

Acid-Catalyzed Hydrolysis of Bridged Bi- and Tricyclic Compounds. XXIX. 7-Oxa-5-oxo-2-bicyclo[2.2.1]heptene: Kinetics and Mechanism

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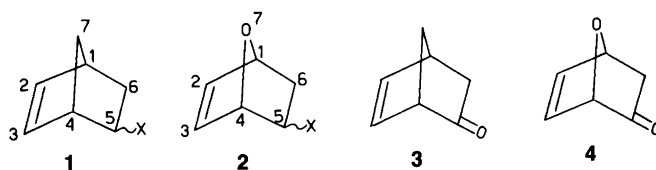
7-Oxa-5-oxo-bicyclo[2.2.1]heptene (7-oxanorborn-2-en-5-one) produces in concentrated (5–8.5 mol dm⁻³) aqueous perchloric acid mainly 1,2-dihydroxybenzene. The reaction is initiated by the pre-equilibrium protonation of the ether oxygen atom and the subsequent rupture of the C(1)–O(7) bond. The mechanism of hydrolysis (hydrolytic isomerization) has both unimolecular (A-1) and bimolecular (A-2) features according to the activation parameters, acidity function correlations and solvent deuterium isotope effect.

Electrophilic additions to the double bond of 5-substituted bicyclo[2.2.1]hept-2-enes (norbornenes)^{1–3} (**1**) and 7-oxa-bicyclo[2.2.1]hept-2-enes (oxanorbornenes)^{4–6} (**2**) have been the subject of enthusiastic investigation, especially during the last few years. This is caused by both theoretical interest in the effect of a substituent at C(5) upon the regioselectivity of addition and practical interest in the addition products, which are important intermediates in the syntheses of biologically active compounds.^{2–7} The substituent effect is generally very similar in the cases of norbornenes and oxanorbornenes, although the methylene and oxygen bridges are sterically and inductively different. The oxygen atom is smaller than the methylene group, a fact which may result in an increased rate of addition to the double bond of oxanorbornene from the *exo* direction,^{6c,8} but the oxygen atom is also much more electronegative than the methylene group, which may cause a decreased electrophilic addition rate in the case of oxanorbornenes. (The latter effect, $k_{\text{CH}_2}/k_{\text{O}} \approx 10^3$, has been detected in the solvolyses of 2-norbornyl and 7-oxa-2-norbornyl halides and brosylates.)⁹

The effects of many 5-substituents upon the reaction rates and products have been studied in our laboratory in

the case of the acid-catalyzed hydration of norbornenes, which reaction is started by the rate-determining protonation of either olefinic carbon atom.² A very interesting substituent is the oxo group, which causes a roughly fifty-fifty protonation of C(2) and C(3) of 5-oxo-2-norbornene (**3**).^{10,11} This group is inductively very electron-attractive,¹² but at a suitable position it may act as a strong electron donor because of its homoconjugative and/or hyperconjugative (frangomeric) effect(s).^{2,5} Recent MO calculations and product analyses of the acid-catalyzed solvolyses of 5-oxo-2-norbornene support the idea of the dominance of the frangomeric effect in this case.^{3b,11,13}

Substitution of oxygen for the 7-methylene in 5-oxo-2-norbornene yields 7-oxa-5-oxo-2-norbornene (**4**), the protonation of which can, at least in principle, occur at four positions: at either olefinic carbon, at the ether oxygen or at the carbonyl oxygen. They all have effects (inductive, homoconjugative, frangomeric, steric etc.) on the protonation of the other atom, thus it is interesting to search for the position whose protonation results in the hydrolysis or hydration of 7-oxa-5-oxo-2-norbornene (oxanorbornone).



