

Epoxy Resin Cure III: Boron Trifluoride Catalysts

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Synopsis

Boron trifluoride forms complexes with nitrogen- and oxygen-containing Lewis bases. These acid-base complexes are sometimes added to epoxy resins to accelerate their cure at elevated temperatures (120°–160°C). Several possible processing concerns with the use of boron trifluoride complexes have been investigated. It was shown that each complex can be readily identified by its distinct fluorine-19 NMR spectrum. All of the boron trifluoride complexes are converted to fluoroboric acid under normal epoxy resin cure conditions. The fluoroboric acid is the true catalyst for epoxy resins. Experimental results show that fluoroboric acid does not catalyze the polymerization of an epoxy resin at room temperature. Finally, it was shown that fluoroboric acid is not hydrolyzed to hydrofluoric acid.

INTRODUCTION

Boron trifluoride monoethylamine ($\text{BF}_3\text{-MEA}$) is sometimes added to epoxy resins to help accelerate their cure at elevated temperatures. Previous workers had suggested that $\text{BF}_3\text{-MEA}$ was useful because it was a latent catalyst, that is, it was inactive at room temperature and required elevated temperatures (120°C or higher) to be activated.¹ If $\text{BF}_3\text{-MEA}$ can truly accelerate the cure rate of epoxies, it is important to determine the purity of commercial sources of $\text{BF}_3\text{-MEA}$ and the amount of $\text{BF}_3\text{-MEA}$ in commercial epoxy prepolymers. Fluorine-19 NMR is useful for such determinations. In fact, fluorine-19 NMR clearly demonstrates that different sources of $\text{BF}_3\text{-MEA}$ have different amounts of fluoroboric acid impurity.² The fluoroboric acid is produced by hydrolysis of $\text{BF}_3\text{-MEA}$.^{2,3} Thus, experiments were performed to determine the role of $\text{BF}_3\text{-MEA}$ in epoxy resin cure. The results indicate that $\text{BF}_3\text{-MEA}$ is not a true catalyst at all. At epoxy resin cure temperatures (120–160°C), it rapidly converts to fluoroboric acid, and it is the fluoroboric acid that catalyzes the epoxy cure.^{2,4} As a result, one might be tempted to conclude that the amount of fluoroboric acid impurity in $\text{BF}_3\text{-MEA}$ samples is not important because all the $\text{BF}_3\text{-MEA}$ will be hydrolyzed to fluoroboric acid anyway, once the epoxy resin is heated to cure temperature.

However, there are two possible concerns: The first is whether fluoroboric acid can catalyze the room-temperature cure of an epoxy resin. In other words, will the shelf life of an epoxy resin be shortened by the presence of fluoroboric acid? The second concern is that fluoroboric acid might be hydrolyzed to hydrofluoric acid (HF). The presence of HF could cause compatibility problems for industrial applications of epoxies.

The purpose of these investigations was to answer those questions and to determine if other boron trifluoride complexes functioned as catalysts.

First, it was important to know if they were present. Fluorine-19 NMR methods were developed to identify different boron trifluoride complexes. Second, it was important to know whether these complexes could also be hydrolyzed to form fluoroboric acid.

Data are presented in this report to indicate that

1. Fluoroboric acid does not catalyze the cure of an epoxy resin at room temperature.
2. Fluoroboric acid is not hydrolyzed to HF.
3. Other boron trifluoride complexes can be identified by fluorine-19 NMR.
4. The boron trifluoride complexes tested can also be hydrolyzed to fluoroboric acid.

EXPERIMENTAL

All fluorine-19 NMR and Fourier transform infrared (FTIR) spectra were recorded as previously described.^{2,4} The effect of fluoroboric acid on epoxy resin shelf life was determined by preparing a mixture of fluoroboric acid, tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM), and diaminodiphenylsulfone (DDS) (1:100:58.7) in acetone. A thin film of this solution was cast on a NaCl plate. The NaCl plate was put in a vacuum desiccator to remove the acetone. This NaCl plate was covered with another NaCl plate, and FTIR spectra were recorded. The NaCl plates were kept at room temperature, and FTIR spectra were recorded daily for the first week and then once a week for the next two months.

