# THE KINETICS OF THE COPPER(II)-IODINE(-I) REACTION IN THE PRESENCE OF CHLORINE(-I) IONS

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Abstract—The kinetics of the reaction between Cu(II) and I<sup>-</sup> to give Cu(I) and I<sub>2</sub> have been investigated in acidic solution in the presence of high chloride ion concentration ( $\mu = 3.13$  M). Under such conditions the precipitation of CuI is avoided. The rate of I<sub>2</sub> production was followed using a "clock" technique, by addition of increments of thissulphate and noting the time of appearance of the blue I<sub>2</sub>-starch complex. At a constant chloride ion concentration 1500 times that of the initial [Cu<sup>2+</sup>], the reaction is second order in both Cu<sup>2+</sup> and I<sup>-</sup>, and is independent of [H<sup>+</sup>]. The rate is almost independent of [Cl<sup>-</sup>], but CuI precipitates when the initial [Cu<sup>2+</sup>] has a value of  $5.6 \times 10^4$  M<sup>-3</sup> s<sup>-1</sup> at 298.2 K ([Cl<sup>-</sup>] = 2.73 M,  $\mu = 3.13$  M) with activation parameters:  $E_{\mu} = 54.8$  kJ mol<sup>-1</sup>, log PZ = 14.347 and  $\Delta S_{298}^* = 21.4$  J K<sup>-1</sup> mol<sup>-1</sup>. The rate determining step is characterised by a large positive salt effect and a mechanism is proposed consistent with these observations.

#### INTRODUCTION

The reaction between  $Cu^{2+}$  and  $I^-$  is used extensively in the iodometric analysis of  $Cu(II)^1$ . As the  $[I^-]$  is reduced, the reaction occurs at a conveniently measurable rate.<sup>2-4</sup> Previous kinetic studies have been complicated by the precipitation of CuI, which gives rise to the characteristic autocatalytic behaviour of an heterogenous system, and reaction orders are not well established. To avoid these difficulties, we have investigated the kinetics of the reaction in the presence of excess chloride ion which effectively complexes the Cu(I) product and the system remains homogeneous.

## **EXPERIMENTAL**

Stock solutions of CuSO<sub>4</sub> ( $2.06 \times 10^{-2}$  M), NaI (0.123 M), HClO<sub>4</sub> (2.11 M), NaCl (5.00 M), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2.05 × 10<sup>-2</sup> M) and NaClO<sub>4</sub> (2.0 M, 5.0 M) were prepared and standardised by conventional volumetric techniques. The "standard run" conditions were  $Cu^{2+}$  (5 mL), I<sup>-</sup> (5 mL), Cl<sup>-</sup> (30 mL) and starch (freshly prepared, 1%, 5 mL) to give the following initial concentrations:  $[Cu^{2+}] = 1.87 \times 10^{-3} M$ ,  $[I^-] = 1.13 \times 10^{-2} M$ ,  $[H^+] = 0.384 M$ ,  $[Cl^-] = 2.73 \text{ M}$ , and an ionic strength,  $\mu = 3.13 \text{ M}$ . All solutions, except Cu<sup>2+</sup>, were added to a cylindrical reaction vessel fitted with a magnetic stirrer and jacketed with circulating water at the desired temperature. A 5 mL microburette containing S<sub>2</sub>O<sub>3</sub><sup>2-</sup> solution was mounted above the reaction chamber. An appropriate volume of  $S_2O_3^{2-}$  was added from the burette and, after temperature equilibration, the reaction was initiated by addition of the Cu<sup>2+</sup> solution. The time of appearance of the blue I<sub>2</sub>-starch complex was noted, and a further aliquot of  $S_2O_3^{2-}$  added. The extent of reaction vs time was thus recorded (Table 1). In much of the preliminary investigation, the calculated (3/4)-life, (1/2)-life and (1/4)-life volumes of  $S_2O_3^{2-}$  were used as aliquots. Under the above conditions, the (1/2)-life for the consumption of Cu<sup>2+</sup> was  $51 \pm 2$  s at 298.2 K.

