β-(p-Methoxyphenyl)-ethylmercuric acetate was prepared by the reaction of the ethylene–mercuric acetate addition compound with anisole.[2a]

Rate Measurements.—Solutions of benzylmercuric acetate in acetic acid were added to a solution of mercuric acetate and perchloric acid in aqueous acetic acid with good stirring. At proper intervals, aliquots (5 ml.) were withdrawn and added to 50 ml. of water in separatory funnels. Unreacted benzylmercuric acetate was extracted with 20 ml. of chloroform three times. To these chloroform extracts, 50 ml. of water and 2 ml. of concd. nitric acid were added and the benzylmercuric acetate remaining was titrated with 0.05 N ammonium thiocyanate solution. Water layers after the extractions were mixed with 40 ml. of 0.3 N potassium iodide and 5 or 10 ml. of 0.05 N iodine solution. After shaking for 10 min., excess iodine was titrated with 0.05 N sodium thiosulfate solution. Thus, decreases of benzylmercuric acetate and increases of mercurous salt were determined. The other rate measurements were carried out by the same method.
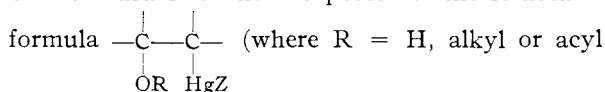

The Kinetics of the Decompositions of Ethylene–Mercuric Salt Addition Compounds with Hydrochloric Acid

By Katsuhiko Ichikawa, Hajime Ouchi[1] and Shigemitsu Araki

The kinetics of decompositions of ethylene–mercuric salt addition compounds ($ROCH_2CH_2HgCl$) with hydrochloric acid has been studied in water–ethanol mixtures and found to be third order (first order in addition compounds, hydronium ion and chloride ion, respectively). In the presence of perchloric acid, it has been demonstrated that R in the addition compound can be replaced by the solvent without decomposition. On the basis of these observations, the reaction mechanisms are discussed.

Since the first preparation of olefin–mercuric salt addition compounds,[2] the easy decomposition of these compounds with hydrochloric acid has proved puzzling. This decomposition gives the original olefins and mercuric salts, despite the fact that the usual reactions expected of the structural

formula $-\overset{|}{\underset{OR}{C}}-\overset{|}{\underset{HgZ}{C}}-$ (where R = H, alkyl or acyl

groups, and Z = inorganic or organic acid radicals) are reported. The addition compounds are also rather stable to non-halogen acids.[3] Recently, Kreevoy reported that the kinetics of the decomposition of propylene–mercuric salt addition compound (CH_3CH-CH_2) in the presence of perchloric

$$\overset{|}{\underset{OR}{}}\quad\overset{|}{\underset{HgI}{}}$$

acid was a second-order reaction between the addition compound and hydronium ion and discussed the mechanism. It was concluded there that the π-

complex form of the addition compounds $-\overset{|}{\underset{\searrow_{\oplus,'}}{C}}{=\!\!=\!\!=}\overset{|}{C}-$,

$$\underset{HgZ}{}$$
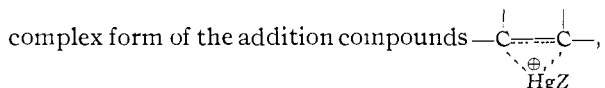
proposed by Lucas, Hepner and Winstein,[4] could not be the intermediate.[5] This complex, however, has been proposed as the intermediate in the reactions of the addition compounds with aromatics or acetoacetic ester in the presence of strong acids.[6-8]

For example

To reconcile these two incompatible conclusions, the kinetics of decompositions of ethylene–mercuric salt addition compounds with hydrochloric acid have been studied.

There are several difficulties in this kinetic study. Mercuric chloride, one of the reaction products, may form complex compounds such as $H_2Hg\text{-}Cl_4$ and $HHgCl_3$ with hydrochloric acid. These compounds are strong acids and therefore the proton concentrations are not affected, but chloride ion concentrations may change. Calculations on the basis of equilibrium constants reported by Damm and Weiss[9] show that mercuric chloride in hydrochloric acid exists largely in the form of the complexes. Despite these considerations, addition of aqueous sodium hydroxide to the mercuric chloride solutions in dilute hydrochloric acid (below 0.2 M) resulted in quantitative precipitations of mercuric oxide. On the other hand, sharp decreases of the yields of mercuric oxide in the range of more concentrated hydrochloric acid definitely indicate complex formation. It is doubtful, therefore, that the complexes are formed in dilute hydrochloric acid solution. As far as the determination of mercuric ion concentration by this method is applicable, however, the reaction order of chloride ion in this decomposition can be determined by checking the effects of initial concentrations of chloride

(1) Department of Chemical Engineering, University of Osaka Prefecture.

