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ESR Spectra of the System of the Transition Metal Compound and Trialkyl Aluminum. II.[*1] The System of the Vanadium Compound and Trialkyl Aluminum[*2]

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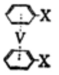
The ESR spectra of the homogeneous organometallic catalyst system of VOA_2-$AlEt_3$ (I) and VCl_4-$AlEt_3$ (II) were measured in benzene, toluene, *n*-hexane and tetrahydrofuran solutions. A superhyperfine structure of nine lines with a *g*-value of 1.9917, and with a hyperfine splitting of 4.2 gauss on each eight line due to the ^{51}V nucleus, was observed in the systems of I and II in the aromatic solvents at any Al/V ratio from 1 to 15. The same type of spectrum was observed in the VA_3-$Al(isoBut)_3$ system in a benzene solution at Al/V ratios higher than 3. In the system of II, the single line was observed at Al/V ratios up to 5. At higher ratios the superhyperfine structure appeared to overlap on the single line. On the basis of these facts, it may be considered that the vanadium atom was reduced to the zerovalent state and was then complexed with aromatic solvents in these systems. This suggests the presence of a sandwich complex such as  where $X{=}H$ or CH_3.

Homogeneous catalytic systems of the vanadium (V) compound and aluminum alkyl for the polymerization of ethylene and its copolymerization with α-olefin have been investigated in detail.[1-4] Natta[5] has shown, by means of electron spin resonance (ESR) measurements, that the active species of vanadium complexes for the syndiotactic polymerization of polypropylene have a valence state of 3. The active oxidation state of the V compound has also been extensively discussed by Lehr.[6] The formation of a chlorine-bridged complex as the reaction product of vanadium tetrachlolide (VCl_4) and triethylaluminum ($AlEt_3$) in the VCl_4-$AlEt_3$ system has been proposed by Sciulydin.[7] The same type of ESR spectrum has, however, been obtained in the system of vanadyl acetylacetonate (VOA_2) and $AlEt_3$, in which chlorine atoms are not present. Therefore, it seems to be worthwhile to study further the chemical structure of the complex produced in the system of the V compound and $AlEt_3$.

The present paper describes ESR measurements

[*1] Part I of this series: Y. Nozawa and M. Takeda, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan. Ind. Chem. Sect.*), **71**, 189 (1968).

[*2] Presented at the 7th symposium on ESR held by the Chemical Society of Japan, Sapporo, September, 1968.

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

2) F. D. Otto and G. Parravano, *J. Polym. Sci.*, **A-2**, 5131 (1964).

3) L. C. Anand, S. S. Dixit and S. L. Kapur, *J. Polym. Sci.*, **A-1**, **6**, 909 (1968).

4) I. Pasquon, *Pure and Applied Chem.*, **6**, 465 (1968).

5) G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, A. L. Segre and P. Centola, *Macromol. Chem.*, **81**, 161 (1965).

6) M. H. Lehr, *Macromolecular*, **1**, No. 2, 178 (1968).

7) S. V. Sciulydin, N. N. Tikhomirova, A. E. Shilov and A. K. Shilova, *Zh. Struk. Khim.*, **2**, 740 (1961).

of the VOA_2-$AlEt_3$ (I) and VCl_4-$AlEt_3$ (II) systems in various organic solvents; the formation of a sandwich complex of the V atom with aromatic solvents will be discussed on the basis of our observations.

Experimental

Reagent and Preparation of Samples. Vanadium trisacetylacetonate was prepared as described in the literature[8] and was purified by recrystallization from benzene. Commercially-obtained vanadium tetrachloride and triethylaluminum (Ethyl Co) were used without further purification. The solvents used were refluxed over a sodium ribbon and distilled immediately before use.

The samples for ESR measurements were prepared in a 30-milliliter glass vessel under a dried nitrogen atmosphere at room temperature. One milliliter of the 1/5 mol/*l* solution of the V compound was taken into the vessel and a predetermined aliquot of an $AlEt_3$ solution with the same concentration as the V compound was added; then the solvent was added to bring the total volume to 20 m*l*. Thus the concentration of the sample solution was 0.01 mol/*l* with respect to the V compound. The solution was introduced into a sample tube for ESR measurements by means of a hypodermic syringe. The concentration of the sample solution for the VOA_2-$AlEt_3$ system in *n*-hexane was small because of the low solubility of the species involved.