The use of the "standard run" conditions allowed a systematic variation of  $[Cu^{2+}]$  (7.49-18.7×10<sup>-4</sup> M),  $[I^-]$  (4.52-11.3×10<sup>-3</sup> M),  $[H^+]$  (0-0.384 M),  $[CI^-]$  (0.910-2.73 M), and  $\mu$  (1.31-3.13 M), by varying the initial volumes. Appropriate amounts of NaClO<sub>4</sub> solution were added to maintain constant ionic strength where necessary. At least two, and usually three, kinetics runs were performed after the variation of any particular reaction parameter. Replacement of Cl<sup>-</sup> by Br<sup>-</sup> as complexing

agent resulted in a much faster reaction. Stock solutions used under these conditions were:  $[Cu^{2+}] = 1.01 \times 10^{-2} \text{ M}$ , 5 mL:  $[Cu^{2+}]_i = 9.16 \times 10^{-4} \text{ M}$ ,  $[I^-] = 6.32 \times 10^{-2} \text{ M}$  at  $\mu = 0.126 \text{ M}$ , NaClO<sub>4</sub>, 5 mL:  $[I^-]_i = 2.30 \times 10^{-3} \text{ M}$ ,  $[H^+] = 2.11 \text{ M}$ , 10 mL:  $[H^+]_i = 0.384 \text{ M}$ ,  $[Br^-] = 5 \text{ M}$ , 30 mL:  $[Br^-]_i = 2.73 \text{ M}$  and starch (5 mL),  $[S_2O_3^{2-}] = 2.07 \times 10^{-2} \text{ M}$ ,  $\mu = 3.13 \text{ M}$ .

#### RESULTS

Some 100 kinetic runs allowed us to determine the variation of reaction rate with respect to  $[Cu^{2+}]$ ,  $[I^-]$ ,  $[H^+]$ ,  $[Cl^-]$ , ionic strength and temperature. In most cases, the order with respect to a particular reagent was determined by the fractional life method.<sup>5</sup>

The reaction rate is independent of  $[H^+]$  in the range 0.073–0.364 M, and even with no added acid, essentially the same (1/2)-life is observed (Table 2).

A slight decrease in reaction rate is observed (Table 2) with decreasing chloride ion in the range 1.36-2.73 M. Below this value, a more marked decrease is observed, and with [Cl<sup>-</sup>] < 1.0 M, CuI precipitation occurs. A further set of reaction rates were measured in non-standard conditions ( $\mu = 4.04$  M, NaClO<sub>4</sub>), with [Cl<sup>-</sup>] varying from 3.64-1.82 M. These data (Table 2) confirm that the rate is independent of [Cl<sup>-</sup>], in the range 2.0-3.6 M and the small rate variation observed in the 1.0-2.0 M range may be due to the presence of colloidal CuI. Decreasing the [Cl<sup>-</sup>] without maintaining constant ionic strength shows that the reaction is characterised by a marked positive salt effect (Table 2).

Table 2 also presents the kinetic data obtained to determine the variation of rate with respect to  $[Cu^{2+}]$  and  $[I^-]$ . The reaction is found to be second order in both reagents and can thus be represented as:

$$\frac{-d[Cu^{2^+}]}{dt} = k_4[Cu^{2^+}]^2[I^-]^2$$
(1)

 $([Cl^-] = 2.73 \text{ M}, \mu = 3.11 \text{ M})$ . The order with respect to  $[Cu^{2+}]$  was confirmed<sup>6</sup> from a linear plot of  $[Cu^{2+}]^{-1} vs$  t obtained from the "standard run" conditions by  $S_2O_3^{2-} vs$  t data (Table 1). Pseudo-second-rate constants,  $k_2$ ,  $M^{-1} s^{-1}$ , were obtained from the slope of such plots and are presented in Table 3. The fourth order rate constant,

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Table 1. Vo	lume of $S_2O_3^{2-}$ v	s time data fo	r the Cu <sup>2+</sup> /I <sup>-</sup>	reaction.* T	= 298.2 K,	$[Cl^-]_i = 2.73 \text{ M},$	$[H^+]_i = 0.384 M_1 =$
		3.13 M. S	$S_2O_3^{2-} = 20.5$	mM. [Cu <sup>2+</sup> ]; :	= 1.87 mM		

