the mixture refluxing vigorously, 0.25 mole of the cyanide dissolved in 35 g. of absolute alcohol. After this addition, another 35 g. of absolute alcohol was added at the same rate. The mixture was allowed to cool and 95% alcohol slowly added until any unreacted sodium had disappeared. Then 500 cc. of water was added, the toluene layer separated and washed several times with 150-cc. portions of water and these washings together with the first aqueous layer diluted to exactly one liter. An aliquot portion of the solution was titrated for cyanide ion with standard silver nitrate solution according to the method of Volhard.

The amine was removed from the toluene by extracting with 15% hydrochloric acid and any amine in the aqueous washings steam distilled and added to this acid extract. Those amines which were very insoluble in water were isolated by fractionation of the toluene layer. The cleavage product resulting from the replacement of the cyanide group by hydrogen was isolated in a few instances and found to correspond to the amount of cyanide ion found by titration.

Summary

A study of the reduction of a variety of cyanides by sodium and alcohol has been made and the extent of the two competing reactions, $RCN \longrightarrow RCH_2NH_2$ and $RCN \longrightarrow RH + NaCN$, determined in each case.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Oxidation of the Benzene Ring of Arylboric Acids by Potassium Permanganate

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When *m*- and *p*-tolylboric acids, $CH_3C_6H_4B(OH)_2$, are dissolved in 0.3 *N* alkali and oxidized with a saturated solution of potassium permanganate, good yields of *m*- and *p*-carboxylphenylboric acids, $HO_2CC_6H_4B(OH)_2$, are obtained.[1]

These preparations can be carried out at room temperatures, though heating near the end of the reaction is advisable. Koenig and Scharrnbeck report a similar preparation of *o*-carboxylphenylboric acid. The product melted at 152° and gave percentages of carbon and hydrogen corresponding to the formula $C_7H_7O_4B$. We have found the method very suitable for the preparation of *m*- and *p*-carboxylphenylboric acids, but we have not succeeded in preparing the *o*-isomer.

Oxidation of *o*-Tolylboric Acid.—When we added the theoretical amount of potassium permanganate (six oxidizing equivalents per mole of tolylboric acid) to an alkaline solution of *o*-tolylboric acid at room temperatures, the permanganate ion was rapidly and completely reduced to manganese dioxide. From the reaction product we obtained an acid melting at 150–154°. When this acid was titrated with alkali using phenolphthalein as the indicator, an equivalent weight greater than a thousand was obtained. In the presence of mannitol an equivalent weight of 130 was obtained. These results show that the acidic group in the reaction product is $B(OH)_2$ and not carboxyl. When the substance was purified the melting point rose to 170°. The product was unchanged *o*-tolylboric acid, m. p. 171° (Koenig and Scharrnbeck give 168°), equivalent weight 136. We varied the *P*H of the solution from that of 1 *N* acid to that of 1.5 *N* alkali, and the temperature from 20 to 0°, and tried the substitution of manganate for permanganate ion. In every case the theoretical amount of oxidizing agent was reduced, but the only arylboric acid obtained was *o*-tolylboric acid. Our results seemed to indicate that oxidation of the benzene ring in *o*-tolylboric acid or in *o*-carboxylphenylboric acid is faster than the oxidation of the methyl group in *o*-tolylboric acid to a carboxyl group.

If our failure to obtain *o*-carboxylphenylboric acid is to be attributed to the oxidation of the benzene ring, *o*-tolylboric acid can rapidly reduce much more than six oxidizing equivalents of permanganate ion per mole of tolylboric acid. We tested this deduction in the following experiment.

A saturated solution of potassium permanganate was added in small portions to a 2% solution of *o*-tolylboric acid in 0.3 *N* alkali. The portions of permanganate solutions contained about a quarter of an oxidizing equivalent per mole of tolylboric acid. Fresh portions of the permanganate solutions were added when the previously added portions had been reduced completely to manganese dioxide. This process was continued until the permanganate was no longer reduced. The experiment was done at room temperatures. In this way we were able to reduce twenty-four equivalents of potassium permanganate per mole of *o*-tolylboric acid. The reduction was quite fast. The individual portions of permanganate were reduced in less than a minute, and this rate was maintained nearly up to the last one or two equivalents.

The large quantities of potassium permanganate reduced

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(1) Michaelis, *Ann.*, **315**, 19 (1901), and Koenig and Scharrnbeck, *J. prakt. Chem.*, **128**, 153 (1930).

clearly showed that the benzene nucleus was oxidized. To test the generality of this reaction we repeated this experiment with some other organic boric acids. We found that many organic boric acids are oxidized by alkaline permanganate at room temperatures, but at very different rates. When the boric acid group was attached to an aromatic nucleus and the oxidation was not very slow, the quantity of permanganate ion reduced indicated that the aromatic nucleus was oxidized.

