

99. *Tracer Studies in Ester Hydrolysis. Part XI.\* The Hydrolysis of Diphenylmethyl Toluene-*p*-sulphinate.*

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The hydrolysis of diphenylmethyl toluene-*p*-sulphinate is very slow in neutral aqueous dioxan, but is acid-catalysed and is rapid in alkaline solution. The sulphur-oxygen bond is broken during alkaline hydrolysis. Alkyl-oxygen fission predominates in solutions containing perchloric acid. The dependence of rate upon acidity, and the values of the deuterium solvent isotope effect, and the entropy of activation, suggest a predominantly *A*-1 mechanism. Hydrogen bromide is a more effective catalyst than perchloric acid; it changes the mechanism because it can convert the ester into the readily hydrolysable sulphinyl bromide; hydrogen chloride is ineffective in this respect. Small amounts of diphenylmethyl *p*-tolyl sulphone are formed as a by-product of acid hydrolysis.

CARBONIUM ions have been shown to be intermediates in the rearrangement of diaryl-methyl arenesulphonates to sulphones in acetic acid.<sup>1</sup> We have therefore examined the hydrolysis of diphenylmethyl toluene-*p*-sulphinate with the expectation of finding evidence for alkyl-oxygen fission in contrast to the sulphur-oxygen fission observed in the hydrolysis of methyl toluene-*p*-sulphinate (Part X \*).

*Results.*—The rate constants for hydrolysis are given in Table 1. Dioxan-water 60 : 40 (v/v) was the usual solvent; the ester is only sparingly soluble in more aqueous mixtures. The first-order rate constants,  $k_1$ , are not proportional either to concentration of perchloric acid or to its protonating power as measured by Hammett's acidity function, but a plot (see Figure) of  $\log k_1$  against  $-H_0$  is linear with a slope of *ca.* 1.6. The values of  $-H_0$  are taken from Part X and ref. 2.

The entropy of activation is +2 e.u. in 60 : 40 v/v dioxan-water (calculated from rate

\* Part X, *J.*, 1962, 2562.

<sup>1</sup> Wragg, McFadyen, and Stevens, *J.*, 1958, 3603.

<sup>2</sup> Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

TABLE 1.

First-order rate constants,  $k_1$  for hydrolysis of diphenylmethyl toluene-*p*-sulphinate (dioxan-water 60 : 40 v/v and 25.2° unless specified).

## (A) Acid solution.

(i) Acid: Perchloric unless specified.

[HX] (M) .....	0.20				0.22	0.33		0.50	
$10^5 k_1$ (sec. <sup>-1</sup> ) .....	2.2 <sub>2</sub>	4.5 <sub>5</sub> *	6.5 <sub>1</sub> †	4.5 <sub>0</sub> ‡	2.5 <sub>7</sub> §	3.6 <sub>7</sub>	11.7 ¶	11.7	14.3 **
[HX] (M) .....	0.56	0.59	0.69	0.69	0.82	1.00			
$10^5 k_1$ (sec. <sup>-1</sup> ) .....	8.8 <sub>4</sub> §	26.5	33.4		68	108			

(ii) Variation of solvent. [HClO<sub>4</sub>] = 0.2M.

Dioxan (v %)	60	65	75	80	85	90
$10^5 k_1$ (sec. <sup>-1</sup> ) .....	2.2 <sub>2</sub>	2.1 <sub>1</sub>	1.6 <sub>1</sub>	1.4 <sub>3</sub>	1.2 <sub>8</sub>	2.4 <sub>3</sub>
$H_0$ .....	1.90	2.00	2.08	2.05	2.01	1.67
3 + log $k_1$ + $H_0$ .....	0.25	0.32	0.29	0.22	0.12	0.06

(iii) Variation of temperature. [HClO<sub>4</sub>] = 0.2M.

