

## Proposed Mechanism for the Curing of Epoxy Resins with Amine-Lewis Acid Complexes or Salts

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### Synopsis

The common assumption in the literature is that amine complexes of Lewis acids (particularly boron trifluoride) cure epoxy resins by virtue of their dissociation to liberate the Lewis acid which then functions as the "true" catalyst. Evidence is presented to indicate that this picture of amine-Lewis acid complex curing may be incorrect. Another mechanism is proposed which is consistent with (a) lack of correlation between adduct stability and reactivity, (b) a similarity in reactivity of  $\text{BF}_3$  adducts and the corresponding fluoroborate salts, (c) the relationship between reactivity of  $\text{BF}_3$  and  $\text{PF}_5$  adducts, (d) a correlation between reactivity and structure of the amine in the complex, and (e) the effect of the anion on reactivity of amine salts. The relative reactivity of the catalysts has been equated with the temperature at which gelation occurs on heating at a fairly constant rate.

### INTRODUCTION

Little study has been given to the mechanism by which amine boron trifluoride adducts<sup>1-3</sup> or amine tetrafluoroborate salts<sup>4</sup> cure epoxy resins. The most relevant statement on the subject, with reference to the amine-boron trifluoride adduct, appears to be the claim<sup>5-8</sup> that the adduct dissociates at a certain temperature and the epoxy resin is then cured by the boron trifluoride which is liberated. Apparently, no suggestion has been offered concerning the mechanism by which curing is effected by amine tetrafluoroborate salts.

Some recent work in our laboratory led us to reexamine this problem. It appears that the suggestions which have been made concerning the curing mechanism of epoxy resins with amine-boron trifluoride complexes are not in agreement with the actual chemistry of amine-boron trifluoride complexes and thus are untenable. In this paper we suggest an alternative mechanism for the curing of epoxy resins by amine-Lewis acid adducts, comprehensive enough to include the action of the corresponding salts, which is believed to be in agreement with results in the literature as well as those reported in this paper.

### Concept of Complex Dissociation

Although articles<sup>5-7</sup> on the mechanism of epoxy resin curing by amine-boron fluoride complexes and manufacturers' literature on the complexes<sup>8</sup>

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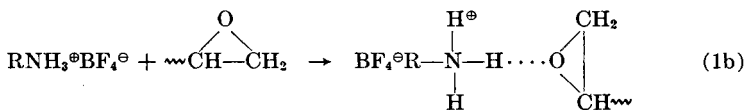
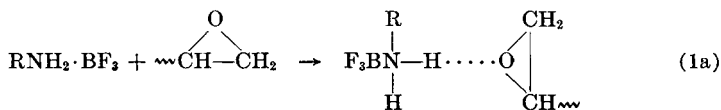
postulate that the resin is cured by the complex at its "dissociation temperature," the dissociation temperature is not defined experimentally. For example, the statement that  $C_2H_5NH_2 \cdot BF_3$  cures epoxy resins at the temperature at which it dissociates ( $90$ – $100^\circ C.$ ) is contrary to fact. The primary amine complexes of boron trifluoride have not been reported to dissociate reversibly in any available literature. The ethylamine–boron trifluoride complex has been reported to decompose rapidly in air when heated above its melting point ( $89^\circ C.$ ),<sup>9</sup> but this report is more properly interpreted as indicating that at this temperature the complex becomes reactive to atmospheric moisture. We have heated ethylamine–boron trifluoride at  $120^\circ C.$  in nitrogen with no indication of decomposition and at  $190$ – $200^\circ C.$  with only very slow decomposition to products containing the  $BF_4^-$  ion. Similarly, the boron trifluoride complexes of ethylenediamine and hexamethylenediamine give only small traces of  $BF_4^-$  ions when heated above  $120^\circ C.$  and finally sublime at  $170^\circ C.$  to give products closely resembling the original complex in composition.<sup>10</sup>

Secondary amine–boron trifluoride complexes are reported to disproportionate to the products  $R_2NH_2^+BF_4^-$  and  $R_2NBF_2$  at widely varying temperatures, depending upon the amine,<sup>11,12</sup> but again there is no dissociation. Since primary and secondary amine–boron trifluoride complexes are not reported to dissociate, it seems clear that dissociation cannot be the primary reaction preceding the cure of epoxy resins by amine–boron trifluoride complexes.

