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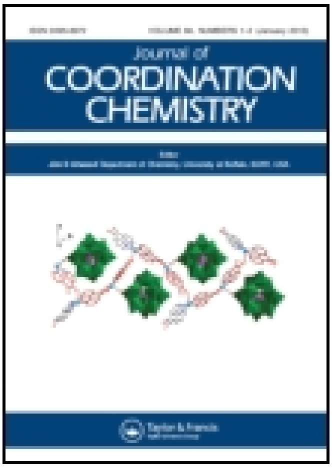

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Study of the reaction between boron trifluoride methanol complex and sodium methoxide

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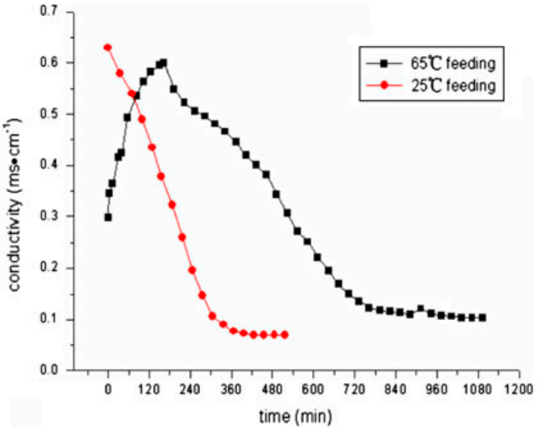

Boron trifluoride methanol complex was added to sodium methoxide at 65 and 25 °C, and the reaction time was 18 and 6 h, respectively. This figure indicates that the feeding stage is the controlling step of the whole reaction.

The reaction between boron trifluoride methanol complex and sodium methoxide in methanol solution was investigated using conductivity as the reaction indicator. The reaction conditions were examined and a mechanism of this reaction was proposed. Moreover, proper reaction conditions were proposed for boric acid preparation using this reaction.

Keywords: Boron trifluoride methanol complex; Sodium methoxide; Mechanism; Boric acid

1. Introduction

Our laboratory has engaged in the separation of boron isotopes and preparation of enriched boron compounds for years. Our basic idea is to produce enriched B-10 boron trifluoride-anisole or enriched B-10 boron trifluoride gas first, and then produce other boron-10

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*Corresponding author. Emails: xujiaohh@163.com, wjzh@tju.edu.cn enriched boron compounds such as enriched B-10 boric acid. For enriched B-10 boric acid production, some methods are plausible. The first method is that BF_3 complex, such as boron trifluoride ether complex, reacts with calcium carbonate or lithium carbonate in water to produce boric acid [1, 2]. The second method is that diethyl ether complex reacts with calcium chloride in methanol; after the produced hydrogen chloride is neutralized, the produced methyl borate is hydrolyzed to boric acid [3]. The last one is that diethyl ether complex reacts with sodium methoxide to produce methyl borate first, and then methyl borate is hydrolyzed to boric acid [4, 5].

The last method interests us. The reaction between sodium methoxide and BF_3 had been investigated as early as 1894 by Lappert [6]. He claimed to have prepared methyl fluoroesters BF_2OCH_3, and $BF(OCH_3)_2$ by the interaction of boron trifluoride and sodium methoxide as follows:

$$BF_3 + NaOCH_3 \longrightarrow BF_2OCH_3 + NaF$$

$$BF_3 + 2NaOCH_3 \longrightarrow BF(OCH_3)_2 + 2NaF$$

However, Meerwein and Pannwitz [7] claimed to obtain the coordination compound, BF_3NaOCH_3, and other researchers [4, 5, 10] obtained methyl borate from this reaction. Not only the discordance of different authors about this reaction, but also the capability of producing methyl borate and further producing boric acid interests us. This article is aimed to clarify the knowledge about this reaction and to find proper conditions to produce boric acid using this reaction. The following details our research about the reaction between BF_3–methanol complex with sodium methoxide in methanol solution.

