

The Estimation of Catalytic Parameters of Metal Acetylacetonates in Isocyanate Polymerization Reactions*

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INTRODUCTION

The use of metal acetylacetonates for promotion of the reaction between isocyanate groups and hydroxyl functions has been described for the most part in patent literature.¹ In the preparation of highly linear, low-gel elastomers by means of addition of polyether or polyester diols to diisocyanates, these catalysts have been used to advantage. Little has been reported, however, on the quantitative catalytic features of these materials. The catalytic parameters for ferric acetylacetonate in the small-molecule, pseudo-unimolecular reaction of phenyl isocyanate and *n*-butanol have been determined by a thermoanalytical technique described earlier,² as have those for the bimolecular reaction reported by Hostettler and Cox.³ Relative catalysis by the iron complex has recently been investigated qualitatively for a polymerization reaction.⁴ In general, methods employed in the past for the investigation of relative catalysis in isocyanate polymerizations include (a) the determination of the decrease in isocyanate through the use of spectrophotometric techniques,⁵ and (b) the "gel-point" method.⁴ The former method may be limited because of the constitution and the optical properties of the base polyol used, while the latter method is tenuous at best. In the present work, some more quantitative aspects of polyaddition catalysis by various metal acetylacetonates are explored through the use of plasticity-time measurements. The increasing viscosity of a "bodying" system or any other easily measured property which changes continuously may be used with equal facility.

In a series of similar reactions, the time required for formation of a certain intermediate in reaction is inversely proportional to the rate of reaction, regardless of the order of reaction, and the following relationship applies:

$$k/k_0 = t_0/t \quad (1)$$

where k and k_0 are the rate constants for the catalyzed and uncatalyzed reactions, respectively, and t and t_0 correspond to the times required for formation of the intermediate species in the catalyzed and uncatalyzed reactions. From the catalysis law, we have the expression:

$$k = k_0 + k_c[C]^x \quad (2)$$

where k_c is the catalytic coefficient, $[C]$ the concentration of catalyst, and x is the order of catalysis. Dividing (2) by k_0 ,

$$k/k_0 - 1 = k_c/k_0[C]^x \quad (3)$$

or

$$\log(k/k_0 - 1) = \log(k_c/k_0) + x \log[C] \quad (4)$$

Thus, by plotting $\log(t_0/t - 1)$ or $\log(k/k_0 - 1)$ against the logarithm of the catalyst concentration, one can determine the catalytic order x from the slope of the plot and the "relative catalytic coefficient," $\log(k_c/k_0)$, from the intercept. The ratio k_c/k_0 is a useful comparative constant and may be stated as the number of times the rate of reaction is increased (over the rate of the uncatalyzed reaction) by a catalyst in "unit concentration." It can be seen that the utility of this term for comparing different catalysts is limited to cases where the orders of catalysis are identical. One unit concentration of catalyst in the present work corresponds to one gram of catalyst per hundred grams of polyester diol, exclusive of the added diisocyanate. To determine molal catalytic coefficients (Table II), one simply multiplies the graphical intercept by the catalyst molecular weight and divides by 11.27 (weight of polyester plus added diisocyanate).

EXPERIMENTAL

The polyester used for these experiments was prepared from a mixture of ethylene glycol (70

* Contribution No. 202.

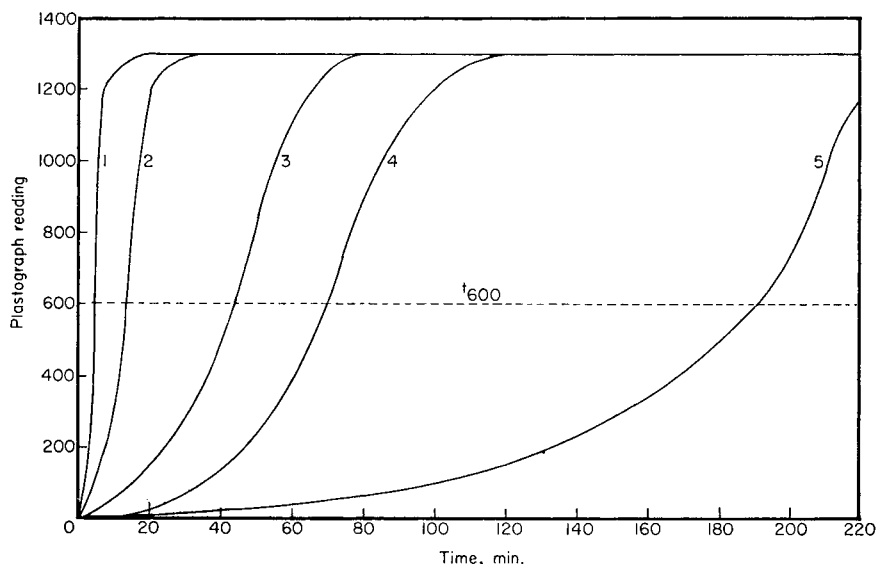


Fig. 1. Plastograph records for the reactions of polyethylene propylene adipate diol and diphenylmethane diisocyanate with ferric acetylacetonate catalyst at concentrations of (1) 0.04, (2) 0.010, (3) 0.005, and (4) 0.0025, pph polyester, and (5) without catalyst.

