[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 39]

Condensation Reactions of Boric Acid

BY WALTER C. SCHUMB AND WINSLOW H. HARTFORD

The only well authenticated complex compounds of boric acid are the borotungstates. The existence of a complex boromolybdic acid has been left in doubt for over a century; repetition of earlier work,[1] supplemented by other experiments, leads to the conclusion that such a complex acid does not exist. Thus, nitric acid added to a solution containing salts of the two single acids gives no coloration, and it was demonstrated quantitatively that the presence or absence of boric acid has no influence upon the precipitation of phosphomolybdate, again indicating that no boromolybdate is formed under these conditions.

In this connection it seemed of importance to observe the relation between the quantities of molybdic oxide dissolved by a given quantity of borate in solution and the change in *p*H accompanying solution of the oxide. If the quantity of acid anhydride dissolved by a given quantity of a dissolved oxysalt (such as sodium carbonate, phosphate or borate) is plotted against the observed change in *p*H, from the character of the curve obtained the extent to which complex formation takes place may be judged. A large degree of solubility accompanied by a relatively small change in acidity is indicative of complex formation.

This technique was employed in the study of the following combinations: Na_2CO_3 with MoO_3 and with WO_3; Na_3PO_4 with MoO_3 and with WO_3; $Na_2B_4O_7$ with MoO_3 and with WO_3; H_3BO_3 with MoO_3. The salts were chosen because they represent a gradation from cases where a definite lack of complex formation exists (Na_2CO_3), through the doubtful cases in which we were interested ($Na_2B_4O_7$), to the cases of very definite complex formation (Na_3PO_4). The case of boric and molybdic acid was studied as a further check upon Berzelius' work above referred to.

The method employed was the rotation of weighed quantities of MoO_3 or WO_3 with weighed quantities of standard solutions of sodium carbonate, trisodium phosphate or borax, contained in tightly stoppered 4-ounce bottles in a large thermostat for the desired period (from six to twenty-four hours), after which the mixtures were filtered through tared Gooches. The filtrate was preserved for the *p*H determination, and any residue remaining in the bottle was carefully washed upon the Gooch with a solution consisting of ammonium nitrate saturated with the appropriate oxide. The Gooches were heated at 150° for at least two hours to remove nitric acid and ammonium nitrate, cooled and weighed. The *p*H of the filtrate was determined electrometrically, using a quinhydrone electrode.[2]

Preparation of Molybdenum and Tungsten Trioxides.—Considerable care was given to the matter of the purity of the molybdenum and tungsten trioxides employed. The former was found to be prepared most conveniently by precipitating the monohydrate from a solution of C. P. ammonium molybdate with concentrated nitric acid, keeping both solutions just below the boiling point. The mixture, after standing for several hours, was filtered and the granular precipitate washed on a Büchner funnel and dehydrated at above 150° for eighteen to twenty-four hours. The product was pure white. As a check on its uniformity the solubility of the substance thus prepared was determined. Four successive saturated solutions were prepared by shaking with an excess of solid for a minimum of twenty-four hours in the thermostat, and 50-cc. samples of each were evaporated to dryness and the residues weighed. The constancy of the results of these determinations—0.490 ± 0.002 g. per liter of solution at 28°—indicates that the product thus prepared is of uniform composition. The *p*H of the saturated solution at this temperature was found to be 3.16. Molybdenum trioxide is much more insoluble than its hydrates, and the above results lead us to believe that its saturated solution is a much weaker acid than is indicated by the results of Rosenheim and Bertheim.[3]

The preparation of molybdenum trioxide by gentle ignition of ammonium molybdate proved unsatisfactory—the product was of grayish color, and tended to form colloidal solutions in water.

Tungsten trioxide was found to be prepared most satisfactorily by precipitation from boiling ammonium tungstate solution by means of nitric acid. The high temperature prevailing prevented the formation of the white colloidal modification of WO_3, and the yellow precipitated monohydrate was relatively easy to filter after standing for some hours on the steam-bath. In order to eliminate any of the colloidal modification that may have been formed, and to dehydrate completely the monohydrate, the product was ignited for ten hours at 775°. This sub-

---

[1] Berzelius' [*Pogg. Ann.*, **7**, 261 (1826)] product, obtained from a solution of molybdic acid in a hot solution of boric acid, consisted doubtless of ammonium molybdate, resulting from impure molybdic oxide. Carefully prepared molybdic oxide does not dissolve under these conditions, but commercial "85% MoO_3" dissolves, leaving on evaporation crystals of impure ammonium molybdate.

[2] Malaprade [*Ann. chim.*, [10] **11**, 104 (1929)] has used a procedure somewhat similar to this in measuring the neutralization of known complex acids.

