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CONTENTS

New Aspects of Some Organometallic Complex Compounds

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THE most important fact for the understanding of many reactions of the organoaluminium compounds is the electron-deficiency of the aluminium atoms in the aluminium trialkyls and similar substances:
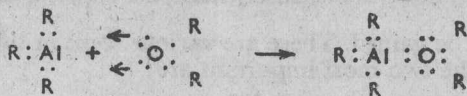
This lack of electrons causes the well-known formation of stable complex compounds of the aluminium trialkyls with electron-donors such as ethers and tertiary amines. In addition, the electron-deficiency is the reason why many aluminium trialkyls are associated to dimers, which I shall discuss in detail later.

It is obvious that the aluminium trialkyl molecules also tend to add negative ions. Indeed, two typical addition products of this kind have long been known: those of negative hydrogen ions, and those of negative alkyl ions such as are realised in the complex anions of $Li^+(Na^+)[AlHEt_3]^-$ and $Na^+[AlEt_4]^-$. It was to be expected also that the most typical negative halogen ions should add to aluminium trialkyls. This indeed is the case, but it had been overlooked for a long time until about 1950 when Dr. Köster[1] discovered in my Institute the addition of sodium fluoride and somewhat later of potassium chloride to triethylaluminium to form $Na[AlEt_3F]$ and $K[AlEt_3Cl]$ respectively. These two discoveries were the starting point for a wide and systematic research on the complex compounds between alkali halides and aluminium trialkyls. It was found that the stability of such complexes depends on the alkali halide used and on the size of the alkyl radicals bound to the aluminium.

Table 1 summarises the results of our investigation with regard to the ethyl compounds only. The stability of these complexes can be compared by several methods. The complexes on the lower left-hand side of the Table are the most stable.

These results can be easily explained in the following way. (1) When such a complex compound is formed we have first to split the alkali halide crystal into the single ions. This requires the lattice energy U_{AX}. (2) The aluminium trialkyls are normally associated to dimers which also have to

be split. The necessary energy is about 10 kcal. mole^{-1} for $\frac{1}{2}[AlR_3]_2$. Thus, in all, $(U_{Ax} + 10)$ kcal. mole^{-1} are required. Then the complexes are formed

TABLE 1. *Stability of aluminium triethyl complexes*
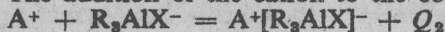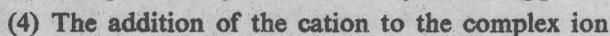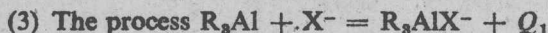*with halides having univalent cations.*

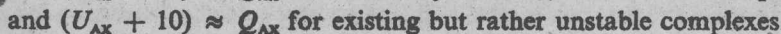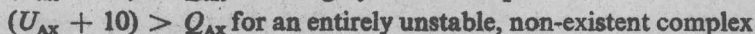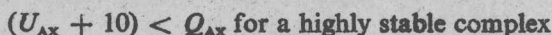|	H$^-$	F$^-$	Cl$^-$	Br$^-$	I$^-$
Li$^+$	+	−	−	−	−
Na$^+$	+	+	−	−	−
K$^+$	(+)	+	+	−	−
Rb$^+$	(+)	+	+	+	−
Cs$^+$	(+)	+	+	+	−
Et$_4$N$^+$	?	+	+	+	+

+ Complex formed.
− No complex formed.
(+) Complex presumably stable, but not yet isolated.

and energy can be gained. There are various steps in this complex formation, of which the two most important are:

(3) The process $R_3Al + X^- = R_3AlX^- + Q_1$

(4) The addition of the cation to the complex ion
$A^+ + R_3AlX^- = A^+[R_3AlX]^- + Q_2$

I shall combine these Q's to Q_{Ax}. Clearly we have:

$(U_{Ax} + 10) < Q_{Ax}$ for a highly stable complex

$(U_{Ax} + 10) > Q_{Ax}$ for an entirely unstable, non-existent complex

and $(U_{Ax} + 10) \approx Q_{Ax}$ for existing but rather unstable complexes

For existing but rather unstable complexes this energy of complex-formation from the ions and the monomer of aluminium triethyl can be estimated with an uncertainty of only a few calories. Such a complex is that of RbBr. It can very easily be split into its components. Therefore we have:

$U_{RbBr} + 10 \approx Q_{RbBr}$ or $Q_{RbBr} \approx 167$ kcal. mole^{-1}
$(157 + 10)$

Very good agreement is reached between our experimental observations and such energy calculations if one starts from this value and assumes that the Q_{Ax} for the different alkali halides are proportional to the reciprocals of the radii of the halogen ions. Of course, this is a simplification because the possible effect of the different cations is entirely neglected. Nevertheless the conclusions are, as you will see, reasonable. Indeed, special estimations demonstrate that the influence of different cations cannot be very great. The radii of the halogen ions are:

r_F 1·33 Å, r_{Cl} 1·81 Å, r_{Br} 1·96 Å, r_I 2·19 Å

$Q_{AF} : Q_{ACl} : Q_{ABr} : Q_{AI} = 1·48 : 1·09 : 1 : 0·90$

Then these ratios are 248 : 182 : 167 : 150 if $Q_{ABr} \approx Q_{RbBr}$
≈ 167 kcal. mole^{-1}.

According to our simplification all fluorides, chlorides, bromides, and iodides would have the same values for these Q's.

The lattice energies of the alkali halides are well known: they are as in Table 2. Thence we calculate the differences $Q_{AX} - (U_{AX} + 10)$, with results given in Table 3. The results are in entire agreement with our

TABLE 2. *Lattice energies* (U_{AX}) *of the alkali halides* AX *from lithium fluoride to cæsium iodide* ($T = 291°$K).

	F	Cl	Br	I
Li	247	203	191	178
Na	218	185	178	165
K	195	170	163	154
Rb	185	163	157	149
Cs	177	155	151	144

TABLE 3. *Energies for complex formation* (kcal. mole^{-1}) *of aluminium triethyl and alkali halides.*

	F	Cl	Br	I
Li	− 9	−31	−34	−38
Na	+20	−13	−21	−25
K	+43	+ 2	− 6	−14
Rb	+53	+ 9	0	− 9
Cs	+61	+17	+ 6	− 4

observations. The minus signs in Table 1 correspond to endothermic, and the plus signs to exothermic, complexes.

In the course of these systematic investigations a new type of complex compound was discovered, the so-called 1:2 complexes such as NaF,2AlEt$_3$,[2] CsCl,2AlEt$_3$, and LiH,2AlEt$_3$. They probably have structures

(A)   (B.)
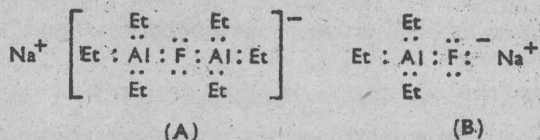
such as (A). This must be a better electrolyte than (B) where the sodium ion can come much nearer to the halogen ion to form a dipole. Indeed the electrolytical conductivity of NaF,2AlEt$_3$ is about 100 times higher than that of NaF,AlEt$_3$.

When we increase the size of the alkyl bound to the aluminium the stability of the complexes decreases. In homologous aluminium trialkyls there is a sharp limit for each alkali halide beyond which no more complex compound exists. For sodium fluoride this lies between aluminium tributyl and trihexyl. NaF,AlBu$_3$ and NaF,2AlBu$_3$ exist, but the corresponding trihexyl compounds do not. For potassium fluoride the limit obviously

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lies much higher and has not yet been reached: even aluminium trioctyl combines with this halide. For other halides the positions of the limits have been well established, as Table 4 shows.