mole-%), propylene glycol (30 mole-%), and adipic acid, had a final hydroxyl number of 55.3 and an acid number of 1.2, and was terminated for the most part with secondary hydroxyl groups. Approximately 0.04% of each of the catalysts was weighed accurately and dissolved in the polyester, and these stock solutions were cut further with more polyester. The mixtures were vacuum-stripped for 2 hr. at 100°C. and 5 mm. Hg prior to use. Metal acetylacetonates were obtained from Union Carbide Metals Company and used without further purification.

One hundred grams of the polyester-catalyst substrate were charged into the small chamber (220 ml.) of a Brabender Recording Plastograph⁶ at 105°. After the system had come to temperature, one molar equivalent of molten, clear diphenylmethane diisocyanate (Naugatuck Chemical) was added and the development of plasticity was recorded against time. Typical plasticity curves are shown in Figure 1. The final plasticities ranged from about 1300 to 1400 (arbitrary units). The time required for reaching a plasticity or Plastograph reading of 600 was arbitrarily selected as the formation time for the intermediate species defined above. It may be argued that this time lies in the latter phases of reaction (80%), but it is still significantly removed from the completion point, in contrast to the gel time used previously as a criterion. These data are recorded in Table I and plotted according to eq. (4) in Figure 2.

Final catalytic orders and coefficients (in molal units) for the metal complexes investigated are summarized in Table II.

It is important to realize that the Plastograph was not designed to yield highly precise measurements. Temperature control is tedious at best and such factors as the exothermicity of reaction and heat build-up due to hysteresis often have to

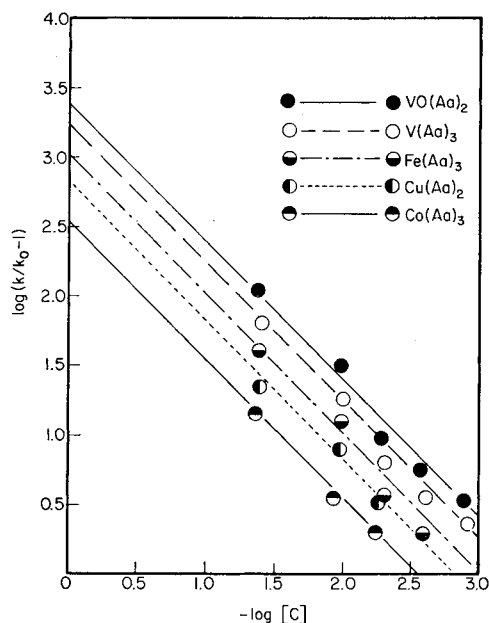


Fig. 2. Plots of catalysis law for various metal acetylacetonates.

TABLE I
Plasticity-Time Data for the Reaction of Polyester
with Diisocyanate at 105°C.

Catalyst	Catalyst concn., pph polyester	$t_{600},^a$ min.	k/k_0
None	—	193	1.00
Cr(Aa) ₃	0.0465	170	1.13
Cu(Aa) ₂	0.0400	8.2	23.6
	0.0103	20.5	9.4
	0.0052	44.0	4.4
Co(Aa) ₃	0.0410	12.0	16.0
	0.0114	43.0	4.5
	0.0057	62.5	3.1
Mn(Aa) ₃	0.0470	7.4	26.1
	0.0118	40.5	4.8
V(Aa) ₃	0.0059	107.0	1.8
	0.0385	2.8	69.0
	0.0095	9.7	19.9
	0.0048	26.2	7.4
	0.0024	41.5	4.65
VO(Aa) ₂	0.0012	59.0	3.3
	0.0420	1.7	113
	0.0104	5.8	33.3
	0.0052	17.3	10.2
	0.0026	29.0	6.65
Fe(Aa) ₃	0.0013	46.0	4.2
	0.0400	4.6	43.5
	0.0100	13.7	14.6
	0.0050	43.2	4.6
	0.0025	69.2	2.9

^a Time elapsed before a plastograph reading of 600 was obtained.