ESR Measurements. The ESR spectrometer used was a JES-3BSX-type apparatus (Japan Electron Optics Co. Ltd.) with 100 kHz field modulation and TE_{011} mode cavity. The *g*-value was determined by the aid of DPPH.

Results

1. The VOA_2-$AlEt_3$ System (I). The ESR spectra of VOA_2 and the VOA_2-$AlEt_3$ system in a benzene solution are shown in Fig. 1 and Fig. 2-a respectively. The eight-line signal with a *g*-value of 1.9843 and with a hyperfine (hf) splitting of 109 gauss was observed in a benzene solution of VOA_2. In the VOA_2-$AlEt_3$ system in benzene, similar line spectra with a *g*-value of 1.9917 and with a hf splitting of 62 gauss were obtained at an Al/V ratio from to 15. The eight-hf signal in each spectra is due to the interaction between an odd electron and the ^{51}V of the nuclear spin moment, 7/2. As is shown in Fig. 2-b, with a lower sweep rate a superhyperfine (shf) structure which apparently has nine-line signal with a splitting of 4.2 gauss was obtained on each line of the eight hf components in this system. The same spectral feature appeared also in the region where the Al/V ratio was higher than 15. The nine-shf structure, however, could not be detected in a benzene solution of VOA_2.

The spectra of this system in toluene are given in Fig. 3, the nine-line shf signal that overlapped on each component of the eight hf lines was also observed at Al/V ratios from 3 to 15. The spectrum was exactly the same as that obtained in the benzene solution.

The ESR spectra of this system in an *n*-hexane solution at an Al/V ratio of 7 are shown in Fig. 4. A signal with a *g*-value of 1.9928 containing an eight-line signal (a splitting of about 66 gauss) was observed on samples with Al/V ratios from 1 to 15. The shf structure could not, however, be detected at all on any eight-hf component. This spectrum is different from those of benzene and toluene solutions in that the eight-hf structure is missing in the former, apparently indicating that the radical species in an *n*-hexane solution is different from those in benzene and toluene.

The ESR signal of the system of VOA_2 and $AlEt_3$ could not be observed at any Al/V ratio when tetrahydrofuran was used as the solvent.

2. The VCl_4-$AlEt_3$ System (II). The ESR spectrum of the VCl_4-$AlEt_3$ system in a benzene

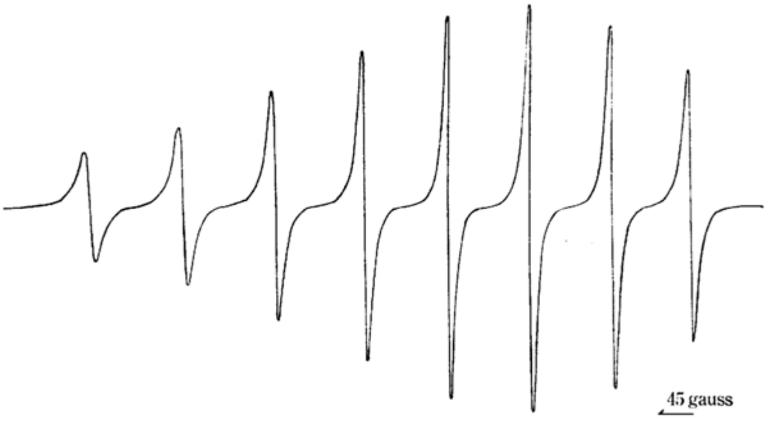


Fig. 1. The ESR spectrum of VOA_2 in benzene solution.

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[8] R. Rowe and M. Jones, *Inorg. Syn.*, **5**, 114 (1957).