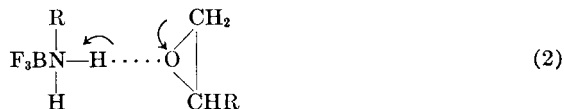
### Outline of Proposed Mechanism

At certain temperature levels the amine–boron trifluoride complex (or amine tetrafluoroborate salt) becomes reactive towards the epoxy resin; curing is caused by reaction with the resin rather than by liberated boron trifluoride. As explained below, amine tetrafluoroborate salts may react as such. The reaction of amine–boron trifluoride complexes, however, may be somewhat more involved, since they may react directly with the resin (as outlined below) or may react first to give a salt. The salt, of course, would then react according to the scheme described below.

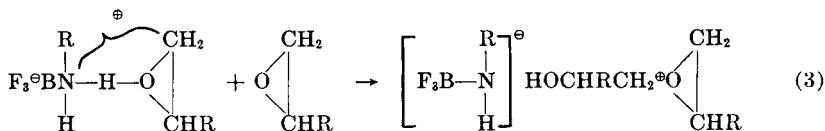
We assume the amine adduct or salt is solvated by the epoxy groups of the epoxy resin. With respect to the amine this means that weak bonds are formed between the oxygen of the epoxy group and the hydrogen atoms located on the amine nitrogen atom according to eqs. (1a) (for the adduct) and (1b) (for the salt).



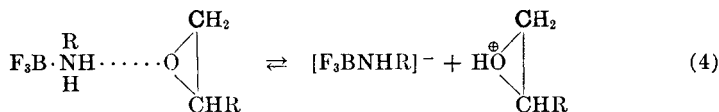
In essence, there is competition between the two bases, the epoxy ring and the amine, for the hydrogen atom. Since the amine is more basic, the hydrogen will still be attached primarily to the nitrogen atom. However, the oxygen atom, since it is contributing a portion of its electrons to the amine hydrogen atom, now has a partial positive charge causing a partial shift of electrons from an adjacent carbon atom according to eq. (2).



The reactivity of the resulting complex towards an attacking nucleophile, such as another epoxy ring, will depend upon the magnitude of charge transfer which will, in turn, depend upon the acidity of the hydrogen atom which is attached to the amine. As the temperature is increased, some point is reached at which reaction according to eq. (3) becomes sufficiently rapid for curing. A similar reaction would occur in the case of a salt catalyst.



Reaction then proceeds (propagation) by attack of other epoxy groups on the oxonium ion. Alternatively, one may consider an equilibrium [eq. (4)] between the epoxy-solvated amine-boron trifluoride complex and a secondary oxonium ion.

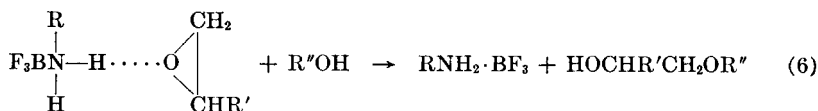


The curing reaction is then initiated by attack of an epoxy ring on the secondary oxonium ion thus formed according to eq. (5) (anions not shown).



Increased cure rate at higher temperature is now caused by a shift of equilibrium (4) to the right, accompanied by an increased reactivity of the secondary oxonium ion. Although no choice can be made between equations (2), (3), or (4), (5), it should be emphasized that in either instance curing is initiated by reaction of the complex (or salt) with the epoxy groups rather than by decomposition of the salt or complex to some species reactive towards epoxy groups.

If the epoxy mixture contains a relatively high concentration of hydroxyl groups, the propagation reaction may be that shown in eq. (6), where an alcohol becomes the attacking nucleophile.



The regenerated catalyst now activates another epoxy ring and eq. (6) is repeated as the propagation step. The mode of epoxy polymerization depicted in eq. (6) is favored by some researchers.<sup>13</sup> According to this mode of reaction, the adduct or salt becomes a true catalyst with no decomposition occurring (at least in the primary polymerization reaction). Again, increased reactivity at higher temperatures is expected for reasons previously discussed for eqs. (2), (3) and (4), (5).

