the products sufficiently dry for analysis and viscometric and M_n determinations. Analytical data and yields for ten representative polymers III are collected in Table I.

Cyclodehydration of Polyhydrazones III. Polypyrazoles VIII. Cyclodehydration was generally accomplished by stirring 0.3–0.5-g quantities of polyhydrazones III with 0.3–0.7 ml of DMF or formic acid to form a sticky, resinous paste, which was placed in a test tube fitted with a tapered joint and vacuum outlet. After removal of most of the solvent at 50° *in vacuo*, the tubes were flushed with nitrogen and reevacuated to remove adsorbed oxygen and were then subjected in a metal bath to the heating cycles given in Table III, raising the temperature to the first heating stage (180°) gradually over a 4-hr period. Throughout the heat treatment, the materials were protected from direct light by covering tubes and bath with aluminum foil. Alternately, concentrated solutions of polymers III in DMF or formic acid were sprayed in repeated passes onto glass plates; the resulting films were predried at 50° under flowing nitrogen and, with their support plates, were subjected to the same heat treatment, using a leakproof vacuum oven. The polypyrazoles obtained by either method were blackish brown, infusible solids. The fluorine-containing types VIIIc, f, and i dissolved only partially in sulfuric acid and formic acid. All other types were completely soluble in sulfuric acid and also largely or completely so in formic acid. Analytical results and viscometric data are collected in Table III.

Polycondensation of Bis(acylaceto)benzenes with Dihydrazines and Cyclodehydration of Resultant Polyhydrazones. Polypyrazoles IX. Polycondensations and subsequent cyclodehydrations to the benzene–aromatic polypyrazoles IXa–e were performed under the experimental conditions described for the ferrocene analogs, employing both the bis-β-diketo compound and the dihydrazine in 0.1 mol $l.^{-1}$ concentration. Thus, 1-4-bis(formylaceto)benzene was condensed with 4,4′-dihydrazino-2,3,5,6,2′,3′,5′,6′-octafluorobiphenyl and 4,4′-dihydrazinodiphenyl sulfone, respectively, to give the hydrazone-type precursor polymers to IXa and b, and the condensation of 1,4-bis(acetylaceto)benzene with 1,4-dihydrazinobenzene, 4,4′-dihydrazino-2,3,5,6,2′,3′,5′,6′-octafluorobiphenyl, and 4,4′-dihydrazinodiphenyl sulfone, respectively, furnished the precursors to IXc, d, and e. The polyhydrazone-type precursor compounds, yellow solids soluble in formic acid, hexamethylphosphoramide, and mostly also in DMF, were heat-treated as described above for the ferrocene analogs (no light protection required). Table IV summarizes exemplifying cyclodehydration conditions and also lists pertinent analytical and viscometric data.

Acknowledgment. The assistance of Dr. R. F. Orloski and Mr. R. K. Crossland in the experimental work, notably in the monomer preparation, is gratefully acknowledged. The author is also indebted to Messrs. S. E. Gordon, W. T. Thompson, and T. H. Mills, who scanned the ir spectra and performed the thermogravimetric and neutron activation analyses.

The Active Oxidation State of Vanadium in Soluble Monoolefin Polymerization Catalysts

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Received November 22, 1967

ABSTRACT: The active oxidation state of vanadium in olefin polymerization catalysts prepared from vanadium tetrachloride and dialkylaluminum chlorides was studied. The data suggest two active complexes containing V(III), one much more active but less stable than the other. The more active catalyst evidently came from an inactive V(III) precursor. The origin of the less active V(III) catalyst is unknown. A potentially active V(II) complex was examined under the same conditions as a similar V(III) complex. No conclusive evidence for catalytic activity in the V(II) complex was found. However, theoretical arguments still suggest a V(II) oxidation state can be active in olefin polymerization.

Many investigators have assigned a formal oxidation state to the active state of vanadium in Ziegler polymerization catalysts. For example, Carrick and his coworkers concluded that some divalent vanadium may be a prerequisite for catalytic activity.[1-3] De Liefde Meijer, *et al.*, looked at similar catalysts and concluded that either V(II) or V(III) could be active.[4,5] Other investigators studying different vanadium catalysts concluded that V(III) is the active state.[6-13] Recently even V(IV) and V(V) oxidation states have been suggested.[12]

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TABLE I
REDUCTION OF VCl_4 BY R_2AlCl AT −78° [a]

R	Al/V	Time, min (hr)	% V(IV)	% V(III)	% V(II)
Et	5	5	5.1	94.9	...
Et	5	5	1.3	98.7	...
i-Bu	5	2.5	7.6	92.4	...
i-Bu	5	2.5	8.5	91.5	...
i-Bu	5	2.5	3.1	96.9	...
Et	4	(17.4)	...	90.0	10.0
Et	4	(16.0)	...	85.5	14.5
i-Bu	4	(17.4)	...	98.4	1.6
i-Bu	4	(16.0)	...	99.8	0.2

[a] In toluene. $[VCl_4] = 0.019$ *M*.

