

# The Effect of Some Catalysts on the Curing of Oxiranes with *p*-Phenylenediamine

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## Synopsis

The effect of some alcohols, acetylacetonates of transition metals, and manganese stearate and naphthenate on the curing reaction of a diglycidyl ether of bisphenol-A with *p*-phenylenediamine is studied. Maximum catalytic activity is shown by the manganese compounds and triethanolamine.

## INTRODUCTION

There has been considerable interest in recent years in the development of a "latent catalyst" for the curing of epoxy resins; most of the work is patented due to its commercial importance.<sup>1-3</sup> A great variety of compounds has been used as catalysts for this reaction.<sup>4-8</sup> The use of acetylacetonates of transition metals<sup>2,3,9</sup> and metal salts<sup>10-13</sup> as curing catalysts for epoxy resins is reported. Though the use of acetylacetonates as catalysts for the anhydride cure of epoxy resins has been described, their use with *p*-phenylenediamine is not reported. It has been shown<sup>14,15</sup> that the addition of amine to epoxide can be accelerated by hydrogen donors. However, there seems to be no report on the use of metal naphthenates or stearates for the curing of the diglycidyl ether of bisphenol-A (DGEBA) with *p*-phenylenediamine (PDA).

In this paper we have studied the effect of the acetylacetonates of Fe(III), Co(II), Ni(II), and Mn(II), manganese stearate and naphthenate, and some alcohols on the curing of DGEBA with PDA.

## EXPERIMENTAL

### Materials

Commercially available chemicals were used without any further purification. The materials used were the acetylacetonates (ac ac) of Mn(II), Fe(III), Co(II), and Ni(II) (Fluka), manganese stearate and naphthenate (Vir-

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al Rasayam), triethanolamine and amyl alcohol (Sarabhai), 1-butanol and cyclohexanol (E Merck), isobutanol (Purex), *tert*-butyl alcohol (Baker), 2-butanol and PDA (Riedel de Haenag Steelze Hannover).

### Preparation of 2,2-bis(4-Glycidoxyphenyl) Propane (DGEBA)<sup>16</sup>

2,2-(4-Hydroxyphenyl) propane (bisphenol-A) 0.5 and 5 mol of epichlorohydrin were refluxed and sodium hydroxide (1.5 mol as a 30% solution) was added over a period of 2 h; water was removed by azeotropic distillation. After addition of NaOH, the reaction mixture was further refluxed for 8 h and cooled at 60°C. The epoxide was extracted with toluene and distilled to get the title compound.

### Thermal Studies

DGEBA and PDA were mixed thoroughly in the ratio of 1:1. Epoxy-amine curing reactions are exothermic and were followed by differential scanning calorimetry (DSC). DSC experiments were carried out using a DuPont 990 instrument at a heating rate of 10°C min<sup>-1</sup> using a sample weight of 4.0 mg. Typical DSC exotherms are presented in Figure 1. In the case of Fe(ac ac)<sub>3</sub>, it was found that the catalytic activity increased from 1 to 3% by weight of resin and then diminished at higher concentrations (Table I). Subsequent experiments with other acetylacetonates and manganese stearate and naphthenate were carried out keeping the amount of catalyst fixed at 3% by weight since this gave the maximum effect. Similarly, the curing exotherms were also obtained using alcohols as accelerators. The exothermic peak temperatures obtained from DSC runs are presented in Table I.

Thermogravimetric (TG) studies were done on a Stanton Redcroft TG750/770 instrument using 5 mg of the sample.

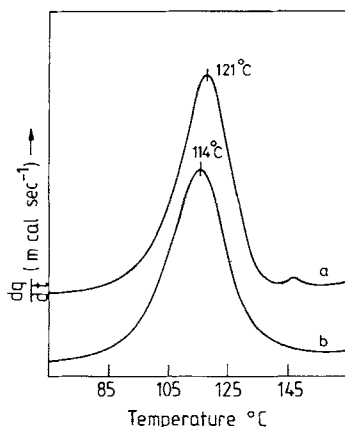


Fig. 1. DSC of a typical curing mixture: (a) DGEBA + PDA; (b) DGEBA + PDA + Ac ac.

