The Acid-catalysed Hydrolysis of Episulphoxides

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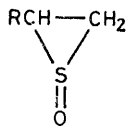
The acid-catalysed hydrolyses of a number of episulphoxides in aqueous mineral acids have been studied. Ethylene, propylene, and styrene episulphoxides hydrolyse by concurrent *A*-2 and nucleophile-catalysed pathways. 3-Methyl- and 3,3-dimethyl-butylene 1,2-episulphoxides hydrolyse in sulphuric acid by an *A*-2 mechanism but in concentrated perchloric acid their rate profiles pass through a maximum and there is a changeover from an *A*-2 to an *A*-1 mechanism. Values of pK_{BH^+} for these two episulphoxides have been determined.

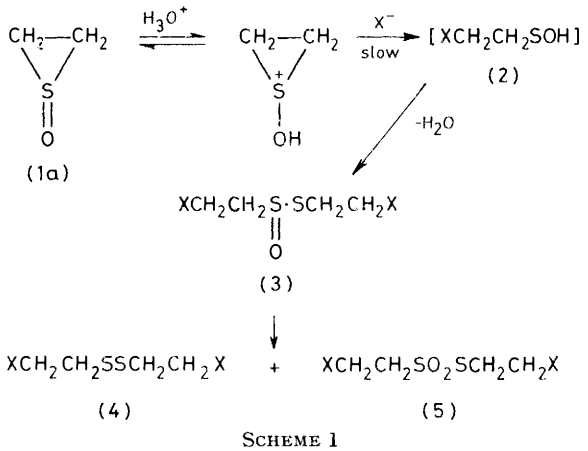
THE formation of episulphones from the corresponding episulphides by oxidation with hydrogen peroxide is well documented.[1,2] Only relatively recently has a successful partial oxidation procedure been reported for the preparation of a number of episulphoxides.[3] Haskell and



(1)

a; R = H d; R = Pr^i
b; R = Me e; R = Bu^t
c; R = Ph f; R = Et

Paige found [3] that ethylene episulphoxide (1) undergoes acid-catalysed nucleophilic attack with opening of the three-membered ring. They proposed a mechanism involving initial protonation on oxygen followed by nucleophilic attack leading to the formation of a sulphenic acid (2) which rapidly undergoes decomposition to form a disulphide (4) and a thiosulphonate (5). Reduction with triphenylphosphine of the crude product from the reaction of ethylene episulphoxide in methanol solution acidified with sulphuric acid gave an 88% overall yield of 2-methoxyethanethiol.



SCHEME 1

A preliminary kinetic study suggested that the hydrolytic ring-opening of ethylene episulphoxide in aqueous perchloric acid (0—3.0M) occurs *via* an *A*-2 type mechanism.[4] Kondo and his co-workers subsequently established that the sulphenic acid intermediate initially decomposes to a thiosulphinate (3) and this disproportionates to a mixture of disulphide (4) and thiosulphonate (5) (Scheme 1).[5,6]

In their initial publication, Kondo and his co-workers concluded that the products obtained in the acid-catalysed hydrolyses of substituted episulphoxides favoured an *A*-1 mechanism.[5] In their subsequent publication, however, they seem marginally to favour an *A*-2 mechanism but regarded the evidence as inconclusive.[6]

In order to clarify this situation we now report a detailed kinetic study of the acid-catalysed hydrolysis (more correctly the hydrolytic ring-opening) of a number of substituted episulphoxides in aqueous solutions of concentrated mineral acids. The protonation behaviour of 3-methyl- and 3,3-dimethyl-butylene 1,2-episulphoxide has also been studied.

EXPERIMENTAL

Materials.—Episulphoxides were prepared by oxidation of the corresponding episulphides using either H_2O_2,[7] a Bu^{t}OH–H_2O_2–V_2O_5 system [8] or perbenzoic acid.[9] Ethylene episulphoxide (1a) had b.p. 42° at 1.0 mmHg (lit.,[10] 53° at 3.0 mmHg), $\nu_{max.}$ 1 060 cm^{-1}; propylene episulphoxide (1b) was a high boiling oil redistilled in a molecular still, $\nu_{max.}$ 1 070 and 1 050 cm^{-1}. *Butylene 1,2-episulphoxide* (1f) was a high boiling oil (Found: C, 46.3; H, 7.7; S, 29.8. C_4H_8OS requires C, 46.2; H, 7.7; S, 30.7%), $\nu_{max.}$ 1 060 cm^{-1}; *m/e* 104 (*M*). Styrene episulphoxide (1c) had m.p. 70—72° (lit.,[10] 59—60°), $\nu_{max.}$ 1 065 cm^{-1}; *3-methylbutylene 1,2-episulphoxide* (1d) was a high boiling oil (Found: C, 49.9; H, 8.6; S, 26.4. $C_5H_{10}OS$ requires C, 50.8; H, 8.5; S, 27.1%), $\nu_{max.}$ 1 060 cm^1, *m/e* 118 (*M*); *3,3-dimethylbutylene 1,2-episulphoxide* (1e) was also a high boiling oil (Found: C, 53.9; H, 9.2; S, 23.8. $C_6H_{12}OS$ requires C, 54.5; H, 9.1; S, 24.2%), $\nu_{max.}$ 1 055 and 1 075 cm^{-1}; *m/e* 132 (*M*). Although the elemental analyses for (1d and e) suggest the presence of trace impurities, these could not be detected from the i.r. or mass spectra of these high boiling compounds.

