Transition Metal Complex Catalysts for the Oligomerization of Butadiene. II. The Reaction of Catalyst Components

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There have been several reports on the remarkable activities of catalysts composed of transition metal complexes and organometallic compounds on the oligomerization of butadiene.¹⁾ The present authors have reported in previous papers²⁾,³⁾ that butadiene dimerizes into 3-methyl-hepta-1, 4, 6-triene with the catalyst system consisting of cabalt(III) acetylacetonate and triethylaluminum, and that it trimerizes into *n*-dodeca-1, 3, 6, 10-tetraene with iron(III) acetylacetonate and triethylaluminum. In these reactions, it has been found that the order of the mixing of the catalyst components and butadiene has a great effect on the rate of the formation of oligomers; this has been explained⁴⁾ as being true because in the presence of butadiene, triethylaluminum reduces cobalt(III) or iron (III) acetylacetonate and makes butadiene coordinate to the low valent metal, while without butadiene, cobalt(III) or iron(III) acetylacetonate and triethylaluminum react to form a complex to which butadiene coordinates only with difficulty. The present investigation was undertaken in order to acquire knowledge about the behavior of catalyst components in these reactions. The structure of the catalysts, the oxidation states of the transition metals, the role of triethylaluminum, and the mechanism of the reactions will be discussed on the basis of the results of the magnetic

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1) Studiengesellschaft Kohle, *Austrian.* 219580 (1962) ; G. Wilke, *Angew. Chem.*, **75**, 10 (1963) ; S. Ohtsuka, T. Taketomi and T. Kikuchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1094 (1963) ; *J. Am. Chem. Soc.*, **85**, 3709 (1963) ; H. Takahashi, *J. Org. Chem.*, **28**, 1409 (1963) ; S. Tanaka, K. Mabuchi and N. Shimazaki, ibid., **29**, 1636 (1964).

2) T. Saito, T. Ohno, Y. Uchida and A. Misono, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1094 (1963).

3) M. Hidai, Y. Uchida and A. Misono, This Bulletin, to be published.

4) T. Saito, Y. Uchida and A. Misono, ibid., **37**, 105 (1964).

susceptibility, infrared spectra, gasometry, and electron spin resonance spectra of the reaction solutions.

Experimental

Reagents.—The reagents used in these experiments were prepared and purified in the way which has been described in previous reports.

Magnetic Susceptibility Measurements.—Most of the reactions were carried out in a specially-made Erlenmeyer flask (100 ml.) with a small cell on its side. Known amounts of cobalt(III) acetylacetonate or iron(III) acetylacetonate (benzene solution) and triethylaluminum (benzene solution), one introduced in the main body of the flask and the other in the side cell separately under an atmosphere of nitrogen, were mixed by inclining the flask. The reaction solution was then transfused into a Gouy tube with a hypodermic syringe.

The magnetic susceptibility was measured using a Gouy balance. The Gouy tube was 250 mm. long and 10 mm. in diameter and was calibrated with distilled water. The sample transfused into the Gouy tube was placed in the field of 10000 gauss, and the measurements ware carried out at room temperature. The calculations of the magnetic susceptibility and the magnetic moment were performed with the following equations:

$$\chi_M = (\chi_g - \sum_i w_i \chi_{gi}) M/w$$

$$\mu_{eff} = 2.84\sqrt{\chi_M T}$$

where χ_M: the moalr susceptibility based on the cobalt or the iron atom
χ_g: the gram susceptibility of the sample solution
$\sum_i w_i \chi_{gi}$: the diamagnetic correction
M: the molecular weight of $Co(acac)_3$ or $Fe(acac)_3$
w: the weight fraction of $Co(acac)_3$ or $Fe(acac)_3$
μ_{eff}: the effective magnetic moment (B.M.)
T: the absolute temperature

Gasometry.—The reaction was carried out in a 300 ml. four-necked flask equipped with a gas burette and a dropping funnel. With a magnetical stirring of the benzene solution of cobalt(III) acetylacetonate or iron(III) acetylacetonate, a certain quantity of a benzene solution of triethylaluminum in the funnel was dropped intermittently, with an allowed interval long enough to complete the gas evolution after each addition. During the measurement, the temperature was kept at 25°C. A change in the order of mixing the components was achieved by interchanging the contents of the flask and the funnel. The gas volume was converted into that at 0°C.