Examination of eqs. (1)–(6) also reveals that the process is essentially the same whether an amine complex or an amine salt is used, i.e., the interaction of a hydrogen atom on a quaternary nitrogen atom with the epoxide ring. Thus, the curing action of amine salts and the corresponding amine complexes would be expected to be very similar. Some differences between the curing action of salts and adducts might be expected, since the replacement of an amine salt hydrogen atom with a Lewis acid may alter the acidity of the remaining hydrogen atoms. However with strong Lewis acids such as  $\text{BF}_3$ , any change should be relatively small. Any change in acidity is also reduced by the fact that the acidity of the original salt has been reduced by its association with the anion. While some degree of correlation of curing of salts and adducts might be expected indirectly from the dissociation theory, the prediction of close similarity is an essential feature of the proposed mechanism.

A suggestion leading to an anion of the type  $(\text{BF}_3\text{NHR})^-$  has been included in an article by Arnold.<sup>6</sup> He assumes the amine–boron trifluoride complex to dissociate to the Lewis acid (boron trifluoride) as the major mode of reaction but he also suggests as a minor reaction its dissociation as a Brønsted acid, i.e.,  $\text{RNH}_2 \cdot \text{BF}_3 \rightarrow \text{H}^+ + \text{RHNBF}_3^-$ . Although this latter dissociation leads to the same type of anion we postulate, there is no evidence for such dissociation in the absence of the participation of the epoxy. Further, such a mechanism cannot be valid for amine salts, since any such dissociation to  $\text{H}^+$  and  $\text{R}_3\text{N}$  would certainly be negligible at temperatures at which the salts will cure epoxies. Thus, our mechanism differs in that reaction of the epoxy groups with adduct or salt, rather than simple dissociation of either the complex or the salt, is assumed.

## RESULTS

Outlined below is the experimental evidence supporting the new mechanism and contradicting the dissociation theory.

### Similarity of Salts and Adducts as Curing Agents

A very close similarity in the action of amine–boron trifluoride adducts and the corresponding amine tetrafluoroborate salts as curing agents for epoxies was established as shown in Table I. Similarly, the  $\text{BF}_3$  adduct of

triphenylphosphine cured the epoxy at 160°C., while the corresponding tetrafluoroborate salt caused curing at 150°C.

In each instance the salt and the adduct cure the resin in the same temperature range. The cure times, i.e., times to reach the recorded temperatures, were never separated by more than 2-3 min. (see Experimental Section).

TABLE I  
Comparison of Curing Temperature for Bisphenol A Epoxy Resins of Amine Salts and Adducts.

Amine	Temperature of cure, °C.		Molality of catalyst
	BF <sub>3</sub> complex	BF <sub>4</sub> <sup>-</sup> salt	
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	55	58	0.124
2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	64	63	0.163
EtNH <sub>2</sub>	140	140	0.174
( <i>sec</i> -Bu) <sub>2</sub> NH	160	160	0.144
Et <sub>3</sub> N	243	241	0.178

### Lack of Correlation between Curing Temperature and Adduct Stability

Absolutely no correlation was obtained between the curing temperature of an adduct (complex) and the temperature at which it forms other products when heated. Data are given in Table II.

TABLE II  
Comparison of Adduct Stability and Curing Temperatures

Complex	Curing temperature, °C.	Decomposition temperature, °C.
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ·BF <sub>3</sub>	55	160 (slight)
EtNH <sub>2</sub> ·BF <sub>3</sub>	140	200 (slight)
<i>i</i> -PrNH <sub>2</sub> ·BF <sub>3</sub>	145	200 (slight)
<i>sec</i> -Bu <sub>2</sub> NH·BF <sub>3</sub>	160	<100 <sup>a</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P·BF <sub>3</sub>	160	<150 <sup>b</sup>
Et <sub>2</sub> NH·BF <sub>3</sub>	210	Reported to react at low temp. <sup>11</sup>

<sup>a</sup> When *sec*-Bu<sub>2</sub>NH·BF<sub>3</sub> is heated at reduced pressure at less than 100°C. it reacts according to the equation:



<sup>b</sup> When (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P·BF<sub>3</sub> is heated at a little below 150°C. at 1 mm. pressure, the free (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P is recovered quantitatively.

From Table II it is apparent that the curing temperature does not correspond to the temperature at which the adduct will become reactive, i.e., will dissociate or form other products.