TABLE I  
 Exothermic Temperatures Obtained from DSC in the Curing Reaction of DGEBA with PDA

Catalyst	Catalyst concentration (wt %)	Exothermic peak temperature (°C) <sup>a</sup>
Uncatalyzed	—	121
Fe(ac ac) <sub>3</sub>	1.0	120
Fe(ac ac) <sub>3</sub>	2.0	120
Fe(ac ac) <sub>3</sub>	3.0	118
Fe(ac ac) <sub>3</sub>	4.0	120
Fe(ac ac) <sub>3</sub>	6.0	120
Fe(ac ac) <sub>3</sub>	8.0	122
Co(ac ac) <sub>2</sub>	3.0	118
Ni(ac ac) <sub>2</sub>	3.0	118
Mn(ac ac) <sub>2</sub>	3.0	112
<i>Tert</i> -butyl alcohol	2.2	118
Cyclohexanol	2.9	119
1-Butanol	2.2	119
2-Butanol	2.2	120
Isobutyl alcohol	2.2	120
Isoamyl alcohol	2.6	120
Triethanolamine	4.4	112
Manganese stearate	3.0	116
Manganese naphthenate	3.0	114
Mn(ac ac) <sub>2</sub> after heating at 300°C for 2 h	2.8	122
MnSO <sub>4</sub> ·H <sub>2</sub> O	4.1	120
Acetylacetone	3.6	114

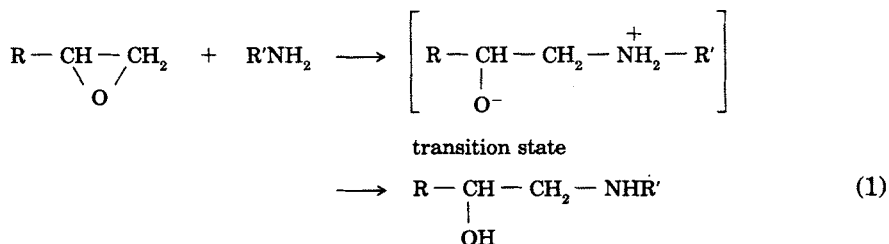
<sup>a</sup> Error ± 1°C.

### Spectral Studies

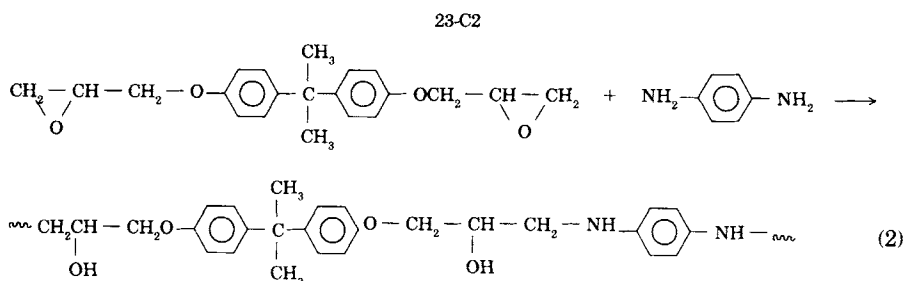
Infrared (IR) spectra were recorded on a Perkin-Elmer Model 597 IR spectrophotometer on a KBr disc or as a KBr pellet. Electronic spectra were recorded on a Beckmann Model 25 double beam spectrophotometer of a 0.1M ethanolic solution of Mn(ac ac)<sub>2</sub> and 0.005M ethanolic solution of Mn(ac ac)<sub>2</sub> + PDA.

### RESULTS AND DISCUSSION

Epoxides readily react with amines to give hydroxy imines.<sup>17</sup> The function of the catalyst is to assist the opening of the oxirane ring:



DGEBA and PDA react to give an extended or cross linked polymer chain



The enhanced reaction rate in the presence of catalysts may be seen from a shift in the peak exotherm to lower temperatures (Fig. 1 and Table I).

Of the catalysts studied in the present investigation, some are effective whereas others are not (Table I). Among the acetylacetonates,  $\text{Mn}(\text{ac ac})_2$  has a maximum effect on the curing reaction (Table I). In view of the exceptional activity of  $\text{Mn}(\text{ac ac})_2$ , the study of the manganese compounds was extended to the stearate and naphthenate.