2. Experimental

2.1. *Reagents and apparatus*

Anhydrous methanol, sodium methoxide methanol solution (30%), anhydrous calcium chloride, and dihydrate calcium chloride are of analytical purity, purchased from Guangfu Fine Chemicals Co. Boron trifluoride gas is purchased from Liufang Gas Co. and the purity is 99.5%. Boron trifluoride complexes and the enriched boron-10 BF_3 complex were obtained in our laboratory. A DDS-11A conductivity meter was used to detect the reaction system's conductivity.

2.2. *Preparation of BF_3–CH_3OH complex*

The complex solution was produced in a jacket packing tower as shown in figure 1. The boron trifluoride entered from the middle of the tower and met the methanol pumping from the methanol tank. Natural abundance BF_3 complex or enriched boron-10 BF_3 complex can be obtained depending on the BF_3 source. The BF_3 mass concentration of the produced solution is within the range of 0.300–0.680.

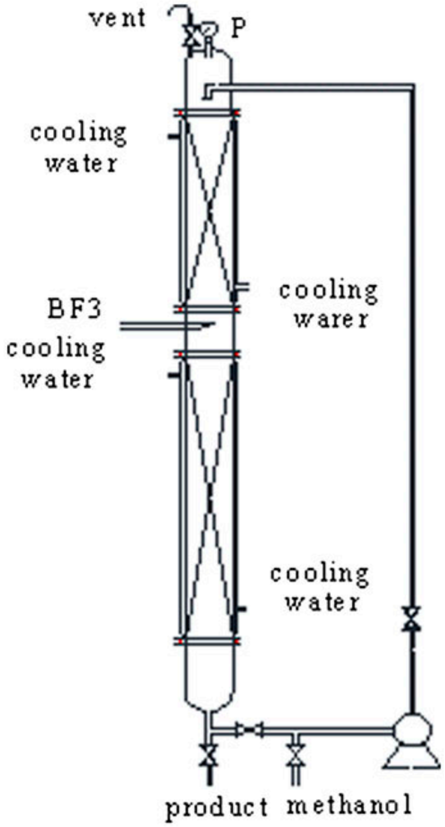

Figure 1. Apparatus for the preparation of BF_3–CH_3OH complex.

2.3. *Reaction between BF_3–CH_3OH and sodium methoxide*

The complex (80.10 g, 0.314MBF_3) was added dropwise to a stirring solution of sodium methoxide methanol (169.79 g, 30%, 0.932M$NaOCH_3$) in a water bath. After addition, the temperature of water bath was set and a conductivity electrode was placed in the flask. The conductivity was recorded every 30 min and about 5 g of mixture was extracted using 10 mL syringe every 40 min. The mixture was weighed and centrifuged; the solid was dried and weighted. Then the solid content of the reaction mixture was calculated.

When the reaction was stopped, the mixture was centrifuged, the wet solid was dried in an oven and the liquid was distilled. Due to the formation of an azeotrope between methyl borate and methanol at 54.6 °C, the distillate of 50–64 °C was collected.

2.4. *Determination of the concentration of sodium methoxide solution*

The concentration of sodium methoxide methanol solution was determined according to HG/T 2561-1994.

2.5. *Determination of BF_3 concentration of the complex*

About 1–2 g (accurate to 0.0001 g) of BF_3 complex was extracted using 5 mL syringe and injected to about 20 g $CaCl_2$ solution (20 wt%) which was neutralized to methyl orange endpoint by HCl solution (0.1 M). Then the mixture was titrated to the methyl orange endpoint using standard sodium hydroxide (0.5 M) and boiled for 30 min till the methyl orange no longer turned red. At last, the mixture was cooled to room temperature; 5–6 g of mannital added and titrated to the phenolphthalein endpoint using standard sodium hydroxide (0.5 M), and this volume of sodium hydroxide was used to calculate BF_3 concentration.

2.6. *Determination of methyl borate and boric acid*

The distillate of 50–64 °C was detected using GC, Agilent, db-1701p column. The methyl borate content was determined by external standard method. The distillate was always directly hydrolyzed and the produced boric acid was used to calculate the methyl borate content of the mixture. The boric acid was determined by IR (TENSOR 27). The purity of the boric acid was determined by acid–base titration using standard sodium hydroxide (0.2 N) after the addition of mannital.

