CATALYTIC SYNTHESIS OF ISOCYANATES BY CARBONYLATION OF NITRO COMPOUNDS IN THE PRESENCE OF $[Rh(CO)_2Cl]_2$ PROMOTED BY PYRIDINE AND PYRIDINE HYDROCHLORIDE

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UDC 542.97:542.91:547.551.43

Aromatic isocyanates are formed in high yield from nitro compounds and CO in the presence of Rh catalysts, activated by pyridine (Py) [1-3].

$$RC_6H_4NO_2 + 3CO \rightarrow RC_6H_4NCO + 2CO_2$$

We established that Py in combination with pyridine hydrochloride (PyHCl) is an efficient activator of rhodium carbonyl chloride. $[Rh(CO)_2Cl]_2$ alone is catalytically inactive: Nitrobenzene (NB) is not reduced in its presence at 205°C and a CO pressure of 50 atm, and phenyl isocyanate (PhI) is not formed, while the $[Rh(CO)_2Cl]_2$, according to the IR spectra of the reaction solutions, remains unchanged (νCO 2105 and 2048 cm^{-1}).

Pyridine activates the dimeric rhodium carbonyl chloride by converting it to the catalytically active monomer: With increase in the Py concentration from 0 to 0.6 mole/liter both the NB conversion and the PhI yield pass through a maximum at 0.1 mole/liter of Py (Fig. 1), while in the IR spectra of the reaction solutions, containing 0.05-0.15 mole/liter of Py, are observed the frequencies of the CO vibrations at 2098 and 2022 cm^{-1}, which are characteristic for $[Rh(CO)_2PyCl]$, which, as is known [4], is easily formed from $[Rh(CO)_2Cl]_2$ and Py. Excess Py (>0.2 mole/liter) deactivates the $Rh(CO)_2PyCl$ by apparently converting it to the dehalogenated Rh form

$$[Rh(CO)_2Cl]_2 \xrightarrow{Py} Rh(CO)_2PyCl \xrightarrow{CO,\ Py} Rh_x(CO)_y Py_z + Py_2COCl_2$$

since the pyridine solution of $[Rh(CO)_2Cl]_2$, after heating at 205° and a CO pressure of 50 atm, lacks in the IR spectrum the frequencies of the CO vibrations that belong to rhodium carbonyl chlorides.

The form of the Pd catalyst active in the carbonylation of nitro compounds is also unstable and on dissociation liberates Py, CO, and halide ion; the addition of an excess of these ligands to the reaction solution stabilizes the catalytically active form of Pd [5]. In a similar manner, it could be expected that the addition of Cl^- ions to the solution should prevent the deactivation of the Rh catalyst. Actually (Fig. 2), when PyHCl is added to the $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2Cl]_2$– Py catalysts in an amount up to 0.11 mole/liter the NB conversion and the PhI yield increase from 0-10 and 0-5 to 100 and 70-90%, respectively. At PyHCl concentrations > 0.11 mole/liter the PhI yield decreases. In the entire studied range of PyHCl concentrations (0-0.216 mole/liter) is observed an extremal dependence of the PhI yield on the Py concentration (see Fig. 1), in which connection the optimum Py concentration in solution is higher at a higher PyHCl concentration. The character of the curves in Figs. 1 and 2 shows that $Rh(CO)_2ClPy$ is apparently not the sole catalytically active monomeric rhodium complex.

After the carbonylation of the NB we isolated from the solutions, containing before reaction 3-30 mmoles/liter of $[Rh(CO)_2Cl]_2$, 1.27-2 moles/liter of Py, and 0.05-0.25 mole/liter of PyHCl, a substance with the composition $RhPy_3Cl_{1.5}$, which is unstable when heated to 100° in the absence of Py.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2556-2561, November, 1980. Original article submitted December 10, 1979.

