Influence of Cu(II) Ions on the Mechanism of the Ring Transformation of S-(2-Oxotetrahydrofuran-3-yl)-N-(4-methoxyphenyl) isothiouronium Bromide

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ABSTRACT: The effect of additional Cu(II) ions on the rate of transformation of S-(2-oxotetrahydrofuran-3-yl)-N-(4-methoxyphenyl)isothiouronium bromide (**1**) into 5-(2-hydroxyethyl)-2-[(4-methoxyphenyl)imino]-1,3-thiazolidin-4-one (**2**) has been studied in aqueous buffer solutions. The reaction acceleration in acetate buffers is caused by the formation of a relatively weakly bonded complex ($K_C = 600$ L·mol^{-1}) of substrate with copper(II) acetate in which the Cu(II) ion acts as a Lewis acid coordinating the carbonyl oxygen and facilitating the intramolecular attack, leading to the formation of intermediate $T^{\pm}$. The formation of the complex of copper(II) acetate with free isothiourea in the fast preequilibrium (K_C) is followed by the rate-limiting transformation (k_{Cu}) of this complex. At the high concentrations of the acetate anions, the reaction is retarded by the competitive reaction of these ions with copper(II) acetate to give an unreactive complex $[Cu(OAc)_4]^{2-}$. The influence of Cu(II) ions on the stability of reaction intermediates and the leaving group ability of the alkoxide-leaving group compared to the Cu(II)-uncatalyzed reaction is also discussed. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 248–255, 2013

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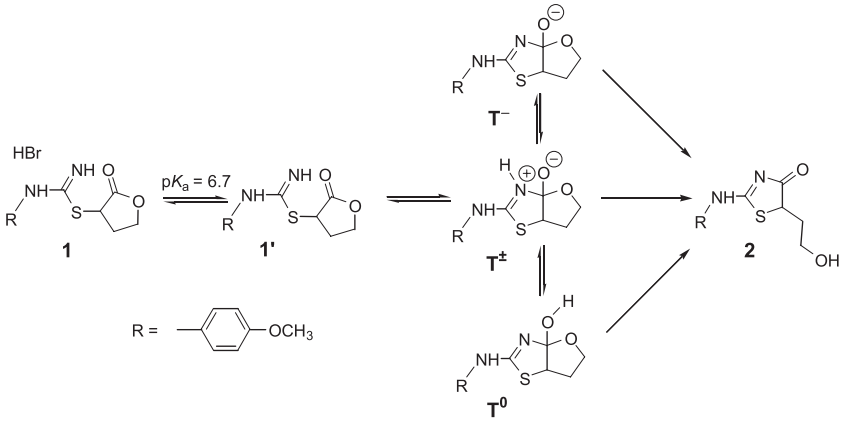
INTRODUCTION

It is well known that many organic [1–3] as well as enzymatic [4,5] reactions in solutions cannot proceed without transition metal ion catalysis or promotion. Especially, the presence of metal ions in active sites of enzymes attracts much attention [6,7] and the elucidation of mechanisms of its action is crucial for



Scheme 1 Reaction pathways for buffer-catalyzed transformation of **1** to **2**.

understanding of reactions occurring in living organisms. Owing to this, the use of simplified small molecules as models is of great importance [8–11]. In particular, the intramolecular models are very advantageous for a deeper understanding of preorganizational effects that are responsible for the high reaction rates of the reactions catalyzed by enzymes [12].

An acyl group transfer belongs to the most common and the most studied reactions in biochemistry and medicinal chemistry [13]. A large amount of work [14–19] has been done in the area of heavy metal ion accelerated acyl group reactions since Kroll observed the participation of heavy metal ions in the hydrolysis of amino acid esters [20]. On the other hand, only a small attention has been devoted to intramolecular models [21].

In the past several years, we have been involved in the preparation and study of structure [22,23] and reaction mechanisms of transformations of isothiouronium salts containing the γ-lactame [24–26] or γ-lactone [27] ring. Recently, we described in detail [28] (Scheme 1) the mechanism of transformation of *S*-(2-oxotetrahydrofuran-3-yl)-*N*-(4-methoxyphenyl) isothiouronium bromide (**1**) to 5-(2-hydroxyethyl)-2-[(4-methoxyphenyl)imino]-1,3-thiazolidin-4-one (**2**) in aqueous solutions over a wide pH range [28]. Multiple breaks in the measured pH profile established the formation of three different kinetically detectable intermediates $T^{\pm}$, T^{0}, and T^{-}, whose rates of formation and breakdown to the product are pH dependent [28].

