Mesoionic Compounds. Part 8.[1] Acid-catalysed Hydrolysis of Aryloxatriazoles

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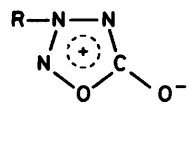
The acid-catalysed hydrolyses of some 3-(*para*-substituted phenyl)oxatriazoles have been studied in aqueous solutions of mineral acids at 120 °C. Analyses of the data by Bunnett, Bunnett–Olsen, and excess acidity criteria are consistent with a gradual changeover from an *A*-2 mechanism at low acid concentration to a predominantly *A*-1 mechanism at high acidities. Values of pK_{BH^+} of these compounds in sulphuric acid have been determined.

BOYER and HERNANDEZ established that alkyloxatriazoles decompose in concentrated sulphuric acid to form the corresponding alcohol, carbon dioxide, and hydrogen azide.[2] Kinetic studies have shown that isopropyloxatriazole (1; R = Pr^i) undergoes ring-opening by an *A*-1 mechanism, whereas methyloxatriazole (1; R = Me) undergoes acid-catalysed hydrolysis by an *A*-2 mechanism in which a proton transfer may be partially rate-limiting.[3,4] The acid-catalysed hydrolysis of ethyloxatriazole proceeds at low acidity *via* a similar modified *A*-2 mechanism to that proposed for the hydrolysis of methyloxatriazole, whereas at higher acidities there is a gradual changeover to a predominantly unimolecular mechanism.



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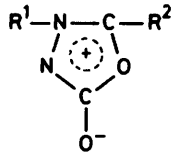

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In contrast to the behaviour of alkyloxatriazoles, Quilico reported that the products of hydrolysis of phenyloxatriazole (1; R = Ph) in concentrated sulphuric acid are phenyl azide and carbon dioxide.[5] In order to provide further evidence of the mechanism of decomposition of aryloxatriazoles in the presence of acids, we have examined the effect of added mineral acids on the rates of hydrolysis of a number of 3-(*para*-substituted phenyl)oxatriazoles and also the protonation behaviour of these compounds in sulphuric acid.

EXPERIMENTAL AND RESULTS

Materials.—Aryloxatriazoles were prepared by the reaction of arenediazonium salts with nitroform followed by cyclisation of the resulting product with glacial acetic acid as described by Quilico [5] and Ponzio.[6] 3-*p*-Nitrophenyloxatriazole after recrystallisation from methanol had m.p. 165° (pale yellow plates) (lit.,[5] 166°); 3-*p*-bromophenyloxatriazole after recrystallisation from ethanol had m.p. 145° (needles) (lit.,[5] 145°); 3-phenyloxatriazole after recrystallisation from aqueous methanol had m.p. 83—84° (pale yellow needles) (lit.,[6] 85°); 3-*p*-methoxyphenyloxatriazole (yield 34%) after recrystallisation from aqueous ethanol had m.p. 135—136° (needles) (lit.,[7] 138—139°) (Found: C, 50.3; H, 3.6; N, 22.2. Calc. for $C_8H_7N_3O_3$: C, 49.7; H, 3.6; N, 21.8%), $\lambda_{max.}$ 310 nm, $\nu_{max.}$ 1 790 cm^{-1}; 3-p-*tolyloxatriazole* (yield 36%) after recrystallisation from ethanol had m.p. 97—98° (needles) (Found: C, 54.0; H, 3.8; N, 23.7. $C_8H_7N_3O_2$ requires C, 54.2; H, 3.9; N, 23.7%), $\lambda_{max.}$ 280 nm, $\nu_{max.}$ 1 790 cm^{-1}.

