

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	$c(\text{HClO}_4)/\text{mol dm}^{-3}$ ^a	X_0 ^b	$k_\psi/10^{-4} \text{ s}^{-1}$
283.2	1.006		3.02(3)
293.2	1.004		10.47(9)
298.2	1.002		18.87(12) ^c
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

$$\Delta H^\ddagger = 83.4(2) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = -17.4(7) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$k_{\text{H}}/k_{\text{D}} = 0.389(17)$$

$$\log(k_\psi/\text{s}^{-1}) = -0.95(3)H_0 - 3.84(3); r = -0.996^e$$

$$\log(k_a/\text{M}^{-1} \text{ s}^{-1}) = 0.87(2)X_0 - 3.78(1); r = 0.998^f$$

$$\log(k_a/\text{M}^{-1} \text{ s}^{-1}) - \log a_w = 1.01(2)X_0 - 3.80(1); r = 0.9991^g$$

$$\log(k_a/\text{M}^{-1} \text{ s}^{-1}) - \log[c_S/(c_S + c_{\text{SH}^+})] = 0.914(15)X_0 - 3.787(10); r = 0.9991^{f,h}$$

$$\log(k_a/\text{M}^{-1} \text{ s}^{-1}) - \log[c_S/(c_S + c_{\text{SH}^+})] - \log a_w = 1.046(12)X_0 - 3.807(8); r = 0.9995^{g,h}$$

^aTemperature corrected. ^bExcess acidity, ¹⁵ temperature corrected. ¹³ ^cCalculated from the activation parameters. ^dMeasured in $\text{DClO}_4(\text{D}_2\text{O})$. ^eCurved; H_0 values at 298.2 K. ¹⁴ ^f $k_a = k_\psi/c_{\text{H}^+}$; 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 $\text{p}K_{\text{SH}^+}$ value of -2.75 (see text).

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_ψ 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),

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

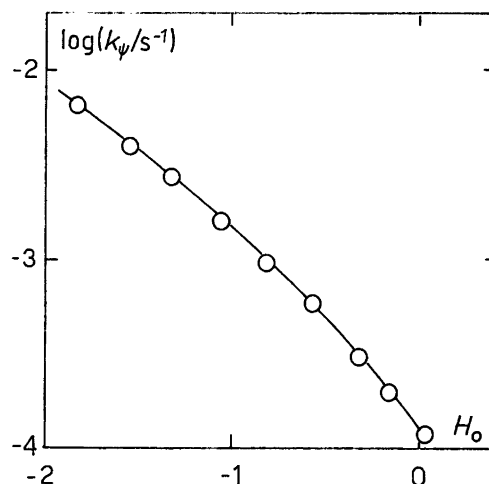


Fig. 1. Log(k_ψ/s^{-1}) vs. H_0 plot for the hydrolysis of oxetane in $\text{HClO}_4(\text{aq})$ at 283.2 K. The H_0 values are at 298 K.¹⁴

† $k_{\text{H}}/k_{\text{D}} = 0.38(2)$ in 0.1 M and $0.39(2)$ in 1.0 M LClO_4 (L_2O) ($\text{L} = \text{H}$ or D) at 298.2 K.¹²

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

if the substrate (S) is partially protonated in the aqueous acid with concentration c_{H^+} , activity of water a_{w} ,¹⁴ and excess acidity X_0 .¹⁵ If the substrate is essentially unprotonated within the acid concentrations employed, the correction term $\log [c_{\text{S}}/(c_{\text{S}} + c_{\text{SH}^+})]$ 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 $\log [c_{\text{S}}/(c_{\text{S}} + c_{\text{SH}^+})]$ 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

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

where m^* is the slope parameter, which depends on the site of proton attack [$m^* = 1.0$ when an ether oxygen is protonated in $\text{HClO}_4(\text{aq})$],^{16,17} 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)

$$\log k_{\text{a}} (-\log a_{\text{w}}) = m^{\neq} m^* X_0 - \log [1 + (c_{\text{H}^+}/K_{\text{SH}^+}) 10^{m^* X_0}] + \log(k_0/K_{\text{SH}^+}) \quad (4)$$

where $k_{\text{a}} = k_{\psi}/c_{\text{H}^+}$ 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 ($\log a_{\text{w}}$ 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: $m^{\neq} = 1.025(8)$, $m^* = 1.01(3)$, $\text{p}K_{\text{SH}^+} = -2.75(19)$ and $\log(k_0/K_{\text{SH}^+}) = -3.806(5)$. 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 $\text{p}K_{\text{SH}^+}$ values. The evaluated $\text{p}K_{\text{SH}^+}$ parameter

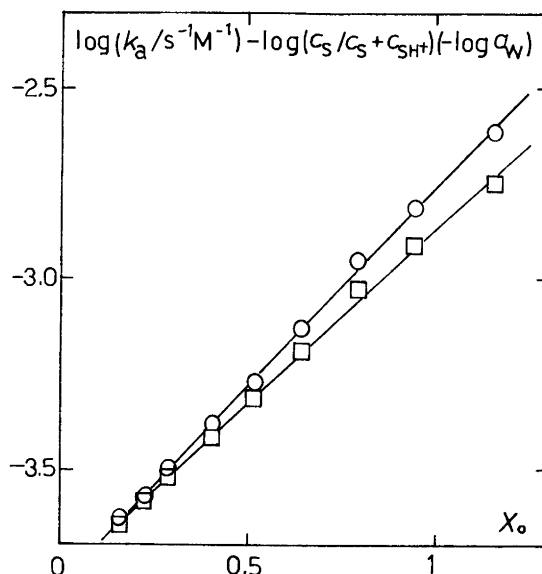


Fig. 2. Excess acidity plots for the hydrolysis of oxetane in $\text{HClO}_4(\text{aq})$ at 283.2 K with inclusion (O) and exclusion (□) of the activity of water (at 298.2 K). The straight lines obey eqns. (2) and (1), respectively.

(-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 $-17 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$.) A problem arises from the exceptional solvent deuterium isotope effect (mean value of this work and Ref. 12: $k_{\text{H}}/k_{\text{D}} = 0.39 \pm 0.02$ 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).¹⁹ 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 ($k_{\text{H}}/k_{\text{D}} \approx 0.5$). 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.²⁰

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% 1,2-propanediol, 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 $\text{HO}[(\text{CH}_2)_3\text{O}]_n\text{H}$, 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 $k_{\text{H}}/k_{\text{D}}$ is exceptional), those of 7-oxa-5-oxo-2-bicyclo[2.2.1]heptene 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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