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TITANIUM REDUCTION IN A SOLUBLE ZIEGLER—NATTA CATALYST

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Summary

The spontaneous reduction of Ti^{IV} to Ti^{III} in soluble Ziegler—Natta catalysts of type $Cp_2RTiCl \cdot R'AlCl_2$ ($Cp = h^5$-cyclopentadienyl, R and R' = methyl or ethyl) was studied both spectrally and chromatographically. Varied were R, R', Al/Ti ratio, total concentration, solvent, and added olefin. Kinetic order in [Ti] could be varied from zero to second order by changing solvent. This can be explained by a mechanism in which a $Cp_2RTiCl—R'AlCl_2$—olefin complex forms in the rate determining step and ligand R is expelled as half alkane half olefin. The expelled olefin may either polymerize or catalyze reduction by forming the rate-determining complex. Different apparent kinetic orders arise from differences in the olefin competitive reactions. The reaction products appear to form in a rapid bimolecular reaction following the rate-determining step. Evidence is presented that neither free radicals nor $Cp_2RR'Ti$ are reduction intermediates. The intermediate is postulated to be a Ti^{IV} transient hydride formed by a reverse insertion step.

Introduction

Soluble Ziegler—Natta polymerization catalysts derived from alkylaluminums and dicyclopentadienyltitanium dichloride, Cp_2TiCl_2 where $Cp = h^5$-C_5H_5, undergo a reaction giving valence reduction of titanium. The kinetics of this reduction have been variously reported as zero [1], half [2—4], first [1, 3] and second order [5—7].

Proposed mechanisms to explain the products and kinetics have included one-electron reduction of titanium by homolytic cleavage of a Ti—R bond with expulsion of $R^{\bullet}$ free radical [8] and a two-electron process involving expulsion of both R groups from Cp_2TiR_2 [3, 4, 9] with (at least transitory) formation of a Ti^{II} species. The reported gaseous products derived from R have ranged all the way from a 50/50 mixture of alkane and alkene [3, 4, 8] to alkane containing some alkene [2] to pure alkane [1, 10].

We have studied the valence reduction of titanium which occurs upon thermo lysis of pure compounds of structure Cp_2RTiCl [11]. It was natural for us to extend the work to valence reduction in the presence of alkylaluminiums to see if we could shed additional light on the kinetics and mechanism of reduction and perhaps clear up some of the apparent conflict in the literature. It has been reporte that the reduction slows and the kinetics change after the reduction is nearly complete [3]. We also found, and report herein, that there is a short period of change in reduction rate and kinetics at the very beginning of the reduction. Although some data in this paper will touch on both the early and late periods, their detailed consideration lies in the future. This paper is intended to treat in detail only the steady middle period during which the majority of valence reduction takes place.

Experimental methods

1. Materials and apparatus

Preparation of compounds Cp_2RTiCl has been described previously [12]. Solutions were made fresh for each run from material stored at —78°C. Alkylaluminums (Texas Alkyls), ethyllithium (Foote Mineral Company) and Grignard reagents (Fisher Scientific) were used as received after assay for alkyl content. Solvents were dried with 3A molecular sieves to < 10 ppm water and deoxygenated with argon containing < 2 ppm O_2. Toluene was used as the solvent unless otherwise indicated. All apparatus was oven dried at 140°C, cooled under argon, purged to < 2 ppm oxygen, and rinsed with the Al, Mg, or Li reagent being used in the experiment prior to addition of the solvent and reactants.

2. Spectrophotometric and gas evolution studies

The reduction reaction was studied by both spectral and chromatographic techniques. The spectra observed were essentially those already reported by Long and Breslow [1] for the system $Cp_2TiCl_2 \cdot Et_2AlCl$ going to $Cp_2TiCl \cdot EtAlCl_2$. For kinetic studies, the optical density of the solution was monitored at 520 nm using a cell which permitted the reagents to be kept in separate compartments until the cell was tilted. This allowed the reaction to be followed from the instant of mixing. For chromatographic studies, fixed volumes of the atmosphere over the solution were injected into a chromatograph calibrated for light hydrocarbon gases. Knowing the solubility of the gases in the solvent, it was possible to calculate the total amount of C_1—C_6 gases in the cell and thus obtain both identity and quantity of these gases. In some experiments, these techniques were applied simultaneously using a spectral cell, detailed elsewhere [13], incorporating a circulating pump and provision for sampling the gas phase into a chromatograph.

