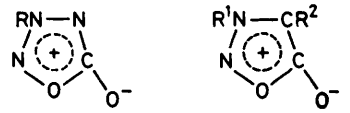
Mesoionic Compounds. Part 7.[1] Acid Catalysed Hydrolysis of Ethyloxatriazole

By **Zainuddin Said** and **John G. Tillett,*** Chemistry Department, University of Essex, Colchester CO4 3SQ

The acid catalysed hydrolysis of ethyloxatriazole has been studied in aqueous solutions of mineral acids at 120 °C. Analyses of the data by Bunnett and Bunnett–Olsen criteria and entropies of activation are consistent with a gradual change-over from an *A*-2 mechanism at low acid concentration to a predominantly *A*-1 mechanism at high acidities. Values of the kinetic solvent isotope effect indicate the involvement of a modified *A*-2 mechanism in which a proton transfer is partially rate determining.

BOYER and HERNANDEZ established that alkyloxatriazoles decompose in concentrated sulphuric acid to form the corresponding alcohol, carbon dioxide, and hydrogen azide.[2] Previous studies of the acid catalysed hydrolysis of methyl- and isopropyl-oxatriazole (1; R = Me or Pr^i) have shown that whereas the latter compound undergoes ring-opening by an *A*-1 mechanism, methyloxatriazole hydrolyses by an *A*-2 mechanism in which proton transfer is probably partially rate determining.[2,3]



(1) (2)

Such behaviour is significantly different to that observed for the hydrolysis of 3-alkylsydnones (2; R^1 = alkyl; R^2 = H) for which the mechanistic changeover occurs later in the alkyl series. Thus both 3-methyl- and 3-isopropyl-sydnone were shown to hydrolyse by an *A*-2 mechanism (with concurrent nucleophilic catalysis) whereas 3-t-butyl- and 3-furfuryl-sydnones are hydrolysed by the corresponding unimolecular mechanism.[4]

In order to determine more precisely the mechanistic cross-over point for the hydrolysis of alkyloxatriazoles we have examined the effect of added acids on the hydrolysis of ethyloxatriazole. Of particular interest at the present time is the demonstration by Yates and his co-workers that for some acid catalysed reactions such as the hydrolysis of esters a changeover of mechanism occurs on changing from a low to a high concentration of acid.[5] The possibility of such an occurrence in the hydrolysis of ethyl oxatriazole has been investigated by extending the kinetic study to very high concentrations of mineral acids.

In previous work we have shown that the values of the deuterium kinetic solvent isotope effect (k.s.i.e.) [$k_1(D_2O)/k_1(H_2O)$ in the range 1.83—2.22] are entirely consistent with the assumed *A*-1 mechanism for the hydrolysis of isopropyloxatriazole. The values obtained for the hydrolysis of methyloxatriazole, however (0.81—0.91) suggest that proton transfer may be partially rate-determining. The deuterium k.s.i.e. for the hydrolysis of ethyloxatriazole has been studied at a number of different acid concentrations for both hydrochloric and sulphuric acid to determine whether this low isotope value is a general characteristic of the hydrolysis of oxatriazoles with primary alkyl group substituents.

EXPERIMENTAL

Materials.—Ethylhydrazine prepared by Condon and Thakkar's modified version [6] of Fisher's original synthesis [7] had b.p. 99—103 °C (lit., b.p. 99—103°). Ethyloxatriazole prepared from ethylhydrazine by the method of Hashimoto and Ohta [8] (yield 38%; solvent chloroform) had b.p. 110—112 °C and 1.5 mmHg, *m/e* 115, 106, 91, 71, 58, and 44, $\nu_{max.}$ 1 780 cm^{-1}.

Kinetic Measurements.—The rates of hydrolysis were determined spectrophotometrically at 255 nm with a Unicam SP 500 spectrometer 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 Table 1. The concentration of acids used were corrected to allow for thermal expansion using data obtained earlier.[1]

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.

