Epoxy Resin Cure. I. Fluorine-19 NMR of Boron Trifluoride Monoethylamine and Fluoroboric Acid

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Synopsis

Fluorine-19 NMR is used to examine the role of boron trifluoride monoethylamine (BF_3–MEA) in epoxy resin cure. Spectra were first recorded in a variety of solvents suitable for dissolving different epoxy resins. All spectra contained a peak due to fluoroboric acid. Spectra of BF_3–MEA in orthodichlorobenzene were then recorded at elevated temperatures. The floroboric acid peak area increased, indicating that the BF_3–MEA was being hydrolyzed. Results indicate that, at temperatures above 100°C, BF_3–MEA is completely hydrolyzed within 5 min to fluoroboric acid.

INTRODUCTION

Boron trifluoride monoethylamine (BF_3–MEA) is important in industry as an additive to epoxy resins. Various reports have identified BF_3–MEA as either a catalyst, accelerator, or crosslinking agent.[1-7] These reports were based primarily on studies with simplified model systems. Instead of observing the BF_3-MEA directly, inferences were drawn based on the well-known chemical properties of boron trifluoride.[8] Because boron trifluoride is a well-known catalyst for a number of reactions, it is often assumed that BF_3–MEA must also be a catalyst for the curing of epoxy resins. Such an assumption is dangerous without experimental evidence. Perhaps the best experimental technique for observing BF_3–MEA is fluorine-19 NMR. The BF_3–MEA is usually present in 0.05–1% of the total weight of the epoxy prepolymer. Most common spectroscopic techniques will not distinguish BF_3–MEA from the large excess of epoxy prepolymer. Fluorine-19 NMR will observe only fluorine-containing molecules, thus eliminating the epoxy prepolymers (which contain no fluorine).

Before BF_3–MEA is studied in an epoxy resin matrix, it is important to describe fully its fluorine-19 NMR spectrum without any other substances present. The present study reports the fluorine-19 NMR spectra of BF_3–MEA in a variety of solvents and at different temperatures. All commercially available sources of BF_3–MEA were found to contain at least 5% fluoroboric acid (HBF_4). Since HBF_4 can also catalyze a number of reactions,[8] its fluorine-19 NMR spectrum also is reported.

The most probable source of HBF_4 is hydrolysis of BF_3–MEA. To better understand the NMR spectrum of BF_3–MEA, it is necessary to investigate

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this hydrolysis. Previous workers have shown that both boron trifluoride (BF_3) and HBF_4 undergo hydrolysis.[9-11]

The hydrolysis of BF_3–MEA has never been investigated. Fluorine-19 NMR is ideally suited for such hydrolysis studies because hydrolysis products can be observed directly. Previously, only HBF_4 and HBF_3OH were observed directly, although other hydrolysis products were suspected.[9-11] Since hydrolysis of BF_3–MEA might affect its shelf life and/or catalytic properties, fluorine-19 NMR was chosen to study its hydrolysis.

Both temperature and water concentration should affect the rate of hydrolysis. Because epoxy resins containing BF_3–MEA are cured at elevated temperatures (120–180°C), a deuterated solvent with a high boiling point is needed. Thus, deuterated 1,2-dichlorobenzene (also known as d_4-orthodichlorobenzene or d_4-ODCB) was chosen.

This report describes the fluorine-19 NMR spectra of BF_3–MEA and HBF_4 at room temperature in a number of deuterated solvents. The hydrolysis of BF_3–MEA and HBF_4 are also described. Results show clearly that, at temperatures above 80°C, BF_3–MEA is rapidly hydrolyzed to HBF_4 (and other hydrolysis products). At the temperatures which epoxy resins are cured, the rate of hydrolysis of BF_3–MEA to HBF_4 is much faster than the rate of epoxy cure. Thus, it is proposed the BF_3–MEA is not a catalyst in such systems, but instead HBF_4 and/or other hydrolysis products serve as catalysts.

EXPERIMENTAL

Fluorine-19 NMR spectra were recorded on a Varian FT80-A NMR at a frequency of 74.832 MHz. The following spectral parameters were used: Sweep width was 4000 Hz, pulse width was 13 μs (90° flip angle), pulse delay was 10 s, acquisition time was 2.047 s, and 16,384 data points were collected. Deuterated solvents were used for field lock in every case. With the exception of spectra recorded in D_2O, hexafluorobenzene was added as an internal standard. All chemical shifts were assigned based on −163 ppm for hexafluorobenzene.[12] Negative chemical shifts are upfield (more shielded) from $CFCl_3$, which is usually taken as 0 ppm.[13,14]

RESULTS AND DISCUSSION

The NMR analysis of BF_3–MEA can be divided into three parts. In the first part, the spectra of BF_3–MEA in different solvents is compared. The peaks present in each spectrum are identified. In the second part, one of these peaks, the one due to HBF_4, is examined more closely. The chemical shift of the HBF_4 peak is shown to depend on the acidity of the sample matrix. The relative size of the HBF_4 peak indicates the degree of hydrolysis of the BF_3–MEA. In the third part, the hydrolysis of BF_3–MEA is reported. The effects of temperature and time on the hydrolysis in a 1,2-dichlorobenzene solvent are examined. Finally the hydrolysis of BF_3–MEA in D_2O is described.

Spectra in Different Solvents

Different epoxy resins are soluble in different solvents. As a result, it is useful to compare the fluorine-19 NMR spectra of BF_3–MEA in a variety of these solvents.