TABLE 1

Hydrolysis of 3-(*p*-nitrophenyl)oxatriazole (k_1/min^{-1})

(a) Effect of added acids at 120°

[HCl]/M	0.964	1.93	2.89	3.85	4.81	5.77
10^4k_1	10.1	9.88	12.2	13.2	15.6	16.6
[HCl]/M	6.72	7.67	8.62	9.57	10.5	10.9
10^4k_1	19.4	25.5	28.9	36.7	44.4	46.9
$[H_2SO_4]$/M	0.959	1.92	2.88	3.83	4.78	5.72
10^4k_1	10.7	9.27	9.51	8.76	8.90	9.87
$[H_2SO_4]$/M	6.65	8.50	11.2	13.1	14.1	15.1
10^4k_1	11.7	12.7	15.0	16.8	21.5	41.7
$[HClO_4]$/M	0.955	1.91	2.86	3.78	4.70	5.64
10^4k_1	8.78	7.33	6.03	5.28	4.60	4.62
$[HClO_4]$/M	6.58	7.51	8.45	9.39	10.3	
10^4k_1	7.51	5.41	7.97	28.8	70.6	

(b) Effect of added salts on the 'spontaneous' reaction at 120°

$[NaHSO_4]$/M	0	1.00	2.00	3.00
10^4k_1	12.2	8.72	5.58	5.21

Kinetic Measurements.—The rates of hydrolysis were determined spectrophotometrically at 255 nm with a Unicam SP 500 spectrophotometer using a sealed ampoule technique. Reactions were followed for at least two half-lives and gave good first-order plots. Values of the first-order rate coefficient k_1 were calculated for each run from the standard equation and are shown in Tables 1—3. The concentrations of acids used were corrected to allow for thermal expansion using data obtained earlier.[4]

TABLE 2

Hydrolysis of 3-(*p*-bromophenyl)oxatriazole (k_1/min^{-1}) at 120°

[HCl]/M	0	0.964	1.93	2.89	3.85	4.81
10^4k_1	5.96	3.15	4.90	7.45	8.62	12.3
[HCl]/M	5.77	6.72	7.67	8.62	9.57	10.5
10^4k_1	15.1	18.4	20.2	21.3	25.0	34.4
$[H_2SO_4]_4$M	0.959	1.92	2.88	3.83	5.72	6.65
10^4k_1	2.87	4.48	4.60	5.88	6.32	7.25
$[H_2SO_4]$/M	7.58	8.50	9.42	11.2	13.1	15.1
10^4k_1	9.26	9.32	9.25	11.1	10.0	4.96
$[HClO_4]$/M	0.964	1.94	2.89	3.85	4.81	5.77
10^4k_1	2.00	4.51	5.48	8.37	10.7	12.7
$[HClO_4]$/M	6.72	7.67	8.62	9.57	10.5	
10^4k_1	15.3	17.6	19.5	21.1	26.1	

Influence of Temperature.—The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation (Table 4) were calculated

from the equation $k = (kT/h) \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT)$ by a least-squares procedure.

Protonation Equilibria.—The absorbances at a number of wavelengths between 190 and 230 nm were recorded at 25 ± 0.2° for the aryloxatriazoles at various concentrations of sulphuric acid at constant concentration of

TABLE 3

Hydrolysis of 3-(*p*-methoxyphenyl)oxatriazole (k_1/min^{-1})

(a) Effect of added acids at 120°

[HCl]/M	0.964	1.53	2.89	3.85	4.81	5.77
10^4k_1	1.82	3.79	4.95	5.83	6.20	7.38
[HCl]/M	6.72	7.67	8.62	9.57	10.5	
10^4k_1	13.3	17.8	21.2	30.9	44.0	
$[H_2SO_4]$/M	0.959	1.92	2.88	3.83	4.78	6.65
10^4k_1	3.34	4.74	7.13	11.7	10.7	13.3
$[H_2SO_4]$/M	7.58	8.50	9.42	11.2	13.1	15.1
10^4k_1	12.7	13.7	13.3	12.3	11.0	9.78
$[HClO_4]$/M	0.955	1.91	2.86	3.78	4.70	5.64
10^4k_1	3.25	5.18	7.19	9.25	8.03	6.61
$[HClO_4]$/M	6.58	7.51	8.45	4.39	10.3	
10^4k_1	8.44	9.51	17.3	57.5	76.4	