2.7. *Determination of the side product*

The side products were determined by energy dispersive X-ray spectroscopy (EDS), 15 keV. The purity of sodium fluoride was determined according to GB/T 1264-1997.

3. Results and discussion

3.1. *Synthesis*

Most authors used BF_3–ether complex as a reactant, but we used BF_3–CH_3OH complex as a reactant. The advantage is that there is no need to isolate methanol when it reacts with sodium methoxide in methanol solution. The BF_3–CH_3OH or enriched boron-10 BF_3–methanol complex was prepared first as shown in figure 1. It was used without further purification.

If boric acid is the target product, reaction (2a) is needed. The first reaction (1a) is to produce methyl borate. The second (2a) is the hydrolyzation of methyl borate to boric acid.

$$BF_3 + CH_3ONa \xrightarrow{CH_3OH} B(OCH_3)_3 + NaF \downarrow \tag{1a}$$

$$B(OCH_3)_3 + 3H_2O \longrightarrow H_3BO_3 + 3CH_3OH \tag{2a}$$

In order to produce boric acid, reaction (1a) should be studied and the following sections focus on reaction (1a).

3.2. *Study of the reaction conditions*

Bowlus [8] claimed that the BF_3–CH_3OH system is featured by high conductivity. Nieuwland *et al.* [9] showed that the conductivity of the system BF_3–CH_3OH is of the same order as that of the system H_2SO_4–SO_3. O'Leary and Wenzke [10] had measured the mole conductivity of the BF_3–CH_3OH system. While the other reactants, reagent methanol, and sodium methoxide, or the product methyl borate have low conductivity compared with the BF_3–CH_3OH solution, it is feasible to choose conductivity as the reaction indicator. The reaction is deemed completed if the system conductivity does not change or changes as slowly as possible. At the same time, the solid content was detected as described in Section 2.3.

3.2.1. Reactant ratio. Lappert [6] reviewed Gasselin's results that, if the mole ratio of BF_3 and $NaOCH_3$ is 1 : 1 or 1 : 2, the main product is the methyl fluoro-esters, BF_2OCH_3, and $BF(OCH_3)_2$, as mentioned in the Introduction. But this result was not confirmed at that time. Our experiment obtained methyl borate from the reaction between BF_3–methanol and sodium methoxide methanol solution. Especially, when the ratio was 1 : 3, the yield of methyl borate was the highest; when the ratio was greater than 1 : 3, the yield dropped sharply; and when the ratio was about 1 : 4, methyl borate was hardly obtained.

When the ratio is less than 1 : 3, sodium methoxide is insufficient to remove the three fluorine of BF_3, which leads to a low conversion of BF_3. When the ratio is greater than 1 : 3 such as 1 : 4, the produced methyl borate will be further consumed by excess sodium methoxide, which leads to low yield of methyl borate. The latter observation was proved indirectly by a patent [11] which reported that methyl borate reacts with sodium methoxide to form $NaB(OCH_3)_4$. The following is the supposed mechanism of the 1 : 4 reaction. Reaction (1b) is endothermic and slow; reaction (2b) is exothermic and rapid; and reaction (3b) is the overall equation. Reaction (2b) was repeated by the addition of methyl borate to sodium methoxide methanol solution; the produced solid is almost equal to the theoretical yield of $NaB(OCH_3)_4$ and the EDS denotes the mole ratio of Na/O is close to 1 : 4. In a patent [11], reaction (2b) was used to isolate methyl borate from its methanol azeotrope and to produce high purity methyl borate by decomposing $NaB(OCH_3)_4$.