In the study of the reduction of Cp_2RTiCl in the presence of $R'AlCl_2$, experiments were run in which both R and R′ were ethyl and in which either R or R′ was methyl. The Al/Ti ratio was varied from 1 to 8, and at Al/Ti = 1, the total concentration was varied by a factor of 10. Typical data are shown in Tables 1 and 2 and Figs. 1—3. In some runs, 1-octene, which is reported to accelerate the reduction [4, 7, 9], was added at a level of 1 to 2 moles/mole of titanium compound. In many of the runs the total mixture was solvolyzed with HCl after the reduction appeared to be complete (see Table 3). After

TABLE 1

GAS EVOLUTION DATA FOR $Cp_2EtTiCl + EtAlCl_2$ AT 23° C

[Ti] (mmoles/l)	[Al] (mmoles/l)	Complex. temp. (°C)	Ethane evolved during steady period (μmol l^{-1} min^{-1})
10	10	0	18
10	10	23	14
25	25	0	51
50	50	0	142
10	80	−30	0.6

TABLE 2

CHANGE IN OPTICAL DENSITY AT 520 nm FOR $Cp_2EtTiCl + EtAlCl_2$ AT 24° C AFTER COMPLEXING AT 0° C

[Ti] (mmoles/l)	[Al] (mmoles/l)	Optical density decrease during steady period (milliunits/min)
5	5	6.8
10	10	18
30	30	35
50	50	69
10	15	5.2
10	20	0.50
10	40	0.25

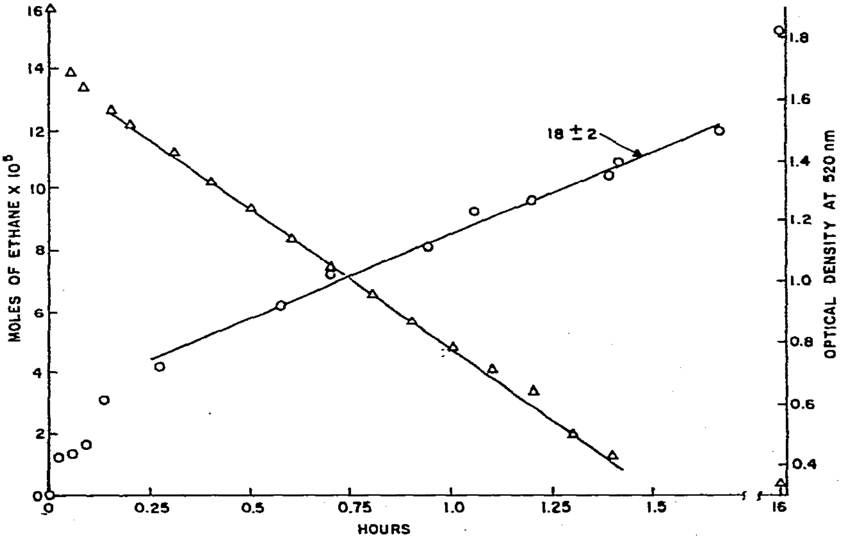

Fig. 1. Simultaneous gas evolution and spectra study. Optical density (Δ) at 520 nm of 50 ml of 0.01 *M* solution of $Cp_2EtTiCl \cdot EtAlCl_2$ at 25°C in 1 cm cell after reagents mixed at 5°C. Ethane evolved (O) measured simultaneously, and least squares line through points after 0.25 h shown. Slope and 95% confidence limits are in dimensions of μmol l^{-1} min^{-1}.

