CARBONYLATION REACTION

COMMUNICATION 18. ACTIVITY OF SOME TRANSITION METAL SALTS IN INITIATION OF CARBONYLATION OF PIPERIDINE WITH CARBON MONOXIDE

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UDC 542.97:547.822.3:546.262.3-31

The carbonylation of amines with carbon monoxide proceeds vigorously in the presence of Hg(II) [1] and Cu(II) [2] salts, and bears a chain character. These salts fulfill the role of reaction initiators, since they generate the active particles (radicals or ion-radicals) that arise via the intermediate formation and oxidation-reduction decomposition of the complexes of the metal salt with the amine, which have the character of charge-transfer complexes [3]. Since the salts of other transition metals can form complexes with amines, it seemed interesting to study the physicochemical properties of these complexes and their activity in the carbonylation of amines. Statements exist that the salts of certain transition metals can be used to effect the carbonylation of amines [4, 5], but this problem has not been studied in detail.

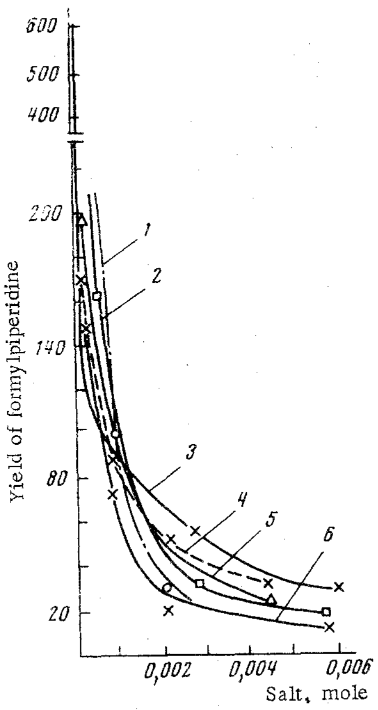

Fig. 1. Yield of formylpiperidine (moles/mole of metal salt) as a function of the number of moles of salt taken for reaction in the carbonylation of piperidine with CO in the presence of: 1) Tl_2SO_4; 2) $AgNO_3$; 3) $SbCl_5$; 4) $SnCl_2$; 5) $CuCl_2$; 6) $Mn(CH_3COO)_2$.

In the present paper we took piperidine, one of the most basic amines (pK_a 11.13), for carbonylation, which reacts easily with CO in the presence of Cu and Hg salts to give predominantly formylpiperidine [1, 2]. As reaction initiators we studied some salts of the metals of periods IV and V, which had variable degrees of oxidation and a variable configuration of the d shell of the metal ion: $CrCl_3 \cdot 6H_2O(3d^3)$, $Mn(CH_3COO)_2 \cdot 4H_2O(3d^5)$, $Co(HCOO)_2 \cdot 2H_2O(3d^7)$, $NiI_2(3d^8)$, $ZnCl_2(3d^{10})$, $AgNO_3(4d^{10})$, $SdCl_6(4d^{10})$, $SnCl_2(4d^{10}5s^2)$, and $Tl_2SO_4(5d^{10}6s^2)$, as a supplement to those previously studied by us: $FeCl_3(3d^5)$ [6], $CuCl_2 \cdot 2H_2O(3d^9)$ [2], $CuCl \cdot H_2O(3d^{10})$, and $Hg(CH_3COO)_2(3d^{10})$ [1]. The obtained results are given in Table 1. From Table 1 it can be seen that all of the studied salts proved to be active initiators for the carbonylation of piperidine with carbon monoxide at 200-300°C and a pressure of 100-120 atm. A decrease in the salt concentration leads to an intensification of the carbonylation reaction and an increase in the yield of formylpiperidine when based on 1 mole of metal salt taken for reaction (Fig. 1). A similar relation was obtained by us previously when the amines were carbonylated in the presence of Cu, Fe, and Hg salts, and also by other authors for the liquid-phase oxidation of paraffins in the presence of transition metal salts [7, 8].

From the data given in Table 1 and those obtained by us previously it can be seen that the most active salts in the carbonylation of piperidine are: $CuCl \cdot H_2O$, $CuCl_2 \cdot 2H_2O$, $SbCl_5$, $CrCl_3 \cdot 6H_2O$, $Co(HCOO)_2 \cdot 2H_2O$, $FeCl_3$, and NiI_2. In their presence the yield of

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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. 2535-2541, November, 1974. Original article submitted December 19, 1973.

