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Semicarbazones and Thiosemicarbazones, XIII [1]: Study of the Hydrolysis of Coordinated Thiosemicarbazones

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Summary. The hydrolysis of coordinated thiosemicarbazones was studied. It was found that the nickel(II) ion promotes the reaction. Steric and electronic influences were found. The hydrolysis of *ATSC* in the trigonal bipyramid compounds $[M(ATSC)_2Cl]Cl$ [M = Fe(II), Co(II), Ni(II)], is higher with the Ni(II) complex, the compound with the shorter M-N distance.

Keywords. Thiosemicarbazones; Hydrolysis; Reactivity.

Semicarbazone und Thiosemicarbazone, 13. Mitt.: Untersuchungen zur Hydrolyse koordinierter Thiosemicarbazone

Zusammenfassung. Bei der Hydrolyse von koordinierten Thiosemicarbazonen wurde festgestellt, daß das Nickel(II)-Ion die Reaktion begünstigt. Es wurden sterische und elektronische Einflüsse gefunden. Die Hydrolysengeschwindigkeit des *ATSC* im trigonal bipyramidalen Komplex $[M(ATSC)_2Cl]Cl$ [M = Fe(II), Co(II), Ni(II)] ist höher mit dem Ni(II)-Komplex, der Verbindung mit der kürzeren M-N-Distanz.

Introduction

Recently we reported the hydrolysis of coordinated acetonethiosemicarbazone [*ATSC*: $(CH_3)_2C=N-NH-C(S)-NH_2$] to give acetone and coordinated thiosemicarbazone [*TSC*: $NH_2-NH-C(S)-NH_2$] [2]. Under the same conditions (*pH**, temperature, H_2O concentration), acetonethiosemicarbazone hydrolyzes after 10 days with a 19% conversion, compared with 31% of the coordinated compound in 20 hours. According to these results, there must be an important influence of the metal ion in the hydrolytic process.

In this work, we confirm the importance of the metal ion in the hydrolytic process, and evaluate the influence of different factors on the rate of reaction.

Experimental

The thiosemicarbazone ligands were prepared by the method described by Sah and Daniels [3]. The thiosemicarbazone complexes were obtained by literature methods, $[Ni(ATSC)_2(NO_3)]\,[NO_3]$ [2],

$[M(ATSC)_2(Cl)]Cl$, M = Fe(II) [4], Co(II) [5], Ni(II) [6]. All other chemicals were purchased from commercial sources.

The products of the reaction were analyzed either on a Perkin Elmer Sigma IB chromatograph with a 18 m × 5 mm column packed with Porapak-Q 80/100 and a thermal conductivity detector, or an a Hewlett Packard 5890 Chromatograph with a 25 m × 0.2 mm column packed with Carbowax 20M and a flame ionization detector.

Temperature was controlled in a bath, with a Polyscience Corporation, model 73, temperature controller. Glass sealed reactors were used.

Hydrolysis Reactions

Method 1 (M1). In a typical reaction 0.1 mmol of the metal thiosemicarbazone complex was dissolved in 25 ml of ethanol (95%), and heated to reflux or to a controlled temperature. The resulting mixture was analyzed by VPC.

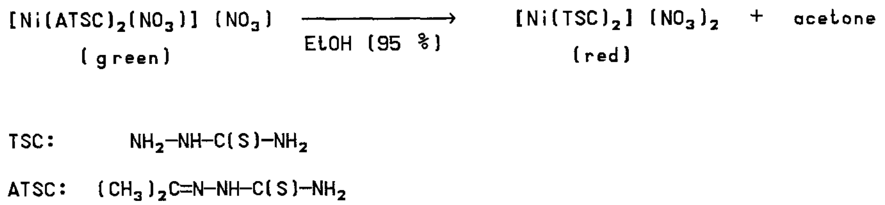
Method 2 (M2). In a typical reaction 0.2 mmol of the thiosemicarbazone was added to a solution of 0.1 mmol of the metal complex in 25 ml of ethanol, and heated to the specified temperature. The resulting mixture was analyzed by VPC.

Results and Discussion

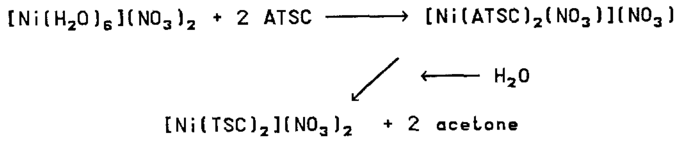
Two different methods were used to study the reaction. In the first one, a coordinated thiosemicarbazone in a well characterized compound was hydrolyzed (M1), see Scheme 1. In the second one (M2) the metal compound was generated in situ and then hydrolyzed, Scheme 2.

When $[Ni(ATSC)_2(NO_3)]$ (NO_3) is dissolved and refluxed four hours in absolute ethanol, no acetone is detected in the reaction medium. Under the same reaction conditions, small amounts of water (0.58%) initiates the hydrolytic process (16.81% after 4 h). As it is shown in Scheme 1 the products of the reaction are acetone and the red compound $[Ni(TSC)_2]$ $(NO_3)_2$ [2].