$$3NaOCH_3 + BF_3 \xrightarrow{CH_3OH} B(OCH_3)_3 + 3NaF\downarrow \tag{1b}$$

$$NaOCH_3 + B(OCH_3)_3 \xrightarrow{CH_3OH} Na[B(OCH_3)_4] \tag{2b}$$

$$4CH_3ONa + BF_3 \longrightarrow Na[B(OCH_3)_4] + 3NaF\downarrow \tag{3b}$$

3.2.2. Feed mode. O'Leary and Wenzke [10] obtained sodium fluoroborate if sodium methoxide methanol solution was added to boron trifluoride methanol complex. They believed that reaction (3c) occurred. We had a similar result, but CH_3OBF_2 cannot be obtained by distillation, while a small amount of methyl borate was obtained. Hence, if

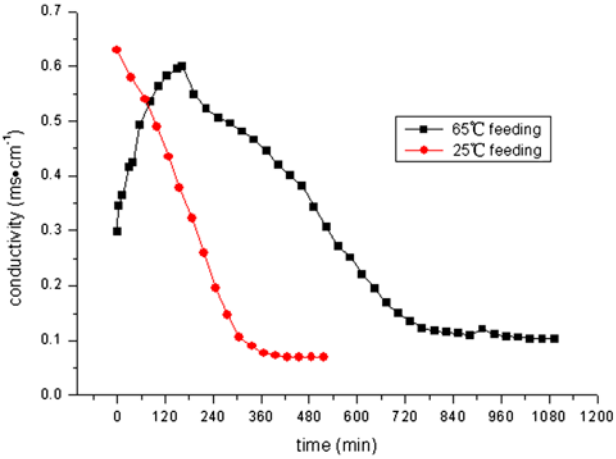

Figure 2. Effect of the different feeding temperatures.

methyl borate is needed, BF_3–methanol should be added to the sodium methoxide methanol solution to avoid the formation of $NaBF_4$.

$$2(CH_3OBF_3)^-H^+ + CH_3ONa \longrightarrow NaBF_4 + CH_3OBF_2 + 2CH_3OH \qquad (3c)$$

When BF_3–methanol solution is dropped to sodium methoxide methanol solution, heat will be liberated. If the adding rate is fast, the temperature will rise quickly. So the effect of the feeding temperature to the reaction was investigated. The experiments were conducted under the same reaction conditions (mole ratio 1 : 3, water bath 65 °C), except changing the feeding temperature. Our results showed that the difference between 12 and 25 °C feeding temperature is little. However, the difference between 25 and 65 °C is great as shown in figure 2.

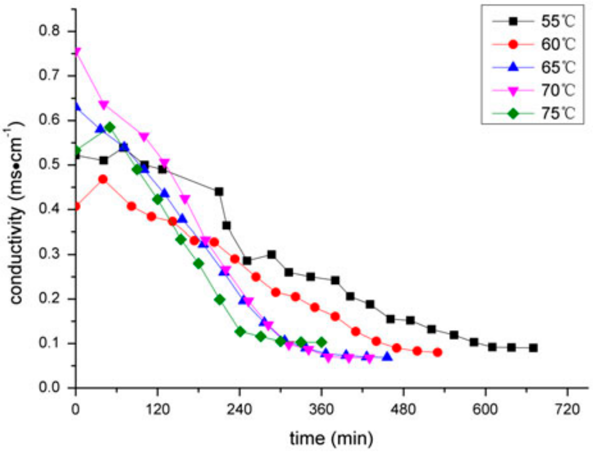

Figure 3. Effect of the different reaction temperatures.

The curves of figure 2 are the conductivity *versus* reaction time at 25 and 65 °C feeding temperatures, respectively. If the complex is fed at 25 °C, the whole reaction time is about 6 h, whereas, if the feeding temperature rises to 65 °C, the whole reaction time will be prolonged to 18 h. There is no rising stage in the 25 °C feeding curve, which could be attributed to too large detection intervals to record it. The reason of the rising stage will be explained later.

3.2.3. Temperature and reaction time. Changmei [3] selected reaction temperature within 55–60 °C. Other researchers [4] chose reflux temperature. Considering the boiling point 54.6 °C of the azeotrope of methanol and methyl borate, the reaction of 1 : 3 ratio from 55 to 75 °C water bath was investigated.

