Catalysis Letters 5 (1990) 127–142

CONCERTED MECHANISMS OF ACID-BASE CATALYSIS IN COORDINATION SPHERE OF METAL COMPLEXES **

K.I. ZAMARAEV *, V.M. NEKIPELOV and E.P. TALSI

Institute of Catalysis, Prospect Lavrentieva, 5 Novosibirsk, 630090, USSR

Received 10 January 1990; accepted 30 March 1990

Concerted processes, Schiff bases, diketonates; alkoxide anions, hydrogen atom transfer; coordination sphere, metal complexes, acid-base catalysis, ligand substitution, urethanes, hemiacetals.

Kinetics and mechanisms of the following reactions in organic solvents have been studied: (i) formation of Schiff bases from aniline and derivatives of salicylic aldehyde coordinated to Cu(II) and Zn(II); (ii) substitution of one β-diketonate ligand coordinated to Fe(III) by another β-diketonate ligand; (iii) formation of coordinated hemiacetals from β-diketonate ligands and alcohols in coordination sphere of Fe(III); and (iv) formation of urethanes in coordination sphere of Fe(III) $(acac)_2$ OR where acac and OR are acetylacetonate and alkoxide anions. Such compounds as aniline, alcohols and phenylacetylene serve as catalysts of these reactions. Their catalytic action is explained by concerted processes of hydrogen atom transfer in cyclic intermediate structures.

1. Introduction

Concerted mechanisms of proton or hydrogen atom transfer are believed to be important for acid-base catalysis of certain reactions of organic chemistry and biochemistry [1–6]. Catalysis by carboxylic acids of the mutarotation of monosaccharides [4] and by the enzyme lysozyme of the hydrolysis of polysaccharides [5,6] seem to serve as typical examples of such reactions.

In this paper we report the data suggesting that concerted mechanisms are also important for certain acid-base reactions proceeding in coordination sphere of metal complexes. The reactions enumerated in the abstract are discussed.

The first of these reactions will be discussed in detail, the remainder only briefly.

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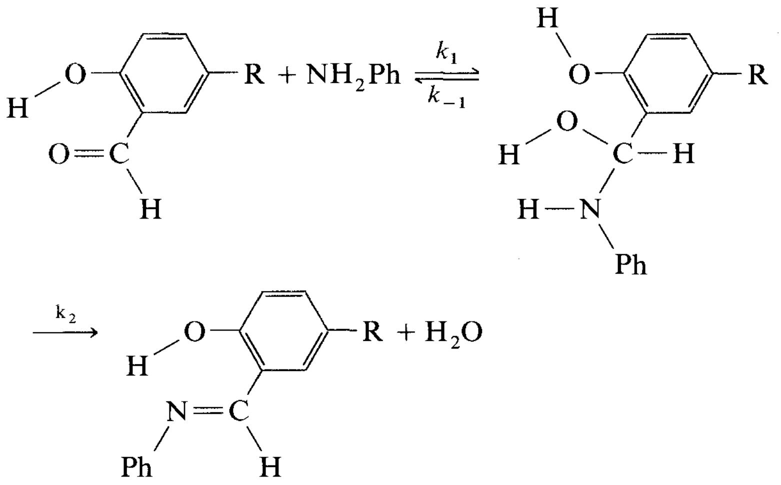
* Author to whom correspondence should be sent.

** Presented in part at the Royal Society-U.S.S.R. Academy Workshop on Catalysis, Oxford, April 1989.

2. Formation of Schiff bases

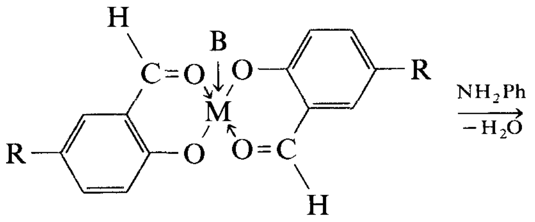
In the absence of metal complexes Schiff bases are believed to be formed from aniline and substituted salicylic aldehydes via the following reaction scheme [1,7]:



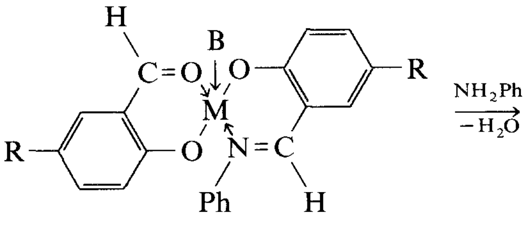
(1)

Note the following important features of the mechanism of this reaction: (1) reaction proceeds via a carbinolamine intermediate and (2) both stages 1 and 2 are accelerated by Brönsted acids and bases.

Reaction (1) can also be enhanced by coordination of an aldehyde to metal atoms, such as Zn(II), Cu(II), Ni(II) and some others [8,15]

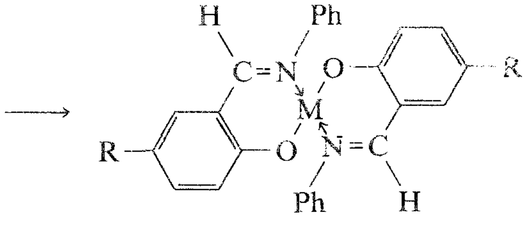


$M(Salald)_2B$



M(Salald)(Salim)B

(2)



$M(Salim)_2$

where M stands for a metal atom and B stands for a Lewis base which along with the anions of salicylic aldehyde (designated Salald) may be also coordinated to M. Various authors assume different metal-to-reagent interactions to play the key role in this enhancement: (1) polarization of the coordinated carbonyl group by a metal atom [9]; (2) metal atom provides conditions for the template synthesis via coordination of both reagents [8].

