

E. Giesbrecht, *Inorg. Chem.*, 12, 2084 (1973). – <sup>(7b)</sup> D. M. Macartney and A. McAuley, *Inorg. Chem.*, 18, 2891 (1979); *ibid.*, 20, 748 (1981). – <sup>(7c)</sup> E. B. Borghi, M. A. Blesa, P. J. Aymonino and J. A. Olabe, *J. Inorg. Nucl. Chem.*, 43, 1849 (1981). – <sup>(8a)</sup> H. E. Toma and J. M. Malin, *Inorg. Chem.*, 12, 1039 (1973). – <sup>(8b)</sup> N. V. Hrepic and J. M. Malin, *Inorg. Chem.*, 18, 410 (1979). – <sup>(8c)</sup> A. P. Szecsy, S. S. Miller and A. Haim, *Inorg. Chim. Acta*, 28, 189 (1978). – <sup>(9)</sup> M. A. Blesa, I. A. Funai, P. J. Morando, J. A. Olabe, P. J. Aymonino and G. Ellenrieder, *J. Chem. Soc., Dalton Trans.*, 845 (1977). – <sup>(10)</sup> M. A. Blesa, I. A. Funai, P. J. Morando and J. A. Olabe, *J. Chem. Soc., Dalton Trans.*, 2092 (1977).

<sup>(11)</sup> N. E. Katz, J. A. Olabe and P. J. Aymonino, *J. Inorg. Nucl. Chem.*, 39, 908 (1977). – <sup>(12)</sup> J. A. Olabe, work in progress. – <sup>(13)</sup> V. L. Goedken, *J. Chem. Soc., Chem. Comm.*, 207 (1972). – <sup>(14)</sup> G.

Schwarzenbach, *Helv. Chim. Acta*, 19, 178 (1936). – <sup>(15)</sup> G. Davies and A. R. Garafalo, *Inorg. Chem.*, 19, 3543 (1980) and references therein. – <sup>(16)</sup> J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, 84, 16 (1962). – <sup>(17)</sup> N. E. Katz, M. A. Blesa, J. A. Olabe and P. J. Aymonino, *J. Inorg. Nucl. Chem.*, 42, 581 (1980). – <sup>(18)</sup> P. J. Morando and M. A. Blesa, *J. Chem. Soc., Dalton Trans.*, in press. – <sup>(19)</sup> A. Haim, *Inorg. Chem.*, 9, 426 (1970). – <sup>(20)</sup> Z. Bradic, M. Pribanic and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 353 (1975).

<sup>(21)</sup> H. E. Toma and J. M. Malin, *J. Am. Chem. Soc.*, 94, 4039 (1972). – <sup>(22)</sup> C. T. Bahner and L. L. Norton, *J. Am. Chem. Soc.*, 72, 2881 (1950).

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## Oxidation of Bis(Bipyridine) Copper(1+) by Oxygen in a Non-Aqueous System. Part I. Nitromethane, Acetonitrile

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### Summary

The oxidation of the cuprous complex, [Cu(bipy)<sub>2</sub>]ClO<sub>4</sub>, in nitromethane (NM) and acetonitrile (AN) solution was studied. The reaction rate was found to be first order in oxygen and second order in the copper(I) complex. When an excess of ligand was present with the cuprous complex, the observed rate constant,  $k_0$ , was found to have a reciprocal dependence on the concentration of free bipyridine. The calculated first dissociation constants,  $K_D$ , ( $7.6 \cdot 10^{-4}$  and  $1.4 \cdot 10^{-5}$  M for AN and NM) at 23 °C indicate that the cuprous complex is more dissociated in acetonitrile. However, the rate of oxidation is 50 times slower in this solvent. Using the  $K_D^{NM}$  value, the rate constants for the oxidation of the undissociated and dissociated species were found to be 21.5 and  $2.1 \cdot 10^3$  M<sup>-2</sup> s<sup>-1</sup>, respectively.

