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Influence of the Nature of the Metal Ion on the Rate of Reduction of Coordinated Azomethine Group

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Abstract—The kinetics of reduction of the azomethine bond in various Schiff bases and their transition metal complexes with sodium borohydride in dimethylformamide and ethanol solutions was studied. The reduction rate depends on both the structure of the starting Schiff bases and the nature of the metal ion. In transition metal *N*-phenylsalicylaldiminates, the rate of reduction of the azomethine group increases in the order Zn(II) < Ni(II) < Cu(II) < Co(II) < VO(II) < Mn(II). Similar trend is observed in other series of metal complexes with Schiff bases. The revealed trends are opposite to the Irving–Williams series of stability of complexes. This fact suggests that the major factor affecting the rate of reduction of the coordinated azomethine bond is the strength of its bonding with the metal ion. Depending on particular metal ion, the complexation can either decelerate or accelerate the reduction.
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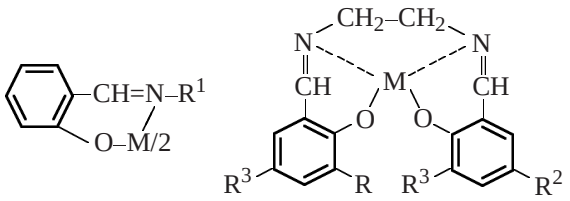
It is well known that metal complexes catalyze reduction of various organic compounds with sodium borohydride. In particular, cobalt(II) β-ketoiminate complexes are used as catalysts for enantioselective borohydride reduction of ketones [1–4], *N*-phosphinylimines [4, 5], and β,β-disubstituted α,β-unsaturated carboxamides [4, 6] to the corresponding alcohols, amines, and saturated carboxamides.

The asymmetric reduction of a series of ketones with borohydride using asymmetric chiral Co(II) bis(salicylidene)ethylenediamine (salen) complexes was studied in [7, 8]. It should be noted that all these complexes used as catalysts contain aldimine groups, which can be reduced with borohydride to secondary amines. It is known that the azomethine bond can be reduced even at 0°C [9]. However, none of these papers consider the possibility of reduction of the azomethine group in the metal complex catalysts in the course of hydrogenation.

In this study we compared the rates of reduction of the azomethine bond in complexes of various metals with Schiff bases derived from salicylaldehyde and mono- and diamines. We examined the kinetic features of the reduction of the starting ligands and metal complexes and suggested the most probable reduction mechanism.

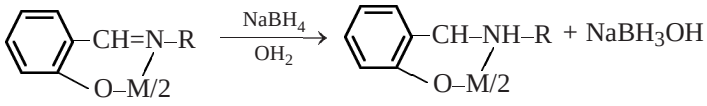


R^1 = Ph ($M[L^1]_2$); R^1 = CH_2Ph ($M[L^2]_2$); R^2 = H, R^3 = H ($M[L^3]$); R^3 = $–OCH_3$, R^2 = H ($M[L^4]$); R^2 = R^3 = $C(CH_3)_3$ ($M[L^5]$); M = VO(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II).

The solvents most commonly used for reduction of various compounds with borohydride are alcohols and water. However, in this case concurrent decomposition of borohydride in the reaction with the solvent should be taken into account in kinetic studies.

We found that, in anhydrous dimethylformamide, borohydride does not noticeably decompose during at least 1-day storage, which consideably simplifies the kinetic studies, because the borohydride consumption in the reaction with the solvent can be neglected.

The reduction of Schiff bases and their metal complexes in dimethylformamide occurs in the presence of water in accordance with the general scheme



The reduction kinetics was monitored by variation of the optical density in the maximum of the $\pi \rightarrow \pi^*$ absorption band of the azomethine group. Figure 1 illustrates variation of the absorption spectrum of the complex VO[L^3] with time.

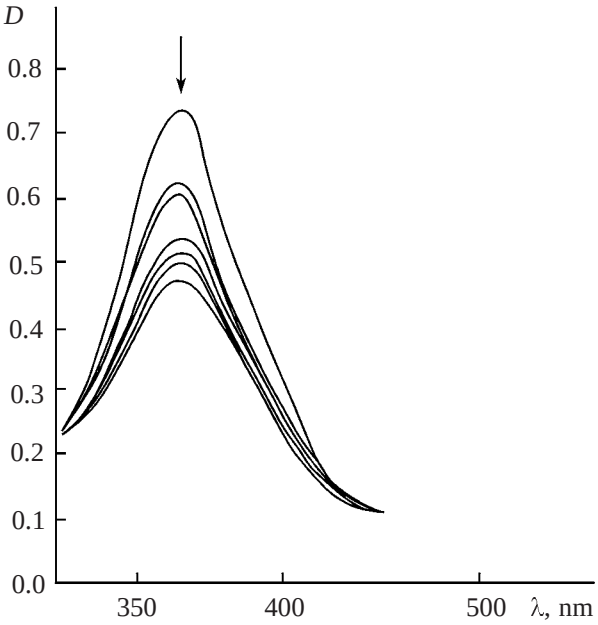


Fig. 1. Variation with time of the absorption intensity in the electronic spectra of VO[L^3]. *T* 35°C, [$NaBH_4$] 0.002 M, [H_2O] 0.073 M. The spectra were recorded at 2-min intervals. The arrow denotes the direction of spectrum evolution. (*D*) Optical density.