TABLE II
REDUCTION OF V(III) BY R_3Al IN TOLUENE AT −78° [a]

R	R_3Al/V	Time, min	% V(III)	% V(II)
Et	0.5	2.5	98.9	1.1
Et	0.5	120	96.9	3.1
i-Bu	0.5	2.6	93.5	4.5
i-Bu	0.5	120	93.0	7.0
i-Bu	1.0	2.5	84.7	15.3
i-Bu	1.0	240	72.7	27.3
i-Bu	2.0	2.6	31.6	69.4
i-Bu	2.0	120	19.4	80.6

[a] V(III) Prepared by reaction of VCl_4 with *i*-Bu_2AlCl (Al/V = 4) at −78°. $[VCl_4] = 0.019$ *M*.

TABLE III
RELATIVE RATES OF POLYETHYLENE FORMATION AT −78° WITH V(III) AND V(II) CATALYST SYSTEMS [a]

Amount, g-atom %			Reaction time, min	Amount g/min/mol of V/l.	Amount g/min/mol of V(III)/l.
V(IV)	V(III)	V(II)			
3.9	96.1	...	6.8	4.3	4.5
2.1	97.9	...	6.8	2.5	2.6
4.1	95.9	...	9.0	2.8	3.0
4.4	95.6	...	9.0	2.1	2.2
				2.9 av	3.1 av
4.5	95.5	...	2.6	7.2	7.5 [b]
4.4	95.6	...	2.6	7.2	7.5 [b]
...	10.2	89.8	60	0.053	0.53
...	9.5	90.5	44	0.039	0.40
...	8.0	92.0	60	0.065	0.81
...	8.4	91.6	60	0.065	0.78
				0.055 av	0.63 av
...	5.2	94.8	12.5	0.017	0.32 [b]
...	3.1	96.9	60	0.022	0.70 [b]

[a] Prepared according to procedures in Figure 1. $[VCl_4] = 0.011$ *M* in toluene. [b] Ethylene introduced approximately seven times faster.

In their study of the catalyst for synthesizing syndiotactic polypropylene, Natta, *et al.*, concluded that a steady-state concentration of a V(III) species accounted for the polymer.[8] Also they proposed that the V(III) catalyst came from a V(IV) precursor, which was present during polymerization. Supposedly, the V(III) catalyst decomposed to catalytically inactive V(II) species.

TABLE IV
ATTEMPTS TO ACTIVATE V(II) COMPLEXES BY ADDITION OF *i*-Bu_3Al [a]

Amount, g-atom % V(III)	Amount, g-atom % V(II)	*i*-Bu_3Al/V	Reaction time, min	Amount g/min/mol of V/l.	Amount g/min/mol of V(III)/l.
11.1	88.9	5	30	0.32	3.0
3.6	96.4	10	6	0.12	3.4

[a] Prepared according to procedure in Figure 1, but aging conducted at room temperature for 20 min. *i*-Bu_3Al was added and the toluene solution cooled to −78° for 15 min before introducing ethylene. $[VCl_4] = 0.011$ *M*.

We report here our work on the catalyst studied by Natta, *et al.*[8,13] In addition we present our data and comments on the question of whether V(II) or V(III) is the active oxidation state of vanadium catalysts.

Results

Reduction Experiments. Dialkylaluminum chlorides rapidly reduced vanadium tetrachloride (Al/V = 5) at −78°. After 5 min only about 10% V(IV) remained. However, further reduction of the V(III) proceeded very slowly. After 16 hr the V(II) content was ≤10% (Table I). The extent of reduction to V(II) depended on the alkyl group, diethylaluminum chloride affording slightly more reduction than diisobutylaluminum chloride. In contrast to the dialkylaluminum chlorides, trialkylaluminum caused rapid reduction of V(III) to V(II) at −78°, the extent of reduction depending on the ratio R_3Al/V (Table II).

Polymerizations. In order to compare V(II) and V(III) solutions for catalytic activity under the same conditions, we prepared them according to the scheme outlined in Figure 1. Both catalyst solutions were stoichiometrically equivalent in alkyl, V, and Al. The vanadium is indicated as the chloride. But this is only a formal designation because the dichloride and trichloride are insoluble in hydrocarbons. The vanadium halides must have formed soluble complexes in these solutions.

The results in Table III show that the V(III) solutions polymerized ethylene about 50 times faster than the V(II) solutions. Since the V(II) solutions contained about 10% residual V(III), the rates of polymerization were recalculated on the basis of V(III) concentration. Thus the essentially 100% V(III) solutions polymerized ethylene about five times faster than the V(II) solutions containing residual V(III). This is a minimum value since a sevenfold increase in ethylene input doubled the rate in the V(III) solutions, but produced essentially no change in rate in the V(II) solutions.

