that the reaction order of the amine is half *vs.* fourth for the bulk reaction. This difference is ascribed to some change in the state of association of ion pairs in dioxane. The activation energy for the reaction decreases from bulk to solution due to the difference in the state of ion pair association. The overall rate may be stated as $-d[COOH]/dt \propto [epoxy][COOH]^{1/2}[R_3N]^{1/2}$. Both the inherent rate and the thermal sensitivity of the reaction rate are affected by the structure of the catalyst.

Discussion of the kinetics of this reaction is based on associated and solvated ion pairs. A coherent mechanism is proposed for the reaction in bulk and solution, and rate laws derived for both cases.

Acknowledgments. The author expresses his appreciation to Messrs. John Parsons and Ernest Scharhag for their help in developing the infrared technique, and to Drs. Seymour Newman and Lee Mahoney for many helpful discussions and suggestions during the course of this work.

Physicochemical Studies of Polyhexene-1. Polymerization Kinetics

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ABSTRACT: A kinetic study of hexene-1 polymerization in cyclohexane solvent with the catalyst system α-$TiCl_3$–$AlEt_2Cl$ was conducted. Correlations in terms of monomer, catalyst and cocatalyst concentrations were proposed for rate of polymerization R_p and average degree of polymerization $\bar{X}_n$, and activation energies of 10.6 and −18.5 kcal/mol, respectively, for these reaction variables were measured. Stationary rates of polymerization and molecular weights were observed and it was concluded that monomer and $TiCl_3$ were involved in chain-breaking processes.

Many kinetic studies of polymerizations catalyzed with Ziegler–Natta-type catalysts have been reported in the literature. Most of these studies involved ethylene and propylene, probably because of their industrial importance, although other monomers such as styrene, butene-1, isoprene, and 4-methylpentene-1 have also been investigated. The most popular catalyst systems studied consisted of $TiCl_4$ or $TiCl_3$ as the catalyst and $AlEt_3$ or $AlEt_2Cl$ as the cocatalyst although $Al(i\text{-}Bu)_3$ has also been used as a cocatalyst.

Most polymers prepared with Ziegler–Natta catalysts are crystalline and, therefore, have poor solubility characteristics. As a consequence they often precipitate out of solution during polymerization and trap the heterogeneous catalyst in a polymer matrix. This impairs kinetic measurements and has caused some workers to consider the possibility that diffusion of monomer to the polymerization sites might interfere with or even control the observed rates of polymerization and others[1] to go to high polymerization temperatures in order to maintain the polymers in solution. Moreover, it is very difficult to analyze accurately the solution properties of these polymers, which should yield valuable information about such important kinetic variables as average molecular weight and molecular weight distribution.

For these reasons we have chosen hexene-1 as our monomer. Hexene-1 is a liquid and it may be polymerized readily with Ziegler–Natta catalysts to a high molecular weight, rubbery polymer which is soluble in most common organic solvents at room temperature. An investigation of the polymerization of hexene-1 to liquid polymer with the catalyst system $TiCl_4$–$AlEt_3$ has previously been reported.[2]

Kinetic studies of α-olefin polymerization with Ziegler–Natta catalysts are also affected by the type, composition, and, sometimes, the method of preparation of the catalyst system. The use of $TiCl_4$ is accompanied by a complex reduction reaction in which titanium is reduced to lower valence states whereas the choice of the system α-$TiCl_3$–$AlEt_3$ avoids this complication and often leads to more stereospecific polymers *via* stationary-state rates of polymerizations.[3] Using $AlEt_2Cl$ as cocatalyst instead of $AlEt_3$ may result in still higher stereospecificity but with polymerization rates which are concomitantly lower and which sometimes do not achieve a stationary state.[4] High rates can be maintained by using Al-reduced $TiCl_3$.

In the present study we have used the catalyst system Al-reduced α-$TiCl_3$ and $AlEt_2Cl$ because we found that $AlEt_3$ and $Al(i\text{-}Bu)_3$ cocatalysts gave us polymerization rates which were too rapid to be measured accurately at low conversions.

Another problem commonly encountered with Ziegler–Natta polymerizations is the difficulty in obtaining reproducible kinetic data owing to the extreme sensitivity of the catalyst components to their environment during catalyst preparation. In order to eliminate this problem all catalysts were prepared under an inert atmosphere in a high-vacuum glove box.

(1) D. F. Hoeg and S. Liebman, *Ind. Eng. Chem., Process Des. Develop.*, 1, 120 (1962).

(2) E. J. Badin, *J. Amer. Chem. Soc.*, **80**, 6549 (1959).

(3) G. Natta and I. Pasquon, "Advances in Catalysis," Vol. 11, Academic Press, New York, N. Y., 1959.

(4) A. D. Caunt, *J. Polym. Sci., Part C*, **4**, 49 (1958).

The usual kinetic variables were measured in the present study, *viz.*, rate of polymerization, R_p, and number average molecular weight, $\bar{M}_n$, as functions of the following kinetic parameters at low conversions: monomer concentration, [m]; $TiCl_3$ concentration, [T]; $Al(Et)_2Cl$ concentration, [A]; total catalyst concentration

$$[C] \equiv [T] + [A]$$

at fixed aluminum-to-titanium ratio

$$r \equiv [A]/[T]$$

and temperature. Under isothermal polymerization conditions, we may write in general

$$R_p \equiv -\frac{d[m]}{dt} = f([m], [T], [A]) \quad (1)$$

$$\bar{M}_n = g([m], [T], [A]) \quad (2)$$

or

$$R_p = F([m], [C], r) \quad (3)$$

$$\bar{M}_n = G([m], [C], r) \quad (4)$$

Experimental Section

Materials. 1. Monomer and Polymer. Hexene-1 was obtained from Matheson Coleman and Bell and was specified as 99% pure with a boiling point range of 63–64°. It was further purified in the same manner as the solvent (described below). Only the middle cut was used in the polymerization.

Polyhexene-1 has been found to have no appreciable crystallinity[5-7] and to have a softening temperature (probably a glass transition) somewhere between −36 and −55°.[7-9] Attempts were made to determine its degree of stereospecificity. Obviously the usual technique of extracting soluble matter from crystalline, insoluble polymer (*e.g.*, polypropylene) with *n*-heptane could not be used since polyhexene-1 is completely soluble in *n*-heptane. Also, the infrared (ir) spectrum of polyhexene-1 did not show peaks which could be identified as being characteristic of isotactic polymer.