TABLE II
Catalytic Parameters for Metal Acetylacetonates

Catalyst	$k_c/k_0 \times 10^{-4}$, kg/mole	Order of catalysis
Mn(Aa) ₃	21.2	1.75
VO(Aa) ₂	5.65	1
V(Aa) ₃	5.30	1
Fe(Aa) ₃	2.98	1
Cu(Aa) ₂	1.53	1
Co(Aa) ₃	1.11	1
Cr(Aa) ₃	(0.01)	—

be reckoned with. However, it has been observed that the average reaction temperature does not vary more than $\pm 4^\circ$ over the course of a reaction, provided that rates are not excessive (i.e., that a plasticity of 600 is reached in not less than one minute), and that the measured Plastograph reading of 600 occurs well before shearing features cause spurious temperature rises. The wide range of response and sensitivity of the system to the catalysts apparently obviates equipment insensitivity. In order to test the limitations of this method in cases where deviations in the mecha-

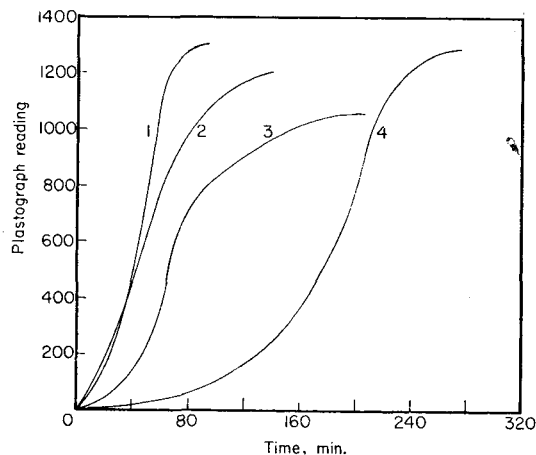


Fig. 3. Plasticity records for polyester-diisocyanate reactions in the presence of (1) 0.005 pph Fe(Aa)₃, (2) 0.005 pph Fe(Aa)₃ + 0.80 pph DECHA, (3) 0.08 pph DECHA, and (4) without catalyst.

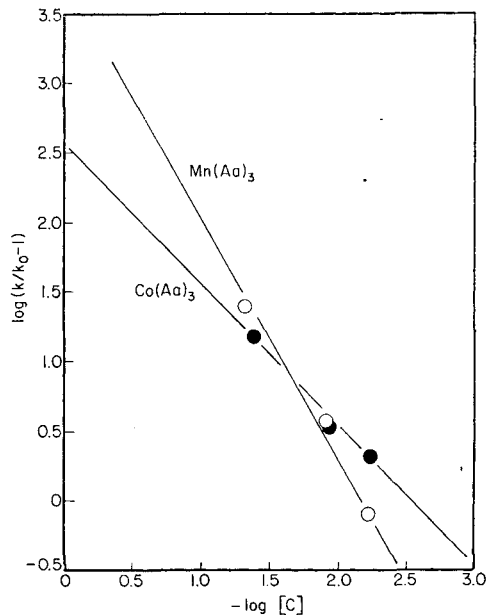


Fig. 4. Comparison of orders of catalysis for cobalt and manganese acetylacetonates.

nism or alteration in the reaction path occur, catalysis by *N,N'*-diethylcyclohexylamine was investigated also. This tertiary amine, in addition to catalyzing the urethane reaction, promotes the various side reactions such as dimerization and trimerization. It has been noticed that in every case equivalent polyol-isocyanate mixtures catalyzed by this amine give gums of lower Mooney viscosity than those obtained with the Me(Aa) catalysts (in the present case, plasticity of less than 1200 Plastograph units), which may harden somewhat on standing. In Figure 3 it is clear

that the Plastograph curve for the system containing 0.08 pph DECHA (diethylecyclohexylamine, parts per hundred polyester) is somewhat different in shape from either the iron-catalyzed or the uncatalyzed reaction curves. Because of this difference, quantitative intersystem comparisons are questionable. It also can be seen in Figure 3 that the combined effect of $\text{Fe}(\text{Aa})_3$ and DECHA is not synergistic; in fact, it is not even additive.

DISCUSSION

Bailey, McGinn, and Spaunbergh have proposed that the catalytic activity of cobalt naphthenate is probably related to the ability of the cobalt atom to coordinate more than one isocyanate in the transition state.⁵ If the catalytic mechanism is ligand-independent, however, this possibility is precluded by the present observations. Catalytic orders are essentially unity (Fig. 2) for all catalysts save manganese acetylacetonate, which has a catalytic order approaching two (Fig. 4). This would indicate that, at least in the concentration range explored, more than one manganese per isocyanate group is needed to provide the proper transition state for reaction. The significance of this phenomenon has not been realized as of this writing.

In preliminary investigations,⁷ some degree of correlation was discerned between catalytic coefficients of bivalent metal acetylacetonates and dissociation constants derived from the relationship of van Pantheleon van Eck.⁸ This, however, applied to a small-molecule reaction in which catalyst isocyanate concentration ratios were quite appreciable (see Reference 2). No such correlation was evident in the present work. It has been suggested,⁹ however, that metal catalysis in isocyanate reactions may be associated with the formation of a triplet state and through this with the paramagnetic properties of the metal. These possibilities are currently being investigated in these laboratories.

