

ate¹⁵ and of a soybean oil¹⁶ give curves similar to those shown in Fig. 1.

There is no apparent correlation between the magnitude of the oxidizing power and properties within the group of coals having high-volatile C bituminous rank. It will be seen, however, that the one coal of higher rank (C-2423) exhibits a definitely lower oxidizing power per unit surface. It seems obvious from Table II that the magnitude of oxidizing power attained is not simply a function of the extent of the surface, but that the nature of the surface (which undoubtedly varies with the rank and source of the coal) is of utmost importance in this respect. It is hoped that this investigation may be extended to cover a series of coals of widely differing ranks.

It is possible that the different petrographic or "banded" ingredients of the coal may differ in

(15) Elm, *Ind. Eng. Chem.*, **23**, 882 (1931).

(16) Clark and Rugg, *Ind. Eng. Chem., Anal. Ed.*, **13**, 243 (1941).

their ability to take on oxidizing power. Such differences, as well as errors in sampling, might contribute to the irregularities in the curves. The present study is being continued with samples of separated banded ingredients of an Illinois coal.

Acknowledgment.—The authors wish to extend their thanks to Drs. F. H. Reed and O. W. Rees for valuable suggestions; to Mr. C. C. Boley for assistance in collecting samples and to Mr. K. F. Bursack and Mr. W. F. Wagner who made the coal analyses and specific surface measurements under the direction of Dr. Rees.

Summary

The oxidizing power exhibited by five Illinois coals has been shown to reach a maximum value and then decrease, suggesting that this "reactive oxygen" may play the role of an intermediate in the oxidative degradation of these coals.

URBANA, ILLINOIS

RECEIVED MAY 1, 1942

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Oxidation of *n*-Butylboron Oxide¹

BY OLIVER GRUMMITT

The reported² auto-oxidation of *n*-butaneboronic acid (*n*-BuB(OH)₂) to the mono-*n*-butyl ester of boric acid (*n*-BuO-B(OH)₂) suggested a parallel study of the auto-oxidation of *n*-butylboron oxide, (*n*-BuBO)₃, which is the trimeric anhydride of the boronic acid. This oxidation, because of the six-electron configuration of the boron atom, offered the possibility of proceeding through the intermediate formation of an oxygen coordination compound (or peroxide) comparable to those postulated for many oxidation processes.³

Preliminary measurements⁴ on several alkylboron oxides showed that oxidation occurred readily but at widely different rates depending upon the nature of the alkyl group (Table I).

Apparently the ease of oxidation decreases with an increasing chain length of the alkyl group and increases sharply in the order primary, secondary,

(1) Presented before the Division of Organic Chemistry at the Detroit meeting of the American Chemical Society, September 12, 1940.

(2) Snyder, Kuck and Johnson, *THIS JOURNAL*, **60**, 105 (1938).

(3) Bailey, "Retardation of Chemical Reactions," Longmans, Green and Co., New York, 1937.

(4) The author wishes to thank Professor J. R. Johnson for his permission to use these data which were obtained during a du Pont Post-Doctorate Fellowship at Cornell University, 1936-1938, and for his suggestions on this problem.

TABLE I

R of R-BO	Time required for the consumption of 2.0 cc. oxygen, 25°, min.
Et	33
<i>n</i> -Pr	36
<i>n</i> -Bu	71
<i>s</i> -Bu	3
<i>t</i> -Bu	2
<i>n</i> -Hex	105

and tertiary. The relative stability of the corresponding boronic acids in air is also of this order.^{2,5}

Experimental Procedure

Apparatus.—The reaction flask is shown in Fig. 1. The total volume of this two-bulb flask is approximately 125 cc. and since none of the dimensions is of critical importance, they are not shown. Connected to the side arm of the flask are two mercury-filled gas burets in series. The first of these burets was made of a 10-cc. delivery pipet calibrated in divisions of 0.05 cc. and a three-way stopcock and was used to measure the consumption of oxygen during the earlier stages of the reaction. The second buret was the orthodox 100-cc. type with 0.2-cc. divisions. Each gas buret was fitted with a leveling bulb and a jacket through which thermostated water could be circulated. The use of two burets permitted accurate readings at the start of the auto-oxidation when an induction

(5) Johnson, Van Campen and Grummitt, *THIS JOURNAL*, **60**, 111 (1938); and unpublished work of Johnson and Grummitt.

period might be present and also allowed total volumes of oxygen up to about 100 cc. to react and be measured with fair accuracy.

