Dismutation of Aluminum Monoalkyldihalides by the Action of Complexing Substances, and their Behaviour in Ternary Catalytic Systems for Anionic Co-ordinated Polymerization Processes

by

G. Natta, A. Zambelli, I. Pasquon, G. Gatti, and D. DeLuca

From the Istituto di Chimica Industriale del Politecnico, Milano, and Centro Nazionale
di Chimica delle Macromolecole, Milano, Italy

Dismutation of Aluminum Monoalkyldihalides by the Action of Complexing Substances, and their Behaviour in Ternary Catalytic Systems for Anionic Co-ordinated Polymerization Processes

By G. Natta, A. Zambelli, I. Pasquon, G. Gatti, and D. DeLuca

Dedicated to Prof. Dr. Dr. h.c. K. ZIEGLER on the occasion of his 65th birthday

SUMMARY:

In the stereospecific polymerization of propylene to isotactic polymer, the behaviour of ternary catalytic systems based on violet $TiCl_3-Al(C_2H_5)Cl_2$-LEWIS base for ratios of LEWIS base/Al from 0 to *ca.* 1 was studied. Under the experimental conditions, all systems prepared with sufficiently weak bases are active in the polymerization, also for values of the ratio LEWIS base/Al somewhat > 1. The systems with strong bases are active only if the ratio LEWIS base/Al < 1. All the active systems show the same degree of stereo-specificity as the binary systems prepared from violet $TiCl_3$ and $Al(C_2H_5)_2Cl$.

The results confirm the interpretation that aluminum monoalkyldihalide is dismuted at least in part by the LEWIS base, with consequent formation of aluminum dialkylmonohalide at least partially non complexed; this compound, in the monomeric, non associated state should participate in the formation of the catalytic complexes. The hypotheses agree with the results of the polymerization of propylene and of butadiene with the aid of similar systems.
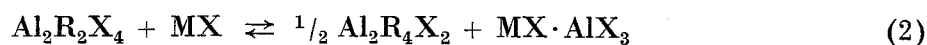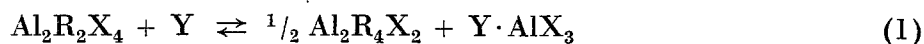
ZUSAMMENFASSUNG:

Bei der stereospezifischen Polymerisation von Propylen zu isotaktischen Polymeren wurde das Verhalten ternärer Katalysatorsysteme von violettem $TiCl_3-Al(C_2H_5)Cl_2$-LEWIS-base untersucht, und zwar im Bereich LEWISbase/Al von 0–1. Unter den experimentellen Bedingungen sind alle Systeme polymerisationsaktiv, die mit genügend schwachen Basen hergestellt werden, sogar für LEWISbase/Al-Verhältnisse > 1. Die Systeme mit starken Basen sind nur etwas aktiv, wenn das Verhältnis LEWISbase/Al < 1. Alle aktiven Systeme haben die gleiche Stereospezifität wie die binären Systeme aus violettem $TiCl_3$ und $Al(C_2H_5)_2Cl$.

Dadurch wird die Deutung gestützt, daß Al-alkyldihalogenid zumindest teilweise durch die LEWISbase dismutiert, mit anschließender Bildung von zumindest teilweise nicht komplexem Dialkylhalogenid. Diese Verbindung sollte im monomeren, nicht assoziierten Zustand an der Bildung der Katalysatorkomplexe beteiligt sein. Die Hypothesen stehen im Einklang mit Ergebnissen bei der Polymerisation von Propylen und Butadien mit ähnlichen Systemen.

I. *Introduction*

In a previous paper[1] some of us had observed that the addition in a 1:2 ratio of a LEWIS base or of another substance able to form addition compounds with aluminum trihalides (*e.g.*, alkaline metal halides or "onium" halides) to aluminum monoalkyldihalides causes one of the following dismutation reactions:

$$Al_2R_2X_4 + Y \rightleftarrows {}^1/_2\,Al_2R_4X_2 + Y \cdot AlX_3 \tag{1}$$

$$Al_2R_2X_4 + MX \rightleftarrows {}^1/_2\,Al_2R_4X_2 + MX \cdot AlX_3 \tag{2}$$

where R = alkyl, X = halogen, Y = LEWIS base, M = alkaline or alkyl "onium" ions.

It had been observed that reaction 1, especially if strong bases are used, is shifted toward the right; moreover, the existence of possible addition complexes of the type: $Y \cdot 2\,AlRX_2$, analogous to $MX \cdot 2\,AlR_3$, isolated and described by ZIEGLER[2] could be excluded.

The results allowed us to assume that the behaviour of the systems prepared by mixing 2 moles of $AlRX_2$ with 1 mole of LEWIS base (or of a salt of the MX type) is similar, in some polymerization reactions and at least under some respects, to that of the corresponding AlR_2X formed in reactions 1 and 2.

In particular, a comparison was made between the results obtained from the stereospecific polymerization of propylene with the aid of the catalytic systems violet $TiCl_3-Al_2R_4X_2$ and violet $TiCl_3-Al_2R_2X_4 + Y$ (or MX); it was thus observed that, when the halogen of $Al_2R_4X_2$ and of $Al_2R_2X_4$ is the same, the systems mentioned above have the same degree of stereospecificity[1, 3, 4]. This result was interpreted by the fact that in both cases the actually active organometallic compound in the formation reaction of the stereospecific catalyst is AlR_2X.

