959. *Nucleophilic Displacements in Organic Sulphites. Part II.*[1] *The Acid-catalysed Hydrolysis of Ethylene Sulphite and of Trimethylene Sulphite.*

By C. A. BUNTON, P. B. D. DE LA MARE, and J. G. TILLETT.

The hydrolysis of ethylene sulphite and of trimethylene sulphite are catalysed by mineral acids. At concentrations of perchloric acid greater than about 1M, the rates increase with acidity more rapidly than does the stoicheiometric concentration of acid. The rates are, however, closely proportional to the stoicheiometric acidity when the total concentration of electrolyte is kept constant by addition of sodium perchlorate; in the presence of added neutral salts, the rates are not proportional to the acidity as measured by Hammett's acidity function, h_0. Nucleophilic anions catalyse the hydrolysis. Some aspects of the mechanistic paths consistent with these experimental features are discussed.

IN PART I [1] it was shown that the acid-catalysed hydrolyses of a number of cyclic sulphites proceed with S-O bond-fission. Preliminary measurements of the kinetics of these reactions have been referred to elsewhere; [2] the present paper amplifies these measurements

---

[1] Part I, Bunton, de la Mare, Greaseley, Llewellyn, Pratt, and Tillett, *J.*, 1958, preceding paper.

[2] Bunton, de la Mare, Llewellyn, Pearson, and Pritchard, *Chem. and Ind.*, 1956, 490.

in the cases of ethylene and trimethylene sulphites, which serve as the simplest examples of 1 : 2- and of 1 : 3-sulphites.

EXPERIMENTAL

The properties of the cyclic sulphites are recorded in Part I.[1] The acids were of Analytical Reagent quality. Their concentrations were determined in the reaction mixtures by titration with standard alkali. Sodium chloride and sodium bromide were dried at 120°. Sodium perchlorate was dried for 4 days at 120°; it was free from halide. Sodium toluene-*p*-sulphonate was a commercial recrystallised specimen. Tetraethylammonium perchlorate was prepared from tetraethylammonium hydroxide by neutralisation with perchloric acid. The precipitate was washed with water until the washings were neutral, then dried at 100°.

The rates of hydrolysis were determined by a conventional sealed-tube method. The conversion of organic sulphite into sulphur dioxide was determined at intervals by breaking samples under excess of standard iodine solution, which was then back-titrated with sodium thiosulphate. The following exemplifies a typical kinetic run, for 0·036M-ethylene sulphite

Time (min.)	0	7	14	21	28	35	42	50	60	75	90	120	180	∞
Titre (ml. 0·0100N-iodine)	7·44	9·64	11·69	13·77	15·46	17·65	18·56	20·21	22·03	24·13	26·04	28·77	32·35	35·53
10^2k_1 (min.$^{-1}$)	—	1·17	1·17	1·22	1·20	1·20	1·20	1·21	1·22	1·20	1·21	1·19	1·21	—

in 1·098M-perchloric acid with 0·25M-sodium chloride at 44·6°. The finite titre for time $t = 0$ represents reaction during the time allowed for warming of the samples to the temperature of the thermostat. Values of k_1 were calculated from $k_1 = 2{\cdot}303[\log a/(a - x)]/t$, where a is the molarity of organic sulphite at time $t = 0$, and x is the molarity of sulphur dioxide liberated at time t. Calculated (35·68) and observed infinity values agreed within experimental error. The fact that the first-order rate-coefficients calculated by the use of the above formula are substantially constant over considerably more than 50% of reaction implies that one mole of material behaving on titration as sulphur dioxide is liberated for each mole of organic sulphite decomposed.

The results are summarised in Tables 1 and 2. Rates are corrected, where the correction is significant, for the rate in neutral solution. Values of H_0 are included for reference, mostly from Long and Paul's review.[3] That for hydrogen bromide has recently been determined by Vinnik, Krugslov, and Chirkov.[4]

DISCUSSION

The kinetic forms observed for ethylene and for trimethylene sulphite are so similar that illustrations for most of the ensuing discussion could be taken from the data for either compound. Many acid-catalysed reactions fall into one of two classes, according to whether the rate of the reaction is proportional to the acidity as measured by the degree of protonation of a weak nitrogen base under the same conditions (*i.e.*, to Hammett's acidity function, h_0) or to the stoicheiometric concentration of acid.[3] In the following discussion, the former class will be described as Hammett-dependent, and the latter as concentration-dependent.