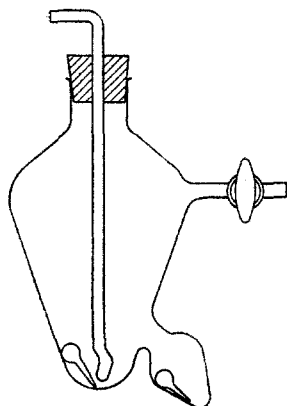


Fig. 1.—Reaction flask.

A small sample of the alkylboron oxide contained in a sealed ampoule made in the shape of a bulb with a fine capillary stem was placed stem-down in the bottom bulb of the reaction flask. A similar ampoule, tared and empty, was placed stem-down in the side bulb. The reaction flask and burets were very carefully dried and filled with dry oxygen so that the small buret contained about 7–8 cc. of gas, the large buret about 70 cc. of gas. The gas buret stopcocks were open to the flask and the leveling bulbs were adjusted so that atmospheric pressure existed in the whole system. The temperature of the system was maintained at 25° by circulating water from a thermostat through the buret jackets and through a container surrounding the flask. When the buret readings no longer changed over a ten-minute period showing that the enclosed gas had reached constant temperature, the stopcock on the large buret was shut off from the reaction flask. The bent rod in the reaction flask was twisted so as to smash the ampoule against the wall of the flask and the time was noted. Frequent adjustments of the leveling bulb on the small buret were made in order to maintain atmospheric pressure and readings were taken at the same time. When 2–5 cc. of oxygen had been consumed, the small buret was shut off and the large buret, by means of its stopcock, was opened to the reaction flask and occasional time-volume readings were made.

When the sample was completely oxidized as shown by a constant volume reading after a period of one-half hour, the stopcock at the connection between the flask and the first buret was closed and the rubber connection removed from the buret. The flask was connected to a vacuum pump through an arrangement of stopcocks which permitted the flask to be evacuated and then filled with dry, oxygen-free nitrogen without opening the flask to the atmosphere. The flask was thoroughly evacuated and rinsed with nitrogen four times while clamped in a vertical position. It was then tilted so that the product drained into the side-bulb, re-evacuated, and again filled with nitrogen. As the pressure approached atmospheric the liquid product filled the empty, tared ampoule. This was then removed, sealed by touching the tip in a flame, and, after weighing, was ready for analysis, molecular weight determination, etc.

The flask shown in Fig. 1 may be useful for other reactions where the reactants are gases and liquids which cannot be exposed to the atmosphere and where the product is also a liquid which cannot be exposed. A somewhat similar device described by Stock and Zeidler⁶ does not permit the product to be removed in an ampoule.

(6) Stock and Zeidler, *Ber.*, **54**, 533 (1921).

Relative Oxidation Rates.—Samples of the various alkyl boron oxides listed in Table I were prepared by dehydration of the corresponding boronic acids with thionyl chloride.⁷ A 0.2–0.3 g. (about 3.0 millimoles) sample was oxidized in the apparatus described above and the time noted for the consumption of 2.0 cc. of oxygen at 25°. Duplicate determinations were made. In each case there was practically no induction period so the data show in an approximate way the relative reactivity of the various compounds with respect to oxygen.