TABLE 4. *Formation of complexes by aluminium trialkyls* (AlR_3) *with alkali halides and its dependence on the size of the alkyl.*

|	Fluoride				Chloride				Bromide			
	Na	K	Rb	Cs	Na	K	Rb	Cs	Na	K	Rb	Cs
Et	++	++	++	++	−	+	+	++	−	−	−	+
Pr	++	++	++	++	−	−	+	++	−	−	−	+
Bu^n	++	++	++	++	−	−	+	+	−	−	−	+
n-C$_6$H$_{13}$	−	++	++	++	−	−	−	+	−	−	−	−
n-C$_8$H$_{17}$	−	++	++	++	−	−	−	+	−	−	−	−

++ 1:2 complexes have also been found.

For practical purposes these alkali halide complexes are important for three reasons:

(1) The 1:2 addition product of sodium fluoride and aluminium triethyl, having rather good electrical conductivity, is a good electrolyte for deposition of extremely pure metallic aluminium by electrolysis.[2]

(2) The formation and thermal splitting of the 1:2 potassium fluoride-aluminium triethyl complex into the 1:1 compound and aluminium triethyl can be used for extracting and recovering aluminium triethyl from mixtures. This is important for the manufacture of higher long-chain alk-1-enes from ethylene.

It is now well-known that aluminium triethyl can be transformed into a mixture of higher aluminium trialkyls by ethylene at about 100 atm. at 100—110°. If we add these higher aluminium trialkyls at the top of a reaction tower filled with a solid nickel catalyst and let them react with ethylene at about 80—90° and 20—40 atm., then further growth of the aluminium alkyl residues is very slow, but another reaction takes place, the so-called "replacement":

$$Et \cdot [C_2H_4]_n \cdot Al_{\frac{1}{3}} + C_2H_4 \rightarrow Et \cdot [C_2H_4]_{n-1}CH = \cdot CH_2 + EtAl_{\frac{1}{3}}$$
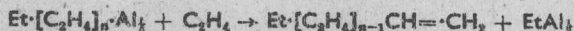
During this step the aluminium triethyl is recovered but it is difficult to separate from certain olefins, especially those with 10—12 carbon atoms. A very convenient way to solve this problem is: (*a*) to add the compound KF,AlEt$_3$ to the olefin–aluminium triethyl mixture, KF,2AlEt$_3$ being formed; (*b*) to distil off the olefins at a moderate temperature *in vacuo* (this is possible with all the olefins of up to 14—16 carbon atoms); (*c*) to split the 1:2 compound into the 1:1 compound and aluminium triethyl at 160—180°/0·1 mm.

(3) Another interesting and important synthetical possibility has been opened up by a detailed study of the alkali halide complexes of dialkyl-aluminium monohalides. It also has a relation to the problem of polymerising ethylene to higher long-chain alk-1-enes.

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One of the first observations in our field was the formation of sodium–aluminium–monoethyl–trichloride on addition of sodium chloride to monoethylaluminium dichloride. It was made by Hall and Nash[6] in England in 1937. The addition product Na[AlEtCl$_3$] is, of course, an analogue of sodium aluminium tetrachloride, NaAlCl$_4$. Hall and Nash used this reaction for separating pure diethylaluminium monochloride from its mixture with the dichloride. The dichloride gives the non-volatile addition product, the monochloride does not. For many years this result was generalised. It was believed that the dichloride gave complexes with alkali halides, and the monochloride did not. This generalisation was an error. The tendency to form stable complexes changes with the alkali halide, and thus Na[AlEt$_2$Cl$_2$] does not exist, but K[AlEt$_2$Cl$_2$] and even K[AlEt$_2$Br$_2$] are quite stable.

When these compounds are heated *in vacuo* they undergo disproportionation:

$$2K[AlEt_2Cl_2] = KCl + K[AlEtCl_3] + AlEt_3$$
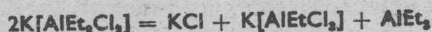
This is a new way of making aluminium triethyl from the diethyl monochloride. The reaction is not so very important in itself, but it becomes highly interesting in the following connection.

Aluminium triethyl undergoes the growth reaction with ethylene to form higher aluminium alkyls, the monochloride does not. Therefore the disproportionation makes a reactive aluminium compound from a non-reactive one, and it does so with full reversibility. For if we mix the distillate with the residue we get back the original complex compound which does not react at all with ethylene. Splitting and recombination gives us an extremely simple possibility to activate and to deactivate the organoaluminium compound toward ethylene at will.