Here, we describe the influence of additional Cu(II) ions on the reaction rate and propose reaction mechanism of the transformation of **1** to **2** in aqueous solutions. Since there are several steps in Scheme 1 that are amenable to general acid/base catalysis, Lewis acid/base catalysis (which is canonical in carbonyl addition/elimination chemistry) should be involved in the transformation reaction too.

EXPERIMENTAL

The preparation and characterization of *S*-(2-oxotetrahydrofuran-3-yl)-*N*-(4-methoxyphenyl) isothiouronium bromide (**1**) and 5-(2-hydroxyethyl)-2-[(4-methoxyphenyl)imino]-1,3-thiazolidin-4-one (**2**) was described elsewhere [27].

Kinetic Measurements

All the kinetic measurements were carried out in a 1-cm closable cell using a Hewlett Packard 8453 diode array spectrophotometer at 25 ± 0.1°C. The observed pseudo-first–order rate constants k_{obs} were calculated from absorbance–time dependences at the wavelengths of 300 nm and at the substrate concentrations of ca. 5×10^{-5} mol·L^{-1}. In all kinetic runs, the standard deviation in the fit was always less than 1% of the quoted value and was more usually between 0.2% and 0.4% of the quoted value. Ionic strength $I = 1$ mol·L^{-1} was adjusted by KCl as in our previous study [28]. However, it is well known that the Cu(II) cation can form various complexes with chloride ions. Fortunately, the stability constants of these chloro complexes in aqueous solutions are only $\beta_1 = 11.6$, $\beta_2 = 3.15$, $\beta_3 = 1.02$, and $\beta_4 = 0.51$ [29]. It means that the stronger ligands as deprotonated substrate **1′** or acetate (for their apparent stability constants K_c and K_{Ac}, see Table I and text below) can easily displace chlorine atoms in these complexes. To investigate the influence of abovementioned chloro complexes on the reaction rate and catalytic efficiency of Cu(II) ions, we have tried to use sodium perchlorate as the noncoordinating salt for

Table I Calculated Constants Using Eq. (2) from Data Presented in Fig. 1

Buffer	pH	K'_c	k'_0 (10^3 s^{-1})	k'_{Cu} (10^2 $L{\cdot}mol^{-1}{\cdot}s^{-1}$)
Dichloroacetate	1.50	0.05305[a]	0.5363[a]	9.59[a]
Chloroacetate	2.65	0.09285[a]	0.7439[a]	38.32[a]
Methoxyacetate	3.40	0.1327[a]	1.1910[a]	53.12[a]
Acetate	4.53	574 ± 68	2.99 ± 0.13	0.518 ± 0.037
Propionate	4.65	455 ± 144	3.56 ± 0.40	0.821 ± 0.081
Pivaloate	4.80	444 ± 41	3.95 ± 0.11	1.121 ± 0.019

[a]Standard deviations for constants are higher than constants itself. It is caused by only small influence of the additional copper(II) ions and insignificant curvature of the dependences (see Fig. 1).

adjustment of the ionic strength. In all acetate buffers, we obtained virtually the same values of the observed rate constants (the difference was always less than 5%). Similar values were also measured in the absence of any salt, i.e., without ionic strength adjustment. From this observation, it is clear that the presence of multiple forms of copper chloro complexes do not complicate the kinetic analysis.

The pH of individual buffers was measured using a PHM 93 radiometer Copenhagen apparatus equipped with a glass electrode. Redistilled water, commercially available substituted acetic acids, copper(II) chloride, copper(II) perchlorate, copper(II) sulfate (Aldrich), and potassium chloride (p.a.) for adjustment of ionic strength of buffer solutions were used.

Buffer solutions were prepared by dilution of 2 $mol{\cdot}L^{-1}$ stock solution prepared by partial neutralization of appropriate acetic acid with potassium hydroxide. Cu(II) ions were added as a solution of copper(II) salt, and ionic strength was maintained at 1 $mol{\cdot}L^{-1}$ by KCl.

In typical kinetic experiment, 2 mL of appropriate buffer solution was pipetted to the quartz cell and after reaching a constant temperature of 25°C, 10 μL of **1** in methanol was added. The reaction was followed for at least five half-lives (see the Supporting Information). The spectrum of reaction mixture after the reaction is the same as the spectrum-containing product **2** in the same medium.