### Introduction

The oxidations of copper(I) complexes studied hitherto show differences in their rate-dependence on the free ligand concentration. Nord<sup>(1)</sup> observed a decrease in rate with increase in ligand concentration, Zuberbühler<sup>(2)</sup> found that the amine and imidazole complexes of copper(I) are oxidized at a rate that is linearly dependent on the respective ligand concentration, whereas Anbar<sup>(3)</sup> found that for the bis(bipyridine) complex the rate is independent of the ligand concentration (above a 1:2 metal to ligand ratio). More recently Crumbliss<sup>(4)</sup>

found that the auto-oxidation of the terpyridine complex proceeds by several paths that involve Cu(terpy)<sub>2</sub><sup>+</sup> and the mono-(terpyridine) complex. Finally, Gorbunova<sup>(5)</sup> reports that in acid aqueous solution the oxidation of Cu(bipy)<sub>2</sub><sup>+</sup> is independent of the free bipyridyl concentration, while in a neutral medium the relaxation time,  $\tau$ , decreases with increasing bipyridine concentration at low [Cu(Bipy)<sub>2</sub>]<sup>+</sup>.

The reaction order with respect to copper(I) has been found to be one for most of the studied systems. However, there are two exceptions, where a second-order dependence with respect to copper(I) is found<sup>(6,7)</sup>.

Because of these considerable differences in the experimental rate laws for the oxidation of copper(I) compounds, we have investigated the reaction of bis(bipyridine)copper(I) perchlorate with molecular oxygen in nitromethane and acetonitrile solution.

### Experimental

The purification of the solvents and preparation of the complex have been described previously<sup>(8,9)</sup>.

A Beckman oxygen sensor was used to follow the oxygen consumption during the kinetic runs. Freshly prepared solution of the copper(I) complex in deoxygenated NM and/or AN were used in the kinetic experiments. When runs were carried out with an excess of ligand, the solutions were prepared by dissolving simultaneously the solid sample of complex and bipyridine. These solutions were left for 30 min to attain the desired temperature. The solutions were degassed with oxygen-free nitrogen to protect them from oxidation. Nitrogen

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was purified by bubbling it through  $\text{Cr}^{\text{II}}$  solutions and then dried by passing it through  $\text{H}_2\text{SO}_4$ ,  $\text{P}_2\text{O}_5$  and  $\text{KOH}$  traps.

The dissociation constants were determined spectrophotometrically at 440 nm using a thermostated Unicam 8000 spectrophotometer. Solutions were prepared in deoxygenated optical cells fitted with serum caps. Since the cuprous complex reacts with the residual oxygen left in the solutions, the absorbance decreases with time. Therefore, extrapolated values of absorbance were used to calculate the absorptivities.

## Results and Discussion

The consumption of oxygen gave first-order rate plots from which  $k_0$  was calculated. An excess of copper(I) complex compared with the dissolved oxygen ensured pseudo-first-order conditions. The first-order rate constant,  $k_0$ , was dependent on the square of the analytical concentration,  $\text{Cu}^{\text{I}}_{\text{A}}$ .

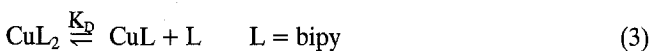
The experimental rate law is represented by the following equations:

$$R = k_1[\text{Cu}^{\text{I}}_{\text{A}}]^2[\text{O}_2] \quad (1)$$

$$k_0 = k_1[\text{Cu}^{\text{I}}_{\text{A}}]^2 \quad (2)$$

A second-order dependence on the analytical concentration of cuprous complex was obtained both in experiments done with and without an excess of free ligand. In each case the complex concentration was varied from  $2 - 9 \cdot 10^{-3}$  M. The values of  $k_1$  are given in Table 1. The activation energy was found to be very small ( $\sim 2$  Kcal/mol).

Since the oxidation rate decreases as the excess of free bipyridine is added (Table 2), it is possible to postulate a dissociation equilibrium:



$K_D$  is assumed to be rapidly established as copper (I) is a labile  $d^{10}$  system. It is inferred from the kinetic data that the coordinatively saturated  $\text{CuL}_2$  would be the less reactive species towards oxygen, while  $\text{CuL}$  would be rapidly oxidized.