RESULTS

Effect of Fluoroboric Acid on Room-Temperature Shelf Life

FTIR was used to monitor the extent of cure of the TGDDM/DDS epoxy resin system. As previously described,⁴ if this epoxy system were to start polymerizing, there would be a decrease in the absorbance at 906 cm^{-1} because of the loss of epoxide, and an increase in the absorbances at 3507 , 3409 , and 1072 cm^{-1} caused by the respective formation of hydroxyl, secondary amine, and ether groups. However, no changes in any of these regions were seen when a mixture of fluoroboric acid, TGDDM, and DDS (1:100:48.7) was kept at room temperature for two months. Thus, it is concluded that fluoroboric acid cannot cause this epoxy system to cure at room temperature and will not affect its room-temperature shelf life.

Hydrolysis of Fluoroboric Acid

Samples of 0.5% and 10% fluoroboric acid in deuterated water were kept at room temperature for one year. The fluorine-19 NMR spectrum indicated that no HF had formed in either sample. The peak caused by HF appears 21.8 ppm downfield from the fluorine-19 NMR peak because of fluoroboric acid. Thus, HF would have been easily identified, had it been present. Next, a sample of 10% fluoroboric acid was kept at 90°C for 20 h, and again, no

HF was seen. All three samples of fluoroboric acid did show some HBF_3OH (which produces a peak 7.9 ppm downfield from fluoroboric acid).

Hydrolysis of BF_3 Complexes

Boron trifluoride readily complexes with nitrogen- and oxygen-containing Lewis bases.⁵ It is conceivable that many of these might be present in epoxy prepolymers. Fluorine-19 NMR spectra of six of these complexes have been measured. Epoxy prepolymers are usually quite soluble in acetone and/or dimethyl sulfoxide (DMSO). Thus, the spectra of the BF_3 complexes with methanol, tetrahydrofuran (THF), dimethyl ether, diethyl ether, piperidine, and monoethyl amine (MEA) were recorded in acetone and DMSO. The spectra of the two complexes with amines (i.e., BF_3 -piperidine and BF_3 -MEA) exhibited a quartet caused by ^{11}B - ^{19}F coupling (Fig. 1 and Ref. 2).

