

# The reaction of dinitrito-2,2'-bipyridylcopper(II) with pyrrolidine in acetonitrile to form *N*-nitrosopyrrolidine

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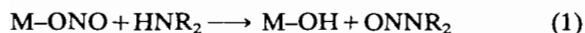
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## Abstract

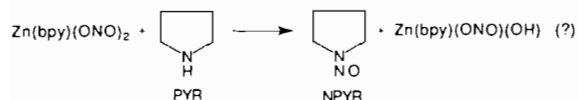
Dinitrito-2,2'-bipyridylcopper(II), [Cu(bpy)(ONO)<sub>2</sub>], reacts with pyrrolidine (PYR) in acetonitrile at 60 °C to form *N*-nitrosopyrrolidine (NPYR) and *N*-nitropyrrolidine (NOPYR). The reaction is first order in [Cu(bpy)(ONO)<sub>2</sub>] with a rate constant of  $(4.4 \pm 1.0) \times 10^{-5} \text{ s}^{-1}$ . Reacting [Cu(bpy)Cl<sub>2</sub>] and [(PPh<sub>3</sub>)<sub>2</sub>N]<sup>+</sup>NO<sub>2</sub><sup>-</sup> with PYR under the same conditions produced NPYR and NOPYR at a rate that was first order in the Cu complex with approximately the same rate constant. The proposed mechanism has Cu(II) slowly reduced by nitrite to a Cu(I) complex and N<sub>2</sub>O<sub>4</sub> which reacts with PYR to form NPYR and NOPYR.

## Introduction

*N*-Nitrosamines are known to form in many different ways [1], but few are known which involve the promotion of *N*-nitrosation by metal ions. The most common metal *N*-nitrosating agents are the transition metal nitrosyl complexes [2–5]. In this case, amines react with the NO<sup>+</sup> group bound to the metal ion. Metal nitrito complexes (M–ONO) might serve as *N*-nitrosating agents if the metal ion would polarize the nitrite group sufficiently to have a reaction between the amine and complex [6].



Many nitrito complexes are known [7] and one, dinitrito-2,2'-bipyridylzinc(II) (Zn(bpy)(ONO)<sub>2</sub>), nitrosates aniline [8] and reacts with pyrrolidine (PYR) to form *N*-nitrosopyrrolidine (NPYR) [6].



The PYR reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> at reflux temperature; while the aniline reaction was carried out in 1,2-dichloroethane at 60 °C. To explain the results found for the aniline reaction, the solvent had to play a role in the reaction. A later study

showed that the soluble nitrite, [(PPh<sub>3</sub>)<sub>2</sub>N]<sup>+</sup>NO<sub>2</sub><sup>-</sup>, slowly reacted with the solvent, CH<sub>2</sub>Cl<sub>2</sub>, at room temperature to form a species, presumably chloromethylnitrite, which did nitrosate PYR [9]. Preliminary to the work reported here, Zn(bpy)(ONO)<sub>2</sub> was found not to react with PYR at 60 °C in CH<sub>3</sub>CN.

Another group of nitrito complexes are the Cu(II) nitrites [10–12], such as Cu(bpy)(ONO)<sub>2</sub> [13]. The structure of this compound has been determined and the nitrite group is bound to the Cu in an unsymmetrical bidentate manner with one O atom of each nitrite bound in the plane with the bpy ligand [12]. The other two O atoms are bound further from the Cu along the axis perpendicular to the plane. This compound when reacted with PYR at 60 °C in CH<sub>3</sub>CN was found to produce NPYR and the results of the experiments are described in this report. The formation of NPYR, however, does not occur by reaction (1), but employs the redox properties of Cu(II) in CH<sub>3</sub>CN.

