A STUDY OF THE KINETICS OF THE DISSOLUTION OF A NIGERIAN TANTALITE ORE IN HYDROCHLORIC ACID

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Abstract

Experiments on the kinetics of dissolution of a Nigerian tantalite ore in hydrochloric acid medium have been undertaken. The effects of temperature, acid concentration, stirring rate and particle size on the dissolution rate have been investigated. Physicochemical characterization of this ore, such as moisture content, loss of mass on ignition, pH and the elemental analysis by inductive coupled plasma-mass spectrometry (ICP-MS) was also carried out. With 12M HCl, about 67.2 % of tantalite ore was dissolved within 120min, using 0.1mm particle size and stirring rate of 270 rpm at 80 ºC .The results of the study indicate that the dissolution reaction is topochemical and is greatly influenced by hydrogen ion [H^+] concentration. Moreover, the leaching data fit a diffusion model. A value of 27.95 kJ/mole was obtained for the activation energy of dissolution of the mineral, which is reasonable for a rate limiting diffusion mechanism.

Keywords: Nigeria, Tantalite ore, Hydrochloric acid, Dissolution.

1.Introduction

Tantalite ore is an economic mineral which contains majorly tantalum and niobium. Other elements found associated with the ore include tin, manganese, iron, germanium and tungsten. The tantalite ore has the general formula: (Mn, Fe) $(Ta, Nb)_2O_6$.(Encycl. Sci. & Tech., 1992).

Pure tantalite is rare, as the presence of elements such as iron and manganese constitute impurities and they vary considerably in their relative proportions. The principal ore of tantalum is found chiefly in granite pegmatities as a detrital mineral and in some places, in important amount having weathered from such rock (Encycl. Sci. & Tech., 1992).

Tantalite ore is found primarily in Australia, Canada, Brazil, South Africa, Nigeria and Central African countries such as Riwanda, Namibia, Uganda, Democratic Republic of Congo-Kinshasa, Gabon and Burundi. The single largest source of tantalum mineral concentrate is produced by Sons of Gwalia limited, from its Green bushes and Wadgina mines in Western Australia. These two combined produce between 25 and 35 % of the world supply, with production in 2001, amounting 1.8 million pounds (Encycl. Analytical Sci., 1986).

Deposits of tantalite ore are also found in Zimbabwe, Mozambique, India and the U.S.A. Research shows that Australia has output of about 17.3 % and Canada 6.9 %. Developing countries like Thailand, Zaire, and Nigeria, all produce 3.6 % of the concentrates (Amethyst Gall., 1996).

Economic deposits of tantalite occur in several parts of Nigeria. The major ones include: Kaduna State (Abia Hill, Tare Naudu, Gerti station); Nassarawa State (Wambe Denga, Akwanga, Kokona-ndegi, Agwa-Doka); Federal Capital Territory (Takwashera, Bize, Kusaki); Kogi State (Okene, Akuta, Ejuku, Takete-Ishanlu Isa and Egbe); Kwara State (Oke-Onigbin) and Oyo State (Igbeti). Precise figure of the total reserves of tantalite in Nigeria is presently not available (History of Min. & Industry in Nigeria, 1987).

In general, tantalum was mostly recycled from the tantalum-related electronics component and new and old scrap products of tantalum-containing cemented carbides and super alloys. In 1998, about 210 metric tons of tantalum were recycled/reused, with about 43 % derived from old scrap. The tantalum recycling rate was calculated to be 21 %, and tantalum scrap recycling efficiency, 35 % (Cunigham, 1998).

Apparently, there is not much work reported on the kinetics of dissolution of tantalite ore in hydrochloric acid. There has been however a lot of work in the literature on the chemical analysis of tantalite ore. The relevant ones include method for the determination of tantalum and tungsten in rocks and meteriorites by neutron activation analysis (Atkins and Smales, 1990); determination of tantalum in ores and mill products after pre-concentration by extraction with methylisobutyl ketone (Donaldson, 1992).