This equilibrium is detected in the visible spectrum of the complex. The absorption maximum at 440 nm is intensified when an excess of ligand is added to the solutions of the cuprous complex. With high concentrations of free bipyridine, limiting absorbance values permit the calculation of the molar absorptivity of  $\text{CuL}_2$  at 440 nm,  $\epsilon = 5.4 \cdot 10^3 \text{M}^{-1}\text{cm}^{-1}$  (ratio

**Table 2.** Calculated values of the first order rate constant corresponding to the oxidation of the dissociated and undissociated species in nitromethane at 23 °C

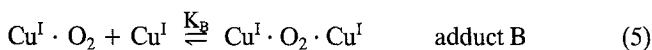
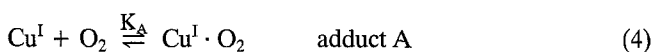
$[\text{L}]_{\text{A}}^*$ $10^3\text{M}$	$[\text{L}]^{**}$ $10^3\text{M}$	$[\text{CuL}_2]$ $10^3\text{M}$	$[\text{CuL}]$ $10^3\text{M}$	$k_{\text{u}} \cdot 10^4$ $\text{s}^{-1}$	$k_{\text{d}} \cdot 10^4$ $\text{s}^{-1}$	$k_0 \cdot 10^4$ $\text{s}^{-1}$
1. $[\text{CuL}_2]_{\text{A}} = 4.64 \cdot 10^{-3}\text{M}$						
-	0.25	4.40	0.25	4.15	22.42	27.6
0.03	0.26	4.41	0.23	4.18	21.18	25.1
0.04	0.27	4.42	0.22	4.19	20.76	24.6
0.12	0.31	4.45	0.19	4.25	18.07	22.2
0.22	0.38	4.48	0.16	4.31	15.12	17.0
0.49	0.59	4.54	0.10	4.42	9.91	11.6
0.77	0.84	4.57	0.07	4.48	7.04	9.6
1.78	1.82	4.61	0.04	4.56	3.32	6.4
4.66	4.67	4.63	0.01	4.60	1.30	4.8
6.07	6.08	4.63	0.01	4.61	1.00	4.8
2. $[\text{CuL}_2]_{\text{A}} = 2.33 \cdot 10^{-3}\text{M}$						
-	0.17	2.16	0.17	1.00	7.75	8.7
0.24	0.33	2.21	0.09	1.05	4.19	4.6
0.49	0.55	2.24	0.06	1.08	2.63	3.4
0.87	0.90	2.27	0.03	1.10	1.61	2.6
1.34	1.36	2.28	0.02	1.11	1.08	2.0
1.54	1.56	2.28	0.02	1.12	0.95	1.8
2.44	2.45	2.29	0.01	1.12	0.61	1.0
5.85	5.86	2.30	0.01	1.13	0.26	1.1

\*  $[\ ]_{\text{A}}$ : analytical concentrations

\*\*  $[\ ]$ : equilibrium concentrations

$\text{CuL}_2/\text{bipy} = 1:100-1000$ ). The molar absorptivity of  $\text{CuL}$  at 440 nm was determined with solutions of  $[\text{Cu}(\text{AN})_4\text{ClO}_4]/\text{bipy}$  (ratio 10-100:1). The mean value was  $\epsilon = 300 \text{M}^{-1}\text{cm}^{-1}$ . The dissociation constant,  $K_D$ , of  $\text{CuL}_2$  was calculated using the absorbance values of the solutions without an excess of ligand, and assuming that the complex  $\text{CuL}$  does not absorb appreciably at 440 nm. The values for the dissociation constant of the complex in nitromethane were  $K_D = 1.1(14^\circ\text{C})$ ,  $1.3(18^\circ\text{C})$ ,  $1.4(23^\circ\text{C})$  and  $1.6 \cdot 10^{-5}\text{M}(28^\circ\text{C})$ , and in acetonitrile  $K_D = 67(18^\circ\text{C})$ ,  $76(23^\circ\text{C})$  and  $85 \cdot 10^{-5}\text{M}(28^\circ\text{C})$ . Therefore, from a thermodynamic point of view  $\text{CuL}_2$  is more stable in nitromethane than in acetonitrile, although both solvents have approximately the same dielectric constant.

The general scheme for the oxidation assumes a simultaneous two-electron reduction of oxygen and can be represented by:



The last equation corresponds to a catalyzed reaction by the solvent, or by a species generated by it.