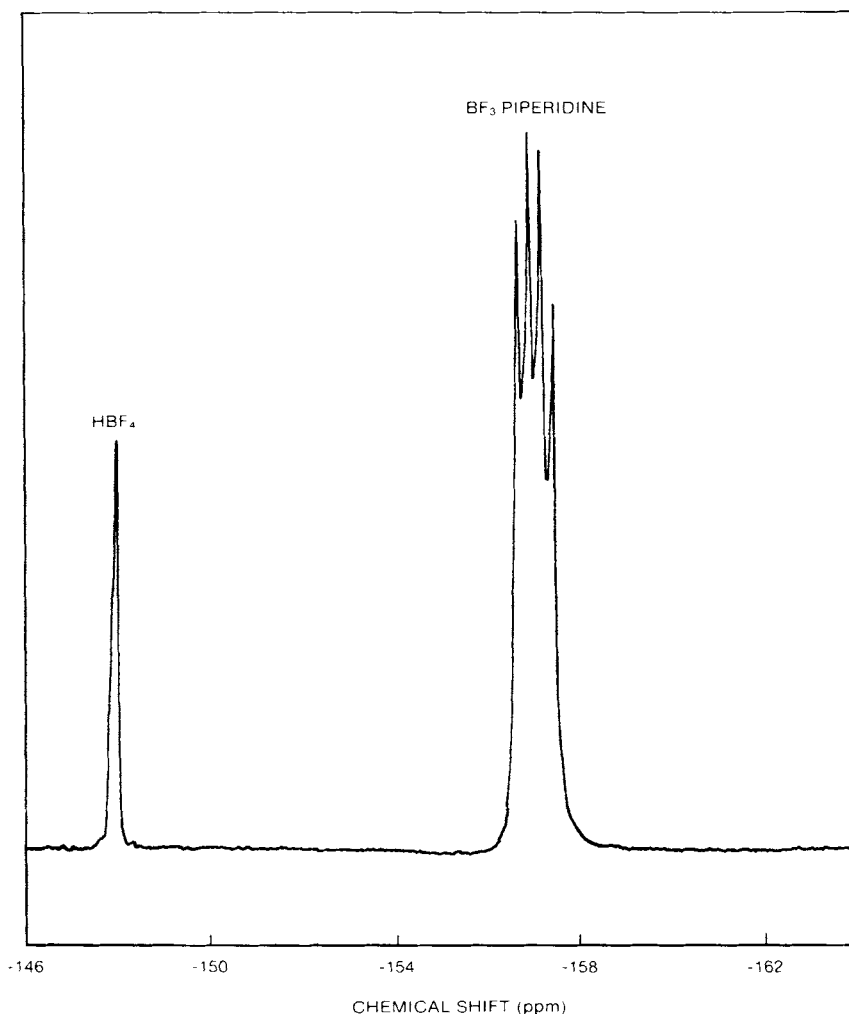


Fig. 1. Fluorine-19 NMR of BF_3 -piperidine in d_6 -acetone.

The spectra of the four complexes with oxygen-containing Lewis bases, however, exhibited one broad peak instead of a well-resolved quartet. A typical example is shown in Figure 2. Thus, BF_3 -nitrogen and BF_3 -oxygen complexes produce different peak shapes. In addition, each complex has a different fluorine-19 chemical shift (Table I). BF_3 -diethyl ether is immediately hydrolyzed to fluoroboric acid when dissolved in acetone or DMSO. Both of these solvents have enough residual moisture to cause the hydrolysis. In addition, BF_3 -THF, BF_3 -methanol, BF_3 -diethyl ether, and BF_3 -dimethyl ether all are rapidly hydrolyzed, in deuterated water (D_2O) and DMSO (d_6 -DMSO). Neither BF_3 -MEA nor BF_3 -piperidine is hydrolyzed in D_2O or d_6 -DMSO at room temperature. Thus water (D_2O or moisture in DMSO) is much more reactive with BF_3 -oxygen complexes than with BF_3 -nitrogen complexes. In every case, only fluoroboric acid (and no HF) was produced by hydrolysis of BF_3 -oxygen compounds.

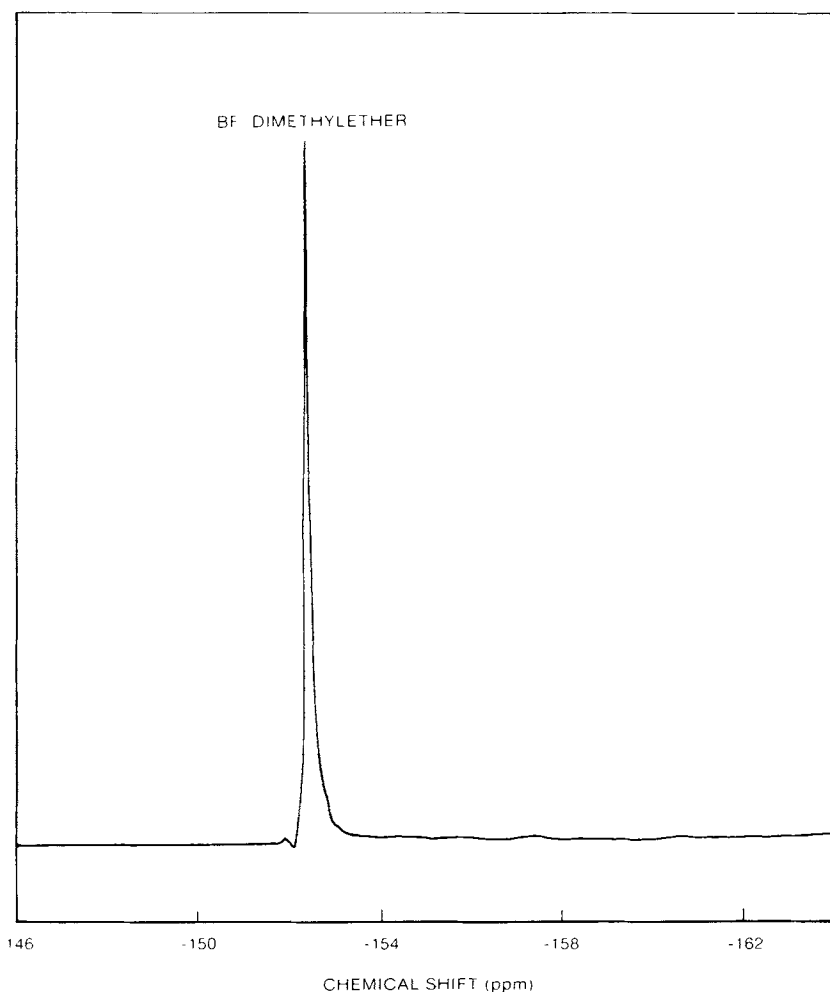


Fig. 2. Fluorine-19 NMR of BF_3 -dimethyl ether in d_6 -acetone.

