ChemClass Journal, 2004 (59-63)

Oxidation of some tris(diimine) iron (II) and tris(substituted diimine) iron (II) complexes by aqueous acidic bromine solution – An assessment of the Marcus model for non-complementary reactions

J.F. Iyun
Department of Chemistry, Ahmadu Bello University, Zaria – Nigeria.

ABSTRACT

The oxidation of $Fe(LL)_3^{2+}$ (LL = phen, 2,2'-bipy, 5,6-$(CH_3)_2$-phen, 4,7-$(CH_3)_2$-phen, 3,4,7,8-$(CH_3)_4$-2,2'-bipy and 4,4'-$(CH_3)_2$-2,2'-bipy) by aqueous acidic bromine solution at I = 0.5M (H_2SO_4/Li_2SO_4) and T = 25°C has been assessed within the framework of the Marcus theory for outersphere reactions. The observed non-conformity of the electron transfer rate constants for both the rate determining step and the overall reactions of these non-complementary reactions to Marcus theory has been rationalized by invoking some of the basic assumptions of the Marcus model.

INTRODUCTION

Apart from a few investigation [1,2], the reaction schemes that have been suggested for the Gibb's function correlation involving mostly tris(diimine) iron(II) complexes [3-7] usually possess favourable rate-controlling electron transfer steps and are mostly complementary reactions. As a means of assessing Gibb's Function Correlations [8] of non-complementary redox reactions therefore and as a continuation of our interest in the dynamics of the redox reactions of the halogens, we have studied the titled reaction.

EXPERIMENTAL

Materials

Solutions of $Fe(LL)_3^{2+}$ (LL = phen, 2,2'-bipy, 5,6-$(CH_3)_2$-phen, 4,7-$(CH_3)_2$-phen, 3,4,7,8-$(CH_3)_4$-2,2'-bipy and 4,4'-$(CH_3)_2$-2,2'-bipy) were prepared by adding known weight of ferrous ammonium sulphate to a solution containing a slight excess (5-10%) of a stoichiometric amount of analar grade of the respective ligands or by dissolution of a known weight of commercially available (G.F. Smith) samples of the complexes in a standard solution of sulphuric acid. After the filtration of the resulting solution, the concentration of the $Fe(LL)_3^{2+}$ solution formed was determined spectrophotometrically by using literature values of λ_{max} and extinction coefficient [1,8,9]. The iron (III) complexes were prepared as reported in literature [10]. Aqueous solution of bromine was prepared and its concentration determined as reported in literature [11].

Stoichiometry

The stoichiometry of each of these reactions was determined by spectrophotometric titration at the appropriate λ_{max} using the mole ratio method.

Kinetics

The rates of the reactions were monitored spectrophotometrically by following the decrease in absorbance at each λ_{max} for each of the complexes [12]. The reactions were carried out under pseudo-first order conditions with bromine concentrations always in more than 100-fold excess over $[Fe(LL)_3^{2+}]$. The ionic strength was maintained at 0.5M (H_2SO_4/Li_2SO_4). Consistent with earlier reports the sulphate medium had no effect on the rates of these reactions. Temperature was maintained constant at 25 $\pm$ 1°C for each run by circulating thermostated water round the reaction compartment. All concentrations were determined before the kinetic runs.

RESULTS AND DISCUSSION

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The 2:1 stoichiometry determined by spectrophotometric titration for all the reactions suggests an overall reaction of the form,

$2Fe(LL)_3^{2+} + Br_2 \rightarrow Fe(LL)_3^{3+} + 2Br^-$

The pseudo-first order plots were linear to only 20-50% with the nature of the deviation from linearity suggesting product inhibition. The second-order rate constants were therefore determined as the initial rates of the reaction and are shown in Table 1. Only reactions of $Fe(2,2'\text{-bpy})_3^{2+}$ and $Fe(1,10\text{-phen})_3^{2+}$ with Br_2 were acid dependent conforming to the equation,

$$k_{obs} = k_o + k_H[H^+] \quad \ldots\ldots(1)$$

The range $0.05 \leq [H^+] \leq 0.40M$. The results are reported in Table 1. Based on literature [13,14], this can be rationalized on the basis of a reversible formation of $HFe(phen)_3^{3+}$ and $HFe(bpy)_3^{3+}$ respectively. The non-acid dependence of the other reactions is most likely due to steric hindrance leading to inaccessibility of the nitrogen atom.

Some acrylonitrile was added to the reaction mixture containing $Fe(LL)_3^{2+}$ and aqueous bromine under the experimental conditions employed in this investigation. This was followed by the addition of a large excess of methanol. A suspension of polyacrylonitrile was formed. The monomer did not polymerize in a solution of $Fe(LL)_3^{2+}$ or bromine respectively. This suggests that free radicals are important intermediates in these reactions.