If free ligand is present, two reactions may produce acetone: the hydrolysis of the ligand by the medium and the hydrolysis of the coordinated ligand. The acetone



Scheme 1. Hydrolysis of the compound $[Ni(ATSC)_2(NO_3)]$ (NO_3) in EtOH (95 %), method M1



Scheme 2. Hydrolysis of the compound $[Ni(ATSC)_2(NO_3)]$ (NO_3) obtained in situ, method M2

Table 1. Influence of the ligand concentration on the reaction[a]

M/L	A^b	B^c	C^d	% Conversion
1/1	2.96	–	2.96	51.03
1/2	6.14	–	6.14	52.93
1/3	8.25	1.09	7.16	61.68
1/4	10.09	2.18	7.91	68.18
1/5	10.90	3.27	7.63	65.78

[a] Four hours under reflux in *Et*OH (95%), using method M2

[b] Total acetone (mg)

[c] Acetone obtained from the hydrolysis of free ligand by the medium (mg), at $pH^* = 9.5$ with an oxalic acid-oxalate buffer

[d] Estimated acetone obtained from the hydrolysis by the Ni(II) ion

Table 2. Effect of different anions[a]

Anion	% of conversion	pH_i^b
Perchlorate	61.57	3.2
Nitrate	52.95	3.5
Chloride	49.17	3.4
Acetate	0.0	6.0

[a] Four hours under reflux, *Et*OH (95%), method M2

[b] Initial *pH* of the solution when the Ni(II) salt is dissolved in *Et*OH (95%)

obtained from the hydrolysis of the coordinated thiosemicarbazone may be evaluated subtracting the estimated acetone generated by the medium to the total acetone. When the ligand to metal relation is increased, the increment in the % of hydrolysis is not significant, see Table 1; according to this result the hydrolysis may be considered a stoichiometric reaction.

To evaluate the possible influence of the anion in the reaction, different Ni(II) salts were used. The results are shown in Table 2.

The higher hydrolysis rate obtained with the perchlorate compound, may be due to the lower pH^*, but a specific influence of the anion is not observed. With Ni(II) acetate, the pH^* produced by the salt is enough to deprotonate the ligand and the compound $[Ni(ATSC\text{-}H)_2]$ precipitates [7].

To compare the effect of different metal ions, the hydrolysis of *ATSC* in $[M(ATSC)_2Cl]Cl$, with M = Fe(II) [8], Co(II) [9] and Ni(II) [10] compounds, was determined. All these compounds have a trigonal bipyramid structure, the same anion and oxidation state. A higher conversion is obtained with the Ni(II) compounds, see Table 3.

It has been proposed that the *M*-N bond weakens the C=N double bond [11], thus rendering the latter more susceptible to hydrolytic cleavage. If this is correct, then a stronger *M*-N bond may favour the attack of the water molecules to the

Table 3. Hydrolysis of $[M(ATSC)_2Cl]Cl^a$, M = Fe(II), Co(II), and Ni(II)

M(II)	% Conversion	pH^{*b}	Average *M*-N distance (*A*)
Fe	9.69	3.2	2.25^c
Co	18.91	3.3	2.23 (1)
Ni	49.00	3.5	2.130 (5)

[a] Four hours under reflux, in *E*tOH (95%), method M1
[b] pH^* after dissolution of the *M*(II) salt
[c] esd's not reported

Table 4. Conversion yield of the carbonyl compounds in mol%

Thiosemicarbazones	Promotor A[a] mol%	Promotor B[b] mol%	No promotor[c] mol%
Acetone	52.95	83.96	8.37
Methyl ethyl ketone	38.31		
4-Methyl-2-pentanone	10.35	46.93	0
2,6-Dimethyl-4-heptanone	0	0	0
Cyclohexanone	49.23		0
Cycloheptanone	38.56	76.36	0
p-Hydroxy acetophenone	21.71	48.42	0
p-Methyl acetophenone	15.41	34.56	0
Acetophenone	11.16	23.84	0
p-Nitro acetophenone	1.11	10.71	0

[a] $Ni(NO_3)_2 \cdot 8H_2O$ EtOH (95%), reflux, 4 hours
[b] $Ni(ClO_4)_2 \cdot 8H_2O$ EtOH (95%), reflux, 5 hours
[c] EtOH (95%), reflux, 5 hours

C=N bond. In accordance to this proposition, the Ni-N distance is significant smaller than the other ones. Another important factor may be the high stability of the red compound $[Ni(TSC)_2]$ $(NO_3)_2$ obtained as a product.

Aliphatic compounds were used to determine the steric influence on the reaction, while aromatic compounds were used to study the electronic influence.