Next we come back to the synthesis of higher olefins from ethylene. In the first step we had the growth reaction, and in the second the displacement, on a nickel catalyst. Such a solid catalyst is not very effective. The reaction rate is rather low. But we had no choice because the resulting mixture of olefins and aluminium triethyl must be free from nickel. Otherwise, during the distillation nickel-catalysed inverse replacement occurs in the absence of excess of ethylene:

$$C_2H_5 \cdot [C_2H_4]_{n-1} \cdot CH=CH_2 + EtAl_3^1 = C_2H_4 + Et \cdot [C_2H_4]_{n-1} \cdot CH_2 \cdot CH_2Al_3^1$$
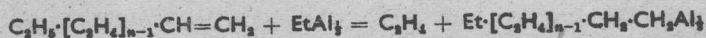
The new findings allow us to use, instead of a solid nickel catalyst, the much more active colloidal nickel added directly to the liquid higher aluminium trialkyl. After the resulting very quick replacement we have a mixture of higher alk-1-enes, aluminium triethyl, and colloidal nickel. Then we use the trick of adding the mixture KCl–K[AlEtCl$_3$] obtained as residue at the beginning of the series of reactions by splitting the complex potassium chloride–diethylaluminium monochloride. It is exactly equivalent to the aluminium triethyl formed as distillate in that splitting. Nickel functions as a catalyst for the replacement or its reverse only in the presence of true aluminium trialkyls. Therefore the deactivation of the

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aluminium triethyl is at the same time a complete deactivation of the nickel catalyst. Besides this, the recovered complex $K[AlEt_2Cl_2]$ is completely insoluble in the olefins. It separates spontaneously as a lower layer. The colloidal nickel goes wholly into the upper layer. Separation of the olefins from the trace of colloidal nickel is very simple. The lower layer, *i.e.*, the complex compound, is split once more, and the whole process can be repeated again and again.

I believe that this series of reactions is one of the nicest applications of a complex organoaluminium compound for solving a quite interesting and important problem of synthetic organic chemistry.

Next I shall consider the autocomplexes of aluminium alkyls and related compounds.

There have been some rather hypothetical considerations in recent publications that the special reactivity of the aluminium alkyls toward ethylene has something to do with the existence of electron-deficient bonds in the dimers of the aluminium trialkyls: primarily the dimers are supposed to react.[4,5]

We have very good experimental proof that such ideas are wrong. The most convincing is that the absorption rate of ethylene by dissolved aluminium triethyl to form butyldiethylaluminium increases when we add more solvent. This rate of absorption is proportional to the square root of the total volume. This is typical for a system $R-R \rightleftharpoons 2R$ with a very low degree of dissociation in which the monomer reacts.

The self-association of aluminium trialkyls and the complex formation with negative ions having the same origin, namely, the tendency of the electron-deficiency to be remedied, we expect a parallelism between the two phenomena.

The alkali halide complexes were less stable the larger the alkyl radicals bound to the aluminium. Therefore we expect a decreasing tendency to dimerise with longer chains on the aluminium. This indeed is the case. It has been demonstrated by Dr. Neumann in my Institute by careful molecular-weight measurements; for 0·05M-solutions in cyclohexane at 5° he found 7% of dissociation for tri-n-butyl- and 10% for tri-n-hexyl-aluminium, but for triethyl- and tripropyl-aluminium it was not measurable.

A consequence of the formation of autocomplexes which I have not yet discussed is the complete interchange of alkyl between aluminium trialkyls with different radicals attached to the aluminium.

If we mix two aluminium trialkyls $[R_3Al]_2$ and $[R'_3Al]_2$ each of them is dissociated:

$$[R_3Al]_2 \rightleftharpoons 2R_3Al \text{ and } [R'_3Al]_2 \rightleftharpoons 2R'_3Al$$

Consequently, mixed dimers $[R_3Al \cdot AlR'_3]$ should also be found. These should be written (I) and if this dissociates again the two processes have the same probability. Therefore an alkyl interchange should occur rather quickly in all those cases where the association is not too strong.

