CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Gaseous Boroxine: Mechanisms of Reactions with Oxygen and Carbon Monoxide[1]

BY GEORGE H. LEE, II, AND RICHARD F. PORTER

Received April 18, 1966

Reactions of gaseous boroxine ($H_3B_3O_3$) with O_2 and CO have been investigated by infrared absorption techniques. Kinetic measurements indicate that the reactions

$$H_3B_3O_3(g) + {}^1/_2O_2(g) = H_2B_2O_3(g) + {}^1/_3B_2O_3(s) + {}^1/_6B_2H_6(g)$$

and

$$H_3B_3O_3(g) + CO(g) = BH_3CO(g) + B_2O_3(s)$$

are first order in $H_3B_3O_3$ pressure and approximately zero order in O_2 and CO pressure. The rates for both reactions are accelerated in reaction vessels coated with $B_2O_3(s)$. Plausible heterogeneous mechanisms for these reactions in B_2O_3-coated vessels are proposed.

Introduction

The chemical behavior of boroxine ($H_3B_3O_3$) has been the subject of a series of recent studies.[2,3] Boroxine reacts with oxygen and carbon monoxide at room temperature to form $H_2B_2O_3(g)$ and $BH_3CO(g)$, respectively. Gaseous $H_3B_3O_3$ should be considered a "high-temperature" molecule since it is a stable product of the thermal reaction of H_2 with B–B_2O_3 mixtures at temperatures above 1000°. The compound also is observed as a product of an explosive reaction of B_5H_9 and O_2. At ordinary temperatures $H_3B_3O_3(g)$ is thermodynamically unstable with respect to B_2H_6 and B_2O_3. However, the gaseous compound does not decompose rapidly, and it may be contained in Pyrex vessels for several minutes at a few millimeters of pressure and room temperature. For this reason exploration of the chemical kinetics of the gaseous species is possible. In this paper results of experimental kinetic studies of the reaction of $H_3B_3O_3(g)$ with $O_2(g)$ and CO(g) are presented.

Experimental Section

Gaseous boroxine was prepared by the explosive oxidation of B_5H_9.[4] *In these experiments one should exercise the utmost in safety precautions. Since occasionally the intensity of this explosive reaction is high enough to fracture the reaction vessel, the appartus should be properly shielded to prevent possible injury to the operator. It is important to keep the B_5H_9 and O_2 sources well isolated from each other to prevent accidental mixing of these reagents during vacuum manipulations.* Pentaborane at a pressure of 10 mm was added to a 125-ml Pyrex bulb with attached stopcock. The gas was frozen at −196° and oxygen was admitted directly into the bulb in sufficient quantity to give a $B_5H_9:O_2$ pressure ratio of 1:3 when the system had warmed to room temperature. The total pressure of reactants was about 40 mm at room temperature. The reaction bulb with reactants was attached to a 9-cm infrared cell with KBr windows. After the cell and the tubing joining the cell to the reaction vessel were evacuated, the reactants were heated to the flash point (about 60°) with a heating mantle. The reaction products were then introduced into the cell by opening the adjoining stopcock. Infrared spectra of the products indicated that boroxine was the only gaseous product, aside from hydrogen. The quantity of boroxine that entered the cell was estimated by allowing a sample to decompose according to the stoichiometric relationship

$$H_3B_3O_3(g) = {}^1/_2B_2H_6(g) + B_2O_3(s) \qquad (1)$$

and measuring the final pressure of B_2H_6. The initial pressure of $H_3B_3O_3$ in the cell was usually between 1.0 and 3.0 mm and the pressure of H_2 was between 30 and 40 mm.