In the paper[1], investigations were restricted to the cases in which the ratios between the reagents corresponded to the stoichiometry of reactions 1 and 2, and to the cases in which the halogen of the MX salt was the same as that of the organometallic compound of aluminum.

The investigations described in this paper also concern the systems prepared from $AlRX_2$ and from a LEWIS base, used in a molar ratio ranging from 0 to 1, and the general case of a halide of any MX type, where X is different from the halogen contained in $AlRX_2$.

It must be stated beforehand that the knowledge of the behaviour of systems prepared with a ratio $Y:AlRX_2 = 1:2$, does not allow *a priori* to draw conclusions about the behaviour of systems in which this ratio is equal to 1:1.

Table 2 reports data of runs carried out with different bases.

The examination of the data of Table 1 suggests that, in the absence of a LEWIS base, no solid polymer is formed; by gradual addition of hexamethylphosphoramide, the catalytic activity increases, reaches a maximum, and then practically tends to zero when the ratio LEWIS base/Al approaches 1. This behaviour seems characteristic of sufficiently strong bases; actually, it also occurs in the case of pyridine (Table 2).

On the contrary, ternary catalytic systems prepared from a weak base such as anisol which yield complexes that can be dissociated more easily are active in the polymerization of propylene, even if the ratio LEWIS base/Al is equal to or slightly above 1 (Table 2).

The data reported in Tables 1 and 2 show that the stereospecificity of the ternary catalytic systems which are active in the polymerization is practically independent both of the nature of the LEWIS base used to prepare the catalyst, and, within wide ranges, of the ratio LEWIS base/Al, at least for the conditions examined. There is also the same degree of stereospecificity shown by the ternary systems violet $TiCl_3-Al(C_2H_5)Cl_2$ — LEWIS base and by the binary systems violet $TiCl_3-Al(C_2H_5)_2Cl$. These results can be interpreted, in analogy with previous reports [1,4], by assuming that the catalytic complexes are in all cases formed by interaction between violet $TiCl_3$ and $Al(C_2H_5)_2Cl$ in the free and non associated state [*].

According to our hypotheses, $Al(C_2H_5)_2Cl$ should be formed, probably in different proportions with all the base/Al ratios examined by reaction of $Al(C_2H_5)Cl_2$ with the LEWIS base. For ratios of LEWIS base/$Al(C_2H_5)Cl_2$ of 0.5 reaction 1 occurs, c.f. [1]; the $Al(C_2H_5)_2Cl$ formed in this reaction, is present in solution in the monomeric and dimeric state, according to equilibrium:

$$Al_2(C_2H_5)_4Cl_2 \rightleftharpoons 2 Al(C_2H_5)_2Cl \tag{5}$$
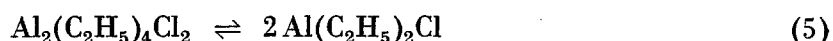
For ratios LEWIS base/$Al(C_2H_5)Cl_2 < 0.5$, the $Al(C_2H_5)_2Cl$ should be formed according to reaction 1, and the resulting system should contain not only $Al(C_2H_5)_2Cl$, but also not dismuted $Al(C_2H_5)Cl_2$; the latter compound in the presence of the former should not exert any influence on the

---

[*] It must be borne in mind, that the differences in activity observed in the systems based on $Al(C_2H_5)_2Cl$ and $Al(C_2H_5)Cl_2$ with LEWIS base (Y) must be attributed at least in part to the presence of the complex $Y \cdot AlCl_3$ in the latter systems [4]. Actually, these complexes when contacting $TiCl_3$ markedly alter the state of dispersion, giving rise to a gathering of the single particles so that $TiCl_3$ looks like a pitch mass.

Therefore, in contrast to the comparison between stereospecificities, the comparison between activities of the different systems is of little significance.

Table 2. Stereospecificity of the catalytic systems violet $TiCl_3$–$Al(C_2H_5)Cl_2$-Lewis base

Lewis base	Lewis base/Al (moles)	Index of isotacticity %[a]
HMPA	0.5	94–95
Pyridine	0.5	94–95
Pyridine	1	no polymerization
Methylal	$^1/_3$	94–95
Ethyl Ether	0.5	94–95
Anisol	1	94–95
Anisol	1.25	94–95

[a] Expressed as % of non extractable polymer in boiling n-heptane. The data refer to average values of polymerization runs carried out at 70 °C. in toluene using violet $TiCl_3$ (α, γ or δ) either in the pure state or containing $AlCl_3$ in a solid solution[3,6], at pressures ranging from 4 to 6 atm.

stereospecificity of the system (under the conditions examined). This interpretation agrees with the results obtained from runs with mixtures of $Al(C_2H_5)Cl_2$ and $Al(C_2H_5)_2Cl$, referred to in a subsequent section.

For ratios Lewis base/Al > 0.5, it still can be assumed that the dismutation of $Al(C_2H_5)Cl_2$ occurs according to reaction 1; however, in this case the Lewis base present in excess is associated with a part of the $Al(C_2H_5)_2Cl$ formed in reaction 1; on the whole, for a ratio Lewis base/Al = 1, reaction 3 occurs, at least in part.

