Asian Journal of Chemistry; Vol. 27, No. 4 (2015), 1274-1278

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17629

Dynamics of Electron Transfer Reaction of Trioxosulfate(IV) Ion with Dinuclear Iron(III)-Salen Complex in Perchloric Acid Medium

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Received: 19 March 2014; *Accepted*: 5 July 2014; *Published online*: 4 February 2015; AJC-16774

The kinetics of oxidation of trioxosulfate(IV) ion, SO_3^{2-}, by $[(Fe(salen))_2adi]$, was investigated in aqueous perchloric acid medium. Stoichiometric results indicate that one mole $[(Fe(salen))_2adi]$ was reduced per two moles SO_3^{2-} oxidized. Under pseudo-first order conditions of SO_3^{2-} being above 20-fold excess of concentration of the oxidant, observed rates were invariant with respect to increase in concentration. Pseudo-first order rate constants were within $(1.68 \pm 0.003) \times 10^3\ s^{-1}$ implying zeroth order dependence of rate on $[SO_3^{2-}]$ and first order dependence on concentration of the oxidant. The rate of reaction increased with increase in $[H^+]$, was unaffected by change in ionic strength and decreased with increase in dielectric constant of the reaction medium. Addition of small amounts of AcO^- and Mg^{2+} ions did not catalyze the reaction. A least squares fit of rate against $[H^+]$ was linear ($r^2 = 0.986$) and with intercept indicating that oxidation of SO_3^{2-} followed two parallel paths. The reaction was analyzed on the basis of a proton-coupled outer-sphere electron transfer mechanism.

Keywords: Kinetics, Dithionite, Electron transfer reduction, Mechanism, Dinuclear iron(III).

INTRODUCTION

Interests in the chemistry of iron complexes involving functionalized coordinated ligands have continued to evolve. This is because iron-salen complexes are also known to exhibit interesting structural, catalytic, electronic, magnetic, optical and bio-active properties[1-4]. The discovery of the importance of iron in many vital cellular metabolic processes in living organisms caused diverging interest in iron chemistry. Bio-activities of iron could be attributed to electron exchange associated with the redox reactions of iron that occur in biological systems. For instance, bridged binuclear iron centres in proteins such as hemerythrin and myohemerythrin are known to function in oxygen transport and storage in invertebrates[5]. Similar properties have also been reported for dinuclear iron(III) complexes[6-9], thus providing structural model for biochemical investigations. For instance iron-salen complexes provide structural mimic for investigating the reactivities of dinuclear Fe(III) species in several proteins. They have been demonstrated to not only damage DNA *in vitro* but also induce efficient apoptosis *in vivo*[10,11]. Potentially, understanding the redox dynamics of bridged dinuclear Fe-salen complexes could help improve the moderation of DNA damage by closely related compounds used for therapeutic purposes. Such model complex is exemplified by a bridged dinuclear iron(III) salen, $[(Fe(salen))_2adi]$, first reported in 1996[12].

Though the investigation of the redox kinetics of $[(Fe(salen))_2adi]$ could provide better insight into the understanding of the action mode of closely related complexes in biological system, to date few reports on this are available in literature. We are currently interested in developing the redox chemistry of $[(Fe(salen))_2adi]$ through studies on the kinetics and mechanism of its reduction with various reductants. In our previous reports we investigated the kinetics of the reduction of $[(Fe(salen))_2adi]$ by dithionate[13] ions which were analyzed on the basis of proton-coupled outer-sphere electron transfer mechanisms. The present report is concerned with an investigation of the kinetics and the proposed mechanism for the reduction of $[(Fe(salen))_2adi]$ by trioxosulfate(IV) ion in aqueous perchloric acid.

EXPERIMENTAL

All reagents were analytical grade and used without further purification. All solutions were prepared with de-ionised water. FTIR spectra were obtained on a Shimadzu FTIR spectrometer. UV-visible spectra were recorded on Unico-2012 and Jenway 6405 UV-visible Spectrophotometer. Absorbances of solutions were obtained on a B.Bran722-2000 spectronic 20D spectrophotometer. $[(Fe(salen))_2adi]$ was prepared by modification of literature procedures[12,13] involving the reaction of $[(Fesalen)_2O]$[13,14] with adipic acid.