Ring-opening of Episulphoxide (1a) *in Methanol.*—Sulphuric acid (2 drops) was added to a solution of (1a) (1.0 g) in dry methanol (25 ml) cooled in an ice-bath. After stirring for 2 h the solution was diluted with water (120 ml) and the resulting mixture extracted several times with chloroform. The chloroform was distilled off to leave *S*-2-methoxyethyl 2-methoxyethanethiosulphinate (3; X = OMe) (1.36 g, 105%) as an oil, $\nu_{max.}$ (neat) 2 950, 1 075, and

TABLE 1

Hydrolysis of ethylene episulphoxide (1a) (k_ψ/s^{-1})

(*a*) Effect of added acids and salts at 25.0°

$[HClO_4]$/M	0.500	1.00 [a]	1.50	2.00	2.50
10^3k_ψ	0.46	1.08	1.83	2.76	4.25
$[HClO_4]$/M	3.00	3.50	4.00		
10^3k_ψ	5.85	8.25	10.8		
$[HClO_4]$/M	1.00	2.00	3.00	4.00	
$[LiClO_4]$/M	3.00	2.00	1.00		
10^3k_ψ	2.71	5.38	8.10	10.8	
$[H_2SO_4]$/M	0.500	1.00	1.50	2.00	2.50
10^3k_ψ	0.89	1.98	3.95	6.28	9.62
$[H_2SO_4]$/M	3.00	3.50			
10^3k_ψ	13.9	15.6			
[HCl]/M	0.200	0.250	0.400	0.500	0.600
10^3k_ψ	1.08	1.36	3.73	4.85	8.29
[HCl]/M	0.800	1.00			
10^3k_ψ	15.4	19.9			
[HBr]/M	0.100	0.150	0.200	0.250	0.300
10^3k_ψ	1.46	3.20	6.04	8.64	13.2

(*b*) Effect of added acids at different temperatures

T/°C	21.5	25.0	30.0	35.0	43.8
10^3k_ψ, 1.00M-$HClO_4$	0.72	1.08	1.85	3.15	7.55
10^3k_ψ, 1.00M-H_2SO_4	1.50 [b]	1.98	3.35	5.65	11.7 [c]

[a] In 99.8% DC_4lO–D_2O, k_ψ 2.47 × 10^{-3} s^{-1}. [b] At 22.5°. [c] At 42.5°.

1 115 cm^{-1}; δ (CCl_4) 6.8 (m, CH_2), 6.65 (s, CH_3), and 6.3 (m, CH_2); *m/e* 198 (*M*).

Ring-opening of Episulphoxide (1a) *with Hydrogen Chloride.*—Anhydrous hydrogen chloride was bubbled through dry ether (40 ml) for 45 min whilst cooling in an ice-bath. Ethylene episulphoxide (1.52 g) in anhydrous ether (40 ml) was added to the ethereal solution and the resulting mixture

TABLE 2

Hydrolysis of propylene episulphoxide (1b) (k_ψ/s^{-1})

(*a*) Effect of added acids at 25.0°

$[HClO_4]$/M	0.500	1.00	1.00 [a]	1.50	2.00	2.50
10^3k_ψ	2.03	4.25	9.33	7.50	12.4	17.1
$[HClO_4]$/M	3.00	3.50	4.00			
10^3k_ψ	22.5	30.9	39.0			
$[H_2SO_4]$/M	0.500	1.00	1.50	2.00	2.50	3.00
10^3k_ψ	2.83	7.22	13.2	22.9	30.3	44.6

(*b*) Effect of perchloric acid (0.500-M) at different temperatures

T/°C	19.0	25.0	30.0	35.0	39.7
10^3k_ψ	1.05	2.03	3.40	5.75	9.07

[a] In 99.8% $DClO_4$–D_2O.

allowed to stand overnight. The mixture was then diluted with water and extracted several times with ether. The extract was dried, the ether removed and, the residual oil purified chromatographically using a silica column and hexane–chloroform (4 : 1) as eluant.

The faster eluate gave bis-(2-chloroethyl) disulphide (4; X = Cl) (0.7 g, 74.0%) as a pale yellow liquid; $\nu_{max.}$ (neat)

TABLE 3

Hydrolysis of styrene episulphoxide (1c) (k_ψ/s^{-1})

(*a*) Effect of added acids at 25.0°

$[HClO_5]$/M	0.250	0.500	0.750	1.00	1.25	1.50
10^2k_ψ	1.92	3.67	5.70	8.47	9.53	13.0
$[H_2SO_4]$/M	0.250	0.500	0.750	1.00 [a]	1.25	1.50
10^2k_ψ	2.97	6.89	10.5	17.5	25.9	29.4
[HCl]/M	0.250	0.500	0.750	1.00	1.25	1.50
10^2k_ψ	3.35	10.6	20.4	39.5	65.0	126

(*b*) Effect of perchloric acid (0.500M) at different temperatures

T/°C	15.3	25.0	35.0	44.3	52.5
10^2k_ψ	1.37	3.67	9.42	21.5	47.4

[a] In 1.00M-D_2SO_4–D_2O, k_ψ 18.1 × 10^{-2} s^{-1}.

2 900, 1 440, 1 280, 1 195, 1 050, 850, 720, and 680 cm^{-1}; *m/e* 95 (M − C_2H_4ClS).

The slower eluate gave *S*-2-chloroethyl 2-chloroethanethiosulphonate (4; X = Cl) (0.53 g, 48.0%) as a viscous

TABLE 4

Hydrolysis of butylene 1,2-episulphoxide (1f) (k_ψ/s^{-1})

(*a*) Effect of added acids at 25.0°

$[HClO_4]$/M	0.500	1.00	1.00 [a]	1.50	2.00	2.50	3.00
10^3k_ψ	0.922	2.17	3.48	3.23	4.60	6.03	8.08
$[HClO_4]$/M	3.50	4.00	5.00	6.00	7.00	8.00	9.00
10^3k_ψ	12.1	15.2	25.8	38.2	48.8	55.7	58.0
$[H_2SO_4]$/M	0.500	1.00	1.50	2.00	2.50	3.00	3.50
10^3k_ψ	1.31	2.85	5.47	8.53	12.7	19.1	25.2
$[H_2SO_4]$/M	5.00	6.00	7.00	8.00			
10^3k_ψ	60.5	85.8	99.8	113			

(*b*) Effect of acids at different temperatures

T/°C	20.0	25.0	30.0	35.0	39.8
k_ψ, 0.500-M-$HClO_4$	0.523	0.922	1.58	2.77	4.68
k_ψ, 0.500-M-H_2SO_4	0.766	1.31	2.28	3.86	6.37

oil; $\nu_{max.}$ (neat) 2 950, 1 450, 1 330, 1 120, 1 020, and 650 cm^{-1}; *m/e* 222 (*M*).