According to this hypothesis, also the species $Y \cdot Al(C_2H_5)_2Cl$ is present in solution in the systems prepared at ratios Lewis base/Al > 0.5; its concentration depends not only on the ratio mentioned above, but also on the strength of the Lewis base.

The complexes $Y \cdot Al(C_2H_5)_2Cl$ are dissociated according to the equilibrium:

$$Y \cdot Al(C_2H_5)_2Cl \overset{K}{\rightleftharpoons} Y + Al(C_2H_5)_2Cl \tag{6}$$
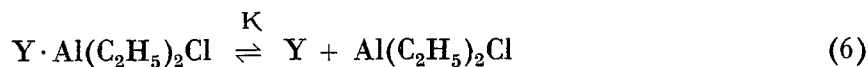
where the numerical value of K obviously depends on the nature of Y; with increasing strength of the Lewis base, K generally decreases.

In order to interpret the results obtained with a ratio Lewis base/Al = 1, it is enough to admit that, in the case of strong bases, the complexes $Y \cdot Al(C_2H_5)_2Cl$ formed in reactions 3 or 4 are too stable (according to reaction 6) to allow the presence of sufficiently high concentrations of $Al(C_2H_5)_2Cl$ in the free state; on the contrary, if the Lewis base is sufficiently weak (such as anisol), reaction 6 is sufficiently shifted toward

the right and the formation of the catalyst complexes can take place by interaction between $TiCl_3$ and $Al(C_2H_5)_2Cl$ in the non associated state.

These results, as well as their interpretation, agree with the data reported below for the polymerization of propylene with the ternary systems $TiCl_3-Al(C_2H_5)_2Cl$-LEWIS base.

Table 3. Polymerization of propylene to isotactic polymer with the use of catalytic systems
δ-$TiCl_3-Al(C_2H_5)Cl_2-Al(C_2H_5)_2Cl$
δ-$TiCl_3$: 7.78 mmoles; n-heptane: 200 ml.; pressure: 5 atm.; t = 50 °C.; time: 5 hrs.

$Al(C_2H_5)Cl_2$ (mmoles)	$Al(C_2H_5)_2Cl$ (mmoles)	$\dfrac{Al(C_2H_5)_2Cl}{Al(C_2H_5)Cl_2}$	Polymer obtained		
			(g.)	Index of isotacticity[a] (%)	$[\eta]$[b] (100 ml./g.)
0	15.56	∞	128.0	97	6.8
7.78	15.56	2	34.4	97.5	5.3
15.56	23.34	1.5	18.7	97	5.2
15.56	15.56	1	11.2	96	4.2
23.34	15.56	0.66	6.6	92	4.3
15.56	7.78	0.5	5.1	89	3.5
15.56	0	0	0	—	—

[a] Expressed as % of non extractable polymer in boiling n-heptane.
[b] Intrinsic viscosity measured in tetralin at 135 °C.

2. Behaviour of the Ternary System Violet $TiCl_3-Al(C_2H_5)Cl_2-Al(C_2H_5)_2Cl$ in the Polymerization of Propylene

In order to further justify the behaviour of the ternary systems violet $TiCl_3-Al(C_2H_5)Cl_2$-LEWIS base prepared at ratios LEWIS base/Al ranging between 0 and 0.5 (in this range not only $Al(C_2H_5)_2Cl$, but also not dismuted $Al(C_2H_5)Cl_2$ are present), polymerization runs have been carried out with the use of the system violet $TiCl_3-Al(C_2H_5)Cl_2-Al(C_2H_5)_2Cl$, prepared with different ratios of $Al(C_2H_5)Cl_2/Al(C_2H_5)_2Cl$.

The results obtained in these runs are reported in Table 3. With increasing $Al(C_2H_5)_2Cl/Al(C_2H_5)Cl_2$ ratio starting from zero it is observed that the catalytic activity increases continuously, in the range covered.

The stereospecificity of the ternary systems considered here increases with the increase of the $Al(C_2H_5)_2Cl/Al(C_2H_5)Cl_2$ ratio, but it rapidly approaches the value of the system $TiCl_3-Al(C_2H_5)_2Cl$ and remains constant here for values of the ratio $Al(C_2H_5)_2Cl/Al(C_2H_5)Cl_2$ higher than ≈ 1.

These results, which agree with the hypotheses to interpret the behaviour of the ternary systems $TiCl_3-Al(C_2H_5)Cl_2$-LEWIS base for ratios

Lewis base/Al $<$ 0.5, also show that the presence of $Al(C_2H_5)Cl_2$ with $Al(C_2H_5)_2Cl$, even in fairly high proportions, does not alter substantially the stereospecificity of the systems prepared from violet $TiCl_3$ and $Al(C_2H_5)_2Cl$.

Table 4. Polymerization of propylene to isotactic polymer with the use of the catalytic systems violet $TiCl_3-Al(C_2H_5)_2Cl$-Lewis base ($TiCl_3$: 0.5 g.; $Al(C_2H_5)_2Cl = 7 \cdot 10^{-3}$ moles; toluene: 200 ml.; t = 70 °C.; $p_{C_3H_6} = 2000$ mm. Hg; time: 1 hr.)