Kinetic measurements: The rate data for reduction of [(Fe(salen))$_2$adi] by trioxosulfate(IV) ion were obtained as the decrease in absorbance of the reacting mixture at 455 nm. At this wavelength only the Fe(III) dimer absorbed with no interference from Fe(II) product, the reductant or organic product. The reactions were followed under pseudo-first order conditions with a large excess of the reductant (20-fold in excess of the oxidant). The kinetic curves obtained under this condition were exponential and the rate constant was obtained from the logarithmic plot of the absorbance difference log(A_t-A_∞) against time (*t*). Pseudo-first order rate constants were determined from the slope of the plot, based on the following equation;

$$(A_\infty - A_t) = (A_\infty - A_0)e^{-k_{obs}\cdot t} \qquad (1)$$

where A_∞ = final absorbance, A_t = absorbance at time *t*, A_0 = initial absorbance and k_{obs} = pseudo-first order rate constant as reported elsewhere[15,16]. Specific rates for replicate runs were reproducible to within ± 6 %.

The presence of intermediate free radical in the reaction was confirmed by gel formation on addition of acrylamide into a portion of partially reacted reaction mixture of [(Fe(salen))$_2$adi] and SO_3^{2-} in excess methanol as reported elsewhere[16]. The stoichiometry of the reaction was determined by spectrophotometric titrations under the following conditions; the concentration of [(Fe(salen))$_2$adi] kept constant at 1×10^{-4} mol dm^{-3}, [H$^+$] = 5×10^{-3} mol dm^{-3}, I = 0.05 mol dm^{-3} (NaClO$_4$) and [SO_3^{2-}] varied at 1.0×10^{-5} mol dm^{-3} ≤ [SO_3^{2-}] ≤ 8.0×10^{-4} mol dm^{-3} at T = 28 ± 1 °C. The final absorbances (A_∞) of separate reaction solutions were plotted against mole ratio, [Red]/[Ox], and the stoichiometry of the reaction derived from the point of inflexion on the curve.

RESULTS AND DISCUSSION

The stoichiometry of the reaction was determined by the mole ratio method. The concentration of [(Fe(salen))$_2$adi] was kept constant at 1×10^{-4} mol dm^{-3} and [SO_3^{2-}] varied between 1×10^{-5} to 8×10^{-4} mol dm^{-3} at constant pH and ionic strength. Final absorbances at completion of reaction were plotted against mole ratios to obtain the mole ratio of the reactants. The result indicated that one mole of [(Fe(salen))$_2$adi] reacted with two moles of SO_3^{2-}. The result is consistent with eqn. 2.

$$[(\text{Fe(salen)})_2\text{adi}] + 2SO_3^{2-} + 2H^+ \rightarrow [(\text{Fe(salen)})_2\text{adiH}_2] + SO_4^{2-} + SO_2 \qquad (2)$$

SO_3^{2-} adopts different stoichiomtries in its reactions. In the reaction with di-μ-oxotetrakis (1,10-phenthroline) a 2:3 stochiometry was reported[17], whereas the reaction of SO_3^{2-} with Mn(III)-Cydta displayed 2:1 mole ratio[18]. Oxidation of iodine by SO_3^{2-} ion followed 1:1 stoichiometry[19], but a 2:1 stoichiometry was reported for the reaction of SO_3^{2-} with HCOO$^-$ [19].

These results are consistent with the fact that oxidation of SO_3^{2-} results in the formation of SO_4^{2-}, $S_2O_6^{2-}$ or a mixture of the two ions for both one and two-electron net oxidations[20-23]. Evidence for reduction of the Fe(III) dimer to Fe(II) analogue was obtained by reacting the resulting solution after the reaction completed with a freshly prepared acidified solution of K$_3$[Fe(CN)$_6$]. Immediate formation of a deep blue precipitate was confirmatory indication of the presence of Fe(II) ions. Evolution of SO$_2$ was confirmed by decolourization of acidified KMnO$_4$ by the gaseous product. Also formation of a white precipitates on addition of aqueous solution of BaCl$_2$ indicated the presence of SO_4^{2-}. The test for free radical initiated polymerization of acrylamide by partly reacted reaction mixture was positive. This suggests the formation and involvement of free radicals in the reaction.

