

**DRIER CATALYST ACTIVITY OF  
1,10-PHEANTHROLINE IN ORGANIC COATINGS**

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# DRIER CATALYST ACTIVITY OF 1,10-PHENANTHROLINE IN ORGANIC COATINGS

## *Lowering of the Activation Energy*

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The over-all activation energy for the oxidative polymerization of a number of alkyd vehicles, in the presence of metallic driers, has been determined. The effect of adding 1,10-phenanthroline to these systems has been observed, and the resultant lowering of the over-all activation energy is discussed in terms of both steric and energetic factors of the complexes formed, and in relationship to conventional theories of the oxidative polymerization mechanism.

The ability of 1,10-phenanthroline to promote the activity of paint driers has been known for many years. Its activity in oleoresinous and latex paints has been explained partly on the basis of the complex species formed by coordination of 1,10-phenanthroline with the metal.

This article offers a kinetic analysis of the drying of an alkyd is an attempt to explain further the mechanism of accelerator action and to uncover further knowledge of the active species when the drier metal is complexed.

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## Literature Background

Unusual activity of 1,10-phenanthroline with manganese salts	(16)
Optimum ratio of 1,10-phenanthroline to metals gives maximum acceleration	(13)
Catalysis of linseed oil by amine-metal catalysts	(11)
Cobalt salts preferred with 1,10-phenanthroline in emulsion systems	(14)
Complex species formed with 1,10-phenanthroline and metal are combined in an oleoresinous system	( 2)

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## Determination of Reaction Rates

The temperature dependence of reaction rates follows a relationship discovered by Arrhenius (1) and amplified by Eyring (4):

$$\kappa = Ae^{-E/RT} \quad (1)$$

which states that the rate constant  $\kappa$  depends on two factors – the  $A$  term which represents the collision or vibrational frequency (3) and includes contributions from entropy and steric effects; and the exponential term which consists of the activation energy  $E$ , the absolute temperature  $T$ , and the gas constant  $R$ . In this work, *rates*, rather than the rate constants, were analyzed kinetically; but inasmuch as the two are related in a comparative study (6), the symbol,  $\kappa$ , is used for measured rates.

A properly controlled kinetic study reveals information on the number of molecules involved in a reaction and the effect of their structural features on the course of the reaction. Unfortunately, rigorous control is rarely attainable in a complex reaction involving commercial materials, and as a result, some of the more valuable information is evasive. In the present case of alkyd drying, the  $A$  term has been analyzed in terms of vibrational frequencies and a combination of entropy and steric effects even though certain restrictions limit the rigorous interpretation of such data (8). The  $E$  term has yielded new knowledge of the activated intermediate, which forms in the oxidation step of drying of unsaturated molecules.

The adaptation of drying data to kinetic analysis was done in the present instance by assuming that the conventional dry hard tack-free drying time of the alkyd represents the same degree of reaction (cure) in all cases studied; the reciprocal of this drying time then represents the over-all rate in *arbitrary units*. The procedure is quantitative only in the intended sense of comparing reaction rates rather than in measuring absolute values of the rate constant; it lacks rigor because the concentrations of reactive species in the plant are unknown and because general agreement has not yet been reached regarding details of the reaction mechanism.

In this work, the metal is considered to be the catalyst; the 1,10-phenanthroline is called the accelerator.

## Test Procedures

Controls and formulations with 1,10-phenanthroline were prepared from a short soya alkyd (Glyptal 2517, General Electric Company), some containing

0.005% manganese and some containing no metal. The 1,10-phenanthroline was present in amine-metal molar ratios of 0.6/1.0 to 2.3/1.0, and in corresponding amounts in the metal-free formulations; it was added as a 38% solution in a butanol-ethylhexanoic acid mixture (1,10-Phenanthroline was introduced in the form of ACTIV-8, a product of the R. T. Vanderbilt Co.) Manganese was introduced as 6% manganese naphthenate.