Infrared Spectra.—The infrared spectra of the samples were measured by a Hitachi EPI-S2 spectrometer for the sodium chloride region and by a Nihon-bunko Model 201 for the potassium bromide region. A certain amount of cobalt(III) acetylacetonate or iron(III) acetylacetonate was weighed in the same reaction apparatus as was used in the gasometry, and then dissolved in benzene. After the air in the flask has been displaced with nitrogen triethylaluminum in benzene was introduced into the solution, which was kept at room temperature and stirred magnetically. Then a part of the miexed solution was transfused into a KRS-5 cell (0.1 mm. path length) with a glass syringe.

Electron Spin Resonance Spectra.—The spectra were recorded in the X-band (9400 Mc.), with 100 kc. modulation, by a Nihon-denshi Model JES-3B ESR spectrometer. The method of sample preparation was similar to that described as having been used for the magnetic susceptibility measurements.

Results and Discussion

Infrared Spectra Analysis.—When triethylaluminum was added to cobalt(III) acetylacetonate, the green color of Co^{3+} faded and the reaction solution changed to purple and then black, with heat and gas generation. Changes in the infrared spectra of the reaction solution were observed with the variation in the amount of triethylaluminum added. A significant change in the absorption band was recognized between 1260 and 1300 cm^{-1}. In this region the following bands were assigned[5]: 1261 cm^{-1} for the C-C stretching + C-CH_3 stretching of cobalt(II) acetylacetonate, 1284 cm^{-1} for that of cobalt(III) acetylacetonate, and 1288 cm^{-1} for that of aluminum(III) acetylacetonate. The changes in these bands of the solution due to the increase in triethylaluminum added are shown in Fig. 1. As triethylaluminum was added to cobalt(III) acetylacetonate, the band at 1284 cm^{-1} gradually decreased, and a new band at 1261 cm^{-1} began to grow; then a new band at 1288 cm^{-1} was also observed. These results indicate the reduction of cobalt(III) acetylacetonate with triethylaluminum and the resultant formation of cobalt(II) acetylacetonate and aluminum(III) acetylacetonate. At a molar ratio of triethylaluminum to cobalt(III) acetylacetonate of

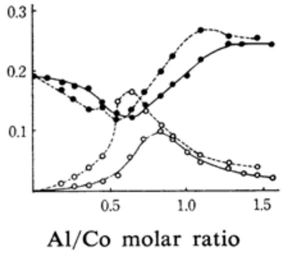

Fig. 1. Variation of the absorbance of IR spectra in 1260—1290 cm^{-1} region upon addition of $AlEt_3$ to $Co(acac)_3$ in benzene (8.12×10^{-2} M) in the presence (—) or in the absence (···) of butadiene.
○ for 1261 cm^{-1}, ● for 1284—1288 cm^{-1}

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[5] K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066, 1272 (1961).

about 0.5, the amount of cobalt(II) acetylactonate formed suddenly increased; then the amount of cobalt(II) acetylacetonate reached a maximum and gradually decreased with the increase in the amounts of triethylaluminum added. The band at 1288 cm^{-1} of aluminum(III) acetylacetonate increased until the amounts of triethylaluminum added reached a level about 1.5 times that of cobalt(III) acetylacetonate. In the presence of butadiene, the addition of triethylaluminum changes the benzene solution of cobalt(III) acetylacetonate from green to purple, and then to wine red. In this case, the formation of cobalt(II) acetylacetonate was less than in the former case, as is shown in Fig. 1, which suggests that the presence of butadiene made the further reduction of cobalt(II) faster by means of complex formation.

When iron(III) acetylacetonate was employed instead of cobalt(III) acetylacetonate, almost the same tendency was observed, as is shown in Fig. 2. In this case the band at 1276 cm^{-1} decreased; new bands were observed at 1288 cm^{-1} and 1265 cm^{-1} with the adddition of triethylaluminum. The band at 1265 cm^{-1} reached a maximum at an Al/Fe ratio of about 0.5 and then gradually decreased in just the same way as the band at 1261 cm^{-1} of cobalt(II) acetylacetonate. The behavior of the band at 1288 cm^{-1} was also similar to the case of the cobalt(III) acetylacetonate and triethylaluminum system. The bands at 1276 cm^{-1} and 1288 cm^{-1} were assigned to the C-C stretching + C-CH_3 stretching of iron(III) acetylacetonate and aluminum(III) acetylacetonate respectively[5]. The band of 1265 cm^{-1} was assigned to the C-C stretching + C-CH_3 stretching of iron(II) acetylacetonate from the infrared observation of iron(II) acetylacetonate prepared by the method described by Buckingham.[6] Thus, in either the presence or absence of butadiene, iron(III) acetylacetonate, as well as cobalt(III) acetylacetonate, may be supposed to be reduced via the bivalent state to the zero valent state by the addition of triethylaluminum, with the resultant formation of aluminum(III) acetylacetonate.