TABLE I
 Fluorine-18 Chemical Shifts for BF₃ Complexes

Complex	Chemical shifts (ppm)			
	<i>d</i> ₆ -Acetone	<i>d</i> ₆ -DMSO	<i>d</i> ₄ -ODCB	D ₂ O ^a
BF ₃ -MEA	-150.39	-149.24	-151.60	-0.5
BF ₃ -methanol	-154.39	b	-156.3	b
BF ₃ -diethyl ether	b	b	-152.28	b
BF ₃ -dimethyl ether	-152.30	b	-156.48	b
BF ₃ -THF	-153.78	b	-155.35	b
BF ₃ -piperidine	-156.94	-155.90	-157.58	-6.25

^a Chemical shifts in D₂O are based on HBF₄ = 0 ppm.

^b The BF₃ complex was immediately hydrolyzed; only HBF₄ was observed.

BF₃-piperidine and BF₃-MEA both are stable in D₂O for several days when kept at room temperature. When heated to 90°C, they are hydrolyzed, but the hydrolysis still takes hours to be completed. Because the fluorine-19 NMR peaks caused by BF₃-MEA and HBF₄ overlap (see figures in Ref. 2), the rate of BF₃-MEA hydrolysis was not quantitated. However, the peaks caused by BF₃-piperidine and HBF₄ do not overlap (Fig. 3a). Thus, the hydrolysis of BF₃-piperidine in D₂O at 90°C was followed quantitatively. Spectra after 2 h and after 20½ h are shown in Figures 3b and 3c. Within 15 min, the concentration of BF₃-piperidine had decreased 11%. The fluoroboric acid increased 33% and a new peak caused by HBF₃OH appeared. During the first hour, the concentration of BF₃-piperidine continued to decrease whereas fluoroboric acid and HBF₃OH increased. After 2 h this trend was continuing but now some HF could be detected. After 4½ h, HBF₂(OH)₂ was also detected. After 2 h, there was no more BF₃-piperidine left. Only fluoroboric acid, HBF₃OH, and HF were present. Figures 3a through 3c show the spectra during the course of the hydrolysis. Figures 4a through 4d show the changes in BF₃-piperidine, fluoroboric acid, HBF₃OH, and HF concentrations during the hydrolysis.

Epoxy prepolymers present a decidedly different (hydrophobic) environment to BF₃ complexes. In the previous study,² deuterated 1,2-dichlorobenzene (*ortho*-dichlorobenzene or ODCB) solvent was used because like epoxy prepolymers, it contains very little moisture (*d*₄-ODCB has 0.03% water as determined by ¹H-NMR). The molar concentration of BF₃-MEA was less than that of the water. Thus, it was possible that the conversion of BF₃-MEA to fluoroboric acid was truly a hydrolysis. However, it is also possible that BF₃ complexes could be converted to fluoroboric acid without water being a coreactant. To test this possibility, solutions containing larger concentrations of BF₃ complexes were prepared. The solutions were 0.5–2.0*M* BF₃, which is a 20–100 molar excess over the water content of the *d*₄-ODCB. The BF₃-oxygen complexes were all quite stable in *d*₄-ODCB at 140°C; however, BF₃-piperidine was not. As shown in Figure 5, after only 20 min, 21% of the BF₃-piperidine had been converted to fluoroboric acid. After 1 h, 25% of the BF₃-piperidine had been converted to fluoroboric acid. Neither HF nor any other fluorinated product was seen except fluo-

boric acid. Although the BF_3 -nitrogen compound, BF_3 -piperidine, and possibly even BF_3 -MEA can be converted to fluoroboric acid without water being a coreactant, BF_3 -oxygen compounds are not converted to fluoroboric acid in the absence of water.