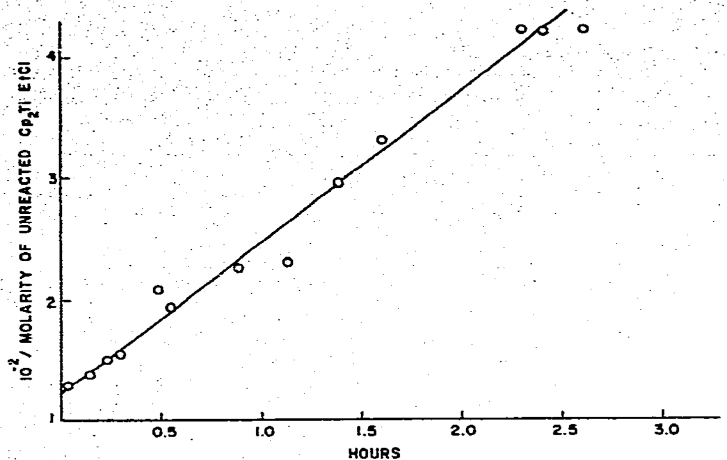

Fig. 2. Second-order plot of ethane evolution from 0.82×10^{-2} molar $Cp_2EtTiCl$ plus 10^{-2} molar $EtAlCl_2$ in hexane at 25° C, assuming complete reaction gives ½ mole ethane and ½ mole ethylene per mole of starting $Cp_2EtTiCl$.

some runs, product studies were carried out on the liquid and solid products which could be isolated following evaporation of the solvent.

Results

Figure 1 shows the optical density change and ethane evolution data for a typical experiment in which R = R′ = ethyl. The main volatile product was ethane, but traces of ethylene, n-butane, and n-hexane were also seen chromatographically. The ethylene, though a minor product, was noted to increase in concentration during the run.

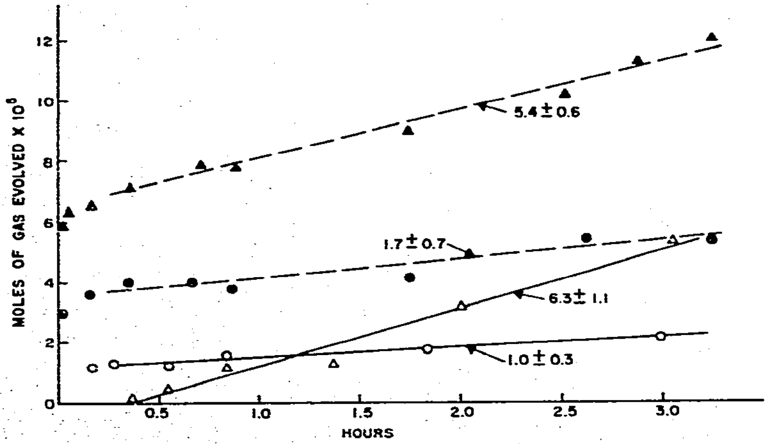

Fig. 3. Gas evolution studies. Ethane (Δ) and methane (○) evolved from 50 ml of 0.01 *M* solutions of $Cp_2RTiCl \cdot R'AlCl_2$ at 23° C after reagents mixed at 5° C. For open emblems, R = Et, R′ = Me, benzene solvent. For closed emblems, R = Me, R′ = Et. Lines represent least squares fit of all points after 0.25 h. Slopes and 95% confidence limits are in dimensions of $\mu mol\ l^{-1}\ min^{-1}$.

TABLE 3

PARTIAL MATERIAL BALANCE

Ligand on Ti (R)	Et	Et	Me
Ligand on Al (R′)	Et	Me	Et
Number of reduction runs	11	4	1
Alkane evolved during reduction as % R initially present	37 ± 6	35 ± 9	41
Number of runs hydrolyzed	7	3	0
Alkane evolved during hydrolysis as % R′ initially present	90 ± 36	105 ± 19	
Products of D_2O solvolysis	C_2H_5D	C_2H_5D, CH_3D	

There are two points relative to Fig. 1 and related runs which should be discussed in more detail. First, we observed the apparent zero order reaction rate already reported by others [1], but noted that it was preceded by a fast initial reaction not previously reported. This fast reaction could be slowed down and observed more easily if the titanium and aluminum reagents were mixed cold and then warmed to reaction temperature. This was done with the runs shown in the figures and tables. Second, some time after an hour, the reduction slowed and the data no longer fell on the zero order line. Frequently, about this time, a haziness developed in the solution which caused some scatter in the optical data.

