# CARBONYLATION REACTIONS

## COMMUNICATION 19. ACTIVITY OF SALTS OF GROUP II METALS OF PERIODIC SYSTEM IN CARBONYLATION OF AMINES WITH CARBON MONOXIDE

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The salts of the Group II metals of the periodic system as catalysts for carbonylation reactions have remained practically unstudied. It was reported that $CaCl_2$ has a low activity in the carbonylation of alicyclic amines [1], and that the complexes of Ca, Ba, and Mg can be used to synthesize carboxylic acid amides from olefins, CO and amines [2]. We established that piperidine at 200-250°C and an initial CO pressure of 100-200 atm is converted to the formyl derivative in the presence of the salts of the mineral and organic acids of Mg, Ca, Sr, and Ba (Table 1). Besides formylpiperidine (in up to 82% yield when based on starting amine), N,N'-dipentamethyleneurea was formed in an amount of 1 mole per mole of metal salt, and also a small amount of tar (4-7% of the starting amine), which, based on the IR spectral data, represented the condensation products of piperidine with formylpiperidine. By means of special experiments it was shown that amines, in the absence of salts of the Group II metals, do not react with CO under our studied conditions. These data completely exclude the possibility of formation and the secondary catalytic effect of metal carbonyls during the contact of the CO with the autoclave material under the synthesis conditions. The most active of the studied catalysts proved to be $CaCl_2$, in whose presence piperidine reacted to the extent of 80-91% and was converted to formylpiperidine in ~82% yield. The activity of the salts of the Group II metals in the carbonylation of piperidine decreased in the order: $CaCl_2 > SrCl_2 > MgCl_2 > BaCl_2 > Ca_3(PO_4)_2 > SrC_2O_4 \sim Be(CH_3COO)_2$. On the example of $BaCl_2$ it was shown that an optimum temperature exists, at which a maximum yield of the carbonylation products is obtained. The reaction rate is slow at lower temperatures; at higher temperatures the processes for the decomposition of the formyl derivative of the amine and polycondensation with the formation of tar are enhanced. Thus, in the presence of $CaCl_2$, piperidine at 300° and higher is completely converted to tarry condensation products, which contain carbonyl groups attached to nitrogen ($\Delta\nu$ 1640-1660 $cm^{-1}$). With increase in the pressure from 50 up to 100 atm the yield of formylpiperidine steadily increases and then it remains constant in the range 100-200 atm (Fig. 1). The amounts of reacted CO and amine change in a similar manner with increase in the pressure.

Diethylamine is carbonylated at a higher temperature than piperidine, in which connection the yield of N,N-diethylformamide does not exceed 20-22% when based on starting amine. The carbonylation is accompanied by the simultaneous conversion of the diethylamine to ethylamine and triethylamine, which is sharply enhanced above 300° (Table 2).

On the example of the carbonylation of piperidine with CO in the presence of $CaCl_2$ at 200° and a pressure of 80 atm it was established that the yield of formylpiperidine in moles per mole of metal salt is inversely proportional to the $CaCl_2$ concentration in the starting amine solution (Fig. 2). The yield of N,N'-dipentamethyleneurea is independent of the $CaCl_2$ concentration. The yield of formylpiperidine as a function of the salt concentration, shown in Fig. 2, makes it possible to conclude that $CaCl_2$, and apparently other salts of the Group II metals, do not catalyze, but rather initiate the studied reaction, while excess salt, in contrast, inhibits the carbonylation. As a result, the same relation between the yield of carbonylation products and the metal salt concentration is observed as when the salts of the transition metals of