In this paper we report the data suggesting that none of these effects is of key importance. As we will show later, reactions with both non-coordinated (reaction (1)) and coordinated-to-metal (reaction (2)) salicylic aldehydes seem to proceed via similar concerted mechanisms of acid-base catalysis. Metal atoms seem to enhance the reaction in two ways: (1) via stabilization of its intermediate-carbinolamine, and (2) via acting as a substituent in the aromatic ring of salicylic aldehyde.

These conclusions were made from comparing the kinetic data for reactions (1) and (2) with the spectroscopic (EPR, NMR, IR) data, from which one can characterize molecular entities which are involved in the reactions.

2.1. EXPERIMENTAL

Reaction (2) was studied for metals M = Cu(II) and Zn(II); substituents R = H and NO_2; bases B = aniline, pyridine, methanol or none and solvents S = chloroform, toluene, cyclohexane and chloroform: toluene (1 : 1 by volume) mixture. Bases and solvents have been purified by standard procedures [10]. p-nitrosalicylic aldehyde, HSalald ($R=NO_2$), was synthesized according to [11]. Complexes $Cu(Salald)_2$ ($R = H, NO_2$) and $Zn(Salald)_2$ ($R = H$) were synthesized according to [12] and [13], respectively. The results of the elemental analysis corresponded to those expected for these complexes. EPR, ^1H-NMR, ^{13}C-NMR, IR and UV-VIS spectra were recorded by using "Bruker-ER-200 D", "Tesla-BS-467", "Bruker-CXP-300", "Specord-75 IR", and "Shimadzu-300 UV" spectrometers, respectively. Chemical shifts for ^1H and ^{13}C NMR were measured relative to the internal reference-tetramethylsilane.

Reactions (1) and (2) were carried out at temperature 298 or 300 in conditions $[NH_2Ph] \gg [HSalald], [MSalald]$, which provided the pseudo-first order reaction kinetics.

Kinetics of reaction (2) for M = Cu(II) was studied with EPR, UV-VIS and that of reaction (1) and reaction (2) for M = Zn(II)-with ^{1}H NMR.

In kinetic studies with EPR, samples of reaction mixture were collected from the reaction vessel at various moments of time and rapidly frozen by putting them into liquid nitrogen. The EPR spectra of the frozen samples contained contributions from various Cu(II) complexes involved in reaction (2). The relative amount of each complex was determined by means of the computer modelling the overall spectrum using programs described in ref. [14]. In kinetic studies with ^{1}H NMR the integral intensity of the line from the aldehyde group of HSalald of Salald$^-$ was measured. Each of the kinetic experiments was repeated for at least three times. The error in determination of the rate constants did not exceed 20% of their values.

2.2. RESULTS AND DISCUSSION

2.2.1. Reactions of NH_2Ph with $Cu(Salald)_2$ and $Cu(Salald)_2Py$. Unimportance of NH_2Ph coordination to the metal.

Figure 1 presents the EPR spectra for $Cu(Salald)_2B + NH_2Ph$ system, R=R, B=NH_2Ph. Reaction was carried out in solution of $CHCl_3$: toluene = 1 : 1 at 300 K. The initial concentration of $Cu(Salald)_2B$ was 0.01 M and that of NH_2Ph–1.5 M. The spectrum of fig. 1 consists of three sets of EPR lines, which

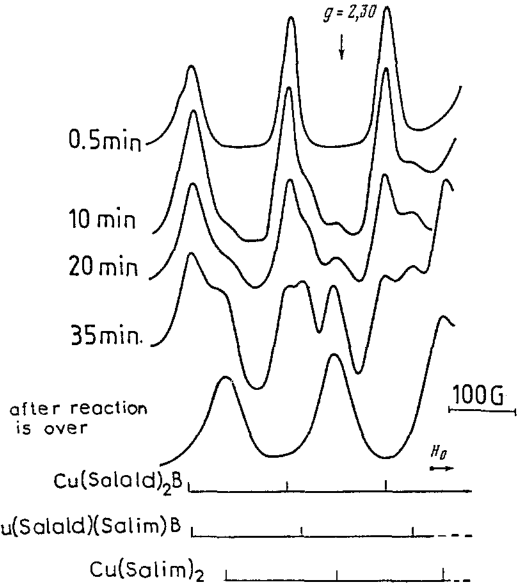


Fig. 1. EPR spectra in parallel orientation at 77 K for 0.01 M $Cu(Salald)_2B + 1.5$ M NH_2Ph (R = H, B = NH_2Ph) in $CHCl_3$: toluene = 1 : 1 solution, frozen at various moments of time after the beginning of the reaction. The assignment of the observed lines to various Cu(II) complexes is given in the bottom of the figure.

are attributed to $\mathrm{Cu(Salald)_2NH_2Ph}$, $\mathrm{Cu(Salald)(Salim)NH_2Ph}$ and $\mathrm{Cu(Salim)_2}$ complexes [15].