In terms of the proposed mechanism (reactions (4)-(7)), the kinetics of the auto-oxidation of the cuprous complex ion can be described by the equations below.

$$R = k_6[\text{B}] + k_7[\text{B}][\text{X}] \quad (8)$$

$$[\text{B}] = K_A K_B [\text{Cu}^{\text{I}}]^2 [\text{O}_2]$$

$$R = K_A K_B [\text{Cu}^{\text{I}}]^2 [\text{O}_2] (k_6 + k_7[\text{X}]) \quad (9)$$

**Table 1.** Calculated values of  $k_1$  in nitromethane and acetonitrile

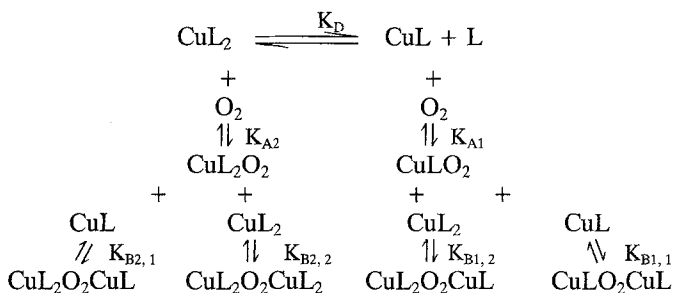
$\frac{[\text{CuL}_2]_{\text{A}}^*}{[\text{L}]_{\text{A}}}$	$k_1$ ( $\text{M}^{-2}\text{s}^{-1}$ )	Temperature (°C)
Nitromethane		
1:0.0	112.5	18
1:0.0	127.9	23
1:0.0	135.0	30
1:0.1	70.6	23
1:0.3	47.6	23
1:0.5	36.1	23
1:1.0	19.1	23
Acetonitrile		
1:0.0	2.2	10
1:0.0	2.4	18
1:0.0	2.7	23
1:0.0	3.0	30

\* Subscript A indicates analytical concentrations

A simpler equation can be considered as a first approximation if  $k_6$  is neglected in relation to  $k_7[X]$ . Replacing  $K_A K_B k_7[X]$  by  $k$ , the equation reduces to:

$$R = k[\text{Cu}^{\text{I}}]^2[\text{O}_2] \quad (10)$$

Since two reactive species were postulated in the oxidation reaction,  $\text{CuL}_2$  and  $\text{CuL}$ , two adducts A must be considered,  $\text{CuL}_2\text{O}_2$  and  $\text{CuLO}_2$ . Consequently, there are four paths to form the adducts B,  $\text{CuL}_2\text{O}_2\text{CuL}_2$ ,  $\text{CuL}_2\text{O}_2\text{CuL}$  and  $\text{CuLO}_2\text{CuL}$ .



Since the concentration of  $\text{CuL}$  is small (Table 2), the contribution to the total oxidation rate of the adduct  $\text{CuLO}_2\text{CuL}$  can be considered negligible. Therefore, equation (2) can be written as:

$$k_0 = k^{\text{I}}[\text{CuL}_2]^2 + k^{\text{II}}[\text{CuL}_2][\text{CuL}] + k^{\text{III}}[\text{CuL}][\text{CuL}_2] \quad (11)$$

$$k^{\text{I}} = K_{A2}K_{B2,2}k_7[X]$$

$$k^{\text{II}} = K_{A2}K_{B2,1}k_7[X]$$

$$k^{\text{III}} = K_{A1}K_{B1,2}k_7[X]$$

Expressing  $\text{CuL}$  in terms of the dissociation constant  $K_D$ , equation (11) can be rewritten as:

$$k_0 = k^{\text{I}}[\text{CuL}_2]^2 + (k^{\text{II}} + k^{\text{III}})\frac{K_D}{[\text{L}]}[\text{CuL}_2]^2 \quad (12)$$

$$k_u = k^{\text{I}}[\text{CuL}_2]^2$$

$$k_d = (k^{\text{II}} + k^{\text{III}})\frac{K_D}{[\text{L}]}[\text{CuL}_2]^2$$

The term inversely proportional to the equilibrium ligand concentration has been substituted by  $k_d$ , and the constant term by  $k_u$ .