## Experimental

### Chemicals

Even though the crystal structure of Cu(bpy)(ONO)<sub>2</sub> has been reported [12], no preparation of the compound has been given in the literature. The compound was prepared by mixing

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a  $\text{Cu}(\text{NO}_3)_2$  solution (2.42 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ /10 ml warm  $\text{H}_2\text{O}$ ) with a solution of 2,2'-bipyridyl (1.56 g/20 ml abs. ethanol) and then adding a solution of  $\text{NaNO}_2$  (1.38 g/20 ml  $\text{H}_2\text{O}$ ). The suspension of green needles which formed immediately was cooled in an ice bath, then filtered. The solid was washed with water and dried overnight over  $\text{P}_2\text{O}_5$  under vacuum. *Anal.* Calc. for  $\text{C}_{10}\text{H}_8\text{N}_4\text{O}_4\text{Cu}$ : C, 38.52; H, 2.59; N, 17.97. Found: C, 38.50; H, 2.45; N, 17.94%. The preparation of  $\text{Cu}(\text{bpy})\text{Cl}_2$  was carried out in a similar manner except  $\text{NaCl}$  was used instead of  $\text{NaNO}_2$ . *Anal.* Calc. for  $\text{C}_{10}\text{H}_8\text{N}_2\text{ClCu}$ : C, 41.32; H, 2.77; N, 9.64. Found: C, 41.35; H, 2.75; N, 9.66%.

Anhydrous acetonitrile (Aldrich) was used with care being taken to remove aliquots under a stream of nitrogen. Pyrrolidine (Aldrich) was used with further purification. Bis(triphenylphosphine)nitrogen(1+) nitrite,  $[(\text{PPh}_3)_2\text{N}]^+\text{NO}_2^-$ , (Aldrich) was recrystallized from acetone-ether.

#### Nitrosation reactions

Each reaction was carried out in a four-neck 50 ml flask with one neck of the flask connected to a Firestone valve (Ace Glass) through a take-off adaptor having a stopcock. The Firestone valve was connected to a vacuum pump and a tank of high purity nitrogen which facilitated degassing and maintaining a constant nitrogen pressure. The second neck of the flask contained a tube with a ground glass joint top. This tube was immersed in the reaction solution and was filled with mineral oil and a thermometer inserted. The thermometer was attached to the thermostating device. The third neck was sealed with a white rubber septum to facilitate removal of samples for analysis. The fourth neck was closed with a ground glass stopper which could be removed for addition of solid reagents while keeping the solution under a stream of nitrogen.

For reactions run at Cu complex concentrations of 5 mM or higher, the Cu complex was weighed into the reaction flask and 50.0 ml of acetonitrile added. The reaction mixture was degassed under nitrogen pressure and heated to the reaction temperature in the dark. After the reaction temperature was attained, the reaction was initiated by injecting an appropriate volume of amine into the flask using a gas-tight syringe. Aliquots of the reaction mixture were removed (usually 10  $\mu\text{l}$ ) and diluted to 1.0 ml in a volumetric flask. A volume of 30  $\mu\text{l}$  was injected into the HPLC which was equipped with a 10  $\mu\text{l}$  sample loop.

For reactions run at Cu concentrations less than 5 mM, the Cu complex was weighed into either a 100, 200 or 250 ml volumetric flask and was diluted to volume with acetonitrile. A volume of 50.0 ml

was pipetted into the reaction mixture and the reaction mixture was treated as above. Aliquots of 30  $\mu\text{l}$  were removed from the reaction mixture with a syringe and were injected directly into the HPLC. Replicate reactions were performed with aliquots from the Cu complex stock solution.

For reactions run with  $\text{Cu}(\text{bpy})\text{Cl}_2$  at concentrations less than 5 mM, the complex was weighed into a volumetric flask, the amine added, and the solution diluted to volume. A 50 ml aliquot of the solution was removed and placed in the reaction flask. The solution was degassed under nitrogen pressure and heated in the dark to the reaction temperature. A weighed amount of  $[(\text{PPh}_3)_2\text{N}]^+\text{NO}_2^-$  was added under a stream of nitrogen to begin the reaction. As with the other reactions, aliquots were removed from the flask and injected into the HPLC. Also, replicate reactions were performed using the same complex-amine stock solution.

#### Instrumental

Reactions were thermostatted with a Therm-o-Watch L61000SS unit from I<sup>2</sup>R, connected to a heating mantle via a variable transformer. Reaction temperatures were maintained by this apparatus to  $\pm 1$  °C.

