Carbonylation of nitro and azo compounds in the presence of iron carbonyl catalysts

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The reactions of nitro and azo compounds with carbon monoxide were studied in the presence of iron carbonyl catalysts. It was shown that these catalytic systems differ substantially from Pd- and Rh-containing catalysts. In the case of the iron catalysts, the products of coupling of molecules are formed as intermediates and azo compounds are the final reaction products. The reactions involving the palladium and rhodium catalysts proceed without the intermediate formation of the coupling products and lead to isocyanates or carbamates. When combined using $PdCl_2$ and $Fe(CO)_5/Al_2O_3$, the catalysts inhibit each other, especially in the presence of pyridine.

Key words: nitro compounds, azo compounds, carbonylation, iron carbonyl catalysts, isocyanates.

In the presence of $Fe(CO)_5$, nitrobenzene reacts with CO at 205 °C and 20 MPa in anhydrous benzene to form azobenzene as the main product:[1]

$$2\ PhNO_2 + 4\ CO \longrightarrow PhN{=}NPh + 4\ CO_2.$$

Finely dispersed iron powder can be used in this reaction instead of $Fe(CO)_5$, and this assumes the preliminary formation of $Fe(CO)_5$.[1]

In the absence of a catalyst, this reaction occurs under more drastic conditions: 250 °C and 300 MPa of CO.[2] The stoichiometric reaction of nitrobenzene with $Fe(CO)_5$ resulting in the formation of azobenzene and azoxybenzene is also known.[3]

Both catalytic reactions mentioned depend weakly on the CO pressure (a maximum conversion of nitrobenzene is observed) and depend strongly on the temperature. For example, the reactions do not occur below 100 °C, while only a black polymer product is obtained above 228 °C. Azobenzene begins to form at temperatures higher than 180 °C.

It has been shown in our previous works[4—8] that the carbonylation of nitro compounds in the presence of Pd- and Rh-containing catalytic systems does not involve the intermediate formation of dimerization products (azo and azoxy compounds) and likely occur *via* the intermediate formation of the nitroso compound and nitrene or nitrene complexes.

In this work, the possible reaction route in the presence of iron carbonyl catalysts has been studied using Al_2O_3-supported iron carbonyl (2% $Fe(CO)_5/Al_2O_3$) as an example.

Experimental

Experiments on carbonylation were carried out in a 0.15-L steel rotating autoclave. Chlorobenzene (10 mL) as the solvent, the necessary amount of the nitro and azo compounds, pyridine, 1-chloronaphthalene (as the internal standard), and the other necessary compounds were placed in the autoclave, the autoclave was purged with CO, an ampule with $Fe(CO)_5/Al_2O_3$ was opened in a CO flow, and the contents of the ampule were extruded into the autoclave with a CO flow. The autoclave was closed rapidly, the autoclave was purged with CO, the pressure was increased to the necessary value, and the autoclave was heated to the working temperature. Reaction products were analyzed using GLC similarly to the procedure published previously.[4]

The 2% $Fe(CO)_5/Al_2O_3$ catalyst was prepared in a U-like device with a T-valve. The device consisted of two sections. Aluminum oxide (98 g) was placed in one of the sections in an argon flow, and freshly distilled iron pentacarbonyl (2 g) was placed in another calibrated section. Then the section containing iron carbonyl was frozen in an argon flow with liquid nitrogen. With continuing cooling, the gas was evacuated from the device by a vacuum pump. When a vacuum was achieved, the device was sealed, cooling was stopped, and the device was left for ~2 h at room temperature until the complete evaporation of $Fe(CO)_5$. Then the device was evacuated at room temperature for 1 h. The catalyst prepared was thrown off in an argon flow in specially prepared ampules purged with argon. The specified amounts of the catalyst were taken by volume.

Results and Discussion

As in the study of the Pd- and Rh-containing catalytic systems, the method of competitive reactions of the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2460—2463, October, 1996.