From the intensities of the appropriate EPR lines we obtain the rate constants k and k' for the consecutive reaction

$$\mathrm{Cu(Salald)_2B} \xrightarrow[\substack{+\mathrm{NH_2Ph}\\ -\mathrm{H_2O}}]{k} \mathrm{Cu(Salald)(Salim)B} \xrightarrow[\substack{+\mathrm{NH_2Ph}\\ -\mathrm{H_2O}}]{k'} \longrightarrow \mathrm{Cu(Salim)_2} + \mathrm{B}. \tag{3}$$

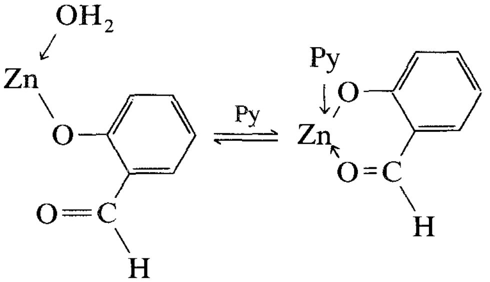
As found, $k = k' = 3.8 \cdot 10^{-4}\ \mathrm{s}^{-1}$, i.e. the rate of Schiff base formation from Salald^- ligand is not sensitive to the nature of the second chelate ligand, Salald^- or Salim^-.

In order to elucidate the role of aniline molecule coordination to copper atom in this reaction we have compared the values of k for the systems, in which aniline and pyridine were used as the axial ligand B in the initial $\mathrm{Cu(Salald)_2B}$ complex. This could be easily done, making use of the difference in the equilibrium constants, K, of the two bases addition to $\mathrm{Cu(Salald)_2}$: $K = 140$ l/mol for Py and $K = 3$ l/mol for $\mathrm{NH_2Ph}$ [15]. The value of k for $\mathrm{Cu(Salald)_2}$ Py was found to be the same as for $\mathrm{Cu(Salald)_2NH_2Ph}$.

Thus inner-sphere coordination of NH_2Ph reactant to metal atom is not important for the reaction. It is non-coordinated rather than coordinated $\mathrm{NH_2Ph}$ molecule that seems to attack the coordinated Salald^-. In other words, one may conclude that, at least in the case of Cu(II) metal, *the template mechanism cannot be responsible for the enhancement of Schiff base formation.*

2.2.2. Reactions of NH_2Ph with $Zn(Salald)_2$ and $Zn(Salald)_2Py_2$. Unimportance of carbonyl group coordination to the metal.

The role in the enhancement of Schiff base formation of the metal atom coordination to the carbonyl group of Salald^- can be elucidated by comparing the rate constants of Schiff base formation for the coordinated and free carbonyl groups. Such comparison can be made for the reaction of $\mathrm{Zn(Salald)_2}$ with aniline in $\mathrm{CHCl_3}$. IR and ^{1}H NMR spectra (see fig. 2) suggest the following equilibrium to exist in solutions of $\mathrm{Zn(Salald)_2}$ in $\mathrm{CHCl_3}$ [15]:



(4)

In the absence of pyridine this equilibrium is shifted to the left. Upon addition of Py from 0.1 to 2 M the equilibrium is gradually shifted to the right. This is

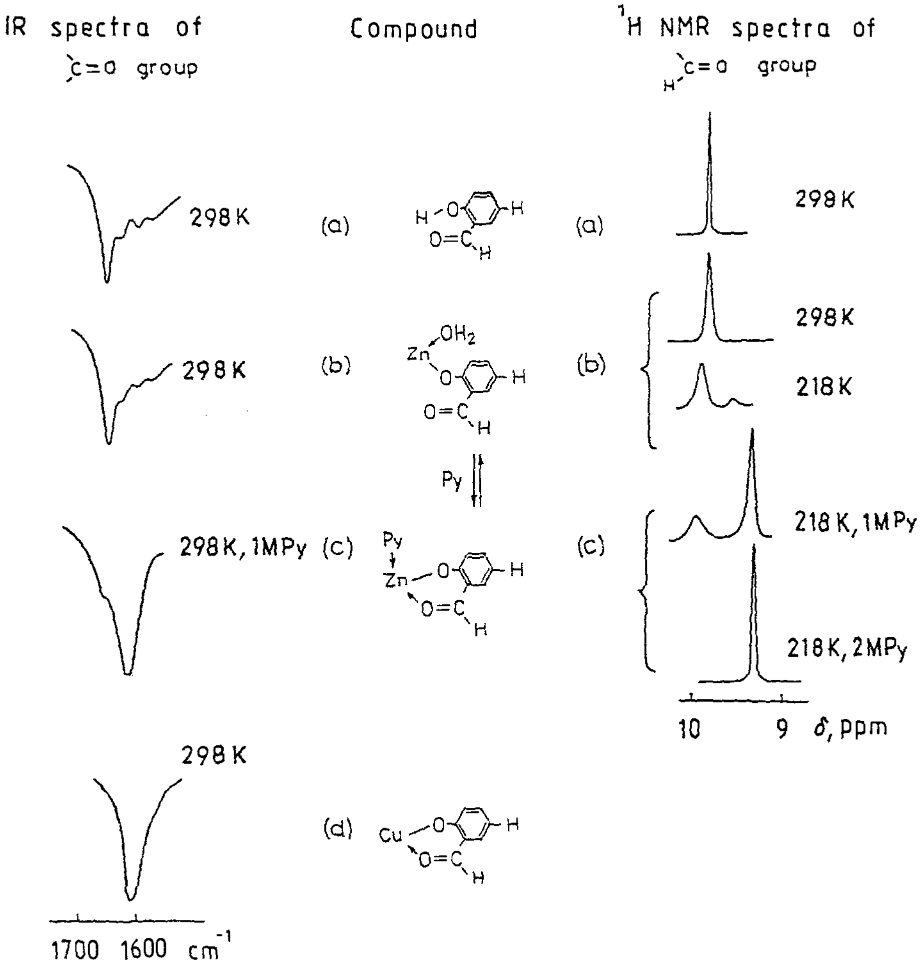


Fig. 2. IR and ^1H NMR spectra at various temperatures of $^{H}\!\!>\!C{=}O$ group in non-coordinated and coordinated-to-metal states for various compounds in $CHCl_3$ solution. To some solutions Py was also added as indicated in the figure.

clearly seen from both IR and ^1H NMR spectra. In the absence of Py, the carbonyl group of Zn(Salald)$_2$ demonstrates the same IR pattern with a 1666 cm^{-1} peak as HSalald does (compare IR spectra (a) and (b) in fig. 2). Upon addition of Py this peak disappears and a new one appears at 1610 cm^{-1}. It has the same frequency as the peaks of well characterized complexes Cu(Salald)$_2$, Ni(Salald)$_2$ and Co(Salald)$_2$ [12] (compare IR spectra (c) and (d) in fig. 2).