Correlation of Rate with Hammett's Acidity Function.—In Fig. 1 are plotted the logarithms of the rates of hydrolysis of ethylene sulphite against values[3, 4, 5] of Hammett's acidity function, in its logarithmic form, H_0. The reaction has been followed well into the region of acidity in which h_0 and [$HClO_4$] are markedly different. Only the effects of variation in the concentration of perchloric acid being considered first, the values lie near to a straight line of slope 0·68, though the graph shows an appreciable curvature, particularly at the higher acidities. A straight line of nearly unit slope would be expected

---

[3] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.
[4] Vinnik, Krugslov, and Chirkov, *Zhur. fiz. Khim.*, 1956, **30**, 827.
[5] McIntyre and Long, *J. Amer. Chem. Soc.*, 1954, **76**, 3240.

Table 1. *First-order rate-coefficients* (*min.*$^{-1}$) *and related data for hydrolysis of ethylene sulphite in water* (*concentrations in moles l.*$^{-1}$).

(*a*) *At* 44·6°.

$\mathrm{HClO_4}$	0	0·030	0·060	0·150	0·350	0·500
10^4k_1	0·065	1·35	2·79	6·89	16·9	25·9
$10^3k_1/\mathrm{H}^+$	—	4·50	4·65	4·55	4·80	5·18
H_0	—	1·52	1·22	0·82	0·46	0·31
$\mathrm{HClO_4}$	1·098	1·500	2·184	3·275	4·373	5·481
10^4k_1	58·6	83·5	141 *	287	476	898
$10^3k_1/\mathrm{H}^+$	5·34	5·56	6·46	8·76	8·80	16·22
H_0	−0·13	−0·44	−0·72	−1·21	−1·74	−2·31

* In 90% $\mathrm{D_2O}$, $10^4k_1 = 213$ min.$^{-1}$.

(*b*) *At* 44·6°, *with added sodium perchlorate.*

$\mathrm{HClO_4}$	0·500	1·000	2·000	3·000
$\mathrm{NaClO_4}$	5·500	5·000	4·000	3·000
10^4k_1	78·6	185	397	610
$10^3k_1/\mathrm{H}^+$	15·7	18·5	19·3	20·3
H_0	−1·00	−1·31	−1·73	−2·00

(*c*) *At* 44·6°, *with other acids.*

Acid	1·226M-$\mathrm{H_2SO_4}$	1·80M-$\mathrm{H_2SO_4}$	0·500M-HCl
10^4k_1	128	235	65·6
H_0	−0·26	−0·59	+0·31
Acid	1·00M-HCl	1·30M-HCl	1·30M-HBr
10^4k_1	208	382	*ca.* 1000
H_0	−0·13	−0·24	−0·24

(*d*) *At* 44·6°, *with added sodium chloride*, 0·25M.

$\mathrm{HClO_4}$	1·098	2·184	3·275	4·373	1·000
$\mathrm{NaClO_4}$	—	—	—	—	5·000
10^4k_1	120	323	742	1760	608

(*e*) *At* 73·05°.

$\mathrm{HClO_4}$	0·108	0·270	0·432	0·539	1·078	2·156
10^4k_1	81·8	202 *	314	380	874	2030
$10^3k_1/\mathrm{H}^+$	75·9	74·8	72·7	70·5	81·1	94·2

* In 90% $\mathrm{D_2O}$, $10^4k_1 = 332$ min.$^{-1}$.

(*f*) *At* 73·05°, *with* 0·270M-*perchloric acid.*

$\mathrm{NaClO_4}$	0·000	0·500	1·000	2·000	3·000	4·000
10^4k_1	202	217	257	302	356	440
NaCl	0·000	0·050	0·100	0·200	0·300	
10^4k_1	202	241	278	354	443	
NaBr	0·000	0·030	0·100	0·200		
10^4k_1	202	234	314	438		
$\mathrm{C_7H_7SO_3Na}$	0·000	0·500	1·000	1·500		
10^4k_1	202	218	228	242		

(*g*) *At* 73·05°, *with* 0·108M-*perchloric acid.*

NaCl	0·000	0·300	0·400	0·600	0·800	1·000
10^4k_1	81·8	110	187	237	290	342

(*h*) *At* 73·05°, *with* 0·284M-*perchloric acid and* 0·47M-*tetraethylammonium perchlorate*, $10^4k_1 = 185$ *min.*$^{-1}$; *with* 0·27M-*perchloric acid and* 0·41M-*tetraethylammonium perchlorate*, $10^4k_1 = 217$ *min.*$^{-1}$.