The following mechanism consistent with our results is proposed:

$$Fe(LL)_3^{2+} + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(LL)_3^{3+} + Br_2^-(rds) \quad \ldots.(2)$$

$$Fe(LL)_3^{2+} + Br_2^- \xrightarrow{k_2} Fe(LL)_3^{3+} + 2Br^- \quad \ldots\ldots(3)$$

Analysis of results

The application of the steady state hypothesis to Br_2^- gives,

$$-\frac{1}{2}\frac{d[Br_2]}{dt} = \frac{k_1 k_2 [Fe(LL)_3^{2+}]^2 [Br_2]}{k_{-1}[Fe(LL)_3^{3+}] + k_2[Fe(LL)_3^{2+}]} \quad \ldots..(4)$$

At the initial stage of the reaction where the product has not formed to any appreciable extent, we can assume that,

$k_2[Fe(LL)_3^{2+}] >> [Fe(LL)_3^{3+}]k_{-1}$

hence equation (4) reduces to

$$-\frac{d[Br_2]}{dt} = k_1[Fe(LL)_3^{2+}][Br_2] \quad \ldots\ldots(5)$$

which is a second-order rate equation. With $[Br_2] >> [Fe(LL)_3^{2+}]$, equation (5) becomes ,

$$-\frac{d[Br_2]}{dt} = k_o[Fe(LL)_3^{2+}] \quad \ldots\ldots(6)$$

where $k_o = k_1[Br_2]$ is pseudo-first order rate constant. From the k_o values determined at the initial part of the reaction, the second-order rate constants k_{obs} were calculated . $k_{obs} = k_1$ in equation (5). If $k_o = k_1[Br_2]$ is substituted into equation (4), equation (7) is obtained:

$$-\frac{1}{2}\frac{d[Br_2]}{dt} = \frac{k_o k_2 [Fe(LL)_3^{2+}]^2}{k_{-1}[Fe(LL)_3^{3+}] + [Fe(LL)_3^{2+}]k_2} \quad \ldots\ldots(7)$$

This is an equation of the form,

$$\frac{dx}{dt} = \frac{k_o k_2 (a-x)^2}{k_{-1}x + k_2(a-x)} \quad \ldots\ldots(8)$$

where a is the initial concentration of $Fe(LL)_3^{2+}$ and x is the amount of Br_2 consumed or half that of $Fe(LL)_3^{3+}$ formed.

Assume that $R = k_2/k_1$ (R = extent of reversibility) and integrating equation (8) gives,

$$(R-1)\ln(a-x)\frac{aR}{a-x} = (R-1)\ln(a-R) + k_o t \quad \ldots..(9)$$

With the values of a and x known as a function of time, different values of R were substituted into equation (9) and the left hand side of the equation plotted against t to obtain k_o. This procedure was carried out for each run in all the reactions investigated. The value of R that gave k_o which was very close to the k_o derived from the initial portion of the pseudo-first order plots (with above 99% correlation coefficient) was taken as the true R value for these runs. The average value of R for all runs for a particular reaction was taken as the R value for that reaction. The values so calculated for each reaction are reported in Table 2.

Using E_o values reported for the Fe(II)/Fe(III) couple involving these phenanthroline complexes and E_o values for the reaction (14, 8e)

$$Br_2 + e \rightleftharpoons Br_2^- \qquad E_o = 0.5V$$

The equilibrium constant

$K = k_1/k_2$ ……..(10)

was calculated using average values of k_1 obtained earlier for each reaction and equation (10) the values of k_{-1} was determined for each system investigated. From the determined value of R and k_{-1} and k_2 was calculated for each system. These values of k, k_1, k_{-1} and k_2 are reported in Table 2.

Linear Gibb's function correlation

Marcus relation (8) for outersphere reactions is given by the expression,

$k_{12} = (k_{11}\, k_{22}\, k_{12}\, f)^{1/2}$ ……..(11)

where $\log f = (\log k_{12})^2/(4\log k_{11} k_{22}/Z^2)$ ……(12)
(Z = the collision frequency for the uncharged reactant molecules in solution usually taken as 10^{11} dm^3 mol^{-1} s^{-1}; k_{12} is the electron transfer rates, k_{11} and k_{22} are the homonuclear exchange rate constants for the oxidant and

Table 1: Second-order rate constants for the $Fe(LL)_3^{2+}$-Br_2 reactions
(LL = 2,2'-bpy; λ = 522nm) T = 25°C, I = 0.5M (H_2SO_4/Li_2SO_4)

