[Contribution from the Chemical Laboratory of Indiana University]

# REACTIONS OF HALOGENS WITH ARYLSULFONATES. I. BROMINATION OF MIXED POTASSIUM 1-METHYLNAPHTHALENESULFONATES[1]

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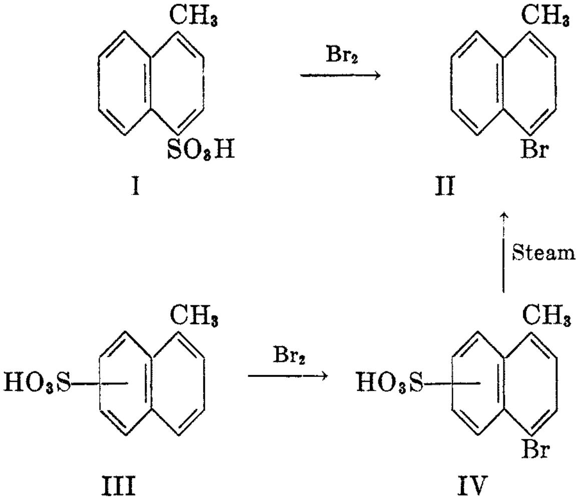
A convenient preparation of a 1-alkyl-4-bromonaphthalene involves the indirect procedure of sulfonating the corresponding 1-alkylnaphthalene in the 4-position and subsequently replacing the sulfonic acid group by bromine in aqueous solution (1–3). In the case of 1-methylnaphthalene, Elbs and Christ (4) have effected the sulfonation by shaking the hydrocarbon with concentrated sulfuric acid. However, they reported the formation of an unidentified isomeric 1-methylnaphthalenesulfonic acid (III) in addition to the major product, 1-methylnaphthalene-4-sulfonic acid (I). This paper is a report of investigations on the stoichiometry of the reactions of aqueous bromine-bromide and bromate-bromide solutions on the mixed potassium 1-methylnaphthalenesulfonates (5) resulting from the sulfonation procedure of Elbs and Christ.



Bromination of the partially purified mixed potassium salts produced 1-methyl-4-bromonaphthalene (II) (apparently arising from the 4-sulfonate) and a 1-methyl-4-bromonaphthalenesulfonic acid (IV) (isolated as the *p*-toluidine salt and presumably arising from the unknown isomer III). The position occupied by the bromine atom in IV was established through desulfonation of IV to yield II. Although attempts to completely establish the structure of IV proved un-

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successful, the presence of a β-sulfonic acid group therein was indicated by lack of appreciable replacement of this group (as the potassium salt) on treatment of IV with excess aqueous bromine.

Isolation of these two different bromine-bearing products from the reaction indicates that both replacement of the sulfonate group by bromine, according to Equation A, and replacement of hydrogen by bromine, according to Equation B,

$$C_{11}H_9SO_3^- + Br_2 + H_2O \rightarrow C_{11}H_9Br + Br^- + SO_4^= + 2\ H^+ \text{ (Equation A)}$$

$$C_{11}H_9SO_3^- + Br_2 \rightarrow C_{11}H_8BrSO_3^- + Br^- + H^+ \text{ (Equation B)}$$

occur. We have attempted to determine the relative extents of these two competing reactions by titrating the acidity formed from treatment of sulfonate aliquots with measured quantities of standard bromine (in bromide) solution (in molar ratios of sulfonate/bromine varying from 9:1 to 1:1). The data obtained (Fig. 1) show that the acidity produced is directly proportional to the bromine added (1.64 hydrions formed per molecule of bromine consumed) and corresponds to reaction of 64% of the bromine by replacement of sulfonate and the remainder by replacement of hydrogen.