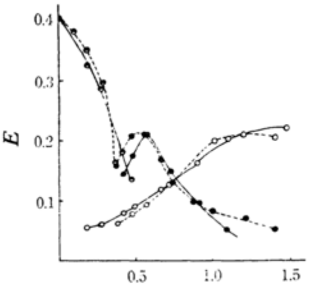

Fig. 2. Variation of the absorbance of IR spectra in 1260—1290 cm^{-1} region upon addition of $AlEt_3$ to $Fe(acac)_3$ in benzene (6.76×10^{-2} M) in the presence (—) or in the absence (···) of butadiene.
● for 1265 cm^{-1}, ◓ for 1276 cm^{-1}
○ for 1288 cm^{-1}

In order to acquire knowledge about the variation in metal-oxygen band through the reaction, the infrared spectra of several reaction, mixture were recorded in the potassium bromide region from 18 μ to 27 μ. When more than 0.5 mol. of triethylaluminum to 1.0 mol. of cobalt(III) acetylacetonate was added, the band at 21.4 μ, assigned to the Co^{3+}-O stretching of cobalt(III) acetylacetonate almost disappered, new bands appeared at 20.5 μ and about 23.6—23.7 μ. The former band was assigned to the Al-O stretching of aluminum(III) acetylacetonate, while the band at 23.6—23.7 μ was assigned to the overlap of the Co^{2+}-O stretching of cobalt(II) acetylacetonate and the out-of-plane bending of aluminum(III) acetylacetonate. Although the exchange of the ligand from cobalt to aluminum was confirmed, a quantitative treatment was unsuccessful because of the overlapping bands.

Gasometry.—When triethylaluminum was added drop-by-drop into the cobalt(III) acetylacetonate - benzene solution, gas evolved. This gas evolution was gradual until the amount of triethylaluminum added reached about a half of the cobalt(III) acetylacetonate in the solution, whereupon a sudden violent gas evolution was observed. The amount of gas evolved by the violent reaction was nearly 1.5—2 times the total amount of that which had been evolved before. The further addition of triethylaluminum made more gas evolve; the gradients of the plots of the evolved gas and the triethylaluminum added before and after the violent gas evolution are nearly equal as shown in Fig. 3. When nearly the same amount of triethylaluminum as cobalt(III) acetylacetonate in the solution was added, the gas evolution ceased. These observations suggest that, in the first step of the reaction, triethylaluminum reacts with cobalt(III) acetylacetonate in the following way to from cobalt(II) acetyl acetonate:

$$AlEt_3 + Co(acac)_3 = AlEt_2(acac) + Co(acac)_2 + \cdot Et$$

It is considered that the diethylaluminum monoacetylacetonate and cobalt(II) acetylacetonate thus formed exist in a meta-stable state with residual cobalt(III) acetylacetonate

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[6] D. A. Buckingham, J. L. E. Cheong, J. E. Ferguson and C. J. Wilkins, *J. Chem. Soc.*, **1963**, 3461.

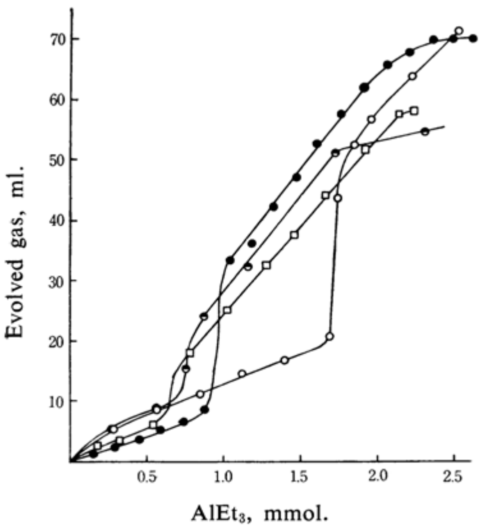

Fig. 3. Plots of amounts of evolved gas upon addition of $AlEt_3$ to $Co(acac)_3$ or $Fe(acac)_3$ in benzene.