Reagents were mixed either by adding $H_3B_3O_3$ (plus H_2) to O_2 or CO at a predetermined pressure in the infrared cell or by the reverse process in which the boroxine was added to the cell first. In the latter case O_2 or CO was added to the cell from a small side arm joined to the cell with a stopcock. The gas pressure in the side arm was high enough to produce a flow of gas into the cell when the stopcock was opened. The pressure of gas introduced into the cell was calculated from the initial and final pressures in the side arm and the volume ratio of side arm to cell. After the reagents were mixed, the progress of the reaction was followed by monitoring the decrease in absorbance of the 918-cm^{-1} band in $H_3B_3O_3$ and the increase in absorbance of bonds characteristic of the products. For $H_2B_2O_3$ and BH_3CO absorbance, measurements were taken with the bands at 885 and 2170 cm^{-1}, respectively. Absorbance measurements were made with a Perkin-Elmer Model 337 grating Infracord. For some experiments the infrared cell was conditioned by deposition of a coating of B_2O_3 on the inner walls. The coating which extended over the Pyrex surface and cell windows was identified from its infrared spectrum. To prepare the cell a mixture of $B_5H_9 + O_2$ from the reaction bulb was first expanded into the cell. The mixture in the bulb was then exploded by the usual procedure. This caused the contents of the infrared cell to flash leaving a B_2O_3 coating. Boric oxide does not absorb strongly at 918 cm^{-1} so the coating did not interfere with the absorbance measurement for $H_3B_3O_3(g)$. Other experiments were conducted with the same cell which had not been preconditioned with a B_2O_3 coating. For these experiments the cell had been treated by washing with methanol and water.

Results

$H_3B_3O_3$–O_2 Reaction.—Since the explosive reaction between B_5H_9 and O_2 gives only a small yield of $H_3B_3O_3$, the initial concentrations of $H_3B_3O_3$ could not be adjusted arbitrarily in these experiments. Therefore, a

---

[1] Work supported by the Army Research Office (Durham) and the Advanced Research Projects Agency.

[2] (a) S. K. Wason and R. F. Porter, *J. Phys. Chem.*, **69**, 2208 (1965); (b) R. F. Porter and S. K. Wason, *ibid.*, **69**, 2461 (1965).

[3] S. K. Wason and R. F. Porter, *Inorg. Chem.*, **5**, 161 (1966).

[4] G. H. Lee, II, W. H. Bauer, and S. E. Wiberley, *J. Phys. Chem.*, **67**, 1742 (1963).