(b) Effect of added acids at different temperatures

	T/°				
Catalyst	110	115	120	125	130
1.93M-HCl	1.11	1.95	3.79	4.72	7.23
9.57M-HCl	9.13	18.4	30.9	58.5	
1.92M-H_2SO_4	2.11	3.16	4.74	8.75	14.6
9.42M-H_2SO_4	5.33		13.3	22.7	33.7
1.91M-$HClO_4$		3.28	5.18	8.81	15.1
9.39M-$HClO_4$	18.2	28.7	57.5	88.9	

oxatriazole. For 3-(*p*-bromophenyl)oxatriazole, values of the ionization ratio *I* (=[BH$^+$]/[B]) were determined from absorbance measurements at 305 nm from equation (1) where D_B is the absorption in a solution in which the base is

$$\log I = \log (D - D_{BH^+})/(D_B - D) \quad (1)$$

completely unprotonated, D_{BH^+} is the corresponding value where it is completely ionised, and *D* is the value in a solution of intermediate acidity. To overcome medium effects, the modification of Davis and Geissman's method [9]

TABLE 4

Arrhenius parameters for the hydrolysis of 3-(*p*-methoxyphenyl)oxatriazole at different acid concentrations

Acid	[Acid]/M	$\Delta H^{\ddagger}$/kJ mol^{-1}	$-\Delta S^{\ddagger *}$/ J K^{-1} mol^{-1}
H_2SO_4	1.92	122 ± 6.9	40.0 ± 17
H_2SO_4	9.42	116 ± 3.5	58.5 ± 8.9
$HClO_4$	1.91	129 ± 4.5	19.9 ± 11
$HClO_4$	9.39	135 ± 9.0	−0.21 ± 2.3
HCl	1.93	116 ± 4.1	59.7 ± 10
HCl	9.57	151 ± 5.4	37.1 ± 12

* Calculated at 120°.

as described by Stewart and Granger [10] was used to obtain the values of *I* for 3-(*p*-tolyl)-, 3-(*p*-methoxy)-, and 3-phenyl-oxatriazole. The wavelengths used were 270 and 310 nm, 300 and 325 nm, and 260 and 300 nm respectively. The changes in optical density with increased acidity for 3-(*p*-nitrophenyl)oxatriazole were found to be too small for accurate determination of the ionization ratio by the spectrophotometric method.

Product Analysis.—Hydrochloric acid (10 ml, 6.0M) was added to *p*-bromophenyl azide (0.6 g) in water (10 ml) and the homogeneous mixture refluxed at 100° (66 h). After cooling, the reaction mixture was filtered to remove tarry impurities (<0.1 g) and extracted with dichloromethane to give a liquid (0.25 g) which solidified on cooling to give 2-chloro-4-bromoaniline, m.p. 65°, identical with an authentic sample. Neutralisation of the acidic filtrate followed by extraction with ether gave a brown liquid (0.1 g) which was also predominantly 2-chloro-4-bromoaniline.

Hydrolysis of *p*-bromophenyloxatriazole (0.6 g) in hydrochloric acid (10 ml, 6.0M) at 110° (5 days) produced similar results to those observed for the corresponding azide. Extraction, as before, with dichloromethane and ether gave two dark brown oily residues (0.2 and 0.1 g, respectively). The crude extracts were purified by analytical t.l.c. on silica gel (eluant benzene). On the basis of their i.r., n.m.r., and mass spectra, the fractions were identified as containing *ca.* 60% and essentially pure 4-chloro-2-bromoaniline, respectively.

Because of low substrate solubility it was not possible to isolate the products from hydrolysis under homogeneous conditions at all acidities. Reaction solutions of oxatriazole (0.7—4 × 10^{-4}M) were heated for the time required for complete hydrolysis in solutions of hydrochloric and perchloric acid. The u.v. spectra agreed well with those obtained for the product of hydrolysis of *p*-bromophenyl azide under similar conditions.