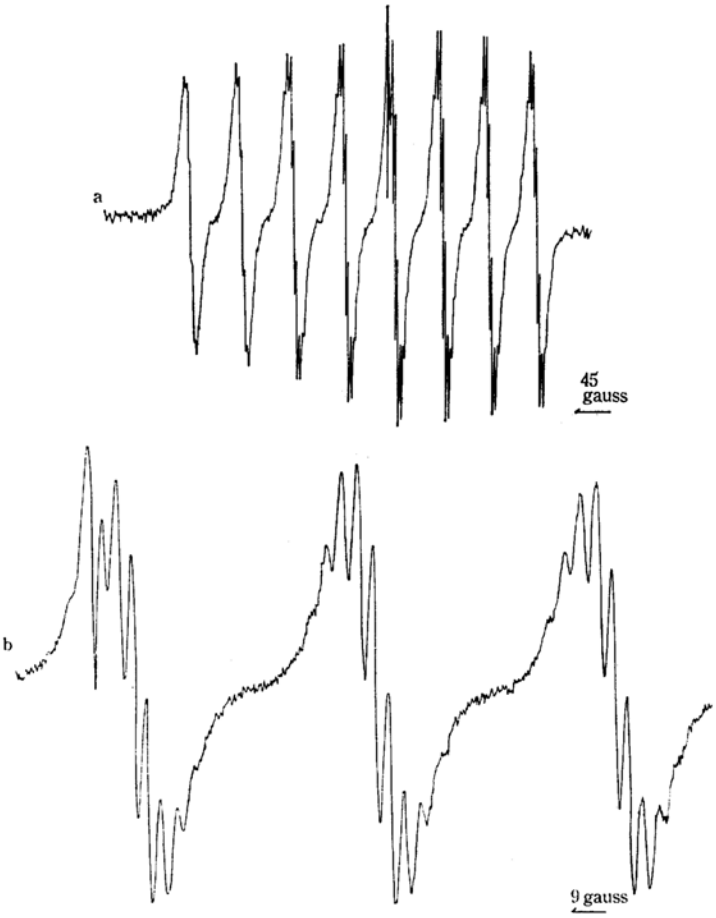


Fig. 2. The ESR spectra of the system of VOA_2-$AlEt_3$ in benzene solution. Al/V=15. When measured with higher sweep (a), lower sweep (b).

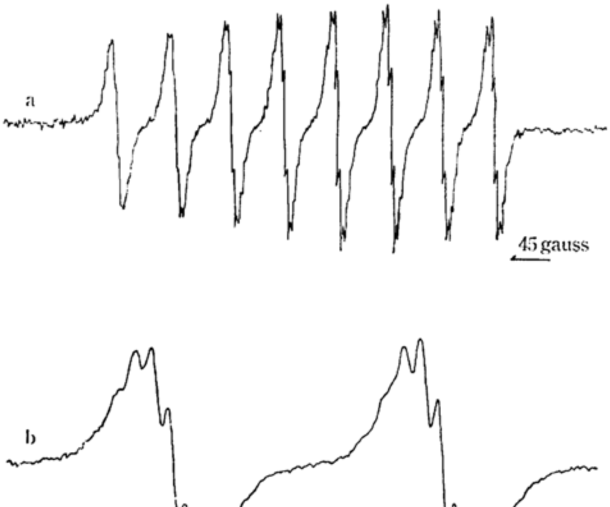


Fig. 3. The ESR spectra of the system of VOA_2-$AlEt_3$ in toluene solution. Al/V=3. When measured with higher sweep (a), and lower sweep (b)

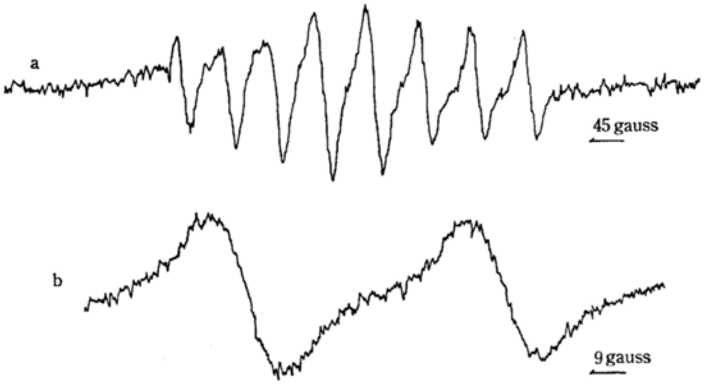


Fig. 4. The ESR spectra of the system of VOA_2-$AlEt_3$ in *n*-hexane solution. Al/V=7. When measured with higher sweep (a) and lower sweep (b).

solution at Al/V ratios up to 5, as shown in Fig. 5, consists of a single line signal with a *g*-value of 1.9775 and has a maximum slope width of approximately 170 gauss. At higher Al/V ratios, as is shown in Fig. 6, an eight line signal with a *g*-value of 1.9917 and containing a nine shf structure on each hf component similar to that found in the system I was superimposed on the single line signal described above.