Lewis base	Lewis base/Al	Polymer obtained	
		Polymer (g.)	Index of isotacticity[a] (%)
Absent	—	9.8	94
Pyridine	1	~0	—
Pyridine	$^1/_2$	6.7	89
Pyridine	$^1/_3$	3.6	90
Trimethylamine	1	~0	—
Triethylamine	1	~0	—
Isopropyl ether	1	1.5	94
Anisol	1	4.9	81

[a] Expressed as % of non extractable polymer in boiling n-heptane.

3. Behaviour of the Ternary Systems Violet $TiCl_3-Al(C_2H_5)_2Cl$-Lewis base in the Polymerization of Propylene

Polymerizations of propylene have been carried out with the ternary systems violet $TiCl_3-Al(C_2H_5)_2Cl$-Lewis base prepared at different Lewis base/Al ratios. The data obtained are reported in Table 4.

First of all, these data show that the sufficiently strong bases used in the ratio Lewis base/Al $\geqslant$ 1, form systems that are practically inactive in the polymerization of propylene under our experimental conditions. These results agree with the hypotheses for interpretation of the behaviour of the ternary systems violet $TiCl_3-Al(C_2H_5)Cl_2$-Lewis base prepared at a ratio of Lewis base/Al = 1 and with bases of different strength.

These data also agree with those reported in a previous paper[4], where it was observed that $Al(C_2H_5)_3$ treated in a 1:1 ratio with Lewis bases having a strength lower than or equal to that of triethylamine, is active (at 70 °C.) in the polymerization of propylene with violet $TiCl_3$. Due to the greater tendency of $Al(C_2H_5)_2Cl$, compared with $Al(C_2H_5)_3$ to add itself to the Lewis base, in this case only the mixtures with bases having strength lower than triethylamine (e.g., isopropyl ether) are active at 1:1 ratios (under our experimental conditions, Table 4).

As already pointed out[4], the heterogeneity of the catalytic systems based on violet $TiCl_3$ implies that the concentration of non associated alkyl aluminum sufficient to originate the formation of catalytic complexes in significant amounts can be very low (under our conditions).

The data reported in Table 4 show that the addition of a LEWIS base in a 1:1 ratio to $Al(C_2H_5)_2Cl$ can decrease the stereospecificity more or less markedly depending on the base used. This could be explained by the possible formation of $Al(C_2H_5)_3$, even if in very small and variable amounts, depending on the nature of the LEWIS base.

The dismutation of $Al(C_2H_5)_2Cl$ by the action of suitable complexing substances was already observed by ZIEGLER[5]. For instance, by adding KCl to $Al(C_2H_5)_2Cl$ the complex $K[Al(C_2H_5)_2Cl_2]$ is obtained; by heating it can be decomposed yielding $Al(C_2H_5)_3$.

By comparing the behaviour of catalytic systems consisting of violet $TiCl_3$ and of various organometallic compounds of aluminum, it can be observed how the addition of a LEWIS base to $Al(C_2H_5)Cl_2$ causes an increase both in activity and stereospecificity of the catalytic system; this can be explained by the formation of $Al(C_2H_5)_2Cl$. On the contrary, the addition of LEWIS bases to $Al(C_2H_5)_3$[4] can alter the activity but not the stereospecificity, since $Al(C_2H_5)_3$ cannot yield dismutation products.

Table 5. Stereospecificity of the catalytic systems violet $TiCl_3-(AlRX_2 + \frac{1}{2} MX)$ in the polymerization of propylene to isotactic polymer

AlRX$_2$	MX	Index of isotacticity[a] (%)
$Al(C_2H_5)Cl_2$	KCl	94—95
$Al(C_2H_5)Cl_2$	$(CH_3)_4NCl$	94—95
$Al(C_2H_5)Cl_2$	$(n\text{-}C_4H_9)_4NBr$	95—96
$Al(C_2H_5)Cl_2$	$(n\text{-}C_4H_9)_4NI$	97—98
$Al(C_2H_5)Cl_2$	$(n\text{-}C_4H_9)_4PI$	97—98
$Al(C_2H_5)Cl_2$	$(CH_3)_3SI$	97—98
$Al(C_2H_5)Br_2$	KCl	95—96
$Al(C_2H_5)I_2$	$(CH_3)_4NCl$	97—98
$Al(C_2H_5)I_2$	$(n\text{-}C_4H_9)_4NI$	97—98
$Al(C_2H_5)I_2$	HMPA	97—98
$(Al(C_2H_5)_2I)$	—	97—98
$(Al(C_2H_5)_2Br)$	—	95—97

[a] Expressed as % of non extractable polymer in boiling n-heptane.
For conditions, c.f., Table 2.

The addition of LEWIS bases to $Al(C_2H_5)_2Cl$ generally causes different decreases in stereospecificity depending on the type of base; they can be explained by the possible formation of $Al(C_2H_5)_3$, even if in very small and variable amounts, owing to the lower tendency of AlR_2X to dismutation.

It can be observed that the stereospecificity of the systems $TiCl_3$–$Al(C_2H_5)_2Cl$-LEWIS base is intermediate between that of the corresponding systems with $Al(C_2H_5)_2Cl$ or $Al(C_2H_5)_3$ respectively.