Toluene and benzene were apparently interchangeable as solvents and gave essentially identical results. In hexane, however, quite different rate results were obtained as shown in Fig. 2. These data from a typical run are plotted to show that the reaction in hexane is quite obviously second order, whereas it was apparently zero order in toluene or benzene. Furthermore, the fast initial reaction seen with toluene and benzene solutions was not observed in hexane. However, the reaction products and the ratios of these products to the reactants, to be described later, were the same for all three solvents.

Substituting a methyl group for the ethyl group on either titanium or aluminum reduced the overall rate of reaction and gave the gas evolution data shown in Fig. 3. From these data, it is seen that the gas evolved during the initial fast reaction came primarily from the aluminum compound. After 15 minutes, the apparent zero order reaction rate constants for ethane evolution and methane evolution were within experimental error of each other regardless of whether methyl was substituted originally on titanium or on aluminum.

An effort was made to account for all of the alkyl groups in the system. The data are summarized in Table 3. It can be seen that the total amount of alkane (ethane plus methane) evolved during the reduction was a constant fraction of the original titanium alkyl present regardless of solvent, Al/Ti ratio, total titanium concentration, variation of the alkyl ligands, and the presence of 1-octene. Further, the additional alkane evolved upon hydrolysis of the reaction mixture after reduction was a constant fraction (essentially 1.0) of the original alkylaluminum present regardless of the same experimental variations. When this hydrolysis was carried out with D_2O rather than H_2O, monodeuteroalkanes were formed exclusively, indicating that all alkyl groups present at the end of the reduction were singly attached to a metal atom.

Some attention was given to the initial fast reaction in toluene. Since the major gas evolved from the beginning was attached to the aluminum group, it appeared possible that the alkylaluminum was reacting with some impurity which contained active hydrogen. Accordingly, a blank experiment was run in which the titanium compound was omitted; essentially no alkane was evolved, showing that the evolution was not caused by active hydrogen in the solvent or on the apparatus. Although the titanium compound appeared to be reasonably pure, the possibility that it might contain some absorbed active hydrogen compound was investigated by subjecting the titanium compound to ultrahigh vacuum drying. This treatment did not affect the initial fast reaction, which was still observed. It is unlikely that an impurity containing active hydrogen was the cause since (1) the fast reaction was not observed in hexane, (2) the mass balances agreed in all three solvents, (3) a sharp spectral change was observed simultaneously with the very fast gas evolution, and (4) the alkyl content at the end of the reduction equalled one alkyl per aluminum at all Al/Ti ratios.

Although the reaction in toluene and benzene appeared to be zero order over the range of about 15 to 80% reduction, the slope of the zero order line at $Al/Ti = 1.0$ was proportional to the initial molarity of the reagents as seen in Tables 1 and 2. Changing the Al/Ti ratio from 1 to 8 led to a steady decrease in the rate of spectral change and of gas evolution as seen in Tables 1 and 2, although the reaction in toluene and benzene remained apparently zero order throughout most of the run. When the reaction was run in deuterobenzene, the ethane evolved contained no detectable amount of deuterium.

When reduction was complete, the greenish color of complexed Cp_2TiCl in the reaction mixture was clearly apparent to the eye and the visible spectrum was that of $Cp_2TiCl \cdot EtAlCl_2$ as reported by Long and Breslow [1]. When air was admitted in the presence of HCl, the characteristic spectrum and color of Cp_2TiCl_2 soon appeared [10]. A limited look for liquid products formed in the reduction was carried out following reduction by carefully evaporating the toluene layer after reaction with HCl. An oil was recovered whose infrared spectrum indicated that it was completely aliphatic hydrocarbon.