Ring-opening of Episulphoxide (1a) *in Aqueous Perchloric Acid.*—Perchloric acid (1.0 ml, 1.0M) was added to episulphoxide (1a) (1.0 g) in water (22 ml) cooled in an ice-bath and the mixture stirred for 4 h. The resulting solution was saturated with sodium perchlorate and extracted three

TABLE 5

Hydrolysis of 3-methylbutylene-1,2-episulphoxide (1d) (k_ψ/s^{-1}) in aqueous mineral acids at 25.6°

$[HClO_4]$/M	1.00	1.50	2.00	2.50	3.00	3.50
10^3k_ψ	0.295	0.458	0.637	0.900	1.29	1.68
$[HClO_4]$/M	4.00	5.00	6.0	7.00	8.00	8.50
10^3k_ψ	2.18	3.05	4.77	7.37	8.58	9.78
$[HClO_4]$/M	9.00	9.50	10.0	10.5	11.0	
10^3k_ψ	8.90	6.58	3.58	3.80	4.50	
$[H_2SO_4]$/M	1.00	1.50	2.00	2.50	3.00	3.50
10^3k_ψ	0.465	0.870	1.29	1.88	2.63	3.52
$[H_2SO_4]$/M	4.00	5.00	6.00	7.00	8.00	9.00
10^3k_ψ	4.85	7.20	11.3	15.2	19.8	20.3
$[H_2SO_4]$/M	10.0	11.0	12.0			
10^3k_ψ	20.0	15.6	10.4			

times with chloroform. The extract was dried and the solvent evaporated off to give a biphasic residue, a yellow liquid (0.58 g) and a gum (0.05 g). Distillation of the yellow liquid in a molecular still gave bis-(2-hydroxyethyl) disulphide (4; X = OH) (0.42 g, 83%) as a liquid; δ 6.43 (OH), 7.60 (CH_2), and 8.08 (CH_2); *m/e* 154 (*M*). The second component was only present in trace amounts (*ca.*

TABLE 6

Hydrolysis of 3,3-dimethylbutylene 1,2-episulphoxide (1e) (k_ψ/s^{-1}) in aqueous mineral acids at 25.6°

$[HClO_4]$/M	1.00	1.50	2.00	2.50	3.00	3.50
10^4k_ψ	0.425	0.670	0.962	1.33	1.70	2.17
$[HClO_4]$/M	4.00	5.00	6.00	7.00	8.00	8.50
10^4k_ψ	2.77	4.42	7.03	9.85	13.3	14.4
$[HClO_4]$/M	9.00	9.50	10.0	10.5	11.0	
10^4k_ψ	14.8	16.4	24.0	29.6	44.9	
$[H_2SO_4]$/M	1.00	1.50	2.00	3.00	4.00	5.00
10^4k_ψ	0.662	1.10	1.73	3.90	6.33	10.2
$[H_2SO_4]$/M	6.00	7.00	8.00	9.00	10.0	11.0
10^4k_ψ	14.4	18.3	21.8	22.6	17.7	13.7

0.05 g) and could not be fully identified. It had $\nu_{max.}$ 3 400, 2 900, 1 260, 1 090, and 1 050 cm^{-1} and was thought to be a polymeric form of the thiolsulphonate (5; X = OH).

Hydrolysis of ethylene episulphoxide (0.5 g) in concen-

TABLE 7

Arrhenius parameters [a] for the hydrolysis of episulphoxides

Episulphoxide	Acid	C_{acid}/M	$\Delta H^{\ddagger}$/kJ mol^{-1}	$-\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
(1a)	$HClO_4$	1.00	79.2	36.4
(1b)	H_2SO_4	1.00	77.1	38.5
(1b)	$HClO_4$	1.00	76.6	39.8
(1d)	$HClO_4$	1.00	81.7	39.8
(1d)	H_2SO_4	1.00	79.6	51.1
(1e)	$HClO_4$	1.00	84.6	46.0
(1e)	$HClO_4$	7.00	83.0	24.3
(1e)	$HClO_4$	10.0	82.5	19.3
(1e)	H_2SO_4	1.00	80.0	57.4
(1e)	H_2SO_4	9.00	72.5	54.5
(1e)	H_2SO_4	10.0	77.5	39.0
(1f)	$HClO_4$	1.00	81.7	28.9
(1f)	H_2SO_4	1.00	80.0	32.3

[a] Standard deviations in $\Delta H^{\ddagger}$ fall in the range $\pm$0.04—2.1 kJ mol^{-1} and in $\Delta S^{\ddagger}$ in the range $\pm$0.4—7.6 J K^{-1} mol^{-1}.

trated perchloric acid (10.0M) produced similar results to those observed in 1.0M-acid. The crude disulphide (4; X = OH) (0.26 g, 104%) and the thiosulphonate gum (5; X = OH) (0.02 g, 6%) were isolated as before.

Kinetic Measurements.—The rates of hydrolysis were determined spectrophotometrically at 239 nm with a Unicam SP 800 spectrometer equipped with a slave recorder and a thermostatted cell compartment ($\pm$0.05 °C). The concentration of the episulphoxide used was *ca.* 1×10^{-4}M. Values of the first-order rate-coefficients k_{ψ} were calculated for each run from the standard equation and are shown in Tables 1—6.

TABLE 8

Kinetic solvent isotope effects for the acid-catalysed hydrolysis of episulphoxides (1d and e) at 25.6°

(1d)	$[HClO_4]$/M	1.00	7.00	9.00	
	$10^3 k_{\psi}$ (D_2O)	0.605	15.3	11.6	
	$k_{\psi}(D_2O)/k_{\psi}(H_2O)$	2.05	2.07	1.30	
	$[H_2SO_4]$/M	1.00	9.00	11.0	
	$10^3 k_{\psi}(D_2O)$	0.860	32.8	22.0	
	$k_{\psi}(D_2O)/k_{\psi}(H_2O)$	1.85	1.61	1.41	
(1e)	$[H_2SO_4]$/M	1.00	7.00	9.00	10.0
	$10^4 k_{\psi}(D_2O)$	1.22	30.7	32.5	25.0
	$k_{\psi}(D_2O)/k_{\psi}(H_2O)$	1.84	1.67	1.44	1.44

In 1.00M-$DClO_4$—D_2O, k_{ψ} $(D_2O)/k_{\psi}(H_2O)$ = 2.04.