[3] Rosenheim and Bertheim, *Z. anorg. Chem.*, **34**, 427 (1903); **37**, 314 (1904).

stance showed no colloidal tendency; it was preferably kept in the dark to prevent the superficial reduction (accompanied by a blue coloration) noted on exposure to light.

Solubility measurements for anhydrous WO_3 appear to be lacking. This property accordingly was measured in the same manner as that used with MoO_3. The solubility at 28° was found to be 0.029 g. WO_3 per liter of solution.[4]

The results of the series of parallel measurements of solubility of acid anhydride and *p*H, carried out with molybdenum trioxide and tungsten trioxide, in solutions of 0.1 molal sodium carbonate, trisodium phosphate, and borax, respectively, are most satisfactorily represented in the form of the accompanying figure, which shows the relation between the quantity of acid anhydride dissolved, and the *p*H of the solution. A total of 124 determinations were made, employing several different samples of acid anhydride, and varying periods of time (to ensure attainment of equilibrium).

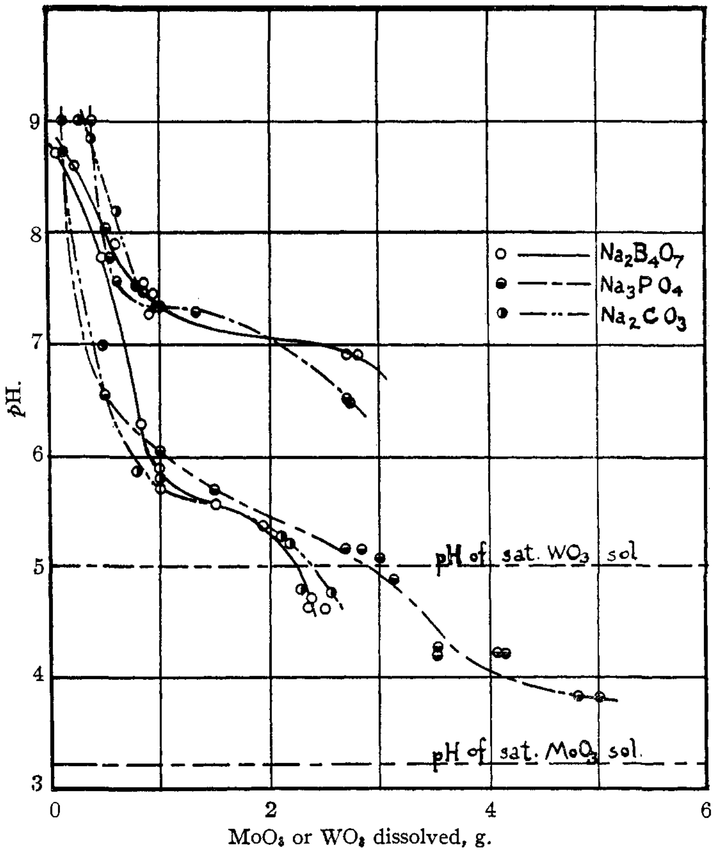

Fig. 1.

Figure 1 gives a clear picture of the reaction of molybdenum and tungsten trioxides with the three salts employed. The upper group of curves is for WO_3, the lower for MoO_3. The curves for MoO_3 are seen to be widely separated at low concentrations of dissolved MoO_3, because of the variation in *p*H of the original solutions. As the buffering action of the MoO_3 begins to appear, the curves become more nearly coincident, and continue so over the interval corresponding to from one to two grams of MoO_3 dissolved. At this point the curve for trisodium phosphate begins to diverge, assuming a less steep slope, and at the same time a trace of the characteristic yellow color of the phosphomolybdate complex becomes apparent in the filtrate. Molybdic oxide continues to dissolve in the phosphate solution, and the *p*H decreases until about 5 g. of the trioxide has dissolved. The curves for the carbonate and borate solutions are distinctly different in character: a rapid drop in *p*H results as MoO_3 continues to dissolve, and at about 2.5 g. of MoO_3 dissolved, the curves abruptly stop.[5]

The virtual coincidence of the borate curve with that of the carbonate (which forms no complex), and the divergence of the curve for the complex-forming phosphate afford a convincing proof that borates do not react with molybdic acid to form a complex.

With tungsten trioxide the abrupt stopping of the carbonate curve and the continuance of the curves for both borate and phosphate, as more trioxide dissolves, indicate clearly the existence of borotungstate and phosphotungstate complexes; while carbonates merely neutralize the weak heavy metal acid in an incomplete manner.

In the case of boric acid and molybdenum trioxide, the study of which led to the development of the method just described, no significant quantity of MoO_3 (if pure) was found to dissolve in boric acid solutions, and the *p*H change was negligible. Complex formation consequently is lacking, since a relatively large change in hydrogen ion concentration in such a case would be expected.

