ORGANIC CHEMISTRY

COMBINED CARBONYLATION OF NITRO AND AZO COMPOUNDS IN THE SYNTHESIS OF ISOCYANATES

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The formation of isocyanates upon the reaction of CO with nitro and azo compounds [1-3] may proceed by various mechanisms. We studied the combined carbonylation of nitro and azo compounds as well as azo compounds taken separately in order to reveal the differences in their reactivity.

Nitro compounds (NC) in the presence of $PdCl_2$, K_2PdCl_4, and $(Pd(CO)Cl)_n$ do not react with CO while azo compounds (AC) react in 80-100% conversion to give 30-40% yields of isocyanates (PdO/Al_2O_3 and palladium black are not active catalysts for this reaction).

Upon the addition of pyridine to the initial solution containing $PdCl_2$, AC and NC, the conversion of the AC decreases while the conversion of NC increases (Figs. 1 and 2). The ratio of the conversions of NC and AC increases with increasing pyridine concentration, while the ratio of the conversions of the individual NC is not altered. Pyridine inhibits the carbonylation of AC significantly less in the absence of NC.

Picolines, lutidines, quinoline, triphenylamine, triphenylphosphine, triethylamine, and benzimidazole have analogous action (Table 1).

Copper halides and oxides as well as chloride and bromide salts of Fe, Co, Ni, Cr, Mo, V, Ti, and Al, in contrast to their oxides, activate the carbonylation of AC in the presence of $PdCl_2$ and pyridine, while potassium halides do not affect the process. Molybdates and vanadates suppress the carbonylation of AC. Molybdic acid and acetyl chloride also activate the catalyst. The activating effect of these compounds (Tables 2-4) on the $PdCl_2$—Py system

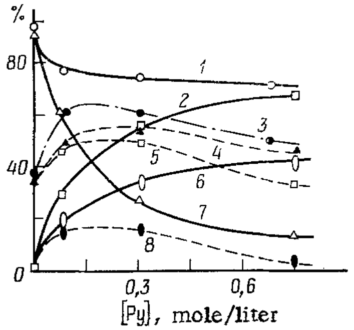

Fig. 1

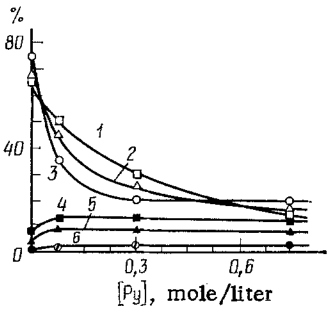

Fig. 2

Fig. 1. Effect of the pyridine concentration in solution on the conversion of azobenzene (1, 7), 3-chloronitrobenzene (6), 3,4-dichloronitrobenzene (2), selectivity of the formation of phenylisocyanate (3, 4), 3-chlorophenylisocyanate (5), and 3,4-dichlorophenylisocyanate (8) in the presence of $PdCl_2$ in the combined carbonylation of nitro and azo compounds (2, 4-8) and carbonylation of only azobenzene (1, 3).

Fig. 2. Effect of the pyridine concentration in solution on the conversion of azobenzene (1-3) and 4-nitrotoluene (4-6) in their combined carbonylation in the presence of $PdCl_2$ (3, 6), $PdCl_2$ + $FeCl_3$ (1, 4), and $PdCl_2$ + $AlCl_3$ (2, 5).

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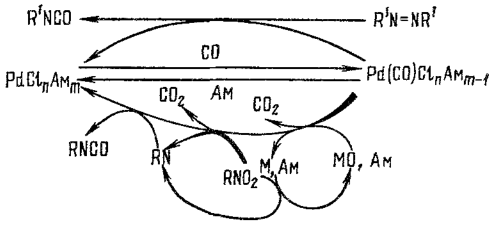
TABLE 1. Effect of Additives on the Combined Carbonylation of 3-Chloronitrobenzene (3-CNB), 3,4-Dichloronitrobenzene (3,4-DCNB), and Azobenzene (AB) in the Presence of $PdCl_2$

Reaction conditions	Additive	Conversion, %			Selectivity (%) for the preparation of isocyanates from		
		3-CNB	3,4-DCNB	AB	3-CNB	3.4-DCNB	AB
170°, 80 atm CO	–	0	10	98	0	0	33
	3,5-Dibromopyridine	0	10	92	0	0	26
	2,6-Lutidine	12	30	48	30	6	64
	2,5-Lutidine	19	34	37	16	7	62
	2-Picoline	27	40	36	48	30	33
	Pyridine	30	54	31	52	15	58
	3-Picoline	31	52	29	45	19	52
	4-Picoline	32	59	26	59	14	49
	4-Ethylpyridine	39	71	25	52	20	54
	3,5-Lutidine	40	69	23	40	18	44
200°, 100 atm CO	–	5	10	100	0	0	18
	Triphenylamine	10	19	73	50	16	33
	Benzimidazole	31	58	7	40	0	80
	Triethylamine	44	98	0	0	0	0
	Triphenylphosphine	57	85	93	4	1	9
	Quinoline	58	90	64	20	0	20
	Pyridine	100	100	57	31	8	67

may result from their capacity to bind pyridine, thereby decreasing its concentration in solution and its inhibiting effect on the carbonylation of AC.