Temp. ....	15.7°	25.2°	35.0°	44.6°
$10^5 k_1$ (sec. <sup>-1</sup> ) .....	5.4 <sub>0</sub>	2.2 <sub>2</sub>	8.8 <sub>4</sub>	26.3

## (B) Alkaline solution.

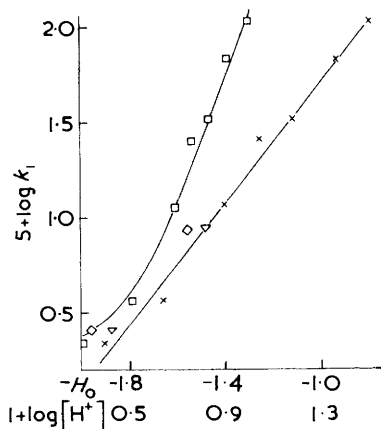
At 0°; [NaOH] = 0.02M;  $k_2 \approx 0.05$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. For the methyl ester in similar conditions  $k_2 \approx 0.11$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

## (C) Initially neutral solution.

At 25.2°. For diphenylmethyl toluene-*p*-sulphinate,  $10^6 k_1 = 1.42$  sec.<sup>-1</sup>; for methyl toluene-*p*-sulphinate,  $10^6 k_1 = 0.0122$  sec.<sup>-1</sup>; for diphenylmethyl chloride,  $10^5 k_1 = 1.28$  sec.<sup>-1</sup>.

\* D<sub>2</sub>O-dioxan. † 0.4M-NaClO<sub>4</sub>. ‡ HBr. § HCl. ¶ 0.27M-NaClO<sub>4</sub>. \*\* 0.1M-NaClO<sub>4</sub>.

measurements with added 0.2M-perchloric acid), and the energy of activation is 25 kcal. mole<sup>-1</sup>. For the methyl ester in 40 : 60 v/v dioxan-water  $\Delta S^\ddagger = -12$  e.u., and  $E = 21$  kcal. mole<sup>-1</sup> (Part X). Hydrogen bromide, but not hydrogen chloride, is a more effective catalyst than perchloric acid.



Plot of  $\log k_1$  against (□)  $\log [\text{HClO}_4]$ , (◇)  $\log \text{HCl}$ , (x)  $-H_0$  for  $\text{HClO}_4$ , and (▽)  $-H_0$  for  $\text{HCl}$ .

The sulphur-oxygen bond is broken during alkaline hydrolysis (Table 2). Hydrolysis catalysed by perchloric acid gives predominant alkyl-oxygen fission, whereas that catalysed by hydrogen bromide gives largely sulphur-oxygen fission. Because hydrolysis in initially neutral solution is autocatalysed by the sulphinic acid we did not attempt to determine the position of bond fission. Small amounts of diphenylmethyl *p*-tolyl sulphone

TABLE 2.

Bond fission.

Dioxan : water 60 : 40 v/v; 25.1°; 0.2M-acid catalyst unless specified otherwise.  
 Isotopic abundances are given in atom % excess above normal.

Isotopic abundance { $\begin{cases} \text{H}_2\text{O} \dots\dots\dots \\ \text{Ph}_2\text{CH}\cdot\text{OH} \end{cases}$	$\text{HClO}_4$					$\text{HBr}$		$\text{NaOH}$	
		0.797	0.734	0.576	0.678	0.54	0.222	0.149	0.00
Alkyl-oxygen fission (%).....	85	80	63*	80†	63‡	25	21	0	0
Sulphone (mole %).....	6.4	5.4	6.4	3.6	4.6	3.2	2.0	0	0

\* At 46.0°. † m-HClO<sub>4</sub>. ‡ Dioxan-water 90 : 10 v/v.

were isolated after acid hydrolysis. The amount, determined by titration, or by sulphur analysis of the crude product, was not more than *ca.* 4% of the total reaction product with perchloric acid as the catalyst, and *ca.* 2% with hydrogen bromide. This sulphone was not formed by interaction between diphenylmethanol and the sulphinic acid, and must have arisen by intramolecular rearrangement of the sulphinic ester or by reaction between free diphenylmethyl cations and the sulphinic acid.