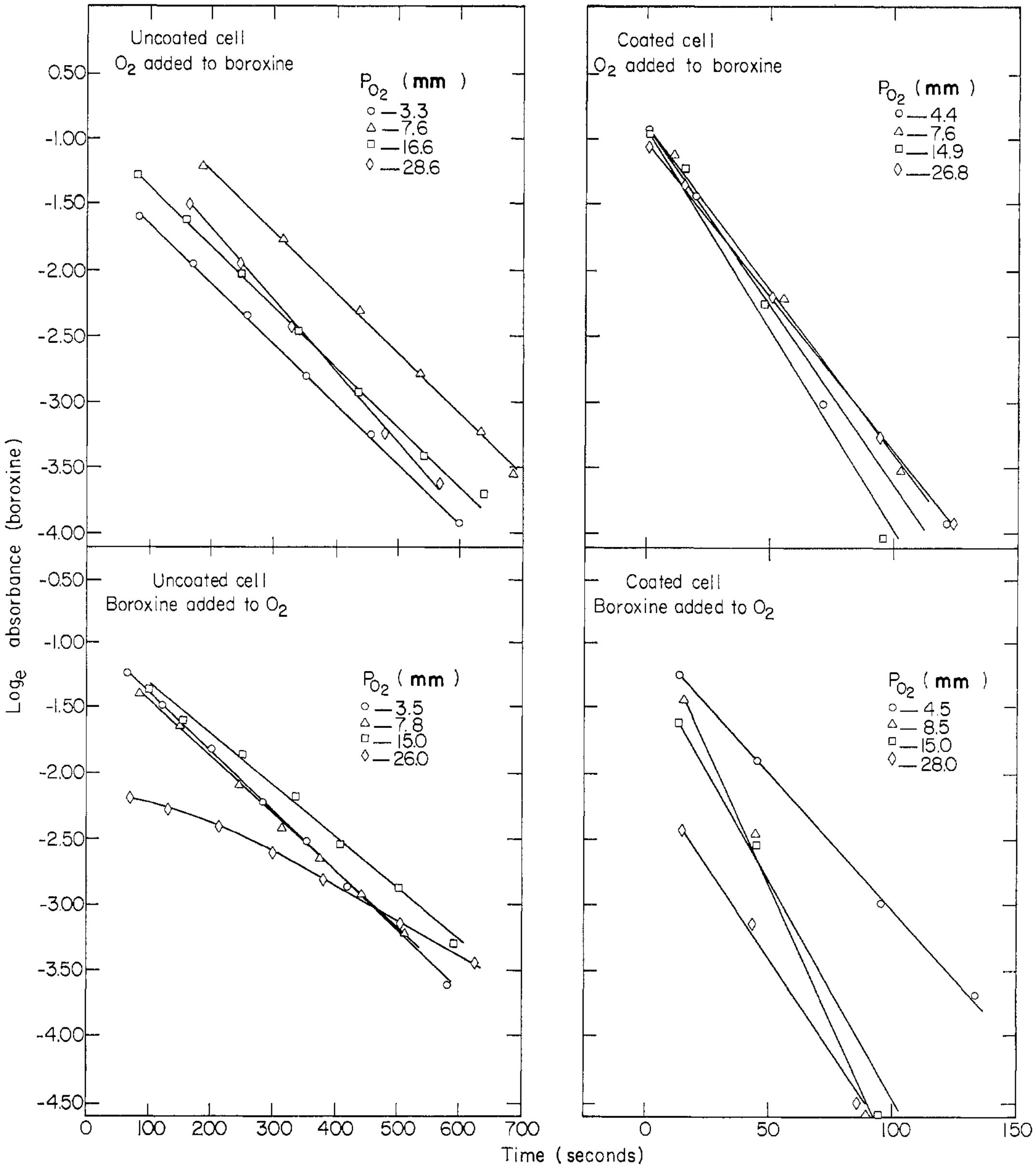

Figure 1.—Graphical determination of rate constants for the reaction of $H_3B_3O_3$ with O_2.

series of kinetic measurements for the $H_3B_3O_3$–O_2 reaction was obtained by noting the rate of disappearance of $H_3B_3O_3(g)$ as the concentration of O_2 was altered. In most cases the pressure of O_2 was in excess of that required by the stoichiometry

$$H_3B_3O_3(g) + {}^1/_2O_2(g) = H_2B_2O_3(g) + {}^1/_3B_2O_3(s) + {}^1/_6B_2H_6(g) \quad (2)$$

The pressure range of O_2 was between about 2 and 30 mm. Plots of the logarithmic dependence of boroxine absorbance *vs.* time for a series of runs are illustrated in Figure 1. The slopes of these curves indicate a pressure dependence on $H_3B_3O_3$ very close to first order. In most cases a rapid drop in $H_3B_3O_3$ pressure was noted when oxygen from the side arm was first added to the cell. This probably resulted from back diffusion of $H_3B_3O_3$ into the side arm. It was noted when boroxine from the reaction vessel was added to the cell containing oxygen, the amount of boroxine entering the cell was limited by the pressure of oxygen. This is expected since the rate of diffusion of $H_3B_3O_3$ should be low when its backing pressure is comparable to the pressure of O_2 in the cell. For these reasons, data recorded for the first few seconds after the gases were mixed were not considered reliable and were not included in quantitative calculations.

First-order rate constants, k_1, defined by the relationship

$$-\frac{\partial \ln P_{H_3B_3O_3}}{\partial t} = -\frac{\partial \ln A_{H_3B_3O_3}}{\partial t} = k_1 \quad (3)$$

were evaluated from the data indicated in Figure 1. In this relationship it is assumed that Beer's law may be applied to $H_3B_3O_3$ at low pressures. Results in terms of the half-life, $t_{1/2} = 1/k_1 \ln 2$, from several experiments with B_2O_3-coated and uncoated Pyrex cells are summarized in Table I. From the data two effects are apparent. The first is the marked increase in reaction rate in B_2O_3-coated cells over that observed in uncoated