TABLE 1. Carbonylation of Piperidine in the Presence of Some Transition Metal Salts at a CO Pressure of 100 atm

Piperidine: metal salt mole ratio	Amount reacted		Amount of formylpiperidine formed, mole
	CO, mole	piperidine, %	
	$CrCl_3 \cdot 6H_2O$, 200°		
1000	0,05	30,8	0,04
500	0,09	38,4	0,08
20	0,13	92,0	0,12
10	0,24	98,0	0,22
	$Mn(CH_3COO)_2 \cdot 4H_2O$, 250°		
750	0,08	30.0	0.07
375	0,08	31,0	0,07
150	0.06	28,4	0,05
75	0,16	44,5	0,12
50	0,11	50,0	0,10
	NiI_2, 300°		
938	0,16	72,5	0,15
469	0,17	88,5	0,17
188	0.07	33,4	0,06
94	0,16	48,0	0,15
136	0,24	85,5	0,20
	$Co(HCOO)_2 \cdot 2H_2O$, 250°		
600	0,06	8.0	0,05
300	0,08	10,0	0,08
120	0,14	52,5	0,12
60	0,16	78.5	0,15
40	0,20	84.0	0,20
	$ZnCl_2$, 200°		
700	0,06	22,4	0,06
350	0,09	35,0	0,09
88	0.11	54,8	0,10
	$SbCl_5$, 250°		
2143	0,13	59,0	0,13
1500	0,13	60,0	0,13
1111	0,12	58,2	0,12
111	0,16	68.4	0,16
50	0,22	98,5	0,22
	$SnCl_2$, 250°		
750	0,07	38.0	0,06
333	0,08	36,5	0,08
136	0,14	65,5	0,12
68	0,16	76,0	0,15
	Tl_2SO_4, 300°		
1500	0,07	29.0	0,07
750	0,12	43,0	0,11
300	0,11	45.5	0,10
214	0,11	49,5	0,10
150	0,07	40.0	0.06
	$AgNO_3$, 300°		
1000	0,09	22,2	0,09
500	0,11	34,0	0,10
250	0,11	34,0	0,10
103	0,11	33,0	0,09
50	0,14	36,0	0,12

formylpiperidine reached 84-98% of the starting piperidine. NiI_2 was active only above 250°C (Table 2). $ZnCl_2$, $SnCl_2$, and $Mn(CH_3COO)_2 \cdot 2H_2O$ had medium activity, and they caused a 50-70% conversion of the piperidine. The optimum temperature for the carbonylation of piperidine in the presence of Tl_2SO_4 and $AgNO_3$ is 300°C, in which connection the yield of formylpiperidine did not exceed 36-50% when based on taken piperidine. However, in contrast to NiI_2, the carbonylation of piperidine in the presence of $AgNO_3$ also proceeded below 250°C (Table 3).

All of the metal salts studied by us have a d shell with a variable degree of filling and are good complexing agents [9]. However, the order of activity observed by us for these salts in the carbonylation of piperidine cannot be explained from the standpoint of the coordination catalysis theory, since, first, a cyclic recurrence of the transformation of the reagents is absent, and, as a rule, the salt is reduced to the metal; second, a correlation is absent between the activity and the stabilization energy of the crystalline field of the ligand, which in period IV is maximum for the metal ions with a $3d^3$—$3d^8$ configuration of the electron shell, i.e., for the ions: Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} [10]. The value of the stabilization energy Dq for the ions with $3d^9(Cu^{2+})$ and $3d^{10}(Cu^+, Zn^{2+})$ configurations is minimum, but the activity of their salts is considerably higher than that of the salts of the metals found in the middle of period IV.