Influence of Temperature.—The entropy ($\Delta S^{\ddagger}$) and enthalpy ($\Delta H^{\ddagger}$) of activation were calculated from the equation $k_{\psi} = kT/k \exp(\Delta S^{\ddagger}/R)\exp(-\Delta H^{\ddagger}/RT)$ by a least-squares procedure (Table 7).

TABLE 9

Chemical shifts ($\Delta\nu$, 1 Hz) of the CH_2 protons of episulphoxides (1d and e) in aqueous sulphuric acid at 23 $\pm$ 1°

		(1d)		(1e)	
$[H_2SO_4]$/M	$-H_0$	ν	log I	ν	log I
1.00	0.26	6.0		12.0	
2.00	0.84	7.0	−1.73	12.5	−2.07
3.00	1.38	8.5	−1.32	13.0	−1.79
4.00	1.85	11.0	−1.00	16.0	−1.15
5.00	2.28	14.0	−0.769	19.0	−0.879
6.00	2.76	18.0	−0.554	23.5	−0.602
7.00	3.32	23.0	−0.349	30.0	−0.368
8.00	3.87	3.00	−0.111	38.0	−0.117
9.00	4.39	38.5	+0.160	47.0	+0.146
10.0	4.91	46.0	+0.426	55.5	+0.421
11.0	5.49	49.0	+0.554	63.0	+0.753
12.0	6.09	58.5	+0.802	68.0	+1.15
13.0	6.70	61.0		71.0	+1.77
14.0	7.29	61.0		72.0	
15.0	7.88	62.0		72.0	
16.0	8.49	61.0		72.0	

Protonation Studies.—The pK_{BH^+} values of 3-methyl- and 3,3-dimethyl-butylene 1,2-episulphoxides (1d and e) could not be determined by u.v. spectroscopy because the spectra of the free bases and their conjugate acids were too similar. The basicities were therefore measured using the n.m.r. technique of Haake and his co-workers.[11] Chemical shifts of the CH_2 protons relative to $(CH_3)_3\overset{+}{N}H$ were measured for the two episulphoxides in aqueous sulphuric acid solutions over the concentration range 1.0—16.0M at 23 $\pm$ 1° (Table 9). The trimethylammonium ion was used as an internal standard to minimise the solvent effects on chemical shifts.[11,12] Spectra were run on a Varian EM-360 spectrometer at 60 MHz. The ionization ratio I (=$[BH^+]/[B]$) at intermediate acid concentrations was calculated from the corresponding chemical shift $\Delta\nu$ and equation (1) where ν_B and ν_{BH^+} are the chemical shifts [relative to $(CH_3)_3\overset{+}{N}H$]

$$I = (\Delta\nu_B - \Delta\nu)/(\Delta\nu - \Delta\nu_{BH^+}) \quad (1)$$

of the free base and conjugate acid forms respectively (Table 9).

DISCUSSION

Protonation Behaviour.—Protonation data can be analysed in a number of different ways. To avoid the necessity of developing a separate scale of acidity for different sets of substrates, Haake and his co-workers suggested that such data could be analysed in terms of the H_0 acidity scale according to equation (2) where M is a measure of the protonation behaviour of substrate B

$$\log I = M(pK - H_0) \quad (2)$$

relative to Hammett bases (primary aromatic amines) used for the determination of H_0.[11] If $M = 1$, B is a Hammett base. It has been shown previously that the value of M for the protonation of dimethyl and methyl phenyl sulphoxides is *ca.* 0.6.[12] The values of M obtained for 3-methyl- and 3,3-dimethyl-butylene 1,2-episulphoxides (1d and e) (Table 10) are of similar magnitude (0.43 and 0.51, respectively). Sulphoxides therefore do not behave like Hammett bases and the pK values obtained from equation (2) are more properly regarded as H_0 values for half-protonation, $(H_0)_{\frac{1}{2}}$, and do not represent true thermodynamic pK values.

TABLE 10

Protonation equilibrium of episulphoxides (1d and e)

	equation (2)			equation (3)		
	M	$(H_0)_{\frac{1}{2}}$	r [a]	M	d/M	r [a]
(1d)	0.43	−4.07	0.998	0.80	−2.28	0.999
(1e)	0.51	−4.06	0.999	0.94	−2.84	0.999
	equation (4)			equation (5)		
	ϕ	pK_{BH^+}	r [a]	m *	pK_{BH^+}	r [a]
(1d)	0.62	−2.13	0.998	0.41	−2.21	0.997
(1e)	0.54	−2.34	0.998	0.50	−2.44	0.999

[a] Correlation coefficient.

Scorrano and his co-workers showed that the protonation behaviour of sulphoxide paralleled more closely

the H_A rather than the H_0 acidity function with values of M close to unity (0.95—0.98).[13] Analysis of the values of log I for the protonation of (1d and e) by equation (3) gave values of 0.80 and 0.94, respectively. These values of M lead to values of $(H_A)_{\frac{1}{2}}$, $(= -d/M)$,

$$\log I = M(H_A + d) \qquad (3)$$

of −2.88 and −2.84, respectively. Because of the closeness of the value of M to unity for episulphoxide (1e), it may be expected to be quite close to the true thermodynamic pK_{BH^+}.

A more general method of determining pK values is to use the linear free-energy approach of Bunnett and Olsen [14] [equation (4)]. Provided the left-hand side of

$$\log I + H_0 = \phi(H_0 + \log[H^+]) + pK_{BH^+} \qquad (4)$$

equation (4) *versus* $(H_0 + \log [H^+])$ is linear, thermodynamic quantitatives can be calculated because the intercept of the plot represents the pK_{BH^+} value referred to infinite dilution in water as the standard state. The slope (ϕ) is a measure of the susceptibility of the equilibrium to changing and concentration. The values of the pK values determined in this way (−2.13, −2.34) are less negative than those based on the H_A scale [equation (3)].