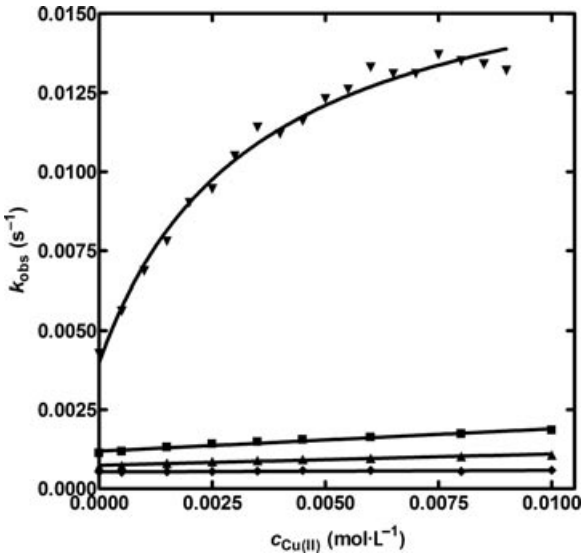


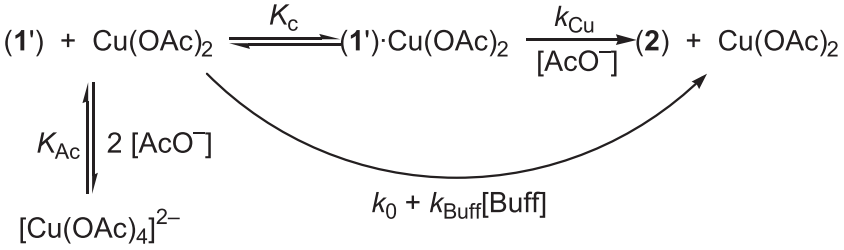
Figure 1 Dependence of the observed rate constants (k_{obs}; s^{-1}) against the copper(II) ion concentration ($c_{Cu(II)}$; $mol{\cdot}L^{-1}$) for **1** measured at 25°C in 0.1 $mol{\cdot}L^{-1}$ acetate, pH 4.53 (▼); 0.1 $mol{\cdot}L^{-1}$ methoxyacetate, pH 3.40 (■); 0.1 $mol{\cdot}L^{-1}$ chloroacetate, pH 2.65 (▲) and 0.1 $mol{\cdot}L^{-1}$ dichloroacetate, pH 1.50 (♦) buffer solutions. The fitted lines were calculated using Eq. (2).

RESULTS AND DISCUSSION

The influence of additional Cu(II) ions on the reaction rate of transformation **1** to **2** was followed spectrophotometrically in solutions of mineral acids (HCl, H_2SO_4, $HClO_4$) and Cl_3CCOOH at pH 2 without ionic strength correction containing increasing amount of Cu(II) ions. The only negligible influence on the rate constant was observed (see the Supporting Information). This small influence is attributable to the small changes in ionic strength of the solutions, which is the most significant in the uni–bivalent sulfuric acid system [30].

Different behavior was observed in methoxyacetate and acetate buffers with a constant buffer concentration of 0.1 $mol{\cdot}L^{-1}$ and with an increasing concentration of Cu(II) ions. The slopes of plots decrease with increasing Cu(II) ion concentration until at sufficiently high Cu(II) concentration the saturation occurs (Fig. 1).

In accordance with the literature [20,31], formation of a complex of copper(II) acetate with the substrate was proposed in the first reaction step. It is obvious that the only the free base of the substrate **1** (whose pK_a is 6.7 [28]) is able to form such a complex. In strong mineral acids, trichloroacetate, dichloroacetate,



Scheme 2 General reaction scheme for the transformation of **1** to **2**.

and chloroacetate buffers, there was no Cu(II) catalysis observed because the starting compound is present almost entirely as the protonated species. Moreover, the acid-catalyzed breakdown of $T^{\pm}$ is the rate-limiting step of the rearrangement at pH 1.5–3 [28]. From this observation, it can also be concluded that the presence of Cu(II) has no influence on a leaving ability of the leaving alkoxide from $T^{\pm}$. A completely different situation was observed in methoxyacetate and especially in acetate buffers (at pH 4.5) where the formation of T^0 is rate limiting [28], and Cu(II) ions can participate on acceleration of this step through activation of the carbonyl group of **1′**.