Oxidation of *n*-Butylboron Oxide.—A 0.2060-g. (2.46 millimoles) sample of *n*-butylboron oxide was quantitatively oxidized in the apparatus previously described. Volume readings were taken at two-minute intervals for the first eighteen minutes, at three-minute intervals for the next thirty-five minutes, and then at longer intervals until no more oxygen was consumed. These data are plotted in Fig. 2. As the curve shows there is no induction period. At the end of 800 minutes 31.5 cc. of oxygen had been consumed as compared to a theoretical consumption of 31.6 cc. (at 25° and 735 mm. pressure) based on the oxidation of *n*-butyl boron oxide to *n*-butyl metaborate (Eq. 1).

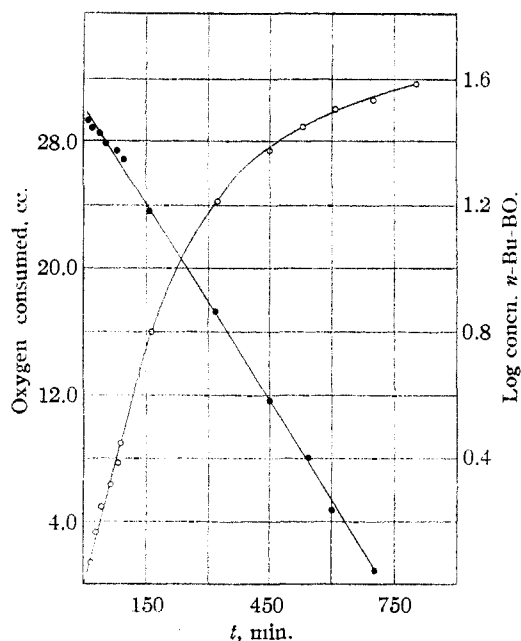


Fig. 2.—Oxidation of *n*-butylboron oxide.

The product from the oxidation of 0.6 g. of *n*-butylboron oxide was distributed into tared ampoules. The saponification equivalent of one of these samples was found to be 98.6; calculated for $n\text{-C}_4\text{H}_9\text{OBO}$, 99.9. A molecular weight determination by freezing point depression in benzene gave 97.6. This determination was very difficult because of the great ease of hydrolysis of the sample; not only must the apparatus and benzene be absolutely dry, but it must be so maintained by slowly passing dry nitrogen into one sidearm of the freezing point tube so as to prevent any air from entering while stirring.

One sample of the ester was hydrolyzed by the dropwise addition of water; some heat was generated and the odor

of *n*-butyl alcohol was apparent. A neutralization equivalent of the boric acid formed was determined by adding mannitol and titrating with standard sodium hydroxide in the presence of phenolphthalein; found 61.5, calculated 61.8. Another sample was hydrolyzed with a slight excess of water, distilled, and the *n*-butyl alcohol identified as the 3,5-dinitrobenzoate derivative, m. p. 63–64°, no depression in a mixed m. p. with an authentic sample.

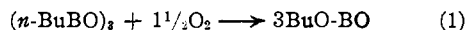
*Anal.*² Calcd. for $C_4H_9BO_2$: B, 10.83. Found: B, 11.05.

Peroxide Tests.—Partially oxidized samples of *n*-butylboron oxide instantly liberated iodine from a slightly acidified solution of 5% potassium iodide in absolute ethanol. Further evidence that peroxides or peroxide-like compounds may be present was obtained by heating three 10-cc. portions of vinyl acetate on the water-bath at 70°; the first sample contained no catalyst, the second contained about 0.1 g. of partially oxidized *n*-butylboron oxide, and the third contained 0.1 g. of benzoyl peroxide. At the end of one-half hour the increase in viscosity, interpreted roughly as a measure of polymerization, was small for the blank, appreciable for the second, and very considerable for the third. It is possible of course that the partially oxidized butylboron oxide furnished other catalytic agents besides peroxides.

