mined and corrected to 760 mm. by means of Trouton's rule, and by comparison with phenol and naphthalene according to the relationship discovered by Ramsay and Young. The molecular heat of vaporization of *p*-cresol not being available, that of *m*-cresol was substituted in the equation $dP/PdT = Q/2T^2$.

3. The values for the boiling point of *p*-cresol at 760 mm. by the three methods of correction were found to be 202.31° (corrected by Trouton's rule), 202.33° (corrected by the above equation) and 202.75° (corrected by comparison with phenol and naphthalene); av., 202.45°. The average of the first two values, 202.32°, is believed to be preferable even though the methods of correction involve the same principle.

The lowest of these values is 1.2° above the commonly accepted value of 201.1° given in the International Critical Tables.

4. A review and criticism of the literature is given.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE UNITED STATES BUREAU OF CHEMISTRY, COLOR LABORATORY]

THE RATE OF CONVERSION OF NAPHTHALENE-2,7-DISULFONIC ACID TO THE ISOMERIC 2,6 ACID AT 160° IN THE PRESENCE OF SULFURIC ACID[1]

BY J. L. HEID

RECEIVED NOVEMBER 15, 1926 PUBLISHED MARCH 9, 1927

In the commercial production of the 2,7-disulfonic acid of naphthalene, the pot method of sulfonation is used. The reaction proceeds in two steps. β-Monosulfonic acid is first produced; this is converted into disulfonic acids by further sulfonation.

As in all these sulfonations, a mixture of isomers is obtained; the product is principally β-monosulfonic acid which is converted to 2,7-disulfonic acid. Small amounts of the 1,6 acid also occur in the sulfonation mass. It is necessary to continue this heating for some time to complete the conversion of the monosulfonic acid, and as this heating is prolonged, the 1,6 and 2,7 acids which are formed gradually undergo a molecular rearrangement to form the symmetrical 2,6 acid, which is more stable under the existing conditions. The reaction has been studied by many investigators, whose reports vary greatly. Ebert and Merz[2] reported that heating for four hours at 160° produced equal quantities of 2,7 and 2,6 acids, and that heating for 24 hours at 180° gave complete conversion to the 2,6 acid. Armstrong[3] and Winne,[4] who also studied the reaction, re-

---

[1] The work here described was completed in June, 1923, in the Bureau of Chemistry Color Laboratory.

[2] Ebert and Merz, *Ber.*, **9**, 592 (1876).

[3] Armstrong, *Ber.*, **15**, 204 (1882).

[4] Armstrong and Wynne, *Proc. Chem. Soc.*, 1885–1895.

ported the presence of 1,6 acid in the sulfonation mass. H. E. Fierz-David and A. W. Hasler,[5] in a paper published since the completion of this work, report the most complete study of this and other naphthalene sulfonation reactions in the literature. Their results indicate that at 160° the sulfonation mixture will come to equilibrium when 27% of 2,6 acid has been formed. Observations in the Color Laboratory indicated that under certain conditions it was possible to obtain a higher percentage of 2,6 acid, but it was not found possible to obtain a complete conversion as reported by Ebert and Merz.[2] Accordingly, it was decided to investigate quantitatively the rate of conversion of the pure 2,7 disulfonic acid of naphthalene to the isomeric 2,6 acid under approximately the conditions existing during the commercial preparation of the 2,7 acid, using an analytical method calculated to minimize the influence of sulfonated tars. The analytical method developed by Haller and Lynch[6] was employed, and the reaction conducted in Pyrex to avoid the catalytic influence of an iron vessel.

Method of Procedure

In order to obtain pure 2,7-disulfonic acid, the crude calcium salt, prepared in the usual manner, was recrystallized once from water and then purified by repeated fractional crystallizations in a mixture of ethyl alcohol and water, increasing the percentage of ethyl alcohol. A slight excess of sulfuric acid was added to the solution of this purified calcium salt and the calcium sulfate removed by filtration. The last traces of calcium sulfate were removed by evaporating to dryness, taking up in 95% alcohol, and filtering.

The free acid was then neutralized with a slight excess of lead carbonate, the solution filtered and evaporated, and the lead salt obtained by crystallization. The solubility of this salt was found to be the same as that prepared by Haller and Lynch[6] by another method through the sulfochloride. The free acid was obtained by precipitating the lead as sulfide with hydrogen sulfide. Upon evaporation, the filtrate gave crystals of free 2,7 acid.

As sulfuric acid seems to promote the molecular rearrangements of these acids, the pure 2,7 acid was mixed with a molecular equivalent of 95% sulfuric acid and placed in a glass vessel equipped with an electrically-driven glass stirrer and heated in an oil-bath at a constant temperature of 160°. Samples were taken at intervals for 24 hours (Table I) and immediately diluted with water.

The lead salts of these samples were prepared in the manner described by Haller and Lynch[6] and filtered while hot from the excess of lead carbonate, the filter paper being extracted four times with boiling water. The filtrates were combined and evaporated to dryness on a steam-bath. The dried mixture was thoroughly ground and mixed, and again dried for four hours at 110° in the electric oven.

As these salts absorb moisture from the air very rapidly, care was necessary in weighing the samples. Approximately 4.1 g. was weighed from a glass-stoppered weighing bottle directly into the tumbling bottle. Water was immediately added from a buret in sufficient quantity to make the ratio of lead salt to water 8.2 g. to 100 cc. This solution was tumbled for 24 hours in a constant-temperature water-bath at 25°

---

[5] Fierz-David and Hasler, *Helvetica Chim. Acta*, **6**, 1133 (1923).

[6] Haller and Lynch, *Ind. Eng. Chem.*, **16**, 273 (1924).

and then removed and immediately filtered. Lead was determined gravimetrically as chromate, and the solubility of the lead salt calculated. From this it was possible to calculate the percentage of 2,6 acid in the sample by reference to the chart prepared by Haller and Lynch.[6] The following table shows the time of heating in hours and the apparent percentage of 2,6 acid present in the mixture.

TABLE I

RESULTS

Time of heating, hrs	1	5	11	15	19	21	24
2,6 Acid, %	5	17	26	31	42	33	30

The results in Table I appear to indicate that the amount of 2,6 acid increased for 19 hours and then diminished, as the lead salt of the later samples is more soluble. However, previous experimental work in the Color Laboratory had shown that as these sulfonations are prolonged, sulfonated tars are formed in very small quantities, causing or accompanied by an increase in the solubility of the lead salts. This would, of course, effect the apparent results in the manner shown. Accordingly, these data indicate that as much as 42% of 2,7 acid can be converted into 2,6 acid by heating in a glass vessel in the presence of sulfuric acid at 160°.

Summary

1. Because of the conflicting character of the literature regarding the conversion of the 2,7-disulfonic acid of naphthalene into the isomeric 2,6 acid, an investigation of the reaction was conducted with a view to eliminating as many as possible of the ordinary sources of experimental error. The experiment was conducted in glassware, as it has been found that iron influences the rate of conversion, the rate of formation of sulfonated tars, and the solubility of the acid salts. The results definitely indicate that as much as 42% of the 2,7-disulfonation acid of naphthalene will be converted to 2,6 acid under the conditions involved before equilibrium is established.

2. A method of purifying 2,7 sulfonic acid is described.

KANSAS CITY, MISSOURI