The Cu(II)-catalyzed reaction exhibits saturation kinetics, which can be explained as follows: First, the observed rate constant increases linearly with $c_{Cu(II)}$ (Fig. 1) because the concentration of a more reactive complex increases too. At sufficiently high Cu(II) concentration, the slope of line appear to approach zero because the whole substrate is present in the form of a reactive complex and a further increase of $c_{Cu(II)}$ has no influence on the reaction rate. This behavior is illustrated in Scheme 2. The second, less probable explanation takes into account that the formation of the complex is rate limiting at low Cu(II) concentrations, whereas at the increased Cu(II) concentration the rate-limiting step changes and the reaction starts to be independent of the Cu(II) concentration [32].

The reaction was also studied in acetate buffers with changing the total buffer concentration at a constant concentration of the Cu(II) ions. These measurements showed unexpected dependences (Fig. 2). While the dependence of k_{obs} vs. c_{Buff} at $c_{Cu(II)} = 0$ is linear the presence of Cu(II) ions causes nonlinearity in the buffer concentration range from 0.01 to 0.2 mol·L^{-1}. Above this buffer concentration, the dependence linearly increases again and its slope approaches to those obtained in acetate buffer in the absence of Cu(II) ions.

This behavior can be explained as follows: The transformation of the substrate to the product takes place through two distinct parallel pathways. The first of them involves simple general acid catalysis [28],

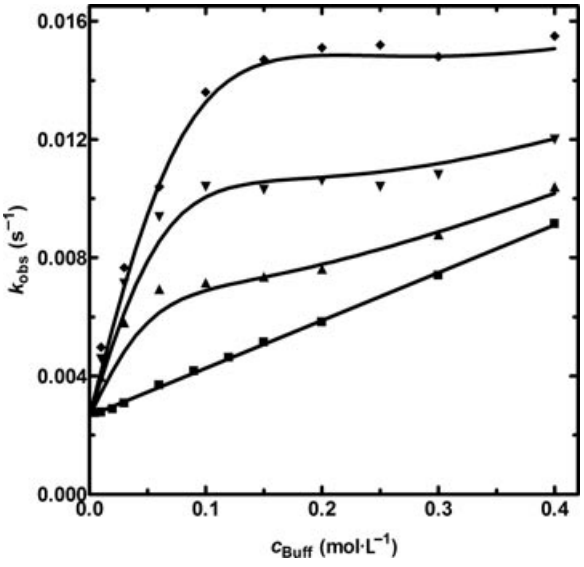


Figure 2 Dependence of the observed rate constants (k_{obs}; s^{-1}) against the buffer concentration (c_{Buff}; mol·L^{-1}) for **1** measured at 25°C in acetate buffer solutions with the constant Cu(II) concentration: 0.001 mol·L^{-1} (▲); 0.003 mol·L^{-1} (▼); 0.006 mol·L^{-1} (♦) and without Cu(II) ions (■). The fitted lines were calculated using Eq. (1) and using linear regression (■).

and the second one involves the formation of relatively weak but a more reactive complex of the substrate with copper(II) acetate (denoted [(**1′**)·Cu(OAc)$_2$]). At low buffer concentrations, the general acid catalyzed transformation is much slower than the analogous transformation of the [(**1′**)·Cu(OAc)$_2$] complex. As the concentration of the acid buffer component (i.e., AcOH) increases, the rate of transformation increases too. However, when increasing buffer concentration, the concentration of the basic buffer component (AcO^-) increases too, which causes rate retardation due to the formation of the more stable but unreactive $[Cu(OAc)_n]^{2-n}$ complex ($n = 3$ and 4; blind alley) [33–36]. In other words, there is a competition between the acetate anion from the buffer and the

substrate for complexation with the copper(II) ions. Therefore, at high buffer concentrations where almost all the copper(II) ions would be complexed to form unreactive $[Cu(OAc)_4]^{2-}$, simple general acid catalyzed transformation of the substrate becomes favorable again and the dependence k_{obs} vs. c_{Buff} linearly increases. Both of these observations are illustrated in Scheme 2, and the general equation (1) could be derived:

$$k_{obs} = k_0 + \frac{k_{Cu} \cdot \dfrac{K_c \cdot [Cu(II)]}{K_{Ac} \cdot [AcO^-]^2 + 1} \cdot [AcO^-]}{1 + \dfrac{K_c[Cu(II)]}{K_{Ac} \cdot [AcO^-]^2 + 1}} + k_{Buff} \cdot [AcOH] \quad (1)$$

where k_0 is the rate constant for the reaction catalyzed by hydroxide and hydroxonium ions [28], k_{Buff} is the rate constant for the buffer-catalyzed reaction (it was taken from the slope of the linear dependence k_{obs} vs. c_{Buff} at $c_{Cu(II)} = 0$), k_{Cu} is the rate constant for the copper(II)-catalyzed reaction, K_c is the stability constant for the complex of copper(II) acetate with the deprotonated substrate **1′,** and K_{Ac} is the apparent equilibrium constant for formation of $[Cu(OAc)_4]^{2-}$.

The multiple regressions of all the dependences measured in acetate buffers (Figs. 1 and 2) provide the values of all the parameters: $k_0 = 2.64 \times 10^{-3}$ s^{-1}; $k_{Cu} = 3.45 \times 10^{-1}$ s^{-1}; $K_c = 600$ L·mol^{-1}; $K_{Ac} = 900$ L^2·mol^{-2}, and $k_{Buff} = 3.23 \times 10^{-2}$ L·mol^{-1}·s^{-1}. The nonideal fit of Figs. 1 and 2 is caused by the fitting of all these dependences together by changing only three parameters k_{Cu}, K_c, and K_{Ac}. Thus-obtained constants are more correct than some average constants that could be obtained by the fitting of single dependences. The obtained value $K_{Ac} = 900$ L^2·mol^{-2} is in good accordance with values published elsewhere [37,38].

In a buffer solution with an increasing Cu(II) ion concentration and constant buffer concentration, some terms in Eq. (1) become constant and therefore Eq. (1) can be simplified to form Eq. (2). This enables the corresponding constants for buffers other than acetate to be obtained. These are quoted in the Table I and correspond to the constants obtained from the multiple regression of dependences measured in acetate buffers:

$$k_{obs} = k_0' + \frac{K_c' \cdot k_{Cu}'[Cu(II)]}{1 + K_c'[Cu(II)]} \quad (2)$$

where $k_0' = k_0 + k_{Buff} \cdot [BH^+]$, $k_{Cu}' = k_{Cu} \cdot [B]$, and $k_c' = K_c/(1+K_{Ac} \cdot [B]^2)$; B is a base buffer component, and BH^+ is an acid buffer component.

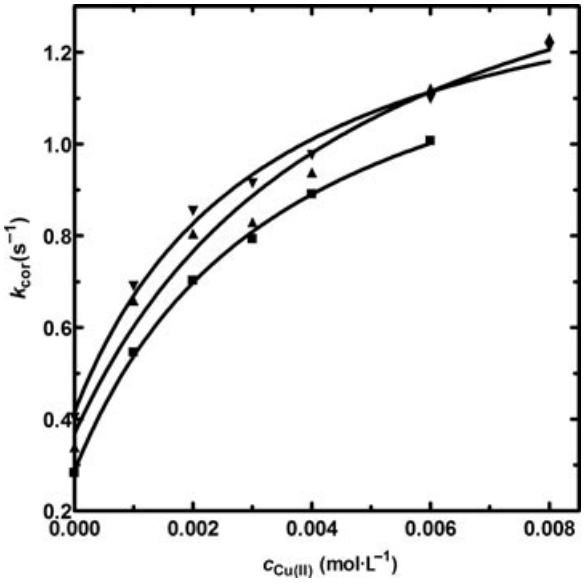


Figure 3 Dependence of the observed rate constants (k_{obs}; s^{-1}) against the copper(II) ion concentration ($c_{Cu(II)}$; mol·L^{-1}) for **1** measured at 25°C in 0.03 mol·L^{-1} propionate, pH 4.80 (▲); 0.03 mol·L^{-1} pivaloate, pH 4.65 (■) and 0.03 mol·L^{-1} acetate, pH 4.53 (▼) buffer solutions. The fitted lines were calculated using Eq. (2).