BF_3–MEA is very soluble in acetone, dimethylsulfoxide (DMSO), and methanol, and slightly soluble in d_4–ODCB. When fresh BF_3–MEA is dissolved in any of the above deuterated solvents, three sets of peaks appear [Fig. 1 (a)–(1d)]. The two largest peaks are caused by BF_3–MEA and HBF_4. As reported previously for BF_3,[15,16] there is spin–spin coupling between [11]B and ^{19}F, making the BF_3 peak a quartet. The same quartet is seen for BF_3–MEA. The [11]B–[19]F coupling constants are large enough to make the quartet clearly resolved. The [11]B–[19]F coupling constants for HBF_4 are so small that the HBF_4 appears as a pseudosinglet in these spectra. Previously, the fluorine-19 NMR of aqueous BF_4 was reported to be a quartet.[17] If the NMR is carefully tuned, the spectrum of HBF_4 in D_2O can be resolved into the expected quartet. The fluorine-19 spectrum of BF_3–MEA in D_2O is shown in Figure 2(a). The HBF_4 overlaps the BF_3–MEA. When the scale is greatly expanded, the HBF_4 shows up clearly as two overlapping quartets. There is an additional [1]H–[19]F coupling because of the proton in HBF_4 [Fig. 2(b)]. The [11]B–[19]F coupling constant in HBF_4 is 1.2 Hz. It should be noted that the chemical shift scale in Figures 2(a) and 2(b) is based on 0 ppm (or 0 Hz) for the center of the BF_3–MEA. Since hexafluorobenzene is not soluble in D_2O, it could not be added as an internal standard.

Figures 1 and 2 show a definite solvent effect on the chemical shifts of BF_3–MEA and HBF_4. This effect is summarized in Table I.

The third peak that appears in each spectrum is a quartet. The chemical shift of this quartet varies considerably in different solvents. This small quartet in D_2O is caused by HBF_3OH. (The acidic proton of HBF_3OH rapidly exchanges with the D_2O so that DBF_3OH is actually being observed.) This interpretation is based on a previous report on the hydrolysis of BF_3 which clearly showed HBF_4 and HBF_3OH to be hydrolysis products.[10] If a chemical shift of -150.39 ppm was arbitrarily assigned to the BF_3–MEA in D_2O, the chemical shift of the downfield quartet becomes -143.27 ppm. In d_6–acetone, this downfield quartet has a chemical shift of -143.18 ppm (BF_3–MEA is -150.39 ppm), and in d_4–ODCB it is at -143.8 ppm (BF_3–MEA is -151.60 ppm). Thus, the small downfield quartet in d_6–acetone is also probably HBF_3OH (actually DBF_3OH or even maybe DBF_3OD). However, the chemical shift of the small quartet in deuterated methanol is -152.68 ppm and is -140.34 ppm in deuterated DMSO. These differences are too large to be caused by solvent effects (compared to solvent effects on BF_3–MEA in Table I). Thus, methanol and DMSO must be capable of displacing the water in HBF_3OH to form BF_3–CH_3OH or BF_3–DMSO. A summary of chemical shift data on these small quartets is given in Table II.