Oxidation of the Naphthylboric Acids.—With both α- and β-naphthylboric acids, $C_{10}H_7B(OH)_2$, eighteen oxidizing equivalents of permanganate ion were reduced per mole of arylboric acid. The reaction was very rapid and stopped abruptly when the eighteen equivalents had been added. The reaction was so fast and ended so abruptly that it could have been used as a method of titration. Phthalic acid was isolated from the oxidation products of both naphthylboric acids. The phthalic acid was identified by a mixed melting point, obtained by immersion into a preheated bath (m. p. of product 213°, m. p. of sample of phthalic acid, 213°, m. p. of mixture 213°). The quantity of permanganate ion reduced corresponds to the equation

$$C_{10}H_7B(OH)_2 + 6MnO_4^- + OH^- = C_8H_4O_2^{--} + 2CO_3^{--} + B(OH)_2O^- + 6MnO_2 + 2H_2O$$

Oxidation of Phenylboric and the Phenetylboric Acids.—Phenylboric acid was very slowly oxidized by the permanganate solution at room temperatures. More than one oxidizing equivalent of permanganate was reduced per mole of phenylboric acid in a week. The experiment was not continued long enough to show that more equivalents of permanganate than correspond to the formation of boric acid and phenol could have been reduced. As phenol is oxidized by permanganate more rapidly than is phenylboric acid, the prolongation of the experiment was not needed to show that more than two equivalents of permanganate could have been reduced.

The three phenetylboric acids, $C_2H_5OC_6H_4B(OH)_2$, reduced more oxidizing equivalents of permanganate ion than correspond to the oxidation of the ethoxy group to carbon dioxide. This reaction needs twelve oxidizing equivalents of permanganate ion per mole of phenetylboric acid. *o*-Phenetylboric acid reduced twenty-four equivalents, *m*-phenetylboric acid reduced the same amount, but the *p*-isomer reduced only eighteen equivalents. The reactions were markedly different in their rates. The *o*- and *p*-compounds reduced the permanganate ion as fast as *o*-tolylboric acid did, but it took a week to reduce twenty-four equivalents of permanganate per mole of *m*-phenetylboric acid.

Oxidation of *n*-Butylboric Acid and β-Phenylethylboric Acid.—*n*-Butylboric acid, $C_4H_9B(OH)_2$, and β-phenylethylboric acid, $C_6H_5CH_2CH_2B(OH)_2$, behaved in similar ways when oxidized with potassium permanganate. Two equivalents of permanganate were reduced very rapidly, after which the reaction became slow. In the case of *n*-butylboric acid a strong odor of butyl alcohol was observed in the reaction product. These reactions are obviously oxidation at the link between the organic radical and the boron atom, *e. g.*

$$3C_4H_9B(OH)_2 + 2MnO_4^- + OH^- + H_2O = 3C_4H_9OH + 3B(OH)_2O^- + 2MnO_2$$

Conclusion

It would seem from these experiments that the $B(OH)_2$ group can make an aromatic nucleus to which it is attached very susceptible to oxidation by permanganate ion. The extent of this susceptibility depends considerably on the other groups attached to the benzene ring. In *o*-tolylboric acid, α- and β-naphthylboric acids, *o*- and *p*-phenetylboric acids, the aromatic nucleus is rapidly oxidized, in phenylboric acid the oxidation is very slow, and in *m*-phenetylboric acid the rate is moderate. That *m*- and *p*-carboxylphenylboric acids are obtained in good yields by the oxidation of the corresponding tolylboric acids shows that *m*- and *p*-carboxylphenylboric acids and *m*- and *p*-tolylboric acids should be classed with phenylboric acid as resistant to nuclear oxidation.

The oxidation of the aromatic nuclei evidently does not follow the removal of the $B(OH)_2$ group by hydrolysis, for the phenetols, toluene and naphthalene are not oxidized by alkaline permanganate at room temperatures. However, it seems likely that the preliminary reaction is the removal of the $B(OH)_2$ group by oxidation. As shown in the case of butylboric acid the removal of this group by oxidation may be very rapid. In the arylboric acids this process produces phenols, which are, in general, rapidly oxidized by alkaline potassium permanganate at room temperatures.

Summary

It is shown that the aromatic nuclei of several arylboric acids are rapidly oxidized by alkaline permanganate at room temperatures.

Phthalic acid was obtained from both α- and β-naphthylboric acids by oxidation with alkaline permanganate at room temperatures.

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