TABLE I

EFFECT OF THE SOLVENTS ON THE COMPOSITION OF STYRENE POLYSULFONE (50°)[a]

Styrene, mol % in feed	Total monomer concn, mol/l.	Added solvent, vol %	Styrene, mol % in copolymer: *o*-Dichlorobenzene	Cyclohexane	Sulfolane	Nitrobenzene	Pyridine	Bulk
80	1.0	89.8	89.4		87.3		98.6	
80	2.0	79.6	80.4		78.9		96.5	
80	3.0	69.4	77.7	77.9	72.7	74.6	96.0	
80	4.5	54.1	73.8	71.7	69.5	72.7	88.6	
80	6.0	38.9	72.4	71.7	69.2	70.9	81.0	
80	7.5	23.6	69.9	69.3	68.8	67.6	75.2	
80	9.0	8.3	67.9	68.4	69.5	68.3	68.9	
80	10.7	0.0						68.4[b]

[a] $[AIBN]_0 = 7.5 \times 10^{-3}$ mol/l. [b] The mean value from two experiments (67.8 and 69.0).

TABLE II

EFFECT OF THE SOLVENTS ON THE COMPOSITION OF STYRENE POLYSULFONE (50°)[a]

Styrene, mol % in feed	Total monomer concn, mol/l.	Added solvent, vol %	Styrene, mol % in copolymer: *o*-Dichlorobenzene	Sulfolane	Pyridine	Bulk
20	3.0	81.3	74.8		91.4	
20	4.5	71.9	71.6	69.2	82.3	
20	6.0	62.5	69.9	69.0	73.5	
20	7.5	53.1	67.9	66.6		
20	9.0	43.8	67.1	66.3	66.2	
20	12.8	0.0				66.6

[a] $[AIBN]_0 = 7.5 \times 10^{-3}$ mol/l.

not occurred. In this case, the copolymer compositions depend on the concentration of the styrene and liquid sulfur dioxide complex, and it should vary with total monomer concentration; *i.e.*, the higher the solvent content the lower the complex concentration. The composition should also depend on the polymerization temperature and the addition of a solvent which has a mutual interaction with liquid sulfur dioxide.

However, an alternative explanation for the dilution effect may be possible if considerable depropagation occurs in these copolymerization systems. It is well known that the radical copolymerizations of liquid sulfur dioxide with a number of aliphatic olefins are characterized by depropagation. As depropagation and propagation are first- and second-order reactions, respectively, the decrease in the rate of depropagation due to dilution is smaller than that in propagation; the result is variable copolymer compositions. In this case, the increase in styrene content by dilution may be interpreted as the result of the increase in the depropagation rate relative to that in propagation.

$$\sim St - SO_2\cdot \longrightarrow \sim St\cdot + SO_2$$

Therefore the possibility of a copolymerization which proceeds by separate monomers (styrene and liquid sulfur dioxide) cannot be discounted completely on the basis of our results, since they can be explained kinetically on the basis of the copolymerization of separate monomers involving a depropagation. The results of the detailed investigation will be presented in the near future.

Acknowledgment. The authors wish to express their thanks to Mr. Yasuhiro Ishioroshi of this university for his discussion on this investigation. The experimental assistance of Mr. Takeshi Hirayama is greatly appreciated.

Minoru Matsuda, Masashi Iino
Chemical Research Institute of Nonaqueous
Solutions, Tohoku University
Sendai, Japan

Received November 26, 1968

Electron Spin Resonance Evidence of Inactive V(III) Precursor to Catalytically Active V(III) in Vanadium Tetrachloride Ziegler Catalysts

In a recent paper[1] on the active oxidation state of vanadium in soluble monoolefin polymerization catalysts, one of us presented data in support of the thesis that catalytically active V(III) species came from inactive V(III) complexes. Earlier, other workers[2] had suggested that the inactive precursor was a V(IV) complex. We now present esr data which support our conclusion that the catalyst precursor was an inactive V(III) complex. Furthermore, the esr results are consistent with the view[1] that the active species was an alkylvanadium(III) complex and that the precursor contained no alkylvanadium bonds.

In the synthesis of syndiotactic polypropylene with a $Et_2AlCl-VCl_4$ catalyst at −78°, steady-state conditions may be reached after 5–10 hr with a minimum of

---

(1) M. H. Lehr, *Macromolecules*, **1**, 178 (1968).

