337. *The Catalytic Action of Metal Alkyl–Metal Halide Complexes. Part I. The Dimerisation of* 1,1-*Diphenylethylene in Benzene– n-Butyl-lithium–Titanium Tetrachloride–Hydrogen Chloride Systems.*

x

line at I and J. The solution was then filtered free from solid impurities through the sintered-glass disc K (No. 4 porosity) and collected in calibrated bulbs, L, and a storage vessel, M, which were then sealed off.

The concentration of n-butyl-lithium was estimated by the double titration method,[6a] high-vacuum techniques being used in the preparation of the solutions and in the reaction of butyl-lithium with benzyl chloride.[6b]

(2) *Kinetic Measurements.*—(a) *Normal method.* A solution of 1,1-diphenylethylene in benzene was introduced into dilatometers by the high-vacuum technique used earlier.[3] Known amounts of titanium tetrachloride, benzene solution of butyl-lithium, and hydrogen chloride, in that order (unless otherwise stated), were then added to the dilatometer by using the technique

FIG. 1. *Apparatus for the preparation of n-butyl-lithium.*

(G) *Butyl chloride*; (E) *benzene.*
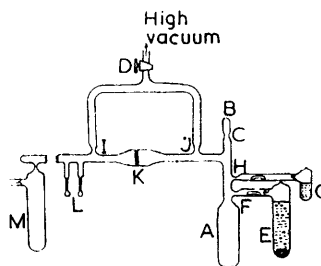
FIG. 2. *Apparatus for mixing monomer, benzene, titanium tetrachloride, butyl-lithium, and hydrogen chloride.*
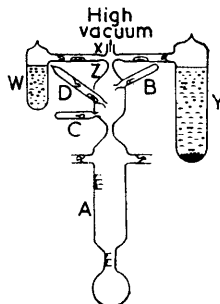
(W) 1,1-*Diphenylethylene*; (Y) *benzene over sodium-potassium alloy*; (B) *titanium tetrachloride*; (C) *butyl-lithium*; (D) *hydrogen chloride.*

FIG. 3. *Apparatus for locating the catalytic activity.*
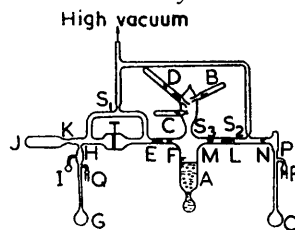
(A) *Benzene solution of* 1,1-*diphenylethylene*; (B) *titanium tetrachloride*; (C) *butyl-lithium*; (D) *hydrogen chloride*; (T) *sintered-glass diaphragm (No. 4 porosity).*

described earlier [1,4] for titanium tetrachloride and hydrogen chloride, the butyl-lithium solution being added in exactly the same way as for titanium tetrachloride. A brown precipitate formed which settled, leaving a clear supernatant liquor. The dilatometers were sealed off and placed in thermostats.

(b) *Method used to locate the catalytic activity.* By means of the apparatus shown in Fig. 2, a known volume of 1,1-diphenylethylene was distilled from W into the graduated vessel A, and the apparatus sealed at X. A known volume of benzene was distilled from Y into A, and the apparatus sealed off at Z. Vessel A was then attached to the system shown in Fig. 3 which was evacuated and sealed off at $S1$ and $S2$. The titanium tetrachloride (B), butyl-lithium solution (C), and hydrogen chloride (D) were introduced into the 1,1-diphenylethylene–benzene solution (A) in the usual way and the vessel was sealed off at S_3. A precipitate formed in A, and this and its supernatant liquor were then dealt with as follows.

A magnetic breaker E was used to break the vacuum seal F, and the apparatus tilted so as to filter the reacting system through the glass sinter T and into the dilatometer G which was

⁶ (a) Gilman and Haubein, *J. Amer. Chem Soc.*, 1944, **66**, 1515; (b) Evans and George, unpublished work.

sealed off at H. The spectroscopic cell I was filled and sealed off, and the dilatometer finally placed in a thermostat. The rest of the filtrate passed into the tube J and was sealed off at K.

The magnetic breaker L was used to break the vacuum seals M and N. A benzene solution of 1,1-diphenylethylene, which had been previously placed in dilatometer O, was then poured through the apparatus, and the catalyst precipitate was washed back into the dilatometer which was sealed off at P and placed in a thermostat.

In this way we obtained two systems: that in dilatometer G contained the supernatant liquid and the original monomer, while that in dilatometer O contained the precipitate and fresh monomer solution.