- ○ 0.278 M of $AlEt_3$ in benzene was added to 3.66 mmol. of $Co(acac)_3$ in 20 ml. of benzene.
- ◓ 0.571 M of $AlEt_3$ in benzene was added to 1.41 mmol. of $Co(acac)_3$ in 20 ml. of benzene.
- ● 0.292 M of $AlEt_3$ in benzene was added to 2.31 mmol. of $Co(acac)_3$ in 20 ml. of benzene.
- □ 0.336 M of $AlEt_3$ in benzene was added to 1.46 mmol. of $Fe(acac)_3$ in 20 ml. of benzene.

by solvation or complex formation. The violent reaction, induced by the further addition of only one drop of triethylaluminum to the solution when about a half of the triethylaluminum was added to the cobalt(III) acetylacetonate, can be understood by considering that the meta-stable state is destroyed by the decrease in the amount of cobalt(III) acetylacetonate to less than that of cobalt(II) acetylacetonate. It is considered that the following reactions occurred in this case:

$$AlEt_2(acac) + 2Co(acac)_3 = Al(acac)_3 + 2Co(acac)_2 + 2\cdot Et$$

$$AlEt_2(acac) + Co(acac)_2 = Al(acac)_3 + Co^0 + 2\cdot Et$$

This mechanism was supported by the infrared observations. Thus, cobalt(III) is supposed to be reduced to cobalt(II), and then to the zero valent state:

$$Co(acac)_3 \rightarrow Co(acac)_2 \rightarrow Co^0$$

Cobalt(I) acetylacetonate is probably too unstable to exist as an intermediate state. The same results were found in the case of the iron(III) acetylacetonate and triethylaluminum system (Fig. 3).

When cobalt(III) acetylacetonate was added to an excess of triethylaluminum, cobalt(III) seemed to be reduced immediately to the zero valent state (Fig. 4).

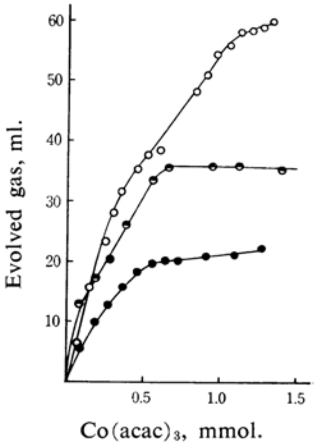

Fig. 4. Plots of amounts of evolved gas upon addition of $Co(acac)_3$ in benzene to $AlEt_3$.

- ○ 0.0734 M of $Co(acac)_3$ in benzene was added to 2.22 mmol. of $AlEt_3$ in 20 ml. of benzene.
- ◓ 0.0914 M of $Co(acac)_3$ in benzene was added to 1.11 mmol. of $AlEt_3$ in 10 ml. of benzene.
- ● 0.0894 M of $Co(acac)_3$ in benzene was added to 1.11 mmol. of $AlEt_3$ in 20 ml. of benzene.

The amount of gas observed in the gasometry was 50—60% of the theoretical value. When the composition of the evolved gas was determined by gas chromatography, it was found that the gas was about 85% ethane and 15% ethylene. The deficiency in gas evolution compared with the theoretical value could be explained by the dissolution of gas in benzene and by the chemisorption of ethylene to the complex formed with the reduced cobalt or iron.

Magnetic Susceptibility Measurements.—The composition and the gram magnetic susceptibility for the sample solution are shown in Table I.

a) When cobalt(III) acetylacetonate in benzene was added to an excess of triethylaluminum, the magnetic moment of the solution was 0.6 B. M. (at Al/Co=7.3). This shows that the cobalt complex in the solution is probably diamagnetic. With the addition of cobalt(III) acetylacetonate, the magnetic moment of the solution increased and reached a maximum at an Al/Co ratio equal to 1. At the same time, the solution turned from brown

TABLE I. COMPOSITION AND MAGNETIC SUSCEPTIBILITY OF THE BENZENE SOLUTION OF $Co(acac)_3$ (OR $Fe(acac)_3$) AND $AlEt_3$

(a) $Co(acac)_3$ was added to $AlEt_3$.
(b) $Co(acac)_3$ and $AlEt_3$ were mixed simultaneously.
(c) $AlEt_3$ was added to $Co(acac)_3$.
(d) $Fe(acac)_3$ was added to $AlEt_3$.