One day after the preparation of each formulation, two sets of five films (0.001 inch dry film thickness) were cast on plate glass and tested at temperatures ranging from 75° to 350° F, using a Gardner Drygraph (7) modified so that the driving mechanism could be operated outside an oven. The dry hard tack-free time was determined. Four years later the process was repeated with greater emphasis on ascertaining the precision of the measurements. Standard deviations (s), calculated for each set of five determinations, rarely exceeded 2% of the measured drying time. Standard deviations of two independent sets at each temperature were slightly higher.

## Results

Drying times are recorded in Table 1 for the original formulations, all of which contained 0.005% manganese. Over-all reaction rates were determined on a relative basis from the reciprocals of the drying times in second, for example  $\kappa = 1.0/(5400 \times 60) = 3.089 \times 10^{-6}$  for the 5400-minute entry. The dimensions of  $\kappa$  depend on the order of reaction, which was not determined. Results of the conversion of drying times to rates appear to Table II.

When logarithms are taken of both sides of Equation 1 the result is.

$$\text{Log } \kappa = \text{log } A - \frac{E}{2.3R} \frac{1}{T} \quad (2)$$

Consequently,  $\log \kappa$  is plotted against reciprocal absolute temperature (Figure 1). The vertical lines representing the data points in Figure 1 show the spread of values for three amine-metal ratios.

Clearly, the 1,10-phenanthroline-accelerated formulations were less temperature-dependent than the conventional formulation ( $E$  dropped from 11, to 7.7 kcal. per mole) for all ratios of amine to metal studied.

The aged series showed the same trend ( $E$  dropped from 13 to 8.0 kcal. per mole); these results are shown in Figure 2. In addition, an  $E$  value of 17 kcal. per mole was obtained for the uncatalyzed alkyd, regardless of the presence or absence of 1,10-phenanthroline. Considerably more curvature was observed in the aged formulations (Figure 2) than in the original formulations, possibly because the reaction became diffusion-controlled at high rates. It is also conceivable, despite the assumption to the contrary, that the curvature resulted from the fact that the drying time did not represent the same degree of cure at all

temperatures or all rates, in view of the possibility of side reactions occurring at higher temperatures.

**Table I. Drying Times (Minutes) of Original Alkyd Films with 0.005% Manganese Drier**

$\theta$ (° F.) <sup>a</sup>	(1000/T) (° K.)	<i>Wt. Ratio 1,10-Phenanthroline/Mn</i>			
		<i>0</i>	<i>1.9</i>	<i>3.8</i>	<i>5.7</i>
		<i>Mole Ratio 1,10-Phenanthroline/Mn</i>			
		<i>0</i>	<i>0.6</i>	<i>1.2</i>	<i>2.3</i>
<i>Drying Times, Min.</i>					
75	3.37	5400	1500	760	650
150	2.95	430	132	130	170
200	2.73	100	70	54	54
250	2.54	55	38	30	28
300	2.37	23	18	16	19

<sup>a</sup> Fahrenheit temperature,  $\theta$ , is converted into absolute temperature by adding 273° C. to the Centigrade equivalent of  $\theta$ .

**Table II. Drying Rates (X10<sup>5</sup>) of Original Alkyd Films**

(1000/T) (° K.)	<i>Mole Ratio 1,10-Phenanthroline/Mn</i>			
	<i>0</i>	<i>0.6</i>	<i>1.2</i>	<i>2.3</i>
<i>Drying Rates, X10<sup>5</sup></i>				
3.37	0.31	1.11	2.9	2.56
2.95	3.88	12.6	12.8	9.80
2.73	16.7	23.8	30.9	30.9
2.54	30.2	43.9	55.5	59.5
2.37	72.4	92.7	104	87.8

