374. *Hydrolysis or Alcoholysis of Resorcinol Ether Sulphonic Acids.*

By G. Spencer Hartley.

Sulphonic acids of resorcinol ethers are reconverted into the ethers in solution in alcohols or moist non-hydroxylic solvents. The velocities of conversion have been approximately measured under various conditions. It appears that the sulphonic acid group must be undissociated, and that it can then react with any hydroxyl group.

In the course of preparations described in the preceding paper, it was noticed that resorcinol ether sulphonic acids, when dissolved in alcohol without neutralisation and heated, appeared to revert to the original ether. " Hydrolysis " of a sulphonic acid under such mild conditions seemed to merit further study. For this purpose, the dioctyl ether sulphonates were selected, because, not only had they been obtained in the purest condition, but also the ether itself crystallises exceptionally well and is thus easily recovered and characterised.

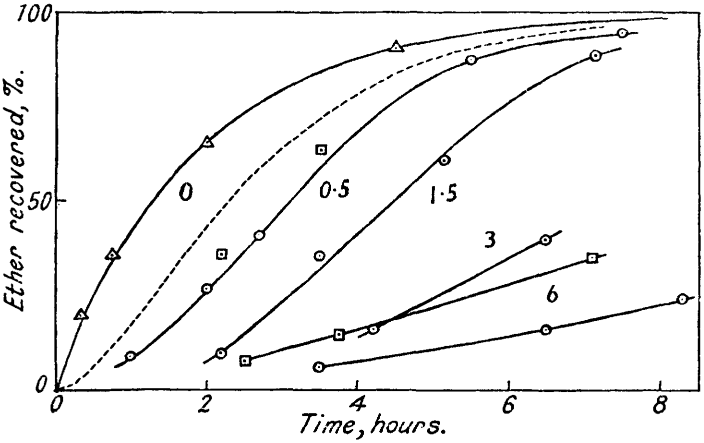
A sample of the disulphonic acid hexahydrate, heated in absolute alcohol at 77° for 6 hours, gave an almost quantitative yield of white crystalline ether on moderate dilution with water and cooling. The recovered ether, once recrystallised, had m. p. and mixed m. p. identical with the original. It was neither dissolved nor emulsified with hot alkali, nor did it couple at once with diazotised aniline when suspended in cold alkali. There was thus no hydrolysis of the ether group itself. From specimens of disulphonic acid and of ether, dissolved in absolute alcohol with the addition of concentrated sulphuric acid in 5 : 1 molal excess and heated at 77° for 12 hours, 96% of ether was recovered in each case. Owing to slight loss in recovery, the equilibrium may lie further to the ether side, but that a trace at least of monosulphonic acid was present in each solution at the end was shown by the very strong foaming power developed on addition of water to the filtrate from the ether.

The rate of complete reaction of the disulphonic acid in ethyl alcohol at 77° was followed, by recovery of the ether, with the results shown in the graph. The rate rapidly decreases with increasing water content. M/20-Solutions of the hexahydrate were used, and the 0·5% of water introduced has been allowed for in the figures given. Additional acid, as hydrochloric acid, had little effect in the driest alcohol, but considerably increased the rate when 6·5% of water was present. In water alone, the solution remained perfectly clear when kept at 100° for 12 hours, even in the presence of hydrochloric acid. On the other hand, when monosulphonate was similarly treated in N-aqueous hydrochloric acid, most of it was recovered as ether. The system is, however, in this case a two-phase one throughout, and the reaction occurs in the small viscous phase, which contains but little water.

In ethylene glycol monoethyl ether (" Cellosolve ") and in *n*-propyl alcohol, the rate of complete reaction of the disulphonic acid is approximately the same as in ethyl alcohol. In *iso*propyl alcohol, it is about one-half as great. At 100°, the reaction in cellosolve proceeds 7 times as quickly as at 77°. Ether could also be recovered after the acid had been heated in dioxan or in methyl ethyl ketone, each containing 5% of water.

It appears from the above facts that the most important condition for the reaction is that the sulphonic acid group should be in the undissociated state, reaction then occurring with any hydroxyl group, either of an alcohol or of a water molecule. Attempts to decide by acid titration between " hydrolysis " and " alcoholysis " as the primary reaction were inconclusive. Although they indicated the formation, in alcohol, of sulphate ester rather than sulphuric acid, further experiment showed that equilibrium between these two possible products is attained far too rapidly for this result to have any significance.

