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THE REACTIONS OF NICKEL(II) CARBOXYLATES WITH A SERIES OF ETHYLALUMINUM CHLORIDES

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Summary

The distribution of nickel in the reaction products from the reactions of nickel(II) stearate with diethylaluminum chloride (Et_2AlCl), ethylaluminum sesquichloride ($Et_3Al_2Cl_3$), and ethylaluminum dichloride ($EtAlCl_2$) in benzene was investigated as a function of the Al/Ni reaction stoichiometry. The products consist of benzene-soluble nickel complexes and a precipitate from which can be extracted $NiCl_2$ and metallic nickel. The percentage of each product is seen to be dependent upon the Al/Ni reaction ratio and the aluminum compound employed in the reaction. It was found that in each case six alkylaluminums are required for complete reaction with one nickel(II) stearate molecule. The compounds Et_2AlCl, $Et_3Al_2Cl_3$, and $EtAlCl_2$ were all found to have greater reducing ability than Et_3Al at room temperature. Alternative interpretations of the chloro compounds' greater reducing abilities are discussed.

Introduction

Several studies have been reported of the reaction of nickel(II) compounds with alkylaluminum species. For instance, nickel(II) chloride is quantitatively reduced to metallic nickel at 105°C by treatment with triethylaluminum [1]. Likewise, at 20°C nickel(II) acetylacetonate is reported to be reduced to metallic nickel by Et_3Al along with gas evolution which consisted primarily of ethane and butane [2]. In addition, the reaction between nickel(II) oleate and ethylaluminum sesquichloride ($Et_3Al_2Cl_3$), which produces a catalytically active solution capable of polymerizing 1,3-butadiene to a polymer containing at least 90% *cis*-1,4-polybutadiene [3,4], has been studied [5]. These workers determined the distribution of nickel reaction products in the precipitate and the composition of liberated gases as a function of the Al/Ni reaction stoichiom-

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etry for a selected number of points. We have recently reported on the symmetry of the soluble nickel species from the above reaction [6]. Based upon the electronic band locations, molar absorptivities of those bands, and the lack of a magnetic moment, the predominant nickel species remaining in solution apparently is a square planar nickel(II) species.

The present paper is an extension of the earlier work in this area. The distribution of nickel among reaction products in solution and the precipitates from the reaction of nickel stearate with diethylaluminum chloride (Et_2AlCl), $Et_3Al_2Cl_3$, and ethylaluminum dichloride ($EtAlCl_2$) as a function of the Al/Ni reaction stoichiometry is reported herein. In addition, reactions of nickel(II) carboxylates with aluminum trichloride and triethylaluminum also are reported.

Results and discussion

Reaction of nickel(II) stearate with Et_3Al

The reaction of nickel(II) stearate with an excess of Et_3Al in benzene at ambient temperature (Al/Ni 14/1, 7/1) produces stable, intensely colored, black solutions. These solutions were centrifuged for long periods of time and exposed to a 4.5 kilogauss magnet for an extended period. In each case, analysis after such treatment reveals that about 90% of the nickel originally present still remains in solution after such treatment. The UV-visible spectrum of these solutions indicates that the intense color is due to an absorption band extending into the visible region from the ultraviolet region. This black solution is also found to be diamagnetic by the NMR method of Evans [7]. Bubbling 1,3-butadiene through such solutions produces only traces of polymer and indicates the solutions to be only weakly active as a polymerization catalyst.

In addition, only a small amount of reduced nickel precipitates from the above solutions which are stable for days at room temperature. This is a somewhat unexpected finding because of the reducing ability of Et_3Al.

Reaction of nickel(II) organic salts with $AlCl_3$

The reactions of nickel(II) acetylacetonate and nickel(II) laurate with a slight excess of $AlCl_3$ were carried out in benzene at room temperature. An orange-yellow precipitate of $NiCl_2$ is formed over a period of 10—30 minutes. White solids isolated from the reaction solutions above are shown by infrared data and melting point determinations to be aluminum(III) acetylacetonate (m.p., found 189—190°C, lit. [8a] 193—194°C) and aluminum(III) laurate (m.p., found 181—183°C, lit. [8b] *, 192—196°C), respectively.