Natta, *et al.*,[13] reported that trialkylaluminum enhanced the activity of the R_2AlCl–VCl_4 catalyst prepared at −78°. We added, therefore, *i*-Bu_3Al to our V(II) solutions to see if we observed a similar effect. We did, but the activity was still low (Table IV). These solutions also contained residual V(III), so the activity was calculated on the basis of V(III) concentration. We found that the activity was the same as in the essentially 100% V(III) solutions (Table III).

Spectra. Figures 2 and 3 show visible spectra for different oxidation states of vanadium in an ethanol–

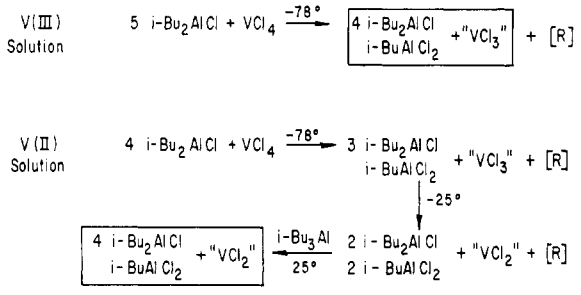

Figure 1. Reaction sequences for preparing similar V(II) and V(III) solutions.

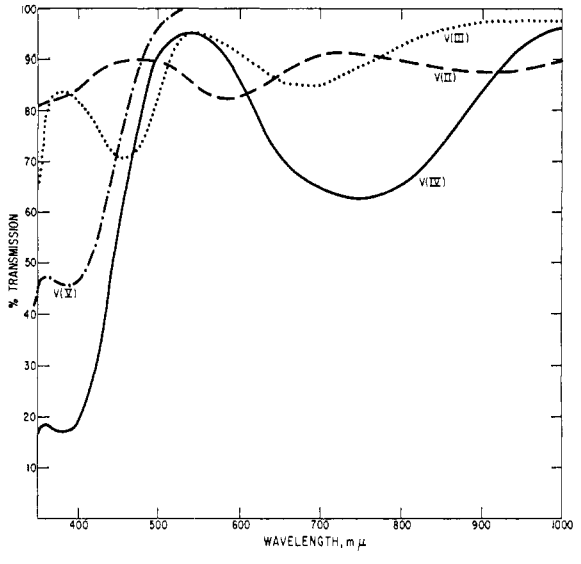

Figure 2. Visible spectra of different vanadium oxidation states: [V] = 0.0078 *M* in (1:6 by volume) ethanol–toluene (temperature of recording indicated in parentheses); V(II) (−22°), V(III) (−25°), V(IV) (−25°), and V(V) (−15°).

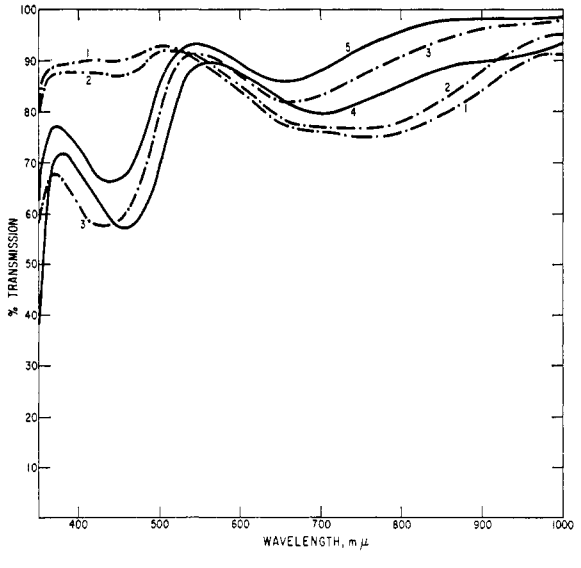

Figure 3. Changes in spectra of V(II) + V(IV) solution *vs.* a V(III) solution. Curves 1–3 for V(II) + V(IV) and curves 4 and 5 are for V(III) prepared from the Et_2AlCl–VCl_4 catalyst. Solution was transferred to cell at −23° to −24° from −78°. Time in parentheses (minutes) indicates beginning of spectrum after transfer. Last curve shows steady spectrum: curves, 1 (0), 2 (1), 3 (25), 4 (0), and 5 (1).

toluene mixture (1:6 by vol). We used this mixture because the catalysts were prepared in toluene, then subsequently treated with ethanol to destroy all carbon–metal bonds without changing the oxidation state.