1-Octene accelerated the rate of reduction as reported [4, 7, 9]. Gas chromatography measurements confirmed that 1-octene was not consumed (polymerized) by this system as reported [7]. All mass balances around the system remained the same as in the absence of 1-octene. However, the reduction rate as measured spectrally (it was too fast to be followed chromatographically) was first order in octene and first order in titanium ($Al/Ti = 1.0$).

In order to examine the possibility that Cp_2TiR_2 might be an intermediate in the reduction process, Grignard alkylation [14] of Cp_2RTiCl and EtLi double alkylation [15, 16] of Cp_2TiCl_2 were briefly examined over the range —80° to 22° C. Although both reactions deserve detailed treatment, only the distinct differences from the reduction behavior with $R'AlCl_2$ will be mentioned here. The rate of reduction was $EtLi > EtMgCl \gg EtAlCl_2$. Both EtLi with Cp_2TiCl_2 and EtMgCl with $Cp_2EtTiCl$ gave more than one mole of gas per mole of titanium. With EtLi, it is clear that more ethane than ethylene was formed. The mixed alkyls $Cp_2MeTiCl$ + EtMgCl and $Cp_2EtTiCl$ + MeMgCl were also examined at 0°C with th finding that, for both mixed pairs, most of the alkane evolved was methane.

Discussion

The results of the study of reduction of Cp_2RTiCl in the presence of $R'AlCl_2$ are consistent with the overall equation, where R = ethyl [3, 4, 8]:

$$2Cp_2(C_2H_5)TiCl \rightarrow 2Cp_2TiCl + C_2H_4 + C_2H_6$$

Since this system is an active ethylene polymerization catalyst [17, 18], the ethylene formed will insert to form butyl, hexyl, octyl, etc., organometallic intermediates. This accounts for the butane [3] and hexane seen chromatographically, for the aliphatic, oligomeric residue [9] observed at the end of the run, and possibly for the cloudiness seen in the optical measurements [17]. For $Cp_2EtTiCl \cdot EtAlCl_2$, for example, the mass balance data suggest that 37% of the titanium-bound ethyl groups go to ethane and, by difference, 37% go to ethylene and 26% are inserted by the ethylene to form oligomers. The HCl hydrolysis results indicate that alkyl groups attached to aluminum are still intact after all alkyl groups on titanium have been lost. The literature results giving olefin/alkane ratios varying from 0 to 0.5 can be accounted for by assuming a varying effectiveness of the different environments on polymerization of the alkene generated.

Perhaps the most confusing aspect of the reduction is that kinetic orders ranging from zero order to second order have been observed. In this paper we show data fitting zero, first and second order rate equations merely by changing the reaction environment. These varying kinetic orders were obtained without changing the type or concentration of titanium or aluminum compounds and without major change in the reduction products or mass balances. Ethylene concentration in the evolved gases, though low, did change significantly.

To explain these results, we propose that the reduction of Ti^{IV} to Ti^{III} in the system $Cp_2RTiCl \cdot R'AlCl_2$ is first order in 1/1 complex of Cp_2RTiCl and $R'AlCl_2$ and first order in olefin, according to eqn. 1. The fact that olefins in general [4, 7, 9], and ethylene specifically [7, 9], accelerate the reduction has been widely observed. The first order dependence on olefin has been shown in this work and previously reported by Shilov et al. [4].

$$\text{Reduction rate} = k[Cp_2RTiCl \cdot R'AlCl_2][\text{olefin}] \qquad (1)$$

Although other reduction mechanisms may be operative under other conditions, we propose that eqn. 1 represents the major reduction pathway in this study when an olefin is present. In the presence of an added, non-polymerizable olefin, the reaction is simply first order in both titanium complex and olefin, as seen for 1-octene.