These data can be interpreted based on the previous report on hydrolysis of BF_3.[10] In this study, it was suggested that free BF_3 reacts immediately with water to give HBF_3OH. The HBF_3OH can then react with water and HF to give HBF_4 and $HBF_2(OH)_2$. Purified KBF_3OH was prepared. Upon
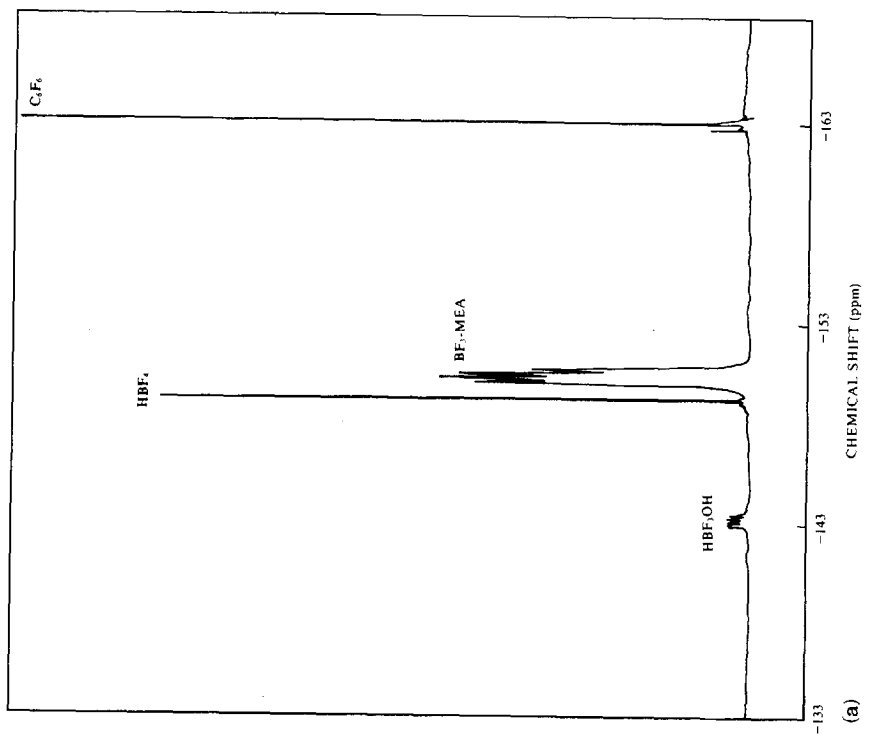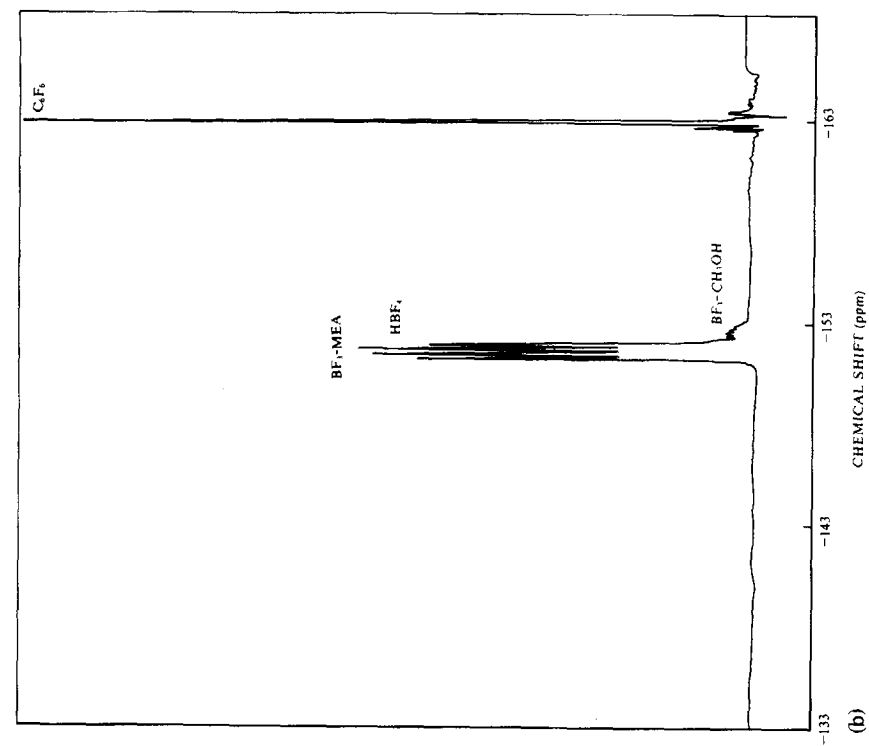
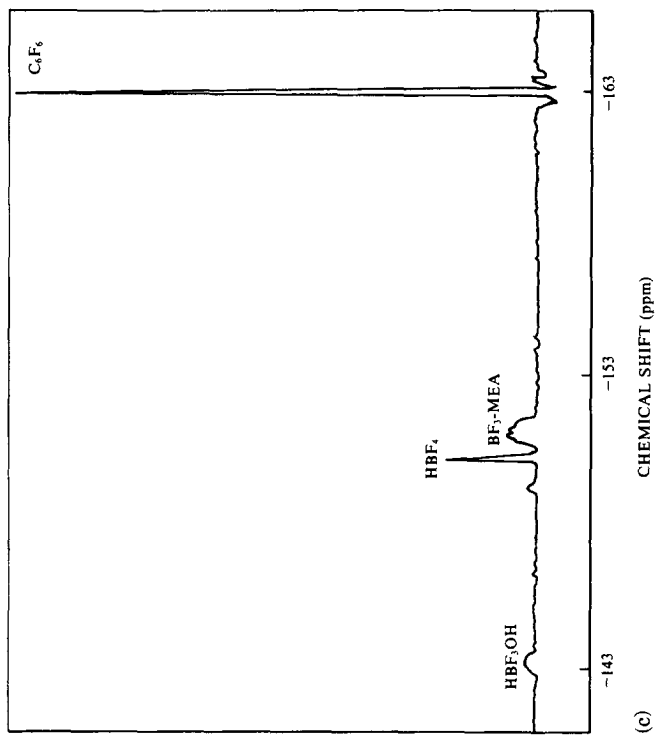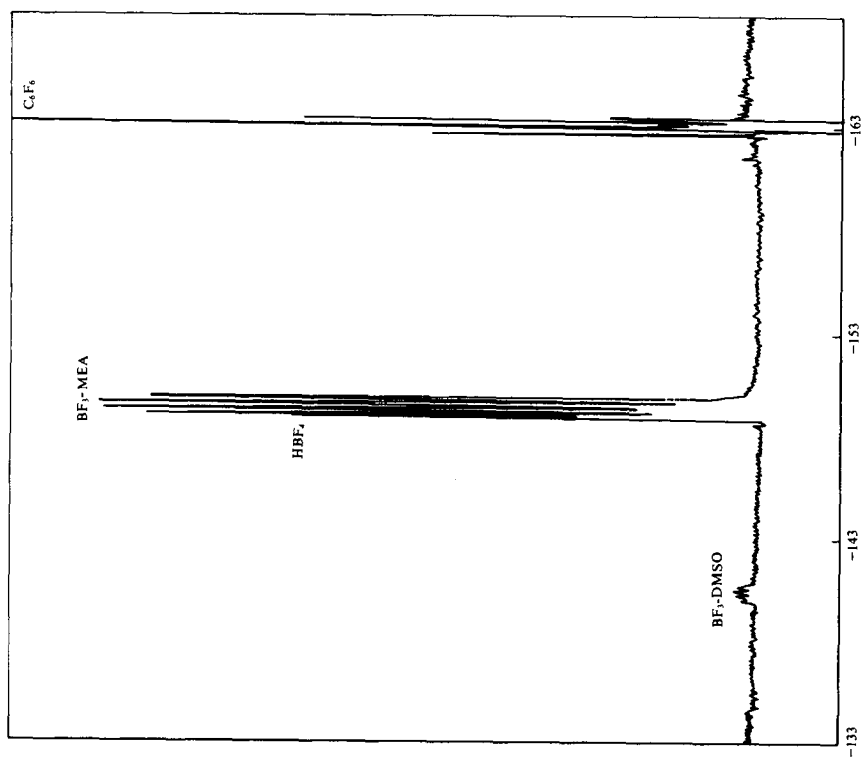Fig. 1. Fluorine-19 NMR spectrum of BF$_3$–MEA in (a) d$_6$–acetone, (b) d$_4$–methanol, (c) d$_6$– DMSO, and (d) d$_2$–ODCB.