In the event that free carboxylic acid is present in solution, the reaction between nickel(II) carboxylates and $AlCl_3$ proceeds in a very different manner. Before $AlCl_3$ addition, nickel(II) laurate dissolves immediately in the presence of free carboxylic acid, producing a green solution with $d \rightarrow d$ electronic absorption maxima at 393, 675, and 1160 nm with molar absorptivities ranging from 7 to 20 $l\ mol^{-1}\ cm^{-1}$ (see Fig. 1). Also, this nickel species was found to be paramagnetic and to possess a magnetic moment of 3.19 BM, in good agreement with

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* The stable compound is assumed to be $Al(OH)(laurate)_2$ since $Al(laurate)_3$ is reportedly unstable to hydrolysis.

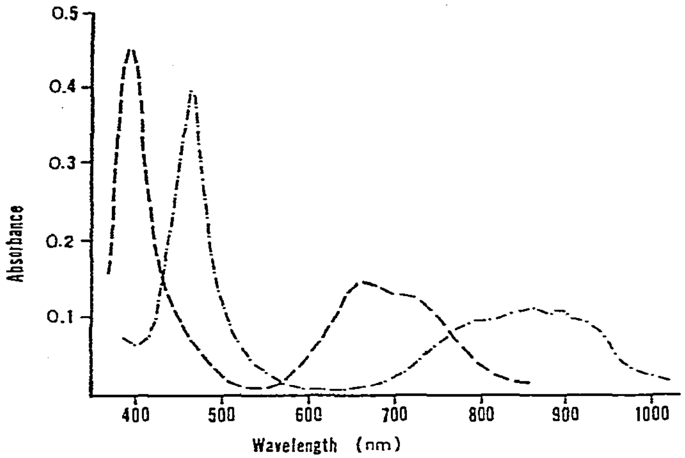


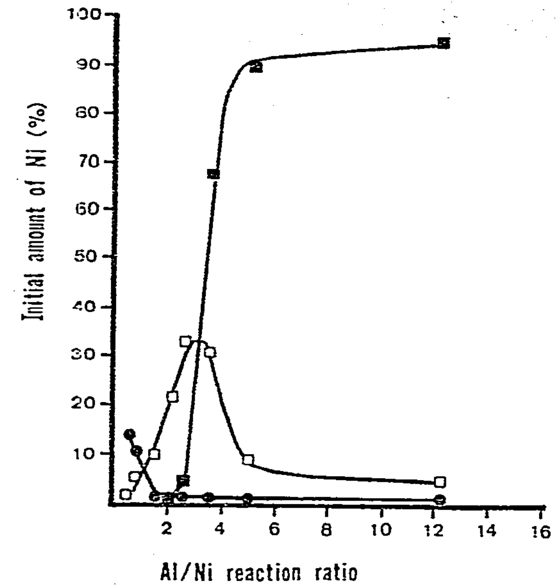
Fig. 1. Visible spectra of nickel(II) complexes. - - - - - -, nickel(II) laurate (0.02 *M*) and 5% lauric acid in benzene; —·—·—·—, nickel(II) laurate and 5% lauric acid in benzene after reaction with $AlCl_3$.

a literature value [9]. These spectral and magnetic data indicate that nickel(II) laurate exists as an octahedral or pseudooctahedral complex under these conditions [10—12]. After introduction of $AlCl_3$, the solution color changes from green to orange-yellow and some $NiCl_2$ precipitates from solution but precipitation rapidly ceases. The result is a stable solution whose visible spectrum is shown in Fig. 1. This spectrum fits that of a weak ligand field octahedral or pseudooctahedral nickel(II) complex. The analysis of nickel concentration and double tube NMR measurements indicate that this complex is paramagnetic with a magnetic moment of 3.32 BM which also supports pseudooctahedral symmetry. A yellow brown solid isolated from the yellow solution was found to have a Ni/Al/Cl ratio of 1/1.05/2.2. Based upon this information, it appears as if the free carboxylic acid stabilizes an intermediate complex in the ligand exchange reaction between nickel(II) carboxylate salts and $AlCl_3$.

Reaction of nickel(II) stearate with Et_2AlCl

Nickel(II) stearate reacts with Et_2AlCl to produce an intensely black solution a few seconds after mixing in benzene. In less than five minutes after mixing, gas evolution becomes noticeable. About 10 to 15 minutes after mixing, a black or dark brown precipitate forms, depending upon the Al/Ni molar ratio. The solution that remains is colorless at Al/Ni molar ratios above 1.5/1. The precipitate may contain water-soluble $NiCl_2$, metallic nickel, and/or unreacted nickel(II) stearate. The exact composition is dependent upon the Al/Ni reaction stoichiometry.