Experimental proof of this interchange has been found in the following way. Aluminium tri-isobutyl is only slightly associated. The same applies

to all aluminium trialkyls with α-substituents, *e.g.*, aluminium tri-iso-octyl. The triisobutyl compound crystallises at about +5° and is a suitable solvent for cryoscopic measurements. The apparent molecular weight of

$$(I) \quad R_2Al \overset{\displaystyle R}{\underset{\displaystyle R}{\cdots\cdots}} AlR'_2$$

$$R_3Al + R'_3Al \qquad\qquad R_2R'Al + R'_2RAl$$
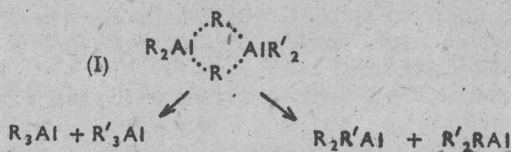
aluminium triiso-octyl in aluminium triisobutyl is one-third of the calculated. So, in the excess of aluminium triisobutyl each molecule of the triiso-octyl compound has formed three molecules of diisobutyloctyl-aluminium:

$$R_3Al + 2AlR'_2 = 3AlR'_2R$$

It seems probable that the formation of autocomplexes plays an important part in this phenomenon. Boron trialkyls are not at all associated and do not show radical interchange below 100°. On the other hand, mixed dimerisation of the type:

$$[R_3Al]_2 + 2BR'_3 \rightleftharpoons 2R_3Al,BR'_3$$
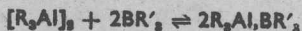
seems to be possible to some extent because aluminium trialkyls and boron trialkyls undergo an extremely quick alkyl-interchange. Aluminium trialkyls are decomposed by water while boron trialkyls are not. Mixtures of equivalent amounts of aluminium triethyl and boron tributyl give ethane and butane in the exact ratio 1:1 immediately on being mixed with water. In such circumstances aluminium trialkyls must be highly efficient catalysts for radical interchange between different boron trialkyls. Indeed, a mixture of 1 mol. each of boron triethyl and boron tripropyl is stable for a long time. Its gas chromatogram shows two peaks. When a trace of aluminium triethyl is added and immediately thereafter destroyed by water the gas chromatogram then shows four peaks corresponding to BEt_3, BEt_2Pr, $BEtPr_2$, and BPr_3. This is a new type of catalysis in which co-ordination compounds play an important part as intermediates.

These observations are of some theoretical interest, and they are important for various reasons.

(1) We know that only the true monomeric aluminium trialkyls were able to add ethylene. Further, the tendency to give these monomers by dissociation of the dimers increases with growing chain-length of the aluminium trialkyls. If so, further growth of longer chains on addition of ethylene should be more favoured than the growth of short chains. This should have a considerable influence on the distribution of the different molecular sizes formed in our growth reaction. The distribution should be broader than that calculated under the assumption that all Al–C bonds in the reacting system have the same chance to catch an ethylene molecule. The complete radical interchange in such mixtures hinders the formation of real $AlBu_3$, $Al(C_6H_{13})_3$, $Al(C_8H_{17})_3$, etc. The lower alkyls are predominantly attached with higher alkyls to the same aluminium. That

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implies that, while the probability of the lower alkyls being present in reactive monomers is increased, that for higher alkyls is lowered. The result must be slightly favoured growth of the longer chains. I believe that we have really found this effect. The annexed diagram shows the distribution of the molecular sizes after hydrolysis of a growth experiment with $C_3H_7Al_3 + C_2H_4$ in the ratio 1:2·2. The distribution is similar to that calculated, but there are some differences in the expected direction.