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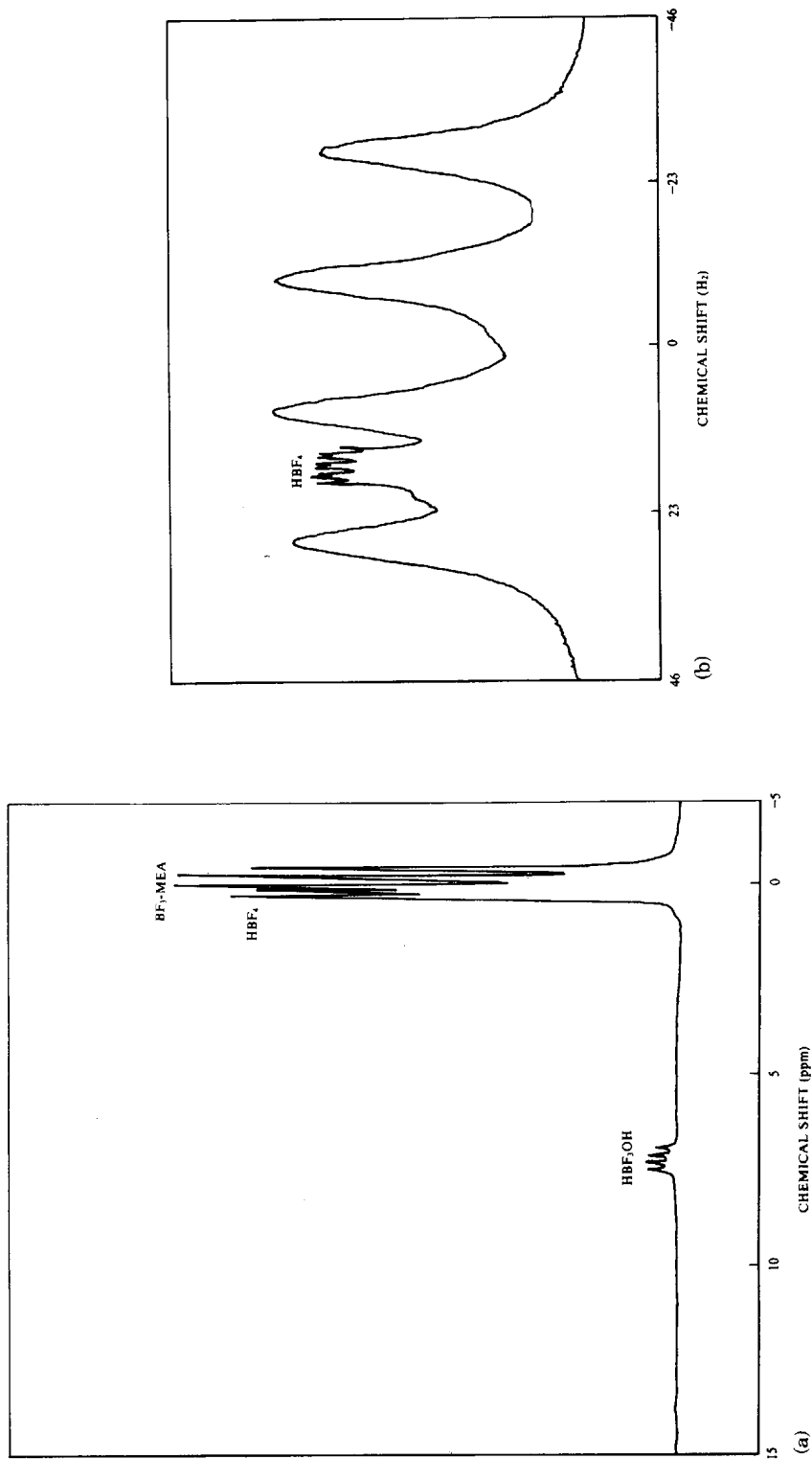
Fig. 2. Fluorine-19 NMR spectrum of BF$_3$-MEA in D$_2$O: (a) full spectrum; (b) scale expanded to show the HBF$_4$ quadruplets.

TABLE I
Solvent Effects on BF_3–MEA Quartet

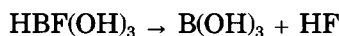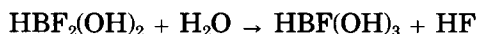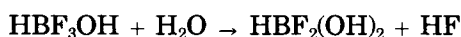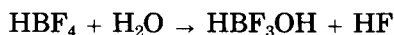| Solvent	Chemical shift of BF_3–MEA (ppm)	$J_{B,F}$ (Hz)
d_6–acetone	−150.39	16
d_6–DMSO	−149.24	19
d–methanol	−151.65	17
d_2–ODCB	−151.60	Not determined

acidification and mixing with BF_3 and HBF_4, the solution had a conductivity and pH identical to aqueous BF_3 which had been allowed to reach equilibrium (a process requiring several days).[10] This can be taken as indirect evidence for the presence of BF_3, HBF_3OH, HBF_4, and possibly even $HBF_2(OH)_2$. The overall reaction sequence would be:

$$BF_3 + H_2O \rightarrow HBF_3OH$$

$$HBF_3OH + H_2O \rightarrow HBF_2(OH)_2 + HF$$

$$HBF_3OH + HF \rightarrow HBF_4 + H_2O$$
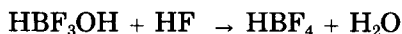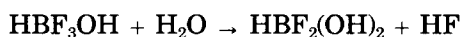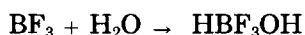
Present fluorine-19 NMR data confirm the presence of BF_3–MEA, HBF_4, and HBF_3OH, but not $HBF_2(OH)_2$. It is possible that the hydrolysis of free BF_3 may be different from the hydrolysis of BF_3–MEA.

To resolve this matter, the literature on the hydrolysis of HBF_4 was reviewed.[9,11] It was suggested in these reports that HBF_4 is hydrolyzed in several steps, as follows:

$$HBF_4 + H_2O \rightarrow HBF_3OH + HF$$

$$HBF_3OH + H_2O \rightarrow HBF_2(OH)_2 + HF$$

$$HBF_2(OH)_2 + H_2O \rightarrow HBF(OH)_3 + HF$$

$$HBF(OH)_3 \rightarrow B(OH)_3 + HF$$

At equilibrium, there would be a mixture of HBF_4, HBF_3OH, $HBF_2(OH)_2$, $HBF(OH)_3$, $B(OH)_3$, and HF. Initially, the HBF_4 and HBF_3OH should be present and identifiable by fluorine-19 NMR. A fresh solution of 0.5% HBF_4 in D_2O shows the two peaks identified in Figure 2(a) as HBF_4 and HBF_3OH (pseudosinglet and quadruplet). After 5 days at room temperature, a new peak, 20.6 ppm downfield from the HBF_4, was observed (Fig. 3). This peak is probably caused by $HBF_2(OH)_2$ or $HBF(OH)_3$.