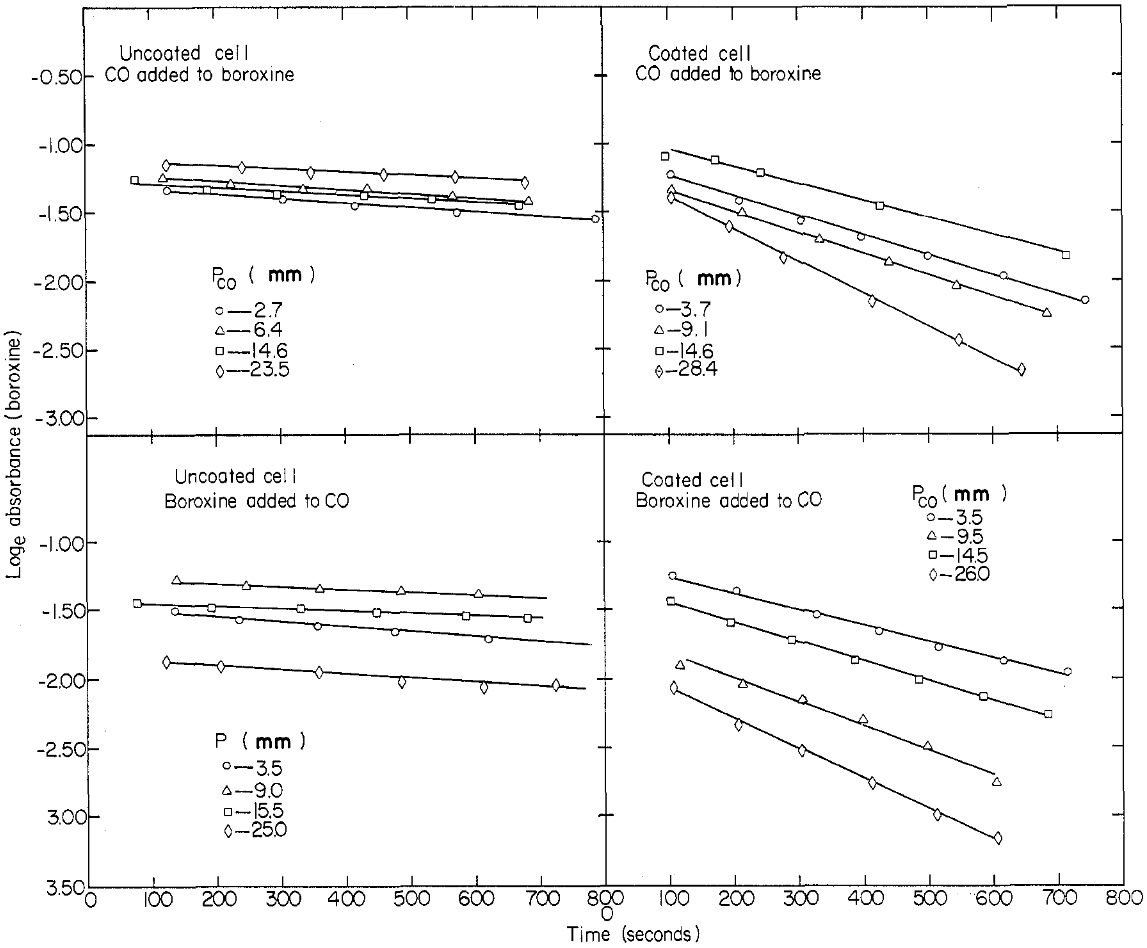

Figure 2.—Graphical determination of rate constants for the reaction of $H_3B_3O_3$ with CO.

