it was vigorous. After twenty-five minutes of heating at 170°, carbon dioxide was no longer evolved. Heating was stopped and the melt was allowed to cool. The copper–bronze powder was removed by filtration with the aid of a small amount of ether. The powder was washed thoroughly with 25 ml. of ether which was combined with the filtrate. Ether was removed by distillation, and the residue was distilled under reduced pressure. A colorless and pungent smelling liquid, boiling between 59 and 60° (28 mm.) was obtained; $n^{20}D$ 1.4344. The yield was 3.2 g. (70%).

Anal.[9] Calcd. for $C_7H_{11}N$: C, 77.01; H, 10.16. Found: C, 77.16; H, 10.16.

β-Isopropylacrylamide.—In a 100-ml., round-bottomed flask were placed 10.8 g. (0.15 mole) of freshly distilled isobutyraldehyde, 30.9 g. (0.30 mole) of malonmonoamide, 25 ml. of dry pyridine and eight drops of dry piperidine. The mixture was heated under reflux (oil-bath temperature was 82°) for twenty-four hours. At the outset of the heating, there was a vigorous evolution of carbon dioxide, which gradually subsided over the twenty-four-hour period. At the end of this time, the mixture was concentrated to dryness under reduced pressure. The residue was diluted with 10 ml. of water and extracted with 250 ml. of ether in five 50-ml. portions. The ether extract was dried over anhydrous magnesium sulfate. Ether was removed by distillation whereupon the residue solidified. The crude, nearly white β-isopropylacrylamide was dried under a reduced pressure of less than 1 mm. overnight. The yield was 11.9 g. (70%), m. p. 79–84°. Recrystallization from 15 ml. of hot benzene gave 9.0 g. of white crystals which melted between 83 and 86° (lit.[2] 82–86°).

β-Isopropylacrylonitrile.—A mixture of 4.4 g. (0.039 mole) of β-isopropylacrylamide and 6.5 g. of phosphorus pentoxide was placed in a 100-ml., round-bottomed flask. The contents were mixed thoroughly. The flask was equipped with a small take-off head for downward distillation and the contents were heated gradually by an oil-bath. The temperature of the bath was brought to and maintained at 200°. At the end of thirty minutes the system was placed under a reduced pressure of about 50 mm. The distillate was collected in a tube immersed in a Dry Ice–acetone-bath. Heating was continued for about two hours and during this time the pressure was lowered gradually to 15 mm. The black residue frothed considerably during this period. At the end of this time, no further distillation took place and heating was stopped. A total of 3.0 g. of colorless β-isopropylacrylonitrile was obtained; $n^{30}D$ 1.4316. Redistillation yielded a product which possessed the following physical constants: $n^{20}D$ 1.4329, b. p. 68° (34 mm.). Reported[10] values for the *trans* compound are: $n^{20}D$ 1.4342, b. p. 48.5° (13.5 mm.).

β-Ethylacrylamide.—Essentially the same conditions were employed for the preparation of β-ethylacrylamide as those described for β-isopropylacrylamide. Crude β-isopropylacrylamide was isolated in the amount of 7.2 g. from 8.7 g. of freshly distilled propionaldehyde and 30.9 g. of malonmonoamide. Subsequent recrystallization from acetone afforded 3.4 g. of glistening, white needles, m. p. 148–148.5° (lit.[2] 148°).

β-Ethylacrylonitrile.—β-Ethylacrylamide was dehydrated with phosphorus pentoxide under essentially the conditions described for the preparation of β-isopropylacrylonitrile. A mixture of 6.28 g. (0.06 mole) of β-ethylacrylamide and 9.2 g. of phosphorus pentoxide yielded 2.3 g. (45%) of colorless β-ethylacrylonitrile, b. p. 72° (72 mm.), $n^{20}D$ 1.4301 (lit.,[11] b. p. 73° (72 mm.), $n^{20}D$ 1.4298 (for the *trans* compound)).

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UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS   RECEIVED JUNE 6, 1949

(10) Bruylants, *Bull. soc. chim. Belg.*, 41, 309 (1932); *C. A.*, 27, 267 (1933).

(11) Bruylants and Jmoudsky, *Bull. sci. acad. roy. Belg.*, [5] 17, 1161 (1931); *C. A.*, 26, 3232 (1932).