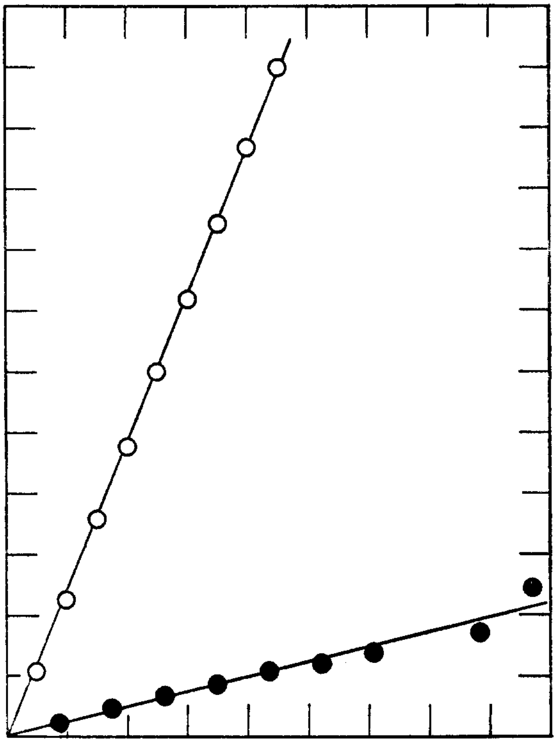

FIG. 1. VARIATION OF TOTAL ACIDITY WITH AMOUNT OF BROMINE ADDED. Ordinate: Change in Milliequivalents of Hydrion Present (varying from 0 to 12 in units of 1). Abscissa: Ml. of Added Bromine-containing Solution (varying from 0 to 18 in units of 2). Open circles: For bromine-bromide. Solid circles: For bromate-bromide.

The titration experiments have also been conducted using a mixture of standard potassium bromate and standard sulfuric acid (in a constant ratio of 3.02 ±.04 moles of acid per mole of bromate) plus excess bromide as a source of bromine *in situ*. The loss in acidity was found to be directly proportional to the bromate added (Fig. 1) (1.03 hydrions lost per bromate ion consumed) and corresponded to 66% of the bromate serving to cause replacement of sulfonate (Equation C) and the remainder to cause replacement of hydrogen (Equation D).

$$3C_{11}H_9SO_3^- + BrO_3^- + 2Br^- \rightarrow 3C_{11}H_9Br + 3SO_4^= \text{ (Equation C)}$$

$$3C_{11}H_9SO_3^- + 3H^+ + BrO_3^- + 2Br^- \rightarrow 3C_{11}H_8BrSO_3^- + 3H_2O \text{ (Equation D)}$$

Material balance studies were made on larger samples of sulfonate in order to correlate, if possible, changes in acidity with products isolable. In a typical experiment with a bromine-bromide mixture, 1.75 equivalents of hydrion were formed per mole of bromine added (corresponding to 75% replacement of sulfonate and 25% replacement of hydrogen) and the yields of II and IV isolated were 46% and 18%, respectively. Likewise in a typical bromate-bromide experiment 0.68 equivalent of hydrion disappeared per g.-ion of bromate added (corresponding to 77% replacement of sulfonate and 23% replacement of hydrogen) and the yields of II and IV isolated were 43% and 23%, respectively. In both cases the correlation between data for titration and for isolation of IV was very good, but the discrepancy between the yield of II obtained and that expected from titration data was always much too large to be caused by mechanical losses inherent in the isolation procedures. The origin of this discrepancy is not yet clear.

## EXPERIMENTAL[3]

*Mixed potassium 1-methylnaphthalenesulfonates.* A mixture of 100 g. of 98% 1-methylnaphthalene (Reilly Tar and Chemical Corp.) and 179 ml. of concentrated sulfuric acid was allowed to stand for five hours, with occasional shaking but without external cooling. The precipitate which formed on dilution with 280 ml. of water was collected, dissolved in 575 ml. of water, filtered, and neutralized with 25% aqueous potassium hydroxide. The potassium salts were collected by repeated partial evaporation of the mother liquor, cooling, and filtration of the resultant precipitate. The combined solids were extracted with two 300-ml. portions of 50% alcohol. The precipitate which resulted on partial evaporation and cooling of the alcoholic extract was filtered and dried at 60–70° for 12 hours; yield, 125 g. of tan solid.

*Anal.* Calc'd for $C_{11}H_9KO_3S \cdot H_2O$: C, 47.50; H, 3.96; S, 11.50.

Found: C, 47.90; H, 3.87; S, 12.42.[4]

*Titration experiments. A. Bromine-bromide method.* A solution of 9.0 g. of bromine (N.F.) and 13.6 g. of c.p. sodium bromide in 70 ml. of water was standardized at the time of use by adding a 3-ml. sample to a mixture of 10 g. of potassium iodide, 100 ml. of 1 *N* sulfuric acid, and 2 g. of sodium carbonate and titrating the liberated iodine with 0.1 *N* sodium thiosulfate, previously standardized with 0.1 *N* potassium permanganate and this in turn standardized with reagent grade sodium oxalate; normality found for bromine solution,

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[3] Microanalyses were performed by Mrs. A. Rosen and Mrs. B. Jarvis. All melting points are uncorrected.

[4] The high sulfur analysis may indicate the presence of potassium sulfate and/or dipotassium 1-methylnaphthalenedisulfonate in the sample.

