Mesoionic Compounds. Part 6.[1] Acid-catalysed Hydrolysis of Alkyloxatriazoles

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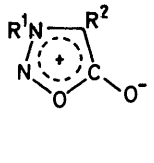
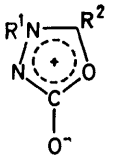
The acid-catalysed hydrolyses of isopropyl- and methyloxatriazole have been studied in aqueous solutions of mineral acids at 120 °C. Analyses of the data by Bunnett and Bunnet–Olsen criteria, solvent deuterium isotope effects and entropies of activation are consistent with an *A*-1 mechanism for the hydrolysis of isopropyloxatriazole. On the other hand the hydrolysis of methyloxatriazole involves a rate-determining proton-transfer mechanism.

THE mechanisms of the acid-catalysed ring-opening of mesoionic sydnones (1) and isosydnones (2) have been studied extensively,[1-5] whereas in contrast very little is known about the acid-catalysed decomposition of the related oxatriazole system (3). Quilico reported [6] that



(1)



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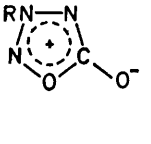


(3)

the products of hydrolysis of phenyloxatriazole (3; R = Ph) in concentrated sulphuric acid are phenyl azide and carbon dioxide, whereas Boyer and Hernandez observed [7] that cyclohexyloxatriazole (3; R = C_6H_{11}) was resistant to dilute sulphuric acid but decomposed in concentrated acid to form cyclohexanol, carbon dioxide, and hydrogen azide. The behaviour of oxatriazoles in strong acid is in sharp contrast to that of the isosteric sydnones which are converted into the corresponding alkyl or aryl hydrazides.

In a preliminary investigation of the acid-catalysed hydrolysis of isopropyloxatriazole, it was found [8] that even in 5.0 molar sulphuric acid at 60 °C, hydrolysis is barely detectable. Above 7.0 molar acid concentration, however, the rate of hydrolysis increases rapidly and the effect of added acids was examined over the range 7.0—10.0 molar. The experimental data are considered to be consistent with an *A*-1 mechanism.

For some acid-catalysed reactions, particularly those involving the hydrolyses of esters, various examples have been reported of a change in mechanism occurring on changing from low to high acid concentration.[9] In order to eliminate this possibility for isopropyloxatriazole we have studied its acid-catalysed hydrolysis at a temperature (120 °C) sufficiently high to permit kinetic measurements in the 1.0—5.0 molar acid concentration range. We have also studied the effect of added acids in aqueous solution on the hydrolysis of methyloxatriazole.

EXPERIMENTAL

Materials.—Methyloxatriazole (3; R = Me) prepared by the method of Hashimoto and Ohta [10] had b.p. 98 °C/1.0 mmHg (lit.,[10] 101/3 mmHg); mass spectrum, *m/e* 129, 105, 99, 56, 44; i.r. 1 800 cm^{-1} (broad). Isopropyloxatriazole (3; R = Pr^i) was prepared by the method of Boyer and Canter [11] and had b.p. 63 °C/0.5 mmHg (lit.,[11] b.p. 60—61.5 °C at 0.45—0.50 mmHg); mass spectrum, *m/e* 101, 91, 77, 71, 63, 58, 44; i.r. 1 800 cm^{-1} (broad).

Kinetic Measurements.—The rates of hydrolysis were determined spectrophotometrically at 255 nm with a Unicam S.P. 500 spectrophotometer using a sealed-ampoule technique. Values of the first-order rate coefficient, k_1 were calculated for each run from the standard equation and are shown in Tables 1 and 2.

TABLE 1

Hydrolysis of isopropyloxatriazole (k_1 in min^{-1}) in water

(a) Effect of added acids at 120 °C

$[HClO_4]$/M	0.918	1.84	2.75	3.63	4.50
10^4k_1	27.9	63.7	164	672	2 052
$[H_2SO_4]$/M	0.922	1.84 [a]	2.77	3.68 [b]	4.60
10^4k_1	24.3	73.7	166	365	798
[HCl]/M	0.927	1.85	2.78	3.71	4.63
10^4k_1	25.4	63.2	144	335	444

(b) Effect of added sulphuric acid (2.00M) at different temperatures

t/°C	105	110	115	120	125
10^4k_1	12.8	24.9	43.6	73.7	125

[a] In D_2O, 10^4k_1 = 135. [b] In D_2O, 10^4k_1 = 811.