Figure 2 presents the distribution of nickel in solution and the precipitate as a function of the Al/Ni reaction ratio. It can be seen that complete transfer of stearate ligands from nickel to aluminum occurs at an Al/Ni ratio of 3/1, since at that ratio or above all of the nickel appears in a form different from starting material. Figure 2 also indicates that at an Al/Ni ratio of 6/1 or greater 95% of the nickel is converted into metallic nickel, but below a ratio of 2/1 very little reduction occurs. In addition, the $NiCl_2$ in the precipitate reaches a



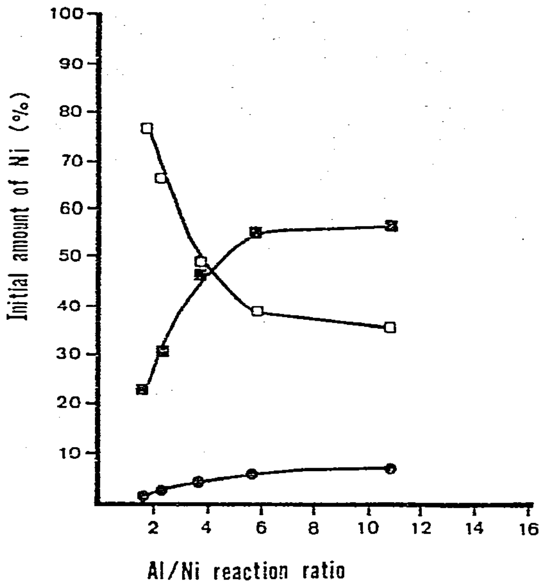


Fig. 2. Distribution of nickel among the reaction products from the reaction of nickel(II) stearate with Et_2AlCl. ■, percentage of metallic nickel; □, percentage $NiCl_2$; ●, percentage of benzene soluble nickel complexes.

Fig. 3. Distribution of nickel among the reaction products from the reaction of nickel(II) stearate with $Et_3Al_2Cl_3$. ■, percentage of metallic nickel; □, percentage $NiCl_2$; ●, percentage of benzene soluble nickel complexes.

maximum of 33% of the initial amount of nickel at an Al/Ni ratio of 3/1 and levels out to a value of around 5% at high Al/Ni ratios. The increased reduction at higher Al/Ni ratios is predictable since the number of ethyl groups available to react with the nickel species is increased.

At low Al/Ni ratios, as much as 14% of the starting amount of nickel remains in solution, but at high Al/Ni ratios the percent of benzene soluble nickel species levels out at 0.35%. However, at Al/Ni ratios of less than 3/1, the solution is not catalytically active for the polymerization of 1,3-butadiene, but it is above this ratio. This indicates that two distinctly different nickel species are present at the two extremes. Attempted concentration and isolation of the catalytically active species failed.

Reaction of nickel(II) stearate with $Et_3Al_2Cl_3$

The visual observations of the reaction are quite similar to those of the reaction of nickel(II) carboxylates with Et_2AlCl. Figure 3 presents the distribution of nickel as a function of the Al/Ni reaction stoichiometry. At Al/Ni ratios of 2/1 and above, the solution after complete reaction is orange to reddish-brown due to the presence of soluble nickel. Visible spectra and magnetic data of the solution indicate that the predominate nickel species present possesses square planar symmetry [6]. Solutions containing this species are very active for the polymerization of 1,3-butadiene. However, only a maximum of about 7% of the starting amount of nickel is converted into this active species.