Distribution of hydrocarbons yielded by hydrolysis of products from
$$C_3H_7Al_3 + 2\cdot2C_2H_4$$

□ *Calc. values.* ■ *Exptl. values.*
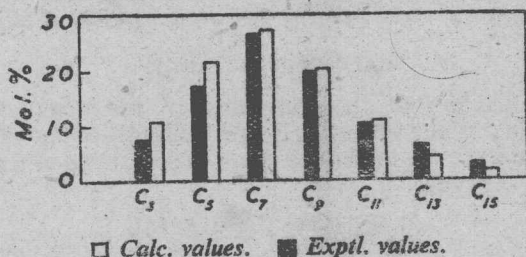
(2) The alkyl interchange between aluminium trialkyls and boron trialkyls probably caused by the intermediate formation of co-ordination compounds between the two trialkyls has yet another consequence. Aluminium trialkyls can add ethylene under reasonable conditions, boron trialkyls cannot. It was to be expected that the aluminium compounds would be able to catalyse the addition of ethylene to boron trialkyls, and this was found to be so: the longer alkyls grown on to the aluminium pass to the boron, unreactive lower alkyls originally bound to boron migrate to aluminium and become reactive toward ethylene. In this way, application of the growth reaction has been considerably widened.

(3) This has been done even more effectively with aluminium trialkyls as catalysts for increasing the reactivity of unreactive aluminium compounds. Obviously there exist also associated mixed dimers between aluminium trialkyls and compounds of the general type R_2AlX, where X is, for instance, halogen, alkoxyl, etc. Such compounds can be written as (II) and therefore alkyl interchange between the R_2AlX compound and


(II)
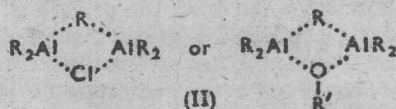
the aluminium trialkyls should be possible. Thus again the trialkyls are able to function as catalysts for the reaction between ethylene and those compounds of dialkylaluminium which do not normally add ethylene at all.

This fact again plays an important part in the synthesis of higher olefins from ethylene. I mentioned the disproportionation of the potassium chloride–dialkylaluminium chloride complexes according to the reaction:

$$2K[AlR_2Cl_2] = KCl + K[AlRCl_3] + AlR_3$$
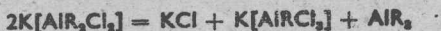
and I now have to explain this in somewhat more detail. This reaction is not entirely smooth. Beside this disproportionation a considerable quantity of the complex is just split into the original components:

$$K[AlR_2Cl_2] = KCl + AlR_2Cl$$
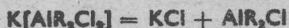
Thus, the real product of thermal decomposition is a mixture of the dialkylaluminium chloride and more or less of the aluminium trialkyl. According to the new catalytic effect this mixture gives the growth reaction with ethylene just as does the aluminium trialkyl itself. It is only necessary that some few per cent of aluminium trialkyl are formed by the thermal decomposition, and the total reaction product can be used as if it were the trialkyl compound.

Of course, the equivalence between the residue of the thermal splitting and the aluminium alkyl compounds in the distillate is not altered by the somewhat more complicated course of that splitting because in each case the $K[AlRCl_3]$ in the residue must be equivalent to the AlR_3 in the distillate. We recognise that the best known way from ethylene to longer-chain alk-1-enes is a very efficient combination of steps each of which has close relations to the co-ordination chemistry of the organoaluminium compounds.

As a final section I shall present some more hypothetical considerations. It was impossible to include in this Lecture all the catalysts discovered in my Institute in 1953, which I called in German "metallorganische Mischkatalysatoren" and which later often were called in English "organometallic complex catalysts." The manifold different catalysts made by mixing compounds of metals such as titanium, zirconium, vanadium, and chromium with organometallic compounds, especially those of aluminium, have been and still are being investigated, probably by some thousands of chemists all over the world; and a great many papers and patent applications have been published. Even to the father of all that trouble it becomes more and more difficult to oversee all the scientific children and grandchildren of his discovery. I have some doubts whether a final and really comprehensive theory of the whole field is yet possible. The attempt to summarise our own results and those of so many others would exceed the possibilities of a short hour. Therefore I will touch this field only at the following point which has a direct relation to the main part of my Lecture.