Table 2. *First-order rate-coefficients for the hydrolysis of trimethylene sulphite in water* (*units as in Table* 1).

(*a*) *At* 35·0°.

$\mathrm{HClO_4}$	0·515	1·03	1·55	2·07	3·09	4·12
10^4k_1	40·7	88·0	150	239	447	989
$10^3k_1/\mathrm{H}^+$	7·90	8·55	9·66	11·55	14·48	24·05
H_0	0·31	−0·08	−0·46	−0·67	−1·12	−1·61

(*b*) *At* 35·0°, *with added sodium perchlorate.*

$\mathrm{HClO_4}$	0·000	1·000	2·000	3·000	4·000
$\mathrm{NaClO_4}$	4·000	3·000	2·000	1·000	0·000
10^4k_1	0	186	392	670	910
$10^3k_1/\mathrm{H}^+$	0	18·6	19·6	22·3	22·8

(*c*) *At* 60·0°.

$\mathrm{HClO_4}$	0·206	0·309	0·412	0·515
10^4k_1	195	255	365	485
$10^3k_1/\mathrm{H}^+$	94·6	82·5	88·6	94·1

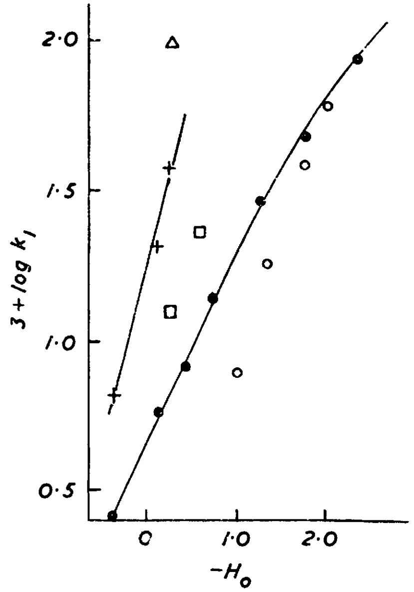
(*d*) *At* 60·0°, *with* 0·412M-*perchloric acid.*

$\mathrm{NaClO_4}$	0·000	1·000	2·000	3·000
10^4k_1	365	499	628	741
NaCl	0·000	0·100	0·200	0·300
10^4k_1	365	495	633	788

NaBr	0·000	0·030	0·100	0·200
10^4k_1	365	442	577	778
$\mathrm{C_7H_7SO_3Na}$	0·000	1·000	1·500	
10^4k_1	365	450	486	

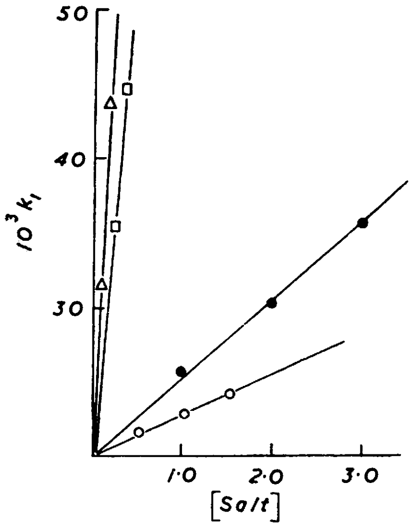
for a Hammett-dependent reaction. Appreciable deviations from this ideal behaviour have, however, been observed for reactions which are accepted as falling into this class.[3] It seems essential, therefore, to use some further criterion to decide whether the reaction now investigated is to be considered as Hammett-dependent. Such a criterion is provided by the influence of added salts. When, at high acidities, the stoicheiometric concentration of acid is kept constant and sodium perchlorate is added, the acidity of the solution as measured by H_0 is very considerably increased.[5] The rates of these acid-catalysed hydrolyses of sulphites are, however, not increased to nearly the same extent. This result is shown in Fig. 1; the full circles refer to experiments in which sodium perchlorate has been added to perchloric acid to make the total concentration of perchlorate ion 6·0M; under these conditions, values of H_0 are known.[5]

FIG. 1. *Acid-catalysed hydrolysis of ethylene sulphite.*



● $HClO_4$, ○ $HClO_4$ + $NaClO_4$, □ H_2SO_4, + HCl, △ HBr.