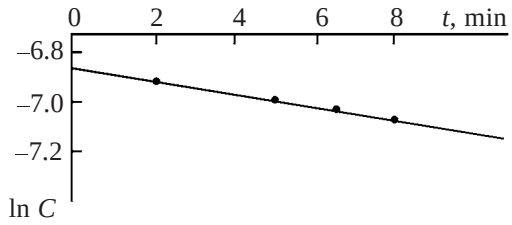


Fig. 2. Logarithm of the substrate concentration as a function of time for the reduction of VO[L^3]. Initial concentrations, M: VO[L^3] 1×10^{-4}, [$NaBH_4$] 0.002, and [H_2O] 0.073.

The reaction rates were measured at large excesses of sodium borohydride and water relative to the substrate (ligand or complex). Under these conditions, the experimental plots of $\ln C$ of substrates vs. time were linear (Fig. 2), suggesting the first reaction order with respect to the substrate concentration.

The pseudo-first-order rate constants k' evaluated from the $\ln C$–t dependences were used for determining the reaction order with respect to water and sodium borohydride concentrations. It was found that the reaction order with respect to these components is also unity (Figs. 3, 4). Thus, according to the experimental data, the reduction rate can be described by the following equation:

$$W = k_{app}[S][H_2O][NaBH_4], \quad (1)$$

where k_{app} is the reaction rate constant; [S], [H_2O], and [$NaBH_4$] are the concentrations of the substrate, water, and sodium borohydride, respectively. The pseudo-first-order rate constant is defined as follows:

$$k' = k_{app}[H_2O][NaBH_4].$$

The expression for the reduction rate corresponds to third-order reactions, but in our case such order is improbable. Among possible reaction mechanisms, the following mechanism leads to the rate equation similar to (1):

$$S + NaBH_4 \overset{K}{\rightleftarrows} [S \cdot NaBH_4],$$

$$[S \cdot NaBH_4] + H_2O \xrightarrow{k} SH_2 + NaBH_3OH,$$

$$W = Kk[S][H_2O][NaBH_4], \quad (2)$$

where *K* is the equilibrium constant of substrate–borohydride complexation, and *k* is the rate constant of the limiting step. Equation (1) corresponds to Eq. (2) at $k_{app} = Kk$. The rates of reduction of the azomethine group in noncoordinated Schiff bases depend on their structure. Whereas *N*-phenylsalicylaldimine is reduced at room temperature at a fairly high rate, the other examined Schiff bases are not reduced under these conditions (see table).

The reduction rates of the coordinated azomethine group strongly depend on the nature of the metal ion. In all the examined series of complexes with Schiff bases, except *N*-phenylsalicylaldiminate complexes, the VO^{2+} and Mn^{2+} complexes are reduced most

Kinetic parameters of hydrogenation[a] of complexes[b] with sodium borohydride in DMF solution

Compound	$[NaBH_4] \times 10^{-3}$, M	$[H_2O]$, M	k', s^{-1}	k_{app}, $l^2\,mol^{-2}\,s^{-1}$	E_{app}, $kJ\,mol^{-1}$
L^1H	0.968	0.089	0.0015	17.41	33.24
$VO[L^1]_2$	0.968	0.089	0.0014	16.25	24.92
$Mn[L^1]_2$	0.23	0.21	0.0005	103.5	66.48
$Co[L^1]_2$	0.968	0.089	0.001	11.61	24.94
$Ni[L^1]_2$	0.968	0.089	0.001	11.61	29.0
$Cu[L^1]_2$	0.23	0.021	0.001	207.03	69.25
$Zn[L^1]_2$	0.968	0.089	0.0017	19.73	38.78
$VO[L^2]_2$	2.02	0.089	0.0005	2.8	
$Co[L^2]_2$	2.02	0.089	0.0002	1.12	0.831
$Cu[L^2]_2$	2.02	0.0089	0.0003	1.68	50.28
$VO[L^3]$	1.7	0.073	0.00057	4.5	27.7
$Mn[L^3]$	0.47	0.017	0.00053	66.33	
$Co[L^3]$	0.98	0.073	0.0003	4.2	
$VO[L^4]$	0.968	0.089	0.005	59	
$Mn[L^4]$	0.2	0.021	0.0013	309	
$VO[L^5]$	4.0	0.089	0.00026	0.738	
$Mn[L^5]$	0.968	0.073	0.000145	2.05	