10^4 M $[Fe(LL)_3^{2+}]$	10^3 M $[Br_2]$	$[H^+]$ M	k_{obs} $M^{-1}s^{-1}$
8.40	3.98	0.05	1.56
8.40	3.98	0.10	1.86
8.40	3.98	0.20	1.96
8.40	3.98	0.31	2.08
4.30	3.98	0.40	2.25
4.30	4.16	0.05	2.16
4.30	4.99	0.05	1.93
4.30	5.94	0.05	1.90
4.30	2.77	0.05	2.00
3.82	1.39	0.05	2.54
3.82	3.65	0.05	1.93
4.80	7.30	0.05	2.12
4.80	1.15	0.05	2.34
4.80	4.37	0.05	2.32
21.3	4.72	0.05	2.37
21.3	1.18	0.05	1.70
21.3	1.24	0.05	1.82
	5.90	0.05	2.06

b. LL = 1,10-phen λ = 510nm

10^4 M $[Fe(LL)_3^{2+}]$	10^3 M $[Br_2]$	$[H^+]$ M	k_{obs} $M^{-1}s^{-1}$
3.82	4.10	0.05	1.64
3.82	4.10	0.10	1.83
3.82	4.10	0.20	2.30
3.82	4.10	0.30	2.60
3.82	4.10	0.40	3.14
6.17	0.59	0.05	3.58
6.17	1.18	0.05	3.45
6.17	2.24	0.05	3.03
6.17	2.95	0.05	3.11

c. LL = 5,6-$(CH_3)_2$ 1,10-phen$)_3^{2+}$ λ = 520nm

3.45	6.80	0.05	41.60
3.45	6.80	0.10	43.00
3.45	6.80	0.20	42.90
3.45	6.80	0.30	41.80
3.45	6.80	0.40	41.30
3.45	6.80	0.05	41.50
3.40	0.61	0.05	43.50
3.40	0.97	0.05	40.10
3.40	1.22	0.05	41.30
3.40	1.46	0.05	41.30

d. LL = 4,4'-$(CH_3)_2$-2,2'-bpy λ = 529nm

1.68	0.89	0.50	295
1.68	1.77	0.50	295
1.68	2.66	0.50	294
1.68	3.55	0.50	299
1.68	4.20	0.30	295
1.68	4.30	0.10	196

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e. LL = 4,7-$(CH_3)_2$-1,10-phen λ = 554 nm

9.75	4.15	0.50	372
9.75	6.92	0.50	395
9.75	9.69	0.50	394
9.75	11.07	0.50	391
9.75	11.07	0.30	387
9.75	11.07	0.10	388

f. LL = 3,4,7,8-$(CH_3)_2$-1,10-phen λ = 500 nm

10^5 M $[Fe(LL)_3^{2+}]$	10^3 mol dm^{-3} $[Br_2]$	$[H^+]$ mol dm^{-3}	k_{obs} dm^3 mol s^{-1}
1.67	0.93	0.50	6344
1.67	1.19	0.30	6301
1.67	1.19	0.10	6299

	ΔE^o (V)	k x 10^9	R	$k_{obs} = k_2$	K_{-1} dm^3 $mol^{-1}s^{-1}$	E^o $(Fe(LL)_3^{3+} / Fe(LL)_3^{2+})$ (V)
$Fe(2,2'bpy)_3^{2+}$-Br_2	-0.53	1.26	0.54	2.1	1.43	1.035
$Fe(1,10\text{-phen})_3^{2+}$-$Br_2$	-0.55	0.48	3.00	3.3	4.75	1.06
$Fe(5,6\text{-}(CH_3)_2\text{-}1,10(phen)_3^{2+}$-$Br_2$	-0.46	16	0.59	41.50	392	0.97
$Fe(4,4\text{-}(CH_3)_2\text{-}2,2'(bpy)_3^{2+}$-$Br_2$	-0.37	53.50	0.16	296	2243	0.88
$Fe(4,7\text{-}(CH_3)_2\text{-}1,10\text{-phen})_3^{2+}$-$Br_2$	-0.36	79.10	0.45	387	137x10	0.87
$Fe(3,4,7,8\text{-}(CH_3)_2\text{-}1,10\text{-phen})_3^{2+}$-$Br_2$	-0.30	8.23	0.27	6300	$1400x10^2$	0.87

reductant respectively and k_{12} is the equilibrium constant).

Equation (11) can be written as

Log k_{12} = 0.5 (log k_{11} + log k_{22}) + 8.46 (ΔE). Where E is the thermodynamic driving force for the reaction.