TABLE I

KINETIC DATA FOR THE REACTION OF $H_3B_3O_3$(g) WITH OXYGEN (T = 23°)

Cell surface	Order of mixing reagents	Run sequence	Initial P_{O_2}, mm	$t_{1/2}$, sec
B_2O_3 coated	O_2 to $H_3B_3O_3$	1	4.4	27.5
		2	16.1	18.7
		3	7.6	27.5
		4	26.8	29.5
		5	14.9	21.1
Uncoated	O_2 to $H_3B_3O_3$	1	7.6	162.7
		2	3.3	162.3
		3	16.6	165.4
		4	28.6	144.1
B_2O_3 coated	$H_3B_3O_3$ to O_2	1	4.5	33.6
		2	15.0	17.9
		3	8.5	13.0
		4	28.0	25.0
Uncoated	$H_3B_3O_3$ to O_2	1	15.0	175.9
		2	7.8	159.7
		3	3.5	148.5

cells. The second is the insensitivity of reaction rate on the initial pressure of oxygen.

$H_3B_3O_3$–CO Reaction.—The reaction between gaseous boroxine and carbon monoxide was studied by the same procedure as that described for the reaction with oxygen. Series of kinetic measurements were made in ordinary Pyrex cells and in cells coated with B_2O_3(s). The partial pressure of CO was in excess of that required by the stoichiometry

$$H_3B_3O_3(g) + CO(g) = BH_3CO(g) + B_2O_3(s) \qquad (4)$$

The dependence of reaction rate on the initial pressure of CO is illustrated in Figure 2. Slopes of these ln A *vs.* time curves indicate the reaction is very close to first order with respect to $H_3B_3O_3$ pressure. Data taken within the first 50 sec after the stopcock joining the boroxine and CO sources was opened were discarded in order to allow for back diffusion and time for gas mixing. A summary of the kinetic results is given in Table II. These data show that the rate of disappearance of $H_3B_3O_3$ in the reaction with CO is nearly independent of initial CO pressure and is greater in cells coated with B_2O_3 than in uncoated cells. In these respects the reaction of $H_3B_3O_3$ with CO is similar to the reaction with O_2 except the reaction with CO is slower under the same conditions of pressure and surface treatment.

Diborane was always observed as a product in these experiments. It was essential therefore to determine how rapidly $H_3B_3O_3$ decomposes in the absence of another reactant. Absorbance measurements indicated that the time required for decomposition of half of a sample of $H_3B_3O_3$ was about 60 min in uncoated cells and about 17 min in coated cells used for the same experiments with CO and O_2.

The stoichiometry for reaction 2 requires that

$$A_{H_3B_3O_3} = A^0_{H_3B_3O_3} - C_1A_{H_2B_2O_3} \qquad (5)$$

and that

$$\frac{\partial \ln A_{H_3B_3O_3}}{\partial t} = \frac{\partial \ln (A^0_{H_2B_2O_3} - A_{H_2B_2O_3})}{\partial t} \qquad (6)$$

where $A^0_{H_3B_3O_3}$ and $A^0_{H_2B_2O_3}$ are initial and final absorbances for $H_3B_3O_3$ and $H_2B_2O_3$, respectively, and C_1 is a constant. Similarly for reaction 4 we may write

$$A_{H_3B_3O_3} = A^0_{H_3B_3O_3} - C_2A_{BH_3CO} \qquad (7)$$

and

$$\frac{\partial \ln A_{H_3B_3O_3}}{\partial t} = \frac{\partial \ln (A^0_{BH_3CO} - A_{BH_3CO})}{\partial t} \qquad (8)$$

where $A^0_{BH_3CO}$ is the final absorbance for BH_3CO and C_2 is a constant. Checks on the rates of disappearance of $H_3B_3O_3$ were made from initial rates based on the appearance of products. Values for $A^0_{H_2B_2O_3}$ and $A^0_{BH_3CO}$ first determined graphically by extrapolation of absorbance data (Figure 3) were, in turn, obtained at 50-sec time intervals by interpolation of absorbance–time curves. Rate data were obtained by plotting ln $(A^0 - A)$ *vs.* time as in Figure 4. The rate constants for the respective reactions were then compared with the rate constants obtained previously. This comparison may be seen in Table III.