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TABLE 1. Carbonylation of Piperidine in Presence of Salts of Group II Metals of Periodic System ($p_{CO}$ 100 atm, amount of metal salt 0.2 g/25 g of amine)

| T., °C | Amount reacted | | Amount of formylpiperidine formed,* moles | Yield of formylpiperidine | | |
|---|---|---|---|---|---|---|
| | CO, moles | piperidine, % | | in mole %·of amine: starting | in mole %·of amine: reacted | in moles per mole of salt |
| $CaCl_2 \cdot 2H_2O$; $CaCl_2$ (anhydrous) | | | | | | |
| 200 | 0,20 | 80,2 | 0,20 | 70,0 | 87,0 | 111,0 |
| 250 | 0,24 | 91,5 | 0,23 | 82,0 | 87,5 | 128,0 |
| $Ca_3(PO_4)_2$ | | | | | | |
| 200 | 0,07 | 20,5 | 0.06 | 21,0 | 96,0 | 92,0 |
| 250 | 0,07 | 21,8 | 0,07 | 25,0 | 98,0 | 108,0 |
| $SrCl_2 \cdot 2H_2O$ | | | | | | |
| 250 | 0,18 | 63,4 | 0,18 | 63,1 | — | 179,0 |
| $SrC_2O_4 \cdot H_2O$ | | | | | | |
| 250 | Traces | Traces | Traces | Traces | | — |
| 300 | 0,04 | 14,0 | 0,02 | 9,2 | 96,0 | 20,0 |
| $Be(CH_3COO)_2$ | | | | | | |
| 300 | 0,02 | 7,0 | 0,02 | 7,0 | — | 13,2 |
| $MgCl_2 \cdot 6H_2O$ | | | | | | |
| 200 | 0,06 | 23,6 | 0,06 | 21,0 | 90,0 | 60,0 |
| 250 | 0,18 | 66,9 | 0,17 | 59,5 | 95,0 | 170,0 |
| $BaCl_2 \cdot 2H_2O$ | | | | | | |
| 220 | 0.08 | 22.0 | 0,07 | 22,0 | 87,5 | 89,0 |
| 250 | 0,14 | 63,4 | 0,11 | 49,5 | 61,0 | 138,0 |
| 290 | 0,06 | 18,2 | 0,03 | 11,0 | 50,0 | 37,0 |

*Besides formylpiperidine, N,N'-dipentamethyleneurea was formed in all cases in a yield of 1 mole per mole of salt.

TABLE 2. Carbonylation of Diethylamine in Presence of $CaCl_2$ ($CaCl_2$ 0.018 mole, $p_{CO}$ 100 atm)

| T., °C | Amount reacted, moles | | Amount formed | | | |
|---|---|---|---|---|---|---|
| | | | N, N-diethylformamide | | ethylamine, moles | triethylamine, moles |
| | CO | diethylamine | moles | in % of starting amine | | |
| 250 | 0,02 | — | — | Traces | — | — |
| 300 | 0,06 | 0,12 | 0,06 | 21,8 | 0,01 | 0,05 |
| 320 | 0.07 | 0,14 | 0,07 | 24,6 | 0,02 | 0,05 |
| 350 | 0,22 | 0,23 | 0,06 | 20,0 | 0,02 | 0,01 |

Periods III-IV are used, which relation characterizes the reaction as proceeding by the chain mechanism [3]. However, in contrast to the transition metals salts, which have a low oxidation-reduction potential and are reduced by the amine by the one-electron transfer mechanism during carbonylation, the salts of the Group II metals are not reduced and remain in solution as the complexes with the amine.

The Group II metals lack d-electrons and do not form carbonyls with CO. As a rule, the complexes of their salts with amines, with a coordination number of 6 [4], are apparently formed via the vacant d-orbitals. However, in contrast to the complexes of amines with the transition metals Cu, Co, Ni, Fe, the activity of which in the carbonylation of amines with CO correlates with the energy value of electron transfer from the ligand (donor) to the metal ion (acceptor) [3], the complexes of the salts of the Group II metals are not charge-transfer complexes, since the energy levels of their d-orbitals are located higher than for the transition metals, and considerable energy is required for complete electron transfer from the ligand to the metal ion ($E_{Mg^\circ} = -2.37$, $E_{Ca^\circ} = -2.86$, $E_{Sr^\circ} = -2.89$. $E_{Ba^\circ} = -2.90$ V). This is confirmed by the electronic absorption spectra, in which the charge transfer bands are absent, and a bathochromic shift of the absorption maxima does not occur, when compared with the spectra of the pure compounds when the polarity of the solvent is increased.