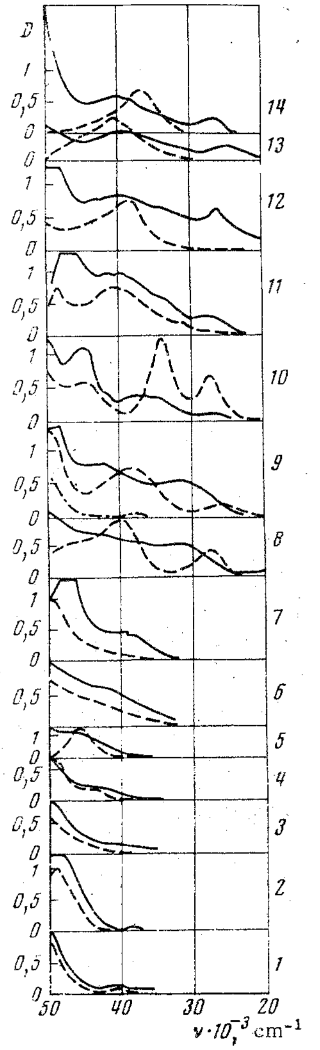

Fig. 2. Ultraviolet spectra of complexes of metal salts with piperidine in methanol at a component concentration of 10^{-3} mole/liter: 1) $AgNO_3$; 2) $Hg(CH_3COO)_2$; 3) $ZnCl_2$; 4) $SnCl_2$; 5) $CrCl_3$; 6) $Mn(CH_3COO)_2$; 7) $Co(HCOO)_2$; 8) $FeCl_3$; 9) $FeBr_3$; 10) NiI_2; 11) $Cu(CH_3COO)_2$; 12) $CuSO_4$; 13) $CuCl_2$; 14) CuCl. The broken lines depict the absorption of the salt in methanol, the solid lines the absorption of the complex.

In a previous paper [3] it was shown that the complexes of $CuCl_2$ with amines, which are formed in the first step of the carbonylation reaction, have a strongly expressed oxidation-reduction character of the charge-transfer complexes (CTC). Consequently, it is possible to assume that the reaction for the carbonylation of amines in the presence of transition metal salts does not proceed via the reaction of the ligand-bonded piperidine and CO in the metal-complexing agent coordination sphere, but rather via the formation and oxidation-reduction decomposition of the intermediately formed complexes, which should also have the character of CTC. It is known that the ease of electron transition from donor (amine) to acceptor (metal ion) in such complexes and, consequently, also their activity, should be primarily determined by the values of the ionization potential of the donor and the electron affinity of the acceptor or the energy of electron transfer. Actually, as a first approximation, for the transition metals of periods IV and V a correlation is observed between the activity of their salts in the studied reaction and the difference in the oxidation-reduction potentials of piperidine and the metal ion: CuCl (1.76) > $CuCl_2$ (1.58), $SbCl_5$ > $CrCl_3$ (0.90) > $Co(HCOO)_2$ (0.96), NiI_2 (0.99), $FeCl_3$ > $ZnCl_2$ (0.48), $SnCl_2$, $Mn(CH_3COO)_2$ (0.66) > Tl_2SO_4, $AgNO_3$, $Hg(CH_3COO)_2$.

However, estimating the values of the energy of electron transfer in the complexes from the oxidation-reduction potential of the amine-metal salt system is very approximate, since it is impossible to take into account the energy of solvation of the electron, and of the other particles that are formed here, by amines. A more accurate estimate can be obtained from the electronic absorption spectra of the complexes, since the energy of electron transition is characterized by the position of the charge-transfer band and its intensity [11]. In the present paper the electronic spectra of the complexes of pyridine with various salts of some transition metals of periods IV and V were studied for the first time. We always observed the formation of complexes when the metal salt was added to the amine, which was usually accompanied either by a shift of the bands of the starting components or the appearance of new bands or shoulders, most frequently in the longer wavelength region of the spectrum when compared with the position of the bands of the components (Fig. 2). If the absorption band of the salt lies at shorter wavelengths ($\lambda < 200$ nm) than the piperidine band, then a short-wave shift of these bands is observed in the spectra of the complexes, for example, for $Hg(CH_3COO)_2$. Based on the obtained data the studied metal salts can be arranged in the following order of descending λ_{max} of the long-wave absorption bands of the complexes with piperidine: CuCl > $CuCl_2$ > NiI_2, $FeBr_3$, $FeCl_3$, $Co(HCOO)_2$ > $CrCl_3$ > $SnCl_2$, $Mn(CH_3COO)_2$, $ZnCl_2$ > Tl_2SO_4, $AgNO_3$, $Hg(CH_3COO)_2$.