In an attempt to crystallize polyhexene-1 a 1% solution in toluene was cooled to −30° and the turbid material which formed was separated from the mother liquor by ultracentrifugation at −20°. A comparison between the ir spectra of this polymeric material and the polymer recovered from the mother liquor, after both had been vacuum dried, showed no discernible differences. Moreover, their spectra were similar to that of the original, untreated polymer. Both polymer fractions were also melted, cooled slowly to room temperature over a period of about 4 hr, and subsequently examined under a polarized microscope. No spherulite formation was detected.

2. Solvent. Spectroanalyzed grade cyclohexane, obtained from Fisher Scientific Co., was used as the solvent after purification by refluxing for 8 hr with metallic sodium, and distilling, under an inert atmosphere of dry nitrogen. Only the middle cut of the distillate was used for polymerization.

All parts of the purification apparatus were cleaned with a dichromate solution, washed with distilled water, dried in an oven overnight, and flamed under vacuum prior to their use.

3. Catalyst. Aluminum-reduced (AA) titanium trichloride (α-$TiCl_3$) was obtained from Stauffer Chemical Co. and diethylaluminum chloride ($AlEt_2Cl$) was obtained from Texas Alkyls Co. Both were used without further purification.

Apparatus. 1. Vacuum Glove Box. Since both catalyst components were extremely sensitive to trace amounts of moisture and oxygen all catalyst preparations were made under an atmosphere of ultra high purity argon (Matheson Co.) in a Whittaker Mark VA glove box after it had been evacuated to a pressure below 5 μ and refilled with argon. No fuming of either catalyst component was detected during catalyst preparation under these conditions and the subsequent kinetic studies with these catalysts were reproducible.

2. Reaction Vessels. It was decided to conduct multiple polymerizations simultaneously or in succession, each to a different conversion, rather than remove aliquots from a single reaction vessel at various times. This decision was based primarily on the requirement that large samples be available for subsequent solution property measurements at various extents of reaction.

Each reaction vessel consisted of a well-stirred, four-necked, 500-ml, round-bottom flask equipped with two breakable, blown glass bulbs containing the catalyst components, a reflux condenser fitted with a mercury check valve, and a thermometer. Six such vessels were placed in an insulated, rectangular aluminum trough containing oil which was well stirred and maintained at the desired reaction temperature to within ±0.2°. The oil bath was placed on a multimagnetic stirrer (Lab-Line No. 1278A) which provided simultaneous agitation for all reaction vessels. All polymerizations were limited to 40% conversion or less in order to avoid poor mixing characteristics resulting from high-viscosity reaction mixtures.

Procedures. 1. Catalyst Preparation and Polymerization. All glass items were cleaned with a dichromate solution, rinsed with distilled water, and dried in an oven overnight. They were then placed in the glove box which contained an analytical balance and both catalyst components. The air in the glove box was then removed by evacuation to a pressure below 5 μ and replaced with argon at a pressure slightly in excess of atmospheric pressure. Purified monomer and solvent were then introduced through an air lock and pipeted into the reaction vessels. The desired amounts of catalyst and cocatalyst were introduced into their respective glass bulbs and the reaction vessels were then completely assembled.

The reaction vessels were subsequently mounted in the oil bath and their contents heated to the desired reaction temperature. The cocatalyst was then added to the monomer solution with agitation followed by the catalyst. This procedure was adopted because preliminary studies had indicated a possible effect of aging on premixed catalysts.

After the desired reaction times had elapsed, the polymerizations were stopped by the addition of excess isopropyl alcohol containing 5% (by volume) concentrated hydrochloric acid. The resulting mixtures were then removed and analyzed.

2. Analysis for Conversion. The polymers which precipitated from the reaction mixtures were separated by filtration, washed with isopropyl alcohol, and freeze-dried to constant weights. Reproducibility within 5% was obtained with polymers prepared under the same conditions. The filtrates were examined for low molecular weight polymer ends; no low ends were found.

3. Analysis for Number Average Molecular Weight ($\bar{M}_n$).

(5) T. W. Campbell and A. C. Haven, *J. Appl. Polym. Sci.*, **1**, 73 (1959).
(6) K. J. Clark, A. Turner Jones, and D. J. H. Sandiford, *Chem. Ind.* (London), 2010 (1962).
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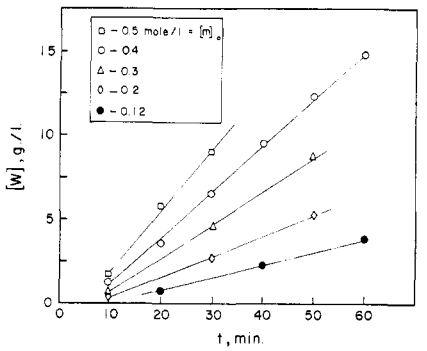

Figure 1. Weight of polymer *vs.* time at 25° for various values of $[m]_0$; $[A]_0 = 0.04$ and $[T]_0 = 0.01$.

Number average molecular weights were measured on a Mechrolab Model 501 high speed membrane osmometer at 37° with toluene as the solvent. Nonaqueous Schleicher and Schuell (type 0-8) membranes were used. They were treated prior to use by successive soakings for 4 hr in each of four solutions; a 50% solution of water–isopropyl alcohol, pure isopropyl alcohol, a 50% solution of isopropyl alcohol–toluene, and finally, pure toluene. They were stored in a closed container filled with toluene until used.

Owing to the rather high molecular weights of the polymers in this study, the precision attainable in measurements of $\bar{M}_n$ was estimated to be approximately ±10% for $10^4 < \bar{M}_n < 10^6$ and ±15% for $\bar{M}_n > 10^6$.