It has been suggested, however, that the H_A scale should be shifted *ca.* 0.3 H_A unit towards less negative values and this would bring the pK values determined by the two methods into closer agreement.[14] The value of pK_{BH^+} obtained in this work for (1d and e) lie in the same ranges as values obtained for open-chain alkyl and aryl sulphoxides (−1.80 to −2.96).[12,15] The values of ϕ for (1d and e) fall into the very narrow range which has been previously observed for other sulphoxides (0.4—0.6) [12] and are in the same range as those observed for amides (0.42—0.55).[14]

The validity of equations (2) and (3) depends on the cancellation of activity coefficient terms. The Bunnett and Olsen approach [equation (4)], although an improvement, has still been criticised because it also requires knowledge of a Hammett-type acidity function which has to be derived using the cancellation assumption referred to above.[16] To obviate these difficulties, Yates and Cox have developed [16] a generalized version of an earlier approach to this problem by Marziano and his co-workers.[17] This approach involves the determination of values of the ' excess acidity ', X, for aqueous solutions of both perchloric and sulphuric acids using a large number of bases of various structural types. The excess acidity, X, which is the difference between the observed acidity and that which the system would have if it were ideal is defined as the activity coefficient ratio term for a hypothetical standard base B* ($X = \log f_{B^*} f_H / f_{B^*H^*}$). Values of pK_{BH^+} can then be calculated from equation (5), where m^* is characteristic of the protonationation behaviour of the type of base. Use of

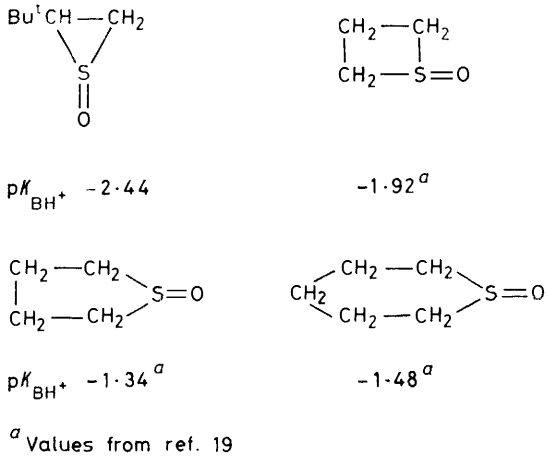
$$\log I - \log C_{H^+} = m^*X + pK_{BH^+} \qquad (5)$$

equation (5) leads to values of −2.21 and −2.44 for the values of pK_{BH^+} for (1d and e), respectively. These values are quite close to those obtained using the Bunnett–Olsen treatment [equation (4)].

Tamres and Searles showed that the basicity of cyclic sulphoxides falls in the order six- ⩾ five- > four-membered ring.[18] A preliminary hydrogen bonding study of the basicity of small ring cyclic sulphoxides indicated that the basicity of ethylene and trimethylene sulphoxides was approximately the same.[4] This was confirmed by Scorrano and his co-workers.[19] The present work shows, however that 3,3-dimethylbutylene 1,2-episulphoxide (1e) is less basic than unsubstituted four-, five-, and six-membered cyclic sulphoxides (Table 11).

TABLE 11

Value of pK_{BH^+} for some cyclic sulphoxides



[a] Values from ref. 19

Ring-opening of Ethylene, Propylene, and Styrene Episulphoxides.—The kinetic behaviour observed for the acid catalysed hydrolyses of episulphoxides (1a—c) is so similar that illustrations for most of the ensuing discussion could be taken from the data for any of these compounds.

The Proton Transfer.—The values obtained for the deuterium kinetic solvent isotope effect $[k_1(D_2O)_4k_1(H_2O)]$ (k.s.i.e.) for the perchloric acid-catalysed hydrolyses of ethylene (2.29), propylene (2.20), and stryene episulphoxides (2.07) are characteristic [20] of reactions which proceed by specific hydrogen ion catalysis.

Rate Dependence on Acidity.—The rates of hydrolysis of all three episulphoxides at first increase linearly with increase in acid concentration but above *ca.* 1.0M increase more rapidly than does acid concentration. This is due to a positive salt effect superimposed on a linear dependence of rate on stoicheiometric acidity as is shown by the linear dependence of rate of hydrolysis on acid concentration for the hydrolysis of ethylene episulphoxide in mixtures of perchloric acid and lithium perchlorate at constant ionic strength (4.00M) [Table 1(a)]. Such behaviour is characteristic of many reactions proceeding by an *A*-2 mechanism, *e.g.* the acid-catalysed hydrolysis of ethyl acetate,[21] methyl phosphate [22] and dialkyl sulphites.[23]

Table 12 summarises the analysis of the hydrolysis data for episulphoxides (1a—c). Bunnett's earlier proposal for the classification of reactions in strong acid media involves a plot of (log $k_\psi + H_0$) *versus* log a_w.[24] Such plots for the hydrolyses of episulphoxides (1a—c) give good linear correlations with values of w (4.0—4.5) which just fall into the range associated with water acting as a proton transfer agent. For some acid-catalysed reactions the Bunnett w^* relationship involving a plot of log k_ψ − log [H^+] *versus* log a_w shows less scatter than the corresponding w plots. This is not so in the present case. The Bunnett w^* plots show some curvature and the correlation is not as good as for the w plots, although the values of w^* (−3.7 to −2.8) fall into the range expected for an A-2 mechanism. The Bunnett–Olsen linear free-energy relationships {(log k + H_0) *versus* (H_0 + log [H^+])} gives a good correlation with values of ϕ (0.54—0.60) at the top end of the range for water acting as a nucleophile.[25] Although the w values for the hydrolyses of episulphoxides fall into the range associated with water acting as a proton transfer agent, in view of the fact that these reactions are not general acid catalysed, such a mechanism seems very unlikely. Similar conflicting conclusions from w and ϕ treatments in borderline cases have been reported for the hydrolyses of amides and related compounds.[26,27] Indeed O'Connor and her co-workers have suggested that the limits of values of w and ϕ may have to be revised for application to each class of substrate.[26] In the present case therefore we feel that the evidence points essentially to an A-2 mechanism.

TABLE 12

Analysis of rate data for the hydrolyses of episulphoxides (1a—c) at 25.0° by use of Bunnett w and w^* and Bunnett–Olsen linear free energy relationships (l.f.e.r.)