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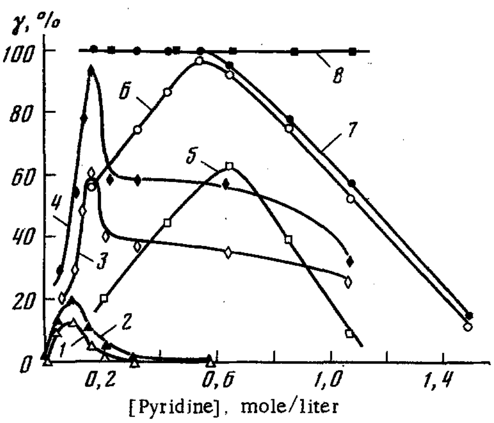

Fig. 1

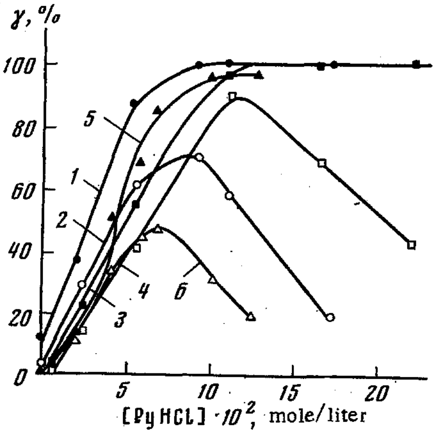

Fig. 2

Fig. 1. Effect of pyridine concentration in solution on conversion (γ) of nitrobenzene (2, 4, 7, 8) and yield of phenyl isocyanate (1, 3, 5, 6) at 205°, a CO pressure of 50 atm, and a PyHCl concentration in mmoles/liter: 1, 2) 0; 3, 4) 48.34; 5, 8) 158.73; 6, 7) 108.23. [Rh-$(CO)_2Cl]_2$ 12 mmole/liter.

Fig. 2. Effect of PyHCl concentration on conversion (γ) of nitrobenzene (1, 3, 5) and yield of phenyl isocyanate (2, 4, 6) at 205°, CO pressure of 50 atm, reaction time of 1 h, and pyridine concentration in mole/liter: 1,2) 0.158; 3, 4) 0.633; 5, 6) in the absence of pyridine. $[Rh(CO)_2Cl]_2$ 12 mmole/liter.

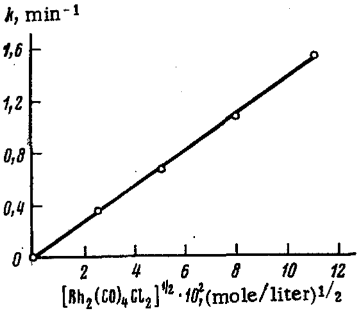

Fig. 3

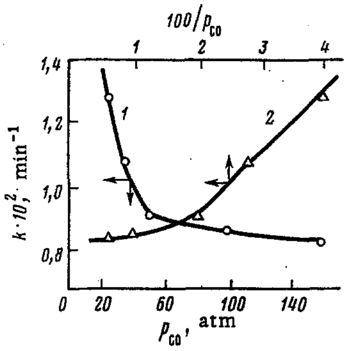

Fig. 4

Fig. 3. Rate constants for carbonylation of nitrobenzene as a function of the concentration of the rhodium carbonyl chloride complex at 205°, a CO pressure of 50 atm, a pyridine concentration of 0.58 mole/liter, and a PyHCl concentration of 0.108 mole/liter.

Fig. 4. Rate constants for the reduction of nitrobenzene as a function of the CO pressure, at 205°, in the presence of the catalyst $[Rh(CO)_2Cl]_2$–Py–PyHCl (6.4:580:108 mmole/liter).

TABLE 1. Synthesis of Aromatic Isocyanates in Presence of Catalyst $[Rh(CO)_2Cl]_2$ – Py – PyHCl under a CO Pressure of 50 atm

$[Rh(CO)_2Cl]_2$	PyHCl	Py	Reaction Temp., °C	Synthesis time, min	Starting nitro compounds	Conversion of nitro compounds, %	Obtained isocyanates	Yield of isocyanate, %
mg								
56	220	600	185	60	Nitrobenzene	60	Phenyl isocyanate	43
56	220	600	205	60	"	98	"	62
56	220	600	215	60	"	100	"	40
56	150	550	205	60	"	100	"	90
30	150	550	205	40	"	63	"	61
30	150	550	205	40	4-Chloronitrobenzene	66	4-Chlorophenyl isocyanate	47
30	150	550	205	40	3-Nitrotoluene	83	3-Methylphenyl isocyanate	45
30	150	550	205	40	4-Methoxynitrobenzene	100	4-Methoxyphenyl isocyanate	36