HPLC analyses were performed on an IBM LC9533 ternary gradient liquid chromatograph equipped with a Rheodyne injector and a variable wavelength UV detector, set at 238 nm. The mixture was separated on a reverse phase Alltech Licrosorb RP10 10  $\mu\text{m}$  column equipped with a guard column. The mobile phase for the initial high concentration work was 69% water, 30% methanol and 1% of a 1% sulfuric acid solution. In the lower concentration work, the mobile phase was 62% water, 37% methanol and 1% of a 1% sulfuric acid solution. In the work in which the *N*-nitropyrrolidine,  $(\text{CH}_2)_4\text{NNO}_2$ , (NOPYR) concentrations were determined, the mobile phase consisted of 55% water, 44% methanol and 1% of a 1% sulfuric acid solution. The increase in the methanol concentration in the mobile phase allowed separation of the nitramine peak from the large peak attributed to the metal complex.

Calibration curves for NPYR (Sigma) and NOPYR were prepared using authentic samples. NOPYR was synthesized by Dr William Muldoon (Department of Chemistry, College of St. Benedict, St. Joseph, MN) and the purity of the sample was verified by HPLC and IR analysis. The calibration curves were linear over the concentration ranges obtained in the experiments. Calibration curves were rechecked periodically and no significant change was observed. Authentic samples were also used to determine the retention times of the species being detected. Vari-

ations of the retention times were generally  $\pm 0.1$  min, with average values of the retention times at 4–5 min.

Conductance measurements were obtained with a YSI model 35 conductance meter. The constant of the dip cell used was determined using a YSI calibrating solution. Conductance measurements of the  $\text{Cu}(\text{bpy})(\text{ONO})_2$  solution in acetonitrile were obtained at 60 °C.

## Results

The reaction of  $\text{Cu}(\text{bpy})(\text{ONO})_2$  with PYR in  $\text{CH}_3\text{CN}$  at 60 °C produces both NPYR and NOPYR in relatively good yields over a 24 h period. A number of reactions have been carried out at several concentrations of  $\text{Cu}(\text{bpy})(\text{ONO})_2$  and PYR. The [NPYR] and [NOPYR] were measured at various times using HPLC techniques. Measuring the [NOPYR] was difficult for it required careful control of the eluent mixture. In some instances, the [NOPYR] was not measured; and in others, the separation of the NOPYR peak from the large peak due to bpy or PYR was only partially complete and only an approximate value was obtained. Figure 1 shows the concentrations of amine products as a function of

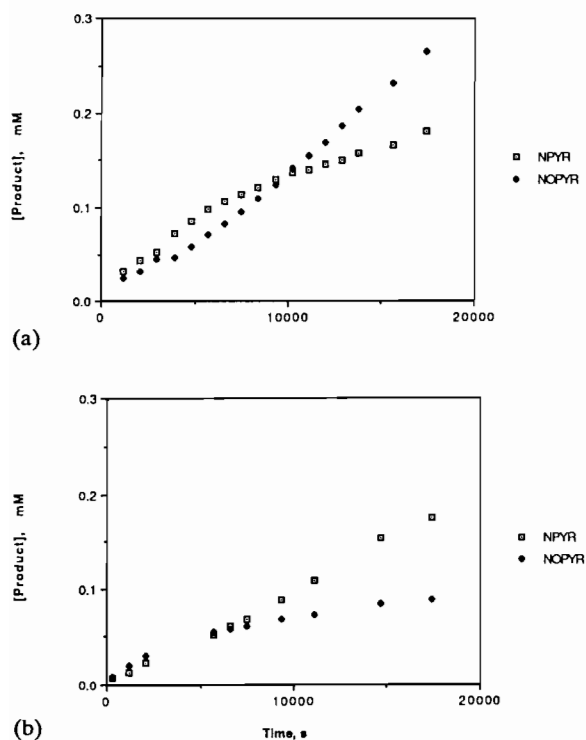


Fig. 1. [NPYR] and [NOPYR] vs. time for the reaction in  $\text{CH}_3\text{CN}$  at 60 °C of 2.4 mM PYR and (a) 1.99 mM, (b) 1.03 mM  $\text{Cu}(\text{bpy})(\text{ONO})_2$ .

time for two different experiments in which product separation was satisfactory. In these experiments the initial rates of formation of NPYR and NOPYR are approximately equal; however, after about 2 h the rates begin to deviate, one slowing down markedly. The initial rate of formation of each product was determined over the first 2 h of reaction. For those experiments with both the [NPYR] and [NOPYR] known, the sum of the initial rates of formation of the two for a given set of reactant concentrations was found to be reproducible within experimental error (*c.*  $\pm 10\%$ ). The results of these experiments are given in Table 1.