TABLE 2

Hydrolysis of methyloxatriazole (k_1 in min^{-1}) in water

(a) Effect of added acids at 120 °C

$[HClO_4]$/M	0.918	1.84	2.75	3.63	4.50
10^4k_1	1.81	2.23	3.81	4.02	5.34
$[HClO_4]$/M	5.40	6.30	7.20	8.10	9.00
10^4k_1	6.46	7.53	8.00	8.05	9.54
$[H_2SO_4]$/M	0.922	1.84	2.77	3.68	4.60
10^4k_1	2.51	4.25	6.57	8.61	10.3
$[H_2SO_4]$/M	5.50	6.40	7.29	9.06	
10^4k_1	12.6	12.8	16.3	18.6	
[HCl]/M	0.927	1.85	2.78	3.71	4.63
10^4k_1	2.65	4.46	7.29	10.2	12.8
[HCl]/M	5.54	6.46	7.38	8.29	9.20
10^4k_1	16.2	18.7	22.2	27.2	30.5

(b) Effect of added sulphuric acid (3.00M) at different temperatures

t/°C	105	110	115	120	125
10^4k_1	1.67	2.41	3.90	6.57	10.6

(c) Kinetic solvent isotope effect at 120 °C

Solvent	Catalyst	10^4k_1	$k_1(D_2O)/k_1(H_2O)$
H_2O	1.85M-H_2SO_4	4.25	
D_2O	1.85M-D_2SO_4	3.73	0.88
H_2O	2.77M-H_2SO_4	6.57	
D_2O	2.77M-D_2SO_4	5.56	0.85
H_2O	4.60M-H_2SO_4	10.3	
D_2O	4.60M-D_2SO_4	9.28	0.90
H_2O	0.927M-HCl	2.65	
D_2O	0.927M-DCl	2.14	0.81
H_2O	1.85M-HCl	7.29	
D_2O	1.85M-DCl	6.64	0.91

Influence of Temperature.—The entropy ($\Delta S^{\ddagger}$) and enthalpy ($\Delta H^{\ddagger}$) of activation were calculated from the equation $k = (kT/h)\exp(\Delta S^{\ddagger}/R)\ \exp(-\Delta H^{\ddagger}/RT)$ by a least-squares procedure. The values obtained for the hydrolyses of isopropyl- and methyl-oxatriazoles were $\Delta S^{\ddagger} = +23.0 \pm 8$ and -61.0 ± 12 J K^{-1} mol^{-1} (calculated at 120 °C) and $\Delta H^{\ddagger} = 137 \pm 3$ and 114 ± 5 J kmol^{-1}.

Correction for Thermal Expansion.—This was determined for a range of acid concentrations using a precision bore capillary tube which was partly filled at room temperature and then immersed in a glass-sided thermostat. The increase in volume with increase in temperature was monitored with a cathetometer. The corrected values of acid concentrations are shown in Table 3.

TABLE 3

Acid concentrations at 120 °C corrected for thermal expansion

$[H^+]^{25\ °C}$	[HCl]	$[H_2SO_4]$	$[HClO_4]$
0.962	0.927	0.922	0.918
1.92	1.85	1.84	1.84
2.89	2.78	2.77	2.75
3.85	3.71	3.68	3.63
4.81	4.62	4.59	4.50
5.77	5.54	5.49	5.40
6.73	6.46	6.40	6.30
7.69	7.38	7.29	7.20
8.65	8.29	8.18	8.10
9.61	9.20	9.06	8.99

TABLE 4

Extrapolated values of H_0 in H_2SO_4 at high temperature

H_2SO_4 (%)	$[H^+]^{25\ °C}$/M	25 °C [a]	100 °C	125 °C
5	0.520	+0.08	+0.18	+0.18
10	1.085	−0.35	−0.21	−0.09
15	1.685	−0.69	−0.47	−0.27
20	2.32	−1.06	−0.78	−0.55
25	3.00	−1.36	−1.05	−0.77
30	3.75	−1.73	−1.39	−1.17
35	4.49	−2.05	−1.68	−1.43
40	5.31	−2.42	−1.98	−1.67
45	6.18	−2.83	−2.34	−2.03
50	7.11	−3.30	−2.72	−2.37
55	8.10	−3.77	−3.13	−2.80
60	9.16	−4.37	−3.59	−3.22

[a] Data from ref. 12.

DISCUSSION

Isopropyloxatriazole.—Before attempting to analyse the kinetic data obtained, the acid concentrations used were corrected for thermal expansion of the reaction solutions from room to reaction temperature as shown in Table 3. It is rather surprising to note that the effective acid concentration decreases by only *ca.* 5% as the temperature is raised from 20 to 120 °C. The first-order rate-coefficients, k_1, for acid hydrolysis are shown in Tables 1 and 2 with the corrected acid concentrations.