(3) *Isolation and Identification of Reaction Products.*—The products were investigated by the method described earlier.[7]

(4) *The Reaction of Butyl-lithium with Titanium Tetrachloride.*—The [LiBu]/[TiCl$_4$] ratio below which free titanium tetrachloride is present in the supernatant liquid was studied by making use of the fact that free butyl-lithium in benzene is colourless, whereas free titanium tetrachloride in benzene is coloured owing to its complex with benzene,[1] which enables it to be detected down to concentrations of 2×10^{-4} mole l.$^{-1}$. Small amounts of titanium tetrachloride (of approx. 0·07 ml.), contained in small bulbs, were successively added under high vacuum to 40 ml. of a colourless solution containing $4·18 \times 10^{-3}$ mole of butyl-lithium in benzene, the same technique being used as that for adding titanium tetrachloride to the reaction mixture. After each addition a brown precipitate formed which was allowed to settle; the supernatant liquid remained colourless for the first five additions, but the sixth gave an intensely yellow liquid showing the presence of free titanium tetrachloride in the benzene solution; 0·411 ml. of a benzene solution of butyl-lithium (0·60M) was then added to the system and the supernatant liquid became colourless. In this way the [LiBu]/[TiCl$_4$] ratio below which free titanium tetrachloride exists in the supernatant liquid was determined.

The [LiBu]/[TiCl$_4$] ratio above which free butyl-lithium is present in the supernatant liquid was investigated by making use of the fact that, although free butyl-lithium in benzene is colourless, yet in the presence of 1,1-diphenylethylene a coloured carbanion is formed.[8] This carbanion is yellow in dilute solution and deep cherry-red in concentrated solutions of 1,1-diphenylethylene. Benzene solutions which were molar in monomer and contained various amounts of titanium tetrachloride and butyl-lithium were made up as described in Experimental, Section 2 (a), and the colour of the supernatant liquid was observed for different [LiBu]/[TiCl$_4$] ratios. For this monomer concentration, free butyl-lithium can be detected by the carbanion colour down to concentrations of 10^{-5} mole l.$^{-1}$.[6] In this way, the [LiBu]/[TiCl$_4$] ratio above which free butyl-lithium exists in the supernatant liquid was determined.

RESULTS

(1) *Products of Reaction.*—The final product of the reaction was analysed and it was found that the monomer was completely converted into the cyclic dimer 3-methyl-1,1,3-triphenylindane; no linear dimer, 1,1,3,3-tetraphenylbut-1-ene, could be detected even in the early stages of the reaction.

(2) *Rates of Dimerisation.*—(a) *Effect of hydrogen chloride.* The change in volume of the solution in the dilatometer was measured with time, and the initial rate determined. It was

TABLE 1.

Batch 1 Run No.	10^4 I.R.*	[M] (mole l.$^{-1}$)	10^3[LiBu] (mole l.$^{-1}$)	10^3[TiCl$_4$] (mole l.$^{-1}$)	10^3[HCl] (mole l.$^{-1}$)	Temp.
1	1·5	1·02	5·1	3·7	0	30·3°
2	62	1·02	5·1	3·7	5·8	30·3°
3	171	1·02	5·1	3·7	33	30·3°

* Initial rate, expressed in moles of dimer formed per l. per hr. M = the monomer, 1,1-diphenylethylene.

found that when the reagents were purified rigorously, a negligible reaction took place in the 1,1-diphenylethylene–titanium tetrachloride–butyl-lithium–benzene system [2b] (see Table 1 and Fig. 4). As the hydrogen chloride concentration was increased the rate increased.

[7] Evans, Jones, and Thomas, *J.*, 1957, 2095.
[8] Evans and George, *Proc. Chem. Soc.*, 1960, 144.

(b) *Temperature dependence.* The effect of temperature is shown in Table 2 and the apparent activation energy was found to be $-11\cdot0 \pm 0\cdot3$ kcal. mole^{-1}.

(c) *Reproducibility.* Runs 1 and 4 (Table 2) were put on at the beginning and the end of the particular batch of runs. The reagent concentrations for them are identical, and it is seen that the rates are the same. This shows that, although the system is heterogeneous, comparison of rates within any one batch of experiments is justifiable. Our method was to allow the precipitate to settle and not to agitate the system.

TABLE 2.