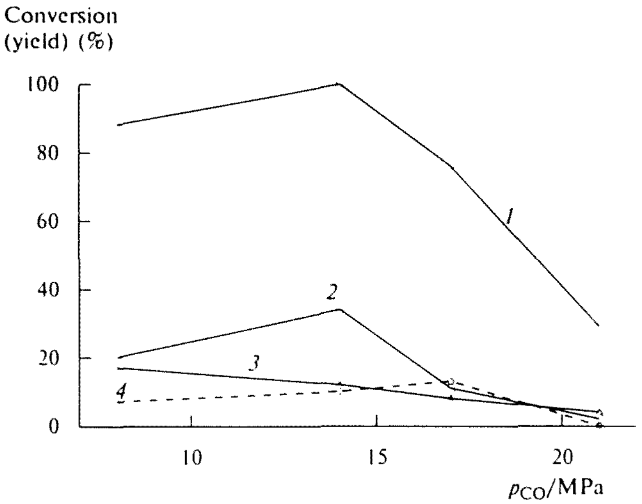

Fig. 1. Effect of the CO pressure on the conversion of the 4-nitrotoluene—azobenzene mixture in the presence of 2% $Fe(CO)_5/Al_2O_3$ + pyridine ($Fe(CO)_5$: Py : 4-nitrotoluene : azobenzene = 1 : 50 : 100 : 50 (mol.); 200 °C; 20 min; $Fe(CO)_5$ (0.05 mmol); chlorobenzene (10 mL); X-product is a mixture of 2-(*p*-tolyl)-5-methylindazole and 2,4-dioxo-6-methyl-3-(*p*-tolyl)-1,2,3,4-tetrahydroquinazoline). Curve *1*, conversion (%) of nitrotoluene; curves *2—4*, yields (%): 4,4′-azotoluene (*2*), 4-toluidine (*3*), and product X (*4*).

initial nitro compound and possible intermediate product (azo compound) in the carbonylation of their mixtures was used to study the effects of experimental conditions, the composition of the catalytic system, and the reaction route in the case of iron carbonyl catalysts.

As seen from the data presented in Tables 1 and 2 and Fig. 1, the activity of the $Fe(CO)_5/Al_2O_3$ catalyst in the transformation of nitro compounds to azo compounds is the same as that of $Fe(CO)_5$.[1] The initial azo compound both individual and in a mixture with the nitro compound undergoes almost no transformation under any reaction conditions, except high temperatures when resins are formed. The curves of dependences of the conversion of nitro compound and the yield of azo compound on the CO pressure are analogous, with a maximum at virtually the same values as that for $Fe(CO)_5$ without a support.[1] Thus, the deposition of iron pentacarbonyl on aluminum oxide did not result in a change in the catalytic properties of iron carbonyl. The activating effect of pyridine on the conversion of the nitro compound, especially on the selectivity of the formation of the azo compound, was observed for the first time.

Since the iron carbonyl catalysts differ qualitatively from the Pd- and Rh-containing catalytic systems and result in the formation of azo compounds rather than isocyanates or carbamates, and on the other hand, the iron compounds are known promoters of the Pd- and Rh-containing catalysts, we have studied their joint effect on the carbonylation of nitro and azo compounds.

Table 1. Effect of the reaction conditions on the conversion of a mixture of 4-nitrotoluene (NT) and azobenzene (AB) in the presence of 2% $Fe(CO)_5/Al_2O_3$ (Cat)

Cat /g	*T* /°C	p_{CO} /MPa	Time /min	Py	Conversion (%)					
					NT				AB	
					C_1	Y_1	Y_2	Y_3	C_2	Y_4
0.5	180	14	20	Yes	100	12	34	10	3	3
2.0	180	14	20	Yes	100	13	39	0	20	16
2.0	190	8	30	Yes	100	15	45	6	18	10
2.0	200	8	30	Yes	100	7	22	19	8	2
2.0	220	8	30	No	100	27	16	4	41	22