Figure 2 illustrates an experiment where the  $[\text{Cu}(\text{bpy})(\text{ONO})_2]$  and [PYR] are approximately ten times that used for the experiments shown in Fig. 1. Unfortunately only the [NPYR] was measured, but it reached a plateau after about 5 h. Changing the solvent from  $\text{CH}_3\text{CN}$  to *p*-dioxane or tetrahydrofuran did not have a major effect on the rate of NPYR production. Once the plateau was reached the [NPYR] very slowly increased over the next 10–12 h. The [NPYR] after 24 h for the three experiments in Fig. 2 was  $15.7 \pm 0.7$  mM. The 24 h concentrations of products were measured for some of the experiments shown in Table 1. In most cases, they were highly variable and could not be related to the initial  $[\text{Cu}(\text{bpy})(\text{ONO})_2]$  and [PYR].

A Cu(II) complex,  $\text{Cu}(\text{bpy})\text{Cl}_2$ , which did not have a nitrite ligand was mixed with added nitrite,  $[(\text{PPh}_3)_2\text{N}]^+\text{NO}_2^-$ , in order to determine if N-nitrosation would occur when PYR was added. Both NPYR and NOPYR formed and their initial rates of formation determined. These are shown in Table 1. When the initial concentration of the appropriate Cu(II) complex for each experiment was divided into the sum of the initial rates ( $\Sigma/[\text{Cu}]_0$ ), a relatively constant number was produced, indicating that the rate of formation of the amine products only had a first order dependence on the Cu complex. The

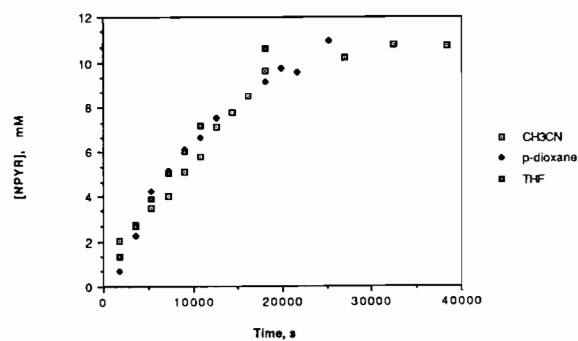


Fig. 2. [NPYR] vs. time for the 60 °C reaction of 10.5 mM  $\text{Cu}(\text{bpy})(\text{ONO})_2$  and 24 mM PYR in  $\text{CH}_3\text{CN}$ , *p*-dioxane and tetrahydrofuran (THF).

TABLE 1. Results of the reaction of [Cubpy(ONO)<sub>2</sub>] or [CubpyCl<sub>2</sub>] and [(PPh<sub>3</sub>)<sub>2</sub>N]<sup>+</sup>NO<sub>2</sub><sup>-</sup> with PYR in CH<sub>3</sub>CN

T (°C)	[Cu] <sub>0</sub> <sup>a</sup> (mM)	[NO <sub>2</sub> <sup>-</sup> ] (mM)	[PYR] (mM)	After 24 h		No. of runs	Initial rates × 10 <sup>9</sup>		Σ <sup>b</sup> (M s <sup>-1</sup> )	Σ/[Cu] <sub>0</sub> × 10 <sup>5</sup> , <sup>d</sup> (s <sup>-1</sup> )	k <sub>calc</sub> × 10 <sup>5</sup> , <sup>e</sup> (s <sup>-1</sup> )
				[NPYR] (mM)	[NOPYR] (mM)		NPYR (M s <sup>-1</sup> )	NOPYR (M s <sup>-1</sup> )			
60	0.5	0	2.4			2	5.4	—	5.4	1.1 <sup>c</sup>	
	1.0	0	1.2	0.25		5	12	7.1	19	1.9	3.5
	1.0	0	2.4	0.91		5	10	7.1	17	1.7	4.1
	1.0	0	4.8			2	8	16	24	2.4	4.6
	2.0	0	2.4	0.56	0.41	2	12	32	44	2.2	3.2
	0.5	1.0	1.8			3	4.0		4.0	0.8 <sup>c</sup>	
	0.5	0.5	2.4			4	4.7		4.7	0.9 <sup>c</sup>	
	0.5	1.0	4.7			2	4.3		4.3	0.9 <sup>c</sup>	
	1.0	1.0	2.4			2	20	0.6	21	2.1	6.3
	1.0	1.0	4.7	0.47		4	14	3.8	18	1.8	3.6
	1.0	2.0	4.7			2	22	0.6	23	2.3	5.8
45	1.0	0	2.4			2	1.6	2.7	4.3	0.43	0.88
30	1.0	0	2.4			2	0.4	0.2	0.6	0.06	0.15