V(IV). Our vanadium tetrachloride contained some V(V), 15% according to an oxidative determination and 9% according to a spectral analysis. Thus three maxima were observed: 385 mμ (ε 99); 650 mμ (ε 23), and 750 mμ (ε 25.6). The 385-mμ peak corresponded to the 385-mμ (ε 880) peak we found for $VOCl_3$ dissolved in a similar solvent mixture. This maximum has been attributed to charge-transfer absorption.[14,15] The other two maxima agree with spectra data for a VO^{2+} ion, in which V^{4+} exists in a distorted octahedral configuration.[14,16,17] Our complex was probably $VOCl_2 \cdot 3ROH$,[18] although a dimer of $VCl_2(OR)_2 \cdot ROH$ is also possible.[19]

V(III).—The standard V(III) solution (VCl_3) showed maxima at 450 mμ (ε 19.3) and 680 mμ (ε 9.4). The vanadium probably existed as $VCl_3 \cdot 3ROH$,[20] since the maxima correspond to similar ones reported for other hexa-coordinated V(III) complexes.[21,22] The addition of *i*-Bu_2AlCl to the standard V(III) solution did not change its spectrum.

Two V(III) catalyst solutions were examined. They were made by reducing VCl_4 with Et_2AlCl in one and *i*-Bu_2AlCl in the other and then subsequently treating them with ethanol. Both solutions had similar spectra. The first solution gave a steady spectrum 1 min after transfer to the cell; the other gave a steady spectrum after 3 min. The solution from the Et_2AlCl–VCl_4 catalyst had maxima at 435 mμ (ε 23.6) and 660 mμ (ε 8.2), and the solution from the *i*-Bu_2AlCl–VCl_4 catalyst had maxima at 455 mμ (ε 20.6) and 675 mμ (ε 8.1). The spectra of the solutions from V(III) catalysts and the V(III) standard solution were similar.

We examined two V(III) catalyst solutions because we have found,[23] as had others[13] before us, that the catalyst prepared with Et_2AlCl was more active. So if a V(IV) species was the precursor to the catalyst, there might be more of it in the Et_2AlCl–VCl_4 solution. However, both solutions appeared to contain only V(III).

V(II). We prepared a V(II) solution by reducing VCl_4 with *i*-Bu_2AlCl and then treating it with ethanol. The ethanolic solution exhibited peaks at 590 mμ (ε 10.8) and 900 mμ (ε 7.1). Although the exact composition of the V(II) complex was unknown, it probably had an octahedral configuration because other V(II) octahedral complexes also exhibit similar spectra.[14,24]

V(II) + V(IV). The oxidation–reduction reaction

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(eq 1) was almost complete in about 25 min at −22° for a solution about 0.004 *M* in each reactant. At −2° the reaction was almost complete in 5 min. Simi-

$$V^{2+} + V^{4+} \longrightarrow 2V^{3+} \quad (1)$$

lar reactions have been studied in aqueous solutions at higher temperatures.[25]

We found that at −22° the initial spectrum (Figure 3, curve 1) was a composite of the spectra we obtained for the V(II) and V(IV) solutions. Since our VCl_4 contained about 15% V(V) the reduction of V(V) took place very rapidly. No absorption at 385 mμ was observed. However, reduction of V(IV) was much slower. After 1 min (Figure 3, curve 2) the V(III) peak at 450 mμ began to grow. After 25 min (Figure 3, curve 3) the spectrum did not change with time. The final spectrum was very similar to that of the V(III) solution.

Magnetic Susceptibility. The V(II) solution prepared by reduction of VCl_4 with *i*-Bu_2AlCl_4 was paramagnetic. The paramagnetic shift of the nmr spectrum of the solvent enabled us to calculate the magnetic moment, μ_{eff} = 3.40 BM. The diamagnetic correction was based on the assumption that the complex was (*i*-$Bu_2AlCl)_2VCl_2$.[8] The calculated magnetic moment is close to 3.88 BM, the spin-free state for three electrons.[26]

Discussion

Catalytically Active State of Vanadium. Most investigators have favored V(III) as the active state of vanadium.[6-13] However, a few,[4,5] and particularly Carrick, *et al.*,[1-3] consider it to be V(II). The possibility of both oxidation states being active also has been suggested.[5] We believe that the evidence for either case is largely circumstantial because of experimental difficulties or limitations. For example it has been suggested that V(III) is the active state because the reduction V(III) → V(II) paralleled the drop in rate of polymer formation.[4] Such an interpretation excludes the possibility that the V(II) catalyst is much less active than the V(III) catalyst. In addition, the number of alkyl groups available to alkylate the vanadium decreases by about one alkyl group per each unit reduction in vanadium valence.[2,27] Hence the alkylating ability of the systems decreases simultaneously as the V(II) concentration increases. Thus the loss of catalytic activity could result from the absence of strong enough alkylating compounds to produce active carbon–vanadium bonds in V(II) species.[28]

Other investigators have concluded that V(III) is the active state in solid cocatalysts of VCl_2 and VCl_3.[9-12] Since reaction must take place on the surface of solid catalysts, probably fewer than 1% of the metal ions are involved in catalysis.[9,29-31] Under these conditions the average bulk oxidation state may be irrelevant. Traces of V(III) on the surface could account for activity of VCl_2, or a weak alkylating agent could account for the absence of activity. It may not be surprising, therefore, that some investigators[32,33] have observed activity with VCl_2 while others[9,12] have not.