Equilibria of the Boric Acid–Mannitol Complexes

BY SIDNEY D. ROSS AND ARTHUR J. CATOTTI

The recent publication by Deutsch and Osoling[1] on the stoichiometry and equilibria of boric acid–mannitol complexes prompts us to report some related results obtained in these laboratories. We have focused our attention on determining the equilibrium constant for the reaction

$$HB + 2M \rightleftharpoons BM_2^- + H^+$$

In determining this constant, we have consciously selected concentrations of both boric acid and mannitol which would permit us to make the simplifying assumption that the concentrations of both B^- and BM^- are negligible in comparison with the concentrations of both H^+ and BM_2^-. For the equilibrium constant, we may write

$$K = \frac{[H^+][BM_2^-]}{[HB][M]^2} \cong \frac{[H^+]^2}{[HB_0 - H^+][M_0 - 2H^+]^2}$$

and K can be calculated from a single pH measurement. The justification for this assumption will be discussed later.

The reagents were C.P. boric acid and mannitol and freshly boiled distilled water. All solutions were thermostatted at 25°, and the ionic strength was kept at 0.10–0.12 M by addition of C.P. potassium chloride. The pH's were measured with a Beckman pH meter. The results are summarized in Table I.

TABLE I

CALCULATED VALUES OF K

[HB]	[M]	[M]/[HB]	[KCl]	pH	$K \times 10^4$
0.0141	0.0534	3.78	0.117	4.20	1.01
.0166	.0985	5.94	.104	3.88	1.09
.0141	.0865	6.16	.117	3.99	0.955
.00532	.0370	6.95	.104	4.56	1.05
.00350	.0257	7.30	.114	4.81	1.05
.00350	.0292	8.30	.114	4.79	0.892
.00851	.0737	8.70	.104	4.17	1.00
.00350	.0374	10.7	.114	4.66	0.990

The average of these values is 1.00×10^{-4} and the maximum deviation from this average value is less than 11%. This agreement is as good as can be expected, since the uncertainty in the pH measurement is 0.02 unit, and a change of 0.02 in pH will change K by as much as 11%.

To check our accuracy, we determined the dissociation constant of boric acid in 0.104 M potassium chloride at 25.0°. The determined values ranged from 6.77×10^{-10} to 8.24×10^{-10}, with the average value being 7.40×10^{-10}. Again, all of the deviations from the average value can be accounted for by an uncertainty of 0.02 unit in the pH measurement. The accepted value for the dissociation constant in pure water is 6.4×10^{-10}, and a higher value is to be expected in our medium of higher ionic strength.[2]

(1) Deutsch and Osoling, THIS JOURNAL, 71, 1637 (1949).

(2) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 89.

Böeseken, Vermaas and Küchlin[3] have also determined the equilibrium constant for this complex formation from data on the potentiometric titration of boric acid in the presence of mannitol. They do not specify the temperature at which the measurements were made but report a value of 1.7×10^{-4} for K. Neither this result nor the result obtained by us are in agreement with that reported by Deutsch and Osoling.[1] The latter workers have defined K differently, but their K can be made equivalent to ours by multiplying it by the dissociation constant for boric acid. This gives for K, 0.33×10^{-4}, a value only one-third that obtained by us. Part but certainly not all of this difference can be attributed to the fact that our measurements were made in solutions of much higher ionic strength.

In making our calculations we have assumed that both B^- and BM^- are negligible compared to H^+ and BM_2. We have chosen concentrations of both boric acid and mannitol such that the hydrogen ion concentration is in every case at least ten times what it would be in the absence of the mannitol. Moreover, by using our determined value for the dissociation constant of boric acid and the Deutsch and Osoling value for the equilibrium constant, K_1, of the reaction

$$B^- + M \rightleftharpoons BM^-$$
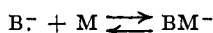
we can calculate the concentrations of B^- and BM^- and correct our equilibrium constant accordingly. We have not reported these revised values, since we strongly question the validity of the value of K_1 as determined by Deutsch and Osoling, and since these corrections would change our values by no more than 10% which is within our known experimental uncertainty.

(3) Böeseken, Vermaas and Küchlin, *Rec. Trav. Chim.*, **49**, 711 (1930).