FIG. 2. *Effect of added salts on the acid catalysed hydrolysis of ethylene sulphite.*



△ NaBr, □ NaCl, ● $NaClO_4$, ○ $C_7H_7SO_3Na$.

Correlation of Rate with Stoicheiometric Concentration of Acid.—The above results, in our view, provide satisfactory evidence that the reaction is not Hammett-dependent. Clearly, however, it is not, in the conventional sense, concentration-dependent either. The values shown in the Tables 1(*a*), 1(*c*), 2(*a*), and 2(*c*) illustrate that the values of k_1/H^+ rise; the factor is nearly three over a range of concentration of perchloric acid, 0·5—4M. If the reaction is carried out under conditions in which the ionic strength is kept constant by addition of sodium perchlorate, however, the rate is very nearly proportional to the concentration of perchloric acid. This is shown by the approximate constancy of the values of k_1/H^+ given in Tables 1(*b*) and 2(*b*).

Effects of Added Salts on the Rate of Hydrolysis.—The above facts suggest that the reaction is essentially concentration-dependent, with a superposed dependence on the concentration of added electrolyte. Since the concentrations involved are fairly high, it might be expected that the rate of the reaction would be affected in a specific manner by different electrolytes. One test of this hypothesis is shown in Fig. 1. The points which represent catalysis by added sulphuric, hydrochloric, and hydrobromic acids fall well above the plot of rate against concentration of perchloric acid; accordingly, at the same molar concentration of acid, the four acids have widely different catalytic power for the hydrolysis [Table 1(*a*), (*c*)].

Catalysis of the reaction by added electrolytes is not confined to the region of high acidity. Fig. 2 illustrates this for various electrolytes.

The salts fall into two fairly well-defined classes. The first, in which the effects are small or zero, includes sodium perchlorate, sodium toluene-*p*-sulphonate, and tetraethylammonium perchlorate. The first two have a small accelerating power on the reaction, and the dependence of rate upon concentration of salt is linear, within experimental error, up to a concentration of *ca.* 2M. Tetraethylammonium perchlorate has very little effect on the rate.

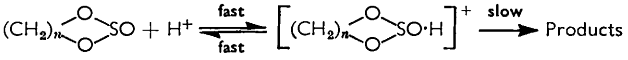
The second class includes sodium chloride and sodium bromide. These salts have a very marked catalytic power, and the rate is very nearly proportional to the concentration of salt. Such catalytic power appears to be associated specifically with the negative ion, and this accords with the catalytic power of hydrogen chloride and of hydrogen bromide, illustrated in Fig. 1. Here it can be seen that, at high concentrations of acid, the points representing catalysis by these substances lie markedly above the plot representing the relationship between the logarithm of the rate and H_0. Still more, of course, do these acids exceed in catalytic power what would be expected from their molar concentrations, the results for perchloric acid at low acidity being taken as standard. Sulphuric acid must be included in this category, and the effects of the negative ions concerned fall in the order $Br^- > Cl^- \gg HSO_4^-(>ClO_4^-)$. This is the order of their decreasing nucleophilic power. It seems reasonable, therefore, to attribute this type of catalysis to nucleophilic attack by the negative ion on the sulphur atom of the protonated sulphite.

Influence of Solvent and Temperature.—The reaction, both at low and at high acidity, is faster in 90% D_2O than in H_2O by a factor of 1·5 or more. The entropy (ΔS^*) and the energy (ΔE) of activation, calculated from formula $k = (e\boldsymbol{k}T/\boldsymbol{h}) \exp (\Delta S^*/\boldsymbol{R}) \exp (-\Delta E/\boldsymbol{R}T)$ for ethylene sulphite are: ΔS^*, $-15·8$ e.u.; ΔE, 20·15 kcal. mole^{-1}; and for trimethylene sulphite: ΔS^*, $-13·0$ e.u.; ΔE, 20·15 kcal. mole^{-1}; both at 1M-perchloric acid.