The carbonylation of NC in solutions of $PdCl_2$ and pyridine is activated by Mo and V oxides, chlorides, and bromides of Fe, Co, Ni, Cr, Mo, P, V, Ti, and Al, molybdic acid, molybdates, vanadates, and acetyl chloride (see Tables 2-4). Potassium halides do not affect the activity of the $PdCl_2$—Py system, while oxides of Cu, Co, Ni, Cr, and Al deactivate the catalyst (see Tables 2-4).

Thus, molybdenum oxide, vanadium oxide, vanadates, and molybdates as well as amines and triphenylphosphine have the common property of facilitating the carbonylation of NC and suppressing the carbonylation of AC, especially in the presence of NC. The ability to bind amines masks this property for molybdic acid, vanadium chloride, molybdenum chloride, and ferric chloride in the presence of the $PdCl_2$—Py catalyst. Amines and vanadium and molybdenum compounds in the carbonylation of NC apparently activate the palladium catalyst, thereby accelerating the reduction of the nitro group similar to iron compounds [2-3]. The scheme gives the major directions for the conversion of NC, AC, and the catalyst during this process [Am) amines and triphenylphosphine, M) V, Fe, and Mo compounds in their intial reduced form and MO) the same compounds in their subsequent oxidized form] involving the removal of an oxygen atom from the nitro group: $PdCl_2$ coordinates Am and CO to form $PdCl_nAm_m$ and $Pd(CO)Cl_nAm_{m-1}$ [4] and then $Pd(CO)Cl_nAm_{m-1}$ carbonylates the AC or reduces MO to M with the formation of CO_2. Then, the NC is reduced by reacting with M or with $Pd(CO)Cl_nAM_{m-1}$. The nitrene formed in the reduction of the nitro compound coordinated on M is converted to an isocyanate as a result of reaction with $Pd(CO)Cl_nAm_{m-1}$; Am participates in the transfer of oxygen from the nitro compound to CO_2. In the absence of Am promotors, M, and MO, the carbonylation of nitro compounds is insignificant. This finding indicates that the reaction of nitro compounds with the promotor is the major process in the reduction of these compounds.



The above scheme explains the inhibiting effect of amines and Fe, V, and Mo compounds on the carbonylation of AC in the presence of NC and its diminution in the absence of NC (see Tables 1 and 2 and Fig. 1 as well as our previous work [3]). This inhibiting effect is observed when it is not masked by the promotion effect due to coordination of Am. These schemes permit us to understand the different effect of the CO pressure on the carbonylation of NC

TABLE 2. Effect of Additives on the Combined Carbonylation of 2-Chloronitrobenzene (2-CNB) and 2,2'-Azotoluene (AT) in the Presence of $PdCl_2$ + Py

Additive	Conversion, %		Selectivity (%) for the preparation of isocyanates from		Additive	Conversion, %		Selectivity (%) for the preparation of isocyanates from	
	2-CNB	AT	2-CNB	AT		2-CNB	AT	2-CNB	AT
–	70	45	68	52	MoO_3	100	29	49	45
V_2O_5	97	21	64	52	$CdMoO_4$	100	31	48	42
$Al(VO_3)_3$	99	25	60	50	H_2MoO_4	100	65	55	63
$NaVO_3$	100	31	56	48	$MoCl_5$	100	97	74	53
VCl_3	100	84	45	72	CH_3COCl	98	70	36	50

TABLE 3. Effect of Additives on the Combined Carbonylation of 4-Nitrotoluene (4-NT) and Azobenzene (AB) in the Presence of $PdCl_2$ + Py

T., °C	Additive	Conversion, %		Selectivity of isocyanate preparation from		T., °C	Additive	Conversion, %		Selectivity (%) of isocyanate preparation from	
		4-NT	AB	4-NT	AB			4-NT	AB	4-NT	AB
190	–	25	66	36	60	200	–	40	73	42	52
	TiO_2	25	66	35	58		CoO	10	17	0	0
	Fe_2O_3	24	65	37	62		Co_3O_4	9	15	0	0
	$FeCl_3$	32	80	50	65		Al_2O_3*	0	0	0	0
	Cr_2O_3	18	50	25	30						

*40 mmoles Al_2O_3 per mole $PdCl_2$.