	Bunnett w		Bunnett w^*		Bunnett–Olsen l.f.e.r.	
Episulphoxide	w [a]	r	w^* [b]	r	ϕ [c]	r
(1a)	4.03	0.996	−3.68	0.988	0.54	0.997
(1b)	4.55	0.999	−2.80	0.983	0.60	0.993
(1c)						

[a] 0.17 > standard deviation (s) >0.10. [b] 0.23 > s > 0.22. [c] 0.04 > s > 0.02.

Consistent with this view, the values of the entropies of activation for the hydrolyses of episulphoxides (1a—c) in perchloric acid (−36 to −40 J K^{-1} mol^{-1}) are in the range normally associated with a bimolecular mechanism.[28] It is of interest to compare these values with those obtained for the hydrolytic ring-opening of other three-membered heterocycles, *e.g.* ethylene oxide (−25 J K^{-1} mol^{-1}) [29] and ethylene imine (−39 J K^{-1} mol^{-1}).[30] The mechanisms of hydrolysis of these other systems have been the subject of much debate but it is now thought that both are hydrolysed by an A-2 mechanism.[24]

The hydrolysis of ethylene episulphoxide in the presence of acids as first reported by Haskell and Paige is unexpected.[3] Although the acid-catalysed equilibration and racemisation of five- and six-membered cyclic sulphoxides is well known,[31] the hydrolytic ring-opening of such compounds has not been observed. Trimethylene and tetramethylene sulphoxides showed no perceptible hydrolysis under the conditions used to follow the hydrolysis of ethylene episulphoxide or at much higher temperatures and concentrations of acids.[4] The rate of hydrolysis of three-membered cyclic sulphoxides is therefore very much greater than that of the corresponding four-, five-, and six-membered ring systems. Such differences in rate cannot arise from differences in basicity since, as discussed above, this has been shown to decrease in the order six- > five- > four- > three-membered ring. The enormous reactivity of the episulphoxide ring relative to that of other cyclic sulphoxides must arise from relief of angular strain on ring-opening.

Nucleophilic Catalysis.—The order of effectiveness of catalysing acids, HBr > HCl > H_2SO_4 > $HClO_4$ for the hydrolysis of ethylene episulphoxide [Table 1(a)] and the magnitude of the relative effects, suggests the occurrence of nucleophilic catalysis. The nucleophile-catalysed oxygen exchange and racemisation reactions of optically active sulphoxides are well documented.[32] The general rate equation for the hydrolysis of sulphoxides in acidic solutions containing halide ions, X^-, can be written as in equation (6), where the terms represent (a) reaction of the neutral species with water, (b) a nucleophile-catalysed spontaneous reaction, (c) an acid-catalysed A-2 reaction, and (d) hydrogen-ion dependent

$$k_\psi = k_0 + k_0'[X^-] + k_{H^+}[H^+] + k_{X^-}[H^+][X^-] \qquad (6)$$

nucleophilic catalysis, respectively. The observed data in Table 1(a) for the hydrolysis of ethylene episulphoxide can be accommodated by terms (c) and (d), the first two terms being negligible under the conditions used. The overall mechanism in the presence of hydrochloric acid can be written as in Scheme 1 (X = Cl). Similar nucleophilic catalysis has been observed in the acid-catalysed hydrolyses of other sulphinyl systems such as sulphinates,[33] sulphinyl sulphones,[34] sulphite ester,[23] and sulphinamides,[35] although these latter cases involve nucleophilic attack at sulphur rather than at carbon as occurs in the present work.

Stereochemistry.—The episulphoxides used in the present work were a mixture of *cis*- and *trans*-isomers and no attempt was made to investigate the stereochemistry of ring-opening. Kondo and his co-workers found that *cis*- and *trans*-but-2-ene episulphoxides undergo ring opening in alcohol as solvent to form exclusively *threo*- and *erythro*-2-methoxy-3-methylthiobutanes respectively, thus confirming that nucleophilic attack occurs stereospecifically with inversion of configuration at the point of attack.[6]

Product Analysis.—We found, as did Kondo and his co-workers, that treatment of ethylene episulphoxide (1a) in methanol with a drop of concentrated sulphuric acid led to the formation of *S*-2-methoxyethyl 2-methoxyethanethiosulphinate (3; X = Cl). Similarly when the episulphoxide was treated with dry hydrogen chloride in

ether, no thiosulphinate could be detected, the product being a mixture of the disulphide (4; X = Cl) and thiosulphonate (5; X = Cl).

Treatment of ethylene episulphoxide with aqueous perchloric acid resulted in the formation of a liquid and a sticky gum. Purification and work-up of these products showed that they were bis-(2-hydroxyethyl) disulphide (4; X = OH) and probably the corresponding thiosulphonate (5; X = OH). The structural assignment of the disulphide was based on its n.m.r., i.r., and mass spectrum and elemental analysis.

Hydrolysis of 3-*Methyl- and* 3,3-*Dimethyl-butylene* 1,2-*Episulphoxides*.—The dependence of rate of ring-opening on acidity for episulphoxides (1d and e) is shown in Figures 1 and 2, and is significantly different from that of ethylene, propylene, and styrene episulphoxides. For both (1d and e) the rate of hydrolysis in sulphuric acid passes through a maximum. The rate profile for the hydrolysis of (1d) in perchloric acid is very similar but with the additional feature of a rate minimum at a

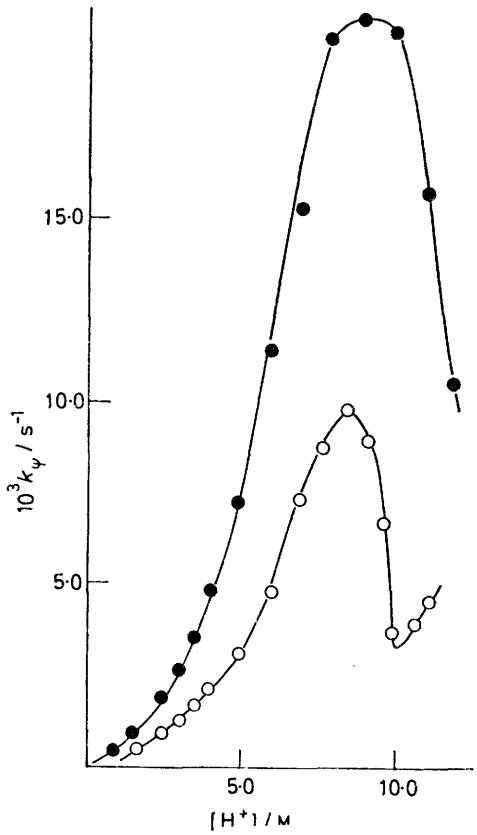


FIGURE 1 Plot of k_ψ *versus* [H$^+$] for the hydrolysis of episulphoxide (1d) in H_2SO_4 ● and $HClO_4$ ○

perchloric acid concentration of *ca.* 10M followed by a further sharp increase in rate. A rate maximum is just discernible for the hydrolysis of (1e) in perchloric acid although this is almost obscured by the very sharp increase in rate occurring in the same region of acidity.