(2) K. A. Hoffmann and J. Sand, Ber., **33**, 1340, 2692 (1900).

(3) See, for example, J. Chatt, Chem. Revs., **48**, 7 (1951).

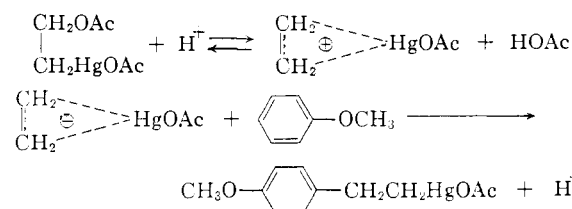(4) H. J. Lucas, F. R. Hepner and S. Winstein, This Journal, **61**, 3102 (1939).

(5) M. M. Kreevoy, ibid., **81**, 1099 (1959).

(6) K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, ibid., **80**, 6005 (1958); **81**, 3401 (1959).

(7) K. Ichikawa, H. Ouchi and S. Fukushima, J. Org. Chem., **24**, 1129 (1959).

(8) K. Ichikawa, K. Fujita and H. Ouchi, This Journal, **81**, 5316 (1959).

(9) K. Damm and A. Weiss, Z. Naturforsch., **10b**, 534 (1955); C. A., **50**, 9917 (1956).

ion on the initial rates, even if complex formation occurs. Tentatively it is assumed that the reactions proceed according to the equation
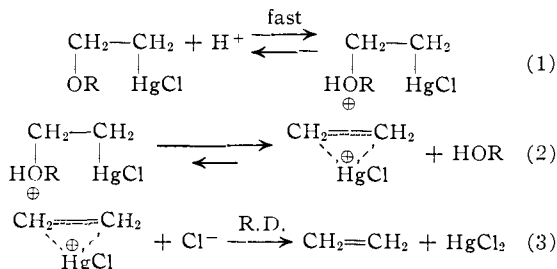
$$ROCH_2CH_2HgCl + H^+ + Cl^- \longrightarrow$$
$$CH_2{=}CH_2 + HOR + HgCl_2$$
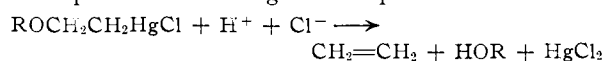
The rates were determined by following the mercuric ion concentrations by the method mentioned above, since the ethylene–mercuric salt addition compounds are soluble in aqueous sodium hydroxide. The best rate expression is $dx/dt = k_3(a - x)(b - x)(c - x)$, where a, b and c are the initial concentrations of the addition compound, hydronium and chloride ion, respectively, and x is the amount of the addition compound which has reacted at time t. In this equation, it is assumed that no Hg(II) complexes are formed. Deviations from this equation, however, were practically negligible up to more than 50% reaction (see Fig. 1). The values of k_3 remained constant even in the presence of added sodium chloride. These observations both in the rate study and the analysis suggest that the assumption is reasonable. However, the addition of mercuric chloride (0.03 M) to the reaction mixture resulted in a decrease of k_3 and, therefore, it is clear that the complex formation must be considered in more concentrated ranges of mercuric salt and hydrochloric acid.

In i-PrO–CH$_2$CH$_2$HgCl (0.05 M)–HClO$_4$ (0.0238 M)–HgCl$_2$ (0.025 M)–75% ethanol and i-PrO–CH$_2$CH$_2$HgCl (0.05 M)–HClO$_4$ (0.0252 M)–75% ethanol systems, no detectable reaction was observed at 25° after 5 hr. It is clear, therefore, that the presence of free chloride ions is required for the decomposition reactions.

The results obtained are shown in Tables I and II.