DISCUSSION

Protonation Behaviour.—The protonation data were initially analysed using the free-energy approach of Bunnett and Olsen [11] [equation (2)]. Provided the plot

$$\log I + H_0 = \phi(H_0 + \log[H^+]) + pK_{BH^+} \quad (2)$$

of the left-hand side of equation (2) *versus* (H_0 + log[H$^+$]) is linear, thermodynamic quantities can be calculated because the intercept of the plot represents the value of pK_{BH^+} referred to infinite dilution in water as the standard state. The slope ϕ is a measure of the susceptibility of the equilibrium to changing acid concentration.

Yates and Cox have recently developed a computerised version of Marziano and Passerini's method [12] for the determination of basicities which does not involve the use of H_0 or H_A functions.[13] This treatment involves the use of ionization data for a large number of weak bases to establish a generalised acidity function for sulphuric acid (the so-called 'excess acidity' X). A plot of the protonation data for aryloxatriazoles according to equation (3)

$$\log I - \log [H^+] = m^*X + pK_{BH^+} \quad (3)$$

gives quite a good straight line correlation and values of pK_{BH^+} fairly similar to those obtained using the free-energy approach (Table 5).

Reaction Products.—Quilico previously reported that the products of hydrolysis of phenyloxatriazole in concentrated sulphuric acid are phenyl azide and carbon dioxide.[5] It is likely, under the conditions used for the present study, that any azide produced would itself decompose further. Griess [14] and Bamberger [15] showed that *para*-substituted aryl azides are converted by strong mineral acids into *ortho*-halogeno- or *ortho*-hydroxyanilines. Polymeric and other side-products were also

observed. More recent studies of the hydrogen halide-catalysed decomposition of 2-azidobiphenyls have given similar results.[16] We chose *p*-bromophenyloxatriazole as a typical aryloxatriazole and examined its hydrolysis and that of the corresponding azide in some detail. Consistent with the results of earlier workers, the major

TABLE 5

Protonation equilibria of 3-(*p*-substituted phenyl)oxatriazoles

	Equation (2)		Equation (3)	
Substituent	ϕ	pK_{BH^+}	m^*	pK_{BH^+}
Me	0.70	−1.38	0.44	−1.60
MeO	0.74	−1.29	0.26	−1.37
H	0.47	−1.61	0.57	−1.61
Br	0.67	−1.61	0.39	−1.78

product isolated from the hydrolysis of both 3-*p*-bromophenyloxatriazole and *p*-bromophenyl azide was 2-chloro-4-bromoaniline (from 6M-hydrochloric acid at 110°). The u.v. spectra of the products of hydrolysis of both the azide and the oxatriazole were found to be similar throughout the range of concentrations of hydrochloric and perchloric acid used, indicating that the products remained unchanged.

Rate Dependence on Acidity.—First-order rate coefficients k_1 as a function of acid concentration are shown in Tables 1—3 and Figures 1 and 2. The five aryloxatriazoles studied show broadly similar kinetic behaviour. At acid concentrations in the range 0—8M [with the exception of 3-(*p*-methoxyphenyl)- and 3-phenyl-oxatriazole which show shallow rate maxima in perchloric acid in this region] the catalytic effect of acids decreases in the order $HCl > H_2SO_4 > HClO_4$. At acid concentrations above 8M, the catalytic effectiveness of the acids decreases in the sequence $HClO_4 > HCl \sim H_2SO_4$, 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 carbocationic character being preferentially

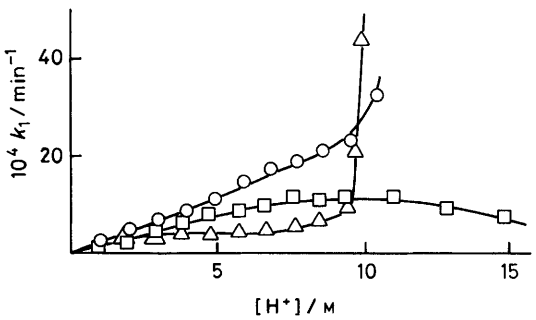


FIGURE 1 Hydrolysis of 3-(*p*-tolyl)oxatriazole in mineral acids at 120°: ○, HCl; □, H_2SO_4; △, $HClO_4$

stabilised by anions of low charge density such as ClO_4^-, whereas the converse is the case for *A*-2 reactions.[17] The kinetic behaviour of the hydrolysis of aryloxatriazoles suggests, therefore, that there is a gradual changeover in mechanism from a bimolecular to a unimolecular mechanism at higher acidities.