The conductivity was recorded from 55 to 75 °C in a water bath with a 5 °C rise of temperature as shown in figure 3. Table 1 is the analysis of the curves of figure 3. Figure 3 shows that the conductivity of the system decreases and approaches a constant value eventually, but the dropping rate of conductivity at different temperatures is different. Table 1 shows that 60 °C is the dividing point; under 60 °C the conductivity decreases slowly compared with that of above 60 °C. However, the difference of 65–75 and 55–60 °C is not significant.

The solid content of this reaction mixture was detected and calculated in figure 4. The solid content rises sharply to a constant value in about 40 min, and is constant the remaining time. The highest point in the conductivity figure almost coincides with the solid content figure at 40 min.

Table 1. Analysis of figure 3.

Water bath (°C)	55	60	65	70	75
Reaction time (h)	10	8	6–7	6	5–6
Slope (ms cm^{-1} min^{-1})	−0.00063 ~ −0.00089	−0.00087 ~ −0.00092	−0.0021	−0.0022	−0.0024

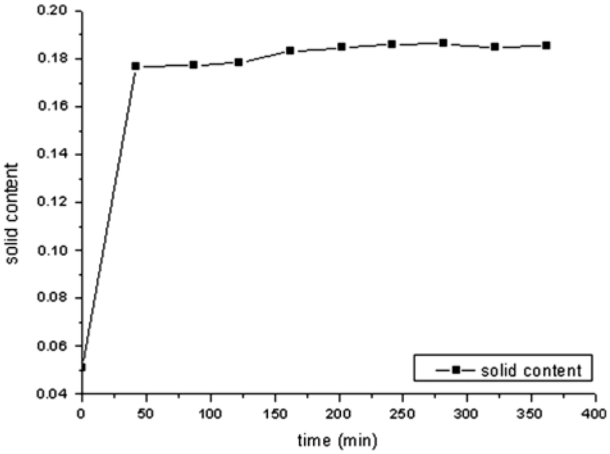

Figure 4. Solid content with time.

3.3. *Analysis*

The IR spectrum of boric acid is shown in figure 5. The strong bands can be assigned as follows: 3206 and 1194 cm^{-1} are ν O–H and δ O–H, respectively; 1458 and 546 cm^{-1} are ν BO and δ B–O, respectively. The purity of boric acid is 99.5%.

The elements of the side product are shown in figure 6. The calculated mass content of F in sodium fluoride is 45.25% and Na is 54.75%; the found result of EDS is F 47 ± 1, Na 53 ± 1%; so the side product is mainly NaF. The impurity may be methanol and boride such as $NaBF_4$. The purity of the side product is about 96%.

3.4. *Mechanism hypotheses*

3.4.1. BF_3–CH_3OH system. Before studying the reaction between BF_3–CH_3OH with Na-OCH_3, one must be aware of BF_3 and its numerous complexes. Boron trifluoride is a strong Lewis acid. It is a typical electron-deficient compound and is easy to form coordination compounds with electron-rich atoms or molecules. Seven elements (N, O, F, H; P, S, and Cl) have been shown with certainty to be capable of coordinating to boron trifluoride [12],

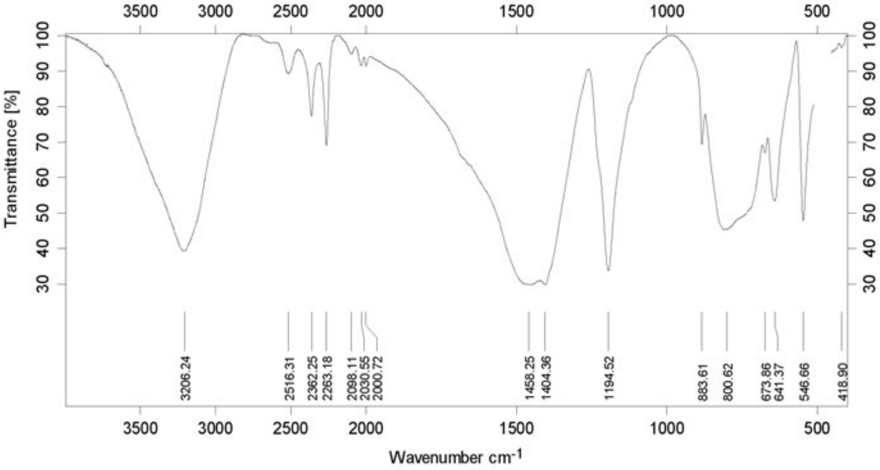

Figure 5. IR spectrum of boric acid.