[a] For L^2H, $Mn[L^2]_2$, $Ni[L^2]_2$, $Zn[L^2]_2$, L^3H_2, $Ni[L^3]$, $Cu[L^3]$, $Zn[L^3]$, L^4H_2, $Co[L^4]$, $Ni[L^4]$, $Cu[L^4]$, $Zn[L^4]$, L^5H_2, $Co[L^5]$, $Ni[L^5]$, $Cu[L^5]$, and $Zn[L^5]$, the absorption maximum of the azomethine bond does not change with time. [b] Geometries of the coordination cores: $Co[L^1]_2$, distorted tetrahedron [10]; $Ni[L^1]_2$, planar square [11]; $Cu[L^1]_2$, planar square–tetrahedron [10]; $Zn[L^1]_2$, tetrahedron [10]; $Co[L^3]$, planar square [12]; $Ni[L^3]$, planar square, dimer [13]; $Cu[L^3]$, planar square, dimer [13]; $Zn[L^3]$, planar square [13].

readily, whereas the Cu(II) and Co(II) complexes are reduced appreciably more slowly. No noticeable transformations in the examined temperature range are observed with the Ni(II), Pd(II), and Zn(II) complexes.

From the temperature dependence of k' (Fig. 5), we determined the apparent activation energies (see table).

Reduction of *N*-phenylsalicylaldiminate complexes $M[L^1]_2$. Noncoordinated *N*-phenylsalicylaldimine is rapidly (k_{app} 17.41 $l^2\,mol^{-1}\,s^{-1}$) reduced at room temperature.

With all the examined metal complexes of this ligand, the reduction rate is fairly high (see table). The Cu(II) complex is reduced by a mechanism that differs from the mechanism of reduction of the other complexes. First the Cu(II) ion is reduced to Cu(I), which is accompanied by decomposition of the complex. A band of the noncoordinated azomethine bond at 340 nm appears in the electronic absorption spectrum, and this is followed by the reduction of this bond with sodium borohydride.

Reduction of *N*-benzylsalicylaldiminate complexes $M[L^2]_2$. *N*-Benzylsalicylaldimine is not reduced with sodium borohydride in DMF solution in the presence of water at 20–60°C. Complexation with

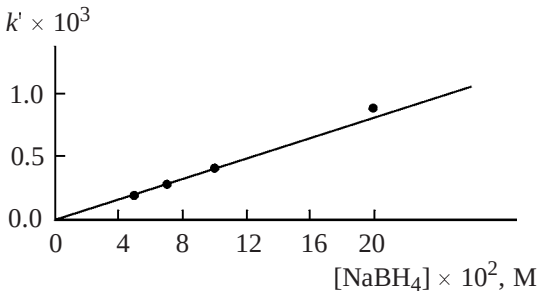


Fig. 3. Pseudo-first-order rate constant k' of the reduction of $VO[L^3]$ at 22°C as a function of $[NaBH_4]$. $[H_2O]$ 0.073 M.

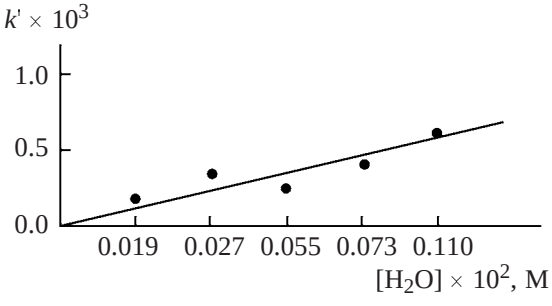


Fig. 4. Pseudo-first-order rate constant k' of the reduction of $VO[L^3]$ at 22°C as a function of $[H_2O]$. $[NaBH_4]$ 0.002 M.

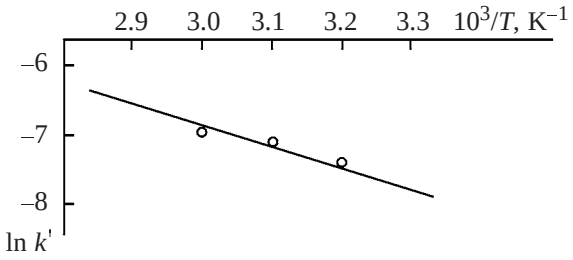


Fig. 5. Plot of $\ln k'$ vs. reciprocal temperature for the reduction of VO[L^3].

VO(II), Mn(II), Co(II), and Cu(II) ions enhances the reactivity of the ligand, so that the reduction rate becomes fairly high, especially for the Mn(II) and VO(II) complexes (see table). At the same time, the azomethine group in the complexes with Ni(II), Zn(II), and Pd(II) is not reduced under these conditions, even at 60°C.