The position of the ^1H NMR line (9.82 ppm) of the aldehyde group of Zn(Salald)$_2$ at 298 K in the absence of Py also coincides with that of the same group in HSalald (compare spectrum (a) and the upper of the spectra (b), fig. 2). However, the line from Zn(Salald)$_2$ is notably broader. At lower temperatures the line from Zn(Salald)$_2$ becomes split into two lines (the lower of the spectra (b) in fig. 2). One of the lines, as before, has the same chemical shift as the line of HSalald at 218 K, while the other (at 9.48 ppm) can be attributed to the aldehyde group, coordinated to the metal. With addition of Py, the intensity of the signal from the coordinated group increases, while that from the noncoordinated group decreases (spectra (c), fig. 2).

We have measured the rate constants, k, at 300 K for Schiff base formation via reactions of aniline (1 M) with $Zn(Salald)_2$ (0.1 M) in $CHCl_3$ without and with Py (0.1–2 M), i.e in conditions when the relative amounts of noncoordinated and coordinated aldehyde groups changed dramatically. However, the same values of $k = 1.1 \cdot 10^{-3}$ s^{-1} were obtained for all these solutions. Thus we come to the unexpected conclusion that, at least in the case of Zn(II) metal, inner sphere coordination of the carbonyl group to the metal is not important for the reaction mechanism.

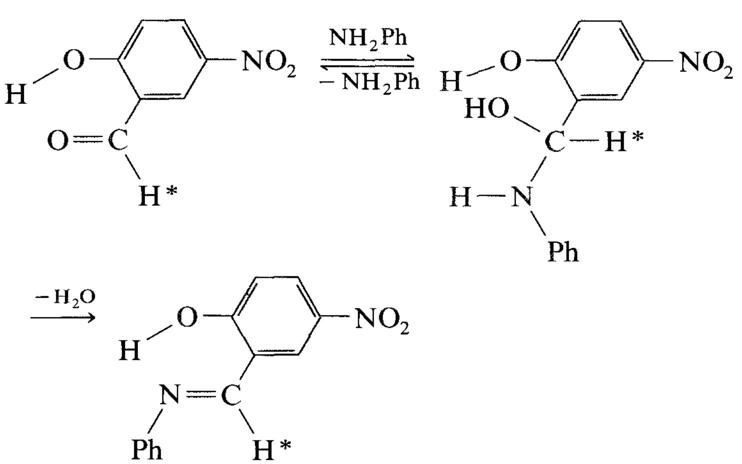
In situations when coordination of neither aniline, nor carbonyl group of $Salald^-$ were found to be important for the reaction, one may assume the following two ways in which metal atoms can influence the reaction:
(a) via stabilization of the carbinolamine which is believed to be the intermediate for the reaction in the absence of metal atoms; (b) via acting as a substituent in the aromatic ring of the salicylic aldehyde.

We have obtained certain evidences in favour of the first of these assumptions.

2.2.3. Reaction of NH_2Ph with HSalald ($R = NO_2$) and $Cu(Salald)_2Py_2$ ($R = NO_2$). Observation of carbinolamine intermediates. Stabilization of carbinolamine via its coordination to Cu(II).

The influence via mechanism (a) was observed for the reaction of aniline with salicylic aldehyde with $R = NO_2$ [15].

For the reaction of non-coordinated aldehyde



(5)

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow{k_2} P$$

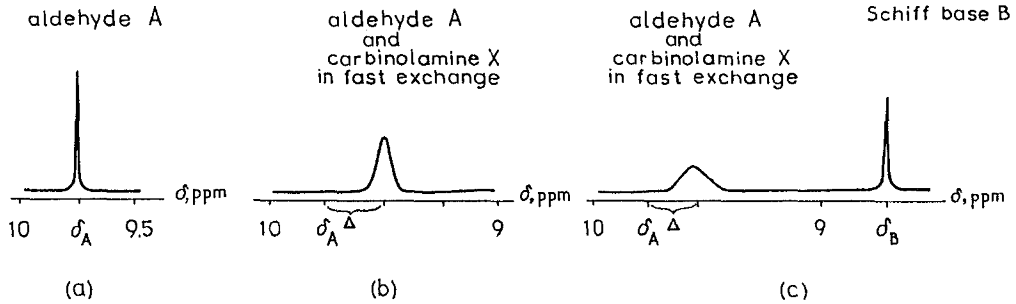


Fig. 3. ^{1}H NMR spectra of CH* group (as indicated in the equation of reaction (5)) for the reaction of 0.01 M HSalald (R = NO_2) with 1 M NH_2Ph in $CHCl_3$ ($T = 300$ K) at various moments of time: (a) before addition of NH_2Ph to HSalald; (b) immediately after the addition of NH_2Ph to HSalald; (c) 2 min after addition of NH_2Ph to HSalald.