The rate profiles for the hydrolyses in sulphuric acid for four of the five aryloxatriazoles studied exhibit shallow rate maxima in the 6—12 mol dm^{-3} region. The exception is 3-(*p*-nitrophenyl)oxatriazole for which the rate levels off (at *ca.* 11 mol dm^{-3}) and there is no discernible maximum. As mentioned above, a rate maximum is also observed at lower acidities for the perchloric acid-catalysed hydrolyses of 3-(*p*-methoxyphenyl)- and 3-phenyl-oxatriazoles. Extensive protonation has been found to occur in the acid-catalysed hydrolyses of the related diarylisosydnones (2; $R^1 = R^2$ = aryl) which are much more basic than the corresponding sydnones.[18,19] It seems reasonable to suppose, therefore, that the rate maxima observed in the hydrolyses of aryloxatriazoles also arise from substantial conversion of the substrate into its conjugate acid. This view is supported by the way in which the

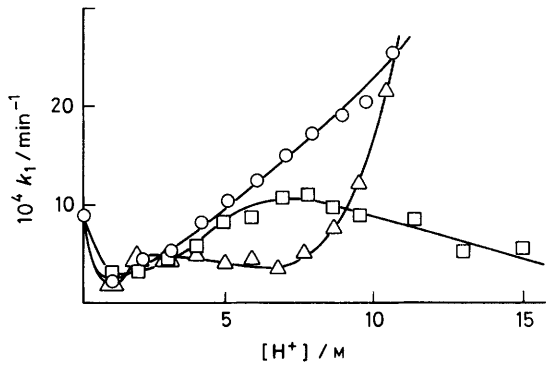


FIGURE 2 Hydrolysis of 3-phenyloxatriazole in mineral acids at 120°: ○, HCl; □, H_2SO_4; △, $HClO_4$

positions of the observed rate maxima vary with both the values of pK_{BH^+} obtained from protonation studies and in a predictable manner with the electronic effects of the substituents.

In addition to the general features of the rate profile referred to above, three of the compounds studied; 3-(*p*-bromophenyl)-, 3-(*p*-nitrophenyl)-, and 3-phenyl-oxatriazole all have a ' spontaneous ' rate of reaction. This causes the appearance of minima in the rate profile for acid-catalysed hydrolysis. The data in Table 1(b) for the effect of added sodium hydrogen sulphate on the rate of the spontaneous hydrolysis of 3-(*p*-nitrophenyl)-oxatriazole shows that there is a considerable negative salt effect on this reaction. A more detailed study of salt effects could not be carried out because of solubility difficulties encountered at high ionic strengths. It is clear, however, that the magnitude of the negative salt effects on the spontaneous reaction are large enough initially to outweigh the positive catalytic effect of the acid, hence the overall rate of hydrolysis is reduced and a minimum is observed. At higher concentrations of acid, however, the salt effect ' tails off ' and acid catalysis begins to predominate.

Analysis of the kinetic data in terms of Bunnett's hydration treatment [20] also leads to the view that there is a changeover in mechanism in the hydrolyses of aryl-

oxatriazoles at high acidity. Plots of log k_1 — log I *versus* log a_{H_2O} derived by Bunnett for a moderate or strongly basic substrate change slope with increasing acidity (Table 6). The value of the slopes (w) obtained in the ' low ' region (1.31—3.37) are characteristic of water acting as a nucleophile in the rate-determining step. In the ' high ' acidity region (>10 mol dm^{-3}), values of w are near zero or slightly negative and are characteristic of a unimolecular (A-1) mechanism in which the solvent is not involved in the rate-determining step.

