XXII.—*Studies on Sulphonic Acids.* No. I. *On the Hydrolysis of Sulphonic Acids and on the Recovery of the Benzenes from their Sulphonic Acids.*

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It has long been known that several of the benzenes—using this term to indicate benzene and its true homologues—may be recovered from their sulphonic acids by dry distillation (Freund, *Annalen*, **120**, 80; Beilstein, *ibid.*, **133**, 36), but the reaction is necessarily by no means of a simple character, and consequently the yield of hydrocarbon is unsatisfactory.*

A method of hydrolysing sulphonic acids which permits of the complete recovery of the parent-compound was (we believe for the first time) employed by one of us in conjunction with C. L. Field, in the course of an examination of coal-tar cresol, and consisted in heating the sulphonate with muriatic acid under pressure (*Chem. News*, 1874, **29**, 282; *Ber.*, 1874, **7**, 406). This method has since been of signal service in the hands of various chemists, but there is the practical objection to its use, except on the small scale, that the decomposition has to be effected in closed vessels; and as the temperature at which

* H. Caro recommends that, instead of the sulphonic acid, its ammonium salt be distilled, and according to V. Meyer (*Ber.*, 1882, **16**, 1468), in the case of thiophene, a much better result is thus obtained.

it takes place is in many cases somewhat high, loss from explosion of the tubes is not unfrequently incurred.

Although it would appear to be obvious that sulphuric might be substituted for muriatic acid to promote hydrolysis, we are acquainted with only one instance of its employment: to recover metaxylene from its sulphonic acid, Jacobsen (*Ber.*, 1878, **11**, 19) recommends distillation of a mixture of 10 parts sodium metaxylenesulphonate, 5 parts sulphuric acid and 1 part water; but we are under the impression that the same chemist has somewhere stated that he had prepared cymene by distilling its sulphonic acid with sulphuric acid.

We were led to investigate the behaviour of sulphonic acids on distillation with sulphuric acid in the course of our study of the hydrocarbons resulting from the action of dehydrating agents upon camphor, our primary object having been to find a method of separating the 1:2:3:5 tetramethylbenzene from admixed hydrocarbons. One of us in 1878 (*Chem. News*, **38**, 5; *Ber.*, **11**, 1697) had devised a process for separating mesitylene and pseudocumene by heating the mixture of their sulphonic acids with muriatic acid at 100°, whereby the mesitylenesulphonic acid alone is hydrolysed, the pseudocumene being afterwards recovered by heating at 130—140°; and it had long been known to him that if mesitylene be dissolved in sulphuric acid, it may readily be recovered by merely passing steam into the solution. It therefore appeared probable that the tetramethylbenzene which is formed on methylating mesitylene would likewise form a highly unstable sulphonic acid. It was found, however, on passing steam into the solution in sulphuric acid of the mixture of hydrocarbons from camphor, that not merely the tetramethylbenzene but all the benzenes could without difficulty be recovered. The knowledge thus gained has nevertheless proved of the greatest service, as it has enabled us, dealing with large quantities, to separate the benzenes from hydrocarbons of other series, and to easily recover benzenes from pure sulphonates.

Our method consists in merely passing steam through the solution of sulphonic acid or sulphonate in sulphuric acid, the acid solution being heated and maintained at the temperature at which hydrolysis takes place with fair rapidity. In commencing the operation, if no hydrocarbon distils over, sufficient heat is applied to concentrate the solution more and more, and when the required degree of concentration is attained, *i.e.*, when the temperature of the liquid is sufficiently high, the flame is so regulated that steam passes through the solution without condensing. It is desirable, as a rule, to add a considerable amount of sulphuric acid, not because the rate of hydrolysis very materially depends upon the presence of a large excess of acid, but in order to retain a sufficient bulk of liquid in the retort or flask when operating at a high temperature. We have usually found it con-

