KINETICS AND MECHANISM OF OXIDATION OF THIOUREA BY TETRAKIS (2, 2'- BIPYRIDINE)-μ- OXODIIRON (III) COMPLEX IN AQUEOUS ACIDIC MEDIA

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Abstract: The reaction between thiourea (TU) and tetrakis(2,2'-bipyridine)-μ-oxodiiron (III) complex ($[Fe_2(bpy)_4O]^{4+}$) hereafter referred to as Fe_2O^{4+} has been studied in aqueous acidic media at hydrogen ion concentration ($[H^+]$) of 0.001 $moldm^{-3}$, constant ionic strength of 0.3 $moldm^{-3}$(NaCl), T= 27 ±1°C and atwave length of maximum absorption (λ_{max}) of 520 nm. The stoichiometry of reaction shows that one mole of oxidant is consumed per mole of reductant. The reaction is first order with respect to oxidant and reductant respectively and is not hydrogen ion and ionic strength dependent. The reaction conforms to the rate law:$\frac{-d}{dt}[Fe_2O^{4+}] = k_2[Fe_2O^{4+}][TU]$. Added SO_4^{2-} and CH_3COO^- inhibited the rate of reaction. The absence of both kinetics and spectroscopic evidence of intermediate complex formation suggest that the reaction proceeds by the outer-sphere mechanistic pathway and a mechanism is proposed.

Keywords: Intermediate, ionic strength, kinetic, oxidant, oxidation, reductant, stoichiometry

Introduction
Thiourea is an organosulphur compound with a wide range of applications in both biological and chemical fields. Most noted of these have been its uses as corrosion inhibitors (Ayres, 1970; Santanu*et al.,* 1997), in industrial equipment such as boilers, to prevent the development of scales due to corrosion (Klern, 1971). As a plant growth stimulator to break bud dormancy and increase crop yield and more recently as a therapeutic agent in the treatment of thyroid dysfunction (Salem, 2010). As a chaotropic agent, it has been used to solubilise membrane and organelle specific proteins for analysis by two-dimensional gel electrophoresis (Rabilloud, 1998). Its reaction with hydrogen peroxide under certain conditions produces a powerful reductive bleaching agent, which is routinely used in the textile industry (Arifoglu*et al.,* 1992; Cagarra*et al.,* 1992). Thiourea has also been used as a vulcanisation accelerator, additive for slurry explosives, viscosity stabilizer for polymer solutions and molality buffer in petroleum and gold extractions (Groenewald, 1977). In pharmacology, It is used as reactant in the production of drugs (sulfathiazole, thiouracil, tetramicol and cephalosporin) (Hilsona and Monhemius, 2006), a class of drugs used in the treatment of hyperthyroidism (Mertschenk and Beck, 1995; Ardiwilaga, 1999**)**.

Moreover, the aforementioned application of thiourea is necessitated by its redox properties. It can be oxidized by a wide range of oxidizing agents to generate various products to include urea, sulphides, oxides of Sulphur, Sulphur and nitrogen (Sandhyamayee*et al*., 2011). The reaction pathway and the final products of the oxidation depends on the kind of oxidant used and conditions of reaction mixtures. Oxidation of thiourea by iodate (Rabai and Beck, 1985), chlorite (Alamgir, and Epstein, 1985) and bromate (Simoyi, 1986) has been found to give complex kinetic behavior. With iodate, the reaction displays oligo-oscillation, in which the concentration of iodide goes through several maxima in a single reaction (Rabai and Beck, 1985). Without gainsay, the current trend in the oxidation of thiourea has been the application of binuclear complex of transition metals as oxidants (Osunlaja*et al.,* 2013; Mohammed *et al.,* 2014) have reported the oxidation of thiourea by μ-superoxo binuclear cobalt(III) complex and diaquotetrakis (2,2'- bipyridine)-μ- oxodiruthenium(III) complex respectively. In this paper we deemed it fit to used tetrakis(2,2' bipyridine) -μ- oxodiiron(III) complex as an oxidant with the aim that the results would be a useful tool for providing more and detail kinetic information about the oxidant. And to identify the kind of products that would be formed and how such products could be harnessed and utilized.