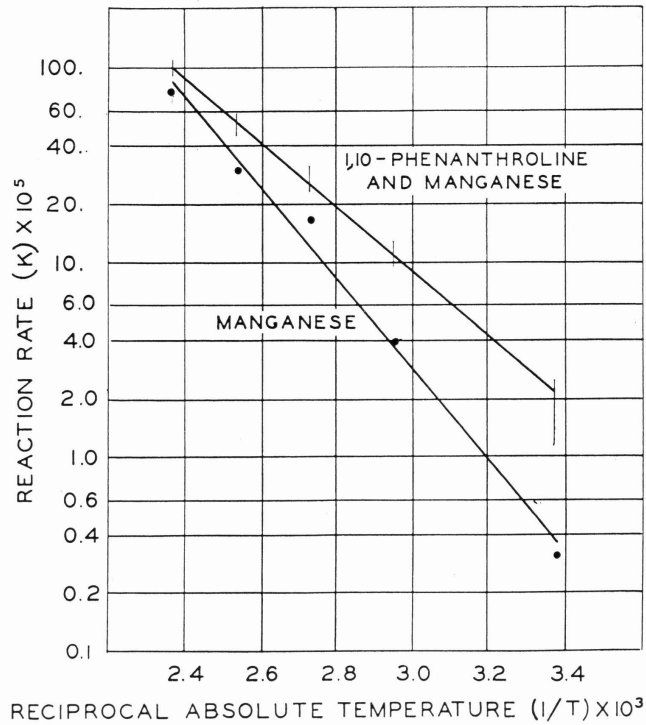


Figure 1. Activation energy of original series

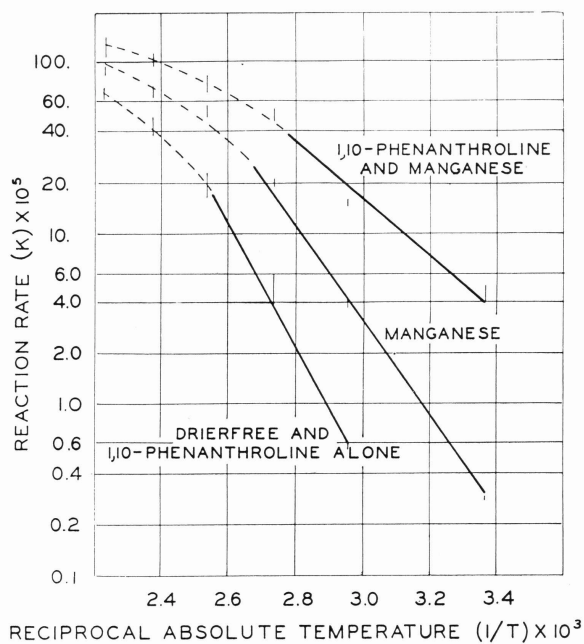


Figure 2. Activation energy of aged series

Other systems produced a similar family of curves when three manganese concentrations and their 1,10-phenanthroline-accelerated counterparts were

tried. Quantitative agreement was only fair, however; a similar soya alkyd in a different solvent gave a different temperature dependence but still revealed a drastic lowering of activation energy on addition of 1,10-phenanthroline. A castor oil alkyd (Glyptal 2480) and a linseed oil alkyd (Glyptal 2452, General Electric Co.) also agreed in qualitative fashion.

The ratio of accelerator to metal is not critical in the range studied.

## Discussion

One result of this work was to learn that complexing manganese by 1,10-phenanthroline reduces the activation energy associated with the oxidative polymerization of conventional coatings. The higher reaction rates of the amine-promoted formulations are accompanied by a decrease in the over-all activation energy  $E$ . The decrease is reflected in a fanning out of the reciprocal temperature plots as temperature is decreased, so that wide differences in reaction rate at low temperatures are observed. The possibility that the convergence of the two lines in Figures 1 and 2 resulted from decoordination of the complex at higher temperatures was ruled out by the independence of  $\kappa$  on amine-metal ratio at the two highest-amine concentrations employed.

Evaluation of the five  $A$  and  $E$  parameters produced the results given in Table III. Both the catalyst and the accelerator (in the presence of catalyst) lowered  $A$  as well as  $E$ .

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**Table III. Activation Energies and Frequency Factors**

	$E$ (kcal.)	$A$ (sec. <sup>-1</sup> ) <sup>a</sup>
Original Films		
With Mn drier	11	300
With drier + 1,10-phenanthroline	7.7	16
Aged Films		
With no drier	17	300,000
With Mn drier	13	6,000
With drier + 1,10-phenanthroline	8.0	10

<sup>a</sup> The  $A$  factor is relative, only. Dimensions are based on assumed first order kinetics.