If the data of Table 2 are plotted as  $k_0/[\text{CuL}_2]^2$  vs  $1/[\text{L}]$ , (equation (12)), one can obtain the slope and a constant value that enables one to calculate the following data:

$$k^{\text{I}} = 21.5 \text{ M}^{-2}\text{s}^{-1} \quad \text{corresponding to the reaction of the undissociated species}$$

$$k^{\text{II}} + k^{\text{III}} = 2.1 \cdot 10^3 \text{ M}^{-2}\text{s}^{-1} \quad \text{corresponding to the sum of the reactions of } \text{CuL}_2\text{O}_2 + \text{CuL} \text{ and } \text{CuLO}_2 + \text{CuL}_2$$

The fact that the plot of  $k_0/[\text{CuL}_2]^2$  vs  $1/[\text{L}]$  is linear provides further evidence that  $\text{CuLO}_2\text{CuL}$  is not involved, see above. Table 2 and 3 give the calculated  $k_u$  and  $k_d$  values for experiments done at 23 °C in nitromethane solution with and without added excess of bipyridine. These data confirm that the presence of  $\text{CuL}$  enhances the oxidation rate.

To explore the role of the nitromethane, kinetic runs were done in nitromethane-acetonitrile mixtures ( $k_0^{\text{NM,AN}}$ ). First,

**Table 3.** Calculated and experimental values of the first order rate constant for experiments done without excess of ligand (nitromethane at 23 °C)

[CuL <sub>2</sub> ] <sub>A</sub> 10 <sup>3</sup> M	[CuL <sub>2</sub> ] 10 <sup>3</sup> M	[L] 10 <sup>3</sup> M	k <sub>u</sub> · 10 <sup>4</sup> s <sup>-1</sup>	k <sub>d</sub> · 10 <sup>4</sup> s <sup>-1</sup>	k <sub>0</sub> · 10 <sup>4</sup> s <sup>-1</sup>
1.49	1.35	0.14	0.39	3.81	2.76
2.22	2.05	0.17	0.90	7.16	8.31
2.33	2.16	0.17	1.00	7.76	8.70
2.34	2.17	0.17	1.01	7.79	7.99
2.88	2.69	0.19	1.56	10.78	10.64
3.18	2.98	0.20	1.91	12.57	13.80
3.93	3.71	0.22	2.96	17.48	21.80
4.63	4.39	0.24	4.14	22.47	27.60
4.65	4.41	0.24	4.18	22.58	27.85
4.66	4.42	0.24	4.20	22.69	27.34
5.37	5.11	0.26	5.61	28.14	42.87
5.69	5.42	0.27	6.32	30.84	49.52
5.91	5.63	0.28	6.81	32.56	44.40
6.11	5.83	0.28	7.31	34.29	47.89
6.72	6.42	0.30	8.86	39.62	62.10
6.84	6.54	0.30	9.20	40.83	59.70
9.29	8.94	0.35	17.18	65.15	100.30

[ ]<sub>A</sub>: analytical concentrations

[ ]: equilibrium concentrations

experiments in pure acetonitrile were done to establish the mode of oxidation in this solvent. Equation (1) accounts for the experimental reaction rate in acetonitrile (Table 1). The value of the rate constant  $k_1^{\text{AN}}$  is  $2.7 \text{ M}^{-2}\text{s}^{-1}$  at 23 °C, and it was obtained for a  $3.7 - 9.0 \cdot 10^{-3} \text{ M}$  concentration range of [Cu(bipy)<sub>2</sub>]ClO<sub>4</sub>. If one compares this value with  $128 \text{ M}^{-2}\text{s}^{-1}$  found in nitromethane it can be seen that there is an approximately fifty-fold decrease in the oxidation rate. Since acetonitrile stabilizes copper(I), the solvation of the mono-complex probably accounts for this reduction<sup>(10)</sup>.

In order to verify the reactivity of  $\text{CuL}$ , kinetic runs were done with solutions of [Cu(AN)<sub>4</sub>]ClO<sub>4</sub> with bipyridine (ratio 400 : 1). These solutions did not present the 440 nm band, so it was inferred that only  $\text{CuL}$  exists in solution ( $\sim 7 \cdot 10^{-5} \text{ M}$ ). The first-order rate constant  $k_0^{\text{AN}}$  is of the order of  $0.53 \cdot 10^{-4}\text{s}^{-1}$ , which corresponds to a  $k_0^{\text{AN}}$  value of a  $4.4 \cdot 10^{-3} \text{ M}$  solution  $\text{CuL}_2$ .