<sup>a</sup>If amount of NO<sub>2</sub><sup>-</sup> is 0, then [Cubpy(ONO)<sub>2</sub>] used; if not, then [CubpyCl<sub>2</sub>] and [(PPh<sub>3</sub>)<sub>2</sub>N]<sup>+</sup>NO<sub>2</sub><sup>-</sup> used. <sup>b</sup>Sum of the initial rates of formation of NPYR and NOPYR. <sup>c</sup>This is a low value since initial rate of formation of NOPYR could not be measured. <sup>d</sup>Average value of Σ/[Cu]<sub>0</sub>, initial rate sum divided by the initial concentration of Cu complex, using seven values that have both NPYR and NOPYR rates measured, is (2.1 ± 0.2) × 10<sup>-5</sup> s<sup>-1</sup>. <sup>e</sup>First-order rate constant (see 'Discussion'). Average value is (4.4 ± 1.0) × 10<sup>-5</sup> s<sup>-1</sup>.

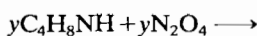
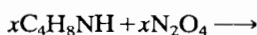
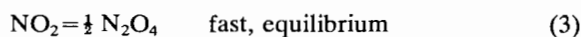
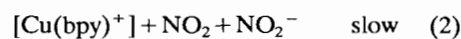
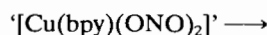
rate of formation did not depend to any great extent on the [PYR] and [NO<sub>2</sub><sup>-</sup>]. For those experiments where the [NOPYR] was not measured, if the Σ/[Cu]<sub>0</sub> is multiplied by two, a number approximating the other values at 60 °C is obtained. This is equivalent to having the initial rates of formation of NPYR and NOPYR equal.

When Cu(bpy)(ONO)<sub>2</sub> is dissolved in CH<sub>3</sub>CN at 60 °C, a green solution forms and some ionization occurs (a 0.99 mM [Cu(bpy)(ONO)<sub>2</sub>] solution has a molar conductance of 16.5 mho cm<sup>2</sup>/mol compared to a highly ionized 0.82 mM [(PPh<sub>3</sub>)<sub>2</sub>N]<sup>+</sup>NO<sub>2</sub><sup>-</sup> solution with a molar conductance of 150 mho cm<sup>2</sup>/mol). When the amine is added to the hot solution, the solution turns yellow and becomes darker as the reaction proceeds. If the [Cu(bpy)(ONO)<sub>2</sub>] is greater than 5 mM, the solution becomes red-brown within 24 h. However, upon cooling the solution returns to a green color. In some reactions with [Cu(bpy)(ONO)<sub>2</sub>] greater than 25 mM, a black to dark red precipitate resulted after 24 h of heating. The precipitate was dissolved in conc. HNO<sub>3</sub> and the %Cu determined spectrophotometrically through formation of the tetraammine complex. Analysis showed the precipitate to be 99+ % Cu, indicating that the final product was Cu metal.

## Discussion

A mechanism which explains the N-nitrosation of PYR by Cu(bpy)(ONO)<sub>2</sub> in CH<sub>3</sub>CN, at least in the

early part of the reaction, is the following:



The reaction medium containing the Cu(II) nitrito complex and PYR has a variety of species which may include [Cu(bpy)(ONO)<sub>2</sub>] and [Cu(bpy)(ONO)]<sup>+</sup>, but most probably, mixed Cu(II) amine complexes, such as [Cu(bpy)(PYR)<sub>2</sub>]<sup>2+</sup> and [Cu(bpy)(PYR)(ONO)]<sup>+</sup>. The latter are presumed to be present since the color of the Cu(II) solution changes immediately upon addition of the amine. NO<sub>2</sub> and a Cu(I) complex might be formed by all of the Cu(II) species and [Cu(bpy)(ONO)<sub>2</sub>] represents them in eqn. (2). In fact, a species such as [Cu(bpy)(PYR)<sub>2</sub>]<sup>2+</sup> with no nitrite ligand might react with unbound nitrite by an outer-sphere mechanism. In the initial stage of the reaction probably one Cu(II) species is predominant.