DISCUSSION

Rate Dependence on Acidity.—A plot of the variation of the first-order rate coefficient k_1 as a function of acid concentration is shown in Figure 1. At acid concentrations in the range 0—8 mol dm^{-3} the catalytic effect of acids decreases in the order HCl > H_2SO_4 > $HClO_4$. The rates of hydrolysis catalysed by perchloric acid are *ca.* 1.5—1.9 times slower, compared at equal molarities of acid, than the corresponding rates for sulphuric acid as a catalyst. A similar difference between the catalytic effects of perchloric and sulphuric acid has been reported for the hydrolysis of methyl benzoate and ethyl acetate [9] and for phenyl and 4-nitrophenyl acetate,[10] and has been associated with an $A_{AC}2$ mechanism. At acid concentrations above 8 mol dm^{-3}, however, the rate of hydrolysis in perchloric acid begins to increase sharply and exceeds first that in sulphuric acid, then that in hydrochloric acid. At acidities above 9.0 mol dm^{-3}, the catalytic effectiveness of the acids decreases in the sequence: $HClO_4$ > HCl ~ H_2SO_4, the reverse of that observed at low acidities. Bunton and his co-workers have suggested that such an order is associated with a unimolecular mechanism, transition states of carbo

cationic character being preferentially stabilised by anion of low change density such as ClO_4^-, whereas the converse is the case for *A*-2 reactions.[9] The kinetic behaviour of the hydrolysis of ethyloxatriazole in concentrated acidic solutions suggests, therefore, that there is a gradual changeover in mechanism from a bimolecular to a unimolecular mechanism at higher acidities.

Application of the simple Zucker–Hammett treatment[11] leads to the same view. Plots of log k_1 *versus* $-H_0$, where H_0 is the Hammett acidity function for aqueous acids, are curved for the acid concentration range 0—8 mol dm^{-3} but at higher acidities such plots become linear with slopes in the range 0.5—0.6. One of the difficulties in the present study in using criteria which utilise H_0 values is the very large difference between the

TABLE 1

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

(a) Effect of added acids at 120 °C

[HCl]/M	0.951	1.90	2.85	3.80	4.74	5.69
10^4k_1	2.71	4.86	6.34	8.24	10.3	14.2
[HCl]/M	6.63	7.57	8.50	9.44	10.4	
10^4k_1	16.2	19.3	23.4	33.9	40.5	
[$HClO_4$]/M	0.942	1.88	2.35	2.82	3.72	4.61
10^4k_1	1.63	2.65	2.87	3.39	4.22	4.77
[$HClO_4$]/M	5.54	6.46	7.38	7.70	7.98	8.30
10^4k_1	5.99	7.73	8.92	9.74	10.7	13.7
[$HClO_4$]/M	8.54	8.77	9.23			
10^4k_1	15.9	23.0	32.0			
[H_2SO_4]/M	0.946	1.89	2.84	3.78	4.71	5.64
10^4k_1	2.15	3.81	6.61	8.05	9.31	11.1
[H_2SO_4]/M	6.56	7.48	8.39	8.84	9.29	9.74
10^4k_1	12.8	13.6	14.0	16.7	17.7	22.0
[H_2SO_4]/M	10.2	11.1	12.0	12.9		
10^4k_1	29.0	43.6	57.7	126		

(b) Effect of added acids at different temperatures

	T/°C					
Catalyst	105	110	115	120	125	130
2.85M–HCl		3.16	4.42	6.34	11.4	16.3
9.44M–HCl		13.6	21.6		57.5	85.2
2.82M–$HClO_4$		1.47	2.49	3.39	6.59	9.96
8.77M–$HClO_4$	5.05	8.22	14.4	23.0	41.8	68.9
2.85M–H_2SO_4	1.69	3.08	4.53	7.02	11.0	15.7
8.84M–H_2SO_4		7.20	14.5	16.6	29.6	47.9
11.1M–H_2SO_4		15.4	26.3	43.6	65.4	105

temperature at which the hydrolysis of ethyloxatriazole was studied (120 °C) and that for which the vast majority of H_0 data is available (25 °C). Very few detailed studies of the variation of H_0 with temperature have been reported. Katritzky and Johnson and their co-workers have, however, determined values of the H_0 scale in aqueous sulphuric acid using primary amine indicators over a temperature range of 25—90 °C.[12] In a previous study[1] we extrapolated this data to provide values of H_0 for sulphuric acid at 100 and 120 °C. The corrected data had very little effect on Hammett slopes and we have therefore in the present work used H_0 data at 25° for all the acids used. Bunnett and Olsen adopted a similar approach in a study of the acid catalysed hydrolysis of *o*-toluonitrile at 133 °C.[13]

Bunnett's earlier proposal for the classification of reactions in strong acid media involves a plot of (log $k_1 + H_0$) *versus* log a_w.[14] The use of this criterion in the present work runs into both the difficulty discussed above