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Experimental

Synthesis. 7-Oxanorborn-2-en-5-one was prepared by the alkaline methanolysis of the Diels–Alder adducts of furan and 1-cyanovinyl acetate.¹⁴ The product was fractionated by distillation through an efficient column, when the purities of the best fractions were over 99%. The IR, ¹H NMR and ¹³C NMR spectra were identical with the published data.¹⁵

Kinetic measurements. The disappearance of oxanorbornenone (ca. 9×10^{-3} M) in concentrated aqueous perchloric acid solutions was followed by GLC during 2–3 half-lives. The samples taken after appropriate intervals were immediately extracted with CH₂Cl₂ and analyzed by GLC (on a Carbowax 20 M capillary column) with 2-norbornanone as internal standard. Each sample was analyzed at least twice and the runs were repeated once. The first-order rate constants calculated from the slopes of a linear plot of $\ln(A_t - A_\infty)$ vs. time (t) (where A is an integral of the GLC peak of the substrate divided by that of the standard) were equal, at least within 6% (av. 3%) in the cases of parallel runs.

Product analysis. Oxanorbornenone (0.5 cm³) was stirred with 7 mol dm⁻³ HClO₄(aq) (50 cm³) in a tightly sealed bottle for 21 h (>20 half-lives) at ca. 87°C. The reaction mixture was cooled and (a) a major part was extracted with CH₂Cl₂ and (b) a minor part was neutralized with concentrated ammonia and centrifugated to remove the precipitated salt. The solutions were then analyzed by GLC by using a Carbowax 20 M capillary column (150°C) in case (a) and a packed Silicon SE-30 column (230°C) in case (b). No product peaks were found in the former case, and only one peak (in addition to the water peaks) was observed in the latter case, but its short retention time hinted that it was due to the destruction of a product component in the hot injection block. It was not identified.

The CH₂Cl₂ solution in case (a) was dried over Na₂SO₄ and the solvent was evaporated under a low vacuum. The solid residue was identified by IR, ¹H NMR (CDCl₃) and ¹³C NMR (CDCl₃ and D₂O) spectroscopy to be mainly 1,2-dihydroxybenzene (catechol). Some additional IR and ¹H NMR peaks as compared with the spectra of authentic catechol showed that minor products were also formed. They were not analyzed, but they were of an acid–base indicator character.

The amount of catechol in the products of the hydrolysis of oxanorbornenone was estimated in 5, 7 and 8.5 mol dm⁻³ HClO₄(aq) by measuring the UV absorbance (271–272.5 nm) of the product formed from the substrate under strictly quantitatively hydrolytic conditions. The molar absorption coefficients (210.5–222.2 m² mol⁻¹) at the corresponding wavelengths were measured for catechol under similar acidic conditions. The maximum amount of catechol in the product was estimated to be $82 \pm 1\%$ in 5 mol dm⁻³, 80% in 7 mol dm⁻³ and 82% in 8.5 mol dm⁻³ HClO₄ at 85–90°C.

The possible formation of other dihydroxybenzenes was tested by analyzing the IR spectra of mixtures which contained 1.3% 1,3-dihydroxybenzene or 0.9% 1,4-dihydroxybenzene in addition to catechol. Not all corresponding signals were found in the spectra of the hydrolysis of oxanorbornenone. These experiments showed that the amount of 1,3- and 1,4-dihydroxybenzenes is < 5% in the product. (They transfer 3.6 and 5.5 times, respectively, less than catechol from 7 mol dm⁻³ acid into CH₂Cl₂ during the extraction.) No isomerization of 1,3- and 1,4-dihydroxybenzenes into catechol was observed during 21 h in 7 mol dm⁻³ acid at 85°C.

Results and discussion

The disappearance rate constants of 7-oxa-5-oxo-2-bicyclo[2.2.1]heptene (oxanorbornenone, **4**) were measured in aqueous perchloric acid at different temperatures and acid concentrations, and in deuterioperchloric acid. The results are listed in Table 1 together with activation parameters, slopes for some linear $\log k$ vs. acidity function correlations and a kinetic solvent deuterium isotope effect.