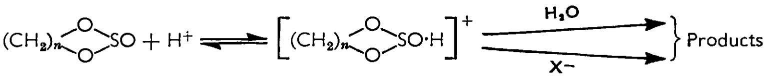
Mechanism of Hydrolysis; Preliminary Considerations.—The present paper records a study, by kinetic methods only, of this acid-catalysed ester-hydrolysis. From such a study, it is possible to make limited deductions concerning the mechanism of the reaction; the accompanying papers amplify the conclusions. The rate-difference in deuterated solvent and water is characteristic [5] of reactions which proceed by a pre-equilibrium proton-transfer, which in this case is probably (1). The proton might be associated either with the terminal or with the ring-oxygen atoms.


. . . . (1)

The reaction is not Hammett-dependent; therefore it is very unlikely that the stage of the reaction which follows the fast proton-transfer is a unimolecular reaction of the *A*-1 class, for such reactions are typically Hammett-dependent.[3, 5] So mechanisms of the type shown in equation (2) are eliminated.


. . . . . (2)

It seems probable, therefore, that some nucleophilic reagent is concerned in the rate-determining covalency change. The most obvious possibility is:


. . (3)

Such a mechanism would accord with the considerable catalytic power of added nucleophilic reagents such as bromide or chloride ions. It would accord also with the negative entropies of activation obtained in the present examples. Such negative entropy factors are often observed[7] in acid-catalysed reactions in which a molecule of the solvent is kinetically concerned in the rate-determining stage of the reaction.

Reactions of the type shown in equation (3), with the solvent water acting as the nucleophilic reagent, should follow the kinetic form:[8]

$$\text{Rate} \propto [\text{S}][\text{H}^+]f_s a_w f_{\text{H}+}/f^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here $f^{\ddagger}$ is the activity coefficient of the transition state, which contains S, H_2O, and a proton; a_w is the activity of water; and the other symbols have their customary significance. In some examples[8] of reactions considered to follow this path, the activity-coefficient ratio, $f_s a_w f_{\text{H}^+}/f^{\ddagger}$, is near unity in the critical experimental region, and hence the rate of reaction is linearly dependent on the concentration of acid, as is required by the Zucker–Hammett hypothesis.

Such a limiting situation is not achieved in the present experiments, and in many examples in the literature similar deviations from what might be called ideal behaviour in terms of the above hypothesis are found. Thus the rate of iodination of acetophenone[9] is accurately proportional to the concentration of acid only up to about 1·5M, and increases more rapidly than the acid-concentration when this is increased further. Similarly the rates of hydrolysis of both methyl formate and ethyl acetate[10] are not strictly proportional to the concentration of acid. In the present experiments, the rate of hydrolysis increases much more rapidly than would be expected if the rate was linearly dependent on concentration of acid, and in fact over a limited range of acidity there is an approximate dependence of rate on the square of the concentration of acid. If sodium perchlorate is added to keep the total concentration of electrolyte constant at 6M, the rate of hydrolysis is then linear with acidity in the range of acid concentration 1—6M. Hence in these particular mixtures the above activity-coefficient term is very nearly constant, though this is not so for mixtures of perchloric acid with salts other than sodium perchlorate.

In considering the effect of the ionic species on the activity-coefficient term, it should first be noted that the effects of added salts on the rate of hydrolysis do not correlate with their effects on the activity coefficient, f_s, of the organic sulphite, as measured by the solubilities of ethylene sulphite in solutions of electrolytes.[11] Both sodium perchlorate and sodium toluene-*p*-sulphonate have a " salting-in " effect on ethylene sulphite, and hence reduce its activity coefficient.[11] The increase in the rate of hydrolysis found when these salts are added cannot, therefore, be associated with an effect on the activity of the organic substrate. Nor can it be associated with a change in the activity of water, for this decreases[12] with increasing concentration of perchloric acid.

It seems in fact that the activity coefficient ratio, $f_s a_w f_{\text{H}^+}/f^{\ddagger}$, is modified by the presence of added electrolytes, by an amount which is to a first approximation proportional to the concentration of the electrolyte, but has a specific value for each particular electrolyte. The catalytic power observed in the present experiments is in the order: $\text{NaClO}_4 \sim \text{C}_7\text{H}_7\text{SO}_3\text{Na} \sim \text{HClO}_4 > \text{NEt}_4\text{ClO}_4$. For perchloric acid, in the range 0·5—5M, the magnitude of the increase in the value of k_1/H^+, and therefore of the activity-ratio term, for a given increase in concentration of electrolyte is of the same order of magnitude as that of the change in the mean ion activity coefficient of perchloric acid.[12, 13] There is, however, no direct association of these quantities in the more dilute solutions.