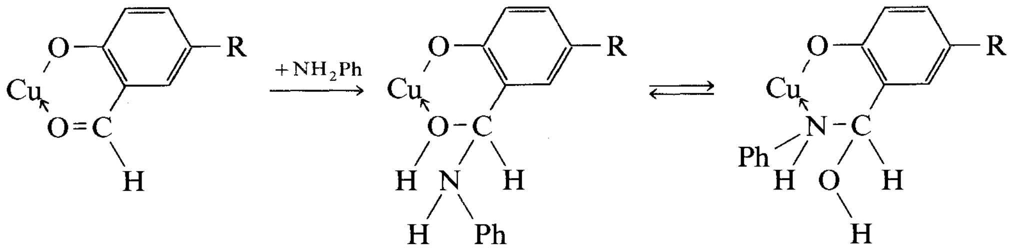
we observed ^{1}H and ^{13}C NMR signals from all the three participants A, X and P of the reaction.

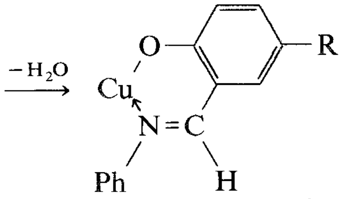
As seen from ^{1}H NMR spectra presented in fig. 3, reaction intermediate X is formed immediately after addition of NH_2Ph to HSalald (R = NO_2). This intermediate is in fast exchange with the aldehyde A. The shift, Δ, of the overall line from A and X with respect to the line from pure A was found to achieve 0.3 ppm ($[NH_2Ph] = 2$ M) and to be proportional to the concentration of aniline, which agrees with X being a carbinolamine. Indeed, the fact that $\Delta \sim [NH_2Ph]$ suggests that $[X] = K[A] \cdot [NH_2Ph]$, i.e. X is the product of NH_2Ph addition to A. The proportionality between [X] and $[NH_2Ph]$ indicates also that $[X]/[A] \ll 1$, i.e. equilibrium of the first stage of reaction (5) is shifted to the left. The second stage of reaction (5) is the rate-determining one.

From the time dependences of the intensities of the lines in spectrum (c) and the width of the line in spectrum (b) of fig. 3, we have estimated the life times of X decay via steps 2 and −1 of reaction (5) at $[NH_2Ph] = 1$ M, $\tau_2 = 1/k_2 = 60$ s, $\tau_{-1} = 1/k_{-1} \approx 10^{-3}$ s.

As is seen, $\tau_{-1} \ll \tau_2$, and thus step −1 determines the overall life time of the carbinolamine intermediate.

The carbinolamine intermediate was also observed with EPR for the reaction of aniline with Salald (R = NO_2) coordinated to Cu(II) [15]. For this reaction the following mechanism was suggested according to EPR and kinetic studies [15]:





$$A \xrightarrow{k_1} X_1 \overset{\text{fast}}{\rightleftarrows} X_2 \xrightarrow{k_2} P \qquad (6)$$

For the sake of simplicity, we have omitted in this equation the notations for the second chelate ligand Salald$^-$ (R=NO$_2$) which is present in all the complexes. The reaction was carried out at 300 K in $CHCl_3$ containing 0.5 M Py, 0.005 M $Cu(Salald)_2$ and 0.10 M NH_2Ph. All the participants, A, X_1, X_2 and P, of this reaction sequence were observed with EPR. The positions of the lines from these compounds are indicated in the EPR spectra of fig. 4. Not going into the details (one can find them in ref. [15]), we will mention only the main conclusions from the analysis of these spectra:

(i) reaction (6) proceeds via the same type of reaction intermediate-carbinolamine, as reaction (5). The rate constants for the first and last stages of reaction (6) are $k_1 = 10^{-2}\ s^{-1}$, $k_2 = 1.1 \cdot 10^{-3}\ s^{-1}$, $[NH_2Ph] = 0.1$ M, i.e. stage 2

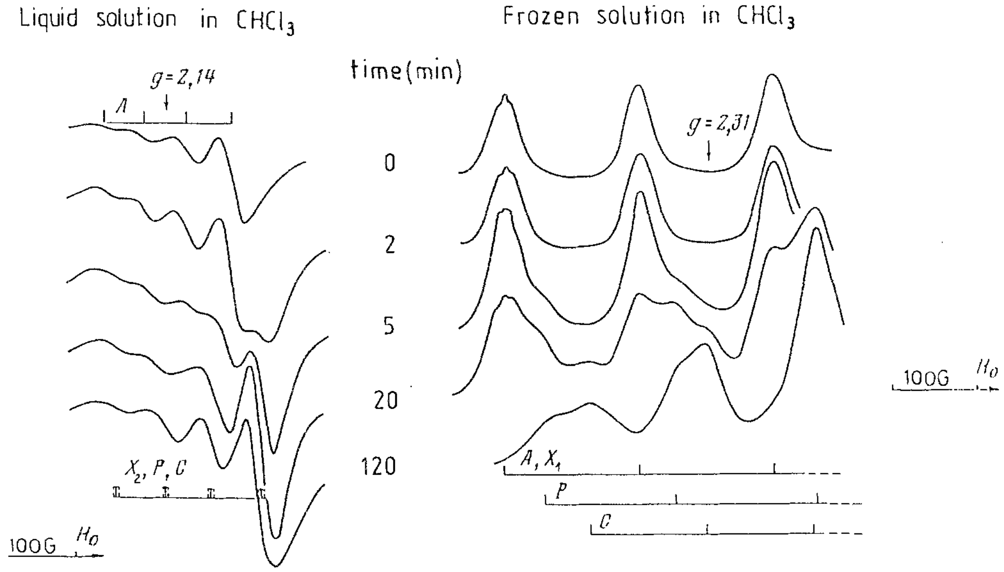


Fig. 4. EPR spectra of compounds A, X_1, X_2 and P in liquid (298 K) and frozen (77 K) solutions of $CHCl_3$ containing 0.5 M Py and 0.1 M NH_2Ph, at various moments of time after the beginning of the reaction (6). Reaction was carried out at 298 K. The composition of compounds A, X_1, X_2 and P is indicated in the equation of reaction (6). Compound C has the composition C=$Cu(Salim)_2Py_2$ (R = NO_2).