TABLE II
Chemical Shifts of Various BF_3 Complexes

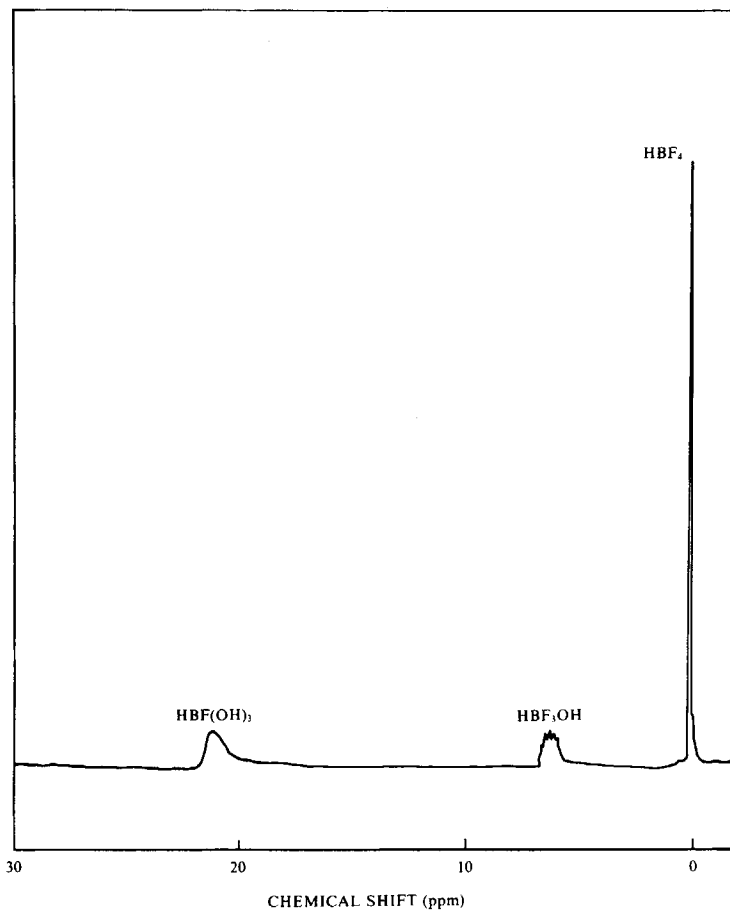| Compound	Chemical Shift (ppm)	$J_{B,F}$ (Hz)
HBF_3OH in d_6–acetone	−143.18	Not determined
HBF_3OH in d_2–ODCB	−143.78	14
BF_3–d–Methanol	−152.60	11
BF_3–d_6–DMSO	−140.34	17

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Fig. 3. Hydrolysis of HBF$_4$ in D$_2$O—HBF$_4$ is arbitrarily assigned to 0 ppm.

Information From HBF$_4$ Peak

Several samples of commercially available epoxy prepolymers were found to contain BF$_3$–MEA. The fluorine-19 NMR of each of these epoxies also showed the presence of HBF$_4$. Similarly, BF$_3$–MEA was obtained from different vendors, and each sample had varying amounts of HBF$_4$. Moreover, the chemical shift of the HBF$_4$ was seen to vary slightly, even though all spectra were obtained using deuterated acetone solvent. It is possible that some of the HBF$_4$ may be present as BF$_4^-$. In general, the chemical shift of an acid will change as it is titrated with a base. This phenomenon is most extensively documented for phosphoric acid and its phosphate anions (H$_2$PO$_4^-$, HPO$_4^{2-}$, and PO$_4^{3-}$). As phosphoric acid is titrated with NaOH, its ^{31}P-NMR chemical shift changes.[18,19] Thus, it was expected that HBF$_4$ and NaBF$_4$ would have different ^{19}F chemical shifts as shown in Figure 4. Both an aqueous solution of HBF$_4$ and a solution of HBF$_4$ in 95% acetone/5% water were titrated with NaOH and ^{19}F chemical shifts were recorded. The results are shown in Figure 5. Thus, the ^{19}F-chemical shift of the HBF$_4$ can be used to measure the acidity of the sample. A comparison of different
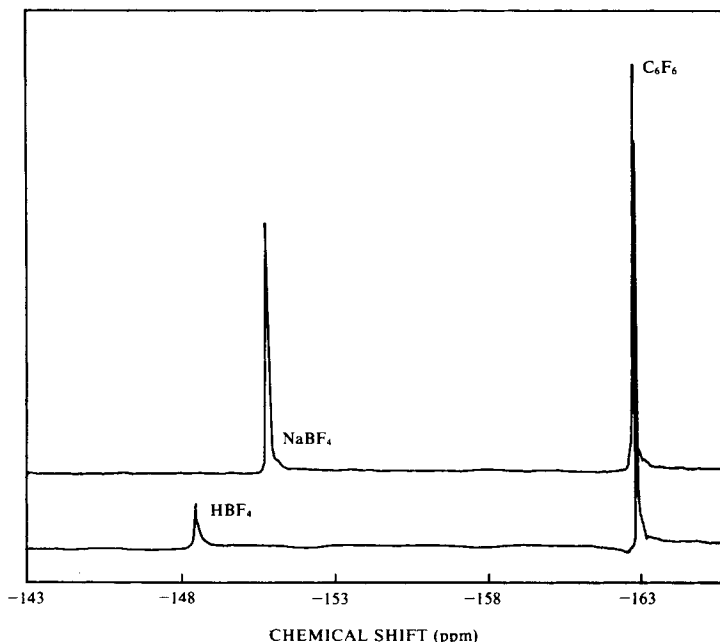
Fig. 4.   pH effect on HBF_4 spectrum in d_6–acetone.

BF_3–MEA samples and epoxy resins containing BF_3–MEA is shown in Table III.

Also shown from the HBF_4 peak is the degree of hydrolysis of the BF_3–MEA based on the relative areas under the HBF_4 and BF_3–MEA peaks. Most commercially available BF_3–MEA samples had 5–10% HBF_4 as determined in this way. BF_3–MEA in epoxy resin samples were 30–60% hydrolyzed to HBF_4. One BF_3–MEA sample was kept at room temperature for 2 years, and the HBF_4 content went from 5% to 30%. Since all samples showed some degree of hydrolysis, it was decided to better characterize the hydrolysis.

Hydrolysis of BF_3–MEA at High Temperature

Since epoxy resins are typically cured at temperatures above 120°C, the effect of elevated temperatures on the hydrolysis of BF_3–MEA was investigated. Initially d_4–ODCB was used as the solvent. Its boiling point is over 160°C, and it contains very little moisture.