4. Ternary Systems — Violet $TiCl_3$–$Al(C_2H_5)Cl_2$ — "Alkyl-onium" Bromide or Iodide; Comparison with Systems Based on Violet $TiCl_3$ and Mixed AlR_2X

Table 5 shows the results from the polymerization of propylene to isotactic polymer with the use of catalytic systems consisting of violet $TiCl_3$ and $Al(C_2H_5)Cl_2$ in the presence of tetra-alkylammonium chloride, bromide and iodide and phosphonium or sulphonium iodide respectively, the ratio "onium" salt/Al being 0.5. The data obtained are compared with those concerning the binary systems based on violet $TiCl_3$ and $Al(C_2H_5)_2Br$ or $Al(C_2H_5)_2I$.

It can be observed that in these case the stereospecificity of the ternary systems is practically equal to that of the corresponding binary system containing AlR_2X with the highest stereospecificity. This result can be interpreted by assuming that similar to reaction 2 in the reaction between $Al(C_2H_5)Cl_2$ and bromide or iodide of an "onium" compound, not only $Al(C_2H_5)_2Cl$ but also $Al(C_2H_5)_2Br$ or $Al(C_2H_5)_2I$ respectively are formed. This hypothesis agrees with the analyses of the reaction products between $Al(C_2H_5)Cl_2$ and, e.g., tetraalkylammonium iodide.

By reacting these compounds in the ratio: "onium" iodide/Al = $^1/_2$ it is possible to separate, e.g., by distillation at 0.1 mm. Hg, a mixture of aluminum alkyl chlorides and iodides, in which the ratio of Al to halides is a little higher than 1. The ratio I/Cl in the distilled product is influenced by the reaction and distillation procedures. The residue consists of a solid product containing Cl, I and Al in various ratios, depending on the operating conditions; the ratio halides/Al is little different from 4.

To confirm these interpretations further, polymerization runs of propylene have been carried out with the use of systems consisting of violet $TiCl_3$ and of mixtures $Al(C_2H_5)_2Cl$–$Al(C_2H_5)_2I$ in various ratios. The data of Table 6 show that with $Al(C_2H_5)_2I$ exceeding an equimolar ratio in the mixture $Al(C_2H_5)_2Cl$–$Al(C_2H_5)_2I$, the stereospecificity of the system is practically identical with that of the binary system violet $TiCl_3$-$Al(C_2H_5)_2I$.

Table 6. Polymerization of propylene to isotactic polymer with the aid of the catalytic system: violet $TiCl_3$–$(C_2H_5)_2AlCl$–$(C_2H_5)_2AlI$; δ-$TiCl_3$: 3.24 mmoles, toluene: 200 ml.; $p_{C_3H_6}$ = 1500 mm. Hg; t = 70 °C.; time: $1^1/_2$ hrs.

$Al(C_2H_5)_2Cl$ (mmoles)	$Al(C_2H_5)_2I$ (mmoles)	$\dfrac{Al(C_2H_5)_2Cl}{Al(C_2H_5)_2I}$	Polymer obtained		
			(g.)	Index of isotacticity[a] (%)	$[\eta]$ [b] (100 ml./g.)
9.72	—	∞	13.8	93	3.9
8.1	1.62	5	9.4	94	4.0
12.96	3.24	4	9.0	94	4.0
6.48	3.24	2	8.0	96	4.1
4.86	4.86	1	6.6	97	3.2
3.24	6.48	0.5	5.8	97	3.0
1.62	8.1	0.2	5.3	97.5	3.8
—	9.72	0	6.5	97.5	3.1

[a] Expressed as % of non extractable polymer in boiling n-heptane.
[b] Intrinsic viscosity measured in tetralin at 135 °C.

It can also be observed that the nature of the cation present in the "onium" salt, be it alkylammonium or alkylphosphonium or alkylsulphonium ion, does not exert any influence on the stereospecificity of the resulting catalytic system.

Equal stereospecificities are obtained by using suitable alkaline halides, (see Table 5) and different $Al(C_2H_5)X_2$ instead of "onium" salts.

5. *Behaviour of systems with $Al(C_2H_5)Cl_2$-LEWIS base in other polymerization reactions*

If we assume that the reaction between $AlRX_2$ and substances able to form complexes with $AlCl_3$ yields $Al(C_2H_5)_2Cl$, according to reaction 1, and that AlR_2X participates in the formation of the catalytic systems, it can be foreseen that not only in the polymerization of propylene to isotactic polymer, but also in other polymerizations with the use of other co-ordinated organometallic catalysts a substantial similarity (concerning the stereospecificity) will be observed between the systems based on $AlRCl_2$ and a LEWIS base and those based on AlR_2Cl.

These hypotheses are confirmed by the data reported in Table 7 for the systems VCl_4-anisol–$Al(C_2H_5)_2Cl$ and VCl_4-anisol–$Al(C_2H_5)Cl_2$-pyridine used in the polymerization of propylene to syndiotactic polymer[7].