TABLE 3. Effect of Additives on the Combined Carbonylation of 3-Chloronitrobenzene (3-CNB), 3,4-Dichloronitrobenzene (3,4-DCNB), and Azobenzene (AB) in the Presence of $PdCl_2$ + Pyridine

Additive	Conversion, %			Selectivity of isocyanate preparation		
	3-CNB	3,4-DCNB	AB	3 CNB	3,4-DCNB	AB
KI	25	40	27	38	10	40
–	29	47	33	40	15	50
KBr	32	54	34	54	18	42
$CoCl_2$	43	60	45	25	10	26
$CrCl_3$	48	61	49	18	4	68
$AlCl_3$	45	65	50	34	–	55
$MoCl_5$	86	100	88	61	–	64
VCl_3	74	100	22	84	0	40
PBr_3	100	100	100	33	6	42
NiO	35	38	17	3	2	12
NiI_2	17	30	45	6	3	18
$NiBr_2$	54	85	78	37	6	70
$NiCl_2$	45	63	37	31	11	36
Cu_2O	12	25	53	41	4	60
CuO	12	24	54	41	4	80
CuI	0	8	67	–	–	47
CuBr	7	23	70	–	–	36
$CuBr_2$	10	37	76	40	6	40
CuCl	33	47	74	–	–	32
$CuCl_2$	28	51	82	–	–	28
$FeCl_3$	45	62	39	81	60	68
$FeBr_3$	46	70	86	12	3	35

and AC (Fig. 3): CO pressure above 80 atm does not affect the conversion of NC and the isocyanate yield (at 80 atm, the conversion and yield are also independent of the initial NC concentration), while an increase in the CO pressure to 235 atm increases the conversion of AC and the isocyanate yield. Indeed, according to this scheme, the AC conversion and isocyanate yield should increase with increasing CO pressure since the rate of AC carbonylation is roughly proportional to $[PdCl_2]P_{CO}[AC]$. The NC conversion and isocyanate yield may be independent of the CO pressure and initial NC concentration since the rate of NC carbonylation may be proportional to [NC][M][Py].

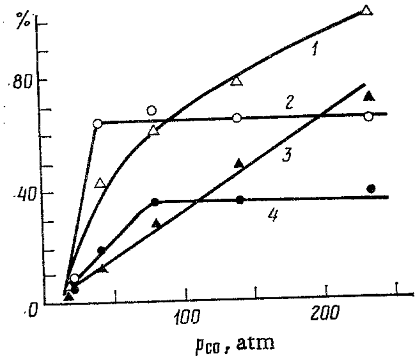


Fig. 3. Effect of the CO pressure on the conversion of azobenzene (1) and 4-nitrotoluene (2), yield of phenylisocyanate (3) and 4-tolylisocyanate (4) in the presence of $PdCl_2$ and pyridine.

In the presence of vanadium and molybdenum compounds, nitro compounds are converted to isocyanates, bypassing the formation of AC, apparently as a result of the carbonylation of the intermediate nitrene complexes with the catalyst [3]. Using the property of a series of organic bases to inhibit the carbonylation of AC in the presence of $PdCl_2$, we found that azo compounds are not intermediates in the conversion of nitro compounds to isocyanates in the absence of vanadium and molybdenum compounds.

EXPERIMENTAL

The carbonylation was carried out in a 0.15-liter steel autoclave in a glass insert (Fig. 2) or without this insert (Figs. 1 and 3, Tables 1-4), in which we loaded 100 mmoles chlorobenzene (solvent) (Figs. 1 and 3, Tables 1-4), or 20 mmoles of this solvent (Fig. 2), 1.5 mmole nitro and azo compounds (Table 4, Fig. 1), 2.4 mmoles of these compounds (Fig. 3, Tables 2 and 3) or 0.33 mmoles of these compounds (Fig. 2), 0.28 mmole $PdCl_2$ (Figs. 1 and 3, Tables 1-4) or 0.06 mmole $PdCl_2$ (Fig. 2), 2.5 mmoles pyridine (Fig. 3, Tables 1-3) or the additives (Table 1) and 0.74 mmole additive/(number of metal ions in the formula) inorganic salt or 0.47 mmole organic additive (Tables 2-4) or 0.28 mmole $AlCl_3$ or $FeCl_3$ (Fig. 2). The autoclave was flushed with CO and the CO pressure was raised to 100 atm (Tables 3 and 4, second part of Table 1) or 80 atm (Table 2, Figs. 1 and 2) and heated at 200°C (second parts of Tables 1 and 3), 190°C (first part of Table 3), 180°C (Fig. 3, Table 2), 170°C (first part of Table 1, Fig. 1), 160°C (Table 4, Fig. 2) for 1 h (Fig. 2), 45 min (Tables 1 and 4, Fig. 1), 30 min (Table 3), or 20 min (Fig. 3 and Table 2). The reaction products were analyzed by gas—liquid chromatography by analogy to our previous work [3].

CONCLUSIONS

1. In the synthesis of isocyanates by the carbonylation of azo compounds, palladium chloride displays activity without promotors, organic bases inhibit the action of palladium chloride, while Lewis acids activate the palladium chloride—pyridine catalyst.

2. Azo compounds are not intermediates in the conversion of nitro compounds to isocyanates in the presence of palladium chloride and pyridine.

3. A scheme was proposed for the activating effect of amines, triphenylphosphine, and compounds of iron, molybdenum, and vanadium added to the palladium catalyst for the synthesis of isocyanates by the carbonylation of nitro compounds.

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