# CARBONYLATION REACTIONS COMMUNICATION 20. SYNTHESIS OF N-SUBSTITUTED PROPIONAMIDES FROM CARBON MONOXIDE, ETHYLENE, AND AMINES IN PRESENCE OF SOME TRANSITION-METAL SALTS

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Previously some esters of  $\beta$ -alkoxypropionic acid were synthesized by the carbonylation of ethylene with CO in alcohol medium in the presence of Hg(OCOCH<sub>3</sub>)<sub>2</sub> [1] or CuCl<sub>2</sub> [2], while some amides of propionic acid were synthesized in an amine medium in the presence of Hg(OCOCH<sub>3</sub>)<sub>2</sub> [3]. The carbonylation of ethylene in an amine medium in the presence of Co, Ni, Fe, and Cu salts has practically not been studied. It is known that amines under the influence of the salts of a number of transition metals of the IV-V periods easily react with CO to give the corresponding formamide [4]. The carbonylation of amines with CO proceeds via the intermediate formation and oxidation-reduction decomposition of the complexes of the transition-metal salt with the amine, which prove to be charge-transfer complexes (CTC) [4]. It is known that ethylene is also capable of forming complexes with transition-metal salts [5], which differ in their structure and bond character from the complexes of the same salts with amines.

$$NH + C_0 X_2 \rightarrow \left[ \begin{array}{c} N \rightarrow C_0 - X \\ | & | \\ H & X \end{array} \right] \rightarrow N' + C_0 X + HX$$

In the present paper it was established that in the range 180-270°C, and a pressure of 100 atm for the  $1:1 \text{ CO-}C_2H_4$  mixture, ethylene was carbonylated in an amine medium in the presence of CO salts to the corresponding propionic acid N-substituted amide in up to  $\sim 70\%$  yield. On the example of the carbonylation of C<sub>2</sub>H<sub>1</sub> in piperidine it was established that the yield of propionic acid N-pentamethyleneamide increased nine times when the amount of Co(CHOO), was reduced from 6 to 1 mmoles (Fig. 1). During reaction the  $Co^{2+}$  is not reduced to  $Co^{0}$  and, based on the IR spectral data, is present in the reaction solution as the carbonyl complexes with the amine, that are analogous to the iron carbonyl complexes [6]. The reduction in the yield of the propionic acid amide when the concentration of the cobalt salt is increased cannot be explained by a change in the degree of complexing of the  $Co^{2^+}$  ion, since even after reaction the amount of amine is at least 100 times greater than the amount of metal salt. Deactivation of the cation of the complex by the condensation products can also not be the reason for retarding the reaction since their amount is small, while the formation rate is independent of the amount of Co(HCOO), used for reaction. Apparently, the reaction for the carbonylation of  $C_2H_4$  with carbon monoxide in an amine medium in the presence of Co salts bears a chain character, while the excess salt exerts an inhibiting effect, the same as in the oxidation reactions of paraffins [7]. A similar inhibiting action by Co salts was observed previously in the carbonylation of allylamine [8]. Previously we had shown that the complexes of amines with the salts of Co and certain other transition metals [4] have a donor-acceptorcharacter, and can undergo homolytic oxidation-reduction decomposition with the formation of active radical particles. Apparently, carbonyl complexes of Co are easily formed in the presence of CO, which under the influence of amines undergo oxidation-reduction disproportionation to give mono- and polynuclear cobalt carbonyl anions, with prior replacement of either one or two CO groups of the carbonyl by the amine [9]:

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$$\operatorname{Co}_2(\operatorname{CO})_8 + \operatorname{B} \rightarrow [\operatorname{Co}(\operatorname{CO})_4 \operatorname{B}]^+ [\operatorname{Co}(\operatorname{CO})_4]^-$$

$$3 \operatorname{Co}_2(\operatorname{CO})_8 + 2 n \to 2 [\operatorname{Co}(\operatorname{B})_n]^{2+} [\operatorname{Co}(\operatorname{CO})_4]_2 + 8 \operatorname{CO}$$