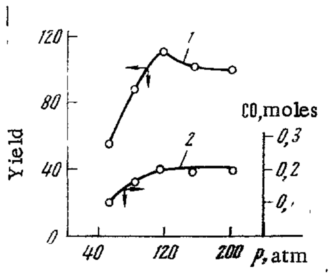

Fig. 1

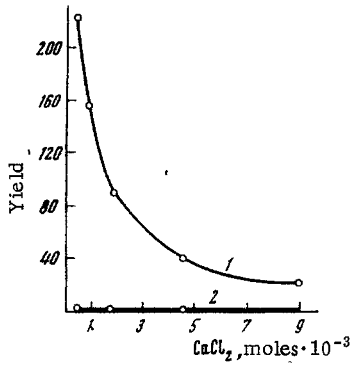

Fig. 2

Fig. 1. Effect of pressure: 1) on yield of formylpiperidine (moles/mole of $CaCl_2$); 2) on amount of reacted CO (moles) in carbonylation of piperidine at 250°.

Fig. 2. Effect of $CaCl_2$ concentration on yield of formylpiperidine (1) and N,N'-dipentamethyleneurea (2) (moles /mole of salt) in carbonylation of piperidine at 200° and an initial CO pressure of 80 atm.

Previously we had shown by the EPR method that when a number of the salts of the transition and nontransition metals is dissolved in piperidine the oxidation of the ligand-bound amine is sharply enhanced by traces of atmospheric $O_2$ dissolved in it, with the formation of either the solvated cation-radicals or the N-oxide radicals [5]. Since when operating in an autoclave it is difficult to remove all of the air dissolved in the amine, it could be assumed that the carbonylation of the amine by CO in initiated by such radical particles and proceeds by the chain mechanism. The role of the salt of the Group II metal apparently consists in activating the amine during its coordination, which facilitates oxidation and the formation of the radical particles. At elevated temperature the latter react with CO and the amine, effecting chain transfer, the same as in the case of the salts of the transition metals. Chain termination occurs as a result of recombination of the radical particles, with the formation of urea and tar, and probably also with excess salt, which at high concentrations acts as an inhibitor of the process.

## EXPERIMENTAL METHOD

The experiments were run in a rotated 0.25-liter steel autoclave, into which in each experiment were charged 0.05-1 g of the metal salt (usually the cp crystallohydrate) and 30-40 ml of the amine, the system was purged with CO, the CO pressure was brought up to 50-200 atm, and the autoclave was heated for 5 h at the given temperature. After cooling, the reaction products were analyzed on an LKhM-8MD chromatograph (7% Apiezon L deposited on Chromosorb W (30-60 mesh), 2-meter column, and carrier gas helium at 40 ml /min). The N,N'-dipentamethyleneurea was separated by filtration, and partially by distillation; it was recrystallized from ethanol and was characterized by the melting point [47°, bp. 180-182° (30 mm)]. The electronic spectra of the piperidine complexes with $CaCl_2$, $MgCl_2$, $SrCl_2$ and $BaCl_2$ were taken on a recording SP-700 spectrophotometer in a quartz cell (layer thickness 0.1 cm) in methanol solution at a salt and amine concentration of $10^{-2}$-$10^{-3}$ M. The IR spectra were taken as a thin layer of the substance between NaCl plates on a UR-20 instrument.

## CONCLUSIONS

1. The salts of the Group II metals cause the carbonylation of piperidine and diethylamine at 200-250° and a CO pressure of 50-200 atm predominantly to the corresponding formyl derivative in up to 82% yield when based on amine taken for reaction.

2. The chlorides are the most effective, the activity of which decreases in the order: $CaCl_2 > SrCl_2 > MgCl_2 > BaCl_2$.

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