Finally, the steric demands of the various aliphatic chains of the catalyzing acid on the reaction course were studied in acetate, propionate, and pivaloate buffers (Fig. 3). The concentration of 0.03 mol·L^{-1} was chosen because of the low solubility of pivalic acid in water, and the ionic strength was adjusted to 1 mol·L^{-1} by the addition of KCl. All the dependences have the same character (Fig. 3), resembling saturation kinetics again. Correction of k_{obs} using Eq. (3) is necessary because of the differences in the pH of the buffers [28]:

$$k_{cor} = k_{obs}\frac{K_a}{K_a + [H^+]} = k_{obs}(1 + 10^{(pK_a - pH)}) \quad (3)$$

This correction (Fig. 4) makes all dependences almost identical, which indicates no influence of steric demands of the catalyzing acid.

The question is, however, what is the structure of the catalyzing complex and hence which atom(s) coordinate(s) to the copper(II) acetate? According to HSAB (Hard and Soft Acid and Base) theory [39], a Cu(II) ion is borderline on the HSAB scale. It means that it can be coordinated to a soft sulfur or carbonyl oxygen as well as to harder nitrogen. If the coordination on a nitrogen atom would take place, then a decrease of electron density at this atom would cause the reaction

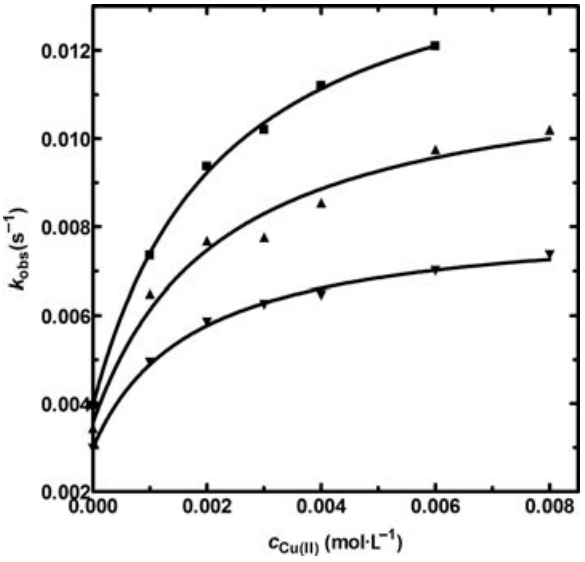


Figure 4 Dependence of the corrected rate constants (k_{cor}; s^{-1}) against the copper(II) ion concentration ($c_{Cu(II)}$; mol·L^{-1}) for **1** measured at 25°C in 0.03 mol·L^{-1} propionate, pH 4.80 (▲); 0.03 mol·L^{-1} pivaloate, pH 4.65 (■) and 0.03 mol·L^{-1} acetate, pH 4.73 (▼) buffer solutions. The fitted lines were calculated using Eq. (2).

retardation. Therefore, the coordination of Cu(II) to the sulfur and carbonyl is more probable like in the case of *N*-acyl thiourea ligands [40]. From the comparison of the moderate acceleration caused by Cu(II) ions during transformation of **1** to **2** with Cu(II)-catalyzed hydrolysis of amino acid glycine esters [20] or other similar reactions [18], it can be concluded that the complex formed has only poor stability [41]. This conclusion is supported by the absence of any new absorbance band in the UV–vis spectra during the reaction and by

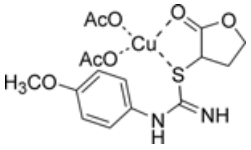
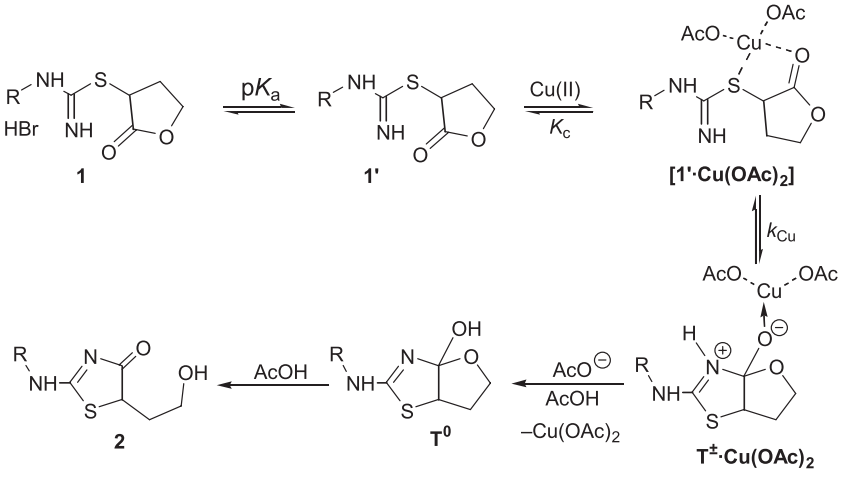