Reaction order: Pseudo-first order plots of log(A_t-A_∞) *versus* time were linear to greater than 75 % extent of reaction. This is indicative of first order dependence of the rate on concentration of the oxidant, ([(Fe(salen))$_2$adi]). Pseudo-first order rate constant values are shown in Table-1. Their invariance with the concentration of SO_3^{2-} within the range 4.0 to 9.0 × 10^{-3} mol dm^3 indicates zeroth order dependence of the rate on [SO_3^{2-}]. In agreement with this, the second order rate constants, k$_2$, varied with change in [SO_3^{2-}]. Least squares fits (r = 0. 995) of a plot of log k_{obs} *versus* log[SO_3^{2-}], gave a straight line with slope of 0.00 supporting zeroth order dependence on [SO_3^{2-}]. Hence, the rate of the reaction at constant pH can be described by eqn. 3,

$$-\frac{1}{2}\frac{d[\text{Fe(salen)}_2\text{adi}]}{dt} = k_{obs}[\text{Fe(salen)}_2\text{adi}] \qquad (3)$$

Zeroth order is not uncommon in reactions of sulfur oxyanions. Reaction of $S_2O_6^{2-}$ with [Fe(salen)(H$_2$O)$_2$]$^+$[16], IO_3^-, Cr(VI) and Ce(IV) were zeroth order dependent on concentrations of the oxidants. In other reactions of this sulfur oxyanions, first order dependence on [SO_3^{2-}] was reported for its reaction with Mn(III) - Cydta[18], dimanganate(III, IV)[24], dodecatungstocobaltate(VII)[25], and Cr(VI)[26]. Zeroth order dependence on [SO_3^{2-}] connotes lack of participation of SO_3^{2-} at the rate determining stage and infers an intramolecular electron transfer process involving [Fe(salen))$_2$adi] or its protonated analogue.

TABLE-1
PSEUDO-FIRST AND SECOND ORDER RATE CONSTANTS FOR SO_3^{2-}-(Fe(salen))$_2$adi REACTION AT T = 28 ± 1 °C, [(Fe(salen))$_2$adi] = 1 × 10^{-4} mol dm^3, λ_{max} = 455 nm, I = 0.05 mol dm^{-3}

10^3[SO_3^{2-}]	10^3[H$^+$]	I [NaClO$_4$]	10^{3}k$_{obs}$, (s^{-1})	k$_2$ dm^{3}mol^{-1}(s^{-1})
4.0	5.0	0.05	1.68	0.42
5.0	5.0	0.05	1.70	0.34
6.0	5.0	0.05	1.68	0.28
7.0	5.0	0.05	1.66	0.24
8.0	5.0	0.05	1.68	0.21
9.0	5.0	0.05	1.68	0.19

Acid dependence: The effect of [H$^+$] on the reaction kinetics was investigated within the range of 3×10^{-3}–11×10^{-3} mol dm^{-3}, with the concentration of oxidant, reductant and ionic strength kept constant. Under these conditions, rate increased with [H$^+$] as shown in Table-2. A plot of k$_2$ *versus* [H$^+$] (Fig. 1) was linear. The intercept on the k$_2$ axis agrees with eqn. 3.

$$k_{H^+} = m + n[H^+] \qquad (3)$$

where m = 0.10 dm^3 mol^{-1} s^{-1} and n = 6 dm^6 mol^{-2} s^{-1}

Increase in reaction rate with increase in [H$^+$] suggests that protonated species played significant role in the reaction. Preprotonated intermediates of the form [(Fe(salen))$_2$adiH$_2$]$^{2+}$ are likely to be formed as precursor complexes before the electron transfer. In addition, SO_3^{2-} establishes various equilibrium states in acidic solutions where protonated species abound {eqn. 5 and 6}[19,28,29].

$$HSO_3^{2-} \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + SO_3^{2-},\ K_a\ (25\ °C) = 1 \times 10^{-7}\ mol\ dm^{-3} \qquad (5)$$

$$2HSO_3^- \overset{Q_d}{\rightleftharpoons} S_2O_5^{2-} + H_2O,\ Q_d\ (25\ °C) = 0.088\ dm^{-3}\ mol^{-1}\ s^{-1} \qquad (6)$$