[6] Wiberg, *Chem. Reviews*, 1955, **55**, 713.

[7] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362.

[8] Chmiel and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 3326; Long, Dunkle, and McDevitt, *J. Phys. Colloid Chem.*, 1951, **55**, 813, 829.

[9] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

[10] Bell, Dowding, and Noble, *J.*, 1955, 3106.

[11] Davies and Tillett, *J.*, 1958, 4766.

[12] Robinson and Baker, *Trans. Proc. Roy. Soc. N.Z.*, 1946, **76**, 250.

[13] Markham, *J. Amer. Chem. Soc.*, 1941, **63**, 874.

Acid-dependence in the Chloride-catalysed Reaction.—If the Zucker–Hammett hypothesis be accepted, reactions which involve a molecule of water undergoing covalency change in the rate-determining stage of an acid-catalysed reaction are typically concentration-dependent, whereas reactions which involve in the rate-determining transition state only a neutral substrate and a proton are typically Hammett-dependent. It is of some interest, therefore, to investigate what happens to the form of the dependence of rate on acidity in the present example, when the molecule of water is replaced by chloride ions in the transition state for the hydrolysis. To examine this, the reaction has been studied in the region of relatively high acidity, with and without chloride ions, present in amount (0·25M) sufficient to increase considerably the rate of reaction, but insufficient, it is considered [cf. 3] to alter differentially the values of H_0 for the solutions. The following are values for the reaction catalysed by 0·25M-sodium chloride at different acidities,[2] it being assumed that the added chloride ions do not differentially affect the rate of attack by water on the protonated sulphite.

$HClO_4$ (M)	1·098	2·184	3·275	4·373	1·000
$NaClO_4$ (M)	—	—	—	—	5·000
H_0 *	−0·13	−0·72	−1·21	−1·74	−1·3
$2 + \log_{10} (\Delta k_1/\text{Cl}^-)$ (l. mole^{-1} min.$^{-1}$) †	0·390	0·862	1·261	1·711	1·24

* In the absence of added chloride ions.

† $\Delta k_1 = \{k_1(\text{Cl}^-) - k_1 \text{ (no Cl}^-)\}$, for otherwise the same experimental conditions; the data are given in Tables 1(*a*) and 1(*d*).

There is a fairly accurately linear relationship between $\log_{10}(\Delta k_1/\text{Cl}^-)$ and H_0, and the slope (0·82) is nearer to unity than is the case for the non-catalysed reaction. The point representing the effect of added sodium perchlorate on the acidity lies below that which would be predicted from the value of H_0 for this solution, but less markedly so than for the non-catalysed reaction. So the chloride-catalysed reaction falls much nearer to the Hammett-dependent category than does the non-chloride-catalysed reaction. The rate-equation that should be followed in the former case is:

$$\text{Rate} \propto [\text{S}][\text{H}^+][\text{Cl}^-]f_{\text{S}}f_{\text{H}^+}f_{\text{Cl}^-}/f^{\ddagger} \quad (5)$$

For this to be Hammett-dependent, it is required that the ratio $f_{\text{S}}f_{\text{H}^+}f_{\text{Cl}^-}/f^{\ddagger}$ follow the protonation of a neutral indicator, and it is not, perhaps, surprising that, though this seems to be approximately true, the test of adding sodium perchlorate reveals significant deviations from exact accordance.

The present paper leaves undiscussed the questions of intervention of reversible or non-reversible stages involving the half-hydrolysed ester of sulphurous acid; and also of the position of bond-fission under the various conditions of catalysis. These matters, and further details of the reaction paths, are discussed in the accompanying papers.

We are indebted to Professor F. A. Long, of Cornell University, and to Professors E. D. Hughes, F.R.S., and Sir Christopher Ingold, F.R.S., for valuable discussion; also to the Department of Scientific and Industrial Research for a grant (to J. G. T.).

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.

[*Received, July* 30*th*, 1958.]