Al/Co	Weight fraction			$\chi_g \times 10^6$
	C_6H_6	$Co(acac)_3$ or $Fe(acac)_3$	$AlEt_3$	
(a) 1.1	0.978	0.0150	0.0053	+2.06
2.0	0.975	0.0155	0.0100	+1.26
3.2	0.969	0.0150	0.0156	+0.081
4.1	0.964	0.0155	0.0202	−0.597
5.9	0.954	0.0153	0.0306	−0.675
7.3	0.951	0.0146	0.0340	−0.695
(b) 0.5	0.964	0.0312	0.0050	+2.32
0.9	0.956	0.0340	0.0096	+4.71
1.0	0.959	0.0309	0.0098	+4.12
2.2	0.972	0.0167	0.0115	+1.50
3.0	0.952	0.0248	0.0237	+0.938
4.0	0.981	0.0084	0.0109	−0.530
4.4	0.927	0.0306	0.0427	−0.205
5.3	0.915	0.0311	0.0535	−0.405
6.7	0.968	0.0102	0.0218	−0.486
6.8	0.947	0.0166	0.0361	−0.624
(c) 1.0	0.944	0.0435	0.0107	+6.75
8.1	0.949	0.0142	0.0366	+0.334
(d) 0.8	0.982	0.0144	0.0036	+1.30
1.3	0.980	0.0147	0.0061	+4.55
2.4	0.972	0.0155	0.0122	+5.07
4.8	0.962	0.0149	0.0228	+1.93
5.8	0.945	0.0190	0.0356	+1.13
8.9	0.949	0.0147	0.0420	+0.285

to black, and a precipitate formed. Here an extraordinarily large μ_{eff} value of 12.1 was observed, which could not be attributed to the paramagnetism arising from first transition metals. If the magnetic moment is considered to be attributed only to the electron spin of the first transition metal, the value can not be expected to be higher than 6. The contribution of orbital motion will probably not be large enough to explain the extraordinarily large magnetic moment. These phenomena can only be explained in terms of the ferromagnetism due to the coagulation of the reduced zero valent cobalt to the unstable metallic state. The above observation suggest that the excess triethylaluminum has the ability to stabilize the cobalt of the zero valent by the formation of a complex like that suggested by Sartori and Costa in such a way as that shown below[9]:

$$Co(acac)_3 + 3AlEt_3 \rightarrow Co^0 \cdots [AlEt_2(acac)]_3 + \frac{3}{2}(C_2H_4 + C_2H_6)$$

As Co^0 has a d^7s^2 ground state, the diamagnetism can be explained by the assumption of a dimer structure or of cobalt hydride, for example. As cobalt(III) acetylacetonate was then added to the reaction mixture which included the above complex, the remaining ethyl groups of $AlEt_2(acac)$ were also used for the reduction of the cobalt atom. The resultant $AlEt(acac)_2$ or $Al(acac)_3$ perhaps has no ability to stabilize Co^0 or to prevent its coagulation.

b) When cobalt(III) acetylacetonate and triethylaluminum were mixed at the same time, it was observed that the magnetic moment was somewhat larger than in the case of a) in the region of an Al/Co ratio greater than four. These results are understood to indicate that small coagulations of cobalt occurred during the mixing.

c) In the case of the addition of triethylaluminum to cobalt(III) acetylacetonate, the magnetic moment also reached a maximum ($\mu_{eff}=12$) at an Al/Co ratio around unity, but the further addition of triethylaluminum to this solution made the μ_{eff} decrease to some degree. This phenomenon can be explained in terms of the fact that the added triethylaluminum dissolved the coagulated cobalt by the complex formation, as has been mentioned above. It may be supposed that the bonds formed by the coagulation of cobalt are either so weak or so active that they have a tendency to enter into the reaction. This was elucidated by the decrease in μ_{eff} caused by the addition of some organic compounds. The addition of butadiene in the solution prepared by adding triethylaluminum to cobalt(III) acetylacetonate in a Al/Co ratio of unity decreased the μ_{eff} value to 7.8. This shows some coordination of butadiene to reduced cobalt, but the amount is not so large that the dependency of the rate of the formation of methylheptatriene on the mixing order ($Co(acac)_3 + AlEt_3 +$ butadiene) is small.[2,4] When methanol was added to the solution of cobalt(III) acetylacetonate and triethylaluminum ($Al/Co=1$) and the mixture was brought into contact with air, the coagulated cobalt dissolved and the solution changed red. From the infrared spectra it was considered that cobalt was oxidized to cobalt(II) acetylacetonate. The magnetic moment ($\mu_{eff}=5.1$) also supported this supposition.

d) When iron(III) acetylacetonate instead of cobalt(III) acetylacetonate was added to triethylaluminum, the curve of the relation between the Al/Fe ratio and the magnetic

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[7] H. Sinn and F. Patat, *Angew. Chem.*, **75**, 805 (1963).