#### B = amine

The cobalt carbonyl anions are powerful oxidizing agents and are capable of protonation via cleavage of hydrogen from the amine, and are converted to complex cations with N-Co and N-C-Co. bonds. Such cations  $\overset{\parallel}{O}$ 

at elevated temperature are apparently capable, the same as the CTC between amines and Co salts, of undergoing homolytic decomposition with the formation of aminyl or formyl radicals and coordination-unsaturated particles of type  $[-Co(CO)_{4}]^{2+}$  or  $[-Co(CO)_{3}]^{2+}$ . The latter are easily reduced by CO to cobalt carbonyl, and in an amine medium again form cobalt carbonyl anions as the result of disproportionation. The aminyl and formyl radicals that are formed in one way or another react with either  $C_{2}H_{4}$  or CO and the amine, thus accomplishing chain transfer and giving the reaction products.

$$\begin{array}{c} N' + CO \rightarrow N - C' \xrightarrow{C_2H_4} N - C - CH_2 - CH_2 \cdot \underbrace{HN}_{||} N - C - CH_2CH_3 + N \cdot \underbrace{O}_{||} N - C - CH_2CH_3 + N \cdot \underbrace{O}_{||} N - C - CH_2CH_3 + N \cdot \underbrace{O}_{||} N - \underbrace{O}_{||} N -$$

Ethylene does not react in piperidine medium in the presence of  $CuCl_2$ ,  $NiL_2$ , or  $FeCl_3$ , and instead the amine is carbonylated, in which connection the  $C_2H_4$  exerts an inhibiting effect: the yield of formylpiperidine drops by two to ten times when compared with the yield obtained in the absence of  $C_2H_4$ , and, with the other conditions kept constant, a higher temperature is necessary for reaction to take place (Table 1).

			Amount reacted			Amount formed		
Amount of salt, moles x 10 <sup>4</sup>	Amine/salt moleratio	T., °C	CO, moles	C <sub>2</sub> H <sub>4</sub> , molês	píper- idine, %	formy1- piper- idine, moles	propi- onic acid amide, moles	tars, in % of starting amine
Ni (HCOO)2•2H2O								
27 27 270	150 150 15	250 270 290	0,04 0,16 0,11	0,0 <b>4</b> 0,0 0,0	$   \begin{array}{c}     11,0 \\     42,2 \\     29,0   \end{array} $	0,08 0,06	0,04 0 0	4,6 5,6 11.1
Cu (HCOO)2•2H2O								
22 13 32	184 310 130	250 250 250	0,11 0,04 0,16	0,10 0,0 0,0	30,0 10,8 42,0	0,04 0,16	0,10 0 0	$4,6 \\ 2,5 \\ 4,3$
CuCl2•2H2O								
12 30 30 59	338 135 135 69	300 300 250 200	0,20 0,20 0,16 0,18	0,0 0,0 0,0 0,0	$53,0 \\ 52,7 \\ 43,3 \\ 47,7$	0,10 0,13 0,15 0,10	0,03 0,03 0	17,6 12,3 7,0 6,5
FeCl <sub>3</sub>								
12 · 30	338 135	250 250	0,05 0,09	0,0 0,0	21,4 29,8	0,01 Tr	0 aces	1,8 13,9
NiI2								
30 30	135 133	250 270	0,12	0,0 0,0	$\begin{vmatrix} 31,6\\34,0 \end{vmatrix}$	0,1 0,12		$4,5 \\ 5,6$
				CoCO <sub>3</sub>				
41	99	250	0,12	0,12	35,2	0,0	0,11	3,4
$Co (HCOO)_2 \cdot 2H_2O$								
5 11 27 40 54 27 27 27 27	810 368 150 100 75 150 150 150	250 250 250 250 250 180 200 270	$\begin{bmatrix} 0,11\\ 0,20\\ 0,20\\ 0,16\\ 0,10\\ 0,20\\ 0,12\\ 0,16\\ \end{bmatrix}$	$\begin{array}{c} 0,11\\ 0,20\\ 0,20\\ 0,16\\ 0,10\\ 0,20\\ 0,12\\ 0,12\\ 0,16\\ \end{array}$	29,8 52,5 57,9 45,5 34,6 47,0 46,5 47,0	0 0 0 0 0 0 0 0	0,10 0,19 0,19 0,16 0,09 0,18 0,13 0,16	4,0 4,0 5,5 4,6 4,9 1,5 1,8 1,9
Mg (HCOO)2•2H2O								
<b>3</b> 3	122	250	0,06	∫ 0,0	6,5	0,02	1 0	3,7
$\mathbf{Z}$ n (HCOO) <sub>2</sub> ·2H <sub>2</sub> O								
26	156	250	0,06	0,0	7,0	0,02	0	5, 5