### The Effect of Metal Acetylacetonates

The greater catalytic activity of  $\text{Mn}(\text{ac ac})_2$  may depend on several factors. The relative solubility of the acetylacetonates in the epoxy-amine mixture may be one of the contributing factors. A second factor which is likely to influence the mechanism is the tendency of these compounds to decompose or dissociate at higher temperatures. Smith<sup>9</sup> has shown that the most effective latent catalysts for the anhydride cure of epoxides undergo thermal decomposition in the temperature range in which the curing reaction takes place, and he concluded that the decomposition products are likely to be the actual catalytic species.

In the present investigation however, the more stable species shows greater catalytic activity.  $\text{Mn}(\text{ac ac})_2$  decomposes at 205°C whereas  $\text{Ni}(\text{ac ac})_2$  and  $\text{Co}(\text{ac ac})_2$  decompose at 95 and 90°C, respectively (Fig. 2). On the other hand,  $\text{Fe}(\text{ac ac})_3$ , which is stable up to 190°C, shows no catalytic activity. The anomalous behavior of  $\text{Fe}(\text{ac ac})_3$  may be attributed to its saturated coordination state. It may be mentioned here that Van Hoene et al.<sup>18</sup> investigated the thermal decomposition of some metal acetylacetonates by mass spectrometric studies in the range 150–400°C and found the order of stability to be  $\text{Ni}(\text{II}) > \text{Fe}(\text{III}) > \text{Co}(\text{II})$ . In the present investigation, TG studies indicate that  $\text{Fe}(\text{ac ac})_3$  and  $\text{Mn}(\text{ac ac})_2$  are more stable than  $\text{Ni}(\text{ac ac})_2$ .

The most likely degradation route for the acetylacetonates is via the formation of metal ion, metal oxide, or other ionic fragments and an organic moiety. Catalytic activity could involve interaction of these decomposition products with the epoxide.  $\text{Mn}(\text{ac ac})_2$  was heated at a temperature of 300°C for 2 h. A weighed amount of the decomposition residue when added to the reaction mixture did not produce any shift in the position of the exotherm (Table I). A typical salt  $\text{MnSO}_4$  also did not show any catalytic activity

(Table I). It may therefore be concluded that the metal ion or the oxide is not the active species.  $\text{MnSO}_4$  has been reported<sup>11</sup> to catalyze the curing with *N,N'*-disubstituted phenylenediamine although in the present case  $\text{MnSO}_4$  showed negligible catalytic activity. The other possible decomposition product, namely acetyl acetone, has been found to catalyze this reaction, even though ketones usually act as retarders for the epoxy-amine reaction due to ketamine formation.<sup>19</sup>

Another possibility is that the reaction proceeds via complex formation between the metal and either the epoxide group or *p*-phenylenediamine. It is known that  $\text{Mn}(\text{ac ac})_2$  forms adducts with one or two molecules of a Lewis base.<sup>20</sup> Figure 3 shows IR spectra taken at intervals of 10 min during the curing reaction. The reaction was studied at 60°C rather than 120°C since the reaction was too fast at higher temperatures. The spectra (Fig. 3) showed no shift in the position of the band at  $910\text{ cm}^{-1}$  (epoxy group), although there was a continuous decrease in the intensity as the reaction progressed. In order to further confirm the absence of complex formation, the acetylacetonates were heated with the epoxy resin in the ratio of 1:2 on a KBr disc at 60°C and the spectra were recorded at intervals of 15 min. In this case also there was no change in the position of the band at  $910\text{ cm}^{-1}$  (Fig. 4). No evidence therefore could be obtained for complex formation between the epoxy group and the metal. If such a complex is formed, it is too short-lived to be detected by IR spectroscopy.