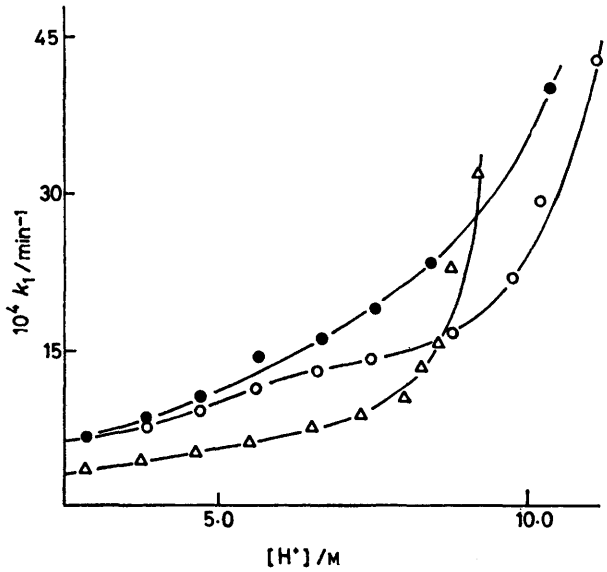


FIGURE 1 Plot of k, *versus* [H$^+$] for the hydrolyses of ethyloxatriazole at 120 °C in HCl, ●; H_2SO_4, ○; and $HClO_4$, △

as to what are the appropriate H_0 values and the related problem that most values of a_w in strong acids have been determined only at 25 °C. The Bunnett plots for the hydrolysis of ethyloxatriazole are shown in Figure 2. At low concentrations of acids (<4 mol dm^{-3}) a good linear correlation is obtained with slopes (*w* values) in the range 3.5—7.7 for all three acids used (see Table 2). Such values of *w* fall into the range normally associated with water acting as a proton transfer agent.

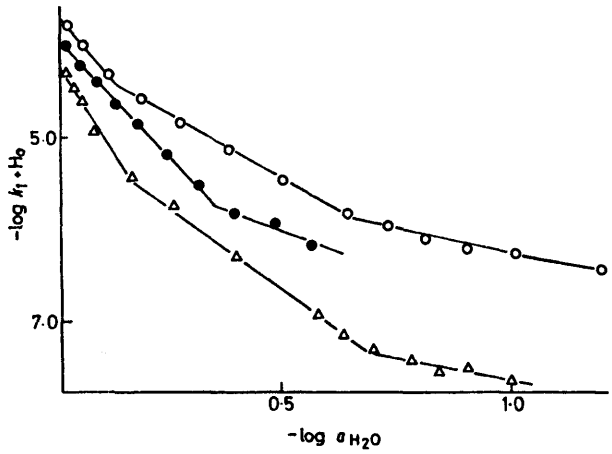


FIGURE 2 Bunnett *w* plot of log $k_1 + H_0$ *versus* log a_{H_2O} for the hydrolysis of ethyloxatriazole in HCl, ●; H_2SO_4, ○; and $HClO_4$, △

Similar values of *w* in the range 4.0—4.9 were obtained for the hydrolysis of methyloxatriazole in 0—9 mol dm^{-3} aqueous mineral acids for which a bimolecular mechanism was proposed.[1] For both perchloric and sul-

phuric acids at *ca.* 4.0 mol dm^{-3} a change of slope occurs in the Bunnett plot corresponding to an intermediate region with a lower value of w. No such behaviour is observed for hydrochloric acid. For all three acids at concentrations higher than 7.5—8.0 mol dm^{-3} the slope

TABLE 2

Analysis of rate data for the hydrolysis of ethyloxatriazole at 120 °C by use of Bunnett w and w^*, and Bunnett–Olsen linear free energy relationships at both ' high ' (>8 mol dm^{-3}) and ' low ' (<5 mol dm^{-3}) acidities

	Low [H$^+$]			High [H$^+$]		
	w	w^*	ϕ	w	w^*	ϕ
HCl	5.0	0.16	1.03	1.7	−0.61	0.79
H_2SO_4	3.5	0.31	1.05	1.1	−0.61	0.64
$HClO_4$	7.7	0.55	1.06	1.4	−1.23	0.66

of the plots of (log k_1 + H_0) *versus* $-H_0$ decrease further to limiting values in the range 1.1—1.8. The corresponding Bunnett plots for the acid-catalysed hydrolysis of isopropyloxatriazole for which an A-1 mechanism has been established showed considerable scatter and only very approximate w values of *ca.* 2 could be obtained. The values of w for the hydrolysis of ethyloxatriazole at high concentrations of acid are more in accord with these values than with those obtained for the hydrolysis of methyloxatriazole referred to above.

