

phthalate of 35 per cent phthalyl content. Very small portions of sodium bicarbonate were added with continuous stirring from a weighed quantity of 20 grams. After somewhat over half of the bicarbonate had been added, the cellulose ester was largely in solution. Further additions of sodium bicarbonate were made at intervals, and the solution was tested after each addition with bromothymol blue indicator. A colorless aqueous solution of the cellulose acetate sodium phthalate was finally obtained; it was adjusted to a pH of 7.0-7.5, where it was kept for determination of viscosity data and preparation of the metallic salts listed in Table VI.

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PRESENTED before the Division of Cellulose Chemistry at the 97th Meeting of the American Chemical Society, Baltimore, Md.

Sulfonation and Nitration Reaction Promoted by Boron Fluoride¹

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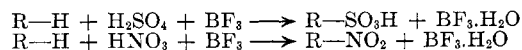
BORON fluoride is a remarkable catalyst (or promoter) for many organic reactions, particularly those of addition or where water is a product of the reaction. In the latter cases boron fluoride may both accelerate the reaction and drive it to completion by combining with the water produced. Combination with water may be by coordination or by hydrolysis. The complex $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ is a heavy, water-white, distillable liquid (?). With large excesses of water, orthoboric acid, hydrofluoric acid, and fluoboric acid may be obtained. Tendency to form coordination complexes is particularly characteristic of boron fluoride. It combines directly with many oxygen- and nitrogen-containing compounds to form such substances as $\text{NH}_3 \cdot \text{BF}_3$, $\text{CH}_3\text{CN} \cdot \text{BF}_3$, $(\text{CH}_3\text{COOH})_2 \cdot \text{BF}_3$, and $(\text{CH}_3\text{CO})_2\text{O} \cdot \text{BF}_3$. The remarkable properties of boron fluoride have merited considerable study by industrial chemists. Since about 1927 several score of patents have been issued covering its many catalytic uses, as in polymerization of olefinic hydrocarbons and in organic condensation reactions. The literature in these fields is too extensive to permit proper review in this paper.

The highly important unit processes of sulfonation and nitration are frequently slow and also proceed incompletely unless the water formed is removed (4). It was felt, therefore, that these processes might be promoted to a great extent by using boron fluoride along with the required sulfuric or nitric acid. These expectations have been fulfilled in many

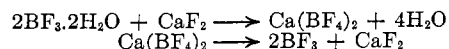
Boron fluoride is shown to be a remarkably effective promoter and dehydrating agent for many sulfonation and nitration processes. In a number of such reactions the boron fluoride may be recovered by distillation as the dihydrate. This work is being continued.

instances. In fact, it has been found possible to sulfonate and/or nitrate many organic compounds quickly and almost completely with stoichiometric amounts of sulfuric or nitric acid when sufficient boron fluoride was added. This is significant particularly since boron fluoride has recently been made available commercially (by the Harshaw Chemical Company) and because in many of the reactions it may be recovered for re-use.

The amounts of boron fluoride required indicate that the reactions proceed as follows:



If, at the completion of the reactions, sufficient water is added to convert the $\text{BF}_3 \cdot \text{H}_2\text{O}$ to $\text{BF}_3 \cdot 2\text{H}_2\text{O}$, the latter may be distilled out under vacuum as a heavy, water-white liquid. Boron fluoride may be recovered from the dihydrate in various ways. In a patented method (6) calcium fluoride is added to form calcium fluoborate which, upon heating, releases gaseous boron fluoride:



¹ This is the twenty-first paper in a series on organic reactions with boron fluoride; the previous paper appeared in *J. Am. Chem. Soc.*, **60**, 654 (1938).

Obviously, the boron fluoride need not be recovered from the crude sulfonated or nitrated material if it is preferred not to do so.

In some cases the promotional effect of boron fluoride was found to be negligible. Thus, no marked advantage attended its use in the sulfonations of chlorobenzene, nitrobenzene, and benzoic acid with 96 per cent sulfuric acid. When beneficial, as in the instances cited below, the use of boron fluoride avoids need for excessive quantities of acid, permits lower reaction temperatures, increases the rate of reaction, and yields products which are quite pure.