Reduction of salen complexes M[L^3], M[L^4], and M[L^5]. Noncoordinated salen is not reduced under the conditions of our experiments (DMF + H_2O). Salen coordinated with the VO(II), Mn(II), and Co(II) ions is active in reduction; the Mn(II) complex is reduced at the highest rate, whereas the Co(II)[salen] complex is reduced at a noticeable rate only above 50°C. The complexes Ni[salen] and Zn[salen], like *N*-benzylsalicylaldiminate complexes of these metals, are inactive in the reduction.

For 3,5-di-*tert*-butyl-substituted salen, only the VO(II) and Mn(II) complexes undergo reduction, whereas the complexes of the other metals are not reduced. The methoxy-salen complexes behave similarly. In this case also the Mn(II) complex is the most active. Somewhat lower reduction rate is observed with the VO(II) complexes, and the Cu(II) complexes are reduced very slowly at 60°C. No reduction is observed under these conditions with the Co(II) and Ni(II) complexes.

Reduction in ethanol. The rate of reduction of the azomethine bond in ethanol solutions is considerably higher than that in dimethylformamide solution. For example, the rate constant k_{app} of reduction of Mn[L^3] in dimethylformamide is 66.33 $l^2\ mol^{-2}\ s^{-1}$, whereas in alcoholic solution it is as high as 106.3 $l^2\ mol^{-2}\ s^{-1}$. The rate of reduction of the vanadyl salen complex in alcohol is also higher than in DMF. The salen complexes of the other metal ions [Co(II), Ni(II), Cu(II), Zn(II)] are not reduced at room temperature.

Thus, in accordance with the studies performed, the rate of reduction of the coordinated azomethine group depends on the nature of the metal ion and structure of the Schiff base. In the case of complexes with *N*-phenylsalicylaldimine, the hydrogenation rate decreases in the following order:

Mn(II) > VO(II) > Co(II) > Cu(II) > Ni(II) > Zn(II).

As for complexes of transition metals with the other Schiff bases, the Mn(II) and VO(II) complexes were also reduced most rapidly, the Co(II) and Cu(II) complexes were reduced more slowly, and the Ni(II) and Zn(II) complexes were not reactive at all in the examined temperature range.

The noncoordinated azomethine bond in different free Schiff bases behaves differently. Whereas noncoordinated *N*-phenylsalicylaldimine is rapidly reduced at room temperature, among salen derivatives only the methoxy compound (L^4H_2) is reduced in DMF at room temperature, with the reaction being very slow.

It should also be noted that *N*-phenylbenzalimine containing no hydroxy grop is not reduced under the conditions we used. The enhancing effect of the hydroxy group on the reactivity of the azomethine group may be due to withdrawal of electron density from the azomethine group, making this group more electrophilic and hence more reactive toward borohydride, or to direct participation of the hydroxy group in the reduction.

However, the azomethine bond in *N*-benzylsalicylaldimine, which is not hydrogenated in the free ligand under common conditions, is reduced upon coordination with the Mn(II) and VO(II) ions, which suggests that these ions exert a catalytic effect.

Presumably, the major factor affecting the reactivity of the azomethine group is the metal–nitrogen bond energy. Indeed, the series of activity of the metal complexes in the reduction of the azomethine bond is opposite to the Irving–Williams series found for the stability constants of various metal complexes. Of course, the systems being compared differ essentially, because the Irving–Williams series described the strength of metal binding with mono- and bidentate ligands (1,2-diaminoethane, oxalic acid, glycine, etc.), whereas our study concerns the reduction of the coordinated azomethine bond. It should also be noted that the geometry of the chelate core has no noticeable effect on the capability of the azomethine group for reduction (see table).

EXPERIMENTAL

Complexes of metals with Schiff bases were prepared by published procedures [10–13].

Dimethylformamide was purified by fractional distillation with a benzene–water mixture, followed by distillation at reduced pressure [14]. Kinetic measurements were performed with Specord M40 (Carl Zeiss, Jena) and UV VIS 240 (Shimadzu) spectrophotometers. The reduction progress was monitored by variation of the optical density in the absorption maxima of the complexes (~360 – 420 nm depending on particular complex), measured in temperature-controlled quartz cells in dimethylformamide solution. The temperature was maintained with an accuracy of ±0.5°C.

The initial concentrations of the reactants were as follows (M): substrates (ligands or complexes) ~10^{-4}, sodium borohydride 10^{-2}–10^{-3}, and water 10^{-1}–10^{-2}.

To determine the initial concentrations of sodium borohydride, we developed a procedure involving titration of a solution of $NaBH_4$ in dimethylformamide with an alcoholic solution of *N*-phenylsalicylaldimine. The end of titration corresponded to the moment when the yellow color of the Schiff base no longer disappeared on stirring.

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