Batch 2 Run No.	10⁴ I.R.	[M] (mole l.$^{-1}$)	10³[LiBu] (mole l.$^{-1}$)	10³[TiCl₄] (mole l.$^{-1}$)	10³[HCl] (mole l.$^{-1}$)	Temp.
1	15·0	0·94	4·8	3·7	0·99	30·3°
2	9·0	0·94	4·8	3·7	0·99	40·0
3	3·9	0·94	4·8	3·7	0·99	55·0
4	15·4	0·94	4·8	3·7	0·99	30·3

In view of the extreme sensitivity of the reaction to hydrogen chloride, we were not surprised to find that when we changed our batch of benzene we did not get exact reproducibility of rates although of course the general behaviour was the same from batch to batch.
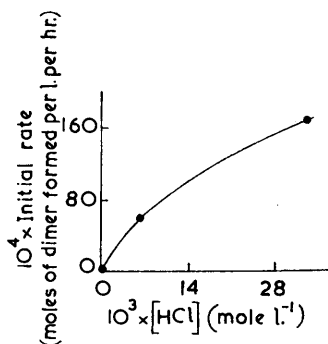
FIG. 4. *Effect of* [HCl] *on initial rate of dimerisation of 1,1-diphenylethylene in benzene at 30·3°, in the presence of titanium tetrachloride–butyl-lithium.*

FIG. 5. *Effect of* [LiBu]/[TiCl₄] *ratio on the rate of dimerisation of 1,1-diphenylethylene.*
● *Initial rate;* ○ *rate at 3% dimerisation.*
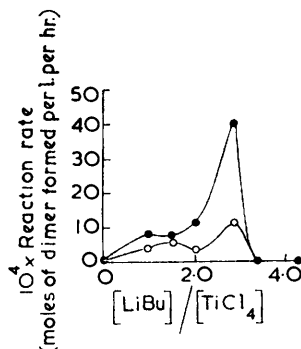
(d) *Effect of* [LiBu]/[TiCl₄] *ratio.* The effect of the [LiBu]/[TiCl₄] ratio on the initial rate is shown in Table 3 and Fig. 5. It is seen that a sharp peak in the plot of initial rate against [LiBu]/[TiCl₄] occurs at a [LiBu]/[TiCl₄] ratio of 2·9. When the butyl-lithium concentration is in excess of this value the initial rate falls to zero, the solution in the dilatometer showing no contraction with time even after 14 days. The reaction rate falls off much faster than corresponds to disappearance of monomer, and suggests that the activity of the catalyst rapidly decreases as the reaction proceeds. The most marked decrease in rate occurs for the catalyst which is most active initially, *i.e.*, for a [LiBu]/[TiCl₄] ratio of 3. This effect is shown in Fig. 5.

(3) *Reaction of Butyl-lithium with Titanium Tetrachloride.*—(a) *The* [LiBu]/[TiCl₄] *ratio below which free titanium tetrachloride is present in the supernatant liquid.* The tetrachloride was added

stepwise to a solution of butyl-lithium in benzene as described in Experimental, Section 4, and the results are given in sequence in Table 4 for the last two additions of titanium chloride and for the subsequent addition of butyl-lithium. It is found that excess of the tetrachloride is present in the supernatant liquid (shown by the yellow colour) when the [LiBu]/[TiCl$_4$] ratio is $\leqslant 1 \cdot 13$.

TABLE 3. *Experiments at* $30 \cdot 3°$ *on the monomer–LiBu–TiCl$_4$–HCl–benzene systems,* *when* [M] $= 9 \cdot 6 \times 10^{-1}$ *mole l.*$^{-1}$ *and* [TiCl$_4$] $= 3 \cdot 7 \times 10^{-3}$ *mole l.*$^{-1}$.

Batch 3 Run No.	10^3[LiBu] (mole l.$^{-1}$)	$\dfrac{\text{[LiBu]}}{\text{[TiCl}_4]}$	Colour of super- natant liquid before addition of HCl	10^3[HCl] (mole l.$^{-1}$)	$10^4 \times$ I.R.
1	0	0	Yellow	1·07	0·3
2	3·5	0·95	Yellow	1·08	8·3
3	5·6	1·5	Colourless	1·07	7·1
4	7·5	2·0	Colourless	1·07	11·3
5	10·5	2·9	Colourless	1·07	40
6	12·6	3·4	Yellow	1·06	0
7	15·9	4·3	Deep yellow	1·07	0
8 *	10·0	∞	Cherry-red	1·07	0

* TiCl$_4$ not present in this run.

TABLE 4.