venient to add a weight of acid about equal to that of the sulphonate taken; when so large an excess of acid is used, no difficulty arises from the separation of solid sulphate, even if barium, calcium, or lead sulphonates be submitted to distillation. Operating in this way, we have not found the slightest decomposition to occur in the case of any of the numerous benzenes whose behaviour we have studied; we have therefore no hesitation in advising the employment of the method in all cases in which benzenes occur mixed with other hydrocarbons from which it is desired to separate them in a state of purity, and also in all cases in which it is desired to recover benzenes from their sulpho-compounds. Two practical illustrations of the value of the method have already been given by ourselves (*Ber.*, 1883, **16**, 2255, 2748*). The yield of hydrocarbon may be said to be theoretical, loss being incurred only (a) through dissolution of a small quantity of hydrocarbon by the water; (b) through incomplete separation of hydrocarbon from the water; and (c) through evaporation of the hydrocarbon. Of these the last only may become serious in the case of the more volatile hydrocarbons, and should be specially guarded against.

The difference in stability of mesitylene- and pseudocumenesulphonic acids led us to anticipate that similar differences would be found to obtain between the sulphonic acids of other hydrocarbons, and we have therefore studied the behaviour of as many as possible. The pure sulphonic acid or sulphonate was introduced, together with a considerable excess of sulphuric acid, into a retort or distillation

* It is well known that it is impossible to obtain the higher homologues of toluene from coal-tar naphtha by fractional distillation, on account of the presence of hydrocarbons of other series. These are in part soluble, and in part insoluble, in sulphuric acid (Jacobsen, *Annalen*, **184**, 200; *Ber.*, **10**, 1009; Nölting, *ibid.*, **17**, 267). Oliveri has stated (*Gazzetta*, 1882, 158) that on warming xylene with sulphuric acid on the water-bath he obtained a hydrocarbon boiling at about 295°, to which he attributes the formula $C_{16}H_{18}$; he appears to regard it as dixylyl, $(C_8H_9)_2$, formed by the action of the acid upon xylene. We also have observed the production of this hydrocarbon from commercial xylene, but have never obtained it on treating xylene, recovered from its sulphonic acid, with sulphuric acid. The hydrocarbon in question is probably a polymeride of an unsaturated hydrocarbon present in commercial xylene.

Moreover, to purify xylene or pseudocumene, it is not sufficient to merely convert the commercial products into sulphonic acids and form salts of the latter. On hydrolysing crude sodium metaxylenesulphonate directly prepared from commercial xylene, we have always observed that a comparatively large amount of black carbonaceous matter remains in the retort, while pure sulphonate does not yield a trace. Crude pseudocumenesulphonate exhibits a similar behaviour. The presence of this "sulphonate" in the mixture obtained on heating commercial xylene with sulphuric acid most seriously affects the separation of orthoxylene from metaxylene in the manner proposed by Jacobsen.

flask provided with a thermometer and steam-tube dipping into the liquid; heat was applied, steam being continually passed through the solution, and the temperature noted at which hydrocarbon began to distil over.

The following results were thus obtained:—

Name of acid.	Temperature of initial hydrolysis.
Benzenesulphonic acid	about 175°
Tolueneparasulphonic acid	„ 150
Metaxylenesulphonic acid } Orthoxylenesulphonic acid } Paraxylenesulphonic acid* }	„ 120
Pseudocumenesulphonic acid	„ 115
Mesitylenesulphonic acid	„ 100
Cymenesulphonic acid	„ 130
1 : 2 : 3 : 5 Tetramethylbenzenesulphonic acid. . } Metamethylisopropylbenzenesulphonic acid }	„ 120
1 : 2 : 4 Dimethylethylbenzenesulphonic acid .. }	

These results justify the hope that it will be found possible to separate many hydrocarbons by “fractional hydrolysis” of mixtures of their sulphonic acids. There are, however, several practical difficulties in the way of effecting this always by mere distillation. Thus the rate at which change takes place at or near the temperature of initial hydrolysis is extremely slow. For example, on distilling a dilute solution of pseudocumenesulphonic acid containing but a small proportion of sulphuric acid, water and hydrocarbon came over at various temperatures in the proportions shown in the following table:—

* On consideration of the results here tabulated, it is obvious that the sulphonic acids which are most stable, are those which are least readily produced when ordinary sulphuric acid is used as sulphonating agent, the only apparent exception being paraxylenesulphonic acid. According to Jacobsen (*Ber.*, 10, 1009) “Beim Schütteln des rohen Theerxylols mit gewöhnlicher Schwefelsäure werden selbst in der Wärme nur geringe Spuren von Paraxylol gelöst.” This, however, is not the case, as paraxylene may be dissolved by well agitating it with ordinary acid almost as easily as pure metaxylene, and therefore it does not materially differ from all other known benzenes in the manner hitherto commonly supposed.