The Proton Transfer.—The values obtained (Table 1) for the deuterium kinetic solvent isotope effect $[k_1(D_2O)/k_1(H_2O)]$ for the hydrolysis of isopropyloxatriazole at 120 °C catalysed by 3.68M-sulphuric acid (2.22) and 1.77M-sulphuric acid (1.83) are somewhat higher than those obtained for perchloric acid at 60 °C (1.42).[8] Such values are characteristic of reactions which proceed *via* specific hydrogen ion catalysis.[13]

Rate Dependence on Acidity.—Plots of log k_1 *versus* $-H_0$ gave quite good straight-line Hammett slopes near unity of 1.21, 0.91, and 0.82 for perchloric, hydrochloric, and sulphuric acid respectively. For these correlations, values of H_0 determined at 25 °C were used (H_0 values at 25 °C) whilst the reactions were carried out at 120 °C and this might affect the value of the Hammett slopes. Rather few studies of the variation of H_0 with temperature have been reported. Johnson, Katritzky, and Shapiro [12] determined the value of the H_0 scale in aqueous sulphuric acid solution using primary nitroaniline indicators over a temperature range of 25—90 °C, and were able to establish empirical relationships between H_0 and temperature. We have extrapolated their data to provide values of H_0 at 100 and 120 °C (Table 4). The plot of log k_1 *versus* $-H_0$ for sulphuric acid using this extrapolated data has a slightly higher slope (0.93), with some curvature, than that obtained with un corrected values of H_0. Both slopes are consistent with an *A*-1 mechanism.

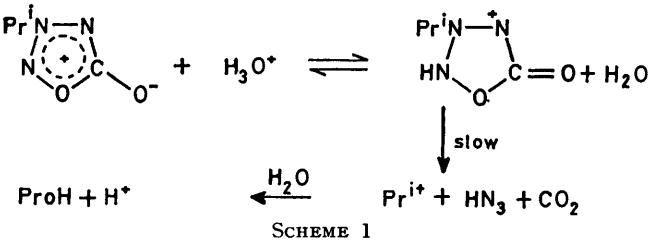
Bunnett's earlier classification of reactions in strong acid media [14] involves a plot of log $k_1 + H_0$ *versus* log a_W. The application of this criterion to kinetic data obtained at high temperature runs into a similar difficulty to that encountered with the Hammett correlation, namely that most of the available values of a_W for strong acids have been determined at room temperature or thereabouts.[14] Studies of the variation of a_W over only limited temperature ranges have been reported for sulphuric [15] and hydrochloric acids,[16] If H_0 values for 25 °C are used, the Bunnett plots give generally rather poor correlations for sulphuric and hydrochloric acids with slopes of around 2.0 with some scatter, whilst the data for perchloric acid are too random to be meaningful. The plot of log $k_1 + H_0$ *versus* log a_W for sulphuric acid using extrapolated H_0 values again gives a rather poor straight line correlation of slope of approximately 0.8.

For some acid-catalysed reactions plots of log k_1 − log $[H^+]$ *versus* log a_W show less scatter than the corresponding *w* plots. This is also the case for the hydrolysis of isopropyloxatriazole for which the following *w** values were obtained: perchloric acid, −7.8, sulphuric acid, −4.8, and hydrochloric acid, −5.0.

The Bunnett–Olsen free-energy approach [17] is particularly susceptible to changes in H_0 with temperature and a plot of log $k_1 + H_0$ *versus* H_0 + log $[H^+]$ for sulphuric acid using extrapolated H_0 values is rather scattered and gives a value of ϕ of approximately 0.1.

Perhaps the most striking feature of the effect of different acids on the hydrolysis of isopropyloxatriazole (Table 1) is the order of effectiveness of added acids, *viz.* $HClO_4 > H_2SO_4 > HCl$. Bunton and his co-workers have suggested that such an order of reactivity is characteristic of *A*-1 reactions and that the transition states of such reactions are preferentially stabilized by anions of low charge density.[18] The value of the entropy of activation calculated for 2.00M-sulphuric acid ($\Delta S^{\ddagger} = +18.8$ J K^{-1} mol^{-1}) is similar to that calculated for hydrolysis at 60 °C ($\Delta S^{\ddagger} = +10.5$ J K^{-1} mol^{-1}) and is also consistent with an *A*-1 mechanism.[19]

The majority of the evidence available therefore suggests that the acid-catalysed hydrolysis of isopropyloxatriazole follows an *A*-1 mechanism in both 1—5.0 molar acid at 120 °C and 7.0—10.0 molar at 60 °C. In the absence of any direct evidence, it is assumed that protonation occurs on N-2 as has been assumed for the acid-catalysed hydrolyses of 3-alkylsydnones.[20] One possible reaction sequence is shown in Scheme 1.