Figure 5 Possible structure of complex of substrate with copper(II) acetate.

the value of the previously mentioned complex stability constant $K_c = 600$ L·mol^{-1}. Coordination to the sulfur [18] is possible, but it would not influence the reaction rate. Very probable is the presence of the complex illustrated in Fig. 5 in which the copper(II) acetate coordinates to both the sulfur and the carbonyl oxygen atom. It is possible to propose that for the reaction acceleration is necessary for coordination of the Cu(II) ion to the carbonyl oxygen [42], and this fact is further discussed. In this case, copper(II) acetate acts as a Lewis acid catalyst and facilitates the attack of the imino group on the carbonyl by withdrawing electrons from the system [9,43,44].

Coordination of copper(II) acetate to the carbonyl oxygen opens a new reaction pathway involving internal attack of the activated carbonyl by the imino group. Thus formed $T^{\pm}\cdot Cu(OAc)_2$ undergoes proton switch (cf. [28]) to T^0. The formation of T^0 the most probably remains the rate-limiting step of the reaction sequence even in the presence of Cu(II) ions. The intermediate T^0 (or some complex with $Cu(OAc)_2$) then quickly decomposes under buffer catalysis to the final product **2** (Scheme 3).

It was recently suggested [31] that there exist a cooperativity between the catalytic effect of copper(II) and acetate anions (bifunctional catalysis) during the



Scheme 3 Probable reaction mechanism for the Cu(II)-catalyzed rearrangement of **1** to **2**.

rearrangement of phenylhydrazones derived from the 3-benzoyl-5-phenyl-1,2,4-oxadiazole. In our case, the acetate anion present in the coordination sphere of Cu(II) could act as an internal base cleaving proton from $T^{\pm}\cdot Cu(OAc)_2$ via a six-membered ring to give an anionic intermediate T^- (cf. Scheme 1). In other words, such bifunctional catalysis could cause a shift to the more basic area in the general Scheme 1 for transformation of **1** to **2**.

Another possibility of the Cu(II) action was suggested in [11,45,46]. This possibility involves bond reorganization in the complex $T^{\pm}\cdot Cu(OAc)_2$ and coordination of the Cu(II) to the oxygen of the leaving group. The leaving group ability (nucleofugality) of the oxygen atom would be improved after this coordination, and formation of the product would be facilitated. We believe that such activation of a leaving alkoxide is not involved in our case because at pH 2 where acid-catalyzed breakdown of $T^{\pm}$ is the rate-limiting step of the rearrangement the Cu(II) has no influence on the reaction rate.

CONCLUSIONS

The influence of additional Cu(II) ions on the rate of the transformation of **1** to **2** has been studied. The transformation in acetate buffers in the presence of Cu(II) ions proceeds via three independent reaction pathways. The first one involves hydroxide and hydroxonium ion catalysis and is characterized by the rate constant k_0. The second one is the reaction pathway catalyzed by the acidic component of the buffer (i.e., AcOH) and is characterized by the rate constant k_{Buff}. The third one is a Cu(II) ion-catalyzed pathway in which the formation of the complex of copper(II) acetate with free isothiourea in the fast preequilibrium (K_c) is followed by the rate-limiting transformation (k_{Cu}) of this complex. The unexpected behavior in buffers with the constant Cu(II) ion concentration and increasing buffer concentration is explained by the competitive formation of $[Cu(OAc)_n]^{2-n}$ ($n = 3$ and especially 4), which retards the transformation at higher buffer concentrations.

The mechanism of copper(II) acetate action is explained by its coordination to the carbonyl oxygen of the substrate. This coordination decreases the electron density on the carbonyl carbon atom and facilitates the nucleophilic attack of the imino group of the isothiourea moiety. The advantageous arrangement of the complex enables proton transfer from the nitrogen atom to the acetate anion can also shift the reaction toward the intermediate T^- and so accelerate the transformation. On the other hand, the effect of the Cu(II) ions involving coordination to the leaving alkoxide group and improving its nucleofugality is improbable.

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