The same analogy, with regard to stereospecificity, was also observed between the systems cobalt compound–$Al(C_2H_5)_2Cl$ and cobalt compound

Table 7. Polymerization of propylene to syndiotactic polymer

Al(C₂H₅)₂Cl (mmoles)	Al(C₂H₅)Cl₂ (mmoles)	Pyridine (mmoles)	VCl₄·anisol (mmoles)	(g.)	Polymer obtained	
					I.R. index of syndio-tacticity[a]	$[\eta]$[b] (100 ml./g.)
4	0	0	1	1	2.5	0.27
0	10	5	1	1.8	0.4	0.4

[a] For the definition and determination of the index of syndiotacticity, see ref. [7].
[b] Intrinsic viscosity measured in tetralin at 135 °C.

The polymerization runs were carried out at −78°C. in 100 ml. of n-heptane and 80 g. propylene; time: 4 hrs.

Table 8. Stereospecificity of catalytic systems containing cobalt in the polymerization of butadiene

Al(C₂H₅)₂X	Al(C₂H₅)X₂	Lewis base	Cis-1.4 units in the polymer %[a]
Al(C₂H₅)₂Cl	—	—	98
—	Al(C₂H₅)Cl₂	Py	98
Al(C₂H₅)₂I	—	—	58
—	Al(C₂H₅)I₂	Py	57

[a] Determined by I.R.[9].

The polymerization runs were carried out in toluene at 0 °C., using Co(acetyl acetonate)₂ as cocatalyst, under the conditions indicated in ref.[8].

−Al(C₂H₅)Cl₂-Lewis base (or alkaline or "onium" salt) used in the polymerization of butadiene to cis-1,4 polymer[8] (Table 8).

It should be pointed out that in these two last types of polymerizations the stereospecificity of the catalytic system is strictly connected with the nature of the AlR₂X. Actually, in the polymerization of propylene to syndiotactic polymer with the use of catalysts based on vanadium compounds, only Al(C₂H₅)₂Cl and not Al(C₂H₅)₂Br or Al(C₂H₅)₂I produces stereospecific catalytic systems[7].

Also the systems with cobalt compounds for the polymerization of butadiene to cis-1.4 polymer are highly stereospecific if the AlR₂X used to prepare the catalytic system is a chlorocompound (Table 8).

III. Discussion of the Results

The dismutation reactions of AlRX₂ by the action of a substance able to form addition compounds with AlX₃ are not in contrast with the thermodynamic data reported in literature.

It is actually known that many LEWIS bases and other complexing substances, such as alkaline halides and alkyl "onium" halides can react with aluminum trihalides, aluminum alkylhalides and aluminum trialkyls to form 1:1 addition compounds[5].

Due to the electronegative character of the halogen atoms, the energy of the dative bond between LEWIS base and aluminum atom increases for the following compounds in the order[*]:
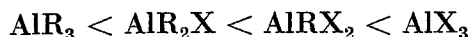
$$AlR_3 < AlR_2X < AlRX_2 < AlX_3$$

Table 9. Heats of complexation (kcal./mole) of $Al(C_2H_5)_3$ [10] and $AlCl_3$ [11] with LEWIS bases

| LEWIS base	$Al(C_2H_5)_3$	$AlCl_3$
Ethyl ether............	11.2	—
Diphenyl ether.........	2.7	4.1
Anisol	2—3	8.2
Pyridine	19.4	47.8

In order to point out better the relative values of these bond energies we report in Table 9 the ΔH of the following complexation reactions for some LEWIS bases (Y):

$$Al_2Cl_6 + 2Y \rightleftarrows 2Y \cdot AlCl_3 \qquad (7)$$

$$Al_2(C_2H_5)_6 + 2Y \rightleftarrows 2Y \cdot Al(C_2H_5)_3 \qquad (8)$$
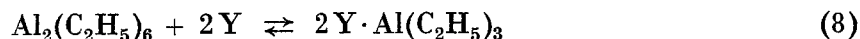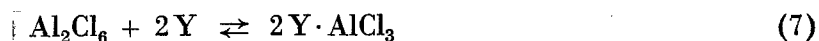
It is observed that the heat evolved from reaction 7 is markedly higher than that from reaction 8, even if the association energy of Al_2Cl_6 is higher than the association energy of $Al_2(C_2H_5)_6$ at least by 9 to 10 kcal.[12, 13] [**].

From the higher stability of the dative bonds in the $Y \cdot AlX_3$ complexes with respect to the corresponding bonds in the $Y \cdot AlX_2R$, $Y \cdot AlXR_2$ and $Y \cdot AlR_3$ complexes, it can be understood how, under the thermodynamic equilibrium conditions, the $Y \cdot AlX_3$ addition compound can be present in

---

[*] e.g., for this reason the reaction:

$$Y \cdot Al(C_2H_5)_3 + {}^1/_2 Al_2(C_2H_5)_4Cl_2 \rightarrow Y \cdot Al(C_2H_5)_2Cl + {}^1/_2 Al_2(C_2H_5)_6$$
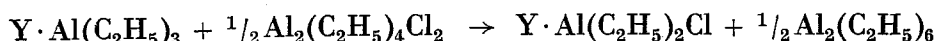
is totally shifted toward the right, even if the association energy of $Al_2(C_2H_5)_6$ is lower than that of $Al_2(C_2H_5)_4Cl_2$.