The disappearance rate constant of oxanorbornenone in 5 mol dm⁻³ acid at 348 K is 0.3 times that of norborn-2-en-5-one (norbornenone, **3**).¹⁰ The ratio is much greater than that (ca. 10^{-3}) for the solvolyses of 7-oxa-2-norbornyl and 2-norbornyl compounds (see above).⁹ This fact does not accord with the protonation of an olefinic carbon atom in the hydrolysis of oxanorbornenone, although the entropies of activation, -32 and -28 J K⁻¹ mol⁻¹, for the hydrolysis of oxanorbornenone and for the rate-determining protonation of the carbon double bond of norbornenone¹⁰ are almost equal. The enthalpies of activation, 107 and 110 kJ mol⁻¹,¹⁰ respectively, are also close to each other.

Clear differences between oxanorbornenone and norbornenone can, however, be found in the slopes of the linear correlations $\log k_\psi$ vs. H_0 , $\log k_\psi + H_0$ vs. $H_0 + \log c(\text{H}^+)$ (the Bunnett–Olsen plot) and $\log [k_\psi/c(\text{H}^+)]$ vs. X_0 (an excess acidity plot).^{16–18} The slopes for oxanorbornenone are -0.77 , 0.25 and 0.85 , respectively, and the corresponding slopes for norbornenone are -1.04 , -0.06 and 1.31 .¹⁰ The latter values are typical of the hydration of the double bond in norbornenes.¹⁹ The clearest contrast is observed between the kinetic solvent deuterium isotope effects. The ratio $k_{\text{H}}/k_{\text{D}}$ is 0.34 for oxanorbornenone and 1.27 for norbornenone,¹⁰ while typical values for the protonation of 5-substituted norbornenes are from 1.1 to 2.4.¹⁹

It is also difficult to explain the formation of the main (ca. 80%) hydrolysis product of oxanorbornenone, 1,2-dihydroxybenzene (catechol **5**, see Experimental section), through the protonation of the carbon double bond. However, its formation through the protonation of the bridge oxygen atom is quite easy to imagine (Scheme 1). The ether oxygen atom is evidently much more basic ($\text{p}K_{\text{a}} = -2.80$ for 7-oxanorbornane) than the carbonyl oxygen atom ($\text{p}K_{\text{a}}$

Table 1. Disappearance rate constants for 7-oxabicyclo[2.2.1]hept-2-en-5-one in aqueous perchloric acid at different temperatures and acid concentrations as well as activation parameters and solvent deuterium isotope effect at 348 K and slopes for the following linear correlations: $\log k_\psi$ vs. H_0 (slope₁); $\log k_\psi + H_0$ vs. $\log a(\text{H}_2\text{O})$ (w); $\log k_\psi + H_0$ vs. $\log c(\text{H}^+) + H_0$ (Φ); $\log(k_\psi/c_{\text{H}^+})$ vs. X_0 (m_1); and $\log(k_\psi/c_{\text{H}^+}) - \log a(\text{H}_2\text{O})$ vs. X_0 (m_2) (r = correlation coefficient).