This order mainly coincides with the order given above for the chemical activity of the transition metal salts as initiators of the reaction for the carbonylation of piperidine, which indicates that a correlation exists between the spectral and chemical properties.* As can be seen from Fig. 2, the absorption bands of the more chemically active complexes lie in the longer wavelength portion of the spectrum. Thus, for example, the absorption bands of the active

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*Together with the intense charge-transfer bands, the spectra of the complexes have weak bands of the d—d transitions, which are located in the visible region. Their position and intensity do not correlate with the chemical activity, and consequently these bands are not discussed here.

TABLE 2. Effect of Temperature on Yield of Formylpiperidine When 0.3 Mole of Piperidine Is Carbonylated in the Presence of 0.032 Mole of NiI_2 at a CO Pressure of 100 atm

T., °C	Amount reacted		Amount of formylpiperidine formed, mole	Yield of formylpiperidine, moles /mole of NiI_2
	CO, mole	piperidine, %		
250	0,04	—	Traces	Traces
280	0,06	14,8	0,05	15,0
300	0,16	48,0	0,15	47,0
350	0,12	32,0	0,10	31,0

complexes of the copper, nickel, and iron salts lie in the region $20\text{-}30 \cdot 10^{-3}$ cm^{-1} or 300-500 nm, whereas the absorption bands of the less active complexes of the tin, thallium, silver, and mercury salts lie at $40\text{-}50 \cdot 10^{-3}$ cm^{-1} or 200-250 nm. Apparently, the determining factor for both the spectral and chemical properties of the studied complexes is the migration of an electron from the donor to the acceptor, in which connection the smaller the energy of electron transfer (shift of the absorption band of the complex toward longer wavelengths) the more active is the metal salt in the reaction for the carbonylation of the amine with carbon monoxide. The only exception is the complex of piperidine with $CrCl_3$, where the absorption band lies in the short wavelength region ($46 \cdot 10^{-3}$ cm^{-1} or 210 nm). Nevertheless, $CrCl_3$ is quite active in the reaction for the carbonylation of piperidine. The reason for this phenomenon is still not clear.

From an examination of the obtained order in the spectral activity of the transition metal salts it may be concluded that the λ_{max} position of the complexes is determined to large degree by the location of the levels of the excited state of the acceptor, since piperidine is the electron donor in all cases. The closer these levels are located to the level of the unshared pair of the piperidine nitrogen atom the greater should be the migration tendency of the electron, both in the ground and in the excited states [11], and the smaller is the energy required for a complete transfer of the electron from the donor to the acceptor and, consequently, for the oxidation-reduction decomposition of the complex with the formation of active particles (radicals or ion-radicals) that are capable of initiating the chain reaction of the amine with CO.

Previously [10] a correlation was observed between the width of the forbidden zone of a semiconductor and its catalytic activity in oxidation-reduction reactions: the greater the width of the forbidden zone the lower is the catalytic activity. In our case the analog of the width of the forbidden zone is the energy of electron transfer from donor to acceptor in the complexes of the transition metals with amines: $E = h\nu = hc/\lambda$, where ν is the frequency of the maximum of the absorption band. This confirms the fact that the correlation observed by us between the λ_{max} of the charge-transfer band of the complexes and the chemical activity of metal salts in the reaction for the carbonylation of amines with CO is not accidental. The correlation observed between the chemical activity of the transition metal salt and the shift of the charge-transfer band, $\Delta\lambda_{max}$, and the change in the intensity $\Delta\varepsilon$, is also interesting in this respect. In the case of the salts of the metals with a low activity (Sn, Tl, Ag, Hg) the formation of the complex with piperidine is accompanied by a slight change in the position and intensity of the bands of its components, whereas for the complexes of the Cu, Co, Ni, and Fe salts the change is substantially greater. Apparently, this is associated with the fact that the smaller the energy of electron transfer the greater is the portion of the electron density that migrates between the fragments, and the greater is the change in their parameters, and in the absorption bands corresponding to them and the intensity.

As a result, the salts of practically all of the transition metals of periods IV and V are initiators of the reaction for the carbonylation of piperidine with carbon monoxide. The reaction apparently proceeds by the chain mechanism and is inhibited by excess metal salt. The complexes of the metal salt with the amine are formed in the first step of the reaction, which bear the character of CTC. The obtained experimental data indicate that a correlation exists between the chemical activity of the transition metal salt in the initiation of the carbonylation reaction and the value of the energy of electron transfer from donor to acceptor in the complexes of the metal salt with the amine, which is characterized by the intensity and position of λ_{max} of the charge-transfer band of the complex. The initiation of the carbonylation reaction is apparently associated with the oxidation-reduction decomposition of the initially formed complex, which leads to the creation of active particles (radicals or ion-radicals) that initiate the chain reaction of the amine with CO.

