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SYNTHESIS OF AROMATIC DIISOCYANATES BY
CARBONYLATION OF DINITRO COMPOUNDS WITH
CARBON MONOXIDE ON PALLADIUM CATALYSTS

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The carbonylation of aromatic dinitro compounds to form diisocyanates is catalyzed by Pd compounds activated by organic, organometallic, and inorganic compounds [1]. The oxides $\text{Fe}_2\text{O}_3 + \text{MoO}_3$ and $\text{Fe}_2\text{O}_3 + \text{V}_2\text{O}_5$ have an activating effect on PdCl_2 [2, 3].

We have studied the influence of pyridine (Py) and transition-metal oxides, and also the effect of temperature and CO pressure, on the activity of PdCl_2 .

At 200°C and 125 atm, PdCl_2 does not catalyze the carbonylation of 2,4-dinitrotoluene (2,4-DNT) (Table 1). When Py is added to the reaction system (PdCl_2 :Py molar ratio 1:1), 1-methylbenzene-2,4-diisocyanate is formed in a yield of 24% under the same conditions. Addition of V_2O_5 or MoO_3 to PdCl_2 -Py in an amount of 10%, based on 2,4-DNT, increases the yield of the diisocyanate, and a mixture of MoO_3 and Fe_2O_3 (weight ratio 1:2) is even more effective. The oxides of Sc, Mn, Ta, Nb, Cr, and Ni reduce the yield of diisocyanate, giving significant amounts of mononitromonoisocyanates, while CuO and Co_3O_4 inhibit the formation of isocyanates, although the 2,4-DNT is reduced.

TABLE 1. Effect of Transition-Metal Oxides on Carbonylation of 2,4-DNT in the Presence of a PdCl_2 -Py Catalyst (200°C, 125 atm)

Additive	2,4-DNT conversion, %	1-Methylbenzene-2,4-diisocyanate yield, %	Mononitromonoisocyanate yield, %	Additive	2,4-DNT conversion, %	1-Methylbenzene-2,4-diisocyanate yield, %	Mononitromonoisocyanate yield, %
None	0*	0	0	Ta_2O_5	100	13	12
»	100	24	12	Nb_2O_5	100	11	15
V_2O_5	100	36	6	Cr_2O_3	96	11	23
MoO_3	100	36	0	NiO	82	10	32
$\text{MoO}_3 + \text{Fe}_2\text{O}_3$	100	58	0	CuO	88	0	8
Sc_2O_3	100	18	13	Co_3O_4	43	0	0
MnO_2	96	16	25				

* PdCl_2 catalyst.

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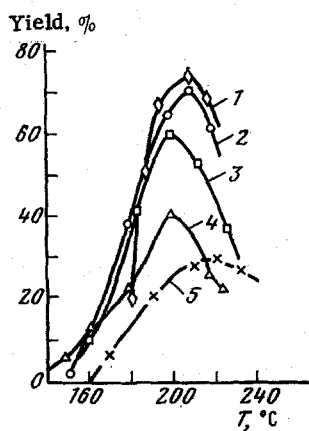


Fig. 1

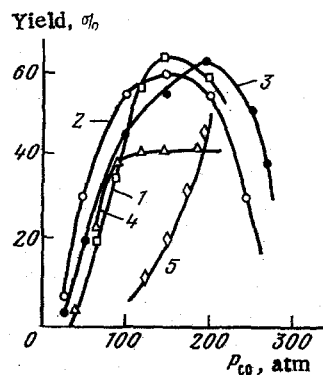
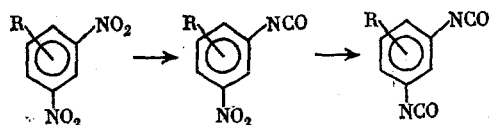


Fig. 2

Fig. 1. Effect of temperature on the yield of 1-methylbenzene-2,4-diisocyanate in the presence of the following catalysts: 1) 7% PdO+5% Fe₂O₃+10% MoO₃/Al₂O₃-Py (1:1); 2) PdCl₂-Py (1:1); 3) PdCl₂-Py-Fe₂O₃-MoO₃ (1:1:0.3:0.6); 4) PdCl₂-Py-10% Fe₂O₃+20% MoO₃/Al₂O₃ (1:1:3); 5) PdCl₂-Py-Fe₂O₃-MoO₃ (1:1:0.5:1). CO pressure, atm: 300 (2), 190 (1), 125 (3), 100 (4), and 50 (5).

Fig. 2. Effect of CO pressure on the synthesis of 1-methylbenzene-2,4-diisocyanate in the presence of the following catalysts: 1) PdCl₂-Py-Fe₂O₃-MoO₃ (1:1:0.3:0.6); 2, 3) PdCl₂-Py-Fe₂O₃-MoO₃ (1:1:0.5:1); 4) PdCl₂-Py-10% Fe₂O₃+20% MoO₃/Al₂O₃ (1:1:3); 5) PdCl₂-Py (1:1). Temperature, °C: 200 (1, 4), 210 (2), 190 (3), and 180 (5).

Thus, the above oxides have the same effect on the PdCl₂-Py catalyst in the carbonylation of 2,4-DNT as in the carbonylation of nitrobenzene to form phenyl isocyanate [4, 5]. In the presence of the oxides of Mn, Cr, and Ni, a considerable amount of mononitromonoisocyanate is formed together with 1-methylbenzene-2,4-diisocyanate, the total yield of mono- and diisocyanates being the same as in the presence of the unpromoted PdCl₂-Py catalyst. Since increasing the temperature decreases the mononitromonoisocyanate yield and simultaneously increases the diisocyanate yield [6], we can assume that the carbonylation of the dinitro compounds proceeds consecutively



Palladium chloride without added Py in the presence of Fe₂O₃+MoO₃/Al₂O₃ (PdCl₂:promoter=1:3) is inactive in the synthesis of 1-methylbenzene-2,4-diisocyanate at 120-160°C and a CO pressure of 100 atm (Table 2). At 120°C, the diisocyanate is not formed in the presence of Py either. At 160°C, the yield of diisocyanate increases with increasing Py concentration, and the yield of mononitromonoisocyanates passes through a maximum at a Py concentration of 0.5%. Thus, as in the case of nitrobenzene [7], the activity of the Pd catalyst in the carbonylation of 2,4-DNT depends on the Py concentration.