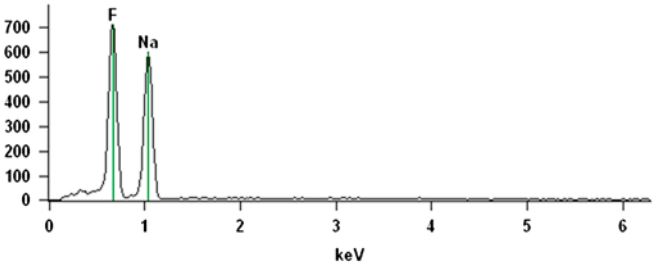

Figure 6. EDS spectrum of side product.

while the stabilities of complexes with BF_3 are different. For example, if oxygen is the donor, the stabilities decrease in the order ethers > alcohols > carbonyl compounds [12]. Many reactions can be attributed to its electrophilicity and the exchange of ligands with different stability.

Boron trifluoride can form 1 : 1 or 1 : 2 molecular adducts with methanol. Some researchers [13, 14] studied the BF_3–CH_3OH system or the complexes $BF_3 \cdot CH_3OH$ and $BF_3 \cdot 2CH_3OH$. They proved that the acidity and high conductivity of this system are due to the formation of some ionic species. Jean Derouault [13] claimed that there exist BF_4^- and $CH_3OH_2^+$ in both $BF_3 \cdot CH_3OH$ and $BF_3 \cdot 2CH_3OH$. Servis [14] reported that at methanol to boron trifluoride ratios of greater than 2 : 1, formation of the conjugate base of the 1 : 1 adduct, $CH_3OBF_3^-$, and the conjugate acid of methanol, $CH_3OH_2^+$, occurs. Our system is similar to the latter.

3.4.2. Feeding stage. With the addition of BF_3–CH_3OH, solid is gradually precipitated. Sodium methoxide is a strong base, so the acid–base reaction was proposed to be the first step as (1d), and it corresponds to the feeding stage. This step is exothermic, so high temperature will suppress it. Figure 2 indicates that this step is the rate controlling step. In other words, if this step is delayed, the whole reaction time will be prolonged. Analysis of the solid content indicates that BF_3 distributes mostly in liquid phase after addition.

$$\begin{aligned} &CH_3OBF_3^- + H^+HOCH_3 + CH_3O^-Na^+ \xrightarrow{CH_3OH} CH_3OBF_3Na(s) \\ &\downarrow + CH_3OBF_3^-Na^+(l) + 2CH_3OH \end{aligned} \tag{1d}$$

Some authors obtained coordination compounds as mentioned in the Introduction. This is true when sodium methoxide is mixed with solvent such as ethyl ether or anisole, it does not dissolve. For example, our experiment showed that the reaction between BF_3–anisole and sodium methoxide in anisole lead to no methyl borate liberated, while methyl borate was obtained when $BF_3 \cdot$anisole reacted with sodium methoxide methanol solution. So the solvent is important to this reaction. Methanol is not just a solvent but supplies CH_3O– group in this reaction.

3.4.3. Heating and keeping. After addition, heating began and 30–40 min was needed to achieve the set temperature. Recording for the figures started at this point. This period of time corresponds to the conductivity rising stage and solid content rising stage. We specify this stage as the reactions 2d–5d. The reactions 2d–4d mainly consumed the dissolved CH_3OBF_3Na and generated solid NaF, which caused the solid content to rise quickly. As for the rise of conductivity, there are two explanations. One is that dissolution of the solid CH_3OBF_3Na leads to the rise of the conductivity. Another is that the generated intermediate featured high conductivity leading to rise of conductivity. With regard to the F removing rate of 2d, 3d, and 4d, there is no direct evidence, but we are inclined to consider (2d) is faster than the others.