In the absence of added olefin, the kinetics are more complicated since a polymerizable olefin, ethylene, is formed during the reduction. The mechanism can be given the following consideration: let C equal the 1/1 complex $Cp_2RTiCl \cdot R'AlCl_2$, E stand for ethylene, and k_1 and k_2 represent the rate constants for reduction and polymerization respectively. Assuming one E is formed for every two titanium atoms reduced, we may write eqn. 2 to express the disappearance of C through reduction and eqn. 3 to account for the appearance and disappearance of ethylene.

$$-\frac{d[C]}{dt} = k_1 [C][E] \tag{2}$$

$$\frac{d[E]}{dt} = 0.5\, k_1 [C][E] - k_2 [C][E] \tag{3}$$

Solving these simultaneously for d[E]/d[C], integrating to get E in terms of C, and substituting in eqn. 2, we obtain eqn. 4 which shows that the reaction can appear to be second order in C, as we observed in hexane.

$$-\frac{d[C]}{dt} = (k_2 - 0.5\, k_1)[C]^2 \tag{4}$$

In an aromatic solvent, the kinetics can be still more complicated since the solvent can compete with the olefin for coordination sites on complex C [17]. If the concept behind eqn. 1 is expanded to include coordination with the π cloud of an aromatic solvent and reduction of titanium from this species simultaneously with, but at a different rate from reduction of the olefin-coordinated species, one obtains eqn. 5 where S refers to the aromatic solvent. If we let K equal the slope of a zero order rate plot, it can be shown that eqn. 5 will appear to be zero order under the condition that eqn. 6 holds.

$$-\frac{d[C]}{dt} = k_1 [C][E] + k_3 [C][S] \tag{5}$$

$$k_1 [E] + k_3 [S] = K/[C] \tag{6}$$

Eqn. 6 clearly specifies two conditions which are required for eqn. 5 to assume an apparent zero order. First, it can be shown that d[E]/dt must be positive, which means that ethylene must build up during the run. Second, K is directly proportional to initial catalyst concentration. Since both of these conditions were experimentally observed, we believe that the above kinetics are valid for our results in toluene and benzene. A different rate of ethylene consumption could give apparent half-order kinetics. Late in the reduction, when [E] becomes relatively high, competition of the aromatic will be minimized and the apparent low kinetic order will tend toward eqn. 1 and approach first order, as observed by us and others [1, 3].

The results of varying the alkyl ligands on Ti and Al suggest that a common intermediate or ratio of intermediates is achieved after 15 min at our conditions. This might result from ligand exchange [6]. It is noteworthy that the $Cp_2RTiCl \cdot R'AlCl_2$ system prefers to eliminate ethane and ethylene rather than methane and ethylene as preferred by the system $Cp_2RTiCl \cdot R'MgCl$. Further, the presence of methyl groups in the system slows the reduction rate [19]. Reichert and Schoetter [2], in an elegant deuterium labelling study, showed that removal of a β-hydrogen from the alkyl ligand is rate-determining. Thus, methyl ligands must either decompose by another, slower mechanism or must first insert an olefin to generate a ligand containing a β-hydrogen. The necessity for an insertion reaction in Shilov's work [4] with methyl compounds, as indicated by the gaseous products, may be an alternate explanation for his reduction rate expression being half order rather than first order as in our eqn. 1. In the present work, little or no propane was observed, probably due to slow insertion rate of ethylene into Ti—Me bonds relative to Ti—Et [18].

The results of varying Al/Ti ratio indicate that it is the 1/1 complex [19] of Cp_2RTiCl with $R'AlCl_2$ or a derivative thereof which is reduced. It is known that 2/1 complexes ($2R'AlCl_2 \cdot Cp_2TiRCl$) form at Al/Ti ratios above 1 [20]. Under conditions where 2/1 complex is preferred over 1/1, both reduction [4, 6] and ethylene polymerization [6, 17, 20] are suppressed. Possibly, both polymerization and reduction occur via a common intermediate, which may be a bimetalic complex or an ion pair.