The low value of K_a indicates that HSO_3^- is a weak acid and the protonated form is predominant in acidic solution. This should result in retardation of the reaction rate as $[H^+]$ is increased rather than increase the rate[18]. It is therefore most likely that the direct acid dependence results from protonation of $[Fe(salen))_2adi]$, (eqn. 7).

$$[salenFe\text{-}adi\text{-}Fesalen] + 2H^+ \overset{Kp}{\rightleftharpoons} [HsalenFe\text{-}adi\text{-}FesalenH]^{2+} \qquad (7)$$

The protonation of the azomethine nitrogens is very facile within the $[H^+]$ range of the reaction (pH 2-2.5) resulting in the dication $[(Fe(salen))_2adiH_2]^{2+}$ which is a better oxidant than $[Fe(salen))_2adi]$.

TABLE-2
EFFECT OF $[H^+]$ ON THE RATE OF $(Fe(salen))_2adi\text{-}SO_3^{2-}$ REACTION AT $[(Fe(salen))_2adi] = 1 \times 10^{-4}$ mol dm^{-3}, T = 28 ± 1°C, I = 0.05 mol dm^{-3}

$10^3[H^+]$	I	$10^3\ k_{obs}\ (s^{-1})$	k_2
3.0	0.05	0.80	0.13
5.0	0.05	1.71	0.29
6.0	0.05	1.80	0.30
7.0	0.05	2.30	0.38
9.0	0.05	3.00	0.50
11.0	0.05	3.30	0.55

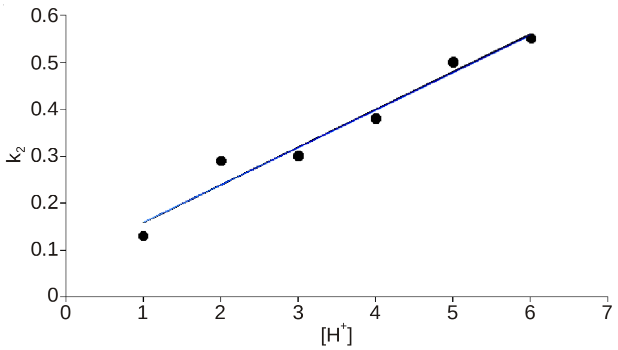


Fig. 1. Plot of k_2 *versus* $[H^+]$

Effect of ionic strength, dielectric constant (D) and added ions: The effect of the ionic strength of the reaction medium was investigated by varying it from 0.05 to 0.15 mol dm^{-3} using $NaClO_4$ at $[(Fe(salen))_2adi] = 1 \times 10^{-4}$ mol dm^{-3}, $[SO_3^{2-}] = 7 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5 \times 10^{-3}$, T = 29 °C and λ_{max} = 455 nm. Table-3 indicates that within this ionic strength range, the rate of reaction remained invariant. Lack of a primary salt effect is indicative of a reaction where the product of the charges of redox partners at the rate determining step is zero. The redox reaction of metabisulphite with $[Fe_2(bpy)_4O]Cl_4$ was reported to be zero order on concentration of metabisulphite and first order on concentration of oxidant and non-dependent on ionic strength[29]. The lack of primary salt effect in $S_2O_5^{2-}$-$[Fe_2(bpy)_4O]Cl_4$ reaction was rationalized on the basis of intramolecular electron transfer involving $[Fe_2(byp)_4O]Cl_4$ or its intermediate species. For the title reaction, this observation is presumably due to the fact that the rate determining step only involves the intermediate product of oxidant.

TABLE-3
EFFECT OF VARYING IONIC STRENGTH OF THE REACTION MEDIUM AT $[(Fe(salen))_2adi] = 1 \times 10^{-4}$ mol dm^{-3}, $[SO_3^{2-}] = 7 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5 \times 10^{-3}$, T = 28 ± 1 °C and λ_{max} = 455 nm

$10^3[SO_3^{2-}]$	$10^3[H^+]$	I	k_{obs}
7.0	5.0	0.05	1.67
		0.07	1.66
		0.09	1.70
		0.11	1.65
		0.13	1.66
		0.15	1.66