Notes. C_1 is the conversion of NT; C_2 is the conversion of AB; Y_1 is the yield of 4-toluidine; Y_2 is the yield of 4,4'-azotoluene; Y_3 is the yield of the X-product; Y_4 is the yield of aniline; NT, 0.67 g; AB, 0.44 g; pyridine, 0.2 g; chlorobenzene, 10 mL. X-product is a mixture of 2-(*p*-tolyl)-5-methylindazolone and 2,4-dioxo-3-(*p*-tolyl)-6-methyl-1,2,3,4-tetrahydroquinazoline.

As seen from Fig. 2, two catalysts, 2% $Fe(CO)_5/Al_2O_3$ and $PdCl_2$, mutually inhibit each other and, as follows from Table 2, pyridine enhances this effect.

Thus, the data obtained demonstrate substantial differences in the behavior of the Pd- and Rh-containing catalytic systems and the iron carbonyl catalysts.

It is known that iron carbonyls form stable complexes with both nitroso compounds[9] and nitrenes.[10—14] Many similar complexes were obtained. The stepwise reduction of a nitro compound by CO results in the primary formation of a nitroso compound and then a nitrene is formed. Since the iron carbonyl complexes with these intermediates are stable, this increases the

Table 2. Effect of the addition of pyridine (Py) on the activity of the catalytic [2% $Fe(CO)_5/Al_2O_3$ + $PdCl_2Py_2$] system (runs *1*, *2*) and [2% $Fe(CO)_5/Al_2O_3$] (runs *3—8*) in the reaction of a mixture of 4-nitrotoluene (NT) and azobenzene (AB) with CO

Experiment	*T* /°C	p_{CO} /MPa	Time /min	Py	Conversion (%)					
					NT				AB	
					C_1	Y_1	Y_2	Y_3	C_2	Y_4
1	200	10	30	No	51	7	9	1	4	0
2	200	10	30	Yes	35	4	3	4	1	0
3	200	8	30	No	55	2	10	7	0	0
4	200	8	30	Yes	100	7	22	19	1	0
5	180	8	20	No	47	14	7	0	2	0
6	180	8	20	Yes	88	17	20	7	3	0
7	180	12	20	No	46	12	0	6	3	0
8	180	12	20	Yes	94	15	27	9	3	0

Notes. C_1 is the conversion of NT; C_2 is the conversion of AB; Y_1 is the yield of 4-toluidine; Y_2 is the yield of 4,4'-azotoluene; Y_3 is the yield of the X-product; Y_4 is the yield of aniline; NT, 0.67 g; AB, 0.44 g; pyridine, 0.2 g; chlorobenzene, 10 mL. X-Product is a mixture of 2-(*p*-tolyl)-5-methylindazolone and 2,4-dioxo-3-(*p*-tolyl)-6-methyl-1,2,3,4-tetrahydroquinazoline.