is the rate-determining step of both reactions (6) and (5). Under similar reaction conditions, $T = 300$ K and $[\mathrm{NH_2Ph}] = 0.1$ M, the observed overall rate constant

$$k = \frac{k_1}{k_{-1}} \cdot k_2 = 1.5 \cdot 10^{-3}\ \mathrm{s}^{-1}$$

for reaction (5) does not differ much from $k_2 = 1.1 \cdot 10^{-3}\ \mathrm{s}^{-1}$ for reaction (6). So, alteration of the rate of the Schiff base formation upon the coordination of the nitrosalicylic aldehyde results from the opposite effect of the metal on the equilibrium constant $K_1 = k_1/k_{-1}$ and rate constant k_2. For the coordinated aldehyde K_1 is bigger while k_2 is smaller than for the non-coordinated one. Thus for nitrosalicylic aldehyde the carbinolamine intermediate is indeed stabilized via its coordination to Cu(II) atom.

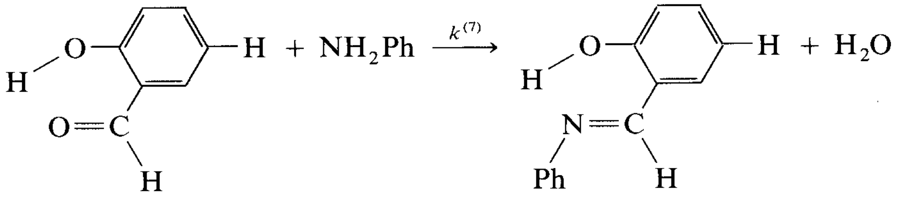
(ii) Carbinolamine intermediate of reaction (6) exists in two different X_1 and X_2 forms, which correspond to different ways of carbinolamine ligand coordination to Cu(II) atom: via the hydroxyl group and via the amine group. These two forms are in fast equilibrium with each other.

It should be noted that under the above mentioned reaction conditions all the complexes which participate in reaction (6) with $\mathrm{Cu(Salald)_2}$ ($\mathrm{R} = \mathrm{NO_2}$) contain most probably two molecules of a base B in the coordination sphere of Cu(II) atoms [15], rather than one molecule of B as it was in the case of the reaction with $\mathrm{Cu(Salald)_2}$ (R = H). Note also that in spectra of fig. 3 the EPR lines of a further product of the Schiff base formation, complex $\mathrm{Cu(Salim)_2Py}$ ($\mathrm{R} = \mathrm{NO_2}$), are also seen.

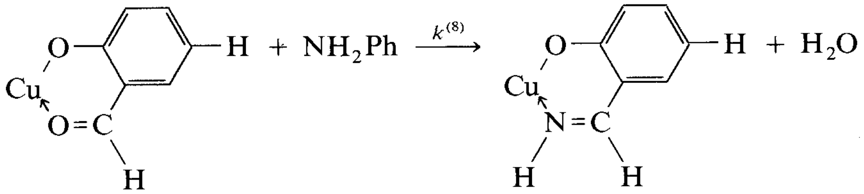
2.3. CATALYSIS OF THE REACTION WITH ANILINE AND METHANOL. EVIDENCES OF ITS CONCERTED MECHANISM.

The rate of the last stage of reaction (6) was expected to be proportional to the concentration of the Cu(II) complex with the carbinolamine, X and independent of the aniline concentration: $w = k_2\,[\mathrm{X}]$. But in fact, we have found out that k_2 is directly proportional to $[\mathrm{NH_2Ph}]$ (see fig. 5). Thus aniline is a catalyst for carbinolamine dehydration to the Schiff base.

In the similar way for reactions:



(7)



(8)

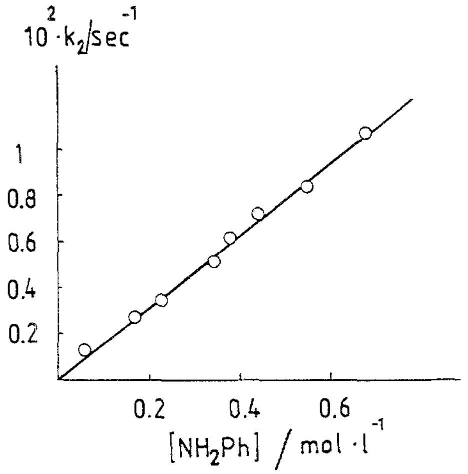
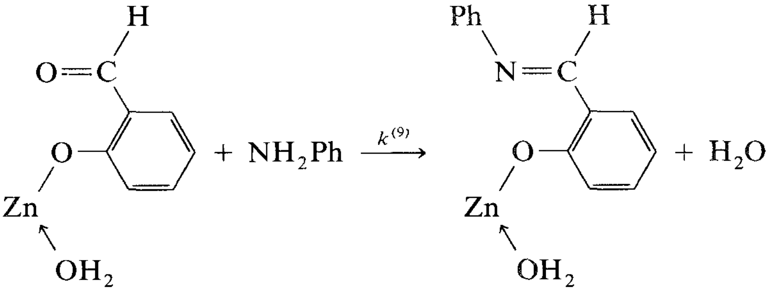
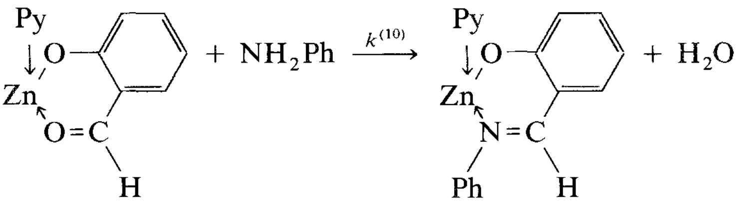