For comparison we measured also some rates of hydrolysis of methyl toluene-*p*-sulphinat and diphenylmethyl chloride in 60 : 40 v/v dioxan-water (Table 1).

*Discussion.*—(a) *Alkaline hydrolysis.* The second-order reaction with hydroxide ion is:  $\text{C}_7\text{H}_7\cdot\text{SO}\cdot\text{O}\cdot\text{CHPh}_2 + {}^{18}\text{OH}^- \longrightarrow \text{C}_7\text{H}_7\cdot\text{SO}\cdot{}^{18}\text{O}^- + \text{Ph}_2\text{CH}\cdot\text{OH}$ . The second-order rate constants for hydrolysis of the methyl and diphenylmethyl esters in 60 : 40 v/v dioxan-water are similar (Table 1). The slightly lower reactivity of the diphenylmethyl ester may be caused by steric hindrance to the approaching nucleophile by the bulky phenyl groups. The rate of the alkaline hydrolysis of the methyl ester is increased almost 40-fold by a change from 60 : 40 to 40 : 60 v/v dioxan-water (Table 1 and Part X).

(b) *Neutral hydrolysis.* The hydrolysis of the diphenylmethyl ester in 60 : 40 v/v dioxan-water is autocatalysed by the sulphinic acid; we measured, therefore, only an initial rate. The methyl ester is very much less reactive in these conditions (by a factor of *ca.* 10<sup>2</sup>; Table 1), and therefore we suggest that it is hydrolysed in neutral solution with sulphur-oxygen fission, whereas the diphenylmethyl ester is generating a carbonium ion intermediate by alkyl-oxygen fission. If this interpretation is correct diphenylmethyl toluene-*p*-sulphinat ionises to a carbonium ion 900 times more slowly than does diphenylmethyl chloride (Table 1).

(c) *Acid hydrolysis.* Strong acids are effective catalysts, *e.g.*, m-perchloric acid increases the rate of hydrolysis by a factor of *ca.* 800, and hydrogen bromide is even more effective. The usual tests for molecularity suggest that the reaction has an A-1 mechanism in perchloric acid.

The entropy of activation, +2 e.u., is in the range usually associated with A-1 mechanisms of hydrolysis,<sup>3</sup> and it is *ca.* 14 e.u. more positive than for the hydrolysis of the methyl ester by the A-2 mechanism (Part X). The energy of activation is also greater than for the methyl ester. The deuterium solvent isotope effect,  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$  is 2.0, and is larger than the value of 1.7 found for the methyl ester. These values are consistent with the suggested mechanistic differences between these reactions.<sup>4</sup>

A plot of  $\log k_1$  against  $\log [\text{HClO}_4]$  is a curve, but against  $-H_0$  it is a straight line of slope 1.6 (see Figure). For the hydrolysis of the methyl ester the corresponding plot against  $-H_0$  has a slope of 0.7 (Part X). Thus the rate of hydrolysis is much more sensitive to increasing acidity for the diphenylmethyl than for the methyl ester. This difference between A-1 and A-2 mechanisms of nucleophilic substitution is commonly observed,

<sup>3</sup> Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2632.

<sup>4</sup> Pritchard and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4162; Bunton and Shiner, *ibid.*, 1961, **83**, 3207.

and it is consistent with either the Zucker-Hammett hypothesis<sup>5a</sup> or with the newer empirical correlation of Bunnett which takes the activity of water explicitly into account in interpreting variations of rate with acidity.<sup>5b</sup> This treatment has been applied to many acid-catalysed reactions, but it cannot be applied to our results at present because the activity of water in acidified 60 : 40 v/v dioxan-water is not known (however, compare ref. 6).