[8] T. Saito, Y. Uchida and A. Misono, This Bulletin, to be published.

[9] G. Sartori and G. Costa, *Z. Elektrochem.*, **63**, 105 (1959).

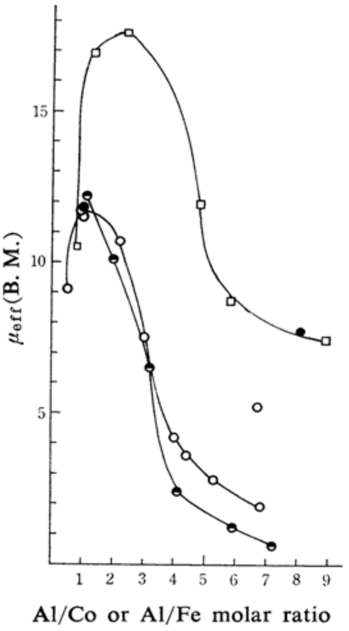

Fig. 5. Variation of the effective magnetic moment with the molar ratio of $AlEt_3$ to $Co(acac)_3$ or $Fe(acac)_3$.
○ $Co(acac)_3$ and $AlEt_3$ were mixed at once.
◓ $Co(acac)_3$ was added to $AlEt_3$.
● $AlEt_3$ was added to $Co(acac)_3$.
□ $Fe(acac)_3$ was added to $AlEt_3$.

moment showed almost the same tendency as in the system of cobalt(III) acetylacetonate and triethylaluminum. In this case, however, the μ_{eff} value of the solution was much larger than in the case of cobalt throughout the Al/Fe ratio range. The extraordinarily large μ_{eff} value of the iron system, even when there is excessive triethylaluminum, may be due to the unstability of the complex between reduced iron and aluminum derivatives of this sort.

ESR Spectra.—With the view of deciding whether the extraordinarily large magnetic moments are aroused by paramagnetism or by ferromagnetism, the electron spin resonance spectra of a benzene solution of cobalt(III) acetylacetonate and triethylaluminum were recorded. A single line signal was observed at a g-value of 2.128. The signal was hardly observed at all in the Al/Co ratio region about 0.5—1, where an extraordinarily large magnetic moment was shown. However, the intensity of the signal increased as the Al/Co ratio became as large as 3—5, which is a tendency opposite to that of the magnetic moment. At an Al/Co ratio of 3—5, the presence of an unpaired electron was supposed, but the spin concentration was quite small. Thus, it is obvious that the large susceptibility is not due to paramagnetism, but to ferromagnetism.

Summary

In order to obtain some knowledge on the behavior of catalysts in the oligomerization of butadiene, the reaction between cobalt(III) acetylacetonate or iron(III) acetylacetonate and trietylaluminum has been investigated by means of magnetic susceptibility measurements, infrared spectra, gasometry, and electron spin resonance spectra.

When triethylaluminum was added to an excess of cobalt(III) acetylacetonate, the infrared spectra and gasometry suggested that the latter was reduced via stable cobalt(II) acetylacetonate to zero valent cobalt and that, at the same time, the former was transformed into aluminum(III) acetylacetonate. The extraordinarily large magnetic moment (μ_{eff}= 12) and the absence of the signal of the electron spin resonance specra suggested the formation of metallic cobalt. The metallic cobalt was active enough to be readily oxidized by the addition of methanol. The addition of butadiene to this solution decreased the magnetic moment to 7.8. This shows some coordination of butadiene to reduced cobalt.

When cobalt(III) acetylacetonate was reduced in the presence of an excess of triethylaluminum (Al/Co>4), the zero valent cobalt was stablilized as a result of the formation of a certain diamagnetic complex with triethylaluminum. However, the addition of cobalt (III) acetylacetonate to this reaction mixture decomposed the above complex, and the very large magnetic moment indicated the formation of metallic cobalt.

Iron(III) acetylacetonate was, like cobalt(III) acetylacetonate, reduced to zero valent iron via stable iron(II) acetylacetonate. In the presence of an excess of triethylaluminum, however, zero valent iron did not form a stable complex with triethylaluminum, and from the ferromagnetism metallic iron was observed toresult.

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