Volume	10 <sup>4</sup> [Cu <sup>2+</sup>	$[Cu^{2+}]^{-1}$		[I]	i, (m <u>M</u> )	n <u>M</u> )		
s203 <sup>2-</sup>			11.3	9.05	6.79	4.52		
 (mL)	( <u>M</u> )	( <u>M</u> <sup>-1</sup> )		Mean t:	ime (s)			
0.75	15.9	629	-	-	-	24.5		
1.00	15.0	668	8	11	16.7	50		
1.25	14.0	714	-	-	34.3	78		
1.50	13.1	763	21.6	28.8	54	115		
1.75	12.1	826	-	45.3	77.3	151		
2.00	11.2	893	41.6	61.7	100.3	220		
2.25	10.3	971	55.3	81.7	132.5	-		
2.50	9.36	1068	70.3	104	163	-		
2.75	8.42	1188	88.6	127.7	195.5	-		
3.00	7.48	1337	110	153.3	-	-		
3.25	6.55	1527	132.3	-	-	-		
3.50	5.61	1782	157.3	221	-	-		
3.75	4.68	2137	184.6					

a Total volume of reaction mixture is 55 mL.

 $k_4$  in eqn (1) was then calculated from the initial  $[I^-]$  using the expression

$$\mathbf{k}_4 = \mathbf{k}_2 [\mathbf{I}^-]_i^{-2}.$$
 (2)

The constancy of  $k_4$  (Table 3) over a 1.7 fold variation in [I<sup>-</sup>] confirms the reaction order established by the fractional life method. Activation parameters<sup>7</sup> were obtained from the variation in  $k_4$ , using the "standard run" conditions, over the 13-25°C temperature range.

The use of bromide rather than chloride ion as a complexing agent resulted in a more rapid reaction and, in contrast to the chloride media, the rate showed a marked dependence on  $[Br^-]_i$  (Table 4). At the same initial halide ion concentration of 2.73 M, the reaction is about 50 times faster in bromide media.

The use of CH<sub>3</sub>CN as a complexing agent (without added halide ion) was also investigated. While water-CH<sub>3</sub>CN (18%) mixtures were effective in maintaining an homogeneous medium, the starch-I<sub>2</sub> indicator complex could not be used as an indicator. Meaningful orders with respect to  $Cu^{2+}$  and I<sup>-</sup> were not obtained (although the reaction under these conditions is approximately second order in Cu<sup>2+</sup>) probably because the rate is very sensitive to [CH<sub>3</sub>CN].

## DISCUSSION

Copper(II) oxidations of halide or pseudohalide ions have several synthetic [e.g.  $(CN)_2$  formation] or analytical applications. From a kinetic aspect, the Cu<sup>2+</sup>/CN<sup>-</sup> system has been the subject of several investigations<sup>8-11</sup> as this is an homogeneous reaction in the presence of excess cyanide ion.

$$2Cu^{2+} + 6CN^{-} \rightarrow 2[Cu(CN)_2]^{-} + (CN)_2.$$
(3)

Although the relationship between the order and the coefficients in eqn (3) is coincidental, Baxendale and Westcott<sup>8</sup> found the rate law to have the form

$$\frac{-d[Cu^{2+}]}{dt} = k[Cu^{2+}]^2[CN^{-}]^6$$
(4)

$$2Cu(CN)_{3}^{-} \rightarrow 2Cu(CN)_{2}^{-} + (CN)_{2}$$
 (5)

was proposed.8

and a rate determining step of

Despite less attention, it is obvious that the  $Cu^{2+}/I^{-}$  system must also be of high order in iodide ion, but the exact factor has been difficult to determine<sup>4</sup> because of the autocatalytic nature of the heterogenous reaction (6)

$$2\mathrm{Cu}^{2+} + 4\mathrm{I}^{-} \rightarrow 2\mathrm{Cu}\mathrm{I} \downarrow + \mathrm{I}_2. \tag{6}$$

For this reaction, Kemp and Rohwer<sup>4</sup> report the rate law:

$$\frac{-d[Cu^{2+}]}{dt} = k[CuI][Cu^{2+}]^{2.62}[I^{-}]^{6.2}$$
(7)

and it is this high power in  $[I^-]$  that enables the iodometric estimation of  $Cu^{2+}$  to be performed in a reasonable time.