One of the difficulties in the present study in using criteria which utilise H_0 or a_{H_2O} values is the very large difference between the temperature at which the hydrolyses of aryloxatriazoles was studied (120°) and that for which the vast majority of such data is available (25°), and the lack of precise information on the protonation behaviour of oxatriazoles. 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—29°.[21] In a previous study [4] we extrapolated this data to provide values of H_0 for sulphuric acid at 100 and 120°. Use of the corrected data had very little effect on the correlation 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°.[22] In Table 6 analysis by the Bunnett treatment for hydrolysis in sulphuric acid has been extended to data for perchloric and hydrochloric acids, for which protonation data are not available, by assuming that the ionization ratio for oxatriazoles is the same in different acids at the same H_0 value. The appropriate protonation data for sulphuric acid have then been combined with kinetic data for the other acids. This procedure has been used satisfactorily to analyse data for the hydrolysis of hydroxamic acids.[23]

TABLE 6

Analysis of rate data for the hydrolyses of 3-(*p*-substituted phenyl)oxatriazoles at 120° by use of Bunnett w and Bunnett–Olsen linear free-energy relationships at both ' high ' (>10M) and ' low ' (<8M) acidities

		Low [H$^+$]		High [H$^+$]	
Substituent	Acid	w	ϕ	w	ϕ
MeO	H_2SO_4	1.38	0.33		
	$HClO_4$	2.08	0.40	−0.18	−0.065
	HCl	1.56	0.28	−0.09	−0.18
Me	H_2SO_4	1.27	0.42		
	$HClO_4$	1.86	0.23	−0.84	−0.29
	HCl	1.31	0.27	−0.48	−0.03
H	H_2SO_4	1.99	0.51		
	$HClO_4$	3.37	0.61	−0.24	0
	HCl	1.96	0.41	−0.17	0.07
Br	H_2SO_4	1.34	0.54		
	$HClO_4$	2.35	0.51	−0.47	−0.15
	HCl	1.72	0.36	−0.32	0.12

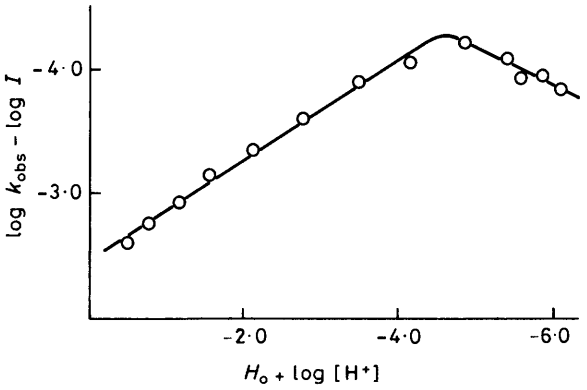


FIGURE 3 Bunnett–Olsen ϕ plot for the hydrolysis of 3-(*p*-tolyl)oxatriazole in perchloric acid at 120°

The plots of log k_1 — log I *versus* (H_0 + log [H$^+$]) for Bunnett's free-energy treatment (Table 6 and Figure 3) again show distinct changes in slope with increasing acidity. In the low acidity region the values of the slope ϕ fall in the range 0.27—0.61. The majority of the values obtained fall clearly in the range originally associated by Bunnett with an A-2 type mechanism. O'Connor and her co-workers have recently suggested that the limits of ϕ for this mechanism for the hydrolyses of amides should be extended to $0.47 \leq \phi \leq 0.98$.[24] A similar conclusion has been reached for the hydrolyses of isosydnones.[18] In the high acidity region the values of ϕ for the hydrolyses of aryloxatriazoles fall in the range associated with a unimolecular mechanism.