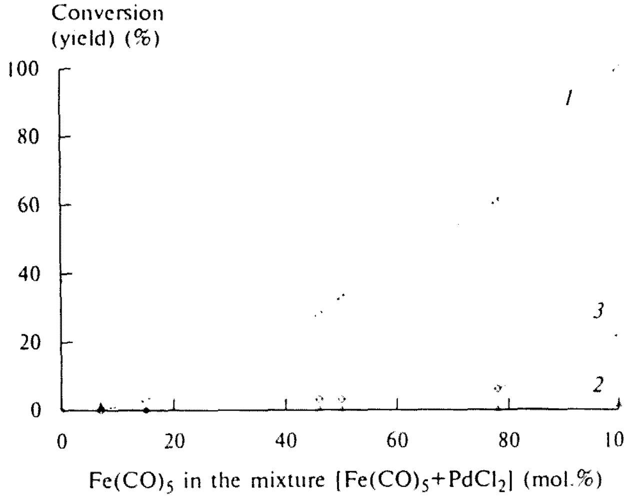

Fig. 2. Effect of $Fe(CO)_5$ (mol.%) in the [$Fe(CO)_5$ + $PdCl_2$] mixture on the conversion of the 4-nitrotoluene—azobenzene mixture in the presence of pyridine (200 °C; 8 MPa of CO; 30 min; azobenzene, 0.44 g; 4-nitrotoluene, 0.67 g; pyridine, 0.2 g; chlorobenzene, 10 mL). Curves *1—2*, conversion (%): 4-nitrotoluene (*1*) and azobenzene (*2*); curve *3*, yield (%) of 4,4′-azotoluene.

probability of the reaction of the nitrene complex with the nitroso compound (to form an azoxy compound followed by its reduction to the azo compound) or the dimerization of two nitrene molecules (including the reason that molecules of nitrene complexes of iron carbonyls contain, as a rule, a pair of nitrene ligands) to form the azo compound. Since iron carbonyl is probably incapable of carbonylating azo compounds, but reduces well azoxy compounds (as well as nitro and nitroso compounds) by carbon monoxide, azo compounds accumulate in the reaction mixture and comprise the main reaction product. In the presence of hydrogen donors and iron carbonyl, nitrenes and azo compounds are also reduced to amines and some other, more complex products with the N—H bond.

In addition to iron carbonyls, stable complexes with nitrenes and nitroso compounds are also typical of ruthenium carbonyls.[15,16] For this case, it is known from the literature that azo compounds form both as the final products of carbonylation of nitroso compounds under mild conditions[17] and intermediates, precursors of isocyanates and carbamates, under more drastic conditions.[18]

In the case of the rhodium catalysts, the formation of azo and azoxy compounds was observed only under very mild conditions of the carbonylation of nitroso compounds (75 °C, 0.1 MPa),[18] when, due to the high initial concentration of the nitroso compound and the relative stability of nitrene complexes, their reaction is possible to form the azoxy compound followed by its reduction to the azo compound.

Thus, the Pd- and Rh-containing catalytic systems and the iron and ruthenium carbonyl catalytic systems constitute two groups, which differ qualitatively with respect to the reaction of nitro compounds with carbon monoxide. In the presence of the first group catalysts, the reaction occurs *via* monomeric intermediates to isocyanates and carbamates, while in the presence of the second group catalysts, the reaction occurs *via* the intermediate formation of dimer products to azo compounds. The reason suggested for this difference is the stability of the catalytic metal carbonyl complexes with nitrenes and nitroso compounds. The Pd- and Rh-containing catalysts are characteristic of the monotonic increase in the conversion of the nitro compound and the yield of isocyanate as the CO pressure increases. For the Fe- and Ru-containing catalysts, the existence of the maximum both of the conversion of the nitro compound and the yield of the azo compound is explained by the displacement of other ligands by CO ligands due to a higher stability of the Fe—CO and Ru—CO bonds compared to that of the Rh—CO and Pd—CO bonds.

The mutual deactivation of the catalysts $PdCl_2$ and $Fe(CO)_5$ can be explained by the redox reaction between them to form inactive palladium black and iron ions; the latter were found in the reaction mixture.

The fact that no isocyanates form in the presence of iron carbonyls and the reaction ceases at the stage of the formation of the azo compound testifies that $Fe(CO)_5$ is not the catalyst of the stage of the carbonylation of nitro compound (and azo compound). This confirms repeatedly the previous conclusion that the Fe-(and Mo-, V-)promoters of the palladium and rhodium catalysts accelerate precisely the stage of the reduction of the nitro group by carbon monoxide and not the stage of the subsequent carbonylation.[5,8]

The authors are grateful to V. E. Wasserberg for help in preparing the catalysts.

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Received February 22, 1996;
in revised form June 5, 1996