The plots of log k_1 − log [H$^+$] *versus* log a_w for the Bunnett w^* relationship (Figure 3) again show distinct changes in slope with increasing concentration of acid. At concentrations of acid < *ca.* 4.5 mol dm^{-3} the values of w^* fall in the range 0.16—0.55 (Table 2). As the concentration of acid increases, the slopes of the plots for all acids decrease to limiting values of w^* of −0.61, −0.61, and −1.23, for hydrochloric, sulphuric, and perchloric acid, respectively, the data for perchloric acid showing a distinct intermediate region. The values of w^* for the hydrolysis of ethyloxatriazole at ' low ' acidity are very similar to those obtained for the hydrolysis of methyl-

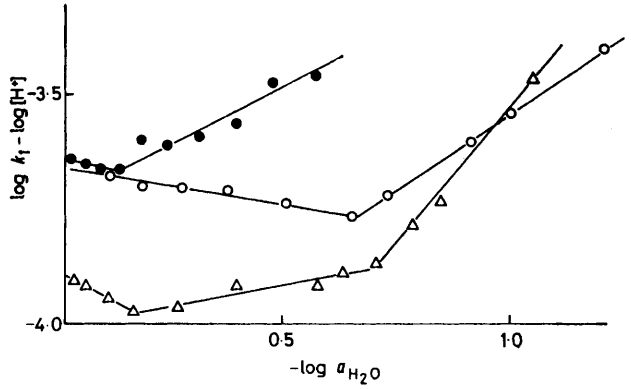


FIGURE 3 Plot of log k_1 − log [H$^+$] *versus* log a_{H_2O} for the hydrolysis of ethyloxatriazole in HCl, ●; H_2SO_4, ○; and $HClO_4$, △

oxatriazole (in the range −0.29 to 0.08) and those at higher acidities are beginning to approach those obtained for the hydrolysis of isopropyloxatriazole (*ca.* −5.0).

The Bunnett–Olsen free energy plot [15] of (log k_1 + H_0) *versus* (H_0 + log [H$^+$]) shows the same distinct regions as the Bunnett w and w^* plots. The slopes ϕ in the ' low ' acid region (*ca.* 1.0) are very similar in magnitude to those observed for the hydrolysis of methyloxatriazole (0.58—1.0). At high concentrations of acids these slopes decrease to limiting values in the range 0.66—0.79 (Table 2). It is not possible to compare these latter values with the data for isopropyloxatriazole for which the ϕ plots either show considerable scatter or no meaningful correlation. For the hydrolysis of a weakly basic substrate the value of ϕ obtained is a composite value, being the sum of ϕ_e and ϕ_r, the values for equilibrium protonation and for the rate-determining step, respectively. In the absence of any protonation data we are unable to calculate values of ϕ_r and hence unable to make any detailed mechanistic deductions from the values of ϕ obtained in the present work.

Analysis of the kinetic data by the various criteria indicates that at relatively low concentrations of acid, the hydrolysis of ethyloxatriazole proceeds *via* a bimolecular mechanism in which a proton transfer may be partially rate determining, a point which we return to in the next section. At higher concentrations of acids there is a gradual changeover to a predominantly unimolecular mechanism. This conclusion is further substantiated by the Arrhenius parameters obtained for the hydrolysis of ethyloxatriazole in different acids (Table 3).

TABLE 3

Enthalpies and entropies of activation for the hydrolysis of ethyloxatriazole at different acid concentrations

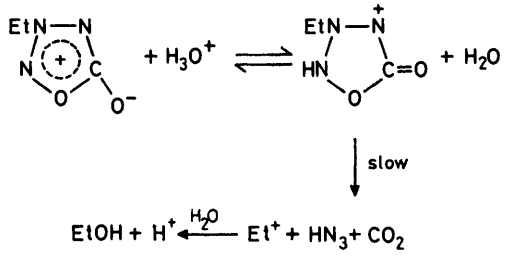
Acid	$\Delta H^{\ddagger}$/kJ mol^{-1}	$-\Delta S^{\ddagger *}$/JK^{-1} mol^{-1}
H_2SO_4, 1.89M	108 ± 3.3	74.9 ± 4.4
H_2SO_4, 9.29M	113 ± 8.8	64.8 ± 22
H_2SO_4, 11.1M	119 ± 2.1	45.6 ± 5.4
HCl, 2.85M	105 ± 5.4	82.8 ± 14
HCl, 9.44M	113 ± 4.2	52.3 ± 10
$HClO_4$, 2.82M	116 ± 4.2	61.4 ± 11
$HClO_4$, 9.23M	128 ± 2.9	24.3 ± 7.9

* Calculated at 120 °C.