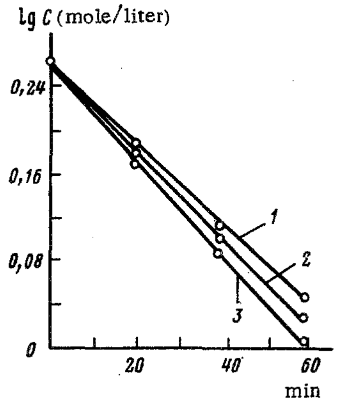

Fig. 5. Change in the concentration of the starting nitrobenzene during the synthesis of phenyl isocyanate at 205°, a CO pressure of 150 atm (1), 100 (2), and 50 atm (3), in the presence of $[Rh(CO)_2Cl]_2$ – Py – PyHCl (6.4:580:108 mmole/liter).

In excess Py, at 0-20°, $Rh(CO)_2PyCl$ is converted to $Rh(CO)_2Py_2Cl$ [4]. At 120-205°, and a CO pressure of 1-50 atm, $[Rh(CO)_2Cl]_2$ reacts with PyHCl in chlorobenzene to give the monomeric complexes $[Rh(CO)_2Cl_2]^-$, $Rh(CO)_2PyCl$, and $[Rh(CO)PyCl_2]^-$, which are catalytically active in the synthesis of isocyanates and during the carbonylation of nitro compounds are found in equilibrium with the starting dimer $[Rh(CO)_2Cl]_2$ [6]. PyHCl in the free state and in rhodium complexes is unstable and dissociates into Py and HCl. All of the above said gives reason to assume that under the conditions of synthesizing isocyanates from nitro compounds and CO the Rh catalyst represents a system of complexes of variable catalytic activity, found in dynamic equilibrium with each other, among which can be the following complexes:

$$\begin{tikzcd}
\underset{(A)}{[Rh(CO)_2Cl]_2} \arrow[r, shift left, "Py"] \arrow[d, shift right, "Cl^-"'] & \underset{(E)}{Rh(CO)_2PyCl} \arrow[l, shift left] \arrow[r, shift left, "Py"] \arrow[d, shift right, "Cl^-"] & \underset{(G)}{Rh(CO)_2Py_2Cl} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift right, "Cl^-"'] & \underset{(K)}{Rh_x(CO)_yPy_z} \arrow[l, shift left, "Cl^-"] \\
\underset{(B)}{[Rh(CO)_2Cl_2]^-} \arrow[u, shift right] \arrow[r, shift left] & \underset{(H)}{[Rh(CO)_2PyCl_2]^-} \arrow[u, shift right] \arrow[l, shift left, "HCl"] \arrow[r, shift left, "Py"] \arrow[d, shift right] & \underset{(I)}{[Rh(CO)Py_2Cl_2]^-} \arrow[u, shift right, "CO"'] \arrow[l, shift left, "CO"] \arrow[r, shift left, "Py"] & \underset{(L)}{RhPy_3Cl_{1,5}} \arrow[l, shift left, "CO"] \\
 & \underset{(D)}{[Rh(CO)PyCl_2]^-} \arrow[u, shift right, "CO"] & &
\end{tikzcd}$$

As a result, the dimeric Rh carbonyl chloride, which is inactive in the carbonylation of NB, when reacted with Py and PyHCl can dissociate reversibly into monomeric Rh complexes, which contain Py, Cl, and either one or two CO molecules as ligands. If it is assumed that the monomeric Rh complexes, for example (B), (E), (H), (G), (D), and (I) are catalytically active in the synthesis of PhI, then the rate of synthesizing PhI, with a selectivity of 70-90%, should be proportional to the concentration of these complexes. The available experimental and literature data do not permit making an unequivocal conclusion regarding the equilibrium composition of the active Rh complexes under the real conditions of synthesizing PhI under CO pressure.