Analysis of Data. Data showing the effect of initial monomer concentration, $[m]_0$, on conversion, $1 - [m]/[m]_0$, with time and $\bar{M}_n$ with conversion are presented in Table I. These data are plotted in Figures 1 and 2. Clearly the weight concentration of polymer obtained, [W], is proportional to conversion since

$$[W] = M([m]_0 - [m])$$

where M is the molecular weight of hexene-1. The effects of $[T]_0$, $[A]_0$, and $[C]_0$ on conversion with time and $\bar{M}_n$ with conversion are shown in Tables II, III, and IV, respectively, and Figures 3-4, 5-6, and 7-8,

TABLE I
DEPENDENCE OF CONVERSION AND MOLECULAR WEIGHT ON INITIAL MONOMER CONCENTRATION[a]

$[m]_0$, mol/l.	t, min	[W], g/l.	$1 - ([m]/[m]_0)$	$\bar{M}_n \times 10^{-5}$
0.12	20	0.792	0.078	3.4
	40	2.267	0.225	3.9
	60	3.876	0.384	3.8
0.20	10	0.434	0.026	5.0
	30	2.748	0.164	6.4
	50	5.371	0.319	5.6
0.30	10	0.735	0.029	7.3
	30	4.601	0.182	8.1
	50	8.751	0.347	8.7
0.40	10	1.236	0.037	3.6
	20	3.617	0.108	10.4
	30	6.566	0.195	10.9
	40	9.675	0.287	9.7
	50	12.311	0.366	9.0
	60	14.883	0.442	9.3
0.50	10	1.762	0.042	11.5
	20	5.843	0.139	12.7
	30	9.013	0.214	12.1

[a] $[A]_0 = 0.04$ mol/l.; $[T]_0 = 0.01$ mol/l.; temperature 25°.

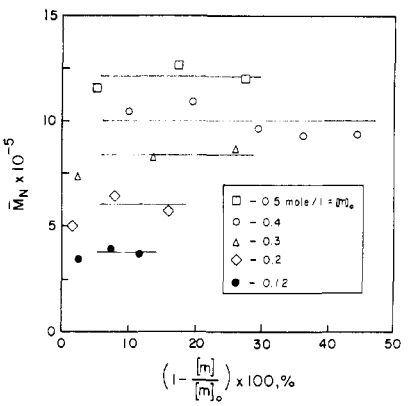

Figure 2. Molecular weight of polymer *vs.* conversion at 25° for various values of $[m]_0$; $[A]_0 = 0.04$ and $[T]_0 = 0.01$.

TABLE II
DEPENDENCE OF CONVERSION AND MOLECULAR WEIGHT ON INITIAL $TiCl_3$ CONCENTRATION[a]

$[T]_0$, mol/l.	t, min	[W], g/l.	$1 - ([m]/[m]_0)$	$\bar{M}_n \times 10^{-5}$
0.0025	10	0.364	0.011	3.2
	30	1.975	0.059	17.3
	50	4.174	0.124	20.5
0.005	10	0.664	0.019	5.2
	30	3.727	0.111	13.2
	50	7.328	0.218	14.4
0.01	10	1.211	0.036	4.6
	30	6.886	0.205	10.2
	50	12.995	0.387	9.8
0.02	10	1.813	0.054	5.2
	30	7.933	0.236	7.3
	50	14.720	0.438	6.6
0.04	10	2.522	0.075	4.1
	30	9.082	0.270	4.3
	50	16.563	0.493	4.4

[a] $[m]_0 = 0.4$ mol/l.; $[A]_0 = 0.01$ mol/l.; temperature 25°.

TABLE III
DEPENDENCE OF CONVERSION AND MOLECULAR WEIGHT ON INITIAL $AlEt_2Cl$ CONCENTRATION[a]

$[A]_0$, mol/l.	t, min	[W], g/l.	$1 - ([m]/[m]_0)$	$\bar{M}_n \times 10^{-5}$
0.0025	10	0.788	0.023	2.9
	30	3.367	0.100	11.1
	50	6.606	0.196	8.7
0.005	10	0.959	0.028	3.1
	30	4.621	0.137	10.4
	50	8.710	0.259	8.9
0.01	10	1.211	0.036	3.6
	30	6.886	0.205	10.2
	50	12.995	0.386	9.9
0.02	10	1.159	0.034	3.4
	30	7.262	0.216	10.8
	50	13.841	0.411	8.7
0.04	10	1.236	0.037	3.6
	20	3.617	0.108	10.4
	30	6.666	0.195	10.9
	40	9.675	0.287	9.7
	50	12.311	0.366	9.0
	60	14.883	0.442	9.3

[a] $[m]_0 = 0.4$ mol/l.; $[T]_0 = 0.01$ mol/l.; temperature 25°.

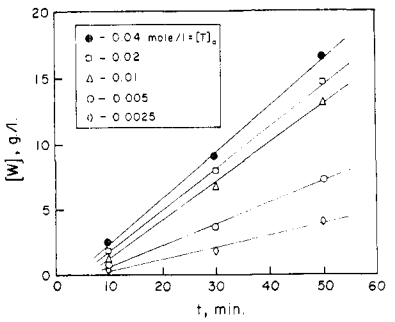

Figure 3. Weight of polymer *vs.* time at 25° for various values of $[T]_0$; $[m]_0 = 0.4$ and $[A]_0 = 0.01$.

TABLE IV
DEPENDENCE OF CONVERSION AND MOLECULAR WEIGHT ON TOTAL CATALYST CONCENTRATION[a]

$[T]_0$, mol/l.	$[A]_0$, mol/l.	t, min	[W], g/l.	$1 - ([m]/[m]_0)$	$\bar{M}_n \times 10^{-5}$
0.0025	0.01	10	0.364	0.011	3.2
		30	1.975	0.059	18.6
		50	4.374	0.124	20.3
0.0075	0.03	10	0.776	0.023	3.9
		30	4.411	0.131	11.8
		50	9.177	0.273	13.4
0.01	0.04	10	1.236	0.037	3.6
		20	3.617	0.108	10.4
		30	6.566	0.195	10.9
		40	9.675	0.287	9.7
		50	12.311	0.366	9.0
		60	14.883	0.442	9.3
0.02	0.08	10	1.942	0.058	5.7
		25	8.063	0.239	7.0
		35	12.777	0.380	6.1

[a] $[m]_0 = 0.4$ mol/l.; $r = 4$; temperature 25°.

respectively. As seen in Figure 6, $\bar{M}_n$ apparently does not depend on $[A]_0$.