About a year ago a Belgian patent[6] of the American Goodrich Gulf Company described the catalysis of a normal-pressure growth reaction of diethylaluminium chloride by a trace of titanium tetrachloride in xylene solution. This system is very closely related to one of our first normal-pressure polyethylene catalysts. The products are obviously the long-chain

dialkylaluminium chlorides because their further reaction with air or oxygen leads to aluminium alkoxides and alcohols. The trace of titanium chloride is by no means sufficient to yield any considerable quantity of an organotitanium compound. It is very likely that the titanium compound functions as a very active catalyst for a real stepwise organometallic synthesis because the distribution of the products after hydrolysis or oxidation is very similar to that distribution in our old growth reaction and because the growth can be interrupted and continued at will by alternately stopping and restarting the ethylene stream. The efficiency of the catalyst is clearly demonstrated by the consideration that diethyl-aluminium chloride itself does not add ethylene at all, aluminium triethyl requires 100°/100 atm., and the new reaction proceeds at about 40°/1 atm. I take this reaction to be the key for the understanding of at least the low-pressure polyethylene formation in the presence of similar catalysts, but under other reaction conditions. There have been theoretical considerations by different authors that complex compounds between organo-aluminium compounds and titanium halides are the active intermediates in such polymerisations. This may be true or false, but in any case the following consequence of our findings should be considered.

In the case of aluminium alkyls, boron alkyls, or diethylaluminium halides, the possible complex compounds (dimers or mixed dimers) certainly do not react with the olefin. Only the true monomeric aluminium trialkyls do. Nevertheless, the formation of supposed mixed co-ordination compounds between aluminium trialkyls and boron trialkyls or diethyl-aluminium halides was very important for the activation of the products not reacting directly with the olefin because without such complex formation we would not have the alkyl interchange between the two types of compounds. For the cases described in detail the activating aluminium trialkyls had a moderate reactivity. Now if highly reactive organotitanium compounds existed they would, through complex compounds with aluminium alkyls and alkyl interchange, lend their own reactivity to the aluminium alkyls. If such a mechanism exists, complex compounds between titanium compounds and aluminium alkyls may have a lower reactivity or no reactivity at all. Nevertheless, it would be possible to understand any observed degree of activation by titanium compounds added.

Some organotitanium compounds have indeed been prepared, for instance, CH_3TiCl_3.[7] Similar compounds with titanium in a lower valency state may also exist. Even though they cannot be isolated as such they may be present in interchange equilibria of the type $Al_3R + Ti^{III}Cl \rightleftharpoons Al_3Cl + Ti^{III}R$. If the left-hand side is highly favoured the Ti_3R would not be found. But if it has a high reactivity toward ethylene and if it gives a second equilibrium,

$$\text{Al alkyl} + \text{Ti alkyl} \rightleftharpoons \text{Al Ti alkyl complex}$$
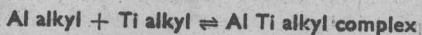
capable of alkyl interchange, the catalysis would be very easily understood without assuming a special and high reactivity for the complex compounds themselves.

I have the impression that such possibilities should at least be earnestly considered in the theory of the complex catalysts. So far as I know, they have been neglected up to the present.

References :

[1] Ziegler, Holzkamp, Köster, and Lehmkuhl, *Angew. Chem.*, 1955, **67**, 213.
[2] Ziegler and Lehmkuhl, *Z. anorg. Chem.*, 1956, **283**, 414.
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The Stability of Metal Complexes

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THERE can be no more appropriate way of beginning this lecture than by recalling that both Part I (Organic Ligands) and Part II (Inorganic Ligands) of the long-awaited "Tables of Stability Constants" have now become generally available.[1] On your behalf, and on that of thousands of chemists who cannot be here today, I should like to express our gratitude and appreciation to Jannik Bjerrum, Gerold Schwarzenbach, and Lars Gunnar Sillén who had the vision to start this great undertaking and the persistence to finish it, and also to The Chemical Society which made its publication possible.