However, even if we limit ourselves only to the first dissociation step of the complex, (A) to (E) (under the influence of Py) or to (B) (under the influence of PyHCl), it can be seen that the concentration of the active complexes should be proportional to the concentration of the starting $[\mathrm{Rh(CO)_2Cl}]_2$ to the 0.5 power. Actually, at a concentration of Py and PyHCl in the reaction mixture that is optimum for the synthesis of PhI the carbonylation rate is proportional to the $[\mathrm{Rh(CO)_2Cl}]_2$ concentration to the 0.5 power (Fig. 3). When the CO pressure is increased from 25 to 50 atm the reaction rate is inversely proportional to the CO pressure, while in the range 50-150 atm it is independent of the pressure (Fig. 4). Based on the starting NB, the reaction for the synthesis of PhI is first order (Fig. 5). On this basis it may be concluded that the rate for the synthesis of PhI, with a selectivity of 70-90%, by the carbonylation of NB at a constant concentration of PyHCl and Py is directly proportional to the concentration of NB and the Rh carbonyl complexes, and is inversely proportional to the CO pressure and has the form

$$W \simeq k_1[\mathrm{NB}]\,[\mathrm{Rh(CO)_2Cl}]_2^{1/2}\left(k_2 + \frac{k_3}{p_{\mathrm{CO}}}\right)$$

where k_1, k_2, and k_3 are constants, and P_{CO} is the CO pressure.

This equation is in agreement with the reaction scheme for the carbonylation of NB, since the rate of the equilibrium transformations between $[\mathrm{Rh(CO)_2Cl}]_2$, CO, and the catalytically active Rh complexes is greater than the rate of synthesizing PhI on these complexes.

$$\begin{tikzcd}
{[\mathrm{Rh(CO)_2Cl}]_2} \arrow[d, shift left, "\mathrm{L}"] & \mathrm{Rh(CO)_2(RNO)Cl} \arrow[r, "\mathrm{L}", "-\mathrm{CO_2}"'] \arrow[d, shift left, "\mathrm{L}"] & \mathrm{Rh(CO)(RN)ClL} \arrow[r, "2\mathrm{L}"] \arrow[d, shift left, "{-\mathrm{CO}, +\mathrm{L}}"] & \mathrm{RhClL_3 + RNCO} \\
\mathrm{Rh(CO)_2ClL} \arrow[u, shift left] \arrow[r, "\mathrm{RNO_2}", "-\mathrm{CO_2}"'] \arrow[d, shift left, "\mathrm{L}"] & \mathrm{Rh(CO)(RNO)ClL} \arrow[u, shift left, "\mathrm{CO}"] \arrow[r, "\mathrm{L}", "-\mathrm{CO_2}"'] \arrow[d, shift left, "\mathrm{L}"] & \mathrm{Rh(RN)ClL_2} \arrow[u, shift left, "+\mathrm{CO}"] & \\
\mathrm{Rh(CO)ClL_2} \arrow[u, shift left, "\mathrm{CO}"] \arrow[r, "\mathrm{RNO_2}", "-\mathrm{CO_2}"'] & \mathrm{Rh(RNO)ClL_2} \arrow[u, shift left, "\mathrm{CO}"] & &
\end{tikzcd}$$

where L = Py or PyHCl.

The catalyst $[\mathrm{Rh(CO)_2Cl}]_2$ − Py − PyHCl is also active in the synthesis of various substituted phenyl isocyanates, and the carbonylation of 3-nitrotoluene, 4-chloronitrobenzene, and 4-methoxynitrobenzene in its presence respectively gives 3-methylphenyl isocyanate, 4-chlorophenyl isocyanate, and 4-methoxyphenyl isocyanate in 36-47% yield (Table 1).

EXPERIMENTAL

The carbonylation of NB and its derivatives was run in a rotated 0.15-liter steel autoclave, into which were charged 0.0195 mole of the nitro compound, 10 ml of chlorobenzene, 3-56 mg of $[\mathrm{Rh(CO)_2Cl}]_2$, 0-220 mg of PyHCl, and 0-1.5 ml of Py. Then the autoclave was purged with CO, the CO pressure was raised to 15-150 atm, and the autoclave was heated at 205° for 5-120 min. The reaction products were analyzed by GLC on an LKhM-8MD chromatograph (length of column 1 m, packed with 5% XE-60 deposited on Chromaton N-AW-DM-CS, 30-60 mesh, and helium as the carrier gas at a flow rate of 40 ml/min), with elevation of the temperature from 60 to 170° at a rate of 20°C/min. The quantitative composition of the products was determined relative to chlorobenzene as the internal standard. The $[\mathrm{Rh(CO)_2Cl}]_2$ and PyHCl were synthesized as described in [7, 8]. The IR spectra were taken on a UR-20 instrument as a thin layer between KBr plates and as KBr pellets. The complex $\mathrm{RhPy_3Cl_{1.5}}$ was isolated at 0° by filtering the reaction solutions that contained before the carbonylation of NB: 3-30 mmoles/liter of $[\mathrm{Rh(CO)_2Cl}]_2$, 1.27-2 moles/liter of Py, and 0.05-0.25 mole/liter of PyHCl (calcd. for $\mathrm{RhPy_3Cl_{1.5}}$: C 45.50; H 3.80; Cl 14.00%. Found: C 45.44; H 4.14; Cl 13.87%), and it was also obtained by heating $[\mathrm{Rh(CO)_2Cl}]_2$ at 70° for 20 min in chlorobenzene, containing 1 mole/liter of Py. The IR spectra of the complexes, obtained by both methods, were identical: ν 1618, 1502, 1458, 1230, 1168, 1092, 1055, 1025, 770, 705 $\mathrm{cm^{-1}}$. The complex $\mathrm{RhPy_3Cl_{1.5}}$ is soluble in Py and is stable when heated. It decomposes when heated without the Py and is insoluble in benzene and chlorobenzene.