### Comparative Reactivity of Aniline Adducts of Boron Trifluoride and Phosphorus Pentafluoride

Phosphorus pentafluoride, like boron trifluoride, is extremely reactive towards oxirane rings at room temperature.<sup>14</sup> Thus, if curing were caused by dissociation, it would be expected to occur with  $\text{PF}_5$  adducts at the temperature at which dissociation of the complex became pronounced. Since phosphorus pentafluoride-amine complexes are much weaker than boron trifluoride complexes,<sup>14</sup> the phosphorus pentafluoride complexes should cure epoxies at much lower temperatures. Experimentally, it was found that the aniline adduct of phosphorus pentafluoride cured a bisphenol A epoxy at 75–80°C., in contrast to aniline-boron trifluoride, which cured the same material at 55°C. Aliphatic amine-phosphorus pentafluoride adducts are also reported<sup>15</sup> to be less active than the corresponding boron trifluoride adducts. These findings are in disagreement with the dissociation theory of epoxy resin curing but are in agreement with our suggested mechanism. Weaker coordination of the complex will mean stronger nitrogen-hydrogen bonds, thus reducing the degree of coordination of the amine hydrogens with the epoxy ring and increasing the temperature necessary for reaction to occur. Thus, weaker coordination should require increased reaction temperatures, in agreement with the experimental findings.

### Relationships between Curing Temperature and Amine Structure

Although a definitive relationship between acidity of an amine and reactivity of its complex might be expected, the importance of other factors limited such a correlation to a given amine type, i.e., to primary, secondary, or tertiary amines. However amine acidities are measured in aqueous solutions and are greatly influenced by the degree of solvation of the different species formed.<sup>16</sup> The relative solvation behavior of an amine in water and in an epoxy (still unknown) might be expected to be vastly different. The greatly different solvation behavior of amines in water and in alcohols, for example, has been indicated.<sup>17</sup> Nevertheless certain generalizations as discussed in the following paragraph may be made.

The reactivity of an amine salt or complex appears to depend upon three factors. These are: (1) amine type (primary, secondary, tertiary), (2) basicity, and (3) steric effects.

Within a given amine type there is some relationship between basicity and reactivity. For example, aromatic primary amines, which are much weaker bases than aliphatic primary amines, in the form of salts or complexes cure epoxies at much lower temperatures than the aliphatic amines salts or complexes, as might be expected from the relative basicity. We have found that secondary aliphatic amine adducts (or salts) require higher temperatures than do primary aliphatic amine adducts (or salts), as might be expected from the generally greater basicity of secondary amines. Tertiary amine complexes (or salts) require higher temperatures than do those of secondary amines, which may indicate a generally greater basicity

of tertiary amines in media where the influence of water is small, perhaps because of the influence of the anion on the proton.<sup>16</sup> However the distinction between reactivity of derivatives of secondary and tertiary amines is somewhat obscured by steric effects. This is illustrated by the curing temperatures of derivatives of tertiary amines, e.g., *i*-Pr<sub>2</sub>EtN (180°C.), and Et<sub>3</sub>N (242°C.), and of secondary amines, e.g., *sec*-Bu<sub>2</sub>NH (160°C.), *i*-Pr<sub>2</sub>NH (160°C.), and Et<sub>2</sub>NH (210–215°C.). The curing temperature is markedly decreased by an increase in the steric requirements of the amine. It may be that this behavior reflects a greater acidity of the amine salt due to relief of steric strain as the amine is converted from a tetra- to a

TABLE III  
Temperature of Cure of Epoxy Resins by Various Salts and Adduct Compounds

Compound	Amt., wt.-%	Cure temperature, °C.	Base pK <sub>a</sub>
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> BF <sub>3</sub>	2.0	55	4.69 <sup>a</sup>
C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	2.25–2.5	58	4.69 <sup>a</sup>
2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub> ·BF <sub>3</sub>	3.54	64	
2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>3</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	3.86	63	
EtNH <sub>2</sub> ·BF <sub>3</sub>	1.96	140	10.63 <sup>b</sup>
EtNH <sub>3</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	2.29	140	10.63 <sup>b</sup>
<i>sec</i> -Bu <sub>2</sub> NH·BF <sub>3</sub>	3.15	160	11.05 <sup>b</sup>
<i>sec</i> -Bu <sub>2</sub> NH <sub>2</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	3.12	160	11.05 <sup>b</sup>
<i>i</i> -Pr <sub>2</sub> NH <sub>2</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	3.06	160	11.01 <sup>b</sup>
Et <sub>2</sub> NH·BF <sub>3</sub>	3.48	210–215	11.09 <sup>b</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PH <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	5.7	150	2.73 <sup>c</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P·BF <sub>3</sub>	4.5	160	2.73 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub> NMe <sub>2</sub> ·BF <sub>3</sub>	4.4	180	5.18 <sup>a</sup>
<i>i</i> -Pr <sub>2</sub> EtNH <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	3.85	180	(11.27) <sup>d</sup>
Pyridine·BF <sub>3</sub>	2.0	225	5.23 <sup>a</sup>
Pyridine H <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	3.0	225	5.23 <sup>a</sup>
Et <sub>3</sub> NH <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	3.36	241	10.65 <sup>b</sup>
Et <sub>3</sub> N·BF <sub>3</sub>	3.0	243	10.65 <sup>b</sup>