The proposal that Cp_2R_2Ti is the species which undergoes reduction in the presence of alkylaluminums appears to be inconsistent with the facts as they now stand. Reduction of Cp_2RTiCl by either RLi of RMgCl, where Cp_2R_2Ti is known to be formed [14—16], has certain characteristics quite different from reduction with $RAlCl_2$: much faster reduction rate, formation of Ti^{II} as well as Ti^{III}, preference for eliminating methane rather than ethane when both possibilities exist, and (at 0° or above) the alkyl groups still attached to metal and recoverable as alkane upon HCl solvolysis were no more than half the amount still attached to aluminum compounds. Although some differences may be ascribed to differences in the metals associated with titanium during the reduction, it seems reasonable that these characteristics common to both Mg and Li reagents are associated with expulsion of two σ-bonded ligands from the same titanium atom. If so, then Cp_2R_2Ti is not an intermediate in the main path of reduction of $Cp_2RTiCl \cdot R'AlCl_2$.

Two other possible mechanisms were considered and discarded for lack of evidence. One was the intermediate formation of an alkylene-bridged species as suggested for reduction of Cp_2ZrCl_2 [21]. Since no dideuterated species were formed after deuterolysis, this possibility seems unlikely in our case. The other was homolytic cleavage of the Ti—R bond with formation of a free radical. Since no deuterated products were formed during reduction in a deuterated solvent, this mechanism is not favored. We previously proposed a coordinated radical mechanism to explain thermolytic reduction of Cp_2RTiCl [11]. This now seems less likely following the report of Braterman and Cross on bond strengths [22]. The striking parallelism of the thermolytic results to the results of this paper suggests to us that the basic mechanism of reduction may be the same whether olefins or alkylaluminums are present or not, and that the function of olefins and alkylaluminums is to catalyze the slow step. It seems from the kinetics and from the labelling studies of Reichert and Schoetter [2] that the rate-determining step is intramolecular abstraction of a β-hydrogen from an ethyl (or longer) ligand. This abstraction process might be thought of as a reverse insertion step to form a Ti^{IV} hydride species and a molecule of olefin, probably coördinated with the titanium. This sort of intermediate has been postulated before to explain auto chain transfer and short-chain branching with Ti^{IV} polymerization catalysts [23—25]. To our knowledge, neither Cp_2HTiCl nor related compounds of Ti^{IV} have been isolated although related Ti^{III} compounds are known. We therefore suggest that an intermediate Ti^{IV} hydride must be extremely reactive and may rapidly react to hydrogenate the alkyl portion of another Ti—R compound evolving RH and reducing both titanium species. Thus, the reduction reaction would be unimolecular in the rate-determining step and bimolecular in the product-determining step.

Conclusions

A satisfactory mechanism for the valence reduction of Cp_2RTiCl in the presence of $R'AlCl_2$ must explain the following:

The reduction is zero or low order in aromatic solvents, 2nd order in aliphatic solvents, and 1st order in the presence of a non-polymerizable olefin.

The alkyl group on Ti is expelled as ½ alkane, ½ alkene.

The alkene builds up during reduction when zero-order kinetics are observed.

The reduction is slowed as Al/Ti is increased above 1.

Alkyl groups attached to Al are not lost during reduction.

There is no evidence of radical attack on solvent.

There is no evidence for formation of Ti^{II}.

There is a strong tendency to eliminate ethyl as ethane rather than methyl as methane when the choice exists, although the opposite tendency exists when $R'MgCl$ is substituted for $R'AlCl_2$.

It is proposed that Cp_2RTiCl in the presence of $R'AlCl_2$ undergoes an intramolecular rearrangement, abstracting a β-hydrogen from R in the rate-determining step when such a hydrogen exists, expelling one R as olefin. The intermediate titanium hydride reacts rapidly with another Cp_2RTiCl to complete the reduction of two moles of titanium and hydrogenate the second R to alkane. The kinetics of the reduction are complicated because both $R'AlCl_2$ and olefins catalyze the slow step, olefin is formed in the reduction and may either act as catalyst or polymerize, and aromatic solvents (which are among the best solvents for Cp_2R-TiCl) compete with the olefin for coordination sites on titanium.

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