Table II

Kinetic Data for the Reaction of $H_3B_3O_3$(g) with Carbon Monoxide (T = 23°)

Cell surface	Order of mixing reagents	Run sequence	Initial P_{CO}, mm	$t_{1/2}$, min
B_2O_3 coated	CO to $H_3B_3O_2$	1	14.6	9.5
		2	28.4	5.0
		3	9.1	7.3
		4	3.7	8.2
Uncoated	CO to $H_3B_3O_3$	1	2.7	35.6
		2	6.1	39.7
		3	14.6	39.4
		4	23.5	52.5
B_2O_3 coated	$H_3B_3O_3$ to CO	1	3.5	9.8
		2	9.5	6.9
		3	14.5	7.9
		4	26.0	5.3
Uncoated	$H_3B_3O_3$ to CO	1	3.5	30.3
		2	9.0	46.8
		3	15.5	58.6
		4	25.0	36.4

Table III

Comparison of Rate Data Obtained by Two Procedures

Reaction	Cell conditions	Initial P_{O_2}, mm	Initial P_{CO}, mm	Disappearance of $H_3B_3O_3$, $t_{1/2}$, sec	Appearance of product, $t_{1/2}$, sec
$H_3B_3O_3$–O_2	Uncoated	15.0	. . .	176	173[a]
		7.8	. . .	160	152[a]
$H_3B_3O_3$–CO	B_2O_3 coated	. . .	3.5	589	573[b] (459)[a]
		. . .	28.4	300	283[b] (238)[a]

[a] Based on evaluation of A^0_{product} from least-squares slope of absorbance curves (Figure 3). [b] Based on evaluation of $A^0_{BH_3CO}$ from limiting slopes of absorbance curves (Figure 3).

Discussion

The catalytic nature of the B_2O_3 surface in the reactions of $H_3B_3O_3$ with O_2 and CO in coated cells is evident from the kinetic data in Tables I and II. From the initial pressures of B_5H_9 and O_2 the quantity of B_2O_3 deposited on the cell walls was calculated to be between 3×10^{-5} and 6×10^{-5} mole, assuming a minimum of 1 and a maximum of 2 moles of B_2O_3 are produced for every mole of B_5H_9 in the explosive reaction. The coating covered a surface with an area, calculated from the cell dimensions, of 134.1 cm². Since B_2O_3 is produced in these reactions with $H_3B_3O_3$, firm conclusions regarding the nature of the catalytic surface in runs with "uncoated" cells cannot be drawn. However, the near independence of reaction rate on initial pressure of O_2 or CO indicates that the reactions are occurring by a heterogeneous path, regardless of the nature of the active surface site. The order of mixing reagents does not alter the rates significantly so it is unlikely that the