In order to investigate the effects of the dielectric constant (D), other parameters were kept constant whilst the dielectric constant of the reaction medium was varied between 55.32 to 72.63 using propan-2-one/H_2O mixture. The results (Table-4) indicated an increase in the rate with decreasing D. This observation differs with the results of varying ionic strength and suggests involvement of two charged species in the rate determining step. Consequently, from eqn. 8 as reported elsewhere[30], a plot of log k *versus* 1/D for the interaction of an ion A with a polar molecule will give a positive slope irrespective of the charge on A. For the reaction of SO_3^{2-} and $[Fe(Salan))_2adi]$, interaction of charged protonated oxidant species with solvent molecules at the rate determining step is most probably the reason for the effects observed on varying the dielectric constant (D).

$$\ln k_o = \ln k_\infty - \frac{e^2 \cdot Z_A Z_B}{DkTr_A r_B}$$

where D = dielectric constant, k = Boltzmann constant, T = temperature, k_o and k_∞ = the rate constant at zero ionic strength and infinite dielectric constant, respectively, Z_A and Z_B = charges on the ions A and B respectively, r_A, r_B represent radius of the two species, respectively.

TABLE-4
EFFECTS OF THE DIELECTRIC CONSTANT (D) at I = 0.05 mol dm^{-3}, $[(Fe(salen))_2adi] = 1 \times 10^{-4}$ mol dm^{-3}, $[SO_3^{2-}] = 7 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5 \times 10^{-3}$, T = 28 ± 1 °C and λ_{max} = 455 nm

D	72.63	66.86	61.09	55.32
10^3k_{obs}	2.76	3.12	4.80	5.60

The catalytic effect of added ions was investigated by adding various amounts of aqueous AcO^- and Mg^{2+} in the range 4×10^{-3} to 14×10^{-3} mol dm^{-3}. Table-5 indicates that the rate of reaction was unaffected by the concentration of these ions. This is a pointer to likely formation of a precursor complex with an inner-sphere character rather than an outer-sphere path[31]. It could also imply that the rate determining step does not involve species with formal charges. Intramolecular electron transfer in the protonated oxidant is the rate determining step in the reaction and therefore was not catalyzed.

Rate dependence on temperature: The rate dependence on temperature for SO_3^{2-} reaction with $[(Fe(salen))_2adi]$ was investigated between 29 and 50 °C. Table-6 shows the temperature dependent rate constants. From the Eyring equation;

$$\log \frac{K_{obs}}{T} = \log \frac{k}{h} + \frac{\Delta S^\#}{2.303R} - \frac{\Delta H^\#}{2.303RT} \qquad (8)$$

TABLE-5
EFFECT OF $[AcO^2]$ AND $[Mg^{2+}]$ ON THE RATE OF REACTION

$10^3[AcO^-]$	6.0	8.0	10.0	12.0	14.0	-
10^3k_{obs}	1.68	1.68	1.70	1.68	1.66	-
$10^3[Mg^{2+}]$	4.0	6.0	8.0	10.0	12.0	14.0
10^3k_{obs}	1.68	1.71	1.67	1.66	1.68	1.70

where k_{obs} = temperature dependent rate constant, k = Boltzmann's constant, h = Planck's constant, $\Delta S^{\#}$ = enthropy of activation, $\Delta H^{\#}$ = enthalpy of activation, R = universal gas constant, T = temperature.

TABLE-6
TEMPERATURE DEPENDENT RATE CONSTANTS

T(K)	$10^3k_{obs}(s^{-1})$	$\log(k_{obs}/T)$	$10^3(1/T)(K^{-1})$
302	1.68	-5.52	3.31
308	1.90	-5.21	3.25
313	2.40	-5.12	3.19
318	2.64	-5.08	3.14
323	3.12	-5.02	3.10

A plot of log (k_{obs}/T) *versus* 1/T was constructed and the activation parameters determined. $\Delta S^{\#}$ was determined as -293.5 J mol^{-1} K^{-1} and $\Delta H^{\#}$ as 1136.9 J mol^{-1}. The relatively large negative $\Delta S^{\#}$ suggests that the redox process is spontaneous in the rate determining step and is largely the result of substantial mutual ordering of the solvated solvent molecules of the equilibrium state and the intramolecular electron transfer[32]. It has also been reported that redox processes mediated by free radical intermediates usually have $\Delta S^{\#}$ values in the range of -90 to -140 J mol^{-1} K^{-1} [33].