10[LiBu] (mole l.$^{-1}$)	10^2[TiCl$_4$] (mole l.$^{-1}$)	$\dfrac{\text{[LiBu]}}{\text{[TiCl}_4]}$	Colour of supernatant liquid	10[LiBu] (mole l.$^{-1}$)	10^2[TiCl$_4$] (mole l.$^{-1}$)	$\dfrac{\text{[LiBu]}}{\text{[TiCl}_4]}$	Colour of supernant liquid
1·05	5·9	1·77	Colourless	1·05	9·3	1·13	Yellow
1·05	7·7	1·37	Colourless	1·11	9·3	1·19	Colourless

(b) *The* [LiBu]/[TiCl$_4$] *ratio above which free butyl-lithium is present in the supernatant liquid.* These observations were carried out on the reaction mixtures given in Table 3, and it is seen that excess of butyl-lithium (indicated by the coloured carbanion, see Experimental, Section 4) is present in the supernatant liquid for runs 6, 7, and 8, *i.e.*, when the [LiBu]/[TiCl$_4$] ratio is $\geqslant 3 \cdot 4$. The yellow colour of the supernatant liquid in runs 1 and 2 ([LiBu]/[TiCl$_4$] ratio $< 1 \cdot 13$) is due, of course, to excess of the tetrachloride (see above).

(4) *Location of Catalytic Activity.*—It was found that the solution in dilatometer *G* (see Experimental, Section 2b), containing the supernatant liquid and the original monomer, did not contract. To test whether this was due to the fact that all the monomer had been completely converted into dimer during the time of filtration (1 hr.), titanium tetrachloride was added to this dilatometer under high-vacuum conditions by using the vacuum seal *Q* (Fig. 3). The system immediately began to contract and gave a volume change equal to that expected for the conversion of 25% of the original monomer into the indane dimer. The dilatometer was then opened and the products were analysed. It was found that all the monomer had been converted into the indane dimer. This means that about 75% of the original monomer had dimerised before filtration was complete, but that the removal of the precipitate had stopped further reaction; the subsequent addition of titanium tetrachloride to the supernatant liquid had then brought about the titanium tetrachloride–hydrogen chloride-catalysed homogeneous dimerisation of the remaining 25% of monomer. The presence of monomer in the supernatant liquid after filtration was also confirmed (Experimental, Section 3) by analysis of that portion of the filtrate which was collected in the tube *J* (Fig. 3).

The precipitate, which was washed back into the dilatometer *O* (Fig. 3) with fresh monomer solution, showed catalytic activity in that the dilatometer solution contracted with time at an appreciable rate: 10% reaction to dimer in 19 hr. Analysis of the product showed it to be cyclic dimer.

(5) *Effect of using Large Concentrations of Butyl-lithium and Titanium Tetrachloride.*—After a dilatometer had been filled with a solution of 1,1-diphenylethylene (0·96 mole l.$^{-1}$), the alkyl (0·22 mole l.$^{-1}$), and the chloride (0·14 mole l.$^{-1}$), a negligible contraction was observed during a week and analysis of the solution showed that no dimerisation had occurred even at these high concentrations of alkyl and tetrachloride in the absence of hydrogen chloride.

DISCUSSION

Heterogeneity of Reaction.—The results show that the butyl-lithium–titanium tetra-chloride–benzene system will not act as a catalyst for the dimerisation of 1,1-diphenyl-ethylene, but that the addition of hydrogen chloride to such systems causes formation of the cyclic dimer. That this reaction does not occur in the homogeneous phase is shown by the following considerations: (a) It cannot be due to the titanium tetrachloride–hydrogen chloride homogeneous reaction since it occurs in systems for which the tetra-chloride has been removed from the supernatant liquid by the alkyl, *i.e.*, systems for which the [LiBu]/[TiCl$_4$] ratio is $\geqslant 1\cdot 19$ [see Results, Section 3 (a)]. Indeed, even if all the original tetrachloride were present in the liquid phase, the reaction rates would be some 25 times faster than could be expected for the titanium tetrachloride–hydrogen chloride homogeneous reaction. (b) This reaction is not due to any butyl-lithium–hydrogen chloride-catalysed homogeneous reaction, since butyl-lithium and butyl-lithium–hydrogen chloride do not act as catalysts in this reaction. (c) The rapid decrease in catalytic activity of these systems shows them to be very different from the homogeneous systems which we have previously studied. (d) The fact that cyclic dimer is produced directly, whereas in the case of the homogeneous reaction linear dimer is first formed, which is then converted into cyclic dimer,[1] also shows that this reaction is not of the normal homogeneous type. (e) Experiments designed to show exactly where the catalytic activity is situated (Results, Section 4) demonstrate conclusively that the activity resides in the precipitate and not in the supernatant liquid.