In a toluene solution of this system, only a single line was observed at Al/V ratios up to 5. At higher ratios (7 and 15), the single line and the eight-line signal were observed again, the two signals overlapping.

The spectrum in an *n*-hexane solution has only a single line signal with a *g*-value of 1.9771, and its maximum slope width is approximately 200 gauss. No other signal (*e. g.*, the nine line shf signal) could be observed when the Al/V ratio was varied from 1 to 15. These single-line spectrum of this system can be exactly assigned to the signal of the VCl_2 compound by reference to those observed in a solid state and in a hydrocarbon solution.[5)]

In view of the present observations, it is clear that the ESR-active species in a benzene and a toluene solution are different from that in *n*-hexane solution, as is the case for the system I. The results observed in both systems are summarized in Table 1.

The addition of various alcohols to the system I and II did not alter the line shapes of the spectra and the *g*-values of the signals, though the signal intensity decreased. This is in sharp contrast to the system of bis-cyclopentadienyltitanium dichloride ($(C_5H_5)_2TiCl_2$) and AlR_3, which will be described again later.

Discussion

As Fig. 1 and Fig. 2 show, the hf splitting of the eight-line signal for the benzene solution of VOA_2 is approximately 109 gauss, but the splitting width changes to 62 gauss in the systems of both I and II when $AlEt_3$ is added. It is, therefore, apparent that vanadium is reduced to a lower oxidation state from its initial state, +4, as a result of the reaction of the original compound with $AlEt_3$. A

TABLE 1. SUMMARY OF *g*-VALUES AND HYPERFINE COUPLING CONSTANTS IN VARIOUS SYSTEMS

System	Solvent	Al/V	*g*-Value	hf constant (8) (gauss)	shf constant (9) (gauss)
VOA_2	Benzene	—	1.9843	109	—
VOA_2-$AlEt_3$ (I)	Benzene	1—15	1.9917	62	4.2
	Toluene	3—15	1.9916	63	4.3
	n-Hexane	1—15	1.9928	66	—
	THF	1—15	—	—	—
VCl_4-$AlEt_3$ (II)	Benzene	1— 5	1.9705	(170)*	—
	Benzene	7—15	1.9917	62	4.3
	Toluene	1— 3	1.9705	(170)*	—
	Toluene	5—15	1.9915	63	4.3
	n-Hexane	1—15	1.9771	(200)*	—
VOA_2-Al(i-But)$_2$	Benzene	3— 8	1.9918	62	4.1
VA_3-Al(i-But)$_3$	Toluene	>3	1.9917	62	4.3

* The values in parentheses are maximum slope width of single resonance line.

correlation of the hf splitting with the oxidation state of ^{51}V has been reported,[9] it was found that the separations for V^{4+}, V^{3+} and V^{2+} in α-Al_2O_3 are 140, 110, and 88 gauss, respectively. The steady decrease in the splittings in this series also supports the idea of the formation of a reduced vanadium compound in the present system.

In the ESR spectrum for the system of VOA_2-Al(isoBut)$_3$ in toluene, eight-line signal with an hf splitting of 63 gauss, each of the signal with an shf structure of nine line similar to the spectra shown in Fig. 2, were also observed at Al/V ratios from 3 to 8. The oxidation state of vanadium is reduced to a lower state by Al(isoBut)$_3$ also.

For the system of vanadium trisacetylacetonate (VA_3) and Al(isoBut)$_3$ in benzene solution, no ESR signal was observed at Al/V ratios of 1 and 2. The oxidation state of vanadium in VA_3 may be regarded as +3, and the species does not give rise to any ESR signal. Apparently, VA_3 is not reduced by Al(isoBut)$_3$ under such conditions. If the Al/V ratio was raised to above 3, however, the same spectra as those of I and II were obtained.