[**] For an exact formulation of the calculation of the bond energies and of the free enthalpies concerning the addition compounds considered here, see for instance ref.[14].

a system prepared from a Lewis base Y and from $Al_2X_4R_2$; therefore, also $Al_2X_2R_4$ or $Y \cdot AlR_2X$ can be present, depending on the ratio Y/AlX_2R used.

This is particularly evident for the systems prepared with $Y/AlRX_2$ ratios equal to 1/2. Actually, in that case the absence of detectable amounts of the $Y \cdot [AlRX_2]_2$ complexes was demonstrated and it can be assumed that reaction 1 will be more favoured than reaction 9:

$$Al_2R_2X_4 + Y \rightarrow Y \cdot AlRX_2 + {}^1/_2 Al_2R_2X_4 \qquad (9)$$
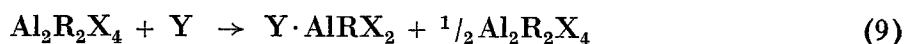
By operating at a $Y/AlRX_2$ ratio equal to 1, either reaction 3 or reaction 10

$$Al_2R_2X_4 + 2Y \rightarrow 2Y \cdot AlRX_2 \qquad (10)$$
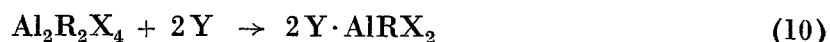
or both could occur.

The data reported in this paper show that, under these conditions, reaction 3 occurs at least in part.

A final remark on the interpretations reported above concerns the kinetic behaviour of the dismutation reactions previously discussed.

We think that the kinetics of these reactions is such that the system is soon brought to its thermodynamic equilibrium. This actually occurs for various systems studied so far, containing organometallic compounds of aluminum, in the presence or in the absence of Lewis bases. For instance, reaction 1 occurs very rapidly even at rather low temperatures; sufficiently strong Lewis bases, such as pyridine, easily react with $Al_2R_4(OR)_2$ to give the corresponding 1:1 addition compounds even if aluminum dialkyl monoalcoholates are strongly associated[5].

We note that also other reactions, in which aluminum alkyls participate, are very rapid; for instance, $Al_2(C_2H_5)_6$ reacts rapidly with $Al_2(C_2H_5)_2Cl_4$ to give $Al_2(C_2H_5)_4Cl_2$.

A quite similar behaviour is observed in the reaction between $Al_2(CH_3)_6$ and $Al(i\text{-}C_4H_9)_3$ (monomeric): these two components react with considerable evolution of heat to yield the corresponding mixed dimeric aluminum alkyls, in which the Al atoms are bound by CH_3 bridges[5].

These reactions occur because the possible different complex equilibriums in which the aluminum alkyls participate are shifted toward those dimeric components that can be less easily dissociated.

IV. *Conclusions*

The results reported in this paper show that $AlRX_2$ cause, to a different degree, a dismutation reaction by the action of LEWIS bases, or of "onium"-alkyl halides or of alkaline halides, practically for wide ranges of the ratio between the complexing substance and $AlRX_2$.

AlR_2X is formed in the dismutation reaction; therefore, on the basis of the results reported in this paper, it must be assumed that, also in the case of the ternary systems which were considered in this paper, prepared from $AlRX_2$ and from a complexing substance, and in analogy to observations in other catalytic systems[4], the monomeric species AlR_2X (not associated or not complexed) always participates in the formation of the catalytic complexes.

Significant amounts of these complexes are formed only if the concentration of AlR_2X in the free, not associated state is sufficiently high. This concentration can be varied by the use of LEWIS bases having a different strength in the dismutation reaction of $Al_2R_2X_4$ and by suitably varying the ratio of LEWIS base to $Al_2R_2X_4$.

The stereospecificity of the different catalytic systems obtained does not depend, in this case, on the nature of the complexing agent and is equal to that of the systems prepared from the corresponding AlR_2X compound.

The various results reported in this paper are in contrast to the interpretations given by other authors[15], with regard to the behaviour of our ternary catalytic systems for the stereospecific polymerization of propylene to isotactic polymer.

It can be generally foreseen that, by reaction between $AlRX_2$ and any other organic or inorganic substance, either monomeric or polymeric, containing atoms or groups with a basic character in the meaning of a LEWIS base, a dismutation of $AlRX_2$ can occur; therefore, it is also possible to obtain organometallic catalytic systems of the co-ordinated type. The only restriction is that groups, able to react with $Al(C_2H_5)_2Cl$ by opening of the organometallic bond, must be necessarily absent in the complexing substance of the catalytic system.

V. *Experimental Part*

The apparatus used and the operating procedure are described in previous papers[1, 3, 4, 7] in which the reagents used, their degree of purity or their origin and the relating preparation methods are also indicated.