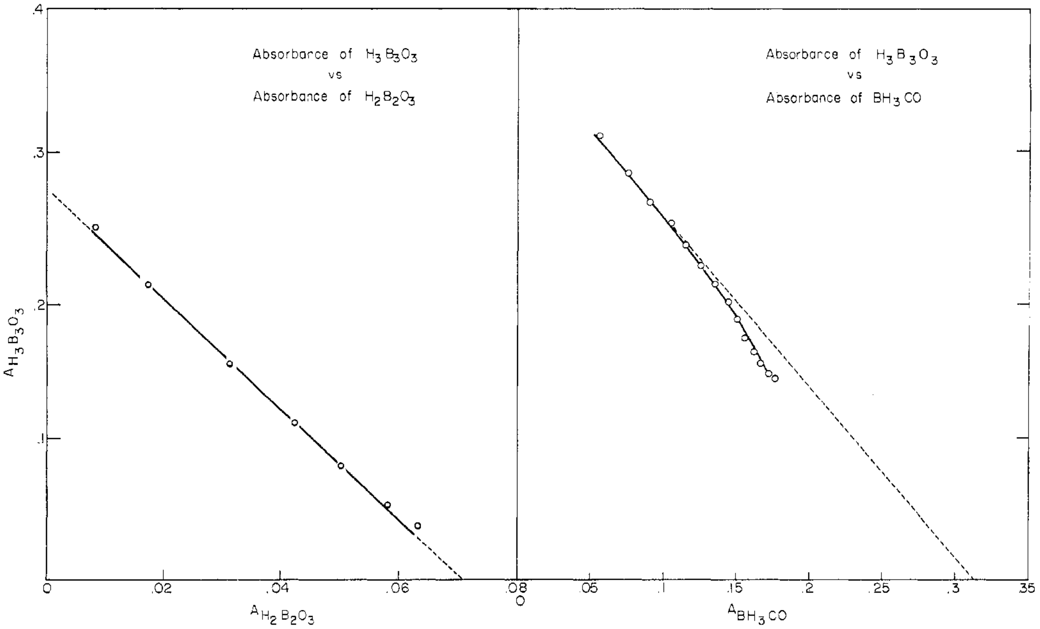

Figure 3.—(a) Plot used for evaluation of $A^0_{H_2B_2O_3}$. (b) Plot used for evaluation of $A^0_{BH_3CO}$.

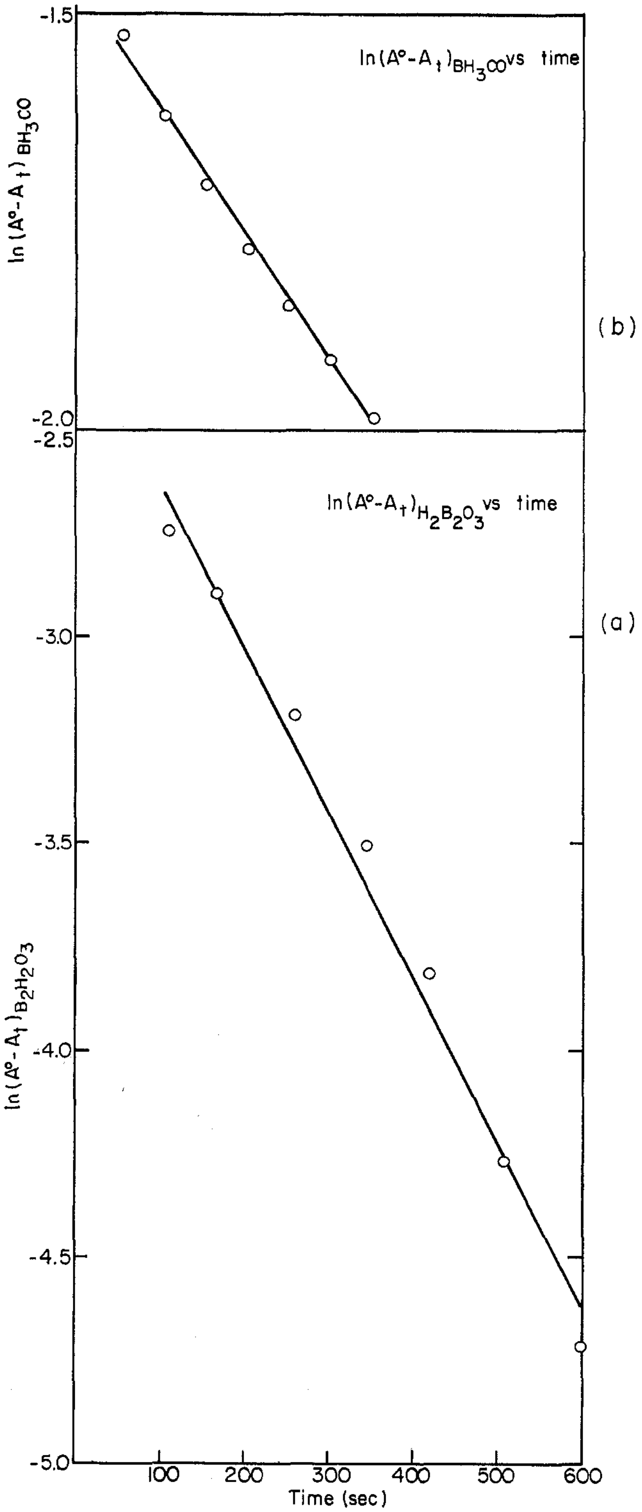

Figure 4.—(a) Graphical determination of rate constant for the $H_3B_3O_3$–O_2 reaction based on appearance of $H_2B_2O_3$. (b) Graphical determination of rate constant for the $H_3B_3O_3$–CO reaction based on appearance of BH_3CO.

