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SEPARATION OF XYLENES¹

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From the literature dealing with the separation of the xylenes it might be inferred that it is a comparatively simple matter to prepare the 3 isomers in a state of chemical purity. This, however, is far from being the case.

It was shown by Fittig² that xylene from coal-tar consists principally of the *meta* derivative together with smaller amounts of the *ortho* and *para* isomers. No attempt was made to separate the hydrocarbons, the evidence that xylene boiling at 130–140° was a mixture being obtained by oxidation to the corresponding acids. Specific directions for the separation of the hydrocarbons were first given by Jacobsen,³ who claimed that *p*-xylene is not sulfonated to any appreciable extent by ordinary conc. sulfuric acid, even on warming; the separation of the sulfonated derivatives of the *ortho* and *meta* xylene depended on the fact that a concentrated solution of sodium salts deposited only the *ortho* derivative, the sodium salt of the *m*-xylene sulfonic acid remaining as a sirup. These claims were later supported by Levinstein,⁴ who described a method for the analysis of xylene in which the treatment with conc. sulfuric acid is repeated until no more of the hydrocarbon is taken into solution. The *p*-xylene remaining undissolved was claimed to be of such purity that the first fractions obtained by steam distillation solidified on cooling.

Later, it was shown by Crafts⁵ that *p*-xylene is sulfonated by conc. sulfuric acid, though less readily than the *o*- and *m*-xylenes. The analytical method developed by Crafts appears to be satisfactory for its purpose, but is inapplicable to the preparation of the pure compounds on a large laboratory scale.

We have found with Crafts that *p*-xylene is readily sulfonated, even in the cold, by 95% sulfuric acid, so that the complete separation by this means alone cannot be obtained. Moreover, we have been unable to reproduce the results of Jacobsen on the separation of the sodium sulfonates of *o*- and *m*-xylene. The sodium salt of 1,3-xylene-4-sulfonic acid, which forms the main product of sulfonation of *m*-xylene, can readily be obtained in a crystalline condition, and in fact crystallizes on neutralizing and saturating with sodium chloride the crude sulfonation mixture.

¹ A paper read at the 64th meeting of the American Chemical Society, September, 1922.

² Fittig, *Ann.*, 153, 265 (1870).

³ Jacobsen, *Ber.*, 10, 1009 (1877).

⁴ Levinstein, *ibid.*, 17, 446 (1884).

⁵ Crafts, *Compt. rend.*, 114, 1110 (1892).

In order to prepare the 3 xylenes in a pure condition, a series of operations must be carried out. These are: (a) fractional distillation; (b) selective sulfonation; (c) fractional crystallization of sulfonic acids or their salts; (d) selective hydrolysis of sulfonic acids at different temperatures. None of these processes by itself would be sufficient to effect a complete separation, and while it may not be necessary to apply all of them, the most successful results can be obtained by so doing.

Experimental Part

The crude materials were obtained, through the courtesy of Dr. J. B. Hill, from the Barrett Company, to whom we express our indebtedness.

m-Xylene, which forms by far the largest proportion of coal-tar xylene, can be obtained in a high state of technical purity by distillation alone. The xylene of 1° boiling range supplied by the Barrett Company contains only a few per cent. of isomeric xylenes, and these were removed by boiling the mixture with dil. nitric acid⁶ which oxidizes the *ortho* and *para* compounds, leaving the *m*-xylene unchanged. The product was purified by washing it with water and with alkali, then distilling, first in a current of steam and finally under atmospheric pressure with the use of a column. It was then sulfonated by stirring at 95° with half its volume of conc. sulfuric acid and the resulting acid solution separated from unsulfonated material, diluted with an equal volume of conc. sulfuric acid and twice its volume of water, and distilled in a current of steam, heat being applied externally in order to increase the concentration gradually and thus raise the temperature. The first runnings consisted of water and any suspended unsulfonated hydrocarbon; when the temperature reached 110°, *m*-xylene began to condense in the distillate, and by 120° practically no more came over. The oil so obtained was pure *m*-xylene boiling at 138–139°.

o-Xylene.—Five liters (4400 g.) of technical *o*-xylene (95% of which boiled over the range 143–144°) and 2.5 liters of conc. sulfuric acid were stirred together at 95° for 4 hours. When the mixture was cooled a small layer of unsulfonated material was separated and the sulfonic acid layer diluted with 3 liters of water and neutralized with 40% sodium hydroxide solution. The solid which separated on cooling was collected on a centrifuge and recrystallized from half its weight of distilled water. The mother liquors from the recrystallization were concentrated to about 1/3 of their volume, and the solid which separated on cooling was again recrystallized from half its weight of water; the resulting crystals were united with the first crop. This product was once again crystallized from distilled water, from which it separated in long, flat needles unmixed with crystals of any other type. The mother liquors from this second crystallization yielded on concentration a further crop of crystals, which on one more crystallization also consisted entirely of flat needles. By further concentration of the mother liquors a solid was obtained which on recrystallization yielded none of the flat needles characteristic of the pure *ortho* derivative.

The crystals of sodium *o*-xylene-sulfonic acid were then dissolved in just enough distilled water in the cold and the resulting saturated solution mixed with an equal volume of conc. sulfuric acid. The mixture is then heated to 110° at which point steam is injected; distillation with steam was continued with external heating until the temperature had risen to about 130° and no more oil condensed with the steam. Almost the entire amount, however, passed over while the temperature of the mixture remained between 110–120°. The oil was separated from the water and distilled, when 1980 g. (45%) of pure *o*-xylene boiling at 144–145° was obtained.

⁶ *Ann.*, 148, 10 (1868).