Fig. 5. Dependence of the rate constant k_2 for reaction (6) on the concentration of aniline. $T = 300$ K, solvent $CHCl_3 + 0.5$ M Py, R = NO_2.



(9)



(10)

pseudo first order rate constants in expressions for the rates $w = k^{(7)}$ [Hsalald], $w = k^{(8)}$ $[\mathrm{Cu(Salald)_2}]$, $w = k^{(9)}$ $[\mathrm{Zn(Salald)_2}]$ and $w = k^{(10)}$ $[\mathrm{Zn(Salald)_2Py_2}]$ were expected to be independent of or directly proportional to the concentration of aniline, depending on whether carbinolamine decomposition or formation is the rate determining step of these reactions and/or whether the formation of carbinolamine is an equilibrium reaction. In reality, all rate constants appear to be directly proportional to the square of $[\mathrm{NH_2Ph}]$ (fig. 6a, curve 1 and fig. 6b). On addition of 1 M CH_3OH to the solution, $k^{(8)}$ increased and became directly proportional to $[\mathrm{NH_2Ph}]$ (fig. 6a curve 2). These facts indicate that aniline is a catalyst for reactions (7), (9) and (10) and both aniline and methanol are catalysts for reaction (8).

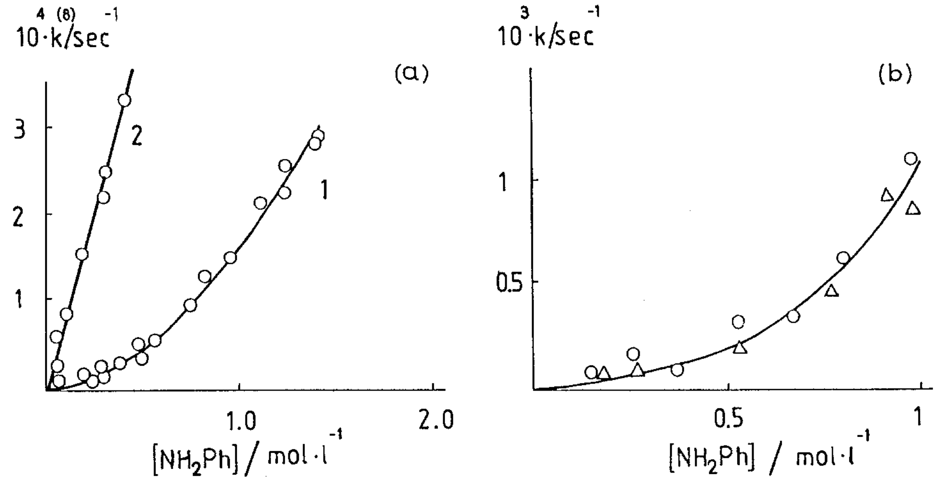


Fig. 6. Dependence of the rate constants on the concentration of aniline for: (a) Reaction (8) at 298 K, solvent $CHCl_3$. CH_3OH was not added (curve 1); 1 M CH_3OH was added (curve 2). (b) Reaction (9) at 298 K in $CHCl_3$–(○), and reaction (10) at 298 K in $CHCl_3 + 2$ M Py–(△).

The influence of the solvent on the rate constants $k^{(7)}$ and $k^{(8)}$ was also studied (table 1). The values of the rate constants show no correlation with the polarity of the solvents. This fact militates against the mechanism of catalysis via the formation of ionic structures.

All the above facts taken together suggest that formation of Schiff bases in the coordination sphere of metal complexes proceeds via concerted mechanisms of the type presented in scheme 1.

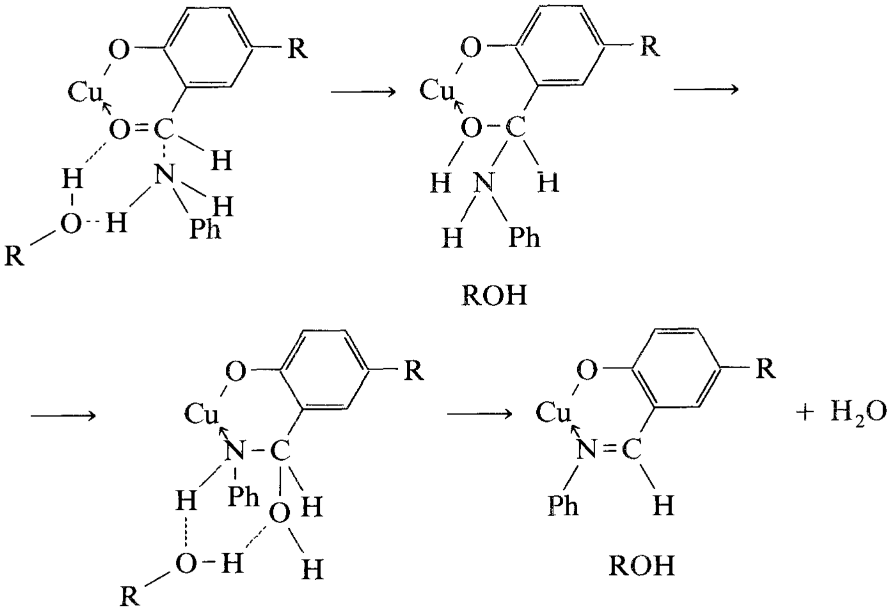
2.4. CONCLUSIONS

The following conclusions concerning the mechanism of Schiff base formation in the coordination sphere of metal complexes may be drawn:

(i) Schiff bases are formed via direct attack of the coordinated salicylic aldehyde ions by free aniline molecules:

Table 1
The influence of the solvent on the rate constant for reactions of HSalald and $Cu(Salald)_2$ with NH_2Ph

Solvent	$k \cdot 10^5$ (s^{-1})	
	For $Cu(Salald)_2$	For HSalald
$CHCl_3 + 1$ M Py $+ 1$ M NH_2Ph	17	2
$CHCl_3 + 1$ M NH_2Ph	17	2
toluene $+ 1$ M Py $+ 1$ M NH_2Ph	20	2.5
$C_6H_{12} + 1$ M Py $+ 1$ M NH_2Ph	100	12



Scheme 1.

(ii) the metal atom can change the rate of this reaction in two ways (a) via stabilization of its intermediate-carbinolamine; (b) via acting as a substituent in the aromatic ring of the salicylic aldehyde;

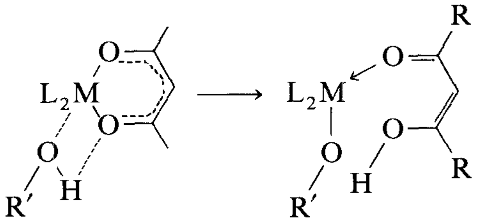
(iii) in contrast to the widely accepted point of view, coordination of neither carbonyl, nor amine groups to metal atoms seems to active them in the reaction studied.

(iv) molecules of aniline and methanol serve as catalysts of the Schiff base formation in both free- and coordinated-to-metal-atom states. Their catalytic action is explicable in terms of a concerted process of hydrogen atom transfer in cyclic intermediate structures.

3. Other reactions

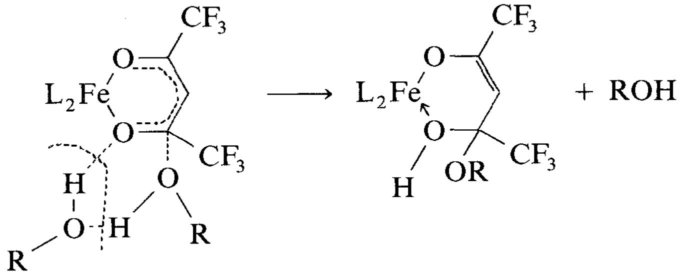
Concerted mechanism of hydrogen atom transfer was found to provide also the occurrence of the following reactions in the coordination sphere of metal atoms:

(1) substitution of one β-diketonate ligand attached to Fe(III) by another in the presence of such catalysts as alcohols, aniline and phenylacetylene [16,17]. The rate determining step of this reaction seems to be scheme 2 [16,17].



(11)

Scheme 2.



(12)

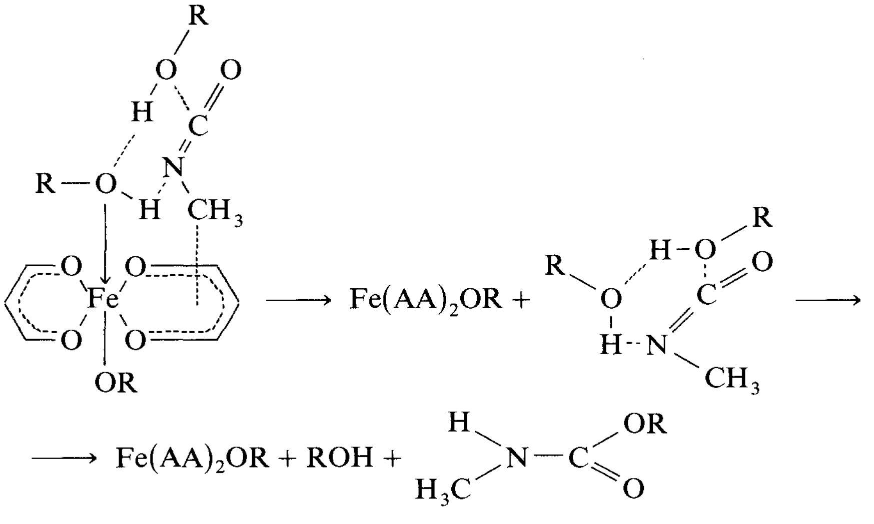
Scheme 3.

In scheme 2 M denotes the metal atom and L_2 stands for other two β-diketonate ligands. The overall rate of the reaction is proportional to the concentration of ROH.

(2) Formation of hemiacetal ligands from β-diketonate ligands and alcohols in coordination sphere of Fe(III) via scheme 3 [18]

In this case the reaction rate is proportional to the square of the concentration of ROH.

(3) Formation of urethane in the coordination sphere of $Fe(acac)_2OR$, where acac and OR are acetylacetonate and alkoxide anions, respectively [19]. The key step of this reaction was suggested to be [19]:



(13)

In this case the reaction rate is also proportional to the square of ROH concentration.

Thus concerted mechanisms of hydrogen atom transfer seem to play an important role in various reactions of organic species coordinated to metal atoms in non-polar solvents.

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