With concentrations of hydrochloric acid greater than 0.05 M, no substantial effect of initial concentration of hydronium and chloride ions on k_3-values is observed. In the presence of more dilute hydrochloric acid, however, k_3-values increase with a decrease of acid concentration (see Fig. 2). This is explained in terms of the activity of hydrochloric acid. The marked increase of rate with increase of ethanol concentration (see Fig. 3) appears to show the same effect of activity.[10]

A possible mechanism which is consistent with the results obtained is proposed in equations 1, 2 and 3.

$$\underset{\substack{|\\OR}}{CH_2}{-}\underset{\substack{|\\HgCl}}{CH_2} + H^+ \underset{\longleftarrow}{\overset{\text{fast}}{\rightleftharpoons}} \underset{\substack{|\\\underset{\oplus}{HOR}}}{CH_2}{-}\underset{\substack{|\\HgCl}}{CH_2} \qquad (1)$$

$$\underset{\substack{|\\\underset{\oplus}{HOR}}}{CH_2}{-}\underset{\substack{|\\HgCl}}{CH_2} \underset{\longleftarrow}{\longrightarrow} \underset{\substack{\diagdown,\oplus,\diagup\\HgCl}}{CH_2{=\!=\!=}CH_2} + HOR \qquad (2)$$

$$\underset{\substack{\diagdown,\oplus,\diagup\\HgCl}}{CH_2{=\!=\!=}CH_2} + Cl^- \xrightarrow{\text{R.D.}} CH_2{=}CH_2 + HgCl_2 \qquad (3)$$

Kreevoy concluded that π-complex formation by equation 2 could not occur in these decompositions, because the rates observed were not the same for CH$_3$CH(OH)CH$_2$HgI and CH$_3$CH(OCH$_3$)CH$_2$HgI.

(10) On the activity coefficient of hydrochloric acid in ethanol–water mixtures see, for example, Y. Oiwa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **78**, 775 (1957).

TABLE I

THIRD-ORDER RATE CONSTANTS FOR DECOMPOSITIONS OF ETHYLENE–MERCURIC SALT ADDITION COMPOUNDS (ROCH$_2$-CH$_2$HgCl) WITH HYDROCHLORIC ACID IN 75% ETHANOL

R	Temp., °C.	Initial concn., M ROCH$_2$-CH$_2$HgCl	HCl	Salt added, M	$k_3 \times 10^2$, mole^2/l.^{2} sec.
Ac–	25.0	0.0250	0.0505		1.96
			.1013		1.41
			.1518		1.27
			.2006		1.23
		.0500	.0257		3.42
			.0255	HgCl$_2$, 0.0304	1.92
			.0500		2.14
			.0975		1.49
			.1028	NaCl, 0.0520	1.50
			.1614		1.39
			.1992		1.34
	0.3	.0500	.1614		0.0789
Me–	25.0	.0500	.0257		3.94
			.0500		3.43
			.0975		3.49
			.1028	NaCl, 0.0520	3.55
			.1614		3.47
			.1992		3.50
	0.3	.0500	.1614		0.163
Et–	25.0	.0500	.0257		4.28
			.0255	HgCl$_2$, 0.0304	3.45
			.0500		3.91
			.0975		3.85
			.1028	NaCl, 0.0520	3.97
			.1614		3.85
	0.3	.0500	.1614		0.176
i-Pr–	25.0	.0500	.0128		8.50
			.0257		6.49
			.0255	HgCl$_2$, 0.0304	4.20
			.0500		5.86
			.0975		5.59
			.1028	NaCl, 0.0520	5.72
			.1614		5.65
	0.3	.0500	.1614		0.290
H–	25.0	.0242	.0121		32.8
			.0242		27.8
			.0500		24.8
			.0975		22.7
			.1614		22.0
	0.3	.0242	.1614		1.33

TABLE II

ACTIVATION ENERGIES AND LOG PZ FOR DECOMPOSITIONS OF ETHYLENE–MERCURIC SALT ADDITION COMPOUNDS (RO-CH$_2$CH$_2$HgCl) WITH HYDROCHLORIC ACID IN 75% ETHANOL

R	E_{act}, kcal./mole	log PZ
Ac–	18.8	11.9
Me–	20.0	13.2
Et–	20.2	13.4
i-Pr–	19.4	13.0
H–	18.4	12.8