The purity of the sulfonic acid was established by fusing the sodium salt with twice its weight of potassium hydroxide, acidifying the product and distilling with steam when *o*-xylenol, melting without further purification at 65°, was obtained (4-hydroxy-1,2-dimethylbenzene is stated to melt at 65°).

***p*-Xylene.**—To 10 kg. of technical *p*-xylene (91% of which distilled between 136° and 137°) was added an equal volume of conc. sulfuric acid with continual stirring, while the temperature was kept at 15–20°. After the mixture had been stirred for 5–6 hours at this temperature the undissolved hydrocarbons, amounting to 5–6 liters were separated and again treated in the same way with an equal volume of conc. sulfuric acid. The undissolved portion, amounting to 2.5–3 liters, was mixed with an equal volume of conc. sulfuric acid and the mixture stirred for 5 hours at 95°. After this had cooled, the lower acid layer was separated and cautiously mixed with an equal volume of conc. hydrochloric acid. Heat was evolved and as the solution cooled the *p*-xylene-sulfonic acid crystallized as fine plates. In certain preparations where the preliminary sulfonation had not been carried out, a certain proportion of *m*-xylene-sulfonic acid crystallized in needles. The crystals were filtered on flannel and dissolved in about 1/4 of their weight of hot distilled water. As the solution cooled the nearly pure *p*-xylene-sulfonic acid separated in large plates and was collected in the centrifuge. The mother liquors which contained *p*- and *m*-xylene-sulfonic acid were hydrolyzed separately and the mixture of hydrocarbons was again subjected to partial sulfonation.

The recrystallized *para* acid, which still contained a small proportion of the *meta* derivative, was dissolved in a minimum quantity of water and the solution mixed with an equal weight of sulfuric acid. The mixture was then heated to 120° when a current of steam was passed in, and the temperature allowed to rise to 145°.

The xylene distilling up to this point consisted largely of the *meta* derivative and was again treated with a subsequent batch. The temperature was then gradually brought to 170°, when the operation was stopped. It was observed that the greater part of the *p*-xylene passed over while the temperature of the mixture lay between 150° and 155°; in fact, on hydrolyzing a perfectly pure sample of *p*-xylene-sulfonic acid under the same conditions no hydrocarbons were formed below 150°. The oil was separated, dried with calcium chloride and cooled to 5° when the greater portion of it solidified. After the supernatant liquid was decanted, the crystals which melted at 10–12° were distilled, when the pure *p*-xylene passed over entirely at 136.5–137°. The yield from 20 kg. of the technical material was 2847 g. (14.2%).

The purity of the *p*-xylene-sulfonic acid was established by fusing the salt with twice its weight of potassium hydroxide and distilling the resulting phenol with steam, when pure *p*-xylenol melting at 73° was obtained in good yield.

Although the original hydrocarbon boiled almost entirely at 136–137° its principal constituent was found to be *m*-xylene. The more easily sulfonated portions on hydrolysis yielded a hydrocarbon boiling constantly at 138–139°; the sulfonic acid was converted through its sodium salt into the corresponding sulfochloride, which on treatment with ammonia yielded the sulfonamide melting sharply at 136–137° (1,3-dimethylbenzene-4-sulfonamide is stated to melt at 137°). The sodium sulfonate on fusion with potassium hydroxide yielded a xylenol which distilled at 94° at 11 mm. and melted at 22–23°, and was therefore pure *m*-xylenol.

No evidence was obtained of the presence of any ethyl benzene.

The unsulfonated material present in xylene has usually been referred to in the literature as consisting of paraffins; the odor, however, so strongly resembles that of menthane that it seems probable that it consists largely of cyclohexane derivatives such as the hexahydroxylenes.

Summary

The literature dealing with the preparation and the separation of the xylenes is contradictory and misleading.

It has been found that fractional distillation, selective sulfonation, crystallization of the sulfonic derivatives and selective hydrolysis of xylene-sulfonic acid all tend to bring about a partial separation of the 3 xylenes present in coal-tar xylene, but that none of these processes alone is entirely suitable for the isolation of the *ortho* and *para* derivatives. A satisfactory procedure is described in which the above processes are combined.

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FLUORO-ACETYL DERIVATIVES OF SUGARS. I

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Introduction

Moissan¹ prepared several organic fluorine derivatives by the action of dry silver fluoride on iodine and chlorine derivatives of organic compounds. A modification of Moissan's method was applied by shaking dry silver fluoride with an ether solution of bromo-acetyl glucose, but no fluorine derivative could be obtained. Fischer and Armstrong² used liquid hydrochloric and hydrobromic acids for obtaining the crystalline chloro- and bromo-acetyl derivatives of several sugars, the time of action being 15-20 hours at room temperature. This procedure suggested the use of water-free hydrofluoric acid. After several unsuccessful attempts in which sirupy reaction products were obtained, it was found that if the time or reaction were shortened to $\frac{1}{2}$ hour, crystalline fluoro-acetyl derivatives could be obtained. The yield was small but the compounds were stable, which facilitated the investigation.

A subsequent paper will deal with the application of the process to other sugars and the description of the properties of the new class of compounds.

Experimental Part

General Method of Preparation.—Ruff and Plato³ have given detailed directions for preparing and handling water-free hydrofluoric acid. The hydrofluoric acid used in this investigation was distilled in a small platinum still. The retort contained about 80 g. of dry potassium hydrogen fluoride,

¹ Moissan, *Compt. rend.*, **110**, 951 (1890); *Ann. chim.*, [6] **19**, 270 (1890); *J. pharm. chim.*, [5] **23**, 329 (1891).

² Fischer and Armstrong, *Ber.*, **34**, 2885 (1901).

³ Ruff and Plato, *ibid.*, **37**, 675 (1904).