Several conclusions are immediately apparent from Figures 1 and 2. First, since high molecular weights are obtained virtually at the outset of the polymerizations, *viz.*, within 5–10% conversion or 10–15 min, and remain relatively constant (within experimental error) thereafter, we may assume that active polymeric intermediates (P) exist which are terminated at various stages of polymerization, otherwise $\bar{M}_n$ would grow steadily

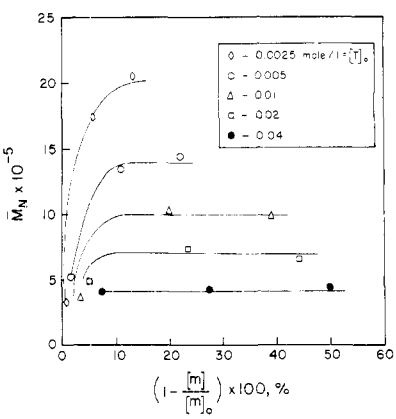

Figure 4. Molecular weight of polymer *vs.* conversion at 25° for various values of $[T]_0$; $[m]_0 = 0.4$ and $[A]_0 = 0.01$.

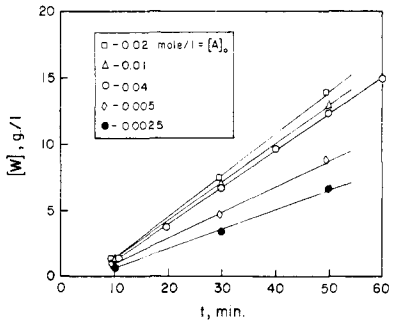

Figure 5. Weight of polymer *vs.* time at 25° for various values of $[A]_0$; $[m]_0 = 0.4$ and $[T]_0 = 0.01$.

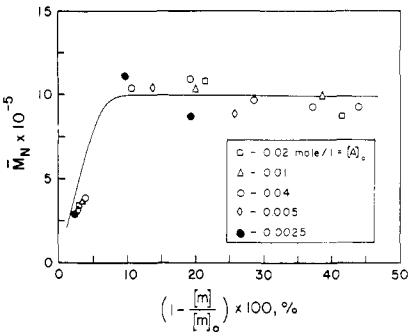

Figure 6. Molecular weight of polymer *vs.* conversion at 25° for various values of $[A]_0$; $[m]_0 = 0.4$ and $[T]_0 = 0.01$.

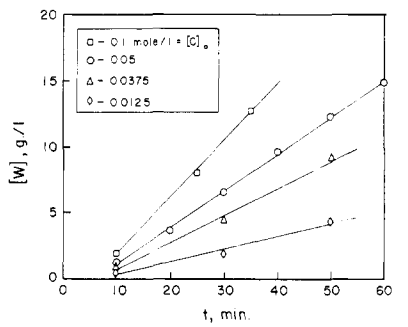

Figure 7. Weight of polymer *vs.* time at 25° for various $[C]_0$; $[m]_0 = 0.4$ and $r = 4$.

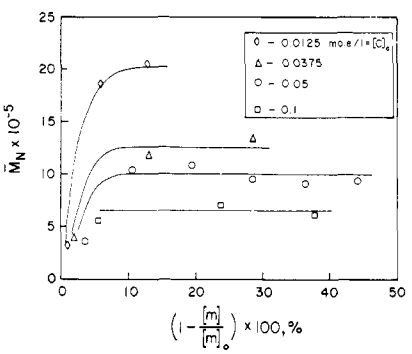

Figure 8. Molecular weight of polymer *vs.* conversion at 25° for various values of $[C]_0$; $[m]_0 = 0.4$ and $r = 4$.

with conversion like in stepwise polymerizations. These active intermediates are active sites on the catalyst surface. Moreover, a stationary state probably exists with respect to the initiation and termination of these chain intermediates because the rate of polymerization

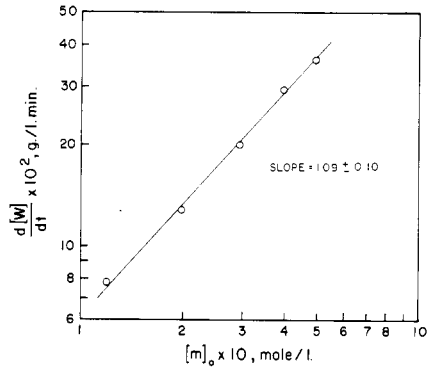

Figure 9. Log polymerization rate *vs.* log $[m]_0$ at 25°; $[A]_0$ = 0.04 and $[T]_0$ = 0.01.

R_p, which is clearly proportional to d[W]/dt, is relatively constant during the early stages of polymerization before [m] has changed appreciably. Finally, we may conclude that the average lifetime (τ) of these growing chain intermediates has an upper limit of the order of 10–15 min, which is at least an order of magnitude less than the overall polymerization time. Thus, Ziegler–Natta catalyzed polymerizations resemble chain addition type polymerizations with somewhat larger values for τ than observed for free radical chain polymerizations. Other workers have reached similar conclusions.

We shall now analyze the data from the classical chain reaction viewpoint. When high molecular weight polymer is formed, since the polymerization is addition type, eq 1 may be written as

$$R_P \approx k_P[m][P] \tag{5}$$

where k_P is the propagation rate constant and [P], which is a function of [T] and [A] ,is the concentration of active chain intermediates (relatively constant). We may also use the concept of an instantaneous average molecular weight or degree of polymerization

$$(\bar{X}_n)_{inst} = \frac{(\bar{M}_n)_{inst}}{M} = \frac{R_P}{R_t}$$

where R_t is the rate at which the chain intermediates are broken or terminated. Clearly R_t is at least proportional to [P] although it may actually be a summation of several terms

$$R_t = \sum_i R_{ti}$$

where each R_{ti} represents a different chain-breaking

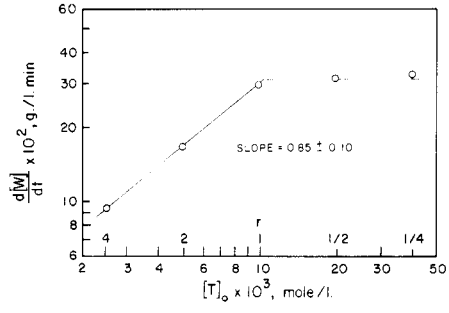

Figure 10. Log polymerization rate *vs.* log $[T]_0$ at 25°; $[m]_0$ = 0.4 and $[A]_0$ = 0.01.