Reaction of Butyl-lithium with Titanium Tetrachloride.—Our results show that when titanium tetrachloride is added to butyl-lithium free tetrachloride is observed only when [LiBu]/[TiCl$_4$] <1, and that in the reverse order of addition free butyl-lithium is observed only when [LiBu]/[TiCl$_4$] >3. In order to explain these results we postulate the following reactions.

(a) When [LiBu]/[TiCl$_4$] >1 (excess of tetrachloride in supernatant liquid)

$$\text{LiBu} + \text{TiCl}_4 \longrightarrow \text{TiCl}_3 + \text{LiCl} + \text{Bu} \quad\ldots\ldots\ldots\ldots \quad (1)$$

It is likely that the precipitate formed by the reaction of butyl-lithium with tetra-chloride consists of TiCl$_3$ and not TiCl$_3$Bu, since Bawn and Gladstone[9] have found that TiCl$_3$Et is liquid at room temperature, and is readily soluble in hydrocarbons.

(b) When [LiBu]/[TiCl$_4$] > 3 (excess of alkyl in supernatant liquid)

$$\underset{\text{ppt.}}{3\text{LiBu} + \text{TiCl}_4 \longrightarrow \text{TiCl}_3(2\text{LiBu})} + \text{LiCl} + \text{Bu} \quad\ldots\ldots\ldots \quad (2)$$

where 2 butyl-lithium molecules form a complex with the trichloride. It is necessary to postulate that a complex is formed, and not lithium chloride, since the slow stepwise addition of small quantities of titanium tetrachloride to a butyl-lithium solution finally gives excess of tetrachloride only when [LiBu]/[TiCl$_4$] < 1 (see Results, Section 3a). This means that these two butyl-lithium molecules can be removed easily from this complex by the tetrachloride as follows:

$$\underset{\text{ppt.}}{\text{TiCl}_3(2\text{LiBu})} + 2\text{TiCl}_4 \longrightarrow \underset{\text{ppt.}}{3\text{TiCl}_3} + 2\text{LiCl} + 2\text{Bu} \quad\ldots\ldots\ldots \quad (3)$$

and this would not be possible if they had reacted with the titanium trichloride to form lithium chloride.

Friedlander and Oita[10] mixed butyl-lithium and titanium tetrachloride in benzene and found that free butyl-lithium was present in the supernatant liquid only when the [LiBu]/[TiCl$_4$] ratio was >3. For a [LiBu]/[TiCl$_4$] ratio of unity, they state that about 50% of the tetrachloride was reduced to the tervalent state, whereas at higher [LiBu]/[TiCl$_4$] ratios less reduction took place.

[9] Bawn and Gladstone, *Proc. Chem. Soc.*, 1959, 227.
[10] Friedlander and Oita, *Ind. Eng. Chem.*, 1957, **49**, 1885.

Reaction Mechanism.—Our results show that the butyl-lithium–titanium tetrachloride system is not active for the dimerisation of 1,1-diphenylethylene unless hydrogen chloride is present. Even when butyl-lithium and titanium tetrachloride concentrations more equivalent to the monomer concentrations were used (Results, Section 5) still reaction was not observed. Thus the dimerisation of this olefin by the addition of the butyl group to the monomer molecule appears to be impossible in these circumstances. It is clear, therefore, that the activating group in the titanium tetrachloride–butyl-lithium–hydrogen chloride system is the proton from the hydrogen chloride.

Hydrogen chloride is in some way involved in the reaction which occurs on the surface of the precipitate. There is also hydrogen chloride in the supernatant liquid, since addition of titanium tetrachloride to this after filtration (Results, Section 4) brings about the homogeneous reaction catalysed by tetrachloride–hydrogen chloride. An equilibrium must exist therefore between the hydrogen chloride in the supernatant liquid and on the precipitate.