In the present system, Cu(I) is stabilised in the presence of Cl<sup>-</sup> (or Br<sup>-</sup>) and CuI precipitation is prevented. Precipitation of CuI is also prevented if the  $[I^-]$  is sufficiently high<sup>12,13</sup> but under these conditions the reaction rate is too rapid for conventional techniques.

In principle, it should be possible, from a knowledge of the Cu<sup>2+</sup>/halide ion stability constants<sup>14</sup> and the variation in rate with respect to the halide ion, to estimate which Cu(II)X<sub>n</sub><sup>2-n</sup> species is involved in the rate determining step. Unfortunately, the results of our calculations are inconclusive but it is obvious that Cu<sup>2+</sup>, CuX<sup>+</sup> and CuX<sub>4</sub><sup>2-</sup> are unlikely candidates for the active Cu(II)halide species.<sup>15</sup> We have chosen CuX<sub>2</sub> as the reactive Cu(II) species in strong halide media to illustrate the possible mechanism, but CuX<sub>3</sub><sup>-</sup> cannot be discounted. CuX<sub>2</sub> has the advantage of providing the appropriate Cu:X ratio for the most stable form of the Cu(I) halide complex.

The following equilibria fit the observed rate laws and

are analogous to those proposed for the  $Cu^{2+}/CN^{-}$  system:<sup>15</sup>

$$Cu^{2+} + 2X^{-} \Leftrightarrow CuX_2 \tag{8}$$

$$CuX_2 + I^- \rightleftharpoons CuX_2I^- \tag{9}$$

$$2\mathrm{CuX}_{2}\mathrm{I}^{-} \rightarrow \mathrm{CuX}_{2}^{-} + \mathrm{I}_{2}. \tag{10}$$

The positive salt effect suggests a rate determining step between two ions of the same charge (eqn 10), and the choice of equilibria has been made on the basis of reactants that will give the least unfavourable electrostatic interactions. We believe that the electron transfer is rate determining rather than substitution of a coordinated water molecule, as all observations suggest that such substitution processes are very rapid in Cu(II) systems.<sup>16</sup>

Although Cu(I)-halide complexes are known to be very sensitive to air oxidation, kinetic runs performed in the open atmosphere, and under  $N_2$  were identical. Deli-