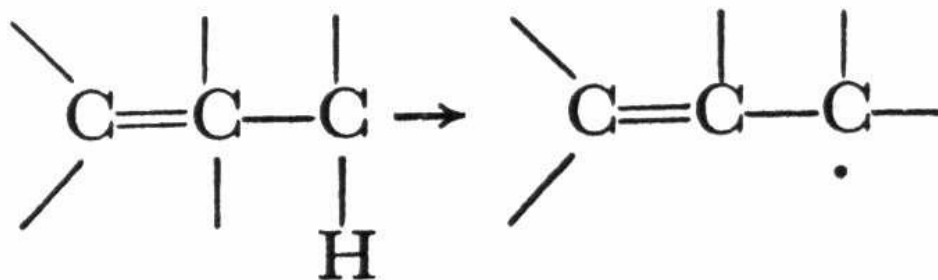
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Fairlough and Hinshelwood (5) have observed that reduction in  $E$  frequently accompanies a reduction in  $A$ , and suggest that  $\log A$  is inversely proportional to  $1/\sqrt{E}$ . The basis of this functional relationship between  $A$  and  $E$  is the assumption that a decrease in the bond strength lowers both  $E$  and vibrational frequency, and therefore permits fewer chances for the activated intermediate to get in phase for reaction before it reverts to the original reactants. Consequently, activation of oxygen by metal would be expected to lower the  $A$  factor by reducing the vibrational frequency of the carbon-oxygen bond.

The absolute magnitudes of the five  $A$  parameters cannot be interpreted in terms of collisions or vibrational frequencies (which are of the order of magnitude of  $10^{13}$  per second); they not only vary widely from system to system, but also they involve extensive extrapolation into an unattainable region.

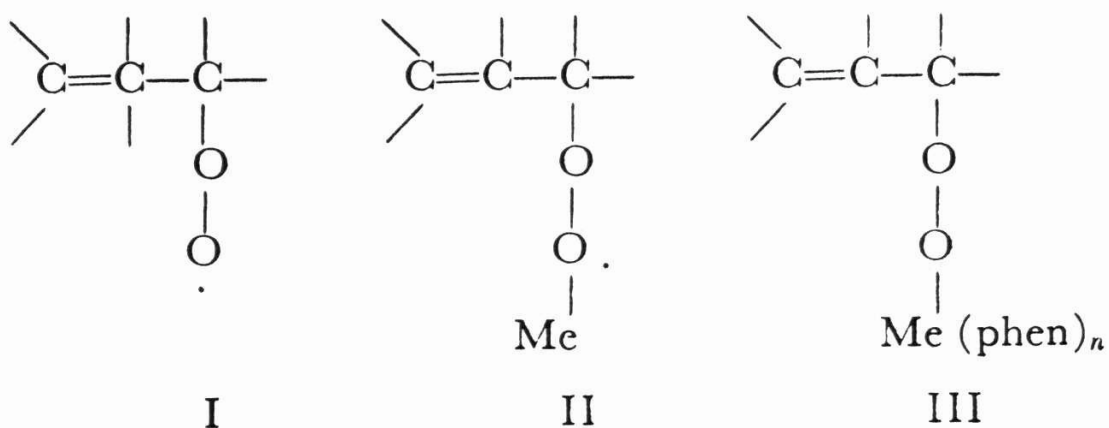
It is best to consider the oxidative polymerization in steps.

**Initiation** of the reaction involves abstraction of a hydrogen atom from the  $\alpha$ -methylene carbon atom (general contained in a 1,4 diolefin-type structure):



There is little doubt that oxygen participates in this step, although it is only possible to speculate on the details of the mechanism. An oxygen molecule replaces a hydrogen atom at the  $\alpha$ -carbon, whereupon the released hydrogen becomes attached to the most likely partner (either to another oxygen to form the  $\cdot\text{OOH}$  radical or to the  $\alpha$ -peroxide, **I**). The lowering of  $E$  by the metal signifies that the activated intermediate **II** (with the metal attached to the oxygen) is formed with less expenditure of energy than is intermediate **I**. Further reduction in  $E$  on complexing suggests that intermediate **III** is formed even more readily than **II**.