SCHEME 1

Consistent with the proposed mechanism, the major products of hydrolysis in the presence of hydrochloric acid were found to be isopropyl chloride and hydrazoic acid.

Methyloxatriazole.—The behaviour of methyloxatriazole in acid solution at 120 °C differs significantly from that observed for isopropyloxatriazole. Thus the order of effectiveness of added acids is $HCl > H_2SO_4 > HClO_4$ which is more consistent with a bimolecular rather than a unimolecular type of mechanism.[18] The value of the entropy of activation calculated for 3.0M-sulphuric acid ($\Delta S^{\ddagger} = -61.0$ J K^{-1} mol^{-1}) is much more negative than the value obtained for the hydrolysis of isopropyloxatriazole and is consistent with this view.

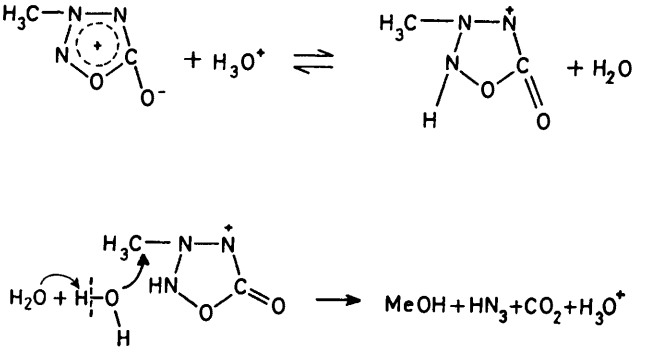
Rate Dependence on Acidity.—The first-order rate-coefficients of hydrolysis, k_1, for catalysis by all three acids used show a linear dependence on stoicheiometric acid concentration whereas the Hammett plots of log k_1 *versus* $-H_0$ are all curved. Use of extrapolated H_0 values at 120 °C has very little effect on the profile of the Hammett plot for hydrolysis in sulphuric acid.

Plots of log $k_1 + H_0$ *versus* log a_W using values of H_0 and a_W determined at room temperature give w values of hydrochloric acid, 4.85; sulphuric acid, 4.0 (using extrapolated H_0 values); and perchloric acid, 4.0. The correlation is less satisfactory for sulphuric and perchloric acid and is slightly curved. Such w values lie in the range said to be characteristic of water acting as a proton transfer agent.[14]

Plots of log k_1 — log $[H^+]$ *versus* log a_W give Bunnett w^* values of −0.29, 0.08, and 0.09 for hydrochloric, sulphuric, and perchloric acid respectively, with the perchloric acid plot showing considerable scatter. Such values are consistent with the mechanistic classification indicated by the Bunnett w values. This is also confirmed by the slopes, ϕ, of the Bunnett–Olsen plot, perchloric acid, 0.58; sulphuric acid, 0.88 (0.92 using extrapolated H_0 values) which gave quite satisfactory correlations.

The Proton Transfer.—The values obtained [Table 2(c)] for the deuterium kinetic solvent isotope effect $k_1(D_2O)/k_1(H_2O)$ (KSIE) for both hydrochloric and sulphuric acid at various acid concentrations lie in the range 0.81—0.91, which is normally associated with a rate-determining proton transfer. It is noteworthy that values of the KSIE previously reported [1-5] for the acid-catalysed hydrolyses of the related sydnones and isosydnones and in this work for isopropyloxatriazole are all greater than unity whether hydrolysis occurs *via* an *A*-1, *A*-2, or nucleophilic catalysis mechanism.

It would be anticipated by analogy with 3-methylsydnone that the hydrolysis of methyloxatriazole should proceed *via* an *A*-2 mechanism involving nucleophilic attack by water on the protonated substrate. Examples are known of *A*-2 reactions for which values of the KSIE are less than unity, *e.g.* for the hydrolysis of amides and related compounds in moderately concentrated acid solution.[21,22] Considered together, however, the KSIE values and the Bunnett kinetic correlations suggest some form of modified *A*-2 mechanism for the hydrolysis of methyloxatriazole. One possible scheme involves a general base-catalysed nucleophilic attack of water on the conjugate acid of the oxatriazole (Scheme 2)



SCHEME 2

as proposed for the hydrolysis of *NN*[1]-diphenylformamidine.[14]

It is of interest to note that in contrast to the behaviour of methyl- and isopropyl-oxatriazole, it has been shown that [3] 3-methyl- and 3-isopropyl-sydnone are both hydrolysed in acid solution by the same (*A*-2) mechanism.

[7/2240 *Received*, 21*st December*, 1977]

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