effects are due to nonhomogeneous mixing. Conditions with regard to the coated cells are better defined since we know the gross composition of the surface. For both reactions the rates in coated cells are increased by a factor of 5 to 6 over those observed in uncoated cells for the same initial pressures of reactants. It seems reasonable to suspect that the active sites are present in the surface structure of the B_2O_3 coating.

On the basis of the foregoing observations, the following mechanism for the $H_3B_3O_3 + O_2$ reaction in B_2O_3-coated vessels is proposed

$$H_3B_3O_3(g) + O_2(B_2O_3\ \text{surface}) \xrightarrow{\text{slow}} H_2B_2O_3(g) + HBO_2(\text{ads.})$$

$$2HBO_2(\text{ads.}) \xrightarrow{\text{fast}} O_2(g) + 2HBO(\text{ads.})$$

$$3HBO(\text{ads.}) \begin{array}{l} \nearrow^{\text{fast}}\ {}^1/_2B_2H_6(g) + B_2O_3(s) \\ \searrow_{\text{fast}}\ H_3B_3O_3(g) \end{array}$$

Earlier work has shown[5] that when $H_3B_3O_3$ reacts with ${}^{18}O_2$, the product is mostly $H_2B_2{}^{16}O^{18}O_2$, indicating that the reactant O_2 molecule is retained in the product. This is consistent with the first step of the proposed mechanism. Subsequent steps in the reaction are postulated to account for the formation of B_2H_6 and $B_2O_3(s)$. To lead to these products H–BO_2 or other intermediates would require a structure that retained an H–B bond. In a separate experiment a sample of $H_3B_3O_3$ containing 91% ${}^{18}O$ was allowed to react with ordinary oxygen. Mass spectral analysis of oxygen in the product gases indicated an enrichment in ${}^{18}O_2$. This qualitative result lends support to the inference that oxygen is regenerated in some stage of the reaction. No infrared spectral evidence could be found for the formation of solid HOBO (metaboric acid) as a stable product. Some variation in rate constants or half-life with change of initial O_2 pressure is expected if the mechanism of oxidation involves competitive absorption of the reactants. In this type of mechanism the rate should not show a strict zero order dependence on oxygen. The rate data (Table I) suggest that this may be the case since the rate appears to have a maximum when the O_2 pressure is between the limits indicated.

For the reaction of $H_3B_3O_3(g)$ and CO we propose the rate-determining step

$$[H_3B_3O_3(g) + CO(B_2O_3\ \text{surface}) \longrightarrow BH_3CO(g) + B_2O_3(s)$$

The rate is not strictly zero order in CO pressure. The data in Table II indicate a rough trend toward a lower half-life as the initial CO pressure is increased. This suggests that the mechanism may depend on competitive adsorption of the reactants. Half-life data from measurements of the rate of disappearance of $H_3B_3O_3$ were in agreement with values obtained from measurements of the rate of appearance of $BH_3CO(g)$ only when the value of $A^0{}_{BH_3CO}$ was obtained from the initial slope of the absorbance curves (Figure 3). The discrepancy encountered in using $A^0{}_{BH_3CO}$ values obtained by least-square fitting of the data may be attributed to the thermal decomposition of BH_3CO subsequent to its formation in reaction 4. It should be noted that BH_3CO produced in these experiments by the homogeneous reaction between B_2H_6 and CO can be neglected[6] in the evaluation of rate data since this reaction at low pressures is much slower than the heterogeneous reaction between $H_3B_3O_3(g)$ and CO.

[5] L. Barton, S. K. Wason, and R. F. Porter, *J. Phys. Chem.*, **69**, 3160 (1965).

[6] A. B. Burg, *J. Am. Chem. Soc.*, **74**, 3482 (1952).