v	ariation of [C	:u <sup>2+</sup> ] <sup>a</sup>	Vari	Variation of [I <sup>-</sup> ] <sup>b</sup>					
[ Cu	<sup>2+</sup> ], t, <sup>c</sup>	t,	[1 <sup>-</sup> ],	t₂ <sup>⊆</sup>	t <sub>k</sub>				
(m <u>M</u> )	) (s)	(s)	- (mM)	(s)	(s)				
1.8	7 12.3	49.7	11.3	12.3	49.7				
1.5	0 13.8	53.3	9.05	15.8	60				
1.1	2 20.3	67.7	6.79	22	88.3				
0.7	5 31.5	98.5	4.52	35	150				
n₫	2.0 ± 0.2	1.8 ± 0.2	n <sup>₫</sup>	2.1 ± 0.2	2.0 ± 0.2				
Va	ariation of [H	¦⁺] <b>º</b>	Vari	ation of $\mu^{\frac{1}{2}}$	5				
[H <sup>+</sup> ]	i t <sub>3</sub> <sup>c</sup>	ty	[c1 <sup>-</sup> ] <sub>i</sub>	μ	tą <sup>c</sup>				
( <u>M</u> )	(s)	(s)	( <u>M</u> )	( <u>M</u> )	(s)				
0.3	33 12.5	52.7	2.73	3.13	12.7				
0.30	07 12	51	2.27	2.65	23				
0.2	30 12	51.5	1.82	2.20	55				
0.1	53 11.5	51.5	1.36	1.74	113				
0.0	77 11.8	51.5	0.91	1.29	195				
- 3	2 11	53							
Va	ariation of [C	1-] <u>Þ</u>	Variat	Variation of $[C1^{-}](\mu = 4.04)^{\frac{1}{2}}$					
[C1]	] <sub>i</sub> t <sub>i</sub> C	t <sub>L</sub>	[c1 <sup>-</sup> ];	t <sub>2</sub> j					
( <u>M</u> )	- (s)	3 (s)	(風)	(s) 5					
2.7	3 12.5	52.6	3.64	20					
2.2	7 13	56	3.18	19.5					
1.83	2 14 K	63	2.73	20					
1.30	5 <sup>4</sup> 16.3	94	1.82	22.5					
ą	[I <sup>-</sup> ], = 1.13	× 10 <sup>-2</sup> <u>м</u> , [с	c1 <sup>−</sup> ], = 2.73 M, [	H <sup>+</sup> ], = 0.38	34 <u>M</u> .				
þ	$[Cu^{2+}]_{i} = 1.$	87 x 10 <sup>-3</sup> M,	$[C1^{-}]_{,} = 2.73 \text{ M}_{,}$	$[H^+]_{,} = 0.$	.384 M.				
-	-1 t. is the ti		the initial cone	1	- dogau				
2	to to to to	original valu	ue, i.e. at least	two half-1	ives.				
đ	The order, n	. with respec	t to the varied	reagent. X.					
-	calculated f	rom the plot	of ln t <sub>3</sub> (or ln	t,) vs ln [	<b>x</b> ].				
	where the slope = $(1-n)$ [5].								
e	$[cu^{2+}]_{i} = 1.4$	87 x 10 <sup>-3</sup> <u>M</u> ,	$[1^{-}]_{i} = 1.13 \times 10^{-1}$	р <sup>-2</sup> м, [с1 <sup>-</sup>	], = 2.73 M.				
£	$[Cu^{2+}]_{i}^{-} = 1.0$	$B7 \times 10^{-3} M$ ,	[I <sup>-</sup> ], = 1.13 x 10	- 0 <sup>-2</sup> м, [н <sup>+</sup> ]	1				
g	No added acid	±. –	1	-	1 -				
ħ	$[Cu^{2+}]_{i} = 1.6$	87 x 10 <sup>-3</sup> M,	$[I^{-}]_{i} = 1.13 \times 10^{-1}$	о <sup>-2</sup> м, [н <sup>+</sup> ]	. = 0.384 M.				
	μ = 3.13 <u>M</u> , 1	NaClO <sub>4</sub> .	1	_	1 -				
i	$[Cu^{2+}]_{i} = 1.4$	в7 × 10 <sup>-3</sup> <u>м</u> ,	$[1^{-}]_{i} = 1.13 \times 10^{-1}$	р <sup>-2</sup> <u>м</u> , [н <sup>+</sup> ]	i = 0.				
i	t <sub>3</sub> = time ta) of its origin	cen for the inal value.	nitial [Cu <sup>2+</sup> ] to	decay to t	wo-fifths				
ķ	Observable p	ecipitation	of Cul.						

Table 2. Variation of rate with respect to initial concentrations. T = 298.2 K,  $\mu$  = 3.13 M

Table 3. Rate constants for the Cu<sup>2+</sup>/I<sup>-</sup> Reaction. [Cl<sup>-</sup>]<sub>i</sub> = 2.73  $\underline{M}$ , [H<sup>+</sup>]<sub>i</sub> = 0.384  $\underline{M}$ ,  $\mu$  = 3.13  $\underline{M}$ , [Cu<sup>2+</sup>]<sub>i</sub> = 1.87 mM

т °с	[K]	[Cu <sup>2+</sup> ] <sub>i</sub> (m <u>M</u> )	[ɪ <sup>¯</sup> ] <sub>i</sub> (m <u>M</u> )	$(\underline{M}^{-1}s^{-1})$	$10^{4}k_{4}^{\underline{b}}$ $(\underline{M}^{-3}s^{-1})$	$\frac{10^{4}k_{4} \text{ calc.}^{\text{C}}}{(\underline{M}^{-3}\underline{s}^{-1})}$
25.0	[298.2]	1.87	11.3	6.7 <sub>4</sub>	5.27	5.63
		1.87	9.05	4.20	5.13	
		1.87	6.79	2.71	5.88	
		1.87	4.52	1.37	6.74	
		1.83	11.3	7.05	5.58	
22.0	[295.2]	1.83	11.3	5.7 <sub>0</sub>	4.4	4.50
19.0	[292.2]	1.83	11.3	4.64	3.63	3.58
16.0	[289.2]	1.83	11.3	3.74	2.94	2.83
13.0	[286.2]	1.83	11.3	2.75	2.16	2.23