In examining the other reaction products, the percentage of $NiCl_2$ is seen to

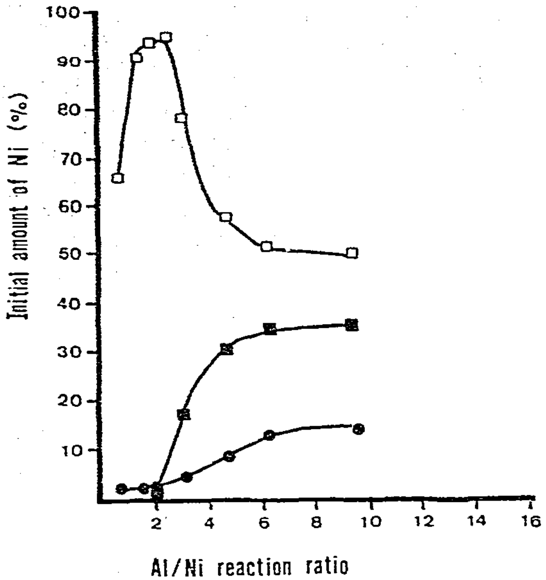


Fig. 4. Distribution of nickel among the reaction products from the reaction of nickel(II) stearate with $EtAlCl_2$. ■, percentage of metallic nickel; □, percentage of $NiCl_2$; ●, percentage of benzene soluble nickel complexes.

decrease rapidly from 80% at low Al/Ni ratios to a value of 36% at higher ratios. In contrast, the percentage metallic nickel steadily increases with increasing Al/Ni ratios until a limiting value of 57% is reached.

Reaction of nickel(II) stearate with $EtAlCl_2$

Again the visual observations of this reaction are very similar to those of the reaction of nickel(II) stearate with Et_2AlCl or $Et_3Al_2Cl_3$. Figure 4 presents the distribution of nickel reaction products as a function of the Al/Ni reaction ratio. The percentage of soluble nickel increases sharply at Al/Ni ratios above 2/1 and reaches a plateau of 14% at high ratios. Visible spectral and magnetic data confirm that the same square planar nickel species is present in this case as in the $Et_3Al_2Cl_3$ reaction [6]. Since $Et_3Al_2Cl_3$ is an equimolar mixture of Et_2AlCl and $EtAlCl_2$, the evidence indicates that the amount of the benzene-soluble nickel species increases in direct proportion to the $EtAlCl_2$ content of the alkylaluminum compound.

Another striking feature noted in Fig. 4 is that an almost quantitative conversion to $NiCl_2$ occurs at an Al/Ni ratio of 2/1. Above a 2/1 ratio, both metallic nickel and the soluble nickel species mentioned above begin to be produced and the amount of $NiCl_2$ in the precipitate begins to decrease to a limiting value of ~52% at high Al/Ni ratios. In addition, the percentage of metallic nickel levels out at ~35% at high Al/Ni ratios.

Conclusions

The reaction of nickel(II) stearate with ethylaluminum chlorides in benzene produces essentially three reaction products which are soluble nickel species,

$NiCl_2$, and nickel metal. The amount of each product is dependent upon the Al/Ni reaction stoichiometry and the identity of the aluminum compound. The data from Figs. 2, 3 and 4 show that little change is noted in the reaction product above an Al/Ni reaction ratio of 6/1 in the reaction of nickel(II) stearate with Et_2AlCl, $Et_3Al_2Cl_3$, or $EtAlCl_2$. Thus, apparently, six alkylaluminum molecules are required for complete reaction with one nickel(II) stearate molecule. At Al/Ni ratios of 6/1 or above, the production of benzene-soluble nickel species increases with the chloride content of the alkylaluminum compound, and the amount of metallic nickel produced increases as the alkyl content of the aluminum compound increases. However, reaction with any of the chloro compounds produces a greater percentage of metallic nickel than does reaction with Et_3Al at room temperature. The maximum amount of $NiCl_2$ in the precipitate is produced at Al/Ni ratios of 3/1 or below in each case, but the maximum amount of nickel metal is produced at Al/Ni ratios of 6/1 and above indicating that carboxylate exchange for Cl is more favorable than and precedes exchange for an ethyl group. Thus, the chlorides facilitate ligand exchange as in the reaction of nickel(II) carboxylates with $AlCl_3$.

The greater reducing ability of Et_2AlCl, $Et_3Al_2Cl_3$, and $EtAlCl_2$ in these systems may arise from the ability of these compounds to bring about rapid ligand exchange while exposing the nickel center to alkylation at the same time. However, an alternative explanation for the stability of the nickel stearate/Et_3Al system is that excess Et_3Al complexes with and stabilizes otherwise unstable alkylated nickel species.