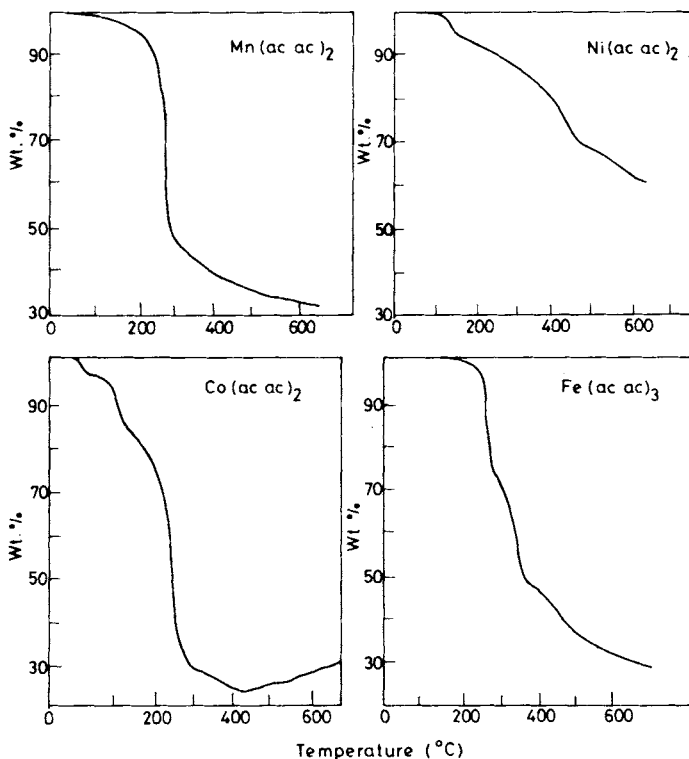


Fig. 2. TG of the metal acetylacetonates.

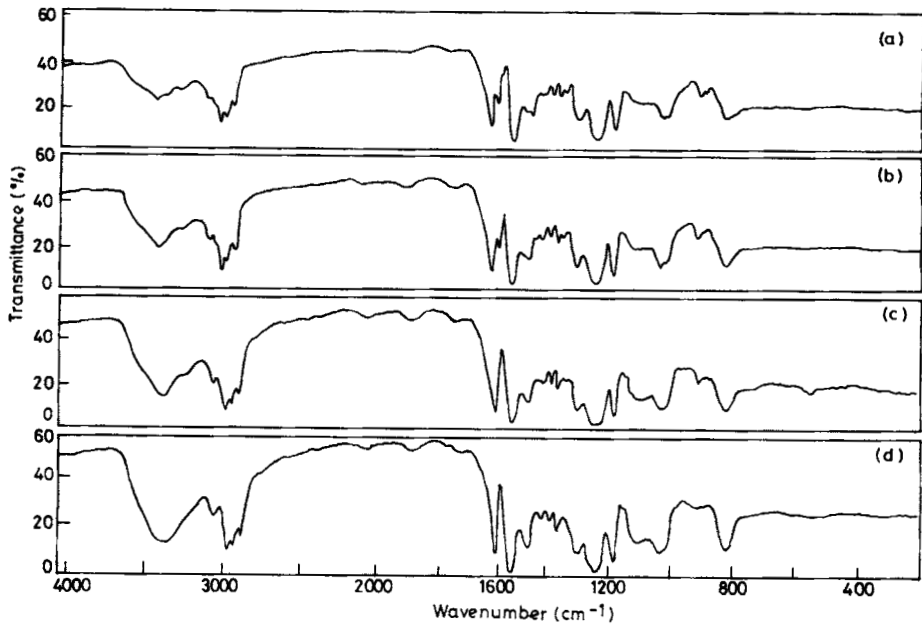


Fig. 3. IR spectra of a mixture of DGEBA + PDA +  $\text{Mn}(\text{ac ac})_2$  recorded at 10 min intervals at 60°C: (a) immediately after mixing; (b) after 10 min; (c) after 20 min; (d) after 30 min.