Similar rate maxima have been observed in the hydrolyses of amides and related compounds and has been attributed to extensive protonation of the substrate.[27] Such an explanation in the present cases is supported by the values of the k.s.i.e. for the ring-opening reaction of (1d) which are 1.85, 1.61, and 1.41 at 1.00, 9.00, and 11.00M-sulphuric acid and 2.05, 2.07, and 1.30 at 1.00, 7.00, and 9.00M-perchloric acid respectively. A similar fall of the k.s.i.e. with increasing acidity

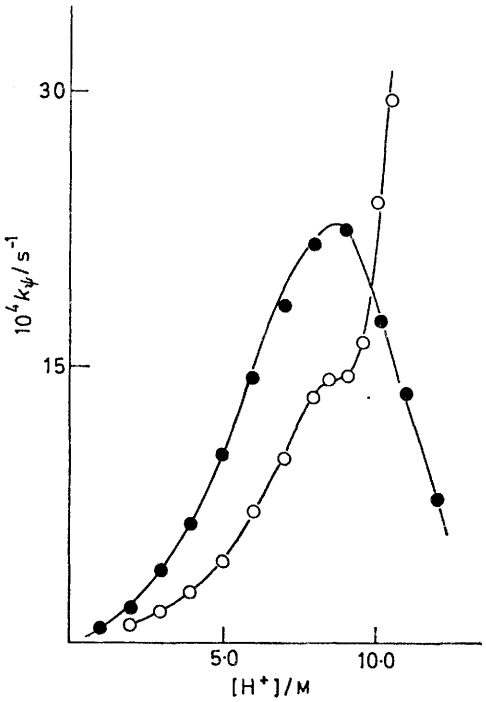


FIGURE 2 Plot of k_ψ *versus* [H$^+$] for the hydrolysis of episulphoxide (1e) in H_2SO_4 ● and $HClO_4$ ○

observed for the hydrolysis of amides has been discussed by Bell[36] and Wiberg[37] in terms of the increasing extent of protonation of the substrate and the weaker nucleophilic reactivity of D_2O compared to H_2O.

The kinetic behaviour of episulphoxides (1d and e) in concentrated acidic media is reminiscent of that of acetate esters.[38] Yates and McClelland found that for the sulphuric acid-catalysed hydrolysis of acetate esters, the dependence of rate on acid concentration was found to fall into four basic types.[38,39] The hydrolysis of primary and secondary alkyl acetates (Types I and II) were found to show rate maxima in *ca.* 50% H_2SO_4 (w/w), associated with essentially complete conversion of the ester into its conjugate acid. At higher concentrations of acid, the rates of hydrolysis of these esters pass through a minimum and then increase (particularly sharply for Type II esters). This increase is associated with a changeover of mechanism from $A_{Ac}2$ to $A_{Ac}1$ and $A_{Al}1$ for primary and secondary alkyl acetates respectively. The rate profile for the hydrolysis of phenyl acetate, which is categorised as a Type III ester, increases monotonically over the range 1.00—12.5M-H_2SO_4.[39] Yates and McClelland suggested that in this case also, there is a changeover of mechanism from $A_{Ac}2$ to $A_{Ac}1$, and this suggestion has recently been confirmed.[40]

For the hydrolysis of (1d) over the entire acid concentration range studied, the rate of reaction in sulphuric acid is greater than that in perchloric acid. At acid concentrations in the range 1.0—7.0M, hydrolysis in sulphuric acid is about twice as fast as that in perchloric acid. This is a somewhat larger increase than has been observed for other bimolecular hydrolyses such as the hydrolysis of ethyl acetate [41] and phenyl acetate.[42] This is to be expected in the present case because, as for

TABLE 13

Analysis of rate data for the hydrolysis of episulphoxides (1d and e) at 25.0° using the excess acidity method

	(1d)		(1e)	
Acid	$m^{\ddagger}m^{*}$	r [a]	$m^{\ddagger}m^{*}$	r [a]
H_2SO_4	0.600	0.998(11)	0.540	0.934(11)
$HClO_4$*	1.04	0.955(4)	1.91	0.979(4)
$HClO_4$†	0.280	0.997(12)	0.23	0.996(12)

[a] Correlation coefficient (no of points in parentheses).
* $HClO_4 \geqslant 9.0$M. † $HClO_4 < 9.0$M.

ethylene and propylene episulphoxides, the observed rate of reaction is a composite rate arising from both A-2 and nucleophile-catalysed pathways. Analysis of the dependence on acidity of the rate of ring opening of (1d and e) in terms of Bunnett w and w^{*} and the Bunnett–Olsen l.f.e.r. approach did not give meaningful correlations either with the standard plots for a weakly basic substrate or using the modified plots for moderately basic substrates. The kinetic data could, however, be satisfactorily correlated with the excess acidity treatment of Yates and his co-workers,[16,43-45] for which the appro-