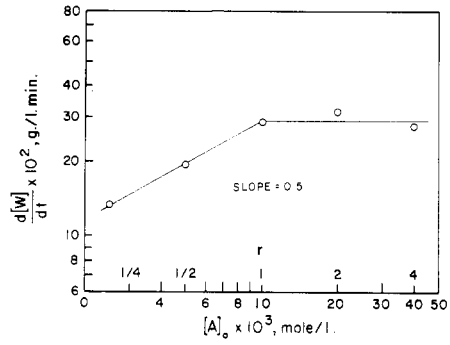

Figure 11. Log polymerization rate *vs.* log $[A]_0$ at 25°; $[m]_0$ = 0.4 and $[T]_0$ = 0.01.

process and each may depend on one or more reaction variable, B_i, such as [m], [T], or [A]. Thus

$$(1/\bar{X}_n)_{inst} = \sum_i \frac{k_{ti}[B_i]}{k_p[m]} \tag{6}$$

It is possible to estimate, roughly, a value for [P]. Typical corresponding values for $[m]_0$ − [m], $[T]_0$ and $\bar{X}_n$ in our experiments were 0.1 mol/l., 0.01 mole/l., and 10^4, respectively, over a reaction period of approximately 60 min. Thus, we can estimate R_t to have, on the average, a value of about 10^{17} polymer molecules/l./min and, assuming a value of 5 min for τ, we find from

$$R_t\tau = [P]$$

that [P] has a value of the order of approximately 10^{-6} mol/l. or 10^{-4} mol/mol of $TiCl_3$. This rough estimate, although it is somewhat lower, compares quite favorably with values for [P] obtained by other workers[3, 10, 11] using more precise methods.

In the present study we examined the effect on both R_p and $1/\bar{X}_n$ of each reaction parameter separately at fairly low conversions since then each concentration may be considered to have a value equal to its initial concentration and also $R_p \approx (R_p)_0$ and $1/\bar{X}_n \approx (1/\bar{X}_n)_{inst}$. These results are shown in Figures 9–15.

From Figures 9–12 it was found that R_p is first order with respect to [m], 0.85 order for $r > 1$ and zero order for $r < 1$ with respect to [T], 0.5 order for $r < 1$ and zero order for $r > 1$ with respect to [A], and 0.75 order with respect to [C]. It is apparent that R_p shows a "saturation" effect at $r = 1$ with respect to both [T]

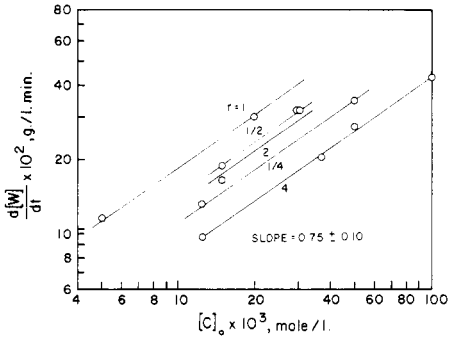

Figure 12. Log polymerization rate *vs.* log $[C]_0$ at 25° for various values of r; $[m]_0$ = 0.4.

(10) J. C. W. Chien, *J. Polym. Sci., Part A*, **1**, 425 (1963).
(11) B. M. Grieveson, *Makromol. Chem.*, **84**, 93 (1965).

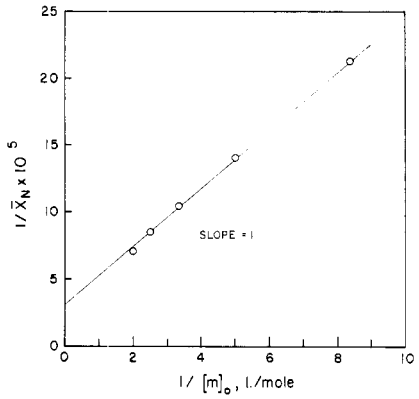

Figure 13. Reciprocal of stationary molecular weight *vs.* $1/[m]_0$ at 25°; $A_0 = 0.04$ and $T_0 = 0.01$.

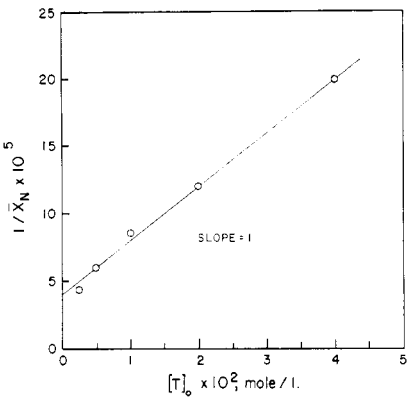

Figure 14. Reciprocal of stationary molecular weight *vs.* $[T]_0$ at 25°; $[m]_0 = 0.4$ and $[A]_0 = 0.01$.

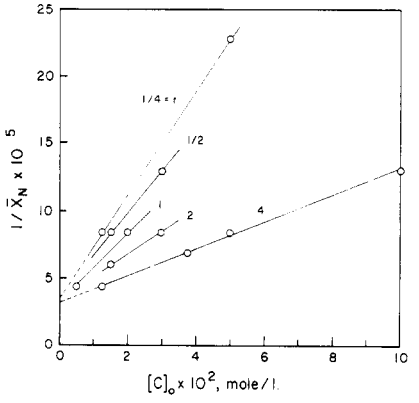

Figure 15. Reciprocal of stationary molecular weight *vs.* $[C]_0$ at 25° for various values of *r*; $[m]_0 = 0.4$.

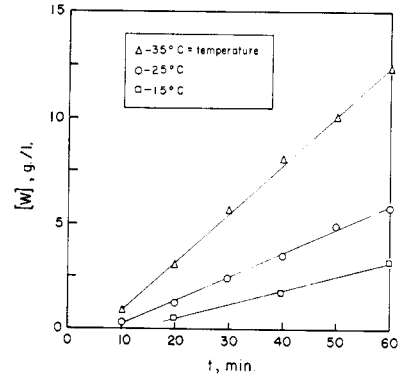

Figure 16. Weight of polymer *vs.* time at various temperatures; $[m]_0 = 0.4$, $[T]_0 = 0.0025$, and $[A]_0 = 0.0025$.