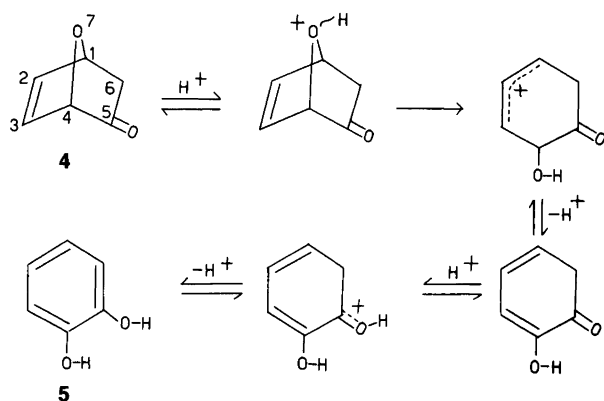
T/K	$c(\text{HClO}_4)/\text{mol dm}^{-3}$	$k_\psi/10^{-6} \text{ s}^{-1}$	Kinetic parameters
328.2	6.97	8.55(20)	
338.2	6.97	27.0(8)	
348.2	6.97	83.7(30)	$\Delta H^\ddagger = 107.1(10) \text{ kJ mol}^{-1}$
348.2	6.97	84.1(20) ^a	$\Delta S^\ddagger = -32(3) \text{ J K}^{-1} \text{ mol}^{-1}$
348.2	7.03	292(10) ^b	$k_{\text{H}}/k_{\text{D}} = 0.34(2)$
358.2	6.97	245(6)	
348.2	4.97	11.1(2)	
348.2	5.49	17.5(4)	
348.2	6.08	34.8(10)	Slope ₁ = $-0.77(2)$ ($r = -0.998$) ^c
348.2	6.37	43.4(9)	$w = 0.83(8)$ ($r = 0.966$) ^d
348.2	6.97	83.7(30)	$\Phi = 0.25(2)$ ($r = 0.980$) ^c
348.2	7.43	156(4)	$m_1 = 0.85(2)$ ($r = 0.998$) ^e
348.2	7.90	265(9)	$m_2 = 1.01(2)$ ($r = 0.998$) ^{d,e}
348.2	7.91	308(6)	
348.2	8.48	711(10)	
348.2	8.56	702(30)	

^aCalculated from the activation parameters. ^bMeasured in $\text{DClO}_4(\text{D}_2\text{O})$. ^c H_0 values at 298 K.^{18a} ^dActivities of water at 298 K.^{18a} ^eExcess acidities, X_0 , are corrected¹⁷ to 348 K from values at 298 K.^{18b}

= -6.8 , -7.5 and -9.5 for cyclohexanone, -pentanone and -butanone, respectively).²⁰

The protonation of the bridge oxygen atom may occur either at the fast equilibrium or at the rate-determining stage. The low isotope effect accords only with the former possibility.²¹ After the pre-equilibrium protonation, either the C(1)–O(7) or the C(4)–O(7) bond can be broken. The former case is more probable, because the developing positive charge would be more destabilized at C(4), next to the carbonyl group, than at C(1). The formation of 1,2-dihydroxybenzene (5) also supports the rupture of the C(1)–O(7) bond (Scheme 1), because the rupture of the C(4)–O(7) bond would evidently produce 1,3- and/or 1,4-dihydroxybenzene(s).

The kinetic solvent deuterium isotope effect of a hydrolysis reaction started by the pre-equilibrium protonation of



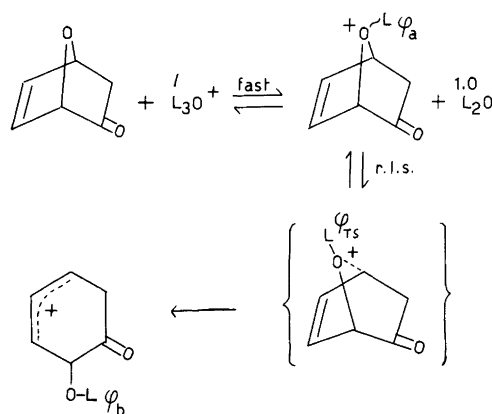
Scheme 1.

the ether oxygen atom can be estimated from the fractionation factors of exchangeable hydrogens.²¹ In the case of unimolecular rupture (A-1 mechanism, Scheme 2) $k_{\text{H}}/k_{\text{D}}$ can be expressed by eqn. (1), where $\varphi_a \leq \varphi_{\text{TS}} \leq \varphi_b$, i.e.