Materials and Methods
Materials
Tetrakis (2,2'–bipyridine)-μ-oxo-diiron(III) chloride ($[Fe_2(bpy)_4O]Cl_4$) hereafter referred to as Fe_2O^{4+} was prepared, purified and characterized following the method of (David, 1973). A stock solution of thiourea "supplied by Sigma–Aldrich Germany" was prepared by dissolving appropriate quantity of thiourea into distilled water in volumetric flask and made up to the mark. Stock solutions of 2.00 $moldm^{-3}$ (HCl)) was made by diluting 8.5 mL of 36% HCl (specific gravity 1.18) in 50 mL standard flask, then made up to the mark with distilled water. The solution was standardized titrimetrically with standard solution of previously dried Na_2CO_3 using methyl red as indicator (Chimere*et al.,* 1985). Stock solutions of sodium chloride, sodium sulphate, sodium acetate, potassium chloride and magnesium chloride were prepared from analar grade salts and their various concentrations were obtained by serial dilution.

Stoichiometry
The stoichiometry of the reactions was determined by spectrophotometric titration at a predetermined $\lambda_{max}= 520$ nm using the mole ratio method (Ukoha and Iyun, 2001; 2002). The concentration of Fe_2O^{4+} was kept constant at 1.0 x $10^{-4}moldm^{-3}$ while that of thiourea was varied between (2.0 – 24) x $10^{-5}moldm^{-3}$ at $[H^+] = 1.0$ x $10^{-3}moldm^{-3}$ and constant ionic strength of 0.3 $moldm^{-3}$(NaCl) at T = 27 ±1.0°C. The reactions were allowed to stand until the repeated absorbances of the reaction mixture at $\lambda_{max}= 520$ nm were constant. The stoichiometry was then determined from the plot of absorbance versus mole ratio of Fe_2O^{4+} : TU.

Kinetic studies
The rate of reaction was studied under pseudo-first order condition with [TU] in at least 50 fold excess over $[Fe_2O^{4+}]$ at the stated conditions by monitoring the increase in the absorbance of the complex at 520 nm using Corning Colorimeter 525. From the slopes of pseudo-first order plots of log (A_∞ - A_t) versus time, the pseudo-first order rate constants (k_1) were determined. The second order rate constant (k_2) were obtained from:

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$k_2 = k_1/[TU]^n$,

where: n is the order with respect to [TU].

Acid dependence studies

The effect of changes in the hydrogen ion concentration on the reaction rate was investigated by keeping the concentration of the other reactants constant while varying the hydrogen ion concentration in the range of $(4 - 14) \times 10^{-4}$ moldm^{-3}.

Effect of ionic strength

The effect of ionic strength on the rates of the reaction was studied over a range of $(1.0 - 6.0) \times 10^{-1}$ moldm^{-3} using NaCl, while other reaction conditions were kept constant.

Influence of added anions

The influence of added sulphate and acetate ions on the rate of reaction were investigated by varying the concentration of these anions whilekeeping [Fe$_2$O^{4+}], [thiourea] and ionic strength constant.

Test for participation of free radicals in the course of reaction

Test for free radicals was carried out by adding 2 g of acrylamide to a partially oxidised reaction mixture containing various concentrations of oxidant, reductant and hydrogen ion. A large excess of methanol was added to the reaction mixture. Control experiment was carried out by adding acrylamide to solutions of oxidant and reductant separately at the same conditions of [H$^+$], ionic strength and temperature. Any polymerisation as indicated by gel formation suggested the presence of free radicals in the reaction mixture (Iyun and Adegite, 1990;Vaidya*et al.,* 1991).

Products analysis

At the completion of the reaction, the reaction mixtures were analyzed for the type of organic and inorganic products formed. The products were confirmed by chemical test and infrared spectroscopy as follows. The FTIR spectra of the binuclear complex of iron(III) and thiourea were obtained separately with a Shimadzu FTIR-84008 spectrophotometer in the region 500-4000 cm^{-1} prior to the reactions. At the completion of reaction, TLC and PTLC were carried out using Fluka silica gel on the product mixture in order to isolate pure organic compound(s) likely to be present in the product. After the isolation of the pure organic compound, the FTIR of the compound was run. The spectral thus obtained, were compared for possible shifts in stretching/vibrational frequencies. Addition of dilute alkaline CuSO$_4$ solution to the products was done to test for the presence of urea. Potassium nitroprusside was added to the reaction mixture to test for the presence of Sulphur.