Sulfonation

BENZENE. Into a one-liter, three-necked flask were placed 78 grams (one mole) of benzene and 104 grams (one mole) of 94 per cent sulfuric acid. The flask was equipped with a mechanical stirrer, reflux condenser, and inlet tube for boron fluoride. Gaseous boron fluoride was passed in with vigorous stirring for 90 minutes when 66 grams had been absorbed. Additional heating over boiling water for 30 minutes caused a loss in weight of 16 grams. The product was remarkably clear, homogeneous, and only mildly yellow in color. Upon dilution with water and steam distillation, only 1.1 grams of unsulfonated benzene were recovered, indicating that sulfonation was about 98 per cent complete. The residual solution was limed, boiled, and filtered with suction. The filter cake was leached three additional times with 500-ml. portions of hot water. The four solutions were evaporated to dryness separately, and the precipitates dried at 100–120° C. and analyzed for calcium (calculated 11.3 per cent for anhydrous and 10.75 per cent for monohydrate). The analyses were as follows:

| Leach No. | Grams of Solute | % Ca |
|-----------|-----------------|-------|
| 1 | 137 | 10.46 |
| 2 | 22.5 | 12.77 |
| 3 | 8 | 15.24 |
| 4 | 3.5 | 17.94 |

A control experiment was performed, omitting the boron fluoride, which showed only 42 per cent sulfonation.

TOLUENE. One mole of toluene was sulfonated with one mole of 94 per cent acid, as described above. The steam distillation indicated 98 per cent reaction. A sample of calcium salt was converted to the phenyl ester which melted at 94–95° C. The product was therefore chiefly the *p*-sulfonic acid (melting point of phenyl ester, 95–96° C., 9).

NAPHTHALENE (COLD). While maintaining the temperature below 30° C., 108 grams of boron fluoride were passed into 1.50 moles of naphthalene and 1.52 moles of 94 per cent sulfuric acid. This required 8 hours, and stirring was continued for an equal period. The product was diluted with water, neutralized with soda ash, and allowed to crystallize. The first crop of crystals weighed 263 grams and was predominantly alpha-sulfonate since the amide melted at 145–147° C. as compared with the literature value (8) of 150°. The second crop of crystals weighed 99.5 grams. This was recrystallized and gave 62 grams of sodium naphthalene sulfonate which was found to be substantially the alpha isomer also.

NAPHTHALENE (HOT). The above experiment was repeated at 160–165° C. Forty-eight grams of boron fluoride were absorbed in 90 minutes. Dilution with water gave 16 grams of β , β' -dinaphthyl sulfone, melting at 174–175° C., compared with 177° (12). The acid was recovered as the sodium salt,

total weight 323.5 grams (theoretical 345 grams). The sulfonamide melted at 212–213° C. which is the accepted value for the beta isomer (1).

PHENOL. Ninety-four grams (one mole) of phenol were treated with 98 grams (one mole) of 100 per cent sulfuric acid. Admission of boron fluoride caused a spontaneous rise in temperature to 80° C. External heat was then applied to maintain a temperature of approximately 100° C. Absorption of boron fluoride amounted to 28 grams in 1.5 hours. The reaction product was diluted to one liter with water, neutralized with soda ash, boiled, saturated with salt, and filtered, and 200 ml. of water were added to the filtrate. Overnight crystallization deposited 173 grams of sodium phenol sulfonate. Analysis showed 2.65 per cent sodium chloride. The methoxy amide melted at 112–113° C., previously reported for the para compound (11).

CARBAZOLE (DISULFONATION). A 42.5-gram sample (0.25 mole, 98 per cent grade) was treated with 54 grams (0.52 mole) of 94 per cent sulfuric acid and 29 grams of boron fluoride at 100° C. The product was taken up in water, neutralized with slaked barium oxide, and filtered, and the filtrate was evaporated to crystallization. The deposit weighed 32 grams and showed 30.9 per cent barium. The mother liquor was evaporated to crystallization and gave a second quantity of crystals which weighed 82.5 grams and contained 32.4 per cent barium. The calculated barium content of the disulfonate monohydrate (10) is 28.5 per cent.

DIPHENYL (DISULFONATION). Attempted disulfonation of 38.5 grams (0.25 mole) of diphenyl with 53 grams (0.51 mole) of 94 per cent acid and 25.5 grams of boron fluoride gave a mixture containing both the mono- and disulfonic acids. They were separated effectively by the procedure of Latschinow (5) and then converted to their potassium salts. The products were identified through the derivatives recommended by Gabriel and Deutsch (3).