In the experiments done in solvent mixtures it must be assumed that the previous three types of adducts were involved. Two regions were found in the dependence of  $k_0^{\text{NM,AN}}$  on the nitromethane concentration (Table 4). Region I comprises low molarities of nitromethane (0.067 – 1.7 M). In this concentration range a plot of  $\log(k_0^{\text{NM,AN}} - k_0^{\text{AN}})$  vs  $\log[\text{NM}]$  indicates a reaction order of 0.5 in nitromethane. In this same range, the apparent molar absorptivity of [Cu(bipy)<sub>2</sub>]<sup>+</sup> does not change as the nitromethane concentration is increased, indicating that the  $K_D$  value remains constant. Hence the concentration of [Cu(bipy)(AN)<sub>x</sub>]<sup>+</sup> does not change in this region. The low value for  $k_0^{\text{NM,AN}}$  at high acetonitrile concentration can be explained, assuming that the mono-bipyridine complex is preferentially solvated by acetonitrile. This preferential solvation becomes the dominant factor in determining the oxidation rate and compensates for the greater dissociation of the complex in this concentration range.

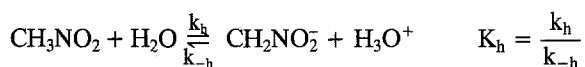
The one-half order in nitromethane obtained in the experiments at low concentrations of this solvent suggests that the solvent is directly involved in the reaction. If the dissociation reaction of nitromethane is considered:

**Table 4.** Experimental values of  $k_0$  for experiments done in nitromethane-acetonitrile mixtures at 23°C\*

Region I			Region II	
$\epsilon_{\text{app}} = 3.6 \cdot 10^3 \text{M}^{-1} \text{cm}^{-1}$				
[NM]	$(k_0^{\text{NM, AN}} - k_0^{\text{AN}})$	[NM]	$(k_0^{\text{NM, AN}} - k_0^{\text{AN}})$	$\epsilon_{\text{app}} \cdot 10^{-3}$
M	$10^4 \cdot \text{s}^{-1}$	M	$10^4 \text{s}^{-1}$	$\text{M}^{-1} \text{cm}^{-1}$
0.07	0.23	2.00	1.62	—
0.13	0.46	3.91	2.70	—
0.20	0.35	9.30	5.12	4.25
0.30	0.54	11.74	6.39	—
0.60	0.72	13.70	10.64	—
0.80	0.75	15.65	12.56	—
1.10	0.91	16.14	14.43	4.75
1.33	0.92	17.61	17.10	—
1.67	1.24	18.10	18.68	—
		(pure solvent)	27.60	5.10

\*  $[\text{CuL}_2]_{\text{A}} = 4.64 \cdot 10^{-3} \text{M}$ 

the concentration of  $\text{H}^+$  and  $\text{CH}_2\text{NO}_2$  can be taken as proportional to the square root of the molar concentration of nitromethane in the solution. The reaction between nitromethane and traces of water is another factor to be considered, since the water content during the oxidation reaction was determined to be in the order of  $10^{-2} \text{M}$ .



It has been published that  $K_h(\text{NM}) > K_h(\text{AN})$  and  $k_h(\text{NM}) > k_h(\text{AN})$  by a factor of  $10^{14}$  and  $10^6$ , respectively<sup>(11)</sup> so acetonitrile may be ignored as a source of protons.

Since the linear dependence between  $(k_0^{\text{NM, AN}} - k_0^{\text{AN}})$  and  $[\text{NM}]^{0.5}$  has a negligible intercept (Figure) it is possible to assume that  $k_6 \ll k_7 [\text{X}]$ . The term dependent on the nitromethane concentration may be interpreted as catalysis of one or both of the following types:

a) the nitromethane ion enhances the reaction by reacting with the copper(I) oxygen adduct and allows the cupric ion to change coordination number and geometry after electron transfer, and/or

b) the reaction may be accelerated by the presence of protons<sup>(12, 13)</sup>, since these facilitate the reduction of oxygen.

However, further experiments are needed in order to distinguish between these two possibilities.

In region II, that is at higher nitromethane concentrations,  $k_0^{\text{NM, AN}}$  is found to increase rapidly. A different interpretation becomes necessary. Presumably  $[\text{Cu}(\text{bipy})(\text{AN})_x(\text{NM})_y]^+$  must be present ( $x$  and  $y$  vary from 0 to 2). This concentration range is characterized by an increase of the apparent molar absorptivity at 440 nm, which corresponds to a decrease of the  $K_D$  value, as the nitromethane concentration increases. Nevertheless, the  $k_0^{\text{NM, AN}}$  values clearly show the effect of the acetonitrile, since the oxidation rate decreases 40% in relation to  $k_0^{\text{NM}}$ , when the concentration of this solvent is 1.0 M.