Results and Discussion

Stoichiometry and product analysis

Results of stoichiometric studies for the oxidation of thiourea (TU) by Fe$_2$O^{4+} shows that one mole of the reductants was consumed by one mole of Fe$_2$O^{4+}. The stoichiometric equation can be represented as equation 1:

Fe$_2$O^{4+} + (NH$_2$)$_2$C=S → 2Fe^{2+} + (NH$_2$)$_2$C=O + S (1)
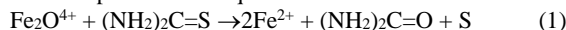
A similar stoichiometry has been reported for the electron transfer reaction of thiourea with μ-superoxobinuclear cobalt (III) complex (Osunlaja*et al.,* 2013). But in the reaction of thiourea with of Ru$_2$O^{4+} (diaquotetrakis (2, 2′-bipyridine) − μ-- oxodiruthenium (III) complex, the stoichiometry of 1:2 (oxidant : reductant) was obtained (Mohammed *et al.,* 2014). The stoichiometry reported in this research is in accordance with thiourea undergoing step-wise two electron oxidation to give the products. The centre of electron transfer is the C=S functional group in thiourea. Loss of electrons is expected to change the stretching/vibrational frequencies especially the υ(C=S) mode into the υ(C=O) mode if thiourea is oxidized into urea as represented in stoichiometric equation above. Spectroscopic evidence of the absence of υ(C=S) in the product as compared to υ(C=S) of thiourea spectra supports

the formation of new functional group identified as $\upsilon(C = O)$ of urea at $1644 \pm 30 \, cm^{-1}$ (Al-Majthouls and Salman, 2012;Osunlaja*et al.,* 2013) as against $700 \pm 50 \, cm^{-1}$ of $\upsilon(C = S)$ of thiourea and its derivatives (Begum *et al.,* 2009).A pinkish-violet colour which gradually turned bluish was obtained with the addition of dilute alkaline CuSO$_4$ solution to the product. This also confirms the presence of urea or its derivatives.

The appearance of an absorption maximum at 520 nm in this study confirmed the formation of Fe^{2+} (Ayoko*et al.,* 1994, 1999; Yusuf *et al.,* 2004; Iyun,2004; Idris*et al.,* 2004). Also the absence of absorption peak at 620nm rules out the presence of mononuclear complex of iron (III) in the reaction medium. When some portion of the products of reactions of Fe$_2$O^{4+} with thioureas were reacted with sodium nitroprusside on a tile violet colour was obtained, thus confirming the presence of sulphur (Murugan, 2013), as one of the products as seen in stoichiometric equations. Similar result was obtained in the reaction of thiourea with chlorite ion in acidic medium (Alamgir and Epstein, 1985).

Kinetic study

Pseudo-first order plot of $\log(A_\infty - A_t)$ versus time (Fig. 1) was linear for greater than 80% extent of the reaction indicating first order with respect to [Fe$_2$O^{4+}]. Also plots of $\log k_1$ versus $\log[TU]$ (Fig. 2) was linear with slopes approximately equal to one suggesting that reaction is approximately first order in [TU]. The kinetic studies of the oxidation of TU by Fe$_2$O^{4+} therefore indicated a second order overall. Similar second order kinetics have been reported for the oxidation of TU by CoO$_2$Co^{5+} (Osunlaj*et al.,* 2013) and Ru$_2$O^{4+} (Mohammed *et al.,* 2014).

