rm S}+c_{\rm SH}^{\perp})]$ at each acid concentration

The ratio of the concentrations of the protonated and unprotonated forms of the substrate can be evaluated using the excess acidity method by employing eqn. (3)¹³

$$\log(c_{SH^+}/c_s) - \log c_{H^+} = m^*X_0 + pK_{SH^+}$$
 (3)

where m^* is the slope parameter, which depends on the site of proton attack $[m^*=1.0$ when an ether oxygen is protonated in $HClO_4(aq)]$, and K_{SH} stands for the thermodynamic dissociation constant of the protonated substrate. The dissociation constant of the protonated oxetane is, however, unknown. Therefore it is estimated by combining eqns. (1)–(3) to get eqn. (4)

$$\log k_{\rm a} (-\log a_{\rm w}) = m^{\neq} m^* X_0$$

$$-\log[1 + (c_{\rm H^+}/K_{\rm SH^+})10^{m^* X_0}]$$

$$+\log(k_0/K_{\rm SH^+}) \tag{4}$$

where $k_{\rm a} = k_{\rm \psi}/c_{\rm H^+}$ and where the term for water activity is excluded in the case of the A-1 mechanism and included in the case of the A-2 mechanism.

A plot of eqn. (4) is nonlinear with respect to X_0 and c_{H^+} , but the best values of the parameters m^{\neq} , m^* , K_{SH^+} and k_0 can be estimated using a nonlinear least-squares minimization, which, however, demands rather well guessed initial values for the parameters, because the effect of the correction terms is small in this case. The parameters evaluated for the A-1 mechanism (log a_w excluded) are not rational (e.g. $m^{\neq} \approx 1$, although the typical value should be > 1), 13 or the compatibility between the experimental points and the calculated curve is poor. On the contrary, the compatibility is excellent and the calculated parameters are reasonable in the case of the A-2 mechanism: $m^{\neq} = 1.025(8)$, $m^* = 1.01(3)$, $pK_{SH^+} = -2.75(19)$ and $log(k_0/K_{SH^+}) = -3.806(5)$. If one slightly exceptional data point $(X_0 = 0.795)$ is eliminated, the values of the parameters do not change markedly. Fig. 2 shows that the linear excess acidity plot fits well to the experimental points in the case of the A-2 mechanism [eqn. (2)], but there is a slight disagreement in the case of the A-1 mechanism [eqn. (1)] if the correction term is calculated [eqn. (3)] using the evaluated m^* and pK_{SH^+} values. The evaluated pK_{SH^+} parameter

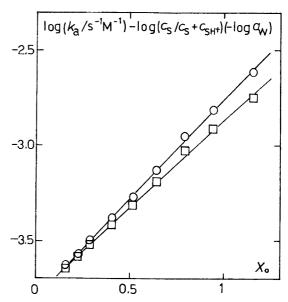


Fig. 2. Excess acidity plots for the hydrolysis of oxetane in $HClO_4$ (aq) at 283.2 K with inclusion (\bigcirc) and exclusion (\square) of the activity of water (at 298.2 K). The straight lines obey eqns. (2) and (1), respectively.

(-2.75) is close to those measured for 7-oxabicyclo[2.2.1]heptane (-2.80) and tetrahydropyran (-2.79), but more negative than that for tetrahydrofuran (-2.08).¹⁸

The negative entropy of activation is also in accord with the A-2 mechanism. (The mean value of this work and Refs. 1b and 5d is -17 ± 3 J K $^{-1}$ mol $^{-1}$.) A problem arises from the exceptional solvent deuterium isotope effect (mean value of this work and Ref. 12: $k_{\rm H}/k_{\rm D}=0.39\pm0.02$ at 298 K), which is within the calculated limits for the A-1 mechanism (0.33–0.48) but not within those for the A-2 mechanism (0.48–0.69). This isotope effect $^{2b,2c,7-9}$ can at least partly be rationalized by an early transition state, when the values for the A-1 and A-2 mechanisms become close to each other ($k_{\rm H}/k_{\rm D}\approx0.5$). The transition state may be early owing to the release of the high ring strain (107 kJ mol $^{-1}$ for oxetane) during the opening of the protonated oxygen bridge.

According to the product analysis (see Experimental), oxetane produces mainly 1,3-propanediol in 1.0 mol dm⁻³ aqueous acid. The product also includes 10% 1,2propanediol, which might be formed from the primary 3-hydroxy-1-propyl cation (A-1 mechanism) via hydride migration and subsequent hydration. However, according to a separate test, 1,3-propanediol produces in the same reaction medium 1,2-propanediol as well as dimeric, trimeric and higher ethers of the form HO[(CH₂)₃O]_nH, which were also found among the hydrolysis products of oxetane. Thus the products are also in agreement with the A-2 hydrolysis mechanism of oxetane, and no contradiction exists between them and the kinetic parameters above, contrary to the hydrolyses of carbonyl-substituted 7-oxabicyclo[2.2.1]heptanes, in which cases the kinetic parameters support the A-2 mechanism but the products

support the A-1 mechanism.^{8,9} In the spectrum of mechanisms of the acid-catalyzed hydrolyses of epoxides, the hydrolysis of oxetane evidently belongs to the A-2 end (although $k_{\rm H}/k_{\rm D}$ is exceptional), those of 7-oxa-5-oxo-2-bicyclo[2.2.1]heptane and 7-oxa-2-oxobicyclo[2.2.1]heptane are representative of the A-2(carbocation) intermediate part,^{8,9} and that of 7-oxabicyclo[2.2.1]heptane belongs to the A-1 end.⁷

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