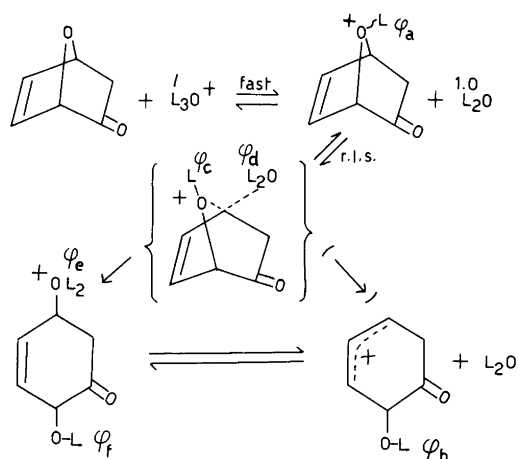
$$k_{\text{H}}/k_{\text{D}} = f^3/\varphi_{\text{TS}} \quad (1)$$

$0.72 \leq \varphi_{\text{TS}} \leq 1.0$. [0.72 is the fractionation factor of the hydronium ion, L_3O^+ ($\text{L} = \text{H}$ or D), at 348 K and 1.00 is that of water in aqueous solutions.]²² Thus the isotope effect takes a value between 0.37 and 0.52, which is in satisfactory agreement with the experimental value of 0.34. In the bimolecular rupture (A-2 mechanism, Scheme 3), an isotope effect can be estimated from eqn. (2), where $\varphi_a \leq$

$$k_{\text{H}}/k_{\text{D}} = f^3/(\varphi_c\varphi_d^2) \quad (2)$$



Scheme 2.



Scheme 3.

$\varphi_c \leq \varphi_f$ and $\varphi_{L2O} \geq \varphi_d \geq \varphi_e$ (the former limits refer to an early transition state and the latter limits to a late transition state), i.e. $0.72 \leq \varphi_c \leq 1.0$ and $1.0 \geq \varphi_d \geq 0.72$. Thus the isotope effect has limits from 0.52 to 0.72 which are markedly higher than the experimental value, 0.34. Partial protonation of the carbonyl oxygen in the transition state can, however, reduce the estimated limits considerably. Briefly, the kinetic deuterium isotope effect supports the unimolecular mechanism, but does not totally eliminate the possibility of the bimolecular mechanism, which is in agreement with the negative entropy of activation.

The observed slope ($w = 0.83$) of the roughly linear Bunnett plot, $\log k_\psi + H_0$ vs. $\log a_w$, where a_w is the activity of water, is between values typical of the unimolecular reaction (-2.5 to 0.0) and of the bimolecular reaction (1.2 – 3.3), but closer to the latter limits.¹⁵ The observed slope ($\Phi = 0.25$) of the satisfactorily linear Bunnett–Olsen plot, $\log k_\psi + H_0$ vs. $H_0 + \log c(H^+)$, is in agreement with the bimolecular reaction ($0.18 \leq \Phi \leq 0.47$) but not with the unimolecular reaction ($-0.34 \leq \Phi \leq 0$).¹⁶ Thus the acid-catalyzed hydrolysis of oxanorbornenone, or more correctly its hydrolytic isomerization (the molecular formulae of the substrate and the main product, catechol, are identical), has features typical of both the uni- and bimolecular mechanisms.

In principle, the contradiction should be solved by the excess acidity correlation [eqn. (3)],¹⁷ which is different

$$\begin{aligned} \log k_\psi - \log c(H^+) - \log [c_s/(c_s + c_{SH^+})](-\log a_w) \\ = m^*m^*X + \log(k_0/K_{SH^+}) \end{aligned} \quad (3)$$

for the unimolecular mechanism (in this case the term $\log a_w$ is excluded) and the bimolecular mechanism (in this case it is included). A correction term $\log [c_s/(c_s + c_{SH^+})]$, which is due to the partial protonation of the substrate (S), can be estimated from eqn. (4)¹⁷ by employing the pK_{SH^+} value of 7-oxanorbornane (-2.80)²⁰ and taking the value

