method on a Tesla BS-467 spectrometer (60 MHz) using HMDS as the internal standard. The accuracy of determining the chemical shift was ±0.05 ppm, and the error of determining the integral intensities was ±2-3%.

## CONCLUSIONS

1. The stereochemistry of the reaction of diethylamine with diacetylene depends on the nature of the solvent and the temperature.

2. The formation of a mixture of the cis and trans isomers is caused by a difference in protonating the transition state and is amenable to both thermodynamic and kinetic control.

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# POLYMERIC METAL COMPLEX CATALYSTS IN HYDROGENATION OF NITROBENZENE

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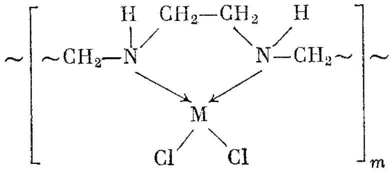
The reaction of polyethylenimine with transition metal halides gives stable coordination compounds [1]. In such macromolecular compounds the metal ions have a specific ligand environment, which is determined by the ratio of the nitrogen and metal ions, and also by the nature of the substituent on nitrogen.



$m = 80-100$; M = Ni (II), Co (II), Sn (II), Pd (II), Rh (III)

The complexes are obtained by reacting a solution of polyethylenimine with a solution of the appropriate metal halide. Polymerlike reactions are characteristic reactions for such complexes, in particular those involving the metal—halogen bonds, in which connection the coordination bonds in the complex are retained [2]. An interesting and practically valuable property of the complexes is their catalytic activity in the hydrogenation of olefins and aromatic hydrocarbons [1, 3].

A further study of the properties of these complexes made it possible to establish that the polyethylenimine complexes (PC) of Ni(II), Co(II), Sn(II), Pd(II), and Rh(III) catalyze the reduction of the aromatic nitro group. They exhibit catalytic activity without prior treatment by such reducing agents as metal hydrides or organometallic compounds.

The hydrogenation of an aromatic nitro group is determined both by the reaction conditions and the nature of the coordinated metal in the complex. The reduction proceeds with

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TABLE 1. Hydrogenation of Nitrobenzene on Complexes $[(-CH_2CH_2-NH-)_2\cdot MCl_n]_m$ when Using 1 g-atom of Metal/100 moles of Substrate

| Metal | T., °C | $p$, atm | Time, h | Composition of products, % | | |
|---|---|---|---|---|---|---|
| | | | | nitrobenzene | aniline | cyclohexylamine |
| Ni(II), Co(II), Sn(II) | 70 a | 50 | 15 | – | 100 | – |
| The same | 70 a | 25 | 15 | – | 100 | – |
| » | 70 a | 10 | 15 | 80 | 20 | – |
| » | 70 b | 25 | 15 | – | 100 | – |
| » | 70 b | 5 | 40 | 100 | – | – |
| Pd(II) | 20 c | 1 | 8 | – | 100 | – |
| Rh(III) | 80 b | 1 | 4 | – | 90 | 10 |

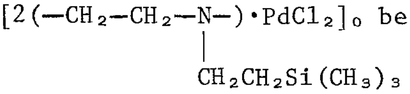
a) Neat.

b) Solvent = 96% ethanol, $[M^{n+}] = 0.03$, $[C_6H_5NO_2] = 3.0$ mole/liter.

c) Solvent = 90% ethanol, $[M^{n+}] = 0.03$, $[C_6H_5NO_2] = 3.0$ mole/liter.

noticeable speed at 20-70°C, a hydrogen pressure of 1-25 atm, and either in solvents or without them.

Based on the data given in [4], the catalytic reduction of an aromatic nitro group is accompanied by the formation of intermediate products. When the PC of the Ni, Co, and Sn chlorides were used we were unable to establish that the reduction of the nitro group is accompanied by the formation of intermediate hydrogenation products. However, when the hydrogenation of nitrobenzene was run using the PC of $PdCl_2$ we were able to record the presence of nitrosobenzene (mass spectrometry) in the reaction mixture. The hydrogenation of nitrobenzene in the presence of the PC of rhodium chloride proceeds to give aniline and cyclohexylamine, the further hydrogenation product of the aromatic ring. The reaction conditions and the results of hydrogenating nitrobenzene are given in Table 1.