TABLE 1. Carbonylation of Ethylene in Piperidine Medium at an Initial Pressure of 100 atm for a  $CO: C_2H_4$  Mixture Equal to One



Fig. 1. Yield of propionic acid N-pentamethyleneamide (moles/mole of salt) as a function of amount of  $Co(HCOO)_2$  used for reaction.

Fig. 2. Effect of temperature on yield of propionic acid N-pentamethyleneamide (moles) (1) and amount of reacted piperidine (2) when ethylene is carbonylated in the presence of piperidine and  $Co(HCOO)_2$  at a initial pressure of 100 atm for the 1 : 1 CO- $C_2H_4$  mixture.

It was shown by the ESR method that the  $Cu^{2^+}$  ion is not reduced noticeably during reaction, and the liquid phase both before and after reaction contains solvated aminyl and nitroxy radicals, analogous to those detected by us previously when the amine complexes of Cu, Co, Ni, and Pd salts, dissolved in the amine, were oxidized with  $O_2$  [10]. If the carbonylation of  $C_2H_4$  in an amine medium is run in the presence of either Cu or Ni formate, then at an amine/formate mole ratio equal to 150-180: 1 the cation of the salt is reduced to the metal and the N-substituted propionamide is formed. The metal cation was not reduced at other ratios between the amine and the formate, and only the N-alkylformamide was formed in small amount. When the Mg and Zn formates were used the propionic acid amides were not formed at all, while the piperidine was carbonylated only to slight degree. In contrast to amines, ethylene has low-lying vacant orbitals, and for this reason its coordination with the metal ions is accomplished both via the simple  $\sigma$ -coordination bond and via the reverse transfer of an electron from the metal to the ligand. When ethylene is carbonylated in an amine medium in the presence of Cu, Ni, or Fe salts a complex with mixed ligands is formed in the first step of the reaction, in whose coordination sphere the molecules of both the amine and  $C_{2}H_{4}$  are present as the ligands. Such complexes are apparently more stable than the donor-acceptor complexes of the salts of these metals with amines due to the stabilizing effect of ethylene as the result of forming a dative bond and shifting the excess electron density from the metal to ethylene. For this reason the carbonylation of piperidine with CO in the presence of Cu, Ni or Fe salts is inhibited when ethylene is added to the reaction system, and a higher temperature is necessary for the reaction to proceed. Ethylene does not enter into the reaction here and the propionic acid amides are not formed. When the Cu and Ni formates are used the latter are formed only as the result of the complete oxidation-reduction decomposition of the complexes, with a reduction of the cation to the metal. Despite the formation of the metal, the reaction proceeds homogeneously in the liquid phase, since it is initiated by the active readical particles and goes with chain transfer.

### EXPERIMENTAL METHOD

The experiments were performed in a rotating 0.15-liter steel autoclave. The charge in each experiment was 0.1-1.0 g of the metal salt and 40 ml of the amine. After blowing the autoclave with CO the pressure of the 1 :  $1 \text{ CO-C}_2\text{H}_4$  mixture was raised to 100 atm and the autoclave was heated at  $150-270^\circ$  for 5 h. The liquid reaction products were fractionally distilled from a Favorskii flask and the obtained fractions were analyzed on an LCM-8MD chromatograph (10% Apiezon L deposited on Chromosorb W, 30-60 mesh; carrier gas helium, and flow rate = 40 ml/min). The fractions that corresponded to the carbonylation products were determined. The solid products were purified by recrystallization.