Thus, the rate law fits into equation 2

$$\frac{-d}{dt}[Fe_2O^{4+}] = k_2[Fe_2O^{4+}][TU] \qquad (2)$$

Where$k_2 = (2.58 \pm 0.02) \times 10^{-2}$ dm^{3}mol^{-1} s^{-1} and [Fe^{2}O^{4+}] = 2.0×10^{-4} moldm^{-3}at [H$^+$] = 1.0×10^{-3} mol dm^{-3},I = 0.3 mol dm^{-3} , T = 27 ± 1^oC and λ_{max} = 520 nm.
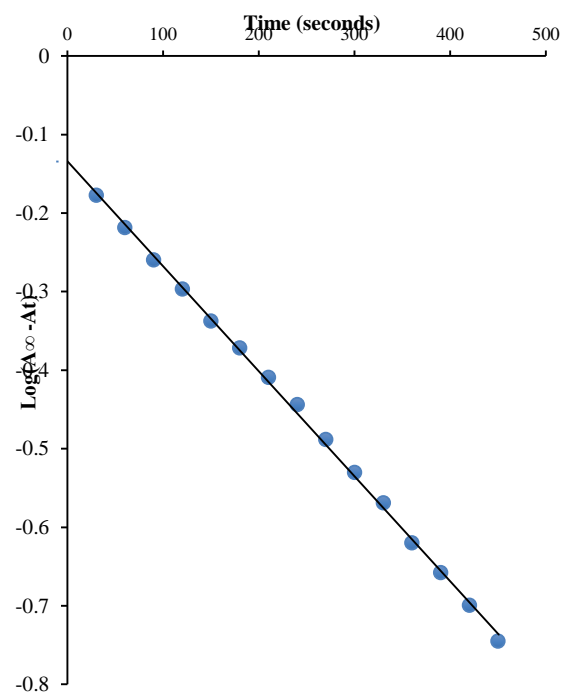

Fig. 1: Typical Pseudo-first order plot for the redox reaction of Fe$_2$O^{4+} with TU at [Fe$_2$O^{4+}] = 2.0 x 10^{-4}moldm^{-3}, [TU] = 4.0 x 10^{-2}moldm^{-3}, [H$^+$] = 1.0x 10^{-3} moldm^{-3}, I = 0.30 moldm^{-3} (NaCl), T = 27.0 ± 1.0^{o}C and λ_{max} = 520 nm

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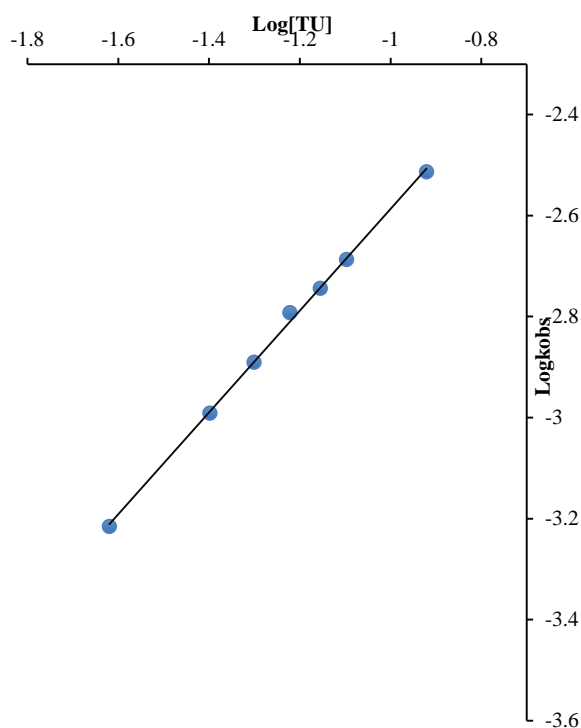**Fig. 2:** Plot of log k_1 versus log [TU] for the redox reaction of Fe_2O^{4+} with TU at $[Fe_2O^{4+}] = 2 \times 10^{-4} moldm^{-3}$; [TU] = (2.4 − 12.0) x $10^{-2} moldm^{-3}$, $[H^+] = 1.0 \times 10^{-3} moldm^{-3}$, I = 0.3 $moldm^{-3}$ (NaCl), T = 27.0 ± 1.0ºC and λ_{max} = 520 nm

Effect of change in hydrogen ion concentration and ionic strength on the reaction

Within the $[H^+]$ range of 4.0×10^{-4} to 1.4×10^{-3} mol dm^{-3}, the rate constant were unaffected by change in hydrogen ion concentration (Table 1). Varying the ionic strength of thereaction medium between 0.1 – 0.6 mol dm^{-3} (NaCl), had no effect on the rates of reaction as shown in Tables 1. Non-dependence of rate of reaction on ionic strength will likely be due to lack of charge on one or both of the reactants in the rate determining step. This result is in accordance with the reaction of Fe_2O^{4+} by 1,2-benzenediol as reported by Idris*et al* (2004).