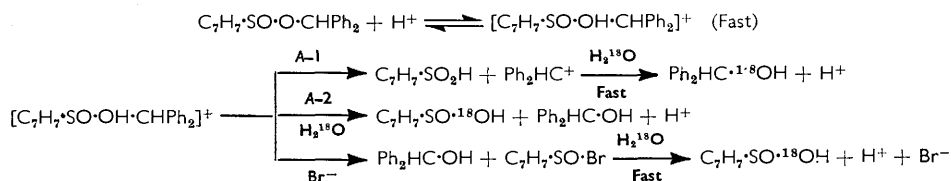
With a constant concentration (0.2M) of perchloric acid there is a minimum rate of hydrolysis in 85 : 15 v/v dioxan-water (Table 1). The protonating power of the medium as measured by  $H_0$  varies similarly (Table 1). We do not attach particular mechanistic significance to this observation because the methyl ester behaves similarly (Part X).

Although these kinetic tests are consistent with an A-1 mechanism of hydrolysis, tracer experiments with  $H_2^{18}O$  show that alkyl-oxygen fission is not complete. In 60 : 40 v/v dioxan-water containing perchloric acid there is *ca.* 20% of sulphur-oxygen fission, probably arising from a bimolecular attack of water on the sulphur atom. The relative amounts of alkyl-oxygen and sulphur-oxygen fission are not affected by a change from 0.2M- to 1.0M-perchloric acid, which suggests that the rates of both processes are affected similarly by limited changes in acid concentration. A decrease in the water content of the solvent decreases the ratio of alkyl- to acyl-oxygen fission from 5 : 1 in 60 : 40 to *ca.* 1.6 : 1 in 90 : 10 v/v dioxan-water.

Added sodium perchlorate speeds the acid hydrolysis, probably by increasing the protonating power of perchloric acid.<sup>7</sup> It has a similar effect on the A-2 hydrolyses of methyl toluene-*p*-sulphinic acid (Part X) and of dialkyl sulphites.<sup>8</sup>

The methyl and the diphenylmethyl ester differ in their susceptibility to halogen acids as catalysts. For the methyl ester (in 40 : 60 v/v dioxan-water) both hydrogen chloride and hydrogen bromide are much better catalysts than is perchloric acid: with 0.2M-acid  $k_{HCl}/k_{HClO_4} \approx 8$ , and  $k_{HBr}/k_{HClO_4} \approx 25$ , and with 0.5M-acid  $k_{HCl}/k_{HClO_4} \approx 19$ . But for the diphenylmethyl ester (in 60 : 40 v/v dioxan-water) with 0.2M-acid  $k_{HCl}/k_{HClO_4} \approx 1$ , and  $k_{HBr}/k_{HClO_4} \approx 2$ , and at higher acid concentrations perchloric acid is a better catalyst than is hydrogen chloride. This difference arises simply because hydrogen chloride is weaker than perchloric acid, and the points for both acids fit on the same plot of  $\log k_1$  against  $-H_0$  (Figure). Hydrolysis of the diphenylmethyl ester is relatively insensitive to halide ions because the predominant reaction is unimolecular alkyl-oxygen fission, unaffected by nucleophiles, and chloride ions are not sufficiently nucleophilic towards sulphur to be able to compete effectively. Bromide ions, in water, are sufficiently nucleophilic towards sulphur for the rate to be greater with hydrogen bromide than with perchloric acid, and hydrolysis then involves predominant sulphur-oxygen fission.

The mechanisms of hydrolysis can therefore be written:



Except for the special catalytic effect of hydrogen bromide there is a strong similarity between the acid hydrolyses of diphenylmethyl toluene-*p*-sulphinic acid and trifluoroacetate.<sup>9</sup>

<sup>5</sup> (a) Long and Paul, *Chem. Rev.*, 1957, **57**, 935; (b) Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, and accompanying papers.

<sup>6</sup> Grunwald in "Electrolytes," ed. Pesce, Pergamon Press, Oxford, 1962, p. 62, and ref. cited therein.

<sup>7</sup> Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

<sup>8</sup> Bunton, de la Mare, and Tillett, *J.*, 1959, 1766; Tillett, *J.*, 1960, 5138.

<sup>9</sup> Bunton and Hadwick, *J.*, 1961, 943.