The reported ineffectiveness of other V(II) compounds can also be explained by insufficiently strong alkylating compounds.[2,6,8,12] Also one can speculate that in some cases the ligands attached to the V(II) were not the right ones to cause enough carbon–metal bond instability (catalytic activity).[28,34]

Carrick, *et al.*,[1-3] interpreted their results as suggesting V(II) is the active state. We think their results are explainable on the basis of a V(III) catalyst. They noted that *i*-Bu_3Al plus VCl_4 (Al/V ≤ 0.4) gave no activity and no V(II).[2] One of the expected products is *i*-$BuAlCl_2$ (eq 2). On the basis of other evidence,[11,13,35]

$$i\text{-}Bu_3Al + 2VCl_4 \longrightarrow i\text{-}BuAlCl_2 + 2VCl_3 + 2Bu \quad (2)$$

we would not expect the monoalkyl to be a strong alkylating agent for solid VCl_3. So lack of activity is not surprising.

Another argument by Carrick, *et al.*, in favor of V(II) was the observation that activity occurred only when V(II) appeared.[2] They also noted that the most active cocatalysts were VCl_4 and $VOCl_3$, the compounds most easily reduced to V(II). Others have shown, however, that the extent of reduction of solid VCl_3 to V(II) by a metal alkyl does not necessarily correlate with polymerization activity.[9]

Still other evidence for V(II) as the active state was based on infrared end group analysis and molecular weight measurements of polyethylenes. The argument here against V(III) as active specie was as follows. If chain termination occurred by the reduction of V(III) to V(II) *via* a bimolecular disproportionation (eq 3), then less than one vinyl group per molecule would be found.

$$2Ph\sim CH_2CH_2VCl_2 \longrightarrow Ph\sim CH{=}CH_2 + Ph\sim CH_2CH_3 + 2VCl_2 \quad (3)$$

Unfortunately, the vinyl group determination depended in part on the accuracy of the assumed intrinsic viscosity number average molecular weight relationship.[36a] Using a more recent relationship[36a] we calculated 0.69 and 0.42 vinyl groups/molecule instead of 1.1 and 0.63, respectively, as reported earlier.[36b] So the recalculated values are consistent with V(III) as the active state and eq 3 as the termination reaction.

In our work we prepared similar homogeneous V(II) and V(III) solutions having the same alkyl/metal ratio (Figure 1). Diisobutylaluminum chloride was used

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TABLE V
RELATIVE RATES OF POLYETHYLENE FORMATION AT −78° WITH V(III) CATALYST SYSTEMS WITHOUT RESIDUAL V(IV)[a]

Amt, g-atom % V(IV)	Amt, g-atom % V(III)	Amt, g-atom % V(II)	Reaction time, min	Amt, g/min/mol of V(III)/l.
...	94.3	5.7	10.0	3.1
0.5	99.5	...	7.8	5.2
...	96.5	3.5	6.0	3.8
...	96.7	3.3	5.7	6.9
				av 4.8

[a] Prepared according to procedure in Figure 1, but toluene solutions aged 10–15 min at −25° before cooling again to −78°. $[VCl_4] = 0.011\ M$.

instead of the corresponding ethyl compound in order to obtain homogeneous V(II) solutions. Chloride ion was the only other anionic ligand present in our solutions. It was chosen because Natta, *et al.*,[37] showed it to be necessary for catalytic activity in ethylene–propylene copolymerizations using vanadium catalysts.

Our polymerization data show that only V(III) solutions exhibited much activity (Table III). Since these solutions did not contain any detectable V(II), V(II) probably did not account for catalytic activity in our V(III) solutions.[38a] The low activity shown by the V(II) solutions could be ascribed to their residual V(III) content. However, if the rate of polymerization based on the residual V(III) were greater than that for the V(III) in the concentrated solutions, then one might conclude that the V(II) also was contributing to the activity. Even then the activity of the V(II) would be considerably less than that of the active V(III). However, we found that the residual V(III) in the V(II) solutions was at most about one-tenth as active as the V(III) in the concentrated solutions. We found, therefore, no direct evidence for catalysis by V(II), unless the residual V(III) was inactive. This seems unlikely because we raised the activity, calculated on the basis of V(III), up to the level of the very active V(III) solutions when we added excess R_3Al (Tables III and IV).

From the foregoing we also arrived at an adjunct conclusion. Our results point to the existence of at least two kinds of catalytically active V(III) species. One was very active, but unstable. The other was less active, but more stable. The unstable $V(III)_a$ species formed initially from the reduction of VCl_4. However, as we show later, the $V(III)_a$ probably came from an inactive V(III) complex not from a V(IV) precursor. With heat or in the presence of R_3Al at −78° (Tables II and III), most of the $V(III)_a$ decomposed to inactive V(II) complexes. Some vanadium was also converted into a stable $V(III)_s$ species. Relative to $V(III)_a$, the $V(III)_s$ was probably more stable both thermally and toward reduction with excess alkylaluminum chloride. For example, we found 6% V(III), presumably $V(III)_s$, in a solution containing mono- and diisobutylaluminum chloride after 1 month at room temperature. We do not know how the $V(III)_s$ species was formed. It could have formed either during the initial reduction of V(IV) to V(III) or during the subsequent incomplete reduction of V(III) to V(II).