<sup>a</sup> Data of Clark and Perrin.<sup>18</sup>

<sup>b</sup> Data of Hall.<sup>16</sup>

<sup>c</sup> Data of Henderson and Streuli.<sup>19</sup>

<sup>d</sup> Calculated according to equations of Clark and Perrin.<sup>18</sup>

tricoordinated form. Only one aromatic secondary amine was tested. Diphenyl amine boron trifluoride reacted with, but did not cure bisphenol A epoxies. Since its reactivity towards other epoxy compounds (such as propylene oxide) was much greater than any other salt or adduct tested (see Table III) secondary reactions apparently killed the propagation step. Substituting one aromatic group for an aliphatic group in a tertiary amine, as in C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>, considerably decreased the curing temperature as expected from the reduced basicity of the amine. A summary of the curing temperature data found for adducts and salts of several types of amines is given in Table III.

### Effect of the Anion on Curing with Amine Salts

Amine salts, to be effective as curing agents for epoxies, must contain large noncoordinating anions. Curing temperatures found for several anilinium salts are listed in Table IV.

TABLE IV  
Curing Temperature of Aniline Salts

Salt	Catalyst molality	Temperature, °C.
$C_6H_5NH_3^+AsF_6^-$	0.173	52
$C_6H_5NH_3^+BF_4^-$	0.175	58
$C_6H_5NH_3^+PF_6^-$	0.176	60
$(C_6H_5NH_3^+)_2SiF_6^{-2}$	0.0887	Poor cure, 180
$C_6H_5NH_3^+Cl^-$	0.177	No cure, 250
$(C_6H_5NH_3^+)_2SO_4^{-2}$	0.088	Poor cure, 230

The salts effective as curing agents (see Table IV) contain anions which have little interaction with the anilinium ion, as indicated by the absence of bonded N—H bonds in the infrared spectra (Fig. 1). (An exception to the rule was the hexafluorosilicate salt whose spectra indicated no amine hydrogen bonding but which was relatively ineffective as a curing agent.) These results appear logical since anions which interact with the anilinium ion will reduce the acidity of the anilinium ion and consequently will reduce its ability to interact with the epoxy ring [eq. (1) and (2)], i.e., reduce the acidity of the complex.

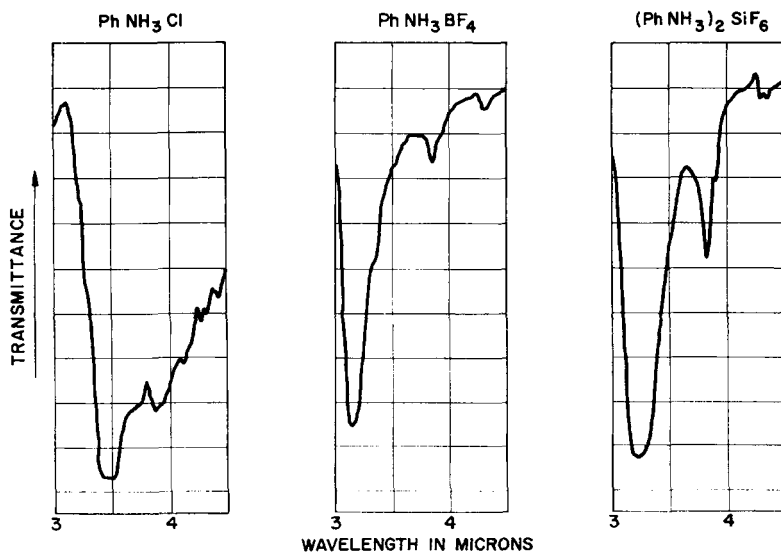
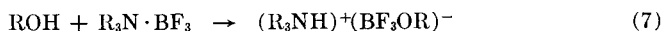


Fig. 1. Absorption spectra of aniline salts in the N—H vibrational region.