In CH<sub>3</sub>CN, Cu(II) is expected to serve as an oxidizing agent [14, 15]. However, allowing a solution of [Cu(bpy)(ONO)<sub>2</sub>] to remain at 60 °C for 24 h

produced no color change and no Cu(I) formation. The addition of PYR to the solution to form the mixed Cu(II) amine complexes makes the reduction of Cu(II) possible. Each of the Cu(II) species would be expected to react with a different rate. As the reaction proceeds the equilibria between the labile Cu(II) complexes, nitrite and PYR would be expected to shift rapidly changing the nature of the reactants and producing a variation in the rate of the reaction.

The formation of  $N_2O_4$ , the active nitrosating agent, should occur rapidly by reaction (3) and favor a high  $[N_2O_4]$  at 60 °C [16]. The  $N_2O_4$  then rapidly reacts with PYR to form either NPYR (reaction (4)) or NOPYR (reaction (5)). The precise nature of the solution at any given time may determine whether reaction (4) or (5), or neither, is favored. In the reaction of  $[Cu(bpy)(ONO)_2]$  and excess PYR, if all of the  $Cu^{2+}$  and nitrite is available to form NPYR and NOPYR and only a Cu(I) complex, then the total  $[NPYR]$  and  $[NOPYR]$  formed would equal the initial  $[Cu^{2+}]$ ,  $[Cu]_0$ , and one-half of the  $NO_2^-$  would remain. If Cu metal forms, then  $2[Cu]_0$  is the maximum total  $[NPYR]$  and  $[NOPYR]$  that can be produced.

In the initial stage of the reaction, the following assumptions may be made:  $[NO_2^-]$  and  $[N_2O_4]$  are small; the  $[NPYR]$  is equal to the  $[HNO_3]$ ; and the  $[NOPYR]$  is equal to the  $[HNO_2]$ . If these are made, then the following relationship may be derived:

$$[Cu] = [Cu]_0 - 2[NPYR] - 2[NOPYR]$$

$[Cu]_0$  is the initial concentration of  $Cu(bpy)(ONO)_2$  and  $[Cu]$  is the concentration of Cu(II) at any time. For experiments where both the  $[NPYR]$  and  $[NOPYR]$  were determined, the first order relationship,  $\ln([Cu]/[Cu]_0)$  versus time may be plotted and  $k$ , the rate constant, obtained. Figure 3 gives some representative plots. The values of  $k$  are given in Table 1 and are approximately twice the values of  $\Sigma/[Cu]_0$ . The production rates of  $HNO_3$  and  $HNO_2$  were not included in the calculation of  $\Sigma/[Cu]_0$  and they are equal, by the above mechanism, to those of NPYR and NOPYR, respectively. Therefore, the values of  $\Sigma/[Cu]_0$  do not include the initial rates of all of the N-containing products, only one-half of them.

Molecular  $N_2O_4$  has been well-described as a N-nitrosating agent in a number of solvents, including  $CH_3CN$ . In that solvent  $N_2O_4$  nitrosates piperidine,  $(CH_2)_5NH$  and diphenylamine at room temperature [17]. At 0 °C in  $CH_3CN$ , aniline reacts with  $N_2O_4$  at measurable rates to give nearly quantitative yields of the diazonium nitrate,  $[PhN_2]^+NO_3^-$  [18]. With secondary amines in organic solvents [19] and in water [17, 20], both the N-nitroso and N-nitro products are obtained. The ratio of the two products