<u>a</u> Estimated from the slope of the linear plot of  $[Cu^{2+}]^{-1}$  vs t (Table 1).

$$\underline{\mathbf{b}} \quad \mathbf{k}_4 = \mathbf{k}_2 [\mathbf{I}]_{\mathbf{i}}^{-2}$$

c Calculated from the activation parameters

$$E_{a} = 54.8 \pm 2.3 \text{ kJ mol}^{-1}, \log PZ = 14.347,$$
  

$$\Delta S_{298}^{\#} = 21 \pm 4 \text{ J K}^{-1} \text{ mol}^{-1}, \Delta H^{\#} = 52.3 \pm 2.2 \text{ kJ mol}^{-1}.$$

Table 4. Volume of  $S_2O_3^{2-}$  vs time data for the  $Cu^{2+}/I^-$  reaction in the presence of bromide ion.  $[Cu^{2+}]_i = 9.16 \times 10^{-4} \text{ M},$  $[I^-]_i = 2.30 \times 10^{-3} \text{ M}, [H^+]_i = 0.384 \text{ M}, \mu = 3.13 \text{ M}, {}^{*} \text{ T} = 298.2 \text{ K}, [S_2O_3^{2-}] = 2.07 \times 10^{-2} \text{ M}$ 

$vo1.s_2o_3^{2-} 10^4[cu^{2+}] [cu^{2+}]^{-1}$				[Br <sup>-</sup> ] <sub>i</sub> (M)			
			2.73	2.27	1.82	1.36	
 (mL)	(M)	(M <sup>-1</sup> )		Mean	time (s)		
0.8	6.06	1650	4	8	18.5	50	
1.0	5.30	1890	-	-	-	100	
1.1	4,92	2030	-	-	-	157	
1.2	4.54	2200	-	-	-	205	
1.3	4.17	2400	-	-	59.5	-	
1.4	3.79	2640	-	-	-	258	
1.5	3.42	2920	18	37	104.5	-	
1.6	3.05	3280	-	-	143.5	-	
1.7	2.68	3730	-	64	188	-	
1.8	2.31	4330	34.5	82.5	242.5	-	
1.9	1.94	5150	-	113	· _	-	
2.0	1.58	6350	60	146		-	
2.1	1.21	8260	85	195	-	-	
2.2	0.85	11800	123.7	268	-	-	
2.3	0.48	20700	191	-	-	-	
	Calcu	ulated Ra	te Constan	ts <sup>b</sup>			
	[Br <sup>-</sup> ] <sub>i</sub>		k <sub>2</sub>		10 <sup>5</sup> k4 <sup>d</sup>		
	( <u>M</u> )		$(M^{-1}s^{-1})$		$(M^{-3}s^{-1})$		
	2.73		99. <sub>8</sub>		<sup>30</sup> .2		
	2.27		35.8		10.8		
	1.82		12.4		3.7 <sub>4</sub>		
 	1.36		3.47	-	1.05		
a Ion	ic strength r	maintaine	d with NaC	104			
<u>b</u> T =	298.2 K, µ	= 3.13 <u>M</u> ,	$[H^+] = 0.$	384 <u>m</u> .			
c Foot	tnote <u>a</u> , Tabi	le 3.					
d Foo	tnote <u>b</u> , Tabi	le 3.					

berate addition of an air or oxygen stream did, however, result in a catalytic system<sup>17</sup> (eqns 11, 12), dioxygen being about 50% more effective than air.

$$2\mathrm{CuCl}_2 + 2\mathrm{I}^- \rightarrow 2\mathrm{CuCl}_2^- + \mathrm{I}_2 \tag{11}$$

$$2H^+ + 2CuCl_2^- + (1/2)O_2 \rightarrow 2CuCl_2 + H_2O.$$
 (12)

Under these conditions, I<sub>2</sub> production is much greater than the stoichiometric amount indicated by eqn (6) and the possibility of using this system for the recovery of iodine from iodide waste is under investigation.

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