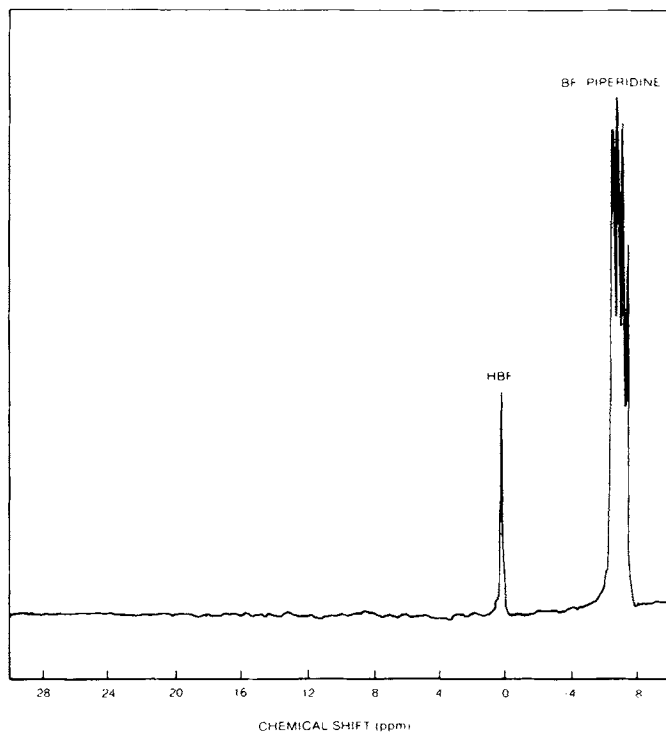
DISCUSSION

It was shown that fluoroboric acid does not affect the room-temperature shelf life of the TGDDM/DDS epoxy resin system. Even though it is an effective catalyst at elevated temperatures, fluoroboric acid is not a catalyst at room temperature.

Because fluoroboric acid is not hydrolyzed to HF, there is no concern that the highly corrosive HF will affect other parts near the epoxy in industrial applications.

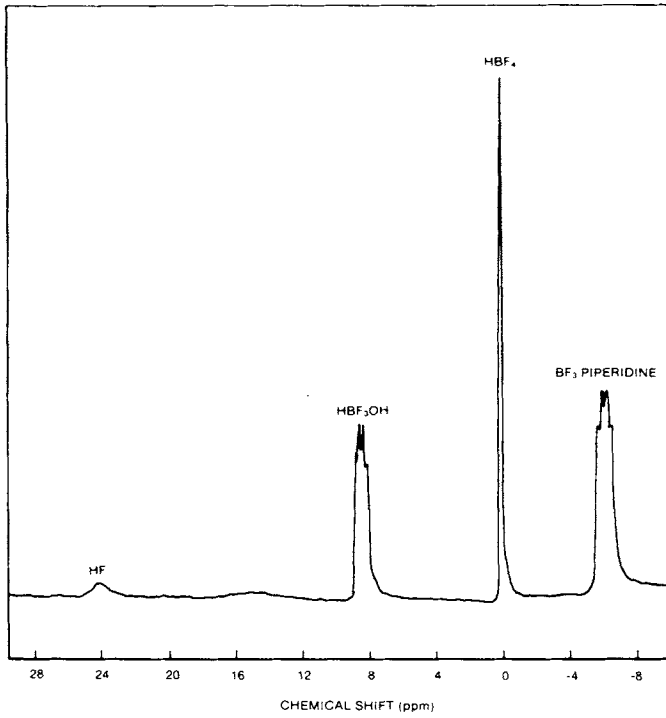
Fluorine-19 NMR has been shown to be an effective tool for identifying different BF_3 complexes. BF_3 -oxygen complexes exhibit a broad peak and are rapidly hydrolyzed to fluoroboric acids if sufficient moisture is present. The BF_3 -nitrogen complexes studied exhibit a quartet and are not hydrolyzed at room temperature. Each BF_3 complex examined had a unique chemical shift.