The species which we characterize as $V(III)_a$ in the polymerization of ethylene is probably the same species that produces syndiotactic polypropylene.[13] We also found these solutions to give syndiotactic polypropylene. And $V(III)_s$ is probably the complex that exhibits low activity toward propylene at room temperature or at −78°.[13,23] It is possible that other unrecognized V(III) species may form during reduction of V(III) to V(II) or at higher temperatures. Such species may be important in forming the less stereoregular polypropylenes.[13,39]

Although we did not observe any catalytically active V(II), it may still be considered a potentially active state. Cossee's theory[28] of catalytic polymerization activity includes V(II) because it allows for activity in transition metal ions with up to three unpaired electrons. In its spin-free state V(II) has three unpaired electrons. And we found that V(II) in a solution prepared by reducing VCl_4 with $i\text{-}Bu_2AlCl$ had an effective moment of 3.40 BM. This value is close to the theoretical value of 3.87 BM for the spin-free state,[26] so our V(II) solution could theoretically have been active.[28]

Gumboldt, *et al.*, recently suggested that V(IV) or V(V) might be catalytically active.[12] Either complex is consistent with Cossee's theoretical arguement for an active state. Nevertheless, we found no conclusive evidence for active V(IV) complexes. For example, our V(III) solutions containing <10% V(IV) did not lose activity on further reduction (Table V). In fact, the activity increased about 55% perhaps because of further alkylation of V(III) species. However, we cannot definitely exclude V(IV) as being active in our examples. At best we can only say that if it was active, its activity was either less than or about the same as the $V(III)_a$ species.

Formation of Catalyst in the Synthesis of Syndiotactic Polypropylene. Natta, *et al.*,[8] concluded that after the reaction of dialkylaluminum chloride with vanadium tetrachloride at −78° the active V(III) soon reached a steady-state concentration according to the scheme given in eq 4–6. They interpreted their polymerization data and the color of their vanadium complexes as indicating the existence of V(IV), and that "all VCl_4 present at −78° in a more or less long time must create catalytically active $RVCl_2$."

$$R_2VCl_2 \longrightarrow RVCl_2 + R\cdot \quad (4)$$

$$RVCl_2 + n\text{-}C_3H_6 \longrightarrow PVCl_2 \quad (5)$$

$$PVCl_2 \longrightarrow VCl_2 + P\cdot \quad (6)$$

If the above reactions are correct then the solutions which we found to contain almost all V(III) really contained an equal mixture of V(IV) and V(II). However, our spectral data (Figures 2 and 3) show that the catalyst solutions were essentially all V(III), and not 50:50 mixtures of V(II) and V(IV).

(37) G. Natta, G. Mazzanti, A. Valvassori, G. Sartori, and D. Fiumani, *J. Polym. Sci.*, **51**, 411 (1961).

(38) (a) We agree with the referee who pointed out that since fewer than 1% of the vanadium species are active any time, it is still possible to account for our results by postulating traces of unstable divalent species as active complex. However, rather than make this inference since we have shown activity in the presence of both stable and unstable V(III) states, we prefer to conclude that the polymerization activity was caused by different V(III) species. (b) See ref 29, p 243, and references therein.

(39) J. Boor, Jr., and E. A. Youngman, *J. Polym. Sci., Part A-1*, **4**, 1861 (1966).

Natta, *et al.*'s, scheme[8] (eq 4–6) is therefore not consistent with our spectrophotometric results and with our observation that V(IV) is practically all reduced to V(III) within minutes. We tentatively suggest that the following reactions to account for these and other results.[5,8,13,39] An explanation of the catalyst stereospecificity has already been advanced.[39] In our scheme no attempt is made to account for the lesser active V(III) catalyst which does not give syndiotactic polypropylene.

$$R_2AlCl + VCl_4 \xrightarrow[\text{fast}]{k_1} RVCl_3 + RAlCl_2 \quad (7)$$

$$4R_2AlCl + 2RVCl_3 \xrightarrow[\text{fast}]{k_2} 2VCl_3\cdot(R_2AlCl)_2 + 2R \quad (8)$$

$$VCl_3\cdot(R_2AlCl)_2 \xrightarrow[\text{slow}]{k_3} RVCl_2\cdot(R_{1.5}AlCl_{1.5})_2 \quad (9)$$

$$RVCl_2\cdot(R_{1.5}AlCl_{1.5})_2 + n\text{M} \xrightarrow[\text{slow}]{k_p} RM_nVCl_2\cdot(R_{1.5}AlCl_{1.5})_2 \quad (10)$$

$$2RM_nVCl_2\cdot(R_{1.5}AlCl_{1.5})_2 \xrightarrow[\text{slow}]{k_t} 2[RM_n] + 2VCl_2\cdot(R_{1.5}AlCl_{1.5})_2 \quad (11)$$