Nitration

NITROBENZENE. To 31 grams (0.25 mole) of nitrobenzene were added 19 grams (0.3 mole) of fuming nitric acid (density 1.5, 92 per cent), and boron fluoride was admitted with stirring until 17 grams had been absorbed. The temperature was not allowed to exceed 80° C. Heating at 100° for 30 minutes followed the admission of boron fluoride. The product was poured into 500 ml. of hot water and stirred until cool. The dinitrobenzene was filtered off and recrystallized from alcohol. The yield was 36.5 grams or 87 per cent of the theoretical (melting point, 89.5–90° C.).

***p*-TOLUENE SULFONIC ACID.** In a similar manner a solution of 19 grams (0.1 mole) of *p*-toluene sulfonic acid in 9.7 grams (0.15 mole) of fuming nitric acid absorbed 8 grams of boron fluoride. The reaction was completed by heating at 100° for one hour. Then 200 ml. of water were added and

TABLE I. YIELDS OF PRODUCTS OBTAINED IN SULFONATION PROMOTED BY BORON FLUORIDE

| Compound Sulfonated | H ₂ SO ₄ BF ₃ | | Treatment | | % reaction* | Product Salt prepd. Identified by: | |
|---------------------|--|-------|-----------|------|--|------------------------------------|-------------------|
| | Moles | Moles | Hours | ° C. | | | |
| Benzene | 1.0 | 1.0 | 1.5 | 40 | 98 ^a | Ca | % Ca |
| Toluene | 1.0 | 1.0 | 0.5 | 100 | 98 ^a | Ca | Phenyl ester |
| | | | 0.5 | 80 | | | |
| | | | 0.5 | 100 | | | |
| Naphthalene | 1.5 | 1.52 | 16.0 | 30 | 94 ^b | Na | Amide |
| Naphthalene | 1.5 | 1.52 | 1.5 | 160 | 93 ^b | Na | Amide |
| Phenol | 1.0 | 1.0 | 1.5 | 100 | 73 ^c | Na | Methoxy amide |
| Carbazole | 0.25 | 0.52 | 0.43 | 2.5 | 100 | Ba | % Ba |
| Diphenyl | 0.25 | 0.51 | 1.25 | 100 | Mono, 26 ^e ; di, 67 ^e | K | Amide |
| | | | | | | K | Sulfonyl chloride |

* Yields were estimated as follows: ^a steam distillation of unsulfonated hydrocarbon, ^b weight of sodium salt, ^c weight of dihydrated sodium salt (ether extraction of unsulfonated phenol from other experiments indicated about 95% reaction), ^d weight of monohydrated barium salt, ^e weight of individual dihydrated potassium salts.

TABLE II. YIELDS OF PRODUCTS OBTAINED IN NITRATION PROMOTED BY BORON FLUORIDE

| Compound Nitrated | HNO ₃ BF ₃ | | | Treatment | | Product | | Identified by |
|---------------------------------|----------------------------------|------|------|-----------|------|---------------------------------|-----------------|---------------|
| | Moles | | | Hours | ° C. | Nature | Yield % | |
| Nitrobenzene | 0.25 | 0.3 | 0.25 | 0.5 | 80 | <i>m</i> -Dinitrobenzene | 87 | M. p. |
| Benzoic acid | 0.25 | 0.3 | 0.37 | 0.5 | 100 | <i>m</i> -Nitrobenzoic acid | 82 | M. p. |
| <i>p</i> -Toluene sulfonic acid | 0.10 | 0.15 | 0.12 | 1.0 | 100 | 2-Nitro-4-toluene sulfonic acid | 92 ^a | Amide |
| Methyl benzoate | 0.10 | 0.15 | 0.12 | 1.0 | 0-10 | Methyl <i>m</i> -nitrobenzoate | 77 | M. p. |
| Phthalic anhydride ^b | 0.10 | 0.15 | 0.28 | 13.0 | 100 | 3-Nitrophthalic acid | 81 | M. p. |

^a From weight of sodium salt.^b Thirty grams acetic acid used as diluent.