References

1. Windemuth, E., U. S. Pat. 2,897,181 (July 28, 1959); (b) Farbenfabriken Bayer A.-G., Brit. Pat. 790,209 (May 2, 1958); (c) J. R. Fischer, U. S. Pat. 2,922,462 (April 19, 1960); (d) H. Ebneth, H. Schultheis, and H. Nordt, U. S. Pat. 2,916,464 (December 8, 1959).
2. Weisfeld, L. B., *J. Chem. Educ.*, **38**, 88 (1961).
3. Hostettler, F., and E. F. Cox, *Ind. Eng. Chem.*, **52**, 609 (1960).
4. Britain, J. W., and P. G. Gemeinhardt, paper No. 16, presented before the Division of Paint, Plastics, and Printing Ink Chemistry, 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

5. (a) Bailey, M. E., C. E. McGinn, and R. G. Spaunbergh, paper No. 36 presented before the Division of Paint, Plastics, and Printing Ink Chemistry, 130th Meeting of the American Chemical Society, Atlantic City, New Jersey, September 1956; (b) M. E. Bailey, A. Khawam, and G. C. Toone, *ibid.*, paper No. 37.

6. Brabender Corporation, Rochelle Park, New Jersey; see A. E. Juve and D. C. Hay, *India Rubber World*, **117**, 62 (1947).

7. Weisfeld, L. B., unpublished data.

8. van Pantheleon van Eck, C. L., *Rec. trav. chim.*, **72**, 50 (1953).

9. Hammond, G. S., personal communication.

Synopsis

The polyaddition process involving a hydroxy-terminated linear polyester and an organic diisocyanate in the presence of a series of metal acetylacetonates has been investigated. The method involved kinetic analysis of plasticity build-up in a Brabender Plastograph. Catalytic orders and relative catalytic constants (k_c/k_0) were determined for $\text{Mn}(\text{Aa})_3$, $\text{VO}(\text{Aa})_2$, $\text{V}(\text{Aa})_3$, $\text{Fe}(\text{Aa})_3$, $\text{Cu}(\text{Aa})_2$, $\text{Co}(\text{Aa})_3$, and $\text{Cr}(\text{Aa})_3$; the constants decrease in that order. Catalytic orders are unity for all complexes save manganese, which is 1.75. No correlation between dissociation potential and catalytic coefficient has been found, and it is believed that catalysis may be associated with the paramagnetic properties of the metal.

Résumé

Le processus de polyaddition comprenant un polyester linéaire portant des hydroxyles terminaux et un diisocyanate organique en présence d'une série d'acétylacétonates de métaux a été examiné. La méthode comprenait l'analyse cinétique de la structure et de la plasticité dans un plastographe de Brabender. Les ordres catalytiques et les constantes catalytiques relatives (k_c/k_0) ont été déterminés pour $\text{Mn}(\text{Aa})_3$, $\text{VO}(\text{Aa})_2$, $\text{V}(\text{Aa})_3$, $\text{Fe}(\text{Aa})_3$, $\text{Cu}(\text{Aa})_2$, $\text{Co}(\text{Aa})_3$ et $\text{Cr}(\text{Aa})_3$, et les constantes décroissent dans cet ordre. Les ordres catalytiques sont un pour tous les complexes sauf celui du manganèse, qui est 1.75. On n'a pas trouvé de corrélation entre le potentiel de dissociation et le coefficient catalytique et on croit que la catalyse peut être associée aux propriétés paramagnétiques du métal.

Zusammenfassung

Die Polyadditionsreaktion zwischen einem linearen Polyester mit endständigen Hydroxylgruppen und einem organischen Diisocyanat in Gegenwart einer Reihe von Metallacetylacetonaten wurde untersucht. Die Methode bestand in der kinetischen Analyse des plastischen Verhaltens in einem Brabender-Plastographen. Die Ordnung der Katalyse und die relativen Katalysekonstanten (k_c/k_0) wurden für $\text{Mn}(\text{Aa})_3$, $\text{VO}(\text{Aa})_2$, $\text{V}(\text{Aa})_3$, $\text{Fe}(\text{Aa})_3$, $\text{Cu}(\text{Aa})_2$, $\text{Co}(\text{Aa})_3$ und $\text{Cr}(\text{Aa})_3$ bestimmt; die Konstanten nehmen in dieser Reihenfolge ab. Die Ordnung für alle Komplexe war bei der Katalyse eins, mit Ausnahme von Mangan mit 1,75. Es wurde keine Beziehung zwischen Dissoziationspotential und katalytischem Koeffizienten gefunden und es wird angenommen, dass die Katalyse mit den paramagnetischen Eigenschaften des Metalls zusammenhängt.

Received September 26, 1960