TABLE I

REDUCTION OF VCl_4 BY R_2AlCl IN TOLUENE AT −78°

Catalyst sample	R	Al/V	Time, min	$[V]_{total}$, *M*	% V(IV) Titration[a]	% V(IV) Esr[b]
A	C_2H_5	5	5.0	4.4×10^{-3}		0.1
B	C_2H_5	5	75.0	1.9×10^{-2}	0[c]	
C	C_2H_5	30	1.0	1.0×10^{-2}		0.2
D	C_2H_5	30	5.0	1.0×10^{-2}		N.d.[d]
E	C_2H_5	30	10.4	1.0×10^{-2}		N.d.
F	i-C_4H_9	5	0.1	8.5×10^{-3}	50.8	54.7
G	i-C_4H_9	5	0.1	8.5×10^{-3}	43.6	59.0
H	i-C_4H_9	5	0.1	8.5×10^{-3}	52.6	52.7
I	i-C_4H_9	5	0.25	1.9×10^{-2}	4.6	3.7
J	i-C_4H_9	5	1.0	1.9×10^{-2}	1.6	0.3
K	i-C_4H_9	5	1.0	1.9×10^{-2}	3.5	1.4

[a] See ref 1 for procedure; figures are the average of two titrations. [b] Using a series of VCl_4–C_2H_5OH solutions as standards. [c] 0.2% V(II). [d] N.d. = not detectable, *i.e.*, ≤0.07% of $[V]_{total}$.

TABLE II

REDUCTION OF VCl_4 BY R_2AlCl AT −78° IN PRESENCE OF ANISOLE AND PROPYLENE[a]

Catalyst sample	R	Time, min	$[V]_{total}$, *M*	% V(IV) Titration	% V(IV) Esr
L	*i*-Bu	10	1.0×10^{-2}	1.8	0.7
M	*i*-Bu	240	1.0×10^{-2}		N.d.[c]
N	Et	10	1.0×10^{-2}	0[b]	N.d.
O	Et	10	1.0×10^{-2}		N.d.

[a] $R_2AlCl:VCl_4:C_7H_8O$ = 5:1:1 in toluene (∼22% by volume propylene). [b] 0.1% V(II). [c] N.d. = not detectable, *i.e.*, ≤0.07% of $[V]_{total}$.

TABLE III

RELATIONSHIP BETWEEN VO^{2+} ESR INTENSITY AND V(IV) CONCENTRATION

Source of VO^{2+}	Concentration range of V(IV), *M*	Intensity[a]/[V(IV)]	No. of measurements
I, VCl_4–C_2H_5OH	10^{-2} to 10^{-4}	3.09 ± 0.21	5
II, VCl_4–$(i\text{-}Bu)_2AlCl$[b]	4×10^{-2} to 4×10^{-5}	3.55 ± 0.48	3

[a] Derivative peak height of $+^3/_2$ line normalized for the receiver gain of the instrument; error reported as standard deviation. [b] Ethanol quenched sample H in Table I as analyzed and subsequently diluted; [V(IV)] determined by titration.

0.1–0.5% vanadium as active species.[2,3] The esr data shown in Table I verify our earlier data that in this system VCl_4 is quickly reduced to the V(III) state. Furthermore, our esr data show that within our limits of detection less than 7×10^{-6} *M* vanadium was present as V(IV) after 5 min. This corresponds to less than 0.07% V(IV) for examples where total vanadium concentration was 1.0×10^{-2} *M* (catalyst samples D and E). It follows that whether or not steady-state conditions are reached after several hours there is either insufficient or no V(IV) present to function as a precursor to catalytically active V(III) species. Therefore, as we proposed earlier,[1] the catalyst species must be derived from inactive V(III) complexes.

The i-Bu_2AlCl–VCl_4 catalyst system also undergoes rapid reduction from V(IV) to V(III) (Table I). According to the esr data we found about 1% V(IV) left after 1 min (catalyst samples J and K). In the anisole modification of this catalyst (Table II) and in the presence of propylene we found 0.7% V(IV) after 10 min, and after 4 hr no detectable (<0.07%) V(IV). The anisole modification of the Et_2AlCl–VCl_4 catalyst gave similar results, no detectable V(IV) after 10 min.

It has been suggested by others[4] that in the anisole-modified catalysts there is no significant chain transfer or chain termination and that the stable catalytic V(III) species form gradually and accumulate during polymerization. Furthermore, they proposed the catalyst precursor was a V(IV) oxidation state. Our esr data (Table II) show that this interpretation cannot be entirely correct. For example, if we calculate the minimum initial catalyst concentrations from the viscosity average molecular weight curve for a i-Bu_2AlCl–VCl_4–anisole system,[5,6] we get 6% active V(III), and after 4 hr we find 10% active V(III) species. But we found that only 0.7% V(IV) remained after 10 min (catalyst sample L) and none was detectable after

---

(2) G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, E. R. Mognaschi, A. L. Segre, and P. Centola, *Makromol. Chem.*, **81**, 161 (1965).

(3) A. Zambelli, G. Natta, I. Pasquon, and R. Signorini, *J. Polym. Sci., Part C*, **5**, 2485 (1967).

(4) A. Zambelli, I. Pasquon, R. Signorini, and G. Natta, *Makromol. Chem.*, **112**, 160 (1968).

(5) See ref 2 for description of calculation.

(6) Reference 4, Figure 18.