Reaction mechanism: Considering the stoichiometry, acid dependence, effect of ionic strength and catalysis, the following mechanism is proposed for the reaction (**Scheme-I**).

$$[(Fe(salen))_2adi] + 2H^+ \overset{K_p}{\rightleftharpoons} [(Fe(salen))_2adiH_2]^{2+} \quad (9)$$

$$SO_3^{2-} + H^+ \overset{K_a}{\rightleftharpoons} HSO_3^- \quad (10)$$

$$(Fe(salen))_2adiH_2^{2+} + HSO_3^- \overset{k_1}{\rightleftharpoons} [(Fe(salen))_2adiH_2^{2+}, HSO_3^-] \quad (11)$$

$$[(Fe(salen))_2adiH_2^{2+}, HSO_3^-] \overset{k_2}{\rightleftharpoons} (Fe(salen))_2adiH_2^+ + HSO_3^* \quad (12)$$

$$(Fe(salen))_2adiH_2^+ \overset{k_3}{\rightleftharpoons} (Fe(salen))_2adiH + H^+ \quad (13)$$

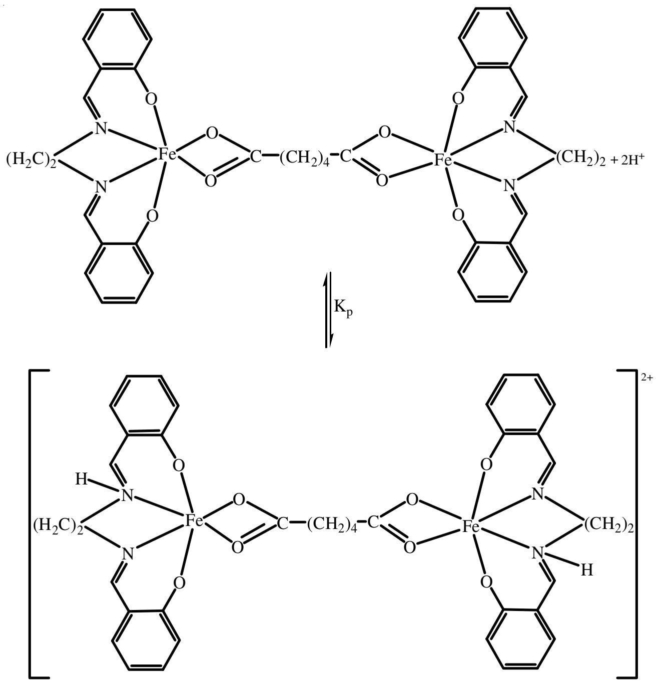
$$(Fe(salen))_2adiH + HSO_3^* \overset{k_4}{\rightleftharpoons} (Fe(salen))_2adi^{2-} + SO_3^* + 2H^+ \quad (14)$$

$$SO_3^* + SO_3^{2-} \overset{k_5}{\rightleftharpoons} SO_4^{2-} + SO_2 \quad (15)$$

$$(Fe(salen))_2adi^{2-} + 2H^+ \overset{k_6}{\rightleftharpoons} (Fe(salen))_2adiH_2 \quad (16)$$

$$\text{Rate} = k_3[(Fe(salen))_2adiH_2^+] + k_6[(Fe(salen))_2adi^{2-}][H^+]^2 \quad (17)$$

Eqn. 9 and **Scheme-I** illustrates the possible protonation of two of the four available azomethine nitrogen atoms symmetrically disposed in $[(Fe(salen))_2adi]$. The postulated $(Fe(salen))_2adiH_2^{2+}$ will easily form an ion-pair complex with HSO_3^-. Destabililization of $[(Fe(salen))_2adi]$ structure due to protonation most likely accelerates the process of electron transfer through the adipato bridge. Free radicals of the form SO_3^* and SO_3^- are not uncommon in SO_3^{2-} reactions[18,34,35].