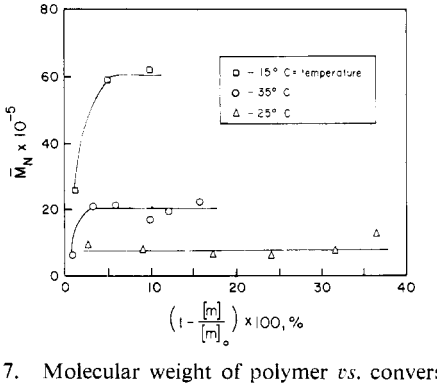

Figure 17. Molecular weight of polymer *vs.* conversion at various temperatures; $[m]_0 = 0.4$, $[T]_0 = 0.0025$, and $[A]_0 = 0.0025$.

and [A] but no change in order with respect to [m], at least within the concentration range examined. From Figures 13–15 it is clear that $1/\bar{X}_n$ shows a first-order dependence on 1/[m], [T], and [C].

The effect of temperature on conversion *vs.* time and $\bar{M}_n$ *vs.* conversion is shown in Tabel V and Figures 16 and 17. If eq 1 and 2 are written in the following somewhat restricted forms

$$R_p = (k_p)_{app} f'([m], [T], [A]) \quad (7)$$

and

$$\bar{M}_n = (k_n)_{app} g'([m], [T], [A]) \quad (8)$$

where $(k_p)_{app}$ and $(k_n)_{app}$ are apparent (lumped) rate constants with Arrhenius-type temperature dependence ($\exp(-E_{app}/RT)$) then the slopes of the respective Arrhenius plots, Figures 18 and 19, give the following apparent activation energies for polymerization rate and molecular weight

$$(E_p)_{app} = 10.6 \pm 3 \text{ kcal/mol}$$

$$(E_n)_{app} = -18.5 \pm 0.5 \text{ kcal/mol}$$

More precisely, the dependence of R_p and $\bar{X}_n$ on the various concentration variables at any temperature as determined in this study, *i.e.*, the specific forms of eq

TABLE V
DEPENDENCE OF CONVERSION AND MOLECULAR WEIGHT ON TEMPERATURE[a]

Temp, °C	*t*, min	[W], g/l.	$\bar{M}_n \times 10^{-5}$
15	20	0.496	25.8
	40	1.709	58.8
	60	3.391	61.8
25	10	0.312	6.3
	20	1.154	20.7
	30	2.412	21.8
	40	3.394	16.6
	50	4.817	19.4
	60	5.815	22.4
35	10	0.885	9.5
	20	3.022	8.1
	30	5.652	6.4
	40	8.028	6.2
	50	10.068	7.7
	60	12.292	13.1

[a] $[m]_0 = 0.4$ mol/l.; $[T]_0 = 0.0025$ mol/l.; $[A]_0 = 0.0025$ mol/l.

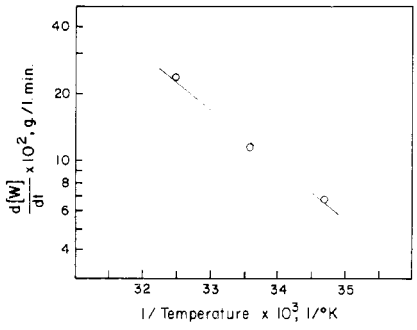

Figure 18. Arrhenius plot for polymerization rate; $[m]_0 = 0.4$, $[T]_0 = 0.0025$, and $[A]_0 = 0.0025$.

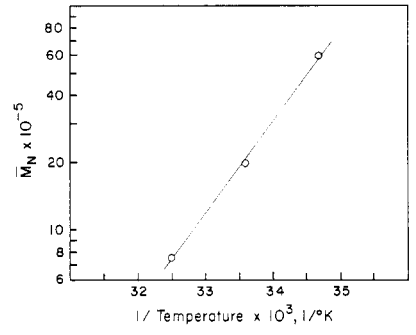

Figure 19. Arrhenius plot for molecular weight; $[m]_0 = 0.4$, $[T]_0 = 0.0025$, and $[A]_0 = 0.0025$.

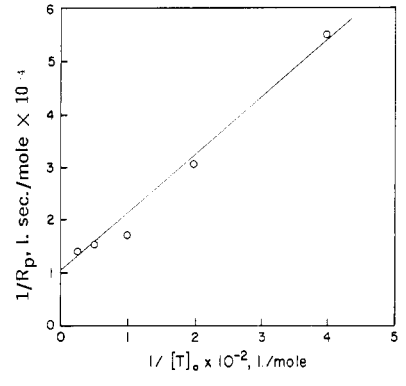

Figure 20. Reciprocal of polymerization rate *vs.* $1/[T]_0$ at 25° $[m]_0 = 0.4$, and $[A]_0 = 0.01$.

1 and 2, may best be represented by the following correlations

$$R_p = \frac{K_1[m][T][A]^{1/2}}{K_2[A]^{1/2} + K_3[T] + 1} \quad (9)$$

$$\bar{X}_n = \frac{k_1[m]}{k_3[T] + k_4[m] + k_5} \quad (10)$$

It is clear that eq 10 correlates the data plotted in Figures 13 and 14 by comparing these plots with its reciprocal

$$1/\bar{X}_n = \frac{k_3[T]}{k_1[m]} + \frac{k_5}{k_1[m]} + \frac{k_4}{k_1} \quad (11)$$

A further check of eq 10 is provided by rewriting its reciprocal, eq 11, in terms of [C] and r. Equation 12

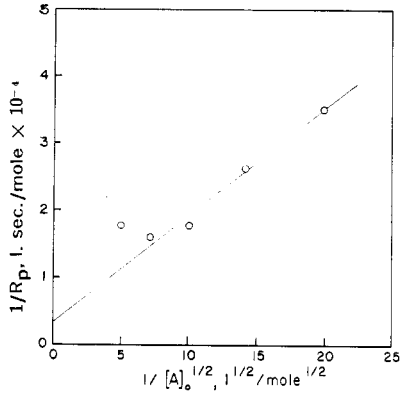

Figure 21. Reciprocal of polymerization rate *vs.* $1/[A]_0^{1/2}$ at 25°; $[m]_0 = 0.4$ and $[T]_0 = 0.01$.

$$1/\bar{X}_n = \frac{k_3}{k_1(r+1)}\frac{[c]}{[m]} + \frac{k_5}{k_1[m]} + \frac{k_4}{k_1}$$

correlates the data plotted in Figure 15 and correctly predicts the observed decrease in slope with increase in r as well as the common intercept.