A sample of BF_3–MEA initially containing 5% HBF_4 was dissolved in d_4–ODCB and placed in the NMR. The temperature of the sample was controlled by a variable temperature controller. The temperature controller was calibrated using a thermocouple placed in d_4–ODCB for temperatures ranging from 60°C to 100°C. A comparison of the fluorine-19 NMR spectra as the BF_3–MEA was heated stepwise from 30°C to 100°C is shown in Figures 6(a)–6(d). At 100°C (and 145°C) the BF_3–MEA peak disappears within 5 min, and only HBF_4 and HBF_3OH are seen. Since epoxy resins containing BF_3–MEA are typically cured for 2 h at higher temperatures (120–180°C), the
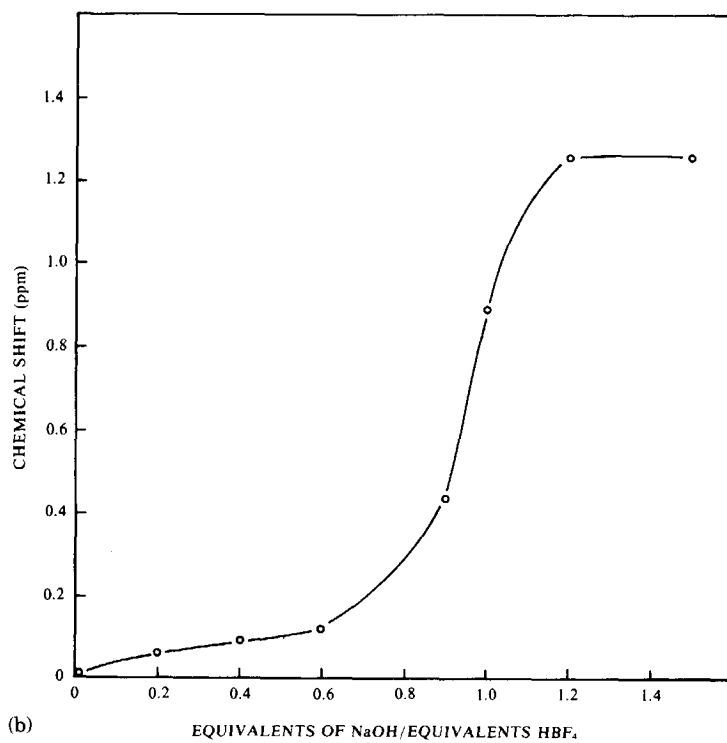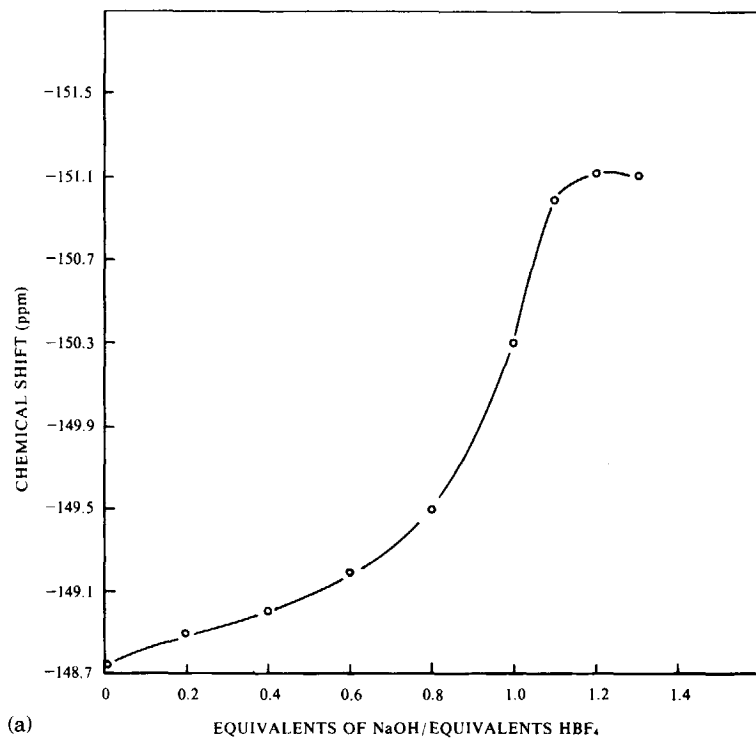
(a)

CHEMICAL SHIFT (ppm)

EQUIVALENTS OF NaOH/EQUIVALENTS HBF₄

(b)

CHEMICAL SHIFT (ppm)

EQUIVALENTS OF NaOH/EQUIVALENTS HBF₄

Fig. 5.   Titration of HBF₄ in (a) d₆–acetone and (b) D₂O.

TABLE III
Chemical Shift of BF_4-Singlet in Various Samples in d_6-Acetone[a]

Sample	Chemical shift (ppm)
Commercial BF_3MEA samples	
Sample 1	−148.3
Sample 2	−148.9
Sample 3	−148.9
Sample 4	−149.0
Sample 5	−149.8
BF_3MEA in epoxy resins	
Resin A	−149.7
Resin B	−150.3
BF_3–MEA mixed with	
Epoxide	−150.1
DDS	−149.8
Epoxide + DDS	−149.5

[a] HBF_4 is at 148.7 ppm; $NaBF_4$ is at 151.1 ppm. The epoxide was bis (N,N-di(d,3-epoxypropyl)-4-aminophenyl) methane. DDS is diaminodiphenylsulfone

BF_3–MEA must be completely hydrolyzed long before the cure is finished. Thus, BF_3–MEA is not acting as a catalyst in these epoxy resin systems.

To distinguish between the effect of moisture content from temperature on BF_3–MEA, the hydrolysis was studied in D_2O. At room temperature, the hydrolysis is very slow. After 24 h, the spectrum is almost identical to that seen in Figure 2(a). The only difference is that the peak caused by HBF_3OH (actually DBF_3OH or DBF_3OD) increased slightly in size. After 24 h, this peak accounts for 4.15% of the total fluorine spectrum as opposed to 3.34% when the BF_3–MEA was first dissolved in the D_2O. After 28 days at room temperature, a new peak arises—at 21 ppm (Fig. 7). When BF_3–MEA is heated to 80°C in D_2O, the rate of hydrolysis increases. The HBF_4 peak increases in size and is shifted upfield by 1.6 ppm, and the 21 ppm peak broadens (Fig. 8) in the first 5 min. Over the next 3 h, the HBF_4 peak continues to increase in size along with the $HBF_3OH(DBF_3OH)$ peak as the BF_3–MEA quartet decreases. The relative peak areas are shown in Table IV. A new peak at 21 ppm is seen after 1.5 h. It is most likely that the peak at 21 ppm is caused by $HBF(OH)_3$, and the peak at 16 ppm is caused by $HBF_2(OH)_2$. These compounds are expected to appear based on previous reports on HBF_4 hydrolysis.[9,11] After 16 h at 80°C, the BF_3–MEA is completely hydrolyzed. Only HBF_4, HBF_3OH, and $HBF(OH)_3$ peaks are seen. It seems that hydrolysis at 80°C occurs slowly in water, but at 100°C or 145°C in d_4–ODCB the hydrolysis is quite rapid. Thus, temperature accelerates the hydrolysis of BF_3–MEA much more than large water concentration.