BF_3 -oxygen complexes probably could be used to accelerate epoxy resin cure. They would be easily hydrolyzed to fluoroboric acid which is the true

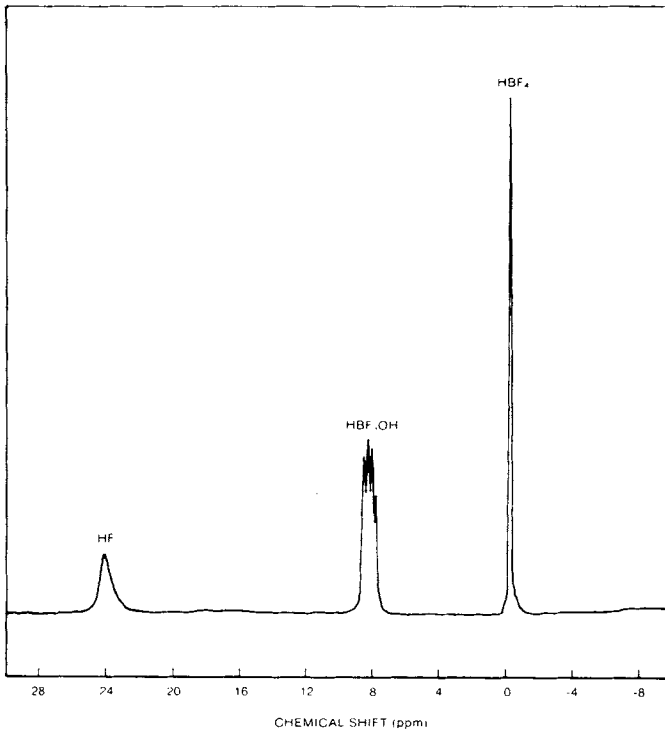


(A)

Fig. 3. (a) Fluorine-19 NMR of BF_3 -piperidine in D_2O . (b) Fluorine-19 NMR of BF_3 -piperidine after 2 h in D_2O . (c) Fluorine-19 NMR of BF_3 -piperidine after 20½ h in D_2O .

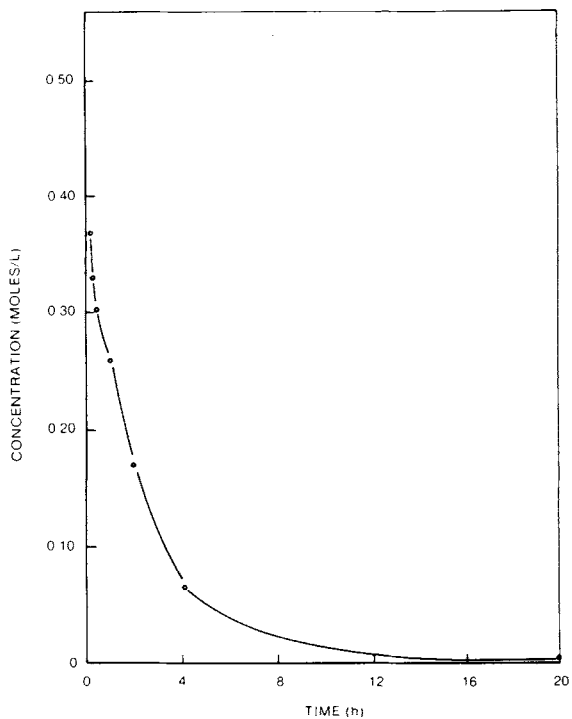


(B)

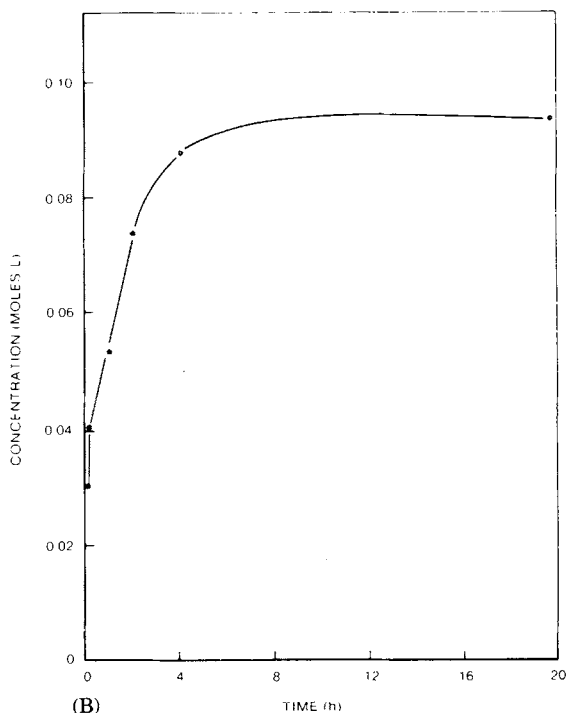


(C)