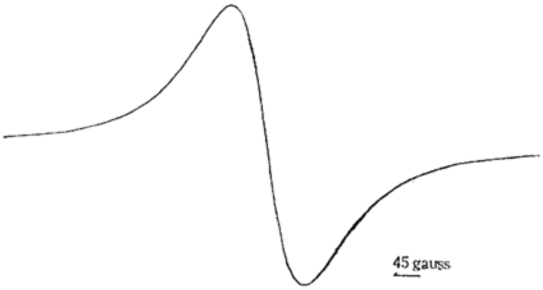
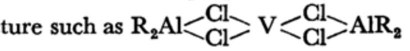


Fig. 5. The ESR spectrum of the system of VCl_4-$AlEt_3$ in benzene solution. Al/V=5.

In the system of II in benzene and toluene, only a single broad line is observed at the Al/V ratio of 5, as is shown in Fig. 5. The spectra may be assigned to that of VCl_2. As Fig. 6 shows, at Al/V ratios higher than 5 the shf structure appears to overlap on the single line. The spectra with an shf structure may be attributed to the signal of vanadium, which has been reduced further from the divalent state to possibly that of zerovalent vanadium.[10]

Note that the nine-line shf structure described above could not be observed when *n*-hexane was used as a solvent instead of benzene and toluene.

Sciulydin[7] reported that the eight-line signal with a *g*-value of 1.992 aws observed in the VCl_4-$AlEt_3$ system in a benzene solution and that each hf component of the eight-line signal gave an shf structure of 11 or 13 lines; be proposed a chlorine-bridged structure such as  $R_2Al{<}^{Cl}_{Cl}{>}V{<}^{Cl}_{Cl}{>}AlR_2$ its hf structure being attributable to interaction between an odd electron of the vanadium atom and four chlorine and two aluminum atoms. However, since we have observed the same spectral features in the VOA_2-$AlEt_3$ system in which no chlorine

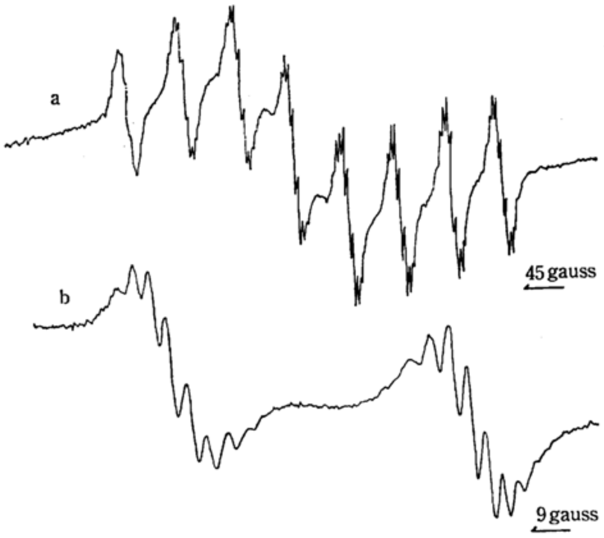


Fig. 6. The ESR spectra of the system of VCl_4-$AlEt_3$ in benzene solution. Al/V=15. When measured with higher sweep (a), and lower sweep (b).

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[9] J. Lambe and C. Kikuchi, *Phys. Rev.*, **118**, 71 (1960).

[10] E. O. Fischer and H. P. Kögler, *Chem. Ber.*, **90**, 250 (1957).

atom is involved, the structure postulated above is not adequate to explain the spectra.

To aid the investigation of the complex formation of the V atom in the system, ESR measurements of the system of chromium trisacetylacetonate (CrA_3) and $AlEt_3$, analogous to the system of the vanadium compound and $AlEt_3$, were carried out. As is shown in Fig. 7, a nine-line spectrum[11] with a *g*-value of 1.986 was detected for the sample in a benzene solution at Al/Cr ratios higher than 4. The same type of spectrum consisting of a seven- or nine-line signal with a *g*-value of 1.987 in various aromatic solvents at the Al/Cr ratio of 10, was also reported by Angelescu *et al.*[12] They proposed the formation a sandwich-type complex of the chromium atom with aromatic species in these systems; they did so on the basis of the evidence that the shapes of the signals and the values of the *g*-factor were in agreement with those of $Cr(C_6H_6)_2^+$ [13] and its derivatives.[14]