Temperature of liquid.	c.c. of hydrocarbon collected.	c.c. of water collected.
115°	Slight film on water	—
115—118	0·1	320
120—140	0·8	230
118—125	0·3	300
122—125	0·6	370
—	0·6	360
—	0·7	400
—	0·6	400
—	0·5	400
—	0·5	370
—	0·75	440
124—128	0·7	450

The same solution was distilled with a larger proportion of sulphuric acid with the following results:—

Temperature of liquid.	c.c. of hydrocarbon collected.	c.c. of water collected.
115°	0·05	400
115—118	0·2	320
118—124	0·7	370
122—123	1·1	350
123—127	1·4	400
130—140	1·9	400

A somewhat large quantity of metaxylenesulphonic acid distilled with acid behaved as follows:—

Temperature of liquid.	c.c. of hydrocarbon collected.	c.c. of water collected.	Percentage of hydrocarbon in distillate.
About 120°	2·5	1000	0·24
120—125	5·5	1020	0·53
125—128	11·0	1020	1·06
128—138	32·0	1000	3·1
138—142	32·0	550	5·5
142—150	35·0	600	5·5
145—155	61·0	1150	5·0
155—157	23·0	1150	2·0

On this account, and as the rate at which hydrolysis proceeds also depends upon the mass of sulphonic acid present, it becomes necessary to distil at a temperature considerably above that at which the sulphonic acid of the particular hydrocarbon which it is desired to isolate begins to undergo change, and it may be therefore that the temperature is so high that the sulphonic acids of other hydrocarbons

are also hydrolysed. For example, if a mixture of mesitylene- and pseudocumenesulphonic acids be distilled at a temperature not exceeding about 105° , the major portion of the mesitylene is recovered free from pseudocumene; but in order to obtain the remainder, the distillation must be carried on at 105 — 115° , and a good deal of pseudocumene then passes over. Just as in ordinary quantitative separations, however, a precipitate is often dissolved and reprecipitated in order to render a separation complete, so in our case the intermediate fraction may be dissolved in sulphuric acid and redistilled: it is then possible to effect an almost complete separation. By combining our method with that which Jacobsen has rendered such service by introducing, namely, crystallisation of the sulphonic acids from a sulphuric acid solution, complete purification of many hydrocarbons may be very readily effected.

Preliminary experiments have shown that the temperature at which hydrolysis takes place in sealed tubes is not always the same as that at which it occurs when the solution is distilled. Thus, the mesitylene was completely recovered on heating its sulphonic acid at about 110° (in toluene vapour), while pseudocumenesulphonic acid remained unaffected, but was decomposed at about 130° . Metaxylenesulphonic acid underwent hydrolysis at 138° (in xylene vapour), a temperature which, however, did not suffice to change ortho- and para-xylene-sulphonic acids; these latter and toluene-parasulphonic acid were hydrolysed at about 160° . Similarly metacymene was found to be more easily recovered than paracymene. We therefore now propose to study with the greatest care the hydrolysis of a variety of sulphonic acids under pressure, taking into account all circumstances which influence the rate of change, such as the amount of free sulphuric acid, mass of sulphonic acid, temperature and time. The results cannot fail to be of value as a contribution to our knowledge of the behaviour of corresponding derivatives of isomeric and homologous bodies, and it is more than probable that it will be possible sooner or later to devise methods which may serve for the quantitative analysis of mixtures of benzenes and of other compounds which are convertible into sulphonic acid.

As yet we have examined but few sulphonic acids of compounds other than benzenes. Naphthalene- β -sulphonic acid begins to undergo hydrolysis at about 135° . Phenolparasulphonic acid at about 116° paracresolorthosulphonic acid apparently at a slightly higher temperature, viz., 120° ; and parisobutylphenolorthosulphonic acid at; about 110° .

It is our intention to extend these experiments to other sulphonic acids, and we expect soon to be able to give some practical illustrations of the use of our method.