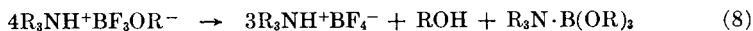


### Role of Tertiary Amine Complexes

Since tertiary amine–boron trifluoride complexes do not contain hydrogen atoms, their behavior would appear at first to fall outside of the scope of our theory. However closer examination suggests a means of including them, by a mechanism which may be applicable to primary and secondary amine complexes as well. Commercial epoxy resins generally contain a variable, although frequently small, amount of hydroxyl groups. The molality of the hydroxyl function is in excess of the catalyst concentrations used. In addition a small amount of adventitious water is normally present. Both protic moieties function as cocatalysts with Lewis acids (which are otherwise ineffective). These cocatalysts may also be reactive towards the tertiary amine–Lewis acid complexes according to eq. (7).

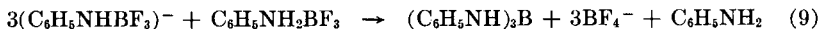


Thus, in comparing complexes of tertiary amines with those of primary or secondary amines one would be comparing the reactivity of two salts. It is not certain that the anions would even differ, since the salt thus produced can react according to eq. (8).<sup>20</sup>



The same kinds of reactions may, of course, occur with primary and secondary amine complexes of boron trifluoride,<sup>10</sup> yielding a reduced catalyst concentration. The effect of this on the curing time would depend upon the particular catalyst, since the amine borate produced is also a catalyst although of generally lower activity.

Similar disproportionations of the anion formed from primary or secondary amine–boron trifluoride catalysts might occur even in the absence of —OH groups. Thus, attempts by us to form salts of the anion  $\text{RNHBF}_3^-$  were unsuccessful. For example, attempts to prepare such an anion, i.e.,  $(\text{C}_6\text{H}_5\text{NHBF}_3)^-$ , from aniline–boron trifluoride, gave instead  $(\text{C}_6\text{H}_5\text{NH})_3\text{B}$ , indicating reaction occurs according to eq. (9).



## EXPERIMENTAL

### Materials

The amine– $\text{BF}_3$  adducts were prepared by reacting equimolar quantities of the amine, dried over calcium hydride, with  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  in dry benzene. The solid complexes were recovered by filtration, washed with fresh benzene, and then dried at reduced pressure. In a few instances the complexes were quite soluble in benzene and were recovered by removing a large portion of benzene, filtering, and washing the solids with petroleum ether before drying. The adduct of aniline and phosphorus pentafluoride was synthesized by treating aniline, in benzene, with gaseous  $\text{PF}_5$ . The reaction was stopped while  $\text{PF}_5$  was still being absorbed (to prevent side reac-

TABLE V  
Salts and Adducts Prepared for Evaluation as Curing Agents  
for Bisphenol A Epoxy Resins

Compound	Melting point, °C.	Solubility
$C_6H_5NH_2 \cdot BF_3$	164-166	Poor
$C_6H_5NH_3^+BF_4^-$	158-160	Poor
$C_6H_5NH_2 \cdot PF_6$	210-240	Poor
$2,6-Et_2C_6H_3NH_2 \cdot BF_3$	75-100	Good
$2,6-Et_2C_6H_3NH_3^+BF_4^-$	118-120	Good
$2,6-Et_2C_6H_3NH_3^+PF_6^-$	118	Good
$EtNH_2 \cdot BF_3$	90	Fair
$EtNH_3^+BF_4^-$	—	Fair
$sec-Bu_2NH \cdot BF_3$	38-42	Good
$sec-Bu_2NH_2 \cdot BF_4^-$	142-144	Good
$i-Pr_2NH_2 \cdot BF_4^-$	140-150	Good
$Et_2NH \cdot BF_3$	Liquid	Good
$i-Pr_2EtNH \cdot BF_4^-$	213-215	Good
$C_6H_5NMe_2 \cdot BF_3$	94-97	Good
$(C_6H_5)_3P \cdot BF_3$	140	Good
$(C_6H_5)_3PH \cdot BF_4^-$	160-170	Good
$i-PrNH_2 \cdot BF_3$	105-110	Fair
$(C_6H_5)_2NH \cdot BF_3$	155-165	Poor
$(C_6H_5)NH_3^+AsF_6^-$	208-214	Fair
$(C_6H_5NH_3)_2^+SiF_6^-$	>230	Fair

tions). The resulting mixture was filtered, the white solids washed with petroleum ether and dried at reduced pressure.