TABLE III. YIELDS OF PRODUCTS OBTAINED IN SUCCESSIVE SULFONATION AND NITRATION PROMOTED BY BORON FLUORIDE

| Compound Treated | H ₂ SO ₄ HNO ₃ BF ₃ | | | | Product (Na Salt) | Yield % |
|------------------|---|------|------|------|--------------------------------------|---------|
| | Moles | | | | | |
| Benzene | 0.25 | 0.3 | 0.11 | 0.24 | <i>m</i> -Nitrobenzene sulfonic acid | 80 |
| Toluene | 0.10 | 0.11 | 0.11 | 0.11 | 2-Nitro-4-toluene sulfonic acid | 82 |

the product was neutralized with soda ash. The neutral solution was heated to boiling, and 200 ml. of cold saturated salt solution were added. The crystalline sodium 2-nitro-4-toluene sulfonate weighed 23.5 grams equal to 92 per cent of the theoretical. The amide melted correctly (2) at 142.5° C.

SUCCESSIVE SULFONATION AND NITRATION OF TOLUENE. One-tenth mole of toluene was sulfonated with 0.11 mole of 100 per cent sulfuric acid and 7.2 grams of boron fluoride as previously described. The crude product was cooled in a bath of ice, and 7 grams (0.11 mole) of fuming nitric acid were added dropwise. After addition of nitric acid the material was heated at 100° C. for one hour. The nitrosulfonic acid was isolated as the sodium salt in the manner described above. The yield of sodium 2-nitro-4-toluene sulfonate was 21 grams or 82 per cent of the theoretical. The amide melted at 141.5-142° C.

OTHER NITRATIONS. Data for other similar nitrations are given in Tables II and III.

Recovery of Boron Fluoride

FROM TOLUENE SULFONIC ACID. Ninety-two grams (one mole) of toluene were sulfonated with 104 grams (one mole) of 94 per cent sulfuric acid and 60 grams of boron fluoride as previously described. The product was a clear, pale-yellow, viscous liquid. Addition of 12 grams of water induced immediate crystallization. The entire product was subjected to vacuum distillation from an oil bath. There were obtained 77.5 grams of distillate, boiling at 75-80° C. at 13 mm. The distillate corresponds to 84.6 per cent recovery of boron fluoride as the dihydrate. The residue from the distillation weighed 169 grams (calculated, 172 grams) and was diluted with one liter of water. There was no insoluble material.

Liming of the hot solution required only 38 grams of calcium oxide. The recovery of calcium sulfonate was 173 grams compared with the theoretical of 191 grams.

FROM NAPHTHALENE SULFONIC ACID. During a period of ninety minutes, 58 grams of boron fluoride were passed into a mixture of 192 grams (1.5 moles) of naphthalene and 158 grams (1.51 moles) of 94 per cent sulfuric acid heated to 160-165° C. Five grams of water were added, and the product was vacuum-distilled directly. There were obtained 80.5 grams of distillate, boiling at 83° C. at 23 mm. The recovery was thus 90 per cent of the theoretical.

The residue was poured into water, yielding 21.5 grams of insoluble material.

FROM SUCCESSIVE SULFONATION AND NITRATION OF TOLUENE. One-half mole of toluene was sulfonated with 0.5 mole of 95 per cent sulfuric acid and 34 grams of boron fluoride.

Nitration was effected with fuming nitric acid without further addition of boron fluoride as previously described. The crude nitrotoluene sulfonic acid was subjected to vacuum distillation which yielded 25 grams of material, boiling at 72-80° C. at 12 mm. This corresponds to 50 per cent recovery of boron fluoride. The residue from the distillation crystallized and weighed 118.5 grams. The theoretical yield of nitrotoluene sulfonic acid is 101.5 grams, indicating that the residue was contaminated.

IDENTIFICATION OF BORON FLUORIDE DIHYDRATE. A sample of distillate from the above experiments was converted to the dioxane addition product for identification. The derivative, after two crystallizations from dioxane, melted at 139° C. The dioxane derivative prepared from an authentic sample melted at 139-140° C. and the mixed melting point was 138-139° C. Meerwein (7) reports a melting point of 142° C.

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THE portion of this paper dealing with sulfonation is abstracted from the Ph.D. dissertation of R. J. Thomas, June, 1939. W. F. Anzilotti performed the experiments on nitration.