It may be added that the method employed in this part of the work is of quite general applicability, and may be used in the study of any reac-

---

[4] The solubility data were subject to a correction for material dissolved from the glass bottles, which was determined in blank runs.

(5) This represents about 90% completion of the reactions

$$Na_2CO_3 + 2MoO_3 = Na_2Mo_2O_7 + CO_2 \text{ and}$$
$$Na_2B_4O_7 + 2MoO_3 + 2H_2O = Na_2Mo_2O_7 + 4HBO_2$$

Malaprade (Ref. 2) has shown that the principal salt formed by neutralization of molybdic acid is the dimolybdate.

tion wherein an insoluble solid is brought into solution with an attendant change in hydrogen ion concentration. Naturally the use of substances which react with the quinhydrone electrode, as employed in these measurements, is excluded.

Summary

1. Experimental evidence is presented leading definitely to the conclusion that boric and molybdic acids do not enter into complex formation.

2. A method is described whereby, through parallel series of measurements of solubility and of *p*H of the saturated solution of MoO_3 or WO_3 in solutions of sodium borate, carbonate and phosphate, respectively, the non-existence of boromolybdate ions and the existence of borotungstate ions in these solutions is demonstrated. The applicability of this method to other cases involving a change in solubility with attendant change in *p*H is suggested.

3. The solubilities of MoO_3 and of WO_3 have been determined at 28°.

4. The most satisfactory methods of preparation of pure MoO_3 and WO_3 are described.

CAMBRIDGE, MASS. RECEIVED JANUARY 16, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE, COPENHAGEN]

Studies of Complex Formation between Aniline and Picrate Ion by Solubility Measurements

BY KAI JULIUS PEDERSEN

When aniline is added to a solution of a picrate the color changes from yellow to orange, showing that a complex is formed. In this paper the stability of the picrate–aniline complex in aqueous solution is determined from (1) the increase in solubility of anilinium picrate when aniline is added, and (2) the increase in solubility of aniline when sodium picrate is added. For comparison, the solubility of anilinium sulfate in aqueous solutions of aniline was also determined, and, finally, that of aniline in solutions of sodium benzoate, anilinium sulfate and potassium sulfate.

Materials

Aniline (Kahlbaum, pro analysi) redistilled, f. p. −6.2°.

Anilinium Picrate.—Two isomeric forms could be prepared from the solution: 35.6 g. of picric acid (pro analysi) dissolved in 1000 cc. of boiling water, and 14.4 g. of aniline added. If it was cooled quickly in ice water the crystals were small and light yellow with a tinge of green, indistinguishable from picric acid. This form could be recrystallized unchanged when dissolved in hot water and cooled quickly. If, however, the original solution or a warm solution of the light-colored form was cooled slowly, larger crystals of a stronger yellow color, like that of potassium picrate, were obtained. If the metastable form was left at room temperature with a little water it gradually transformed into the stable form. The resemblance of the two forms to picric acid and potassium picrate, respectively, is so striking that we may take it as a sign of similarity in molecular structure. The most obvious explanation, that the form which looks like picric acid is a molecular compound of this acid and aniline, does not seem to hold, because it has been found[1] that the color changes when organic nitro compounds form addition products with aromatic molecules. The solubility measurements were (with one exception) carried out with the stable form. This was first recrystallized twice from water.

Sodium Picrate.—The monohydrate was prepared from sodium carbonate and picric acid, both pro analysi; recrystallized once; dried in the air.

Anilinium Sulfate.—From aniline and sulfuric acid; recrystallized; dried *in vacuo* over concd. sulfuric acid.

Sodium Benzoate.—Solutions were prepared by neutralizing benzoic acid pro analysi with sodium hydroxide solution.

The saturated solutions were prepared in glass-stoppered bottles whose necks were covered with ground-on glass bells. The bottles were rotated in a water thermostat at 18.15°.

Samples of the saturated solutions of the two anilinium salts were sucked from the bottle, which was not taken from the thermostat, through a porous glass filter into a pipet. The anilinium ion was titrated with 0.025 *N* barium hydroxide or 0.1 *N* sodium hydroxide. Phenolphthalein was used as indicator. The end-point was distinct even in the yellow picrate solutions.

The solutions saturated with aniline were apt to form a rather stable suspension of aniline particles. However, when the sample was sucked into the pipet through a plug of cotton wool a clear solution was obtained. Usually 10 cc. was taken from the saturated solution and diluted to 100 cc. in a graduated flask; 10 cc. of this dilute solution was pipetted into a glass-stoppered bottle, and 5 cc. of 2 *N* potassium bromide and a small excess of 0.1 *N* potassium bromate (one mole of aniline uses 6 equivalents of bromate)

---

[1] Pfeiffer, "Organische Molekülverbindungen," 1922, pp. 218–245.