TABLE 7

Analysis of rate data for the hydrolyses of 3-(*p*-substituted phenyl)oxatriazoles at 120° by use of the excess acidity treatment [equation (5)]

Substituent	$m^*m^\ddagger$	m^*	$m^\ddagger$
MeO	0.36	0.26	1.37
Me	0.55	0.44	1.24
H	0.70	0.57	1.23
Br	0.44	0.35	1.13

Recently the excess acidity treatment derived for the determination of the basicities of weak bases has been developed by Cox and Yates to cover kinetic studies.[25]

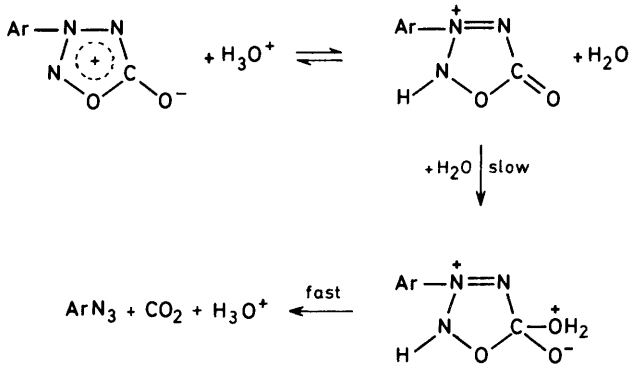
$$\log k_1 - \log \frac{[S]}{[S] + [SH^+]} - \log [H^+] = m^\ddagger m^* X + \log (k_0/K_{SH^+}) \quad (4)$$

$$\log k_1 - \log \frac{[S]}{[S] + [SH^+]} - \log [H^+] = m^\ddagger m^* X + \log a_{Nu} + \log(k_0/K_{SH^+}) \quad (5)$$

Equations (4) and (5) have been derived for A-1 and A-2 reactions respectively, where m^* is obtained from protonation studies, $m^\ddagger$ is characteristic of the type of reaction, and log a_{Nu} for the A-2 reaction represents nucleophilic activity and is commonly equivalent to

$r\log a_{H_2O}$ where r is the number of water molecules involved in forming the transition state.

A plot of the left-hand side of equation (5) exhibits downward curvation, typical of an A-2 reaction. If this is modified by the subtraction of log a_{H_2O}, good linear plots are obtained (Table 7) with slopes in the

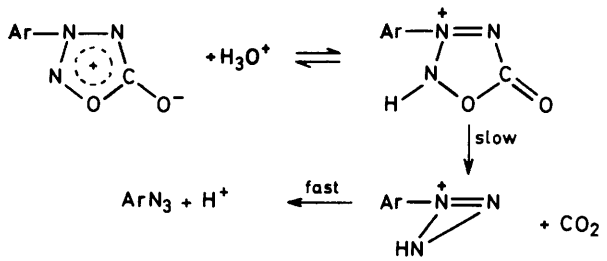


SCHEME 1

range 1.13—1.37 characteristic of an A-2 process. Similar behaviour has been observed for the hydrolysis of methyl benzoate in aqueous sulphuric acid.[26]

Analysis of the kinetic data by the various criteria indicates that there is a changeover in mechanism for the hydrolyses of aryloxatriazoles in perchloric and hydrochloric acids from an A-2 mechanism at low acidity to a predominantly A-1 mechanism at high acidities. Hydrolysis in sulphuric acid appears to occur *via* an A-2 mechanism throughout the entire acid concentration range. These general conclusions are further substantiated by the Arrhenius parameters for the hydrolysis of 3-(*p*-methoxyphenyl)oxatriazole (Table 4).

The enthalpies of activation do not vary greatly at different acid concentrations. The values of the entropies of activation, $\Delta S^{\ddagger}$, however, do show significant



SCHEME 2

trends. In both perchloric and hydrochloric acids $\Delta S^{\ddagger}$ becomes more positive with increasing acidity as expected for a changeover to a unimolecular mechanism.[27] Consistent with the kinetic behaviour, $\Delta S^{\ddagger}$ for hydrolysis in sulphuric acid does not change in this direction; on the contrary, the value becomes more negative.

Mechanism of Hydrolysis.—The available evidence suggests that at low acidity the hydrolyses of aryloxatriazoles proceed *via* an A-2 mechanism in which a water molecule is involved in the rate-determining step. It seems reasonable to suppose that the corresponding azide is formed first and this subsequently decomposes further. One possible mechanism leading to azide formation is shown in Scheme 1. An outline mechanism for the unimolecular (A-1) decomposition of aryloxatriazoles is shown in Scheme 2.

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