

412. *The Hydrolysis of Aryl Sulphonates. Part I.*

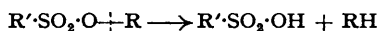
By C. A. BUNTON and (Mrs.) Y. F. FREI.

The hydrolysis of phenyl toluene-*p*-sulphonate has been investigated in aqueous dioxan, with heavy oxygen as an isotopic tracer. The reaction is shown to involve a bimolecular attack by hydroxide ion on the sulphur atom, with fission of the sulphur-oxygen bond.

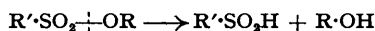
THE chemical behaviour of alkyl sulphonates $R'SO_2 \cdot OAlk$ towards nucleophilic reagents is analogous to that of alkyl halides and sulphates, and they alkylate hydroxy- and amino-compounds by reactions which involve breaking of the alkyl-oxygen bond (Ferns and Lapworth, *J.*, 1912, 273). Hydrolysis may occur by the S_N1 or the S_N2 mechanism, depending on the structure of the compound and the experimental conditions, but no acid catalysis has been observed (Démény, *Rec. Trav. chim.*, 1931, 50, 60).

The optical results of work by Kenyon and his collaborators on the hydrolysis of alkyl sulphonates are adequately explained in terms of alkyl-oxygen fission, and this conclusion is proved by tracer studies in water containing an excess abundance of ^{18}O (Ader, Thesis, London, 1949).

The reduction of alkyl sulphonates by lithium aluminium hydride also involves alkyl-oxygen bond fission, with the formation of a hydrocarbon (Schmid and Karrer, *Helv. Chim. Acta*, 1949, 32, 1371; Kenner and Murray, *J.*, 1950, 406):



However, these authors showed that aryl sulphonates are reduced by this reagent to phenols, a reaction which presumably involves fission of the sulphur-oxygen bond:

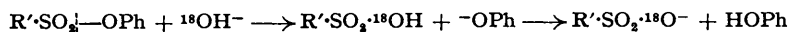


It was expected that this alternative mode of nucleophilic substitution, involving attack on the sulphur atom, should be realised in the hydrolysis of compounds whose structure restricts attack on the carbon atom involved in the oxygen-carbon bond. Nucleophilic attack on a

phenyl group is usually difficult, as in the hydrolysis of the halogeno-benzenes. It is now shown that the hydrolysis of an unsubstituted phenyl sulphonate involves nucleophilic attack on the sulphur atom, with breaking of the sulphur-oxygen bond.

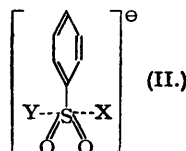
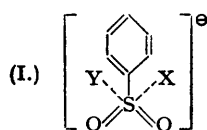
The hydrolysis of phenyl toluene-*p*-sulphonate is very much slower than that of alkyl sulphonates. The reactions were carried out in alkaline aqueous dioxan, with water enriched in ^{18}O , and this tracer did not appear in the isolated phenol.

No phenol was isolated from an experiment carried out in 60% aqueous dioxan for 3 weeks at 120° , in the absence of alkali; therefore the reaction occurs by attack of the hydroxide ion on the sulphur atom:



A similar nucleophilic attack on a hexavalent sulphur atom occurs very readily in reactions of the sulphonyl halides with amino- and hydroxy-compounds.

The nucleophilic attack on the sulphur atom, which only occurs in this special case among sulphonic esters, requires a transition state in which the groups X and Y may be either in one plane with S and O atoms (as I) or opposite to each other in a plane perpendicular to the O-S-O plane (as II).



EXPERIMENTAL.

The experiments were carried out in aqueous dioxan (4 : 6 by vol.), to which the required amounts of solid potassium hydroxide were added; a correction was applied for the dilution of ^{18}O by the normal oxygen of the potassium hydroxide.

The phenol was isolated, and, after distillation, dried intensively over phosphoric oxide. It was reduced to water by Russell and Fulton's method (*Ind. Eng. Chem. Anal.*, 1933, 5, 384). The first portion of the water to pass through the cracking train was rejected. The remainder was purified by static distillation *in vacuo*, and the ^{18}O content determined by equilibration with dry carbon dioxide (Cohn and Urey, *J. Amer. Chem. Soc.*, 1938, 60, 679), followed by a mass-spectrometric determination of the oxygen isotope abundances in the carbon dioxide. These analyses were carried out on a 180° mass spectrometer of conventional design. A blank test with the cracking train showed that a 10% dilution of the isotopic tracer occurred.

The experimental results, summarised in the Table, show that fission of the sulphur-oxygen bond occurs to an extent of at least 98% of the reaction, and that phenol does not exchange its oxygen with water under these conditions,

Expt. no.	Volume of solvent (c.c.)	Moles of ester	Moles of KOH	Time (days)	Temp.	Isotope abundances (atoms % excess),		
						original *	phenol	
1	180	0.016	0.025	20	100°	0.528	0.006	
2	200	0.02	0.25	8	100	0.517	0.011	
3	130	0.02	0.25	6	120	0.502	0.013	
4	200	0.02	—	40	120	No reaction.		
5	100	Phenol, moles 0.01	Na salt, moles 0.012	KOH, moles 0.1	6	120	0.525	0.005

* Corrected for dilution by KOH.

The figures quoted for the excess isotope abundances are obtained by comparing the intensities of the peaks 44 and 46, representing $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ and $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ respectively. The peak 45 due to $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ is ignored as it will always be very small in comparison with $^{12}\text{C}^{16}\text{O}^{18}\text{O}$. If the ratio 44 : 46 = *R*, then the abundance of ^{18}O is given by $n = [100/(2KR + 1)]$ atoms %, where $K = 1.038$ at 25° .

The abundances quoted are the excess above the value obtained for normal carbon dioxide, the values for the normal and enriched samples being determined at the same time for each analysis.

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