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**Propagation** of the reaction, on the other hand, requires that (hydro) peroxide (I) to cross link with another unsaturated molecule. Even though the propagation step is the most fruitful one of the development of high molecular weight polymer, it is not likely to be catalyzed by metal; hence, the initiation of the reaction via an oxygenated intermediate provides a more easily understood picture.

**Termination** via the joining of two radicals can be minimized by the shielding effect of the metal, especially if the activation energy is low for the formulation of a metal-oxygen bond. A large concentration of radicals is an undesirable feature because the recombination of two radicals inevitably terminates the chain at that point.

Consequently, one can conclude that the metal accelerates the initiation and hinders the termination of the reaction. Inasmuch as both of these steps involve the polarization of an oxygen atom by the metal, the selection of the rate-determining step is not as critical as if the steps required different explanations. Drier catalysts are known to decrease  $E$  for the initiation step, as was just concluded.

The most satisfactory explanation of the trends in  $A$  involves the entropy (a measure of randomness embodied in term  $A$ ) of activation,  $\Delta S$ . Apparently,  $\Delta S$ , for the uncatalyzed reaction is the lowest of the three formulations (owing to the random approach of oxygen); the amine-shielded metal requires the highest degree of orientation of the approaching oxygen molecule in order to make the effective contact with the drying-oil molecule. An equally logical explanation of the decreased  $A$  factor is steric hindrance of the amine groups around the metal. Inasmuch as the metal is never completely free of coordinating groups even in the absence of amine, the steric effect, although both would be expected to contribute to  $\Delta S$  in the same manner.

A third interpretation of the decreased  $A$  factor is based on the hypothesis that the vibrational frequency of the metal-oxygen bond should coincide as

closely as possible with the  $1455\text{ cm}^{-1}$  frequency of the  $\alpha$ -methylene C-H bond (10). This idea cannot be tested with the present accumulation of data.

The influence of catalyst and accelerator on the over-all reaction rate via  $E$  is more potent than the effect of these agents on  $A$  at the temperatures encountered in air drying and force drying. If a detailed analysis of the mechanism were possible, it would reveal whether the catalyst affects  $E$  for the initiation stage of the reaction ( $E_i$ ) or the polymerization stage ( $E_p$ ). In the absence of data showing the concentration of the immediate species as a function of time, one must speculate on which  $E$  is depressed by the catalyst. A reasonable assertion is that  $E_i$  is the kinetically sensitive term because thermal polymerizations, which occur without catalyst and in the absence of oxygen, are characterized by much higher activation energies than those encountered in oxidative drying.

Another way of reasoning that the role of drying catalysts is to generate active intermediates (rather than to induce them to combine) is as follows: Alkyds refrain from polymerizing as long as oxygen is excluded, and react only when exposed to air (12). This reaction is catalyzed by the drier.

The rate-determining step in the oxidation of drying involves the formation of an activated intermediate with the carbon atom alpha to a double bond. Inasmuch as catalysts have been known for a long time to shorten the induction period of the drying reaction, the explanation offered here is based on peroxide formation. Recent deductions by Mayo (9) that the reaction of molecular oxygen with alkyl radicals is exceedingly rapid lead to the conclusion that a nucleophilic substitution of oxygen for hydrogen takes place at the  $\alpha$ -carbon atom. The catalyst assists by polarizing the oxygen molecule (lower  $E$ ) but makes more stringent demands on the orientation of oxygen with respect to the carbon atom (lower  $A$ ); the 1,10-phenanthroline sheath lends further aid in the energetic sense, but requires even more precise orientation.