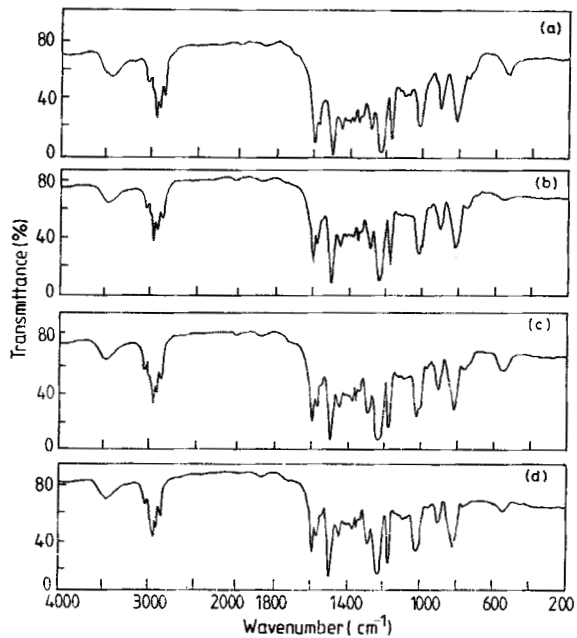


Fig. 4. IR spectra of a 1:2 mixture of  $\text{Mn}(\text{ac ac})_2$  + DGEBA recorded at 15-min intervals at 60°C: (a) immediately after mixing; (b) after 15 min; (c) after 30 min; (d) after 45 min.

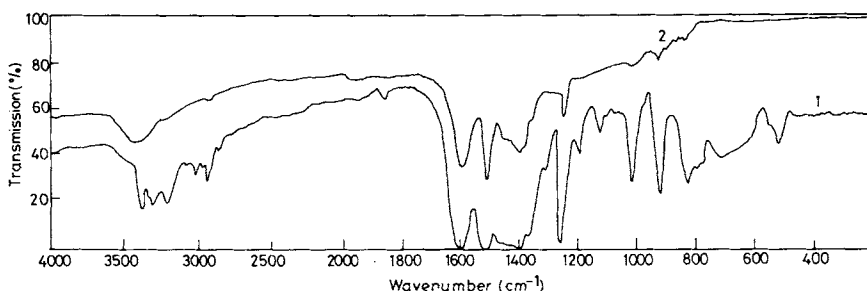
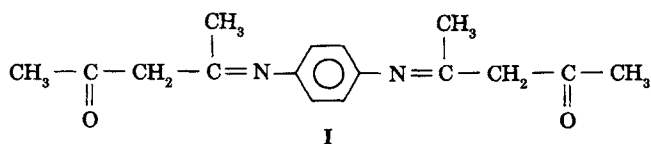
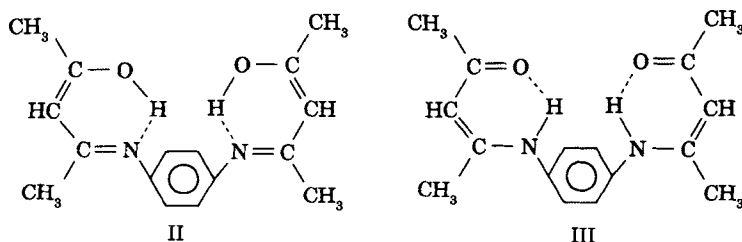


Fig. 5. IR spectra of 1:2 mixture of  $\text{Mn}(\text{ac ac})_2 + \text{PDA}$  recorded: (a) immediately after mixing; (b) after heating at  $120^\circ\text{C}$  for 1 h.

It is possible that PDA itself could form a complex with the metal ion<sup>20</sup> or displace acetylacetonate from the coordination sphere. A mixture of  $\text{Mn}(\text{ac ac})_2$  and PDA in the ratio of 1:2 was heated at  $120^\circ\text{C}$  for 1 h and the IR spectrum was recorded (Fig. 5). Marked changes in the IR spectra were observed. The spectrum of the mixture is characterized by the disappearance of the N—H stretching peaks at  $3300$  and  $3380\text{ cm}^{-1}$ .  $\text{Mn}(\text{ac ac})_2$  may react with PDA to form the compound I:



It is well known that acetylacetonate reacts with primary amines to form Schiff's bases.<sup>21</sup> Compound I can exist in more than one tautomeric form (II & III).<sup>22</sup> It can act both as a proton donor and acceptor and is expected to be a good catalyst for the epoxy-amine reaction. Figure 6 shows the visible spectrum of a  $0.1\text{M}$  solution of  $\text{Mn}(\text{ac ac})_2$  in ethanol.  $\lambda_{\text{max}}$  of  $\text{Mn}(\text{ac ac})_2$  is shifted from  $450\text{ nm}$  to a lower wavelength ( $400\text{ nm}$ ) in the presence of PDA. Martell et al.<sup>23</sup> have reported that the frequencies of the principal absorption bands in the visible region occur at much shorter  $\lambda$  and are more intense for Schiff bases.  $\lambda_{\text{max}}$  of the  $\beta$ -diketone is found displaced  $100\text{ nm}$  or more towards longer  $\lambda$  than that of the Schiff base derived from the same  $\beta$ -diketone.