Reactions 7 and 8 are based on known reactions for $TiCl_4$.[38b] The fate of the liberated alkyl groups may be the same as in the $TiCl_4$ reduction, or may involve coupling.[1] The product in the VCl_4 sample must be a complex because VCl_3 is insoluble in hydrocarbons. The complex very likely involves alkylaluminum chlorides.[2,4,5,27] Although we have shown the active complex as containing the sesquialuminum chloride, this is arbitrary. The actual ratio R/Cl in the aluminum part of the complex can be expected to vary, depending on the over-all R/Cl ratio in the system.[27] The aluminum and vanadium atoms are probably joined by chlorine bridges[2,5] in both inactive and active complexes. Transfer of alkyl from aluminum to vanadium leads to active complex (eq 9)[28] a penta-coordinated alkyl vanadium having one site open for coordination before achieving an octahedral structure. No attempt was made to determine whether or not all V(III) becomes active at one time or another. Other evidence[8,39] indicates, however, that fewer than 1% of the vanadium species are active at any time, and our unpublished calculations agree approximately with this figure. Therefore, we can not ignore the possibility in our suggested scheme that some V(III) is reduced to V(II) without the formation of active complex.

According to Cossee,[28] coordination of monomer produces an unstable octahedral complex, which collapses by adding an alkyl or a growing polymer chain to a monomer. This is the propagation step (eq 10) which results in reformation of active complex. We assume that chain termination occurs by a bimolecular disproportionation (eq 11), though an unimolecular diassociation into V(III) hydride and long chain olefin is also conceivable.

From the above observations that fewer than 1% of the vanadium species are active at any time and that steady-state conditions are present,[8] it follows that $k_p \gg k_t \geqslant k_3$. And all of these rate constants must be very small compared to those for the alkylation (k_1) and reduction (k_2) to V(III), eq 7–8. This is because reduction to V(III) occurs within minutes (Table I) while polymerization proceeds very slowly over several days.[8,39]

Experimental Section

Alkylaluminum Compounds. All were used as received from Texas Alkyls.

Vanadium Compounds. Vanadium trichloride was obtained from Alfa Inorganics, Inc. The vanadium tetrachloride was purchased from the Stauffer Chemical Co. In this material we found 85% V(IV) and 15% V(V) by our oxidative procedure. From spectrophotometric results on VCl_4 and $VOCl_3$ in ethanol–toluene solutions at −15°, we calculated 91% V(IV) and 9% V(V). The VCl_4 was stored in dilute hexane solutions instead of in toluene because it attacks the latter. Also we stored the solutions below 0° to retard thermal decomposition. The vanadium oxytrichloride was obtained by distilling a commercial sample.

Toluene was distilled first from a solution of blue sodium benzophenone complex to remove oxygen and stored under nitrogen. The toluene was sieved just before use.

Ethylene was high purity grade, purchased from Gulf and purified further as described in the polymerization section.

Analytical Reagents. The ceric and ferric ammonium sulfates were reagent grade chemicals from Baker and Adamson.

Average Oxidation State Determinations. We used modifications of procedures described elsewhere.[12,40] Instead of destroying the carbon–metal bonds with methanol,[40] we used ethanol. And instead of titrating directly with ceric sulfate,[40] we added sulfuric acid and ferric sulfate to convert all vanadium into V(IV),[12] then titrated potentiometrically the two end points with ceric sulfate.[12] After adding the alcohol at −78°,[40] we allowed about 30 min for the mixtures to warm up before adding the acid and iron. Under these conditions no significant oxidation of V(II) took place.[40] In titrating we also added orthophosphoric acid after the first end point, in order to facilitate the oxidation of V(IV) by Ce(IV) at room temperatures.[41]

In determining the average oxidation state of vanadium it was necessary to avoid spurious reductions of ferric ion by residual carbon–metal bonds. Giuffre and Cassani claimed that alcoholysis did this without oxidizing the vanadium.[40] Our results support their claim. We found no differences within experimental error (duplicate runs usually agreed within 2–3%) among the following procedural variations: (1) adding the sulfuric acid and ferric sulfate separately instead of together, but with the acid first; (2) adding acid and iron together at −78° instead of at room temperature; and (3) performing the ethanolysis at −27° instead of at −78°.

We used a solution of ethanol, water, acid, and iron as a blank. Generally the blank amounted to less than 1% of the first end point.