His conclusion appears to be incorrect, since this result would be obtained if the reverse rate in equation 2 is much slower than the others. Actually, in aqueous ethanol, we found that β-acetoxyethylmercuric chloride was converted to β-ethoxyethylmercuric chloride completely in the presence of 0.5 M perchloric acid on standing at room temperature for five days. This result cannot be explained
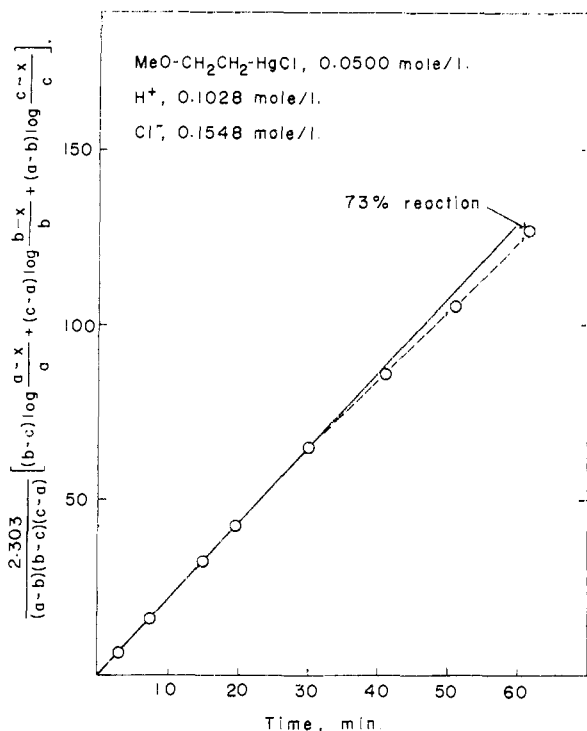
$$\frac{2.303}{(a-b)(b-c)(c-a)}\left[(b-c)\log\frac{a-x}{a}+(c-a)\log\frac{b-x}{b}+(a-b)\log\frac{c-x}{c}\right]$$

MeO-CH$_2$CH$_2$-HgCl, 0.0500 mole/l.

H$^+$, 0.1028 mole/l.

Cl$^-$, 0.1548 mole/l.

73% reaction

Time, min.

Fig. 1.—Typical example of third-order plot for the decomposition of ethylene–mercuric salt addition compound in 75% ethanol at 25°.

$k_3 \times 10^2$

HO-CH$_2$CH$_2$HgCl

i-PrO-
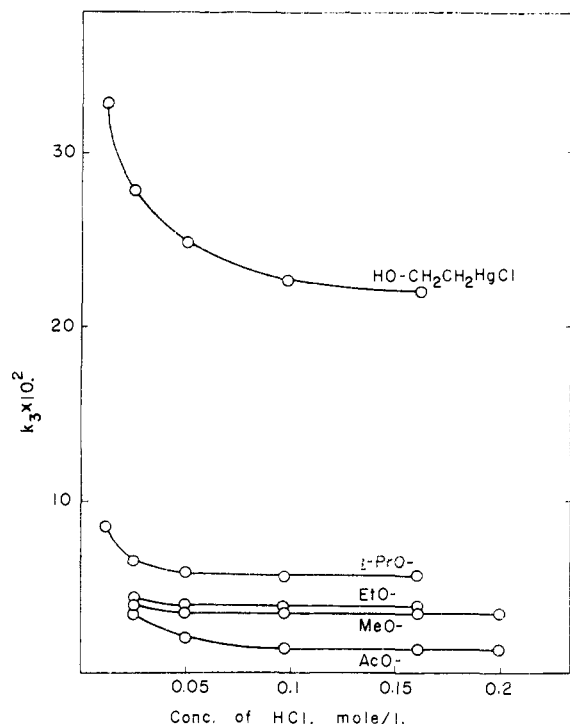
EtO-

MeO-

AcO-

Conc. of HCl, mole/l.

Fig. 2.—Effects of hydrochloric acid concentrations on the decomposition rates in 75% ethanol at 25°.

without assuming π-complex formation as in equation 2, because a solvolytic substitution of the protonated acetoxy group cannot be expected. For example, ethyl acetate does not form ethyl ether under the same conditions.
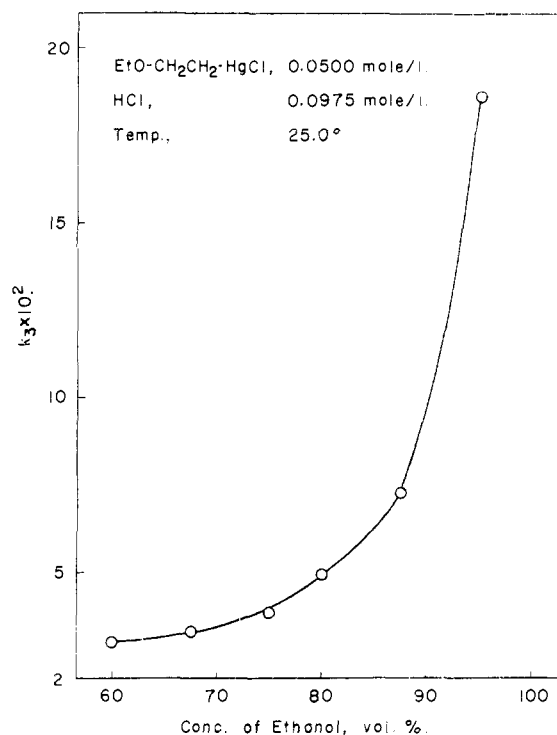

$k_3 \times 10^2$

EtO-CH$_2$CH$_2$·HgCl,   0.0500 mole/l.