It is likely that the chlorine of the hydrogen chloride will be attracted to the titanium ions on the surface of the precipitate, to give a very active acid grouping. For a given concentration of hydrogen chloride the catalytic activity of the system is a maximum when 2 molecules of butyl-lithium are associated with the titanium trichloride. We consider this association to be such as not to involve replacement of the chlorine atoms by butyl groups, but to have sufficient interaction to cause a significant increase in the unsaturated nature of the titanium, and hence a marked increase in the catalytic activity of the complex. As the [LiBu]/[TiCl$_4$] ratio is increased above 3, the initial rate of reaction is reduced to zero. This loss of catalytic activity is, we believe, due to the removal of hydrogen chloride by the excess of alkyl in the irreversible reaction

$$\text{LiBu} + \text{HCl} \longrightarrow \text{LiCl} + \text{BuH} \qquad \qquad \text{. . . . . (4)}$$

Proton transfer from the hydrogen chloride on the catalyst surface to a monomer would produce the $CH_3 \cdot CPh_2{}^+$ ion, and give a resulting negative charge on the surface. This monomer ion, held to the surface by Coulombic attraction, could transfer a proton back to the surface, and so re-form the monomer molecule, or it could react with another monomer molecule to form a dimer ion which would also be held to the surface by Coulombic attraction. The return of a proton from the dimer ion to the surface would result in the formation of a dimer molecule. The fact that under these conditions only cyclic dimer is detectable in the reaction product, suggests that the surface tends to cause the two monomers to combine in this special way.

Order of Addition of Reagents.—If hydrogen chloride is added to the reaction mixture before the butyl-lithium (instead of afterwards, as is the normal case), we find that the initial rate is much slower. We believe this to be due to the fact that, when the alkyl is added to a system which already contains hydrogen chloride it reacts with it according to equation (4), and it is this reduction in the concentration of hydrogen chloride and butyl-lithium which slows down the reaction. When this alkyl is added to the titanium tetrachloride–olefin system before the hydrogen chloride, however, it is incorporated into the precipitate according to equation (2) and the system to which the hydrogen chloride is then added does not contain any free butyl-lithium by which it could be removed. The rapid fall in catalytic activity of the system in the initial stages (Fig. 5) may be due to reaction between the hydrogen chloride and the complexed butyl-lithium molecules in the precipitate. It is significant in this respect that the greatest initial fall in catalytic activity is for those systems ([LiBu]/[TiCl$_4$] ratio = 3) which have the greatest number of complexed butyl-lithium molecules, *i.e.*, 2.

Colour of Supernatant Liquid.—We found that for olefin–butyl-lithium–titanium tetrachloride–benzene systems in which the [LiBu]/[TiCl$_4$] ratio was between 1·19 and 2·0 the colourless supernatant liquid became yellow on addition of hydrogen chloride. To

examine this further, such a system was filtered by the high-vacuum technique [Experimental, Section 2 (b)], and the yellow filtrate divided into two parts. To one portion titanium tetrachloride was added. No precipitate was formed, showing the absence of free butyl-lithium in the supernatant liquid. This was also confirmed by the fact that the spectrum of the solution (Fig. 6) did not show the characteristic peak of the 1,1-diphenylhexyl anion.[8] Another portion of the filtrate was treated with butyl-lithium (more than enough to neutralise the hydrogen chloride present), and a dark brown precipitate

Fig. 6. *Spectrum of the supernatant liquid of a 1,1-diphenylethylene–butyl-lithium–titanium tetrachloride–hydrogen chloride–benzene system of* [LiBu]/[TiCl$_4$] *ratio* 1·3.
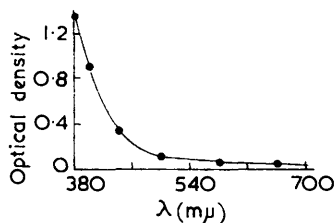
was formed immediately. This suggests the presence of some titanium tetrachloride in the supernatant liquid after the addition of hydrogen chloride. If this is the case, its amount, as estimated from the spectrum, is less than 10% of the total tetrachloride. For olefin–butyl-lithium–titanium tetrachloride–benzene systems in which the [LiBu]/[TiCl$_4$] ratio was between 2·0 and 3·0, the colourless supernatant liquid underwent no change on addition of hydrogen chloride; excess of butyl-lithium, therefore, prevents this action of hydrogen chloride on the precipitate.

Effect of Temperature.—Since the activity of the catalyst requires the association of hydrogen chloride with the precipitate, and the most active precipitate contains two butyl-lithium molecules complexed with titanium trichloride, it is not surprising that an increase in temperature reduces the catalytic activity of the system, and gives an apparent activation energy of −11·0 kcal. mole^{-1}.