Experimental

Chemicals

All reactions and transfers were carried out under dry, deoxygenated nitrogen in an inert atmosphere box. Benzene, used as the solvent for the reactions described herein, was dried, purified, and deoxygenated by fractional recrystallization followed by fractional distillation over sodium and benzophenone under dry nitrogen. Nickel(II) stearate was obtained from Research Organic/Research Inorganic Chemical Corporation and was washed repeatedly with alcohol to remove traces of stearic acid and dried for 14 h at 60°C under vacuum and stored over P_2O_5. Nickel(II) laurate (% Ni found 12.95; calcd. 12.85) was synthesized according to a literature method [13] and was purified and dried in a similar manner as nickel(II) stearate. Nickel(II) acetylacetonate (% Ni found 23.35; calcd. 23.01) was synthesized, purified, and dried according to a literature method [14].

The aluminum compounds triethylaluminum (Et_3Al), ethylaluminum sesquichloride ($Et_3Al_2Cl_3$), diethylaluminum chloride (Et_2AlCl), and ethylaluminum dichloride ($EtAlCl_2$) were obtained from Texas Alkyls or Alfa Inorganics in lecture bottles. Reagent grade aluminum trichloride was obtained from J.T. Baker Chemical Co. and was used without further purification. The alkylaluminum compounds were analyzed for aluminum and chloride contents and their NMR spectra were obtained before use. A typical analysis of $EtAlCl_2$, as an example, gave the following result: % Al found 20.86, calcd. 21.23; % Cl found

55.31, calcd. 55.91. All alkyls used for the reactions reported herein gave analyses close to the theoretical (±0.5%).

Reaction of nickel(II) stearate with alkylaluminum compounds

Nickel(II) stearate in benzene suspension (0.5—1 mmol, 20 ml) was treated, under an inert atmosphere with stirring, with the desired amount of aluminum compound which was transferred by syringe. After allowing 20 minutes for reaction, each reaction tube was centrifuged, the solution was removed, the precipitate was washed repeatedly with fresh benzene, and the washings were combined and analyzed. Next, the precipitate was washed with deionized water three times to extract $NiCl_2$. These washings were collected and analyzed for nickel, aluminum, and chloride. After this treatment, the precipitate was extracted three times with benzene containing 10% octanoic acid to remove any unreacted nickel(II) stearate. The above treatment leaves ferromagnetic metallic nickel, if it was produced by the reaction, that can be extracted with one molar nitric acid and analyzed.

Analysis of nickel, aluminum, and chloride

The nickel and aluminum concentrations were determined by atomic absorption using an Instrumentation Laboratories Model IL 253 spectrometer. A nitrous oxide/acetylene flame and an oxygen/acetylene flame were used in the determination of aluminum and nickel, respectively. A known amount of each solution was diluted to the concentration range 2—30 ppm and was hydrolyzed using dilute nitric acid. The absorbance values were determined from the average of three time averaged readings. Each unknown was bracketed by standards of slightly lower and higher concentrations.

Chloride was analyzed by the Volhard titration method.

Spectral measurements

Visible spectra were obtained using a Beckman DK-1 or a Cary 17 UV-visible spectrophotometer. Quartz UV cells fitted with air-tight teflon stoppers were used for air sensitive solutions.

NMR spectra were obtained using a Varian A-60D NMR spectrometer. Magnetic properties of solutions were investigated using the coaxial double-tube NMR method of Evans [7]. The measured separation in Hertz, Δf, of the inner tube and outer tube reference signal is related to the mass susceptability, χ_{mass}, by eq. 1, where f is the probe frequency (60 MHz), m is the mass of paramagnetic

$$\chi_{\text{mass}} = \frac{-3\Delta f}{2\pi f m} + \chi_o + \frac{\chi_o(d_o - d_s)}{m} \quad (1)$$

substance per ml of solution, χ_o is the mass susceptibility of the solvent, and d_o and d_s are the densities of the solvent and solution, respectively. The measured mass susceptibility must be corrected for the ligand diamagnetism which is negative, but the correction term is positive. The corrected mass susceptibility, χ_{corr}, is related to the effective magnetic moment, μ_{eff}, by eq. 2, where μ_{eff} is in

$$\mu_{\text{eff}} = 2.84\ \text{BM}((\chi_{\text{corr}} \cdot \text{MW})T)^{1/2} \quad (2)$$

Bohr magnetons, MW is the molecular weight, and T is the absolute temperature.

In this work, the probe temperature was determined using the temperature dependent shifts of ethylene glycol. The inert reference used in this work was 3% toluene.

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