HCl,   0.0975 mole/l.

Temp.,   25.0°

Conc. of Ethanol, vol. %.

Fig. 3.—Effects of ethanol concentrations on the decomposition rates at 25°.

The different rates for CH$_3$CH(OR)CH$_2$HgI and ROCH$_2$CH$_2$HgCl appears to be due to the differences in the affinity of mercury for iodine and chlorine. However, the mechanism proposed here can be applied to the case studied by Kreevoy and also suggests strongly that the addition of mercuric salt to olefins (the reverse process of this decomposition reaction)[11] proceeds through an ionic mechanism.

Experimental

β-Acetoxyethylmercuric Chloride.—A mixture of mercuric acetate (80 g.) and acetic acid (80 g.) was treated with ethylene (3 l./hr.) at room temperature until yellow mercuric oxide was no longer formed on adding the reaction mixture to aqueous sodium hydroxide. The reaction mixture was filtered to remove a small amount of mercurous salt (impurity in mercuric acetate). To the filtrate, 600 ml. of cold water and then 170 ml. of 10% aqueous potassium chloride solution were added. The β-acetoxyethylmercuric chloride formed (42 g.) was filtered, dried and then recrystallized from ligroin; m.p. 64–65°.

Anal.[12] Calcd. for C$_4$H$_7$ClHgO$_2$: Hg, 62.08. Found: Hg, 62.00.

The other alkoxyethylmercuric chlorides were prepared from the corresponding alcohols by similar methods. Melting points and the results of mercury analyses are:

R	M.p., °C. Found	M.p., °C. Reported	Hg content, % Calcd.	Hg content, % Found
Me	68–68.5	Not rept.	67.97	67.61
Et	87–89	92[a]	64.88	65.01
i-Pr	85–86	Not rept.	62.07	62.20

[a] W. Schoeller, W. Schrauth and W. Essers, Ber., 46, 2869 (1913).

(11) See, for example, E. R. Allen, J. Cartlidge, M. M. Taylor and C. F. H. Tipper, J. Phys. Chem., 63, 1437 (1959); A. G. Brook and G. F. Wright, Can. J. Research, B28, 623 (1950).

(12) The American Pharmaceutical Association, "The National Formulary," 10th Ed., J. B. Lippincott Co., Philadelphia, Pa., 1955, p. 606.

β-Hydroxyethylmercuric chloride was prepared according to the method of Cotton and Leto by the reaction of ethylene with aqueous mercuric nitrate; m.p. 152–153° (reported[13] 153–155°).

Determination of Mercuric Ion Concentrations in Hydrochloric Acid.—Out of mercuric chloride solutions in 75% ethanol containing hydrochloric acid, aliquot samples (10

DETERMINATIONS OF MERCURIC ION CONCENTRATIONS IN 75% ETHANOL CONTAINING VARIOUS AMOUNTS OF HYDROCHLORIC ACID

HgCl$_2$, M	HCl, M	HgO obtained, %
0.025	0.00	99.0
	.10	98.7
	.15	98.7
	.20	98.3
	.25	96.6
	.50	94.5
.035	.05	99.8
	.15	99.8
.01	.05	94.4
	.10	93.6
	.20	93.5
.05	1.00	88.7

(13) F. A. Cotton and J. R. Leto, This Journal, **80**, 4824 (1958).

ml.) were withdrawn and added to 10 ml. of cold 10% aqueous sodium hydroxide. Mercuric oxide formed was filtered, washed twice with cold water, dissolved in 10 ml. of 5 N nitric acid and titrated with 0.2 N potassium thiocyanate. In cases where the concentration of mercuric chloride was lower, lower values for mercuric oxide were obtained because of the solubility of mercuric oxide in water.

Rate Measurement.—Aliquots (10 ml.) were withdrawn at intervals and added to 10% aqueous sodium hydroxide. The amount of mercuric oxide formed was determined by the method described above.