For both reactions uni- and bi-molecular mechanisms coexist; they have different positions of bond fission and are different chemical reactions which fortuitously lead to the same hydrolysis products.

### EXPERIMENTAL

*Materials.*—Diphenylmethyl toluene-*p*-sulphinic acid was prepared from the alcohol and the sulphinyl chloride in pyridine.<sup>1</sup> It was recrystallised from ether at 0° and had m. p. 84° (Found: C, 74.9; H, 5.3; S, 10.0. Calc. for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>S: C, 74.5; H, 5.6; S, 10.0%). On prolonged heating at ca. 90° it rearranged to the sulphone.

The preparation of the aqueous dioxan solvent and the reagents is described in Part X.

*Kinetics.*—Hydrolysis was followed by acid-base titration as described in Part X.

The results for a reaction catalysed by perchloric acid are:

Dioxan-water 60:40 v/v; 25.2°; [HClO<sub>4</sub>] = 0.82M. Portions (5 c.c.) were removed and the acid was partially neutralised with 20.86 c.c. of 0.194M-sodium hydroxide. The residual acid was titrated with M/100-sodium hydroxide, with the tabulated results. These led to 10<sup>5</sup> *k* = 68 sec.<sup>-1</sup> (calculated graphically).

Time (min.)	3	7	11.5	16	21	25.5	30	35	40.5	46	∞
Titre (c.c.)	11.3	14.7	16.8	18.1	19.1	20.7	21.8	22.1	24.0	24.1	27.0, 26.6, 26.8
log ( <i>a</i> - <i>x</i> ) (obs.)	1.190	1.083	1.000	0.937	0.887	0.786	0.696	0.578	0.455	0.439	
log ( <i>a</i> - <i>x</i> ) (calc. from <i>k</i> <sub>1</sub> )	1.163	1.085	1.010	0.918	0.843	0.770	0.687	0.600	0.500	0.405	

The rates of the hydrolyses in initially neutral solution of the sulphonic esters and of diphenylmethyl chloride were measured conductometrically.

*Bond Fission.*—The ester was hydrolysed in dioxan-H<sub>2</sub><sup>18</sup>O. After complete reaction, crude diphenylmethanol was isolated by extraction from alkaline solution with ether. The ether layer was washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>) and after evaporation the diphenylmethanol was sublimed at 60–70° (bath)/10<sup>-3</sup> mm. The purified diphenylmethanol had a sharp m. p. and contained no sulphur. In one experiment, at 46.0° with 0.2M-perchloric acid, an oily residue was left after sublimation, and the yield of diphenylmethanol was small; the determination of the position of bond-fission is therefore somewhat unreliable here.

The oxygen isotopic content of the purified diphenylmethanol was determined by Rittenberg and Ponticorvo's method,<sup>10</sup> by heating the alcohol in a sealed tube with phenylenediamine hydrochloride and carbon dioxide,<sup>11</sup> or by a modification of the latter method in which the alcohol was heated with phenylenediamine dihydrochloride and guanidine hydrochloride (we are grateful to Professor D. Rittenberg for suggesting the use of guanidine hydrochloride).

The amount of sulphone was estimated by two methods. After complete reaction, titration of the acid produced and comparison of this amount with that calculated from the ester concentration gave a maximum value for the amount of sulphone. This method is insensitive, particularly with the higher concentrations of mineral acid, and therefore the amount of sulphone was also calculated from the sulphur content of the crude diphenylmethanol determined by microanalysis. Diphenylmethyl *p*-tolyl sulphone was also isolated from the reaction mixture by crystallisation (it is much less soluble than diphenylmethanol in ethanol) and was characterised by m. p., mixed m. p., and infrared spectrum.

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<sup>10</sup> Rittenberg and Ponticorvo, *Internat. J. Appl. Radiation Isotopes*, 1956, **1**, 208.

<sup>11</sup> Dahn, Moll, and Menassé, *Helv. Chim. Acta*, 1959, **42**, 1225.