The enthalpies of activation were found to be essentially independent of the nature or concentration of the acid used. The values of the entropies of activation $\Delta S^{\ddagger}$, however, showed a significant change. At low concentrations of acid (<3.0 mol dm^{-3}) values of $\Delta S^{\ddagger}$ in the range −61 to −83 J K^{-1} mol^{-1} were obtained. As the concentration of acid is increased, however, the values of $\Delta S^{\ddagger}$ become markedly less negative as expected for a changeover to a unimolecular mechanism.[16] Furthermore the values of $\Delta S^{\ddagger}$ confirm that a change in mechanism occurs at a lower acid concentration with perchloric acid than with sulphuric or hydrochloric acid as catalyst. One possible reaction sequence for the A-1 mechanism of hydrolysis of ethyloxatriazole is shown in Scheme 1. 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.[17]

The Proton Transfer.—The values obtained for the deuterium k.s.i.e., $k(D_2O)/k(H_2O)$, for the hydrolysis of

ethyloxatriazole are shown in Table 4. The values for hydrolysis in various concentrations of hydrochloric acid lie in the range 1.13—1.23 which although consistent with specific hydrogen ion catalysis are atypically low for such reactions. The values in sulphuric acid (and the



SCHEME 1

single value obtained in perchloric acid) are all slightly less than unity and lie in the range 0.81—0.96 approaching unity at high concentrations of acid. Such values fall in the range normally associated with a rate-determining proton transfer. The values of the k.s.i.e. for the hydrolysis of methyloxatriazole in both sulphuric and hydrochloric acids also fall into this range. The consistently low values of the k.s.i.e.s for the hydrolysis of both methyl and ethyloxatriazoles and the Bunnett w and w^* parameters for these substrates suggest that some modified form of A-2 mechanism is involved in which a proton transfer is partially rate determining. One possible reaction scheme involves a general base catalysed nucleophilic attack of water on the conjugate acid of the oxatriazole (Scheme 2) as has been proposed for the hydrolysis of NN'-diphenylformamidine.[14] Such

TABLE 4

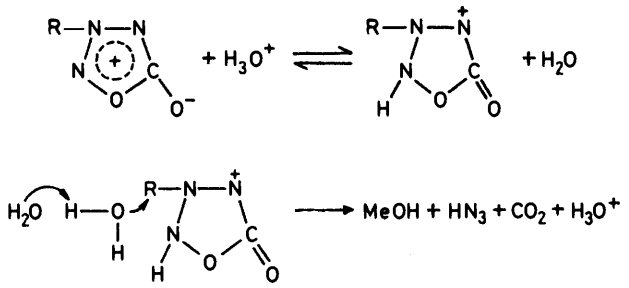
Kinetic solvent isotope effect for the hydrolysis of ethyloxatriazole at 120 °C

[HCl]/M	1.91	2.85	6.63	7.57	9.44
$10^4k_1(H_2O)$	4.36	6.34	16.2	19.3	33.9
$10^4k_1(D_2O)$	4.92	7.17	18.7	23.7	40.6
K.s.i.e.	1.13	1.13	1.15	1.23	1.20
$[H_2SO_4]$/M	1.89	2.84	7.48	11.1	†
$10^4k_1(H_2O)$	3.81	6.61	13.6	43.6	2.87
$10^4k_1(D_2O)$	3.09	5.42	13.1	41.2	2.20
K.s.i.e.	0.81	0.82	0.96	0.95	0.77

† In $DClO_4$, 2.35M.

a mechanism has been confirmed for the hydrolysis of the formamidine by the observation of general acid catalysis.[18]

Another anomaly appears to be the low value of the k.s.i.e. for the hydrolysis of ethyloxatriazole at high concentrations of acid where it is assumed that a predominantly A-1 mechanism operates. These values are in contrast to the ' normal ' values obtained (1.83—2.22) for the hydrolysis of isopropyloxatriazole by an A-1 mechanism. This suggests that perhaps proton transfers to methyl- and ethyl-oxatriazole are less rapid than to the more basic isopropyloxatriazole ring. It is of interest to note that the k.s.i.e. for the A-2 and A-1 mechanisms of hydrolysis in perchloric acid of the corresponding 3-alkylsydnones (2) lie in the ranges 1.25—1.5 and 1.60—1.73, respectively, values which although



SCHEME 2

greater than unity are lower than expected empirically for reactions of these types.[19] Further work is necessary to determine whether such typical isotope effects are a characteristic of these ring systems.

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