We do not know the composition of the principal product(s) of the oxidation. Crystals of  $[\text{Cu}(\text{bipy})_2\text{NO}_2]\text{ClO}_4$  have been isolated and identified<sup>(14)</sup>. However, this compound is considered as a secondary product, since the crystals were separated after 18 hours of reaction. The g.l.c. technique was used to detect possible organic products generated during the cleavage of the nitromethane. A small maximum appears during analysis of the mother liquors before the principal peak due to nitromethane. However, this peak does not correspond to methanol, formaldehyde, formic acid or methyl formate.

Another product of the reaction should be, by stoichiometry,  $\text{H}_2\text{O}_2$ . This is not detected at the end of this reaction. However, reports exist that indicate that the reaction of the copper(I) complex with  $\text{H}_2\text{O}_2$  takes place. Therefore, the produced hydrogen peroxide must react with the excess of copper(I) complex present in the solution<sup>(3, 15)</sup>.

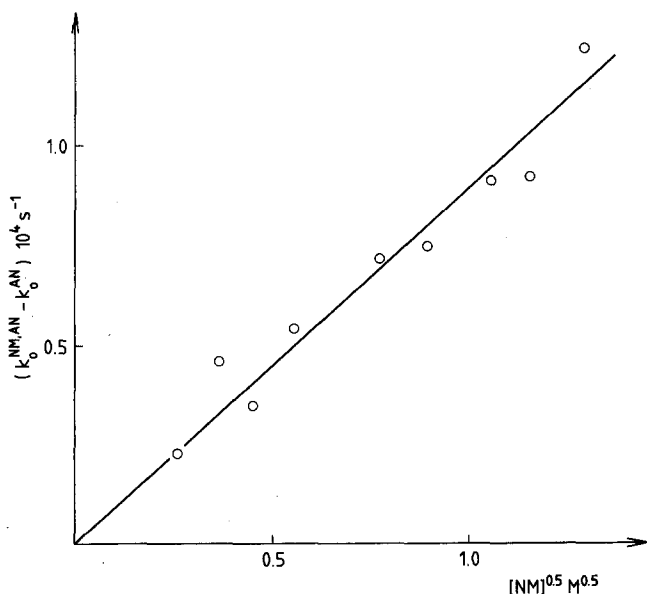
Further work related with the isolation of primary products is in progress.

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#### References

- (1) H. Nord, *Acta Chem. Scand.*, 9, 430 (1955). — (2) A. Zuberbühler, *Helv. Chim. Acta*, 50, 466 (1967). — (3) I. Pecht, M. Anbar, *J. Chem. Soc. A*, 1902 (1968). — (4) A. L. Crumbliss, A. T. Poulos, *Inorg. Chem.*, 14, 1529 (1975). — (5) N. V. Gorbunova, A. P. Purmal, Yu. I. Skurlatov, S. O. Travin, *Int. J. Chem. Kin.*, IX, 983 (1977). — (6) P. M. Henry, *Inorg. Chem.*, 5, 688 (1966). — (7) J. A. Arce, E. Spodine, W. Zamudio, *J. Inorg. Nucl. Chem.*, 37, 1304 (1975). — (8) J. Zagal, E. Spodine, W. Zamudio, *J. Chem. Soc., Dalton*, 85 (1974). — (9) A. A. Schilt, R. C. Taylor, *J. Inorg. Nucl. Chem.*, 9, 211 (1959). — (10) H. C. Mruthyunjaya, A. R. Vasudeva Murthy, *J. Electroanal. Chem.*, 15, 200 (1967).
- (11) R. G. Pearson, R. Dillon, *J. Am. Chem. Soc.*, 75, 2434 (1953). — (12) J. S. Valentine, A. B. Curtis, *J. Am. Chem. Soc.*, 97, 225 (1975). — (13) R. D. Gray, *J. Am. Chem. Soc.*, 91, 56 (1969). — (14) M. T. Garland, E. Spodine, W. Zamudio, *J. Applied Cryst.*, 14, 475 (1981). — (15) S. Bhaduri, N. Y. Sapre, *J. Chem. Soc., Dalton*, 2585 (1981).



**Figure.** Dependence of the first-order rate constant on the concentration of nitromethane.