When there is an increase in the bulk of the substituents on the carbon atom of the imino group in the aliphatic carbonyl compounds, the percentage of conversion is reduced, Table 1, following the order: acetone > methyl ethyl ketone > 4-methyl-2-pentanone > 2,6-dimethyl-4-heptanone, Table 4.

In a study of the hydrolysis of thiosemicarbazones in aqueous solution at a $pH = 7$ [12], a steric influence was not observed. In this case, the conversion follows the other: acetone = methyl ethyl ketone ≈ diethyl ketone. This difference suggests that in the actual Ni complexes there is a steric restriction to the nucleophilic attack, which may be due to the presence of the five-membered chelate ring formed,

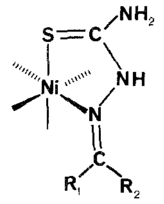


Fig. 1. Five-membered chelate ring formed by the coordination of the ligand to the metal ion

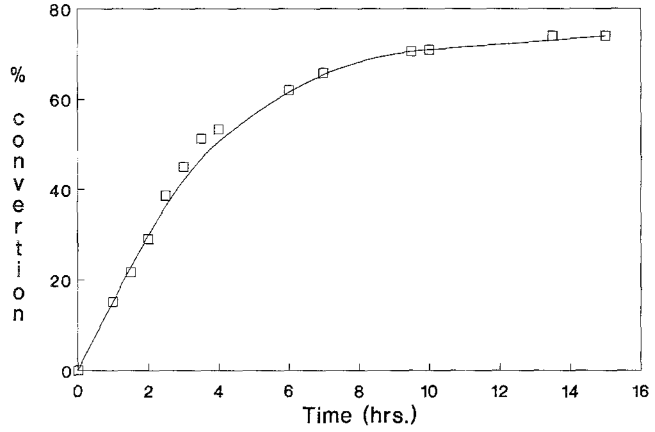


Fig. 2. Plot of % of conversion versus time

Fig. 1. It can also be suggested that in this case the metal promotes the hydrolytic process, because of the electron withdrawing effect from the five-membered ring formation. The arrangement found in the five-membered ring is similar to the one suggested in the study of hydrolysis of isoquinaldehydethiosemicarbazones [13], for which an intermolecular hydrogen ion catalysis was thought to occur.

With the aromatic thiosemicarbazones, the presence of an electron withdrawing substituent in the aromatic ring diminishes the hydrolytic process. This may be due to a reduction of the coordinating capability of the imino nitrogen atom.

The *pH* is an important factor in the hydrolysis of imines [12]. Unfortunately the compounds here studied are not enough soluble in adequate buffers [14]. To diminish this lack of control, a non-rigorous kinetic study of the reaction was done with $[\mathrm{Ni}(ATSC)_2(\mathrm{NO_3})](\mathrm{NO_3})$. This compound was selected because no *pH** changes were observed during the reaction. The reaction was followed until equilibrium was reached (ca. 15 h), see Fig. 2.

The values obtained may be adjusted to a reversible pseudo first order to the right and second order to the left kinetics. The integrated equation for this kinetics is [15]

$$k_1 = \frac{X_e}{([A]_o - X_e)\,t} \times \ln\frac{[A]_o X_e + ([A]_o - X_e)}{[A]_o (X_e - X)},$$

with $[A]_o$ = initial concentration of A; X_e = concentration of the products at equilibrium; X = concentration of products at time t.

If $\ln\,[[A]_o X_e + ([A]_o - X_e)]/[[A]_o (X_e - X)]$ is plotted versus time a straight line is obtained, see Fig. 3.

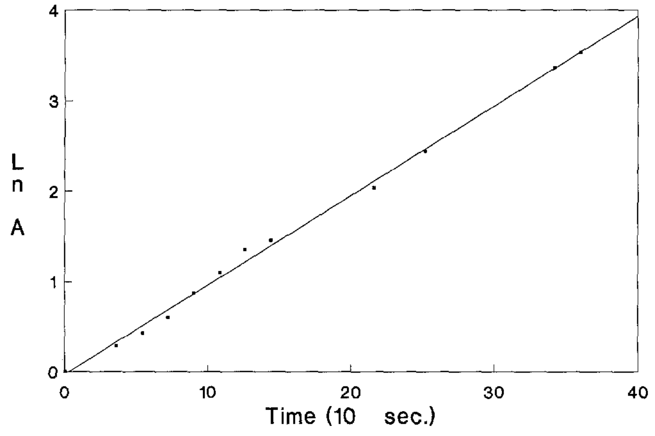


Fig. 3. Plot of ln A versus time, where $\ln A = \ln [[A]_0 X_e + ([A]_0 - X_e)]/[[A]_0 (X_e - X)]$, according to a reversible pseudo first order to the right and a second order to the left kinetics

Conclusions

According to these results it is possible to suggest that the hydrolysis is promoted by the Ni(II) ion. The reaction is stoichiometric and reversible with a pseudo first order to the right and second order to the left. The reaction is influenced by steric and electronic parameters. It is reasonable to propose that Ni(II) promotes the reaction by weakening the C=N double bond.

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