The conductivity began to decrease smoothly and the solid content kept constant in the remaining 5 h. This period still corresponds to reactions 2d–4d and a physical process 5d. The fact that the solid content is constant can be attributed to that solid dissolved (5d) and the solid consumed is equal to the solid generated. The decrease of conductivity still has two explanations. One is that the consumption of CH_3OBF_3Na is larger than the liberation of CH_3OBF_3Na from the solid, another is the consumption of the high conductivity intermediate which led to the decrease of the conductivity. The long time of this period is due to the rate decrease which resulted from the reduction of $NaOCH_3$ and CH_3OBF_3Na after consumption in the first 40 min.

$$\left[\begin{array}{ll} CH_3OBF_3^-Na^+(l) \xrightarrow{CH_3OH} CH_3OBF_2 + NaF\downarrow & (2d) \\ CH_3OBF_2 + CH_3O^-Na^+ \xrightarrow{CH_3OH} (CH_3O)_2BF + NaF\downarrow & (3d) \\ (CH_3O)_2BF + CH_3O^-Na^+ \xrightarrow{CH_3OH} (CH_3O)_3B + NaF\downarrow & (4d) \\ CH_3OBF_3Na(s) \xrightarrow{CH_3OH} CH_3OBF_3^-Na^+(l) & (5d) \end{array}\right.$$

If we suppose 5d is not affected by temperature, the fact that the reaction rate does not rise much with temperature rise indicates that reactions 2d–4d are not thermodynamically controlled but kinetically. In other words, this system is not sensitive to heating temperature above 60 °C.

Although, some researchers [15] claimed to have prepared BF_2OCH_3 and $BF(OCH_3)_2$, and studied the property of these two compounds, we cannot isolate these two intermediates. Maybe there is equilibrium between these two compounds and $B(OCH_3)_3$ as follows:

$$2BF(OCH_3)_2 \leftrightarrows BF_2OCH_3 + B(OCH_3)_3 \qquad (6d)$$

The production of BF_2OCH_3 (mp 41.2°, bp 85.2 °C) by passing BF_3 to $B(OCH_3)_3$ was repeated in our laboratory. This compound is solid in room temperature, but fumed if exposed in air. Purification through distillation was difficult. It dissolved in methanol, and methyl borate was obtained if distilled with methanol as described in (7d). So we think this compound cannot be separated when methanol is present.

$$3BF_2OCH_3 + 2CH_3OH \overset{heat}{\leftrightarrow} 2HBF_3CH_3OH + B(OCH_3)_3 \qquad (7d)$$

3.4.4. Side reactions. There are two competing reactions which lead to side products, and lead to completely different reaction products if conditions are changed. If BF_3–CH_3OH is overdosed, reaction (8d) will occur, which explains reaction (3c), and explains why the yield of methyl borate decreases sharply when the mole ratio is more than 1 : 3. If $NaOCH_3$ is overdosed, reaction (9d) will occur, which accounts for the 1 : 4 ratio results.

$$BF_3 \cdot CH_3OH + NaF \xrightarrow{CH_3OH} NaBF_4 + CH_3OH \qquad (8d)$$

$$NaOCH_3 + B(OCH_3)_3 \xrightarrow{CH_3OH} Na[B(OCH_3)_4] \qquad (9d)$$

4. Conclusion

The reaction conditions for the reaction between BF_3 and $NaOCH_3$ were investigated. When the mole ratio of BF_3 and sodium methoxide is 1 : 3 and water bath is 55 °C or above, the reaction between BF_3 and sodium methoxide will mainly produce methyl borate and sodium fluoride.

A mechanism of this reaction was proposed. The first step is an acid–base reaction and is the controlling step. The reaction is kinetically controlled, and it is not sensitive to temperature. Although the initial F removing is quick, the complete removal is time consuming.

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