Experiments with the anhydrous potassium disulphonate as starting material for the reaction in acidified alcohol gave erratic results, doubtless owing to the very low solubility of this salt in organic solvents. For this reason, dioxan is preferable for recovery of ether from sulphonation residues (see preceding paper), since, when concentrated aqueous hydrochloric acid is added, a separate aqueous phase is present in which the salts dissolve, and out of which the dioxan extracts the undissociated acids.



△ M/20-*Potassium monosulphonate* + N/3-HCl.
⊙ M/20-*Disulphonic acid.*
▢ M/20-*Disulphonic acid* + N/3-HCl.
The figures attached to the curves denote volume percentages of water.

With an M/20-solution of the anhydrous potassium monosulphonate in N/3-absolute-alcoholic hydrogen chloride, results were obtained which closely fitted the unimolecular reaction velocity equation. The curve on the extreme left of the figure is drawn according to this equation (ordinate $= 1 - e^{-kt}$) with the constant $k = 0{\cdot}54$ (hr.$^{-1}$). On the assumption that the reactivity of each sulphonic acid group in the disulphonic acid is the same, and uninfluenced by the presence of the second group, we should expect a unimolecular constant for the first stage of the reaction of the disulphonic acid equal to twice that for the second. This would lead to the prediction that the complete disulphonic acid reaction would follow the broken curve, for which the ordinates are $1 + e^{-2kt} - 2e^{-kt}$. Allowance being made for the effect of the 0·5% of water introduced with the disulphonic acid, there is reasonable agreement with experiment, indicating that the reactivities of the two groups are at least approximately equal, and thus confirming the assumption (see preceding paper) that they occupy equivalent positions.

It is well known that aromatic sulphonic acids can be hydrolysed by superheated steam in the presence of sulphuric acid, and that hydrocarbons can be separated by making use of the differences in temperature required for this hydrolysis (Armstrong and Miller, J., 1884, **45**, 148; Friedel and Crafts, *Compt. rend.*, 1889, **109**, 95). Sulphonic acids of alkylated phenols are more readily hydrolysed in this way than those of hydrocarbons (Steinkopf and Bruckner, Houben's " Methoden der organische Chemie," 1930, p. 1299) and nitrated resorcinoldisulphonic acid still more easily (Kauffmann and de Pay, *Ber.*, 1904, **37**, 725). It was of interest, therefore, to see whether other sulphonic acids could be hydrolysed or " alcoholysed " under the mild conditions here described.

Specimens of phenyl cetyl ether 4-sulphonic acid, *p*-tolyl cetyl ether 3-sulphonic acid, and 1 : 2-dioctyloxybenzene-4-sulphonic acid were dissolved in cellosolve, the last two as potassium salts with addition of hydrogen chloride in cellosolve. After being heated for 3 hours at 100° and diluted with water, all gave clear solutions on heating. After refluxing for 12 hours (136°), 6% of *p*-tolyl ether was recovered. After refluxing for 72 hours, hydrolysis was evident in all, though by no means complete. Pure ether could only be recovered from the *p*-tolyl compound, and again 6%. Tests with diazotised aniline in alkaline solution showed the presence of free phenolic groups in all cases. Evidently ether hydrolysis accompanies that of the sulphonic acid groups. Benzenesulphonic acid was refluxed for 12 hours with cellosolve and the mixture distilled. There was no trace of water-insoluble substance in the distillate until nearly all the cellosolve had been removed.

EXPERIMENTAL.

The sulphonates and sulphonic acids used are described in the preceding paper.

Absolute ethyl alcohol was refluxed for several hours with magnesium turnings and distilled. Commercial pure *n*- and *iso*-propyl alcohols were similarly treated. Commercial cellosolve was fractionally distilled, and the fraction (90% of the whole) of b. p. 133—136° used. Dioxan and methyl ethyl ketone were commercial pure products, redistilled.

The specimen solutions were sealed up in test-tubes, kept in the refrigerator until required, and then heated in the vapour of boiling water or rectified spirit for the desired period. The tubes were then quickly cooled, broken open, and water added at intervals, with cooling in between, till an equal volume had been added. After standing for one hour at 0°, the ether was filtered off on a small paper, washed with a little cold 50% alcohol, scraped off into a small weighed vessel, and dried at 100° to constant weight. Sudden and excessive dilution of the reaction mixture with water was avoided, as the ether was then difficult to filter and retained some sulphonic acid. Tests with synthetic mixtures showed that the ether weights were accurate to 0·0005 g. The amount of ether obtainable from complete hydrolysis of the specimens used was 0·05 g. For half reaction, the accuracy is thus about 2%.

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