Scheme-I: Possible protonation of two of the four available azomethine nitrogen atoms of $[(Fe(salen))_2adi]$

Following steady state approximation

$$[(Fe(salen))_2adiH_2^+] = k_2[(Fe(salen))_2adiH_2^{2+}, HSO_3^-] - k_{-2}[(Fe(salen))_2adiH_2^+][HSO_3^*] - k_3[(Fe(salen))_2adiH_2^+] = 0$$

$$\Rightarrow [(Fe(salen))_2adiH_2^+] = \frac{k_2[(Fe(salen))_2adiH_2^+, HSO_3^-]}{k_3 + k_{-2}\ [HSO_3^*]}$$

Also

$$[(Fe(salen))_2adiH_2^+, HSO_3^-] = k_1[(Fe(salen))_2adiH_2^{2+}][HSO_3^-] - k_{-1}[(Fe(salen))_2adiH_2^{2+}, HSO_3^-] - k_2[(Fe(salen))_2adiH_2^{2+}, HSO_3^-] = 0$$

$$[(Fe(salen))_2adiH_2^{2+}, HSO_3^-] = \frac{k_1[(Fe(salen))_2adiH_2^{2+}][HSO_3^-]}{k_2 + k_{-1}} \quad (19)$$

Substituting eqn. 17 into eqn. 16 gives

$$[(Fe(salen))_2adiH_2^+] = \frac{k_2k_1[(Fe(salen))_2adiH_2^{2+}][HSO_3^-]}{k_2 + k_{-1}\{k_3 + k_{-2}[HSO_3^*]\}} \quad (20)$$

also

$$[(Fe(salen))_2adiH_2^{2+}] = K_p[(Fe(salen))_2adi][H^+]^2 + [(Fe(salen))_2adiH_2^{2+}][HSO_3^*] = 0$$

$$\Rightarrow [(Fe(salen))_2adiH_2^{2+}] = \frac{K_p[(Fe(salen))_2adi][H^+]^2}{k_1[HSO_3^-]} \quad (21)$$

Substituting eqn. 21 into eqn. 20 gives

$$[(Fe(salen))_2adiH_2^+] = \frac{k_2k_1K_p[(Fe(salen))_2adiH^+]^2}{k_2 + k^{-1}\{k_3 + k_{-2}[HSO_3^*]\}} \quad (22)$$

in addition

$$[HSO_3^*] = k_{-4}[(Fe(salen))_2adiH][HSO_3^*] + k_{-4}[(Fe(salen))_2adi^{2-}][SO_3^*][H^+]^2 = 0$$

$$\text{Therefore, } [HSO_3^*] = \frac{k_{-4}[(Fe(salen))_2adi^{2-}][SO_3^*][H^+]^2}{k_{-4}[(Fe(salen))_2adi]} \quad (23)$$

and

$$[(Fe(salen))_2adi^{2-}] = \frac{[H^+]^2}{k_5} \quad (24)$$

Substituting eqn. 24 into eqn. 23 gives

$$[HSO_3^*] = \frac{k_5k_4[SO_3^*]}{k_{-4}[(Fe(salen))_2adiH]} \quad (25)$$

assuming that $k_{-4}[(Fe(salen))_2adiH] \approx \frac{k_3}{[H^+]}$, then eqn. 25 becomes

$$\frac{k_5k_4[SO_3^*][H^+]}{k_3} \quad (26)$$

Substituting eqn. 26 into eqn. 22 gives

$$[(Fe(salen))_2adiH_2^+] = \frac{k_2k_1K_p[(Fe(salen))_2adi][H^+]^2}{\dfrac{k_2 + k_{-1}\{k_3 + k_{-2}kk_4[H^+]}{k_3}} \quad (27)$$

dividing eqn. 27 by k_2 gives

$$\text{Rate} = \frac{k_1K_p[(Fe(salen))_2adi][H^+]_2}{\dfrac{1 + k_{-1}[k_3 + k_{-2}k_5k_4[H^+]]}{k_2}} \quad (28)$$

Conclusion

Analysis of the kinetic data has afforded interesting points for deciding the intimate mechanism for the reaction. Lack of catalysis by AcO^- and Mg^{2+} ions point to an inner-sphere pathway. However, it is actually because the rate determining step is the intramolecular electron transfer in $(Fe(salen))_2adiH^+$ and not any collision between two molecules. This phenomena is in agreement with an outer-sphere process. Lack of Debye-Huckel primary salt effect is also supportive of an outer-sphere electron transfer mechanism involving the oxidant species only. On the strength of these results, it looks very plausible that the reaction follows the outer-sphere proton-coupled electron transfer route.

ACKNOWLEDGEMENTS

The authors thank the Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka for some financial support of this work. Thanks are also due to Mr. Richard Ugwuanyi Ndubisi for technical assistance.

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