Epoxy resin prepolymer would be expected to contain at least as much moisture as d_4–ODCB. Since the epoxies are cured at high temperatures, the BF_3–MEA is expected to be rapidly hydrolyzed. The rate of epoxy cure has been studied by Fourier transform infrared (FTIR) spectroscopy.[20] The results in this study show that epoxy resin is cured much slower than BF_3–MEA is hydrolyzed. Moreover, when HBF_4 is mixed with epoxy resin components in the absence of BF_3–MEA, the epoxy resin cure is accelerated considerably. Thus, it is concluded that BF_3–MEA is not a catalyst for epoxy resin cure. HBF_4 and/or its hydrolysis products act as the catalyst.

(a)   CHEMICAL SHIFT (ppm)

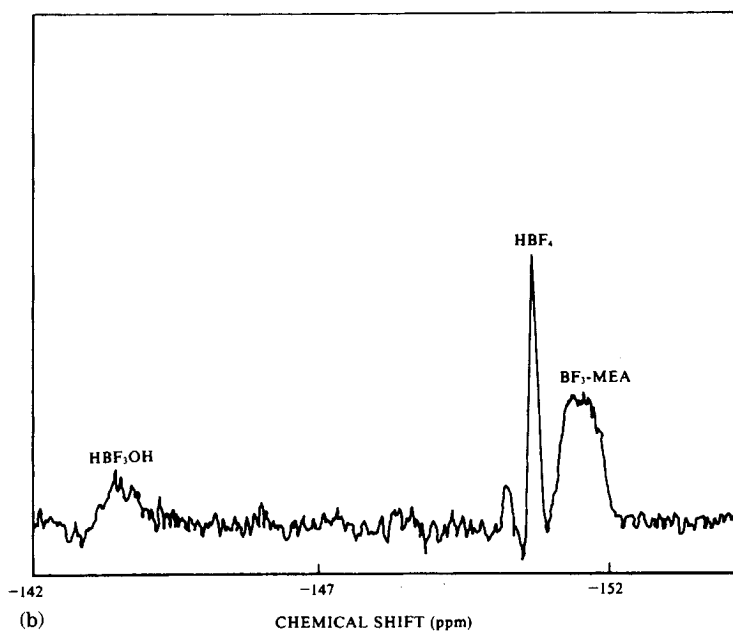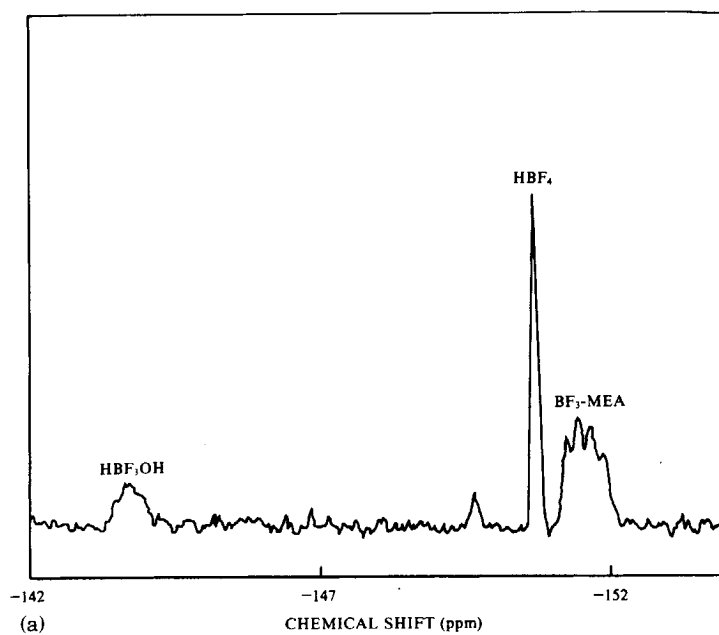(b)   CHEMICAL SHIFT (ppm)

Fig. 6.   Effect of elevated temperature on BF$_3$–MEA hydrolysis: (a) 30°C; (b) 60°C; (c) 80°C; (d) 100°C.

(c)   CHEMICAL SHIFT (ppm)