Table 1: Pseudo-first and second order rate constants for the redox reaction of TU by Fe_2O^{4+} in aqueous HCl medium, λ_{max}= 520nm, T =27.0 ±1.0ºC, I = 0.30 moldm^{-3} (NaCl), $[Fe_2O^{4+}]$= 2 x 10^{-4} moldm^{-3}

10^2[TU] (moldm^{-3})	10^3[H^+] (moldm^{-3})	10 [I] (moldm^{-3})	$10^3 k_1$ (s^{-1})	$10^2 k_2$ (dm^{3}mol^{-1}s^{-1})
2.4	1.0	3.0	6.09	2.53
4.0	1.0	3.0	10.02	2.51
5.0	1.0	3.0	12.87	2.57
6.0	1.0	3.0	16.14	2.69
7.0	1.0	3.0	18.02	2.60
8.0	1.0	3.0	20.58	2.57
12.0	1.0	3.0	30.67	2.56
5.0	0.4	3.0	12.70	2.54
5.0	0.6	3.0	12.65	2.53
5.0	0.8	3.0	12.58	2.52
5.0	1.0	3.0	12.62	2.53
5.0	1.2	3.0	12.57	2.52
5.0	1.4	3.0	12.76	2.55
5.0	1.0	1.0	12.00	2.40
5.0	1.0	2.0	12.98	2.59
5.0	1.0	3.0	13.00	2.60
5.0	1.0	4.0	13.68	2.73
5.0	1.0	5.0	12.74	2.55
5.0	1.0	6.0	12.71	2.54

Table 2: Dependence of rate constant on addition of anions for the redox reaction of the Fe_2O^{4+}.TU system at I = 0.3 moldm^{-3} (NaCl), [TU] = 5.0 x 10^{-2}moldm^{-3}, $[Fe_2O^{4+}]$ = 2.0 x 10^{-4}moldm^{-3}, λ_{max} = 520 nm, $[H^+]$ = 1.0 x 10^{-3}moldm^{-3}, T = 27.0 ± 1.0ºC

10^3[SO_4^{2-}] (moldm^{-3})	$10^4 k_1$ (s^{-1})	$10^2 k_2$ (dm^{3}mol^{-1}s^{-1})
00.0	13.10	2.60
10.0	11.90	2.38
25.0	11.40	2.28
50.0	9.20	1.84
75.0	6.65	1.33
100.0	4.45	0.89
125.0	2.44	0.49
10^3[CH_3COO^-](moldm^{-3})		
00.0	13.10	2.62
10.0	12.15	2.43
25.0	11.55	2.31
50.0	9.80	1.96
75.0	8.90	1.78
100.0	7.80	1.56
125.0	6.40	1.28

Effect of added anions

The rate of reaction was inhibited when SO_4^{2-} and CH_3COO^- were added (Table 2). Inhibition of the reaction rate by the added anions shows that the added ions have hindered the approach of reactant species in a simple collision process. The observed inhibition in reaction rate by the added anions in effect suggests that the reactant species are not linked together in the activated complex

Test for free radicals

Test for free radicals using acrylamide in excess methanol for the reactions gave no gel formation confirming non-participation of free radicals in the reaction.