Catalytic Oxidation of *n*-Butylboron Oxide.—Samples containing approximately 0.1% of the catalyst were made by distilling *n*-butylboron oxide at reduced pressure into receivers containing inverted tared ampoules and a weighed portion of the catalyst. Before letting nitrogen into the system the receivers were gently warmed to dissolve the catalyst. Both hydroquinone and phenyl- β -naphthylamine dissolved readily, but cobalt linoleate and ammonium vanadate were only partially soluble. Nitrogen was admitted and the ampoules sealed and weighed in the usual way. These samples were then oxidized according to the procedure described before. The samples containing hydroquinone, cobalt linoleate, and ammonium vanadate gave time-oxygen consumed curves which substantially duplicated that shown in Fig. 2, but phenyl- β -naphthylamine inhibited the oxidation; for example, in 200 minutes only 1.2 cc. of oxygen had been consumed compared to 15.0 cc. in the absence of the catalyst and at the end of 13.5 hours where the oxidation normally would be completed only 10% of the theoretical amount of oxygen had been consumed.

Results and Discussion

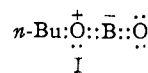
Oxidation of *n*-butylboron oxide was found to proceed quantitatively according to the equation



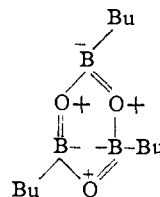
the product being the *n*-butyl ester of metaboric acid. This substance is an oily liquid with a faint ester odor. Like esters of boric acid it hydrolyzes immediately on contact with the atmosphere forming *n*-butyl alcohol and a mixture of metaboric and boric acids.⁷

(7) Schiff, *Ann., Supp.*, **5**, 185 (1887), reported similar properties for methyl and ethyl metaborates which were prepared by the action of boric acid on the alkyl borate or alcohol.

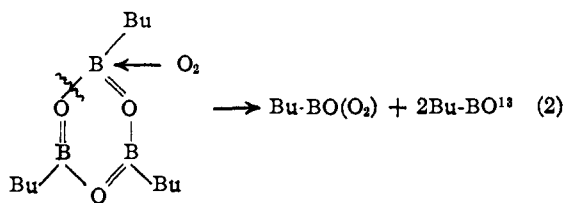
Since *n*-butyl metaborate is monomeric,⁸ the oxidation process has been accompanied by a depolymerization reaction. The failure of *n*-butyl metaborate to retain the trimeric structure of *n*-butylboron oxide is probably due in part to the contribution of resonating forms such as I⁹ in which the boron atom can no longer function as an acceptor center.



This function is necessary in order that the boron atom coordinate with oxygen to form the trimeric butylboron oxide^{2,10,11}



The course of the oxidation of *n*-butylboron oxide is shown in Fig. 2, in which the volume of oxygen consumed is plotted against time. The shape of this curve differs from typical S-shaped auto-oxidation curves for benzaldehyde, linseed oil, etc.,³ in that the induction period¹² is absent. This probably means that the concentration of peroxidic intermediate necessary for an appreciable rate of oxidation is established very rapidly. This intermediate could arise through the attack of a boron atom by oxygen with subsequent cleavage of the ring (2); the peroxide could then



(8) Metaboric acid itself has been reported to be monomeric. Mellor, "Comprehensive Treatise of Inorganic Chemistry," Longmans, Green, and Co., New York, N. Y., 1924, Vol. 5, p. 48.

(9) Other resonating forms include $n\text{-Bu}:\overset{+}{\text{B}}::\overset{-}{\text{B}}::\overset{-}{\text{O}}$, $n\text{-Bu}:\overset{+}{\text{O}}::\overset{-}{\text{B}}::\overset{-}{\text{O}}$, and $n\text{-Bu}:\overset{+}{\text{O}}::\overset{-}{\text{B}}::\overset{-}{\text{O}}$. In the absence of bond length data the principal form cannot be selected, although ordinary valence considerations favor the first of these.

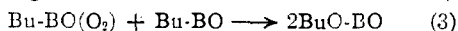
(10) Kinney and Pontz, *THIS JOURNAL*, **58**, 197 (1936), found that certain arylboric oxides are trimeric.

(11) Burg, *ibid.*, **62**, 2228 (1940), found that methylboric oxide is trimeric.

(12) The initial period of time in which the rate of oxygen absorption is zero or very low.