(d)   CHEMICAL SHIFT (ppm)
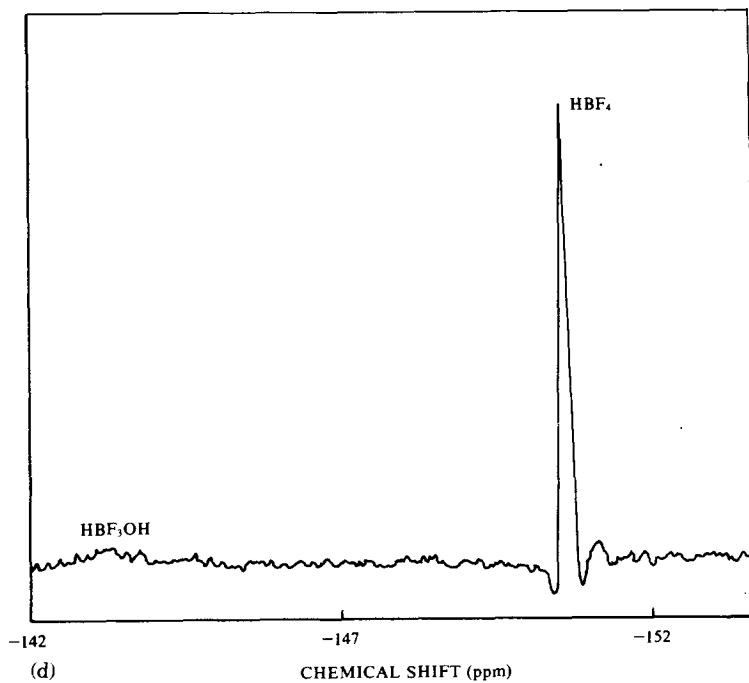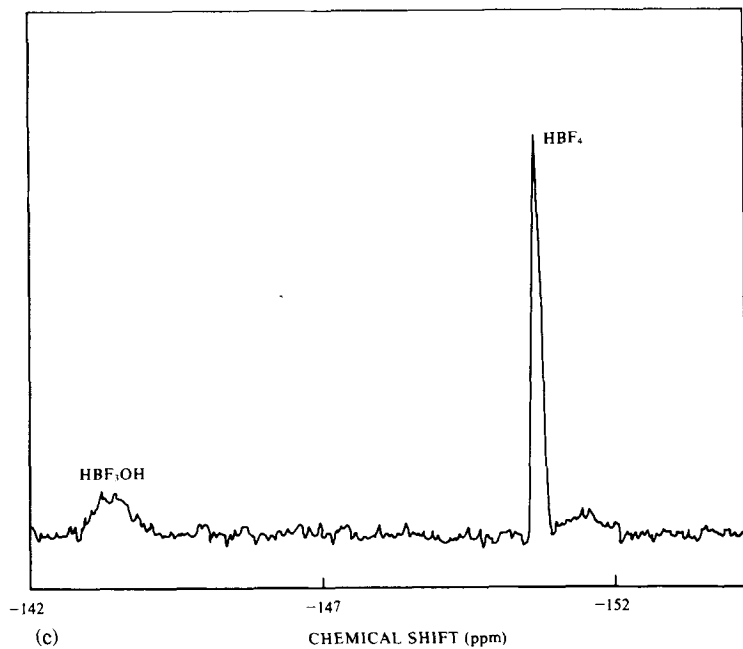
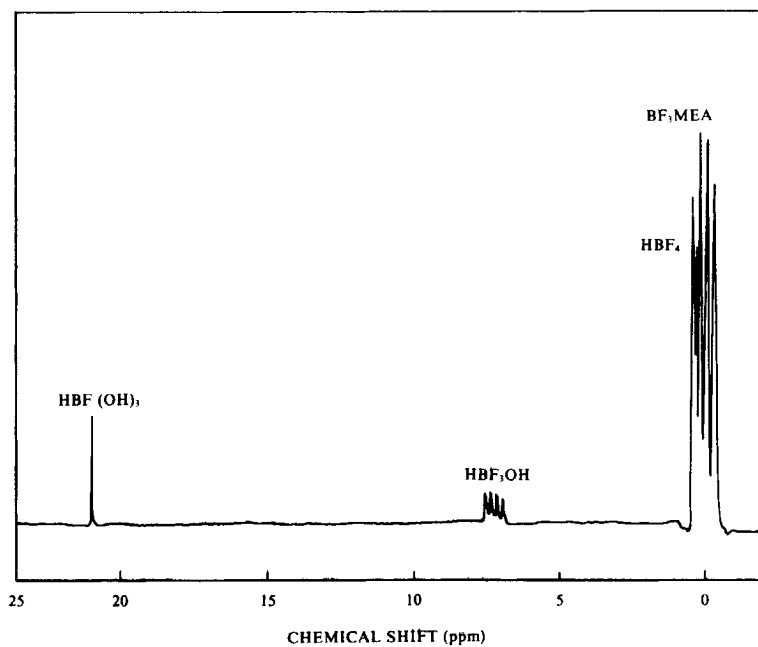Fig. 6 (*continued from the previous page.*)

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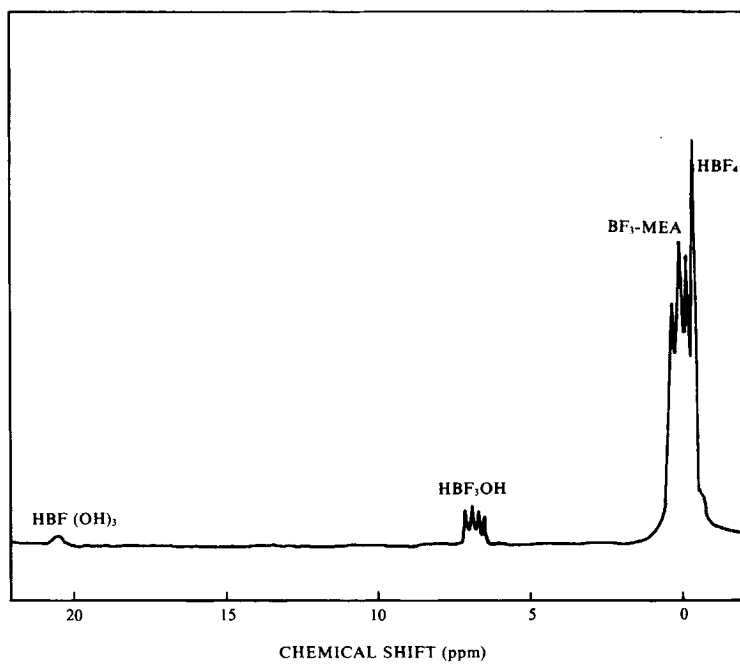Fig. 7.   Room temperature hydrolysis of BF$_3$–MEA in D$_2$O. This is the spectrum after 28 days.

Fig. 8.   High temperature hydrolysis of BF$_3$–MEA in D$_2$O. This is the spectrum after 10 min at 70°C.

TABLE IV
Hydrolysis of BF_3–MEA in D_2O at 80°C

Peak	$t=0$	$t=10$ min	$t=1.5$ h	$t=3$ h	$t=16$ h
BF_3–MEA					
+ HBF_4	88.2	84.9	71.5	58.9	38.1[a]
HBF_3OH	10.5	14.2	24.9	34.2	53.5
$HBF(OH)$	1.28	0.94	1.90	2.83	8.4
$HBF_2(OH)_2$	0	0	1.80	4.12	0

[a] Only HBF_4 is present after 16 h.

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