Short Communication

Acid-Catalyzed Hydration of Cyclopentene

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Acid-catalyzed hydration of aliphatic alkenes, cycloalkenes and bicycloalkenes is still a subject of interest.[1-4] The mechanism of hydration has been established to be $A\text{-}S_E2$ or Ad_E2, i.e., the slow protonation of the double bond produces a carbocation, which is rapidly captured by a nucleophile, mostly water. Distinctive features of this mechanism are negative entropies of activation, solvent deuterium isotope effects greater than unity and linear $\log k_1$ vs. H_0 correlations.[1-5]

A rather similar mechanism of reaction, although via a π complex, has been proposed for the addition of acetic acid to norbornene and norbornadiene catalyzed by trifluoromethanesulfonic acid (k_H/k_D = 1.58 and 1.60, respectively).[6] However, the corresponding addition of acetic acid to cyclopentene was concluded, because of its exceptional solvent isotope effect (k_H/k_D = 0.75), to involve a different mechanism: formation of a solvent-separated ion pair from the intimate ion pair is now the rate-limiting stage.[6] This kind of variation of mechanism appears rather strange. Since no kinetic and mechanistic study on the acid-catalyzed hydration of cyclopentene could be found in the literature despite a systematic search, such an investigation seemed worth carrying out.

The disappearance of cyclopentene (Fluka AG, purity ≥ 99.5 %) in aqueous perchloric acid was followed spectrophotometrically (Cary 17 D,

Table 1. Rate constants for disappearance of cyclopentene in aqueous perchloric acid at different temperatures and acid concentrations; activation parameters, solvent deuterium isotope effects and slopes for the plots of $\log k_1$ vs. H_0 (*slope*$_1$) and $\log k_a$ vs. X_0 (*slope*$_2$) at 298.2 K (r = correlation coefficient).

T/K	[$HClO_4$]/ mol dm^{-3}	H_0[a]	X_0[b]	$k_1/10^{-4}$ s^{-1}	Activation parameters, isotope effects and slopes
283.2	5.96			0.322(4)	$\Delta H^{\ddagger}$ = 90.4(9) kJ mol^{-1}
288.2	5.96			0.613(3)	$\Delta S^{\ddagger}$ = −26(3) J mol^{-1} K^{-1}
293.2	5.96			1.205(22)	
298.2	5.96			2.27(3)	
303.2	5.96			4.41(3)	
308.2	5.96			7.60(3)	
298.2	6.51			6.79(4)	
298.2	6.45[c]			5.27(39)	k_H/k_D = 1.28(10)
298.2	4.00	−1.81	1.09	0.0655(18)	*slope*$_1$ = −1.47(3),
298.2	5.01	−2.32	1.52	0.422(5)	r = −0.9994
298.2	5.96	−2.89	1.99	2.27(3)	*slope*$_2$ = 1.47(2),
298.2	7.05	−3.58	2.65	24.2(8)	r = 0.9997
298.2	8.03	−4.25	3.33	285(5)	

[a]Ref. 15. [b]Ref. 16. [c]Measured in $DClO_4(D_2O)$.

195 nm), and a strictly linear correlation of ln $(A_t - A_\infty)$ with time was always observed ($r \geq 0.999$). The hydration product was shown by GLC as well as by ^1H and ^{13}C NMR spectroscopy to be cyclopentanol. The amount of cyclopentene remaining after ten half-lives was determined to be 3±2 %, and thus the rate of hydration of cyclopentene is practically equal to its rate of disappearance. The rate constants at different temperatures and acid concentrations are listed in Table 1.

The activation entropy of hydration (-26 J K^{-1} mol^{-1}) is typical for the slow protonation of a double bond, as is also the solvent isotope effect (k_H/k_D = 1.28). The latter value is smaller than those generally measured for the hydration of aliphatic alkenes, methylenecycloalkanes and bicycloalkenes,[1-4] but agrees with those for cyclohexene (1.06), 1-methylcyclohexene (1.13–1.16) and 1-methylcyclopentene (1.20–1.23).[1,3,4] The change of solvent from water to acetic acid may decrease its value: e.g., k_H/k_D for norbornene is 2.13 in aqueous acid and 1.58 in glacial acetic acid.[1,6] Thus, the isotope effect for cyclopentene in aqueous acid (1.28) may be changed to 0.75 in acetic acid without change of the reaction mechanism. The origin of the low isotope effect for cyclopentene is possibly a change of conformation during the protonation of the substrate:[3,4] an envelope form of the initial state is transformed into a twisted form of the carbocation.[7-9]

The rate of hydration of cyclopentene is close to that of cyclohexene: k(cyclopentene)/k(cyclohexene) = 2.2 in 5 mol dm^{-3} $HClO_4$ at 298 K.[1] The ratio is similar to that observed for the addition of acetic acid to the double bonds, catalyzed by strong acids.[6,10] The logk_1 vs. H_0 plot for cyclopentene is linear and its slope (-1.47) is also close to that (-1.57) measured for cyclohexene.[1] More informative than the correlation above is, however, the fairly linear logk_a vs. X_0 correlation ($k_a = k_1/c_{H^+}$ and X_0 = excess acidity),[11] since its slope ($m^{\neq}m^* = 1.47$) provides the possibility of estimating the degree of proton transfer in the transition state: $\alpha = m^h$ = slope/m^*, and a value of 1.8 can be estimated for m^* in the formation of the carbocation.[12] The degree of proton transfer is thus 0.82 for the hydration of cyclopentene, which is rather similar to the α values for isobutene (0.84)[13] and substituted norbornenes (0.75 ± 0.05)[14] determined by a different method.

The kinetic parameters above show that the hydration of cyclopentene is, at least in aqueous acid, a typical A-S_E2 reaction in which the transition state for the slow proton transfer is carbocation-like.

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