Magnetic Susceptibility. The procedure using nmr spectroscopy was similar to those reported,[42,43] except that instead of measuring a single concentration of paramagnetic substance we took values at several concentrations. A Varian A-60 spectrometer was used to make the nmr measurements. The magnetic moment and number of unpaired electrons were calculated using equations given by Selwood.[44,45]

(40) L. Giuffre and F. Cassani, *Chim. Ind.* (Milan), **46**, 179 (1964).
(41) L. S. A. Dikshitulu and G. G. Rao, *Talanta*, **9**, 857 (1962).
(42) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(43) H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.*, **1**, 208 (1964).
(44) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, pp 135–136.
(45) See ref 44, pp 158–159.

Polymerizations. The polymerizations were run in a one-necked 24/40 ⅋ 250-cc flask equipped with a Teflon-coated magnet and a three-way stopcock attached to a side arm. All operations were carried out with dry equipment and under nitrogen. Toluene and alkylaluminum chloride solutions were added at room temperature. After cooling the flask in a Dry Ice bath, hexane solution of vanadium tetrachloride was slowly added. It made no difference if the vanadium solution was precooled to −78° before reduction. If trialkylaluminum solution was used, it was added next. Ethylene was passed through molecular sieves and bubbled through a kerosene solution of trihexylaluminum before introducing it into the reaction flask. The ethylene was introduced through a needle placed about 1–2 cm above the stirred solution. It was not feasible to leave the needle below the surface because polymer collected rapidly on the open tip and soon plugged it. The polymer was recovered from the organic phase that was separated during the work-up of the mixture for the valence state determination.

Visible Spectra. Visible spectra were obtained using a Beckman DK28 spectrophotometer. The cell well was kept under a nitrogen blanket and cooled with a circulating acetone–Dry Ice bath.

All vanadium solutions were prepared so that [V] = 0.0078 *M* in ethanol–toluene (1:6 by volume), and all operations were performed under nitrogen. The solutions were either prepared at or cooled to −78°. We transferred the cold solutions using a dry syringe, jacketed with Dry Ice, to a 1-cm or 0.5-mm cell at about −25°.

V(II). This solution was prepared by reducing VCl_4 with *i*-Bu_2AlCl (Al/V = 5) in toluene at −78°. The solution was aged 1 hr at room temperature. Finally it was quenched with ethanol at −78°, and stored in a sealed vial at −25°.

V(III). Vanadium trichloride was added to an ethanol–toluene mixture by first mixing at −78°. A homogeneous solution was obtained by stirring the mixture overnight at room temperature. It was stored in a sealed vial at −25°. Prior to analysis, the solution was cooled to −78° and treated with a toluene solution of *i*-Bu_2AlCl (Al/V = 5). About 30 min later the solution was transferred to the spectrophotometric cell.

V(IV). A 0.5 *M* hexane solution of VCl_4 was cooled to −78°. Ethanol and then toluene were added to give a 0.0078 *M* solution. This was stored in a flask at −25°.

V(V). Ethanol was added to toluene solution of $VOCl_3$ cooled to −78°. The cold solution was next transferred to a cell for analysis.

V(II) + V(IV). The standard V(II) and V(IV) solutions described above were cooled to −78° and mixed in equal amounts. About 2 min after mixing the solution was analyzed with the spectrophotometer. About 45 sec passed in recording each spectrum, so we indicated in Figure 3 the starting time of each spectrum.

Acknowledgments. I wish to thank Drs. M. P. Dreyfuss and W. J. Kroenke for their helpful comments on the manuscript and Mrs. Lois Y. Farrand and Mr. K. E. Andrews for their laboratory assistance.

The Structon Theory Applied to Inorganic Crystals and Glasses Containing Macroions

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ABSTRACT: The over-all structures and many of the properties of matter in condensed systems can be related, often quantitatively, to the types, relative numbers, and properties of the *structons* of which they are composed. (Each structon type is an atom of a specified element, having a specified set of close-neighbor atoms.) This theory is applied to the structures of polyanions in silicate and other related types of crystals and glasses. In many cases the types and relative numbers of the structons present in the crystal or glass can be determined from the over-all composition, using well-established principles. Two useful functions, the *charge density function* and the *reticulation function*, are introduced. Both are closely related to structure and macroscopic properties. Some general principles concerning the types of structons present in polyanions containing Si, B, P, and Al are briefly discussed. Differences between crystals and glasses, with respect to their structures and structon compositions, are also dealt with.

The fundamental principles of atomic structure and interatomic bonding have been shown to hold in crystals,[1-4] as well as in small molecules and ions. Quite properly, they are also generally assumed to hold in glasses. These principles lead directly to the often verified conclusion that many silicate (and borate, phosphate, aluminate, borosilicate, phosphosilicate, aluminosilicate, etc.) crystals and glasses contain macroanions.[4,5] In crystalline substances in these classes, polyanions of the chain, ribbon, sheet, and network types have been found. Many glasses certainly contain macroanions with irregular branched chain, cross-linked chain, and network structures. Between the macroanions (or within them, if they have network structures), in both crystals and glasses, small cations are located in such a manner as to satisfy, as well as possible, their coulombic and other attractions and re-

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