I have heard these two volumes described as "the solution chemist's Bible". I don't know which volume is to be regarded as the Old Testament, and which the New Testament: certainly we can identify the Book of Revelation with the excellent introductory chapter by Professor Sykes—and all of us will have our private views as to which parts are apocryphal!

Any really logically planned and comprehensive account of the stability of metal complexes ought to start with some description of the experimental methods used and proceed with the problems of computing stability constants (or some other meaningful measure of relative stability) from these laboratory data. It would next review the new results, assess their reliability and significance, and examine how they fitted into the pattern of previous studies. Finally it should deal with attempts to interpret the new material theoretically and—most important of all—try to show how this additional knowledge embellishes, or causes us to modify, our picture of inorganic chemistry as a whole.

If time had permitted I should certainly have liked to discuss some of the newer methods or improved techniques of measuring the stability of metal complexes, such as Anderegg's mercurous–phenanthroline electrode,[2] Biedermann's application of conductivity measurements to the precise determination of hydrogen-ion concentrations, especially in the more acid range from 0·1 to 0·6M,[3] or Schwarzenbach's kinetic method for investigating labile proton-complexes,[4] and the use of reversible mercury electrode–ligand systems for measuring the concentrations of various other ions.[5] Among numerous kinetic measurements from which it is possible to derive stability data one new approach will interest those whose special field is the role of metal complexes in biological systems. Koltun and Gurd have shown that the first-order rate constant for the hydrolysis of p-nitrophenyl acetate by imidazole is reduced by the presence of copper or zinc, and that its metal–imidazole complexes are catalytically inactive. It thus proves possible to calculate values for the successive stability

constants which are in good agreement with those obtained by more conventional methods. They extended the principle to the determination of the stability of complexes of copper and zinc with glycylglycine and with benzyloxycarbonyl-L-prolyl-L-histidinylglycine amide.[6]

One task at least I need not contemplate; for in his address to the International Symposium on the Chemistry of Co-ordination Compounds held in Rome during September, 1957, Professor Sillén dealt very authoritatively with the reliability that can be placed on published values of step-wise equilibrium constants obtained in different ways and made some very pungent remarks on the care and discrimination needed in obtaining the primary experimental data and in carrying through the laborious calculations which generally take up so much more time than that spent at the laboratory bench.[7] It will be obvious to many of us here that such comments were, and still are, very pertinent.

One of the commonest errors in many papers is the identification of $\log K_1$ with the value pH on the formation curve when $\bar{n} = 0.5$, and the identification of $\log K_2$ with pH ($\bar{n} = 1.5$), and so on. Bjerrum's approximate relationship should never be applied to a formation curve without considering the errors introduced if the successive step-constants are insufficiently separated.[8] If we remember that the formation curve has probably been "smoothed" to start with, it is hardly surprising that so-called stability constants obtained in this way may, to say the least, be but a poor representation of what might have been good experimental material. If, further, such crude values of K_n are obtained for measurements at a series of temperatures, no reliance at all can be placed on the values of derived thermodynamic quantities—especially in view of the discrepancies which have been repeatedly demonstrated between calorimetrically determined enthalpy changes and those calculated from even the most meticulous measurements of stability constants.[9] If Editors cannot all afford to follow the generous practice of Scandinavian journals in presenting experimental data *in extenso*, at least Referees should insist on sufficient information being presented to enable the critical reader to check, refine, or even to correct the author's conclusions.

This passing reference to thermodynamic studies of complex formation does not suggest that this is a topic unworthy of a more extended review and I am pleased to see that a few papers in this field are to be presented during the present Conference.[10] However, it is no secret that a number of laboratories are on the point of publishing enthalpy data obtained calorimetrically and it will be the task of some future speaker to record to what extent this additional material has clarified the picture . . . or simply made "confusion worse confounded".

It occurs to me, however, that I am being too parochial in limiting my observations to the stability of complexes derived from equilibrium measurements in solution. A glance at the abstracts of papers to be presented at this Conference shows at once that the devotees of solution chemistry, if I may so define it, are definitely less numerous than the exponents of what, for want of a clearer description, I will call preparative co-ordination chemistry. Now the work of the solution chemist has