It has been shown that the major product of decomposition of  $\text{Ni}(\text{ac ac})_2$ ,  $\text{Co}(\text{ac ac})_2$ ,<sup>18</sup> and  $\text{Fe}(\text{ac ac})$ ,<sup>18,24</sup> is acetone, and acetylacetonate was identified only in trace amounts. However, acetylacetonate is the primary product in the decomposition of  $\text{Mn}(\text{ac ac})_2$ .<sup>25</sup> This could be the reason for the greater catalytic activity of  $\text{Mn}(\text{ac ac})_2$ .

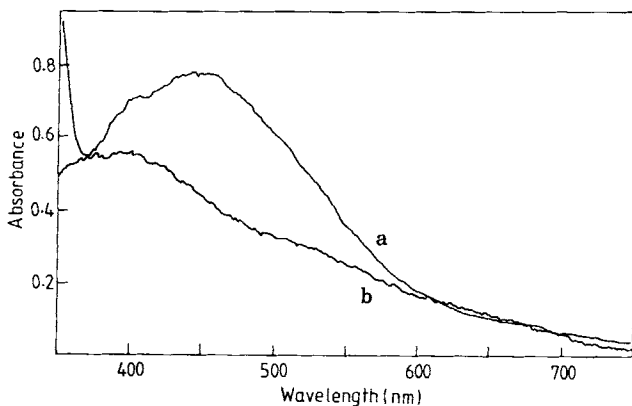
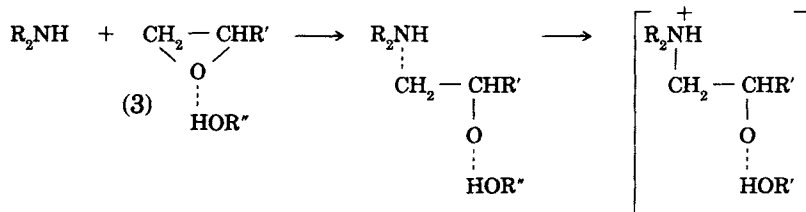


Fig. 6. Visible spectra of: (a) 0.1M solution of  $\text{Mn}(\text{ac ac})_2$  in ethanol; (b) 0.005M solution of PDA +  $\text{Mn}(\text{ac ac})_2$  in ethanol.

### The Effect of Alcohols

Schechter et al.<sup>14</sup> as well as Kakuri and Noguchi<sup>15</sup> have shown that the amine-epoxide reaction is accelerated by the addition of alcohol, water, or other hydrogen donor in the system and suggested a mechanism involving opening of the epoxide ring with the aid of hydrogen bonding in the transition state:



The acceleration of epoxide-amine reactions has been related by Gough and Smith<sup>19</sup> to the ability of the accelerator to form a hydrogen bond. Of the alcohols studied in the present investigation, triethanolamine shows the greatest catalytic activity followed by *t*-butyl alcohol. The efficiency of an alcohol can be considered approximately proportional to its acidity.

Triethanolamine has three alcoholic groups per molecule available for hydrogen bonding and from purely statistical considerations it is expected that triethanolamine should show greater catalytic activity. Alcohol accelerators have the unique property that for the same equivalent hydroxyl concentration, the accelerating effect increases as the number of hydroxyl groups per molecule increases.<sup>26</sup> This is supported by the results in the case of triethanolamine.

### CONCLUSIONS

Acetylacetonates of some transition metals and some alcohols have been found to be effective catalysts for the curing of a DGEBA resin with PDA. Maximum catalytic activity was exhibited by  $\text{Mn}(\text{ac ac})_2$ . This activity may be due to the formation of a Schiff's base adduct of acetylacetone with PDA. In the alcohol series, triethanolamine showed maximum catalytic activity.



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