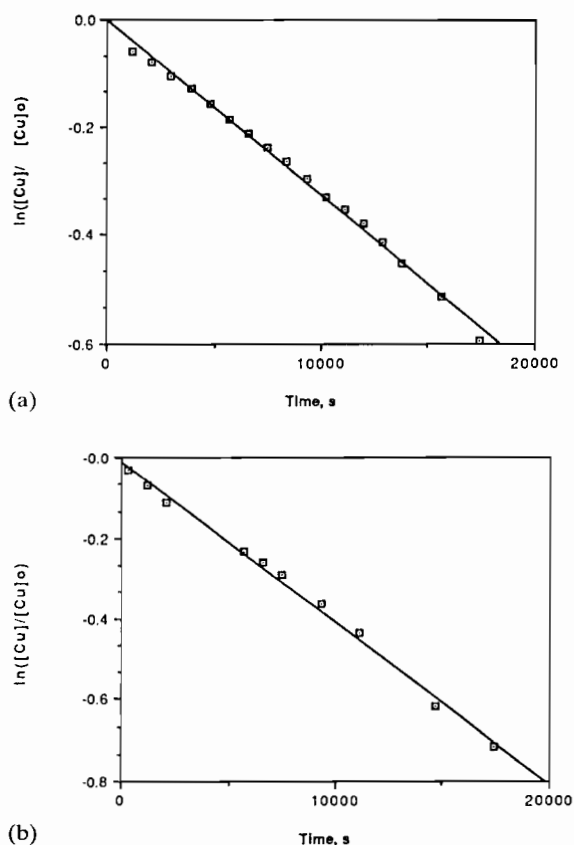


Fig. 3. First-order plot for the reaction in  $CH_3CN$  at 60 °C of 2.4 mM PYR and (a) 1.99 mM, (b) 1.03 mM  $Cu(bpy)(ONO)_2$ . Slope of the line for the top graph,  $-3.44 \times 10^{-5} s^{-1}$ ; correlation coefficient 0.996; bottom graph: slope,  $-3.98 \times 10^{-5} s^{-1}$ , correlation coefficient 0.998.

may depend on a variety of factors, such as amine basicity [17] and the ionic strength of the reaction medium.

By the above mechanism the nitrosating agent,  $N_2O_4$ , is being supplied at a slow rate by one Cu(II)/nitrite complex, or several with approximately the same rate constant, to cause reduction of Cu(II) to Cu(I). Since the spectra of  $[Cu(bpy)(ONO)_2]$  in the solution and solid states are identical [21], this complex maintains nitrito bonds in solution. As mentioned above, when PYR is added, the color of the solution changes and the PYR binds to the Cu(II), possibly assisting in the loss of a nitrite. The bonding mode of the nitrite in the mixed Cu(II) complexes, maybe in the nitrito mode; however, the mechanism does not require nitrito bonding. It only involves the homolytic cleavage of the  $NO_2$  group from the Cu. An activation energy of 22 kcal/mol for the N-nitrosation reaction was calculated using the variable temperature data given in Table 1. This is much

less than the 61 kcal/mol given for the Cu–O bond energy [22].

The Cu(II) nitrito complex did not react directly as a nitrosating agent, through loss of the  $\text{NO}^+$  group, in the manner shown in eqn. (1). In fact, Ni(II) nitrito complexes, such as  $[\text{Ni}(\text{N,N}\text{-dien})_2(\text{ONO})_2]$  and  $[\text{Ni}(\text{tetmen})(\text{ONO})_2]$ , did not react with PYR in  $\text{CH}_3\text{CN}$  at 60 °C. Apparently the +2 metal ion is not strong enough to polarize the nitrito group to form the  $\text{NO}^+$  species. Possibly a metal of higher charge which forms nitrito complexes (maybe Cr(III)?) might do so. The reaction of the Cu(II) nitrito complex requires that a lower oxidation state be readily accessible in order that  $\text{NO}_2$  might form.

Organic soluble nitrite can react with secondary amines to form *N*-nitrosamines in the presence of Cu(II) complexes. A mixture of PYR and  $[(\text{PPh}_3)_2\text{N}]^+\text{NO}_2^-$  allowed to stand in  $\text{CH}_3\text{CN}$  for 24 h at 60 °C did not result in any NPYR formation. However, when  $[\text{Cu}(\text{bpy})\text{Cl}_2]$  was present PYR and NOPYR formed. The kinetic results show that the reaction is very similar to that between PYR and  $[\text{Cu}(\text{bpy})(\text{ONO})_2]$ . There did not appear to be any  $\text{Cl}^-$  catalysis or major ionic strength effect. The latter may account for the difference in formation rates of NPYR and NOPYR.

The thermochromic nature of the Cu complex solution is unusual. The yellow and red–brown are characteristic of Cu(I), but the color reverts back to green upon cooling. These changes, along with electrochemical studies of the Cu(II)/amine/nitrile system in  $\text{CH}_3\text{CN}$ , are to be examined in the future.

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