The influence of temperature on the yield of 1-methylbenzene-2,4-diisocyanate was studied for the following catalysts: PdCl₂-Py (1:1); PdCl₂-Py-Fe₂O₃-MoO₃ (1:1:0.5:1 and 1:1:0.3:0.6); PdCl₂-Py-Fe₂O₃+MoO₃/Al₂O₃ (1:1:3); and PdO+Fe₂O₃+MoO₃/Al₂O₃ (Fig. 1). In all cases the yield and selectivity for diisocyanate formation increase with increasing temperature and pass through a maximum at 200-220°C. The maximum diisocyanate yield depends on the composition of the catalyst and the pressure of CO; this is in accord with the data in [8].

TABLE 2. Influence of Pyridine Concentration on the Activity of PdCl₂-Py Catalysts Containing 10% Fe₂O₃ + 20% MoO₃/Al₂O₃ in the Carbonylation of 2,4-DNT (PCO 100 atm, time 2 h, concentration of nitro compound 10%)

PY concentra- tion, %	T., °C	2,4-DNT conversion, %	Yield, %	
			diisocyanate	mononitro- monoisocyanates
0	120	47	0	0
1	120	53	0	3
2	120	55	0	2
5	120	60	0	0
10	120	65	0	0
0	160	52	0	2
0,2	160	61	1	3
0,5	160	79	8	19
1	160	95	14	17
2	160	97	19	16
5	160	100	21	11

At a CO pressure of 25 atm, practically no diisocyanate is formed on any of the catalysts studied (Fig. 2). As the CO pressure is increased, the diisocyanate yield on the PdCl₂-Py-Fe₂O₃-MoO₃ catalyst passes through maxima at 150 atm (200°C) and 200 atm (190°C). In the case of the PdCl₂-Py-Fe₂O₃+MoO₃/Al₂O₃ catalyst, increasing the CO pressure from 30 to 100 atm increases the diisocyanate yield by a factor of 10, after which it remains practically unchanged in the 100-200 atm range.

Other dinitro compounds also undergo reaction in the presence of the studied catalysts at elevated pressure (Table 3).

We may conclude that effective catalysts for the production of diisocyanates by carbonylation of aromatic dinitro compounds must contain a Pd compound, an organic base (Py), and V₂O₅ or MoO₃ as essential components.

EXPERIMENTAL

The experiments were conducted in a 50-ml steel autoclave with a magnetic stirrer and in a 150-ml steel rotary autoclave. The autoclave was charged with 10 ml of o-dichlorobenzene, 1-2 g of the dinitro compound, PdCl₂, and Py (nitro compound: PdCl₂: Py = 10:1:1), and with the metal oxides in powder form or supported on Al₂O₃. The autoclave was purged with CO, pressurized with CO, and heated for 2 h. The reaction products were analyzed in a LKhM-8MD or Tsvet chromatograph (1-m column packed with 5% KhE-60 on Chromaton N-AW-DMCS, 0.16-0.2 mm; the carrier gas was He, 40 ml/min). The compounds were identified against standards. The quantitative composition was calculated relative to the internal standard o-dichlorobenzene. The diisocyanates were isolated from the reaction mixture and characterized by IR spectroscopy ($\nu_{\text{NCO}} = 2270-2285 \text{ cm}^{-1}$) and by elementary analysis.

The transition-metal oxides were prepared as described in [9]. The supported oxides were prepared by impregnating γ -Al₂O₃ powder with aqueous solutions of FeCl₃, (NH₄)₂MoO₄, and PdCl₂, followed by drying at 200°C and calcining in an air stream at 500°C for 5 h.

TABLE 3. Synthesis of Aromatic Diisocyanates by Carbonylation of Nitro Compounds in the Presence of 7% PdO + 5% Fe₂O₃ + 10% MoO₃/Al₂O₃ (I) and PdCl₂-Fe₂O₃-MoO₃-Py (1:0.5:1:1) (II)

Starting nitro compound	Diisocyanate yield, %			Mononitromonoisocyanate yield, %		
	I 210°, 300 atm	II 170°, 300 atm	II 220°, 50 atm	I 210°, 300 atm	II 170°, 300 atm	II 220°, 50 atm
1,3-Dinitrobenzene	75	60	28	8	30	7
2,4-Dinitrotoluene	72	90	30	5	1	5
4,6-Dinitro-1,3-dimethyl- benzene	65	65	45	7	0	0
2,4-Dinitro-1,3,5-tri- methylbenzene	64	-	20	12	-	0

CONCLUSIONS

1. The catalytic activity of PdCl_2 in the synthesis of aromatic diisocyanates by carbonylation of dinitro compounds depends on the presence of an organic base (pyridine) and a transition-metal oxide in the reaction system, and on the temperature and pressure.
2. The oxides V_2O_5 and MoO_3 activate the PdCl_2 -pyridine catalyst, the oxides of Sc, Cr, Mn, and Ni reduce the yield of diisocyanates, and Co_3O_4 and CuO inhibit their formation.
3. The yield of aromatic diisocyanates in the presence of Pd catalysts increases with increasing CO pressure and passes through a maximum at 190-200°C.

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