G. Natta, A. Zambelli, I. Pasquon, G. Gatti, and D. DeLuca

With regard to the polymerization of propylene to isotactic polymer promoted by binary catalytic systems consisting of violet $TiCl_3$ and of organometallic compounds of aluminum, we only wish to emphasize the great influence exerted by the degree of purity of the violet $TiCl_3$ used. In particular, the presence of tetravalent titanium compounds, which easily defile $TiCl_3$, depresses the stereospecificity of the catalytic systems based on violet $TiCl_3$ and $Al(C_2H_5)_2Cl$ or $Al(C_2H_5)_3$.
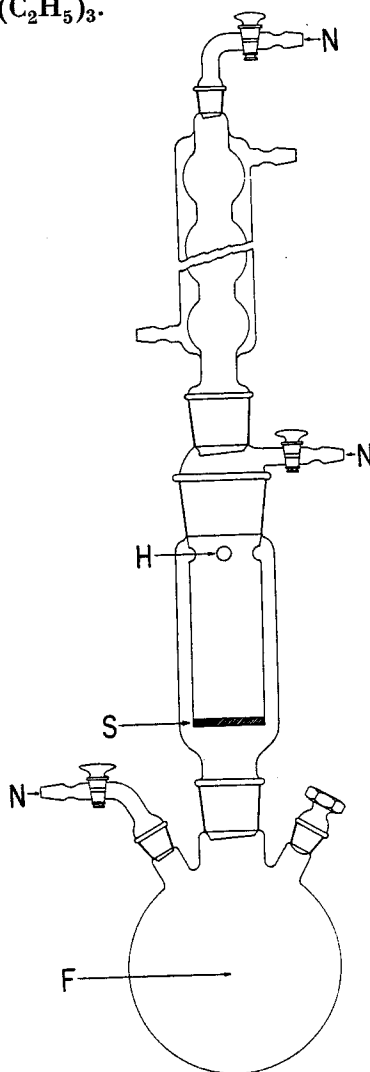

Fig. 1. Extractor in inert atmosphere

The substance to be extracted is put on the sintered glass filter (S). Solvent vapours from the flask (F) pass through the holes (H) and after condensation reflux by performing the extraction on (S). The nitrogen atmosphere is maintained by the tubes (N)

The influence of such impurities on the ternary catalytic systems is much less marked, probably because the impurities interact with the Lewis base or with the secondary products of the reaction between $AlRX_2$ and complexing substances. In order to eliminate these inconveniences, in our runs we used samples of violet $TiCl_3$, previously washed under nitrogen atmosphere by boiling toluene extraction in modified Kumagawa extractors (Fig. 1). Amounts of $LiAlH_4$ sufficient to reduce impurities of Ti^{IV} extracted by the solvent were added to the toluene contained in the flask; thus their re-cyclization with the solvent was avoided.

Dismutation of Aluminum Monoalkyldihalides by Complexing Substances

The extraction was carried on until the $TiCl_3$ sample was no longer able to colour the toluene it contacted. Then the samples were removed from the extractor, and by siphoning under nitrogen put into containers equipped with side taps and maintained under inert diluent.

If toluene in contact with $TiCl_3$ exhibits colouring, washing was repeated. The $TiCl_3$ necessary for each polymerization was collected (previous motion of the container) as a suspension, by a graduated pipette.

In order to obtain fairly well reproducible samples of $TiCl_3$ it is suitable to use suspensions that do not contain more than 5 g. $TiCl_3$/100 ml. diluent.

Preparation of the catalytic systems

The catalytic systems were prepared by pre-reacting the organometallic compounds of aluminum with the complexing substances in order to avoid secondary complexations reactions of $TiCl_3$.

[1] A. ZAMBELLI, J. DIPIETRO, and G. GATTI, J. Polymer Sci. A 1 (1963) 403.

[2] K. ZIEGLER, R. KÖSTER, H. LEHMKUHL, and K. REINERT, Liebigs Ann. Chem. 629 (1960) 33.

[3] G. NATTA, I. PASQUON, A. ZAMBELLI, and G. GATTI, J. Polymer Sci. 51 (1961) 387.

[4] I. PASQUON, A. ZAMBELLI, and G. GATTI, Makromolekulare Chem. 61 (1963) 116.

[5] K. ZIEGLER, "Organoaluminum Compounds" and relating bibliography in H. ZEISS, "Organometallic Chemistry", Reinhold, N.Y. (1960).

[6] G. NATTA, P. CORRADINI, and G. ALLEGRA, J. Polymer Sci. 51 (1961) 399.

[7] A. ZAMBELLI, G. NATTA, and I. PASQUON: Paper presented at the IUPAC Symposium on Macromolecular Chemistry, Paris (1963).

[8] Fr.Pat. 1,322,557 (30.5.1961) Erf.: G. NATTA, L. PORRI, I. PASQUON, and A. ZAMBELLI.

[9] D. MORERO, A. SANTAMBROGIO, L. PORRI, and F. CIAMPELLI, Chim. e Ind. [Milano] 41 (1959) 758.

[10] E. BONITZ, Chem. Ber. 88 (1955) 742.

[11] M. H. DILK, D. D. ELEY, and M. G. SHEPPARD, Trans. Faraday Soc. 46 (1950) 267.

[12] A. W. LAUBENGAYER and W. F. GILLIAM, J. Amer. chem. Soc. 63 (1961) 477.

[13] W. FISCHER and O. RAHLFS, Z. anorg. Chem. 205 (1932) 1.

[14] F. G. A. STONE, Chem. Reviews 58 (1958) 101.

[15] H. W. COOVER Jr., Paper presented at the IUPAC Symposium on Macromolecular Chemistry, Paris (1963).