CONCLUSIONS

1. Pyridine and pyridine hydrochloride activate $[\mathrm{Rh(CO)_2Cl}]_2$ in the synthesis of isocyanates by the carbonylation of aromatic nitro compounds; in the presence of the catalyst $[\mathrm{Rh(CO)_2Cl}]_2$ − Py − PyHCl (weight ratio 1-2:18:5), at 205°, a CO pressure of 50 atm, and a time of 40 min, nitrobenzene, 3-nitrotoluene, 4-chloronitrobenzene, and 4-methoxynitrobenzene are converted to the corresponding isocyanates in 36-90% yield.

2. The activating effect of Py and Py·HCl apparently consists in the formation from $[Rh(CO)_2Cl]_2$ of catalytically active monomeric rhodium complexes, which contain Py, Cl^-, and CO as ligands.

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EFFECT OF CATALYST COMPOSITION AND REACTION CONDITIONS ON SYNTHESIS OF PHENYL ISOCYANATE BY CARBONYLATION OF NITROBENZENE

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UDC 541.12.038:541.128:542.91:547.551.43

Previously we had established [1] that the carbonylation of aromatic mononitro compounds using $PdCl_2$–pyridine–MoO_3 as the catalyst gives isocyanates in high yield and a study was made of the effect of the nature of the metal oxide on the activity of the Pd catalyst.

In the present paper, on the example of carbonylating nitrobenzene (NB), we studied the effect of the catalyst composition, temperature, contact time, and initial concentration of the starting NB on the synthesis of phenyl isocyanate (I).

$$C_6H_5NO_2 + 3CO \rightarrow C_6H_5N{=}C{=}O(I) + 2CO_2$$

The catalyst $PdCl_2$–pyridine–MoO_3 represents a homogeneous-heterogeneous system. Under the reaction conditions, as was shown previously [2], from $PdCl_2$ and pyridine are formed catalytically active complexes of the type $Pd(pyridine)_2Cl_2$ that are soluble in chlorobenzene. Molybdenum oxide is insoluble in chlorobenzene, but it increases the activity of the $PdCl_2$–pyridine catalyst by a factor of 3 (Table 1), which is apparently due to the faster rate of carbonylating NB in the coordination sphere of the pyridine complex of Pd, adsorbed on the MoO_3 surface, when compared with that of the same complex in solution. Actually, when MoO_3 is deposited on γ-Al_2O_3, despite a fivefold decrease in the amount of MoO_3, the carbonylation rate does not decrease (Fig. 1). A fivefold decrease in the amount of $PdCl_2$ in the $PdCl_2$–pyridine–20% MoO_3/Al_2O_3 catalyst leads to a ninefold decrease in the reaction rate (see Table 1).

Compound (I) forms at an initial rate of 1.5 moles/liter·h when NB is carbonylated on the $PdCl_2$–pyridine–MoO_3 catalyst (1:4:2) at 185° and an initial CO pressure of 100 atm. With increase in the reaction time both the NB conversion and the (I) yield increase and after 60 min respectively reach 100 and 95% (see Fig. 1). We will mention that under the same conditions, without adding MoO_3 to the $PdCl_2$–pyridine complex, the NB conversion was a total of 46%, and the yield was 40%. With further increase in the reaction time the NB conversion remains constant, while the yield of (I) drops due to tarring.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2561-2564, November, 1980. Original article submitted December 10, 1979.