These considerations can be shown by an example, although they need not be restricted to the example chosen. The approach of a free-oxygen molecule to the unsaturated functional group (to form intermediate I) may be random; any orientation of the oxygen, perhaps even including a broadside approach (15), could induce the hydrogen to depart from the  $\alpha$ -carbon. On the other hand, the approach of a metal-activated oxygen molecule (to form intermediates II and III) requires at least a head-tail restriction on the possible orientations of the metal-bound oxygen; any approach in which the attached metal spearheads the attack would be fruitless, and the only allowed orientations would be those which are contained in a solid angle of gyration somewhat less than  $180^\circ$ . In short, a wide cone of reaction (reaction zone) determines the allowed orientations.

The orientation required to form intermediate II may be referred to a hemispheric, inasmuch as the potent orientations require the oxygen hemisphere of a rotating metal peroxide radical to face the carbon atom being attacked. The  $A$  factor is lowered by this requirement because fewer collisions are effective than if the oxygen is unattached to metal.

When the metal is complexed, the orientation requirement becomes even more stringent. Instead of hemispheric orientation of the entering oxygen molecule, an orientation directly along the line of approach apparently is needed in the formation of intermediate III. The metal and a good portion of the oxygen are shielded by the amine, with the result that the cone of reaction is sharp – i.e., the reaction zone subtends a much smaller solid angle. Steric hindrance drastically restricts the angle of approach.

The only arbitrary aspect of this picture involves the catalyst in its role as a reaction initiator rather than in the role of an accelerator of the propagation reaction. In the early stages of drying when no peroxide are present, the accelerations must involve initiation, and a reasonable mechanism can be written around the activation of oxygen.

The decrease in  $E$  (from 11-13 to 8) strongly suggests that the electrostatic field of the heterocyclic nitrogen atoms splits the energies of the five  $3d$  orbitals of manganese in such a fashion that at least one orbital has been made more attractive, energetically, to oxygen. This bonus in energy is more than offsets the steric or orientation requirements.

The vibrational frequency of the Mn-O- bond in the oxidized form of the drier is matched with the potent vibrational mode ( $1455\text{ cm}^{-1}$ ) of the alkyd molecule (10), so that the insertion of oxygen into the molecule can take place in concert with the abstraction of hydrogen. Complexing does not appear to aid in this aspect of drying.

In the cases under the consideration the accelerator appears to have little or no effect on the course of the reaction. The metal facilitates the formation of an  $\alpha$ -oxygenated intermediate with interesting results:

At low temperature the number of molecules which react

via far exceed those which react

via the intermediate

At progressively higher temperatures the population of drying oil molecules, which are sufficiently activated to react without the aid of a catalyst, becomes the over-riding factor. As a result, calculated activation energies must be viewed as nominal, rather than quantitatively exact.

The similarity in behavior of accelerated and normal catalysis suggests that 1,10-phenanthroline assists the metal in polarizing the oxygen thereby rendering it more capable of spearheading an attack on the  $\alpha$ -carbon (15).

When all the temperature plots are considered in perspective, a suggestion is detected of a critical temperature and critical rate beyond which the catalyst and accelerator are useless. Despite the curvature of Figure 2 all lines seem to converge on the point,  $T = 350^{\circ}\text{F}$ .  $\kappa = 3 \times 10^{-3}$ . Beyond this temperature or rate, both the catalyst and the accelerator would retard drying if the limiting influences of diffusion had not set in long before that point. No attempt has been made to interpret the coincidence of the three lines at this point, but the fact that they cross is a natural consequence of the lowering of  $E$  at high rates.

## Conclusions

The presence of conventional manganese drier lowers the over-all activation energy for the drying of the alkyds studied.

Complexing of the metal with 1,10-phenanthroline further reduces the activation energy. The ratio of the accelerator to the metal is not critical in the range studied.

The addition of 1,10-phenanthroline to noncatalyzed alkyds has no effect on the activation energy; complexing with the metal is necessary in order to depress  $E$ .

Aging of the vehicle for 4 years has no significant effect on the results of complexing, except to render the drying behavior slightly less amenable to kinetic analysis.

The trends in both steric and energetic factors are consistent with the proposed mechanism of drying whereby the substitution of an oxygen molecule on the  $\alpha$ -carbon atom is enhanced by the presence of an ionic, oxidizable species.

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