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THE SPRAGUE ELECTRIC COMPANY
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Boron Trifluoride Catalyzed Esterification of p-Aminosalicylic Acid

BY JOSEPH J. SCHAEFER AND LEONARD DOUB

The effectiveness of p-aminosalicylic acid (4-amino-2-hydroxybenzoic acid) in experimental tuberculosis chemotherapy[1,2] led us to prepare a number of its esters. These compounds have been prepared by reduction of the corresponding nitro esters,[3] but since p-aminosalicylic acid has become commercially available, it was desirable to investigate direct esterification. Conventional methods of esterification under various conditions

(1) Lehmann, *Lancet*, **250**, 15 (1946).
(2) Youmans, *Quart. Bull., Northwestern Univ. Med. School*, **20**, 420 (1946).
(3) *Cf., e. g.*, Jensen, Rosdahl and Ingvorsen, *Acta Chir. Scand.*, **2**, 220 (1948).

led to very low yields,[4] the primary product being m-aminophenol.

Boron trifluoride as an esterification catalyst, following the work of Sowa and Nieuwland,[5] was tried and found to give excellent results. Approximately 70% yields were obtained with several alcohols. In general we used 4.5 moles of boron trifluoride for each mole of p-aminosalicyclic acid. In accord with the procedures of Sowa and Nieuwland, this provides one-half mole excess of boron trifluoride over that necessary for complex formation with the functional groups.

Experimental

Preparation of the Esters of 4-Amino-2-hydroxybenzoic Acid.—To a suspension of 153 g. (1.0 mole) of 4-amino-2-hydroxybenzoic acid in 1000 ml. of the anhydrous alcohol, 565 ml. (4.5 moles) of boron trifluoride-ethyl ether complex was added slowly, keeping below 40°. The resulting clear solution, after standing at room temperature for several days, was evaporated under reduced pressure to a thick slurry, and 500 ml. of water was introduced. Solution was effected by adding 10 N sodium hydroxide with cooling until alkaline to phenolphthalein. After charcoaling and filtering, solid carbon dioxide was added with agitation to precipitate the ester. This precipitate was removed by filtration and dissolved in dilute hydrochloric acid, charcoaled and filtered. The filtrate was neutralized with potassium bicarbonate. The ester precipitated, was filtered off and crystallized from ethyl alcohol.

ESTERS OF 4-AMINO-2-HYDROXYBENZOIC ACID

Ester	Reaction time, days	Yield, %	M. p., °C.	Empirical formula	Nitrogen, % Calcd.	Found
Methyl	10	74	121–124[4]	$C_8H_9NO_3$	7.73	7.88
Ethyl	10	71	114–115[3]	$C_9H_{11}NO_3$	8.38	8.27
Iso-propyl	30	75	73–75[3]	$C_{10}H_{13}NO_3$	7.18	7.43 7.40

(4) Rosdahl, *Svensk Kem. Tid.*, **60**, 12 (1948), reports the preparation of the methyl ester with sulfuric acid in methyl alcohol. In our hands this procedure gave less than 10% yield.
(5) Sowa and Nieuwland, THIS JOURNAL, **58**, 271 (1936).

RESEARCH LABORATORIES
PARKE, DAVIS & COMPANY
DETROIT 32, MICHIGAN   RECEIVED JULY 1, 1949

The Melting Point of Potassium Hydroxide

BY RALPH P. SEWARD AND KENNETH E. MARTIN

The melting point of potassium hydroxide has been reported as 360° by Hevesy[1] and 380° by Scarpa.[2] A determination of the melting point of potassium hydroxide was suggested by the observation that a sample which had been heated several hours to remove water was found to remain solid above 400°. The observations which are recorded below indicate the melting point to be $410 \pm 1°$.

The "reagent" quality potassium hydroxide employed, from titration with standard acid, was found to be 86.5% potassium hydroxide and 1.0% potassium carbonate, which agreed with the maker's analysis. On heating to constant weight at a

(1) Hevesy, *Z. physik. Chem.*, **73**, 667 (1910).
(2) Scarpa, *Atti Acad. Lincei*, [5] **24**, 745 (1915); *C. A.*, **9**, 2828 (1915).