(13) An alternative initial step could involve peroxide formation from the action of oxygen directly on monomeric butylboron oxide if one assumes an equilibrium: $(\text{Bu}\cdot\text{BO})_3 \rightleftharpoons 3\text{Bu}\cdot\text{BO}$. There is no evidence, however, for this dissociation.

oxidize monomeric butylboron oxide to form the metaborate in a reaction analogous to the interaction of benzoyl hydrogen peroxide with benzaldehyde to give two molecules of benzoic acid (3).



Some evidence in support of the intermediate peroxide is gained from experiments with partially oxidized butylboron oxide which show that it liberates iodine from alcoholic potassium iodide and catalyzes the polymerization of vinyl acetate as do other peroxides.

Efforts to establish a reaction mechanism on the basis of kinetic measurements were unsuccessful. When a sample of *n*-butylboron oxide was exposed to oxygen without agitation, the rate of oxygen absorption followed the unimolecular law as shown by the straight line in Fig. 2 obtained by plotting the logarithm of the concentration of *n*-butylboron oxide against time. The concentration of *n*-butylboron oxide was determined on the basis of the oxygen consumed in accordance with equation (1). This agreement with the unimolecular law is superficial, however, because mechanical agitation of the reaction mixture in other experiments not only increased the rate of oxidation but gave data which could not be interpreted kinetically. Apparently the rate of diffusion of unoxidized material to the surface of the reaction mixture is the rate-determining step in the absence of agitation.

The effect of catalysts on the rate of oxidation was observed in experiments with cobalt linoleate and ammonium vanadate as positive catalysts, and hydroquinone and phenyl- β -naphthylamine as typical anti-oxidants. The only one of these catalysts which had an appreciable effect on the rate of oxidation was phenyl- β -naphthylamine, which inhibited the reaction almost completely. It is interesting to note that aromatic amines are more effective anti-oxidants than phenols for aliphatic aldehydes.¹⁴ This is a further point of resemblance between the alkylboron oxides (or boronic acids) and aliphatic aldehydes, Johnson, *et al.*,² having already pointed out that both types of compounds combine with oxygen, reduce ammoniacal silver oxide, and form cyclic trimers.

Summary

n-Butylboron oxide undergoes quantitative oxidation and depolymerization in the presence of dry oxygen to form monomeric *n*-butyl metaborate. There is evidence for the intermediate formation of a peroxidic substance. A possible reaction mechanism has been suggested, but could not be confirmed by rate measurements because the kinetics were complex. Phenyl- β -naphthylamine retards the oxidation but hydroquinone does not.

(14) Bailey, *Proc. Royal Irish Acad.*, **45B**, 373 (1939).

CLEVELAND, OHIO

RECEIVED MARCH 23, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF SOILS, UNIVERSITY OF MISSOURI]

The Electrochemical Properties of Mineral Membranes. V. Beidellite Membranes and the Determination of Sodium¹

BY C. E. MARSHALL² AND C. A. KRINBILL²

Introduction

Previous papers in this series³ have dealt with the use of preheated montmorillonite membranes in the potentiometric determination of potassium and ammonium and with the application of this method to the electrochemical study of colloidal systems as typified by the clays. The hydrogen

montmorillonite membranes used were preheated to 490°. This treatment conferred remarkable properties of stability and selectivity. The membranes were of high resistance (1-10 megohms), yet showed excellent reproducibility toward potassium and ammonium ions. Acids attacked them chemically and highly reproducible values could only be obtained at pH values above 4. Sodium salts alone gave poor reproducibility and asymmetry potentials were troublesome. However, mixtures of sodium and potassium salts measured against potassium chloride as standard gave values which suggested that the

(1) Contribution from the Department of Soils, Missouri Agricultural Experiment Station, Journal Series No. 820. Read before the Colloid Chemistry Division at the 103rd meeting of the American Chemical Society in Memphis on April 23, 1942.

(2) Associate Professor and Research Assistant in Soils, respectively.

(3) Marshall and Bergman, *THIS JOURNAL*, **63**, 1911 (1941); *J. Phys. Chem.*, **46**, 52 (1942); **46**, 325 (1942).