A plot of k_{12} against ΔE is given in Figure 1. $k_{12} = k_1$ is the rate constant for the reaction:

$Fe(LL)_3^{2+} + Br_2 \rightarrow Fe(LL)_3^{3+} + Br_2^-$ …(13)

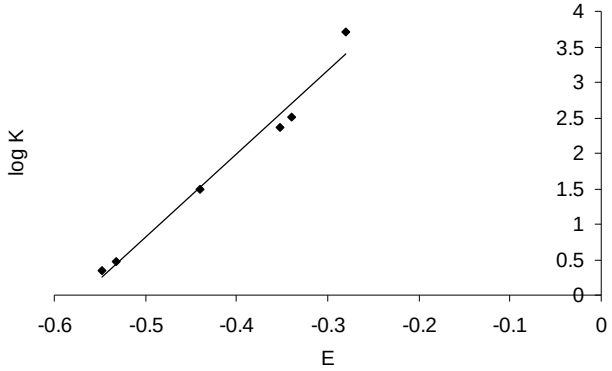
the rate determining step

($E^o(Br_2^-/Br_2)$ = 0.51V and

$k_{11}(Fe(LL)_3^{3+}/Fe(LL)_3^{2+} = 3.3 \times 10^8$ dm^3mol^{-1} ……..(14).

The slope of the plot in Figure is 1.35. Marcus equation (8) predicts a slope of 8.45 hence there is a poor agreement between theory and experiment as had earlier been noted [9,17] for some Fe^{2+} - $M(LL)_3^{3+}$ reactions (LL = 22'-bpy or 1,10-phen derivatives).

Marcus theory of adiabatic electron transfer proceeds from the assumption that within activated complex for electron transfer, the probability of electron transfer is unity. Other additional assumptions made are that the work terms of the self-exchange and cross-reactions are the same and that the electron-transfer reagents may be treated as spherical, structureless reactants with the motion shell of the inner coordination being harmonic. Various attempts have been made to assess these assumptions with the aim of modifying Marcus relation to allow a better fit between theory and experiment [9]. For the reactions under investigation charge and size effects are relatively



Marcus plot : Plot of log K Vs E

unimportant. It has earlier been suggested that the large discrepancies usually observed for the iron, osmium and ruthenium polypyridine complexes do not merely result from the presence of polypyridine ligands but depends on the complex as a whole [9].

Iron, ruthenium and osmium polypyridine complexes manifest several properties as a class. In the divalent state, relatively strong mixing of the metal *d* and the ligand π^* orbitals occur so that significant metal electron density exists on the ligands. This mixing of orbitals may probably account for the high self exchange rates (3.3×10^8 $mol^{-1}dm^3s^{-1}$) that has been reported for the iron(II) polypyridine(tris(diimine) complexes [16]. The assessment of the slowness of the $Fe^{2+}_{(aq)}$ –$M(LL)_3^{3+}$ (M = Fe, Ru, Os) cross-reactions led

to the conclusion that it is as a result of the fact that the cross reactions cannot proceed via a detailed pathway, which is common to the exchange process for both reactants, $\pi \rightarrow \pi^*$ pathway is highly favoured for the $Fe(LL)_3^{3+}/Fe(LL)_3^{2+}$ exchange reaction [9], whereas Br_2^-/Br_2 is likely to be $\sigma \rightarrow \sigma$.

Such a mismatch of orbitals, which characterize all the reactions investigated in this work could result in the breakdown of the Marcus model for the following reasons:

i. the non-adiabaticity of electron transfer i.e. $P_{12} \neq (P_{11}\ P_{22})^{1/2}$ (P is the probability of electron transfer. This implies that the overlap of orbitals between Br_2 and $Fe(LL)_3^{2+}$ complexes may be much poorer than the geometric mean of the overlap of orbitals involving the exchange reactions of these reactants.

ii. Inherent in the Marcus theory is the assumption that the interaction between reactant and product surfaces is large enough for the probability of crossing to be unity, but not so large that the height of the barrier is appreciably lowered. It is conceivable that the $\pi \rightarrow \pi$ interaction most probably for the $Fe(LL)_3^{2+}$-$Fe(LL)_3^{3+}$ exchange reaction may result in splitting energy too large for the assumption of the original Marcus treatment to apply. If this is the case, the exchange reaction would be effectively too rapid. That is, its rate will not be determined by zero interaction barrier but by a barrier lowered by the interaction energy. In cross-reactions where the special $\pi \rightarrow \pi$ interaction operative in exchange reaction is not possible, the zero interaction approximation determines the appropriate intrinsic barrier to electron transfer.

ACKNOWLEDGEMENT

The provision of the facilities with which this research was carried out by the Ahmadu Bello University is gratefully acknowledged.

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