Fig. 3. (continued from previous page)

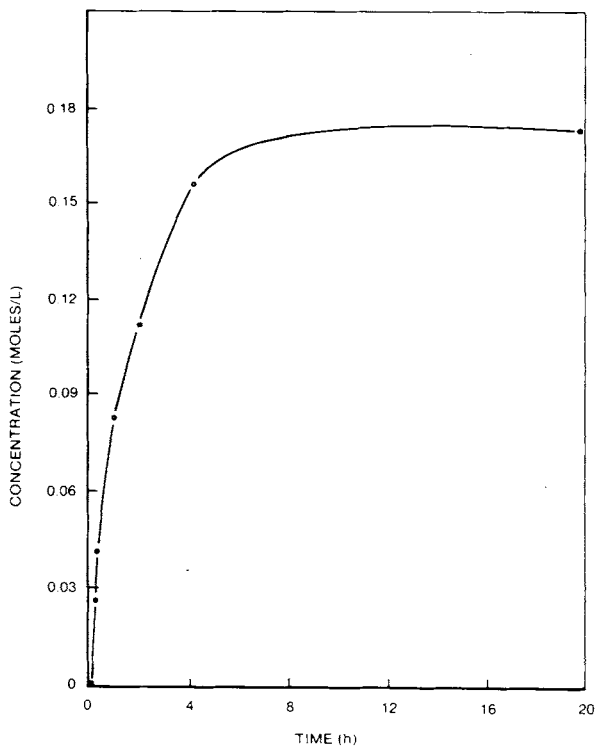


(A)

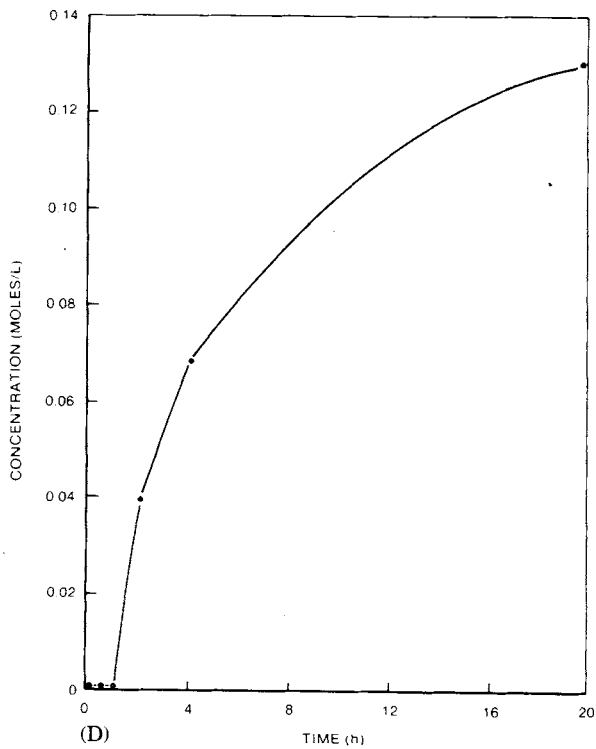


(B)

Fig. 4. (a) Change in BF₃-piperidine concentration in D₂O. (b) Change in fluoroboric acid concentration in D₂O. (c) Change in HBF₃OH concentration in D₂O. (d) Change in HF concentration in D=H₂O.



(C)



(D)

Fig. 4. (continued from previous page)