Test for intermediate complex formation

In ascertaining the presence or absence of the formation of interrmediate complexes in the course of the reactions of Fe_2O^{4+} and the thiourea, Michaelis-Menten plot of 1/ k_1 versus 1/ [TU] (Fig. 3) was made, as applied by Kumar *et al* (1991). The linearity of the plot with negligible intercept, indicated that the intermediates participating in these reactions have no appreciable equilibrium constants thereby ruling out the formation of intermediate complexes in the reactions.
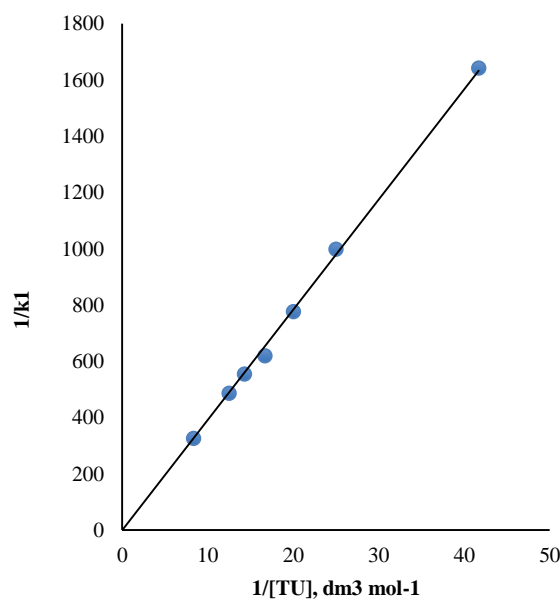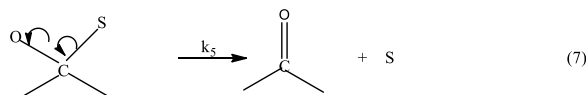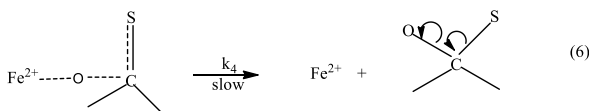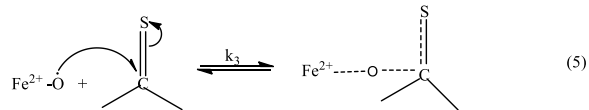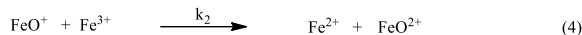

Fig. 3: Michaelis- Menten plot of $1/k_1$ versus 1/[TU] for the oxidation of TU by Fe_2O^{4+} at $[Fe_2O^{4+}]$ = 2.0 x 10^{-4}moldm^{-3}, [TU] = (2.4 – 12.0) x 10^{-2}moldm^{-3}, $[H^+]$ =1.0 x 10^{-3}moldm^{-3}, I = 0.3moldm^{-3} (NaCl), T = 27.0 ± 1.0ºC and λ_{max} = 520 nm

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Mechanism of reaction

Within the limit of experimental condition employed in this research, the mechanism of the reaction is propose as follows.

$$Fe^{2+}\text{-}O\text{-}Fe^{2+} \underset{}{\overset{K_1}{\rightleftharpoons}} FeO^+ + Fe^{3+} \qquad (3)$$

$$FeO^+ + Fe^{3+} \xrightarrow{k_2} Fe^{2+} + FeO^{2+} \qquad (4)$$

$$(5)$$

$$(6)$$

$$(7)$$

Rate $= k_4[Fe^{2+}\text{-}O\text{-}C=S]$ $\qquad (8)$

Application of steady state hypothesis to $[Fe^{2+}\text{-}O\text{-}C=S]$ gives:

$$k_3[Fe^{2+}\text{-}O][\text{-}C=S]\text{-}k_{-3}[Fe^{2+}\text{-}O\text{-}C=S]\text{-}k_4[Fe^{2+}\text{-}O\text{-}C=S] = 0 \qquad (9)$$

$$[Fe^{2+}\text{-}O\text{-}C=S] = \frac{k_3[Fe^{2+}\text{-}O][\text{-}C=S]}{k_{-3}+k_4} \qquad (10)$$

$$Rate = \frac{k_4 k_3[Fe^{2+}\text{-}O][\text{-}C=S]}{k_{-3}+k_4} \qquad (12)$$

If $\quad \dfrac{k_3[Fe^{2+}\text{-}O]}{k_{-3}+k_4} \approx [Fe^{2+}\text{-}O\text{-}Fe^{2+}]$

Rate $= k_4[Fe^{2+}\text{-}O\text{-}Fe^{2+}][\text{-}C=S]$ $\qquad (13)$

Conclusions

The following conclusions are made with respect to this investigation:

(i) Absence of spectroscopic evidence suggests that a precursor complex is probably not formed prior to the act of electron transfer and that the electron transfer may occur by the outer-sphere path.

(ii) Michaelis-Menten's plots of $1/k_1$ versus $1/[thiourea]$ was found to be linear without positive intercept suggesting the absence of a pre-association step. This also favours the outer-sphere mechanism.

(iii) The negative result of polymerization test suggests the absence of free radical intermediate in the reaction or the equilibrium constant for the formation of such radicals can be assumed to be negligible.

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