4 hr (catalyst sample M)! Therefore, a significant part (~40%) of the accumulated catalyst species could not have been derived from V(IV) complexes, but must have come from inactive V(III) complexes.

Attempts to detect V(IV) in solutions of VCl_4 by esr spectroscopy have been unsuccessful at temperatures above 9°K.[7] However, the esr spectrum of the VO^{2+} ion is easily observed and has been well characterized.[8] We converted, therefore, any V(IV) present in our catalyst solutions into VO^{2+} ion by quenching with ethanol. In this way we could monitor the various catalyst systems as a function of time and measure any changes that were occurring in V(IV) concentration.

The VO^{2+} ion exhibits the esr spectrum shown in Figure 1a. The spectrum is characterized by eight lines of hyperfine interaction resulting from the $3d^1$ electron interaction with the ^{51}V nuclear spin of $^7/_2$, and by variation of line widths of each line resulting from hyperfine interaction with each component of nuclear quantum number m_I.[8a]

Our esr results also show that within experimental error all V(IV) was converted into the oxovanadium(IV) cation. This follows from a comparison of partly reduced catalyst solutions (catalyst sample H in Table I) with standard solutions of oxovanadium(IV) cation (Table III). The standard was prepared by treating vanadium tetrachloride with ethanol.[1] Dilutions of the standard were made with a toluene–ethanol mixture (9:1 v/v) to cover a concentration range of 10^{-2} to 10^{-4} *M* V(IV). The quenched catalyst solution containing 52.6% V(IV) by titration was likewise diluted to cover a concentration range of 4×10^{-3} to 4×10^{-5} *M* V(IV). As a measure of intensity the derivative height of the $+^3/_2$ hyperfine component was used because it is less influenced by line broadening than the rest of the spectrum.[8a] After normalizing the measured intensities for the instrument receiver gain, we found that the average intensity per mole of VO^{2+} for the two sets of solutions (Table III) agreed within experimental error. It follows, therefore, that we observed essentially all the V(IV) present in our catalyst solutions as the oxovanadium(IV) cation.

We determined the minimum limit of detectable VO^{2+} by dilution of sources I and II (Table III) until we could no longer see a VO^{2+} esr signal. Both sources had identical esr signals. Both methods indicated that the minimum detectable VO^{2+} concentration was about 7×10^{-6} *M*. Figure 1 compares the spectra of a 4.2×10^{-5} *M* solution (Figure 1a) and a 7.0×10^{-6} *M* solution (Figure 1b). It is clear that even with the noise present 7.0×10^{-6} *M* VO^{2+} was detectable. Figure 1c shows no detectable VO^{2+} in a 30:1 $Et_2AlCl:VCl_4$ catalyst after 5 min (catalyst sample D). We verified this conclusion by searching for the esr signal with 25 scans using a C-1024 time-averaging computer. The broad signal seen in Figures 1b and 1c was due to an impurity in the esr resonance cavity.

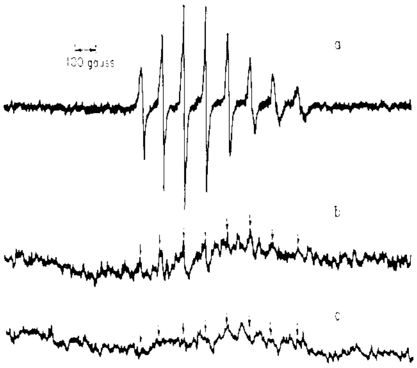

Figure 1. Esr spectra of VO^{2+} ion from VCl_4 in 9:1 toluene–ethanol: (a) $[VO^{2+}] = 4.2 \times 10^{-5}$ *M*; (b) $[VO^{2+}] = 7.0 \times 10^{-6}$ *M*; (c) catalyst sample D from Table I.

A Varian E-3 esr spectrometer operating at 9.52 GHz and 100 kHz modulation was used to obtain the esr spectra. The solutions were contained in 4-mm o.d. quartz tubes outfitted with a joint and three-way stopcock. The solutions were prepared and transferred under nitrogen, and a nitrogen atmosphere was maintained in the tubes. The reported data were obtained at room temperature in the standard E-4531 multipurpose cavity. Similar experiments were conducted with catalyst and standard solutions using the E-4557-9 variable-temperature accessory. These results were also in agreement with the data reported here.

Marvin H. Lehr, Charles J. Carman
The B. F. Goodrich Research Center
Brecksville, Ohio 44141

Received January 17, 1969

---

(7) R. J. Johannesen, G. A. Candela, and T. Tsang, *J. Chem. Phys.*, **48**, 5544 (1968).

(8) (a) R. N. Rogers and G. E. Pake, *ibid.*, **33**, 1107 (1960); (b) H. M. McConnell, *ibid.*, **25**, 709 (1956); (c) D. Kivelson and Sai-Kwing Lee, *ibid.*, **41**, 1896 (1964); (d) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).