Clearly we may conclude that no chain-breaking process which depends on the concentration of $AlEt_2Cl$ was observed. However, a chain-breaking process involving monomer cannot be ruled out since the intercept of Figure 13 is not zero which implies that $k_4 > 0$. Moreover, we cannot establish whether or not the kinetic constant representing spontaneous chain breaking, k_5, is zero since in either case eq 11 and 12 correctly represent the data in Figures 13, 14, and 15.

Most interesting is the [T]-dependent chain-breaking process suggested by eq 10. This dependence has been observed by other workers[1,3,10,12] and may be attributed to the presence of a chain-transfer agent which originates from the catalyst or is a reaction product thereof.

Equation 9 certainly correlates the dependence of R_p on [A] measured since it predicts that R_p should be half-order in [A] for low values of [A] ($r < 1$) and then become zero order for high values ($r > 1$). Regarding the dependence of R_p on [T], it predicts zero order for high values ($r < 1$) and first order for low values ($r > 1$) of [T]. However, it is obvious from eq 9 that if $K_3[T]$ is not "small enough" relative to the other terms in the denominator R_p may have the appearance of being fractional order, *e.g.*, 0.85, with respect to [T].

Equation 9 may be tested graphically since its reciprocal predicts that $1/(R_p)_0$ plotted against $1/[T]_0$ for

$$\frac{1}{R_p} = \frac{M}{\frac{d[W]}{dt}} = \frac{K_2}{K_1[m]}\frac{1}{[T]} + \frac{K_3}{K_1[m]}\frac{1}{[A]^{1/2}} + \frac{1}{K_1(m)[T][A]^{1/2}} \quad (13)$$

constant values of $[m]_0$ and $[A]_0$ and against $1/[A]_0^{1/2}$ for constant values of $[m]_0$ and $[T]_0$ should give straight lines. Such plots are shown in Figures 20 and 21. Moreover, if equation 9 is rewritten in terms of [C] and r we obtain

(12) F. D. Otto and G. Parravano, *J. Polym. Sci., Part A*, 2, 5131 (1964).

TABLE VI
A COMPARISON OF VARIOUS CORRELATIONS FOR RATE OF POLYMERIZATION[a]

Monomer	Catalyst	Cocatalyst	K_2	K_3	K_4	K_5	n	p	q	a	b	c	Ref
Ethylene	$TiCl_4$	$Al(i\text{-}Bu)_2Cl$	0	0	>0	>0	2			0	0	1	*b*
Propylene	α-$TiCl_3$	$AlEt_3$				>0	1	1	0			0	3, *c*
		$AlEt_3$ / $Al(i\text{-}Bu)_3$	0	0	0	0	1	1	0	0	0	0	1
Styrene	α-$TiCl_3$	$AlEt_3$	>0	0	>0	>0	1	1	1	1	0	2	*d*
			>0	0	0	0	1.5	1	0	0.5	0	1	12
Hexene-1	α-$TiCl_3$	$AlEt_2Cl$	>0	>0	>0		1	1	0.5	0.5	1	1	Present study

[a] The coefficients and exponents refer to eq 15. [b] A. Schindler, *J. Polym. Sci., Part C*, **4**, 81 (1964). [c] G. Natta, I. Pasquon, J. Svab, and A. Zambelli, *Chem. Ind.* (Milan), **44**, 621 (1962). [d] K. Vesely, *Pure Appl. Chem.*, **4**, 407 (1962).

TABLE VII
A COMPARISON OF VARIOUS CORRELATIONS FOR DEGREE OF POLYMERIZATION[a]

Monomer	Catalyst	Cocatalyst	B	k_2	k_3	k_4	k_5	α	β	γ	Ref
Ehylene	α-$TiCl_3$	$AlEt_2Cl$	H_2	0	>0	>0	>0	0	0	1	11
Propylene	α-$TiCl_3$	$AlEt_3$	m	>0	>0	>0	>0	0.5	0.5	1	3
		$AlEt_3$ / $Al(i\text{-}Bu)_3$		0	>0	0	>0	0	1	0	1
		$AlEt_2Cl$		>0	>0	0	0	0.5	1	0	10
Styrene	α-$TiCl_3$	$AlEt_3$	A	0	>0	>0	0	0	1	0.5	12
Hexene-1	α-$TiCl_3$	$AlEt_2Cl$		0	>0	>0		0	1	0	Present study

[a] The coefficients and exponents refer to eq 16.

TABLE VIII
A COMPARISON OF VARIOUS ACTIVATION ENERGIES FOR RATE OF POLYMERIZATION

Monomer	Catalyst	Cocatalyst	$(E_p)_{app}$,[a] kcal/mol	Reference
Ethylene	$TiCl_3$	$AlEt_3$	7.6	*b*
		$AlEt_2Cl$	7.8	*b*
			13.5	*c*
		$Al(i\text{-}Bu)_3$	8.3	*b*
Propylene	$TiCl_3$	$AlEt_3$	11–14	3, *d*
		$AlEt_2Cl$	13.0	*d*
		$Al(i\text{-}Bu)_3$	14.2	*d*
4-Methyl-pentene-1	$TiCl_3$	$AlEt_2Cl$	15	*e*
Styrene	$TiCl_3$	$AlEt_3$	8.1–13	*f*
		$AlEt_2Cl$	9.4	*f*
Hexene-1	$TiCl_4$	$AlEt_3$	9.5	2
	$TiCl_3$	$AlEt_2Cl$	10.6	Present study

[a] Heat of solution of monomer in solvent was not deducted. [b] S. S. Medvedev and A. R. Gantmakher, *J. Polym. Sci., Part C*, **4**, 173 (1963). [c] M. N. Berger and B. M. Grieveson, *Makromol. Chem.*, **83**, 80, (1968). [d] A. P. Firsov and N. M. Chirkov, *Polym. Sci., USSR*, **6**, 1870 (1964). [e] R. J. Ehrig, J. J. Godfrey, and G. S. Krishnanmurthy, *Polym. Preprints*, **5**, 1184 (1964). [f] G. M. Burnett and P. J. Tait, *Polymer*, **1**, 151 (1960).

$$\left(\frac{[C]}{R_p} - \frac{(r+1)K_2}{K_1[m]}\right)[C]^{1/2} = \left(\frac{r+1}{r}\right)^{1/2}\frac{K_3}{K_1[m]}[C] + \frac{[r+1)^{3/2}}{r^{1/2}K_1[m]} \quad (14)$$

which may be viewed as a specific form of eq 3. Equation 14 predicts that a plot of

$$\left(\frac{[C]_0}{(R_p)_0} - \frac{(r+1)K_2}{K_1[m]_0}\right)[C]_0^{1/2} \text{ vs. } [C]_0$$

for constant $[m]_0$ and r should give a straight line. Such a plot, which requires that the ratio K_2/K_1 be determined for its construction, is shown in Figure 22. This ratio and, in fact, all three constants K_1, K_2, and K_3, may be easily determined from the slopes and intercepts of Figures 20 and 21 together with eq 13; it was found that K_2/K_1 has a value of approximately 22 mol sec/l.