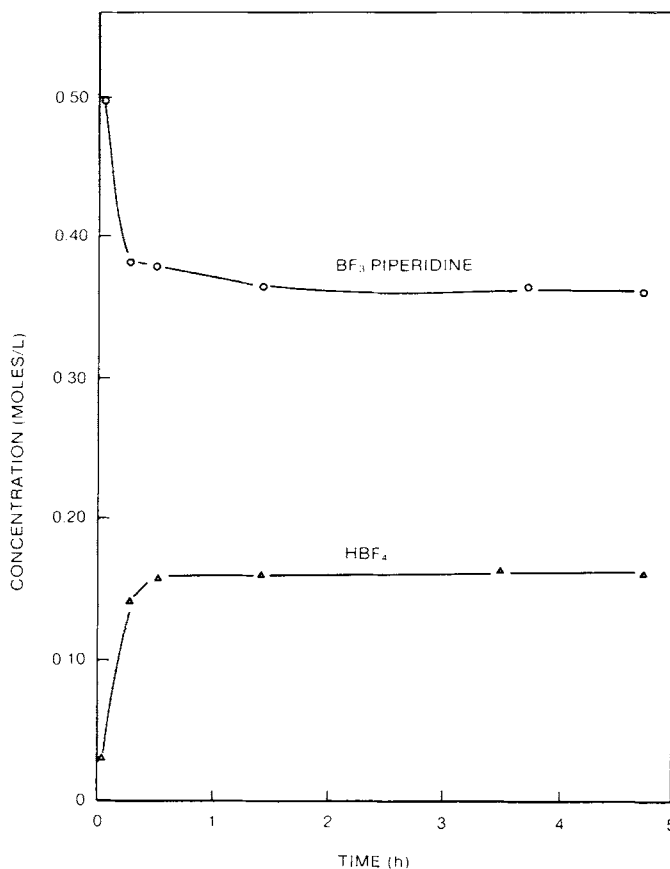
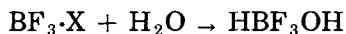


Fig. 5. Reaction in d_4 -ODCB.

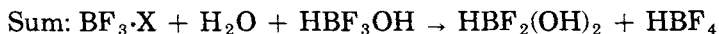
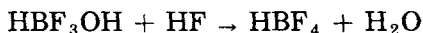
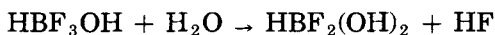
catalyst. The only difference between BF_3 -oxygen complexes and BF_3 -nitrogen complexes is that moisture would be required for the BF_3 -oxygen complexes to produce the desired fluoroboric acid. However, very little moisture would be needed to hydrolyze the small, catalytic amount of the BF_3 -oxygen complex. In fact, it probably would be necessary to carefully dry the epoxy components (TGDDS and DDS) and then cure the epoxy in a very dry environment to prevent a BF_3 -oxygen compound from being converted to fluoroboric acid. This clearly would not be done in an industrial environment. Thus, an epoxy resin should cure quite well regardless of whether a BF_3 -oxygen or a BF_3 -nitrogen complex were used.

Of merely scientific interest is the fact that BF_3 -nitrogen complexes are converted to fluoroboric acid at high temperatures without water being a reactant. As long as fluoroboric acid is produced, its formation mechanism is not important. The epoxy resin cure will still be accelerated as desired.

However, it is interesting to speculate as to how a BF_3 complex can be converted to fluoroboric acid. If the reaction is performed in water, HBF_3OH is produced. If a BF_3 -oxygen complex is hydrolyzed, no HF is produced. However, the previously suggested hydrolysis reactions *cannot* be occurring,^{3,4} i.e.:

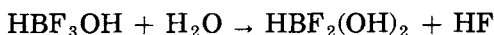
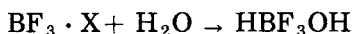


where X can be methanol, diethyl ether, dimethyl ether, or THF.



This requires that $\text{HBF}_2(\text{OH})_2$ be present. Alternatively, the $\text{HBF}_2(\text{OH})_2$ could be hydrolyzed in two steps to produce $\text{B}(\text{OH})_3$ and 2 mols of HF. Not only was $\text{HBF}_2(\text{OH})_2$ not seen, but the HF concentration was too low for $\text{HBF}_2(\text{OH})_2$ to have been hydrolyzed in this manner.

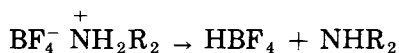
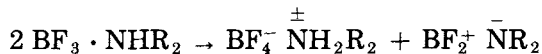
Thus, it is possible that the HBF_4 is produced as follows:



Because no $\text{HBF}_2(\text{OH})_2$ is observed, it must be rapidly converted to fluoroboric acid, thus:



This does not explain how fluoroboric acid can be produced nonhydrolytically (i.e., without water). Perhaps it is produced as follows:



with the fate of the $\text{BF}_2 \text{NR}$ not determined at this time.

Regardless of how the fluoroboric acid is produced, it is important only that it be produced without an excess of the highly corrosive HF. Under epoxy resin cure conditions (140°–160°C in a humid environment), the boron trifluoride complexes investigated will be converted to fluoroboric acid. The fluoroboric acid will catalyze the epoxy resin cure.⁴

References

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