From Table 1 it can be seen that the PC of Ni, Co, and Sn are catalytically active in the reduction of nitrobenzene when $P_{H_2} > 10$ atm. The reduction proceeds with noticeable speed on the PC of Pd and Rh when $P_{H_2} = 1$ atm. It was shown by special experiments that varying the nitrogen—metal ratio in the complex from 2:1 to 6:1 has no effect on the hydrogenation rate of the aromatic nitro group. This fact testifies in support of the outer sphere coordination of the nitrobenzene molecule [5] relative to the active center of the catalyst complex. The structure of these intermediate complexes was not studied by us. The elemental composition of the PC after using it as a catalyst remained unchanged. Thus, the found elemental composition for the complex  $[2(-CH_2-CH_2-\underset{CH_2CH_2Si(CH_3)_3}{\underset{|}{N}}-)\cdot PdCl_2]_o$ before its use in the hydrogenation reaction was: C 36.82; H 7.89; Pd 22.75%; after the hydrogenation of nitrobenzene it was: C 36.54; H 7.51; Pd 22.80%. The chemical stability of the PC of the transition metal halides under the hydrogenation conditions is responsible for the constancy of their catalytic effect after many repetitions of the catalytic cycle. For example, the hydrogenation of nitrobenzene on the complex $[-(-CH_2CH_2NH-)_2-\cdot PdCl_2]_m$ (20°, $P_{H_2}$ 5 atm, 100 moles of substrate/g-atom of Pd, 60-90 min) was repeated 8 times, and a 100% conversion of nitrobenzene to aniline was achieved in all cases.

## EXPERIMENTAL

The complexes were obtained as described in [1]. The hydrogenation was run in an autoclave at 10-50 atm, and in a glass reactor at 1-5 atm. The quantitative composition of the catalyst was determined by GLC on an LKhM-8MD chromatograph, using an internal standard, a 2 m × 4 mm column packed with E-301, and a temperature of 160°. The mass spectra were obtained on an LKV-20-91 instrument.

## CONCLUSIONS

The complexes based on polyethylenimine and the chlorides of Co, Ni, Sn, Pd, and Rh are active in the hydrogenation of nitrobenzene.

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# THERMAL STABILITY OF DIIRON HEXACARBONYL COMPLEXES OBTAINED FROM AROMATIC AZINES

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Up to now the reactivity of binuclear iron carbonyl complexes with nitrogen-containing bridges has received very little study [1].

The diiron hexacarbonyl complexes from aromatic azines are capable of effecting the nonstoichiometric conversion of thiols to disulfides [2]. The thermal stability of carbonyl complexes is an important characteristic when studying their chemical and catalytic properties.

We studied the thermal stability of the diiron hexacarbonyl complexes obtained from the following aromatic azines: $(C_6H_5CH{=}N)_2Fe_2(CO)_6$ (I); $(C_6H_5CCH_3{=}N)_2Fe_2(CO)_6$ (II); $(p\text{-}BrC_6H_4\text{-}CCH_3{=}N)_2Fe_2(CO)_6$ (III); $[(C_6H_5)_2C{=}N]_2Fe_2(CO)_6$ (IV); $(o\text{-}C_6H_4CH_2{-}N{-}N{=}CHC_6H_5)Fe_2(CO)_6$ (V). The synthesis of these complexes is described in [3].

According to the x-ray structure data, the binuclear iron carbonyl complex, obtained from 4,4'-dimethylbenzophenone ketazine, has two three-electron nitrogen-containing bridges and the $Fe_2(CO)_6$ grouping.

The fact that this complex and the studied compounds (I)-(IV) have identical spectral data gives reason to state that these complexes also have a similar structure, which includes $N_2Fe_2(CO)_6$, a fragment in which the Fe atoms are linked by an intermetallic bond.

Complex (V) differs in structure from compounds (I)-(IV). One bridge benzene ring coordinates one Fe atom on the $\eta^2$ type, and forms a $\sigma$ bond with the other Fe atom. The N=C double bond in the second benzene ring does not take part in the coordination with the metal [4]. This compound is the first example of an o-metalated complex, in which only one N atom is coordinated with the metal [5].

TABLE 1. Temperature Characteristics of Complex

| Complex | mp, °C (based on DTA curves) | Incipient decomp. temp., °C | |
|---|---|---|---|
| | | argon | air |
| (I) | 105 | 170 | 105 |
| (II) | 106 | 170 | 120 |
| (III) | 140 | 170 | 120 |
| (IV) | 143* | 170 | 120 |
| (V) | 115 | 115 | 105 |

*From data in [8], mp 136-138°.

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