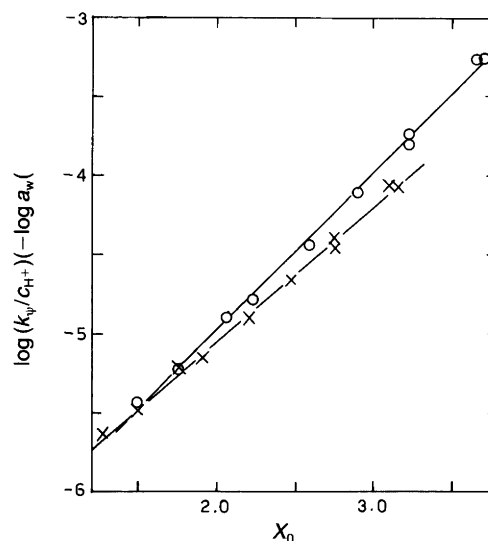


Fig. 1. Excess acidity plots for the hydrolysis of 7-oxabicyclo[2.2.1]hept-2-en-5-one in $HClO_4(aq)$ at 348.2 K with inclusion (O, c_{H^+} , X_0 and a_w values at 298.2 K) and exclusion (x, all values at 348.2 K) of the activity of water [eqn. (3)].

$$\log (c_{SH^+}/c_s) - \log c_{H^+} = m^*X + pK_{SH^+} \quad (4)$$

of m^* as 0.6–1.0,²³ but its inclusion makes the linearity of eqn. (3) a little worse (e.g. $r = 0.996$ and slope $m^*m^* = 1.55 \pm 0.05$ if $m^* = 1.0$). Therefore the correction term is eliminated. The inclusion of the term $\log a_w$, when $m^*m^* = m_2 = 1.01$ and $r = 0.998$, or its exclusion, when $m^*m^* = m_1 = 0.85$ and $r = 0.998$, has no noticeable effect on the linearity of the correlation [eqn. (3) and Fig. 2] and thus does not solve the problem of the molecularity of the reaction. The reason is evidently the rather linear correlation ($r = 0.997$) between X_0 and $\log a_w$ within the narrow limits of acid concentrations used.

According to the product analysis (Experimental section), the amount of the main product, 1,2-dihydroxybenzene, is ca. 80% (maximum). Thus it is possible that part of the reaction occurs through the protonation of the carbon double bond (Ad_{E2} mechanism), although this is not very probable owing to the observed disappearance rate ratio of oxanorbornenone and norbornenone as well as the measured isotope effect (see above). This reaction might produce decomposed compounds^{11,24} which are very water soluble. The degree of protonation of an olefinic carbon atom should increase at higher acid concentrations, because the slope of $\log k_\psi$ vs. H_0 for this process is more negative (ca. -1)¹⁰ than that for the reaction via protonation of the oxygen bridge (ca. -0.77 , Table 1). However, such an increase was not observed in 5, 7 and 8.5 mol dm^{-3} acids (Experimental section). An attempt to correct eqn. (3) by subtracting the estimated $k(Ad_{E2})$ values (fixed at 0.20 k_ψ in 7 mol dm^{-3} acid) from the k_ψ values also made the excess acidity correlation a little worse ($r = 0.997$ and $m^*m^* = 0.76 \pm 0.02$). Thus the portion of the reaction that takes

place through the protonation of the carbon double bond seems to be insignificant.

In summary, the acid-catalyzed hydrolytic isomerization of 7-oxa-5-oxo-2-bicyclo[2.2.1]heptene (**4**) mainly takes place through the pre-equilibrium protonation of the oxygen bridge followed by the rate-limiting rupture of the C(1)–O(7) bond and finally produces 1,2-dihydroxybenzene. The reaction has both unimolecular and bimolecular features. Thus, if a water molecule attacks the protonated substrate, it or some other water molecule must be eliminated at a later stage. Such a reaction, with uni- and bimolecular characteristics is, however, not unique: the hydrolyses of epoxides and trimethyleneoxides have similar features.²⁵ The role of the water molecule in these reactions evidently lies between that of a specific solvation agent and a nucleophilic reagent, to a degree which depends on the substrate and has an effect on the kinetic parameters.

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