Propionic Acid N,N-Diethylamide. A mixture of 40 ml of diethylamine and 0.5 g of  $Co(HCOO)_2$  was heated for 5 h at 250, 280, and 300°. Here 0.04-0.05 mole of  $C_2H_4$  and 0.09-0.11 mole of CO were absorbed. The diethylamine reacted to the extent of 17-28%, and its conversion was: 11.5-19.5% to N,N-diethylforma-mide ( bp 170-173°) 5-9% to propionic acid N,N-diethylamide ( bp190-193°) and 1-3% to N,N,N',N'-tetra-ethyleneurea ( bp 210-215°). The yield of tar was 2.8-3.9% of the starting amine.

<u>Propionic Acid N-sec-Butylamide.</u> A mixture of 40 ml of sec-butylamine and 0.5 g of Co(HCOO)<sub>2</sub> was heated for 5 h at 200°. Here 0.29 mole of CO and 0.29 mole of  $C_2H_4$  were absorbed. The amount of reacted amine was 0.29 mole (74.2%), with the formation of 0.28 mole of propionic acid N-sec-butylamide, bp 220-222°, mp 34°. Found: C 65.24; H 11.52; N 11.21%.  $C_7H_{15}NO$ . Calculated: C 65.12; H 11.63; N 10.85%. The yield of tar was ~3% of the starting amine.

Propionic Acid N-Pentamethyleneamide. A mixture of 40 ml of piperidine and 0.5 g of  $Co(HCOO)_2$  was heated for 5 h at 250°. Here 0.20 mole of CO and 0.20 mole of  $C_2H_4$  were absorbed. The amine reacted to the extent of 58%, with the formation of 0.19 mole of propionic acid N-pentamethyleneamide, bp 231-232°,  $n_D^{20}$  1.4829. Found: C 68.10; H 10.42; N 10.15%.  $C_8H_{15}NO$ . Calculated: C 68.08; H 10.63; N 9.92%. The yield of tar was 5.5% of the starting amine.

<u>N-Propionylmorpholine</u>. A mixture of 40 ml of morpholine and 0.5 g of Co(HCOO)<sub>2</sub> was heated for 5 h at 200°. Here the extent of reaction was: 0.2 mole (43%) of morpholine, 0.14 mole of CO, and 0.07 mole of  $C_2H_4$ . The morpholine was converted to formylmorpholine, bp 240-242°,  $n_D^{20}$  1.4815;  $d_4^{20}$  1.1265, and to the extent of 50% to N-propionylmorpholine, bp 121-123° (10 mm),  $n_D^{20}$  1.4831,  $d_4^{20}$  1.0962. Found: C 58.20; H 10.00; N 10.10%.  $C_7H_{13}NO_2$ . Calculated: C 58.70; H 9.09; N 9.78%.

Propioanilide. A mixture of 40 ml of aniline and 0.5 g of Co(HCOO)<sub>2</sub> was heated for 5 h at 180 and 200°. Here ~0.17 mole of CO and ~0.03 mole of  $C_2H_4$  were absorbed. The aniline reacted to the extent of 35-38%, and its conversion was: 16-17% to propioanilide, bp 221-223° and mp 105; 70-72% to formanilide, bp 270-274; and 9-10% to N,N'-diphenylurea, mp 240°. The yield of tar was 2-3% of the starting amine.

Effect of Temperature on Synthesis of Propionic Acid N-Substituted Amides. The effect of temperature was studied on the example of the reaction of  $C_2H_4$  with CO and piperidine in the presence of 0.0027 mole of Co(HCOO)<sub>2</sub>. Reaction is practically nil up to temperatures of 150° (Fig. 2). Both the piperidine conversion and the yield of propionic acid N-pentamethyleneamide steadily increase with increase in the temperature in the range 150-270°, pass through a maximum at 220-250° (the amine conversion is 50-52%, and the yield of the amide is ~70 mole% of the starting amine), and they they decrease.

## CONCLUSIONS

The carbonylation of ethylene with CO using aliphatic, alicyclic or amomatic amines as the medium, in the presence of the salts of certain transition metals, proceeds at  $200-250^{\circ}$  and an initial pressure of 100 atm for the 1 :  $1 \text{ CO-C}_{2}H_{4}$  mixture to give the corresponding propionic acid N-substituted amide in a yield of up to 70 mole % when based on the amine taken for reaction.

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