1.48. A sample of 40 g. (*ca.* 0.14 mole) of the foregoing mixed potassium sulfonates was dissolved in about 200 ml. of hot water, filtered (through paper), cooled, and diluted to 500 ml. in a volumetric flask. If the solution appeared hazy at this point, it was refiltered through Celite. Aliquot portions (25 ml.) of the sulfonate solution were placed in Erlenmeyer flasks and treated with measured volumes (1–9 ml.) of the standard bromine solution. The flasks were stoppered and allowed to stand at room temperature for 15–30 minutes until the bromine color had been dissipated. The contents were diluted with 100 ml. of water and titrated with 0.5 *N* sodium hydroxide using phenolphthalein as indicator. Results are shown in Fig. 1. A blank run (no bromine added) on the sulfonate showed a negligible alkalinity with standard acid.

*B. Bromate-bromide method.* Aliquot sulfonate samples, prepared as previously, were treated with measured volumes (1–18 ml.) of 0.120 *M* c.p. potassium bromate solution and of 1 *N* sulfuric acid (volume calculated to give 3.02 ±.04 moles of sulfuric acid per mole of added bromate in each case). Each sample was placed in a water-bath maintained at about 55°, treated with 2 g. of sodium bromide, stoppered, and allowed to react for 15–30 minutes. The cooled sample was diluted and titrated with sodium hydroxide as before. Results are shown in Fig. 1.

*Material balance experiments. A. Bromine-bromide method.* A solution of 20 g. (*ca.* 0.072 mole) of sulfonate in 250 ml. of water was treated with a mixture of 10 g. (0.063 mole) of bromine and 15.1 g. of sodium bromide in 78 ml. of water and allowed to stand at room temperature for 45 minutes with occasional shaking. The reaction mixture was diluted with 1 liter of water and neutralized with 1.022 *N* sodium hydroxide (108 ml. required). The precipitated oil was extracted in carbon tetrachloride. The organic layer was washed with water, dried with calcium chloride and evaporated; yield, 6.5 g. (46%) of crude oil, 1-methyl-4-bromonaphthalene; b.p. mainly 140–142° (8 mm.). The *picrate* of the distilled product had m.p. 126–128° [reported (1) m.p. 128–129°].

The aqueous layer was treated with 3 g. of *p*-toluidine and 10 ml. of concentrated hydrochloric acid. The precipitate which formed on cooling the mixture was separated and dried at 60°; yield, 4.6 g. (18%) of *p-toluidinium 1-methyl-4-bromonaphthalenesulfonate,* m.p. 258–272° (decomp.). The product gave a negative halide test prior to sodium fusion but a positive test after fusion.

*Anal.* Calc'd for $C_{11}H_9BrO_3S \cdot C_7H_9N$: N, 3.43; Neut. equiv., 408.
Found: N, 3.69; Neut. equiv., 409.

*B. Bromate-bromide method.* To 45 g. (*ca.* 0.16 mole) of sulfonate in 560 ml. of water was added 392 ml. of 0.120 *M* potassium bromate (0.047 mole), 284 ml. of 0.995 *N* sulfuric acid, and 45 g. of sodium bromide. The mixture was heated at 55° for 30 minutes, cooled, and neutralized with 1.022 *N* sodium hydroxide (245.6 ml. required). The 1-methyl-4-bromonaphthalene was extracted and purified as previously; yield, 13.5 g. (43%). Treatment of the aqueous solution with 12 g. of *p*-toluidine and 48 ml. of concentrated hydrochloric acid gave 13.3 g. (23%) of *p-toluidine salt;* m.p. 260–272° (decomp.) after crystallization from dilute alcohol; Neut. equiv., 410.

*Desulfonation of 1-methyl-4-bromonaphthalenesulfonic acid* (IV). A suspension of 13.1 g. (0.032 mole) of the preceding *p*-toluidine salt in 100 ml. of water was neutralized with 25% aqueous sodium hydroxide and steam-distilled until all of the *p*-toluidine had been removed. The residue was treated with 50 ml. of concentrated sulfuric acid and steam-distilled further (at 130–160°). The latter distillate (about 3 l.) was saturated with sodium chloride and extracted with petroleum ether. The organic layer was dried with calcium chloride and evaporated to give 5.5 g. (77%) of oil. The *picrate* of this oil melted at 124–126°, undepressed on admixture with the picrate of 1-methyl-4-bromonaphthalene (m.p. 126–128°) obtained from the bromination experiments.

## SUMMARY

1. Bromination of a crude mixture of potassium 1-methylnaphthalenesulfonates has resulted in the isolation of a 1-methyl-4-bromonaphthalenesulfonate as well as 1-methyl-4-bromonaphthalene itself.

2. Titration of the acid produced in the bromination indicates that simultaneous replacement of sulfonate and hydrogen from the naphthalene nucleus occurs.

3. Material balance studies show quantitative consistency only in the case of formation of the 1-methyl-4-bromonaphthalenesulfonate.

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