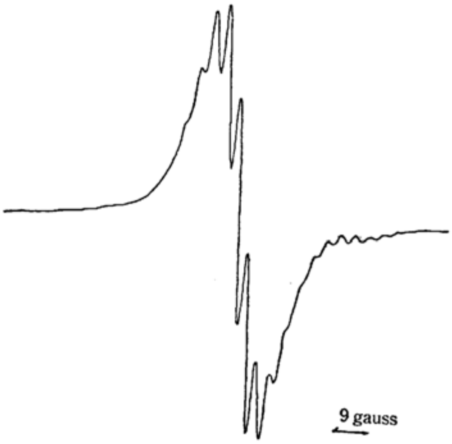
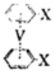


Fig. 7. The ESR spectrum of the system of CrA_3-$AlEt_3$ in benzene solution. Al/Cr=4.

By analogy with Angelescu's interpretation, the formation of a certain complex similar to $Cr(C_6H_6)_2^+$ may be expected for the system of the V Compound and $AlEt_3$ also. In fact, the shape of nine line signal observed in the system I and II (benzene and toluene being used as solvents) was apparently similar to that of the CrA_3-$AlEt_3$ system in various solvents.

Hence, we propose that the V compound in these systems is in the form of a sandwich-type complex with aromatic solvent molecules, as in the cases of CrA_3 and $AlEt_3$. The shf structure appearing in the spectra may, then, be attributed to the hf interaction between an odd electron and 12 (or 10) equivalent protons on the aromatic ring. Such an interaction would give rise to 13 equally-spaced lines with an intensity ratio of 1, 12, 66, 220, 495, 792, 924, 792, 495, 220, 66, 12 and 1 if $V(C_6H_6)_2$ is produced in the systems. Only nine-line signal was observed, however, this disagreement may be attributed to the poor signal-to-noise ratio of the spectra.

On the other hand, Hausser[15] has measured the ESR spectrum of $V(C_6H_6)_2$ in a mixed solvent (toluene and methylcyclohexane, (1 : 1)); he has observed eight-line signal due to the ^{51}V nucleus with a *g*-value of 1.9920, having an hf separation of 63.5±1 gauss and an shf structure of nine line with a splitting of 4.0±0.1 gauss superimposed on each hf component. The results obtained in our experiments are in good agreement with those obtained by Hausser with respect to the *g*-value, the shf splitting constant, and the pattern of the spectra.

In conclusion, the presence of an shf structure on eight-line spectrum observed in these systems (I and II) suggests the formation of a sandwich structure such as  where X=H or CH_3, in which the chlorine-bridged structure proposed by Sciulydin is not involved.

Previously, in the system of $(C_5H_5)_2TiCl_2$-AlR_3 the six-line spectrum caused by hf interaction between an odd electron of the Ti^{3+} and the Al^{27} nucleus had been observed when methyl alcohol and the like were added to this system. This fact was interpreted by assuming the structure of the product to involve a di-*μ*-alkoxo bridge between the Ti and Al atoms.[16] On the other hand, as has been mentioned before, the *g*-value and the line shape of the spectra for the systems of I and II did not change when methyl alcohol was added, except for the decrease in the signal intensity. Therefore, as far as the results of the ESR measurement are concerned, it seems that the V atom does not form a di-*μ*-alkoxo bridge complex with the Al atom upon the addition of alcohol.

Conclusion

From the study of the ESR spectra in the systems of VOA_2-$AlEt_3$ (I) and VCl_4-$AlEt_3$ (II), the formation of a sandwich complex of zerovalent vanadium with aromatic solvents has been suggested; the

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11) M. Takeda, K. Iimura, Y. Watanabe and Y. Nozawa, Preprints for the 14th Symposium on High Polymer (Oct.), 1965.

12) E. Angelescu, C. Nicolau and Z. Simon, *J. Am. Chem. Soc.*, **88**, 3910 (1966).

13) R. D. Feltham, P. Sogo and M. Calvin, *J. Chem. Phys.*, **26**, 1354 (1957).

14) B. Elschner and S. Herrog, *Z. Naturforsh.*, **12a**, 860 (1957).

15) K. Hausser, *ibid.*, **16a**, 1190 (1961).

16) Y. Nozawa and M. Takeda, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **71**, 189 (1968).

formation of an oxo-complex involving Al and V atoms could not be deduced in these systems, even in the presence of alcohol, as long as the ESR spectra of such systems were used as the criterion.

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