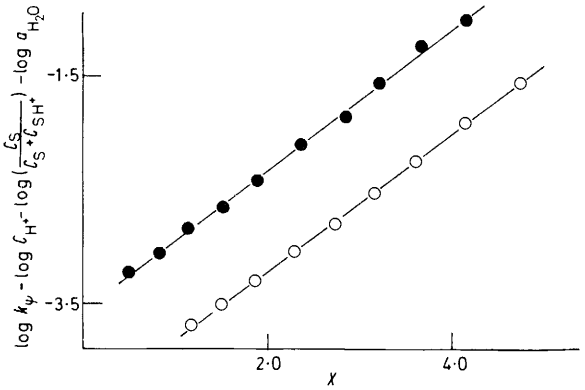


FIGURE 3 Plots of the left hand side equation (8) of $-\log a_{H_2O}$ *versus* X for the hydrolyses in sulphuric acid of episulphoxides (1d) ● and (1e) ○

priate kinetic equations for A-1 and A-2 reactions of dominantly unprotonated substrates are (7) and (8),

$$\log k_\psi - \log C_{H^+} - \log I = m^{\ddagger}m^{*}X + \log(k_0 K_{SH^+}) \quad (7)$$

$$\log k_\psi - \log C_{H^+} - \log I = m^{\ddagger}m^{*}X + \log a_{Nu} + \log(k_0 K_{SH^+}) \quad (8)$$

where $m^{\ddagger}m^{*}$ is a composite parameter and m^{*} is characteristic of the protonation behaviour of the substrate and defined by equation (5).

Plots of the left-hand side of equation (8) for the hydrolyses of (1d and e) in sulphuric acid show the typical curved behaviour expected of an A-2 process.[44] If it is assumed that one molecule of water is involved in the rate-determining step, values of log a_{H_2O} can be subtrated from the left-hand side of equation (7) and the resultant plotted against X. A good straight line correlation (Figure 3 and Table 13) is obtained throughout the entire range of sulphuric acid studied for both episulphoxides. The values of the slopes lead to values of $m^{\ddagger}$ of *ca.* 1.2 for both (1 d and e) which are characteristic of A-2 reactions.[43]

A plot of the left-hand side of equation (7) for the hydrolysis of (1d and e) in perchloric acid is curved at low acidity but at high acidity becomes essentially linear (Figure 4). Similar behaviour has been observed

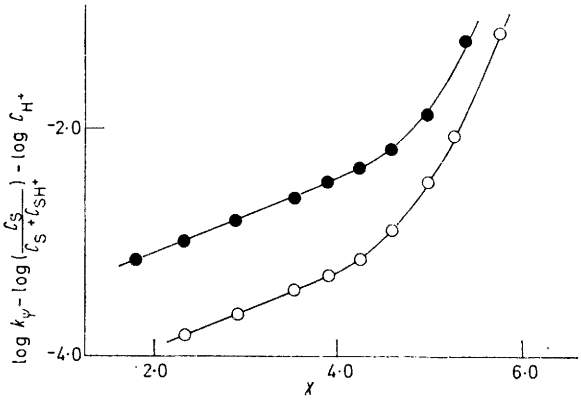


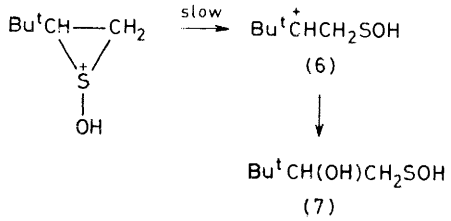
FIGURE 4 Plots of the left hand side of equation (7) *versus* X for the hydrolyses in perchloric acid of episulphoxides (1d) ● and (1e) ○

for the mechanistic changeover from $A_{Ac}2$ to $A_{Ac}1$ for the sulphuric acid-catalysed hydrolysis of benzoate esters.[45] The value of the slopes of the plots of equation (6) for the hydrolysis of (1d and e) in perchloric acid at high acidity (Table 13) lead to values of $m^{\ddagger}$ of 2.3 and 3.0, respectively. Similar values of $m^{\ddagger}$ (*ca.* 2.5) have been observed for the acid-catalysed hydrolyses of acetals which are hydrolysed by an A-1 mechanism.

The value of the k.s.i.e. and analysis of the kinetic data by the excess acidity method suggest therefore that episulphoxides (1d and e) hydrolyse in sulphuric acid by an A-2 mechanism whilst in perchloric acid there is a changeover to an A-1 mechanism which is just perceptible in the acidity range studied for (1d) but which occurs at much lower acidities for (1e). Such a preferential changeover in mechanism in perchloric acid is predicted by the work of Bunton and his co-workers.[41] The values of the entropy of activation $\Delta S^{\ddagger}$ (Table 7) become increasingly positive with increasing perchloric acid concentration for the hydrolysis of (1e) as expected for an A-1 mechanism.[28]

These observations suggest that the rate-determining step in the ring opening of episulphoxide (1e) in very concentrated perchloric acid is a simple unimolecular heterolysis of the protonated sulphoxide to form the intermediate (6) which rapidly reacts with water to form

the sulphenic acid (7) (Scheme 2). This can then undergo further reactions as in Scheme 1. In principle, with an unsymmetrically substituted episulphoxide like (1e), fission of either C–S bond could occur leading to a mixture of products, although it is more likely that the predominant pathway will involve the secondary carbocation



SCHEME 2

ion (6) rather than the alternative primary carbocation. The trace quantities of the product isolated from the ring opening of episulphoxide (1e) in 10M-perchloric acid appeared from its i.r. spectrum to be a mixture of disulphides, thiosulphinates, and thiosulphonates.

It is interesting to note that open-chain sulphoxides such as t-alkyl phenyl sulphoxides undergo a comparable fragmentation in aqueous perchloric acid according to the stoicheiometry of equation (9).[46] Diphenyl disulphide

$$4\ PhSOBu^t + 2H_2O \longrightarrow Ph_2S_2 + PhSSO_2Ph + Bu^tOH \quad (9)$$

and *S*-phenyl benzenethiosulphonate were isolated as the major reaction products.

Hydrolysis of Butylene 1,2-Episulphoxide (1f).—The acid-catalysed hydrolysis of episulphoxide (1f) showed intermediate kinetic behaviour (Table 4) and was not studied in great detail. At concentrations of $HClO_4$ and $H_2SO_4 < 7.0$M, the rate profile is similar to that observed for episulphoxides (1a—c). At higher concentrations of acids, however, the rate profile begins to curve over suggesting that a rate maximum may occur at still higher acidities.

[0/718 *Received*, 15*th May*, 1980]

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