The salts were obtained by reacting aqueous fluoroboric acid with the stoichiometric quantity of amine and removing volatiles at reduced pressures. The solids thus obtained were refluxed in benzene with the use of an azeotrope trap to insure complete removal of water, then filtered and the solids dried at reduced pressure. The salts and adducts used are listed in Table V with their melting points and solubilities in bisphenol A epoxies at the 3-5% level. Good solubility was not essential for cure.

The epoxies used were Araldite 6005 (Ciba Products, Inc.), Epon 820, and Epon 826 (Shell Development Co.). Araldite 6005 and Epon 826 are primarily the diglycidyl ether of bisphenol A, while Epon 820 contains some longer chain units and 4-5% phenyl glycidyl ether as a reactive diluent. The hydroxyl content of these resins is relatively low and not listed in the manufacturer's literature. Private communications from Shell indicated Epon 820 to contain 0.06 hydroxyl equivalent/100 g. while Epon 826 contained 0.05 hydroxyl equivalent/100 g. Epon 820 also contained some phenolic endgroups. There appeared to be little or no difference in the reactivity of these resins towards the catalysts tested.

### Procedure

The desired amount of catalysts, usually 2-4 wt.-%, depending on its molecular weight, and 5-10 g. of the resin were weighed into an 18 × 150

mm. test tube which was then placed in an oil bath. The bath was slowly raised in temperature while the tube contents were agitated with a glass rod to detect gel point which was taken as the curing temperature. The heating rates were generally about 1°C./min. Close control of the heating rate did not appear to be critical.

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### Résumé

L'hypothèse communément admise dans la littérature est que les complexes d'amines des acides de Lewis (particulièrement le trifluorure de bore) modifient les résines époxy grâce à leur dissociation par laquelle ils libèrent l'acide de Lewis qui alors fonctionne comme catalyseur vrai. On démontre que cette image des complexes acides de Lewis avec des amines est incorrecte. Un autre mécanisme est proposé qui est en accord avec (a) l'absence de corrélation entre la stabilité du produit d'addition et la réactivité, (b) la similitude de réactivité des produits d'addition du fluorure de bore et des sels fluoroboriques correspondants, (c) la relation entre les réactivités des produits d'addition du BF<sub>3</sub> et du pentafluorure de phosphore, (d) une corrélation entre la réactivité et la structure de l'amine dans le complexe et (e) l'effet de l'anion sur la réactivité des sels d'amines. La réactivité relative de ces catalyseurs est mise en équation avec la température à laquelle la gélification se passe par chauffage à une vitesse suffisamment constante.

### Zusammenfassung

Nach der allgemein üblichen Annahme in der Literatur härten Aminkomplexe von Lewissäuren (besonders Bortrifluorid) Epoxyharze durch ihre Dissoziation unter Freisetzung der Lewissäure, welche dann als der "wahre" Katalysator wirkt. Es wird gezeigt, dass dieses Bild von der Amin-Lewissäurekomplexhärtung möglicherweise nicht korrekt ist. Es wird ein anderer Mechanismus vorgeschlagen, welcher konsistent mit (a) dem Fehlen einer Korrelation zwischen Adduktstabilität und -reaktivität, (b) einer Ähnlichkeit der Reaktivität von  $\text{BF}_3$ -Addukten und den entsprechenden Fluorboratsalzen, (c) der Beziehung zwischen der Reaktivität von  $\text{BF}_3$ - und  $\text{PF}_5$ -Addukten, (d) einer Korrelation zwischen Reaktivität und Struktur einesamins im Komplex und (e) dem Einfluss des Anions auf die Reaktivität von Aminalsalzen ist. Die relative Reaktivität der Katalysatoren wurde zur Temperatur in Beziehung gesetzt, bei welcher die Gelbildung beim Erhitzen mit einer ziemlich konstanten Geschwindigkeit eintritt.

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