Conversion of β-Acetoxyethylmercuric Chloride to β-Ethoxy-ethylmercuric Chloride.—In the absence of perchloric acid, β-acetoxyethylmercuric chloride was recovered unchanged from ethanol solution after standing for one week. However, in the presence of perchloric acid, the acetoxy compound was converted to the ethoxy compound. β-Acetoxyethylmercuric chloride (3.2 g.) was dissolved in 95 ml. of ethanol containing 30 ml. of 20% perchloric acid. After 5 days, the solution was neutralized with 0.5 N aqueous sodium hydroxide and cooled to −10°. The crystals formed (1.59 g.) melted at 89–90°. Mixed m.p. with authentic sample of β-ethoxyethylmercuric chloride showed no depression.

YOSHIDA, KYOTO, JAPAN

Transition Metal Catalysts. I. Ethylene Polymerization with a Soluble Catalyst Formed from an Aluminum Halide, Tetraphenyltin and a Vanadium Halide[1]

BY WAYNE L. CARRICK, RUDOLPH W. KLUIBER, EUGENE F. BONNER, LLOYD H. WARTMAN, FRANK M. RUGG AND JOSEPH J. SMITH

RECEIVED AUGUST 24, 1959

A mixture of an aluminum halide, tin tetraphenyl and a trace of a vanadium halide in cyclohexane forms a clear solution which contains an active catalyst for the low pressure polymerization of ethylene. In this catalyst the optimum weight concentration of the vanadium halide is only 0.1 to 5 parts in 10^3 parts of total components, and polymerization will take place when the concentration is as low as one part in 10^6. Each molecule of the vanadium compound can catalyze the formation of as many as 2000 *polymer* molecules. The polyethylene obtained is linear in molecular structure, high in molecular weight and narrow in molecular weight distribution. The narrow distribution suggests that catalysis is homogeneous and due to a single catalytic species.

Introduction

Organometallic mixed catalysts for ethylene and α-olefin polymerization were first disclosed in a publication by Ziegler, Holzkamp, Breil and Martin[2] describing the polymerization of ethylene at low pressures with a mixture of titanium tetrachloride and an aluminum alkyl. Since then many other catalyst mixtures have been reported which polymerize ethylene at low pressures to a high molecular weight, linear polymer.[3,4] Some of these also polymerize α-olefins to stereoregular polymers. These catalysts ordinarily are formed by combining a reactive organometallic compound with a transition metal compound of groups IV through VI of the periodic table. The catalyst-forming reaction is very complex, and attempts to define the active species generally have led to ambiguous re-

sults. At present, there is no general agreement as to whether the reaction is ionic[5] or radical,[6,7] heterogeneous[6] or homogeneous,[8] which transition metal valence is optimum,[9-11] or if the polymer molecule grows from a transition metal center[6,7,10,11] or some other site.[8,12] However, most investigators do agree that a transition metal compound is a necessary part of the active catalyst species.

The general problem of the mechanism of olefin polymerization by organometallic mixed catalysts has been under investigation in this Laboratory for several years, and numerous catalyst combinations have been examined. Studies on the organic derivatives of transition metals, interactions of cata-

(1) This work was presented before the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13 to 18, 1958. Address inquiries to W. L. Carrick.

(2) K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, **67**, 541 (1955).

(3) Soc. Chem. Ind., Reports on the Progress of Applied Chemistry, **42**, 436 (1957).

(4) J. K. Stille, *Chem. Revs.*, **58**, 541 (1958).

(5) G. Natta, *Chim. e ind. (Milan)*, **37**, 888 (1955).

(6) H. N. Friedlander and K. Oita, *Ind. Eng. Chem.*, **49**, 1885 (1957).

(7) C. D. Nenitzescu and A. H. Ciresicahuch, *Angew. Chem.*, **68**, 438 (1956).

(8) G. Natta, P. Pino, G. Mazzanti, U. Gianini, E. Mantica and M. Peraldo, *J. Polymer Sci.*, **26**, 120 (1957).

(9) D. S. Breslow and N. R. Newbury, This Journal, **81**, 81 (1959).

(10) D. B. Ludlum, A. W. Anderson and C. E. Ashby, *ibid.*, **80**, 1380 (1958).

(11) W. L. Carrick, *ibid.*, **80**, 6455 (1958).

(12) F. Patat and H. Sinn, *Angew. Chem.*, **70**, 496 (1958).