TABLE 3. Effect of Temperature on Yield of Formylpiperidine When 0.3 Mole of Piperidine Is Carbonylated in the Presence of 0.006 Mole of $AgNO_3$ at a CO Pressure of 100 atm

T., °C	Amount reacted		Amount of formylpiperidine formed, mole	Yield of formylpiperidine, moles /mole of $AgNO_3$
	CO, mole	piperidine, %		
200	0,07	16,9	0,06	10,0
250	0,10	25,4	0,09	15,3
300	0,14	36,0	0,12	20,4
350	0,16	96 *	0,06	11,2

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*Pronounced tarring.

It is possible to assume that initiators of the reaction for the carbonylation of amines can be not only the transition metal salts, but any compounds that form CTC with amines that have a low energy of electron transfer from donor to acceptor. These complexes should be capable of oxidation-reduction decomposition with the formation of either radicals or ion-radicals.

EXPERIMENTAL

Into a 0.25 liter rotated steel autoclave were charged 0.3-0.4 mole of piperidine and 0.1-2 g of the transition metal salt, the system was purged with 99% pure CO, the CO pressure was raised to 100-120 atm, and the mixture was heated at the reaction temperature for 5 h. The liquid reaction products were separated from the formed metal by filtration, and analyzed on an LCM-8 MD chromatograph (10% Apiezon L deposited on Chromosorb W, 30-60 mesh; carrier gas = helium). The electronic spectra of the complexes were taken in methanol at a concentration of 10^{-2}-10^{-3} mole/liter on a recording SP-700 spectrophotometer in a quartz cell at a layer thickness of 0.1 cm.

CONCLUSIONS

1. The salts of all of the transition metals of periods IV and V of the periodic system are active initiators for the carbonylation of piperidine with carbon monoxide at 200-300°C and a pressure of 10 atm. The salts of Cu, Sb, Cr, Co, and Ni have the highest activity, and in their presence the yield of formylpiperidine reached 84-98% when based on amine taken for reaction.

2. Based on the data of the electronic spectra, a correlation was found to exist between the chemical activity of the transition metal salts and the value of the energy of electron transfer from donor to acceptor in the complex of this salt with the amine, which is characterized by the position and intensity of the absorption maximum of the charge-transfer band.

LITERATURE CITED

1. B. K. Nefedov, N. S. Sergeeva, and Ya. T. Éidus, Izv. Akad. Nauk SSSR, Ser. Khim., 807 (1973).
2. B. K. Nefedov, N. S. Sergeeva, T. L. Klusova, E. F. Sevost'yanova, and Ya. T. Éidus, Izv. Akad. Nauk SSSR, Ser. Khim., 1536 (1973).
3. B. K. Nefedov, V. A. Petukhov, and Ya. T. Éidus, Izv. Akad. Nauk SSSR, Ser. Khim., 2705 (1973).
4. T. Saegusa, S. Kobayashi, K. Hirota, and Y. Ito, Bull. Chem. Soc. Japan, 43, 2610 (1969).
5. T. Tsuda, Y. Isegawa, and T. Saegusa, J. Org. Chem., 37, 2670 (1972).
6. B. K. Nefedov, N. S. Sergeeva, and Ya. T. Éidus, Izv. Akad. Nauk SSSR, Ser. Khim., 2718 (1973).
7. D. G. Knorre, Z. K. Maizus, and N. M. Émmanuél, Dokl. Akad. Nauk SSSR, 101, 895 (1955); Zh. Fiz. Khim., 29, 710 (1955).
8. V. K. Tsiskovskii and N. A. Kiseleva, Zh. Prikl. Khim., 23, 1001, 1007 (1950); 24, 527 (1951).
9. A. A. Grinberg, Introduction to the Chemistry of Complexes [in Russian], Khimiya, Leningrad (1971).
10. O. V. Krylov, Coordination Mechanism in Heterogeneous Catalysis, in: Complex Formation in Catalysis [in Russian], Nauka (1968), p. 141.
11. R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950); 74, 811 (1952).