A comparison may be made between the results of this study with those of other workers by writing eq 1 and 2 in the forms

$$R_p = \frac{K_1[m]^n[T]^p[A]^q}{(K_2[A]^a + K_3[T]^b + K_4[m] + K_5)^c} \quad (15)$$

$$\bar{X}_n = \frac{k_1[m]}{k_2[A]^\alpha + k_3[T]^\beta[B]^\gamma + k_4[m] + k_5} \quad (16)$$

which represent somewhat generalized versions of eq 9 and 10. Tables VI and VII give values for the coefficients and exponents in eq 15 and 16 found by various workers so that they may be specialized to represent the appropriate correlation proposed in each particular case. A similar comparison of activation energies is made in Table VIII.

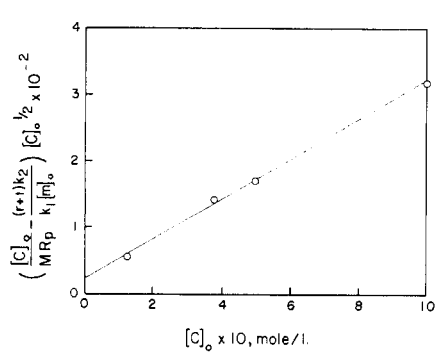

Figure 22. A function of $[C]_0$ defined in eq 14 *vs.* $[C]_0$ at 25°; $[m]_0 = 0.4$ and $r = 4$.

The "saturation" or autoinhibitory behavior of R_p with respect to [A] and [T] has been observed by others;[12,13] so has its half-order dependence on [A].[12] These phenomena can be accounted for satisfactorily by a simple catalyst formation scheme involving a competition for active surface sites between a polymerization-inhibiting species and monomeric $AlEt_2Cl$, subsequent to its decomposition from the dimeric form in solution. We postulate that the active sites are exposed titanium atoms having the requisite geometric characteristics and that the inhibitor has its origin in the catalyst perhaps, as previously suggested,[4] owing to the presence of $AlCl_3$.

Such a scheme may be written as

$$A_2 \rightleftarrows 2A \quad K_1'$$
$$S + A \rightleftarrows C_a \quad K_2'$$
$$S + I \rightleftarrows C_i \quad K_3'$$

with the constraint

$$[S]_0 = [S] + [C_i] + [C_a]$$

This leads to

$$\theta_a = \frac{(K_1')^{1/2}K_2'[A_2]^{1/2}}{(K_1')^{1/2}K_2'[A]^{1/2} + K_3'[I] + 1} \quad (17)$$

where A_2 = dimeric aluminum alkyl, $(AlEt_2Cl)_2$; S = initial sites on the catalyst surface which are capable of complexing aluminum-containing compounds; I = inhibiting species which are capable of complexing with S to form inactive sites; C_a = active sites which become polymerization intermediates; C_i = inactive sites which cannot cause polymerization; θ_a = fraction of the catalyst surface covered with active polymerization sites.

If we now assume that most of the original catalyst is present as dimer in solution and that the concentration of the inhibitor is proportional to the concentration of catalyst added, we obtain an expression for [P], with the aid of

$$[P] = \theta_a[T] \quad (18)$$

which is identical with that deduced from eq 5 and 9.

Acknowledgments. The authors wish to express their gratitude to the National Science Foundation and to the Plastics Institute of America for their support of this work. The authors also wish to thank Professors A. A. Volpe and F. T. Jones for their helpful discussions and suggestions.

(13) See Table VI, footnote *d*.

Esterolytic Catalyses by Copolymers Containing Imidazole and Carboxyl Functions

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ABSTRACT: The electrostatic interactions involved in the imidazole–carboxylic acid copolymer-catalyzed solvolyses of 3-acetoxy-N-trimethylanilinium iodide (ANTI), *p*-nitrophenyl acetate (PNPA), and 3-nitro-4-acetoxybenzoic acid (NABA) were studied and compared with the monomeric analog γ-4(5)-imidazolebutyric acid. The effects of copolymer composition of the 4(5)-vinylimidazole–acrylic acid copolymers on their catalytic activities were investigated in detail. These effects became apparent by inspecting the dependencies of their activities on the monomer sequence distributions, which were found to control the overall catalytic activities of the copolymers for the charged esters. The most catalytically active species toward ANTI is the carboxylate–imidazole–carboxylate triad.

The efficiency and specificity of esterolytic, enzymatic catalyses are, in some cases, caused partly by electrostatic attraction between groups carrying ionic charges of opposite sign, one in a substrate and the other in an active site of an enzyme. Typical examples could be acetylcholine esterase[2] and ribonuclease[3] in their catalytic action toward charged substrates or inhibitors. This type of electrostatic effect has been also observed to enhance the rates of solvolyses of negatively charged substrates catalyzed by partially protonated polymers containing nucleophilic functions.[4-8]

A copolymer of 4(5)-vinylimidazole with acrylic acid was of interest because it had both binding sites (carboxylate anions) and catalytically active groups (neutral

(1) Taken from the dissertation submitted by H. Maki in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Michigan. Mitsui Petrochemical Ind., Ltd., Research Center, Wakimura, Kuga-gun, Yamaguchi, Japan.

(2) I. B. Wilson in the "Enzymes," Vol. IV, P. D. Boyer, H. A. Lardy, and K. Myrback, Ed., Academic Press, New York, N. Y., 1960, pp 501–520; F. Bergmann, *Advan. Catal.*, **10**, 130 (1958); N. Engelhard, K. Prchal, and M. Nenner, *Angew. Chem. Intern. Ed. Engl.*, **6**, 615 (1967).

(3) C. H. Hirs, M. Halmann, and J. H. Kycia in "Biological Structure and Function," Vol. I, Academic Press, New York, N. Y., 1962, p 41.

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