The extraction of tantalum and niobium is more selective from hydrofluoric acid sulphuric acid solution, because the chloro-complexs of iron(II) , molybdenum (VI), tin (IV), antimony (V), and

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arsenic (III) are co-extracted from hydrofluoric acid-hydrochloric acid media (Stevenson and Hicks, 1983) whereas, with 1M hydrofluoric acid and 0.5M sulphuric acid, tantalum is ~96 % extracted into MIBK and niobium is only ~2 % extracted (Nishumura, et al., 1982).

Many researchers have developed several methods of obtaining or extracting tantalum in various materials (Pawel and Campbell, 1981; Gypen and Denythere, 1982; Albert *et al.,* 1983; Balaji, 1984; Jamosbek and Lechora, 1986;).Their aims are among other things to establish some defined physico-chemical parameters that would be favourable to the leaching or extraction of tantalum and developing methods for separating the metal from other impurities, such as niobium and tungsten.

This work presents a detailed study on the application of the hydrochloric acid for the dissolution of a Nigerian tantalite ore mineral. The kinetic of dissolution of the tantalite is also discussed. Hydrochloric acid is cheaper and easier to handle when compared to hydrofluoric -sulphuric acid mixture which could be explosive. To the best of our knowledge, no similar work on the leaching of Nigerian tantalite ore has been reported.

2. Experimental

(a) Material

A tantalite ore from Oke-Onigbin, Kwara State (Nigeria) was used for this study. The elemental analysis of tantalite ore was carried out by inductively coupled plasma-mass spectrometry (ICP-MS).

The reagents used for this research work are mainly BDH products of analytical grades. Doubly distilled water was used for the preparation of all HCl solutions.

(b) Equipment

A 500 ml Rasotherm conical flask, covered with a glass lid and put on a pre-calibrated Bibby Stuart hot plate and stirrer-model CB 162, was used for the leaching experiments.

(c) Physicochemical studies

(i) Moisture content determination:

1g of the tantalite ore was weighed and put into the crucible. The whole was then put inside the Gallenkamp, model DV-160 oven BS for about 5 hours, at 105° C. After heating for about 5 hours, the sample was withdrawn from the oven and was quickly transferred into the desciccator in order to prevent further moisture absorption from the atmosphere. Later the cooled products were then reweighed. The difference in mass which was the mass of the moisture content was then determined.

(ii) Loss of mass on ignition

The weighed crucible and oven-dried tantalite ore was put inside the muffle furnace and roasted at high temperature of about 500-600 °C for about 2 hours. After roasting, the sample was withdrawn from the furnace and allowed to cool for about an hour. Later, the cooled product was then reweighed.

(iii) pH determination

10 g of the tantalite ore was put inside a conical flask. This was followed by the addition of 25 ml distilled water and the mixture was stirred vigorously for about 5 minutes and then allowed to equilibrate. The pH of the supernatant solution was then measured using, KENT EIL 7055 pH meter. The pH measurement was monitored daily over a period of one week.

(d) Leaching procedure

A sieved tantalite ore sample of particle diameter 0.1 mm was used for this experiment at different concentrations of HCl and at different contact times and fixed temperature of 55° C. 0.5 g of the sieved sample of tantalite ore was put into a 100 ml of 0.5M HCl acid. The magnetic stirrer was introduced into the Bibby Stuart hot plate. The sample mixture was heated at temperature of 55 °C and stirred at a rate of 200 rpm.

The same procedure was repeated for other concentrations of HCl: 1M, 2M, 4M, 8.42M and 12M. Each concentration of HCl was contacted with 0.5 g of tantalite ore for 5, 10, 30, 60 and 120 min. respectively.

At the end of the leaching process for a given contact time, the mixture was allowed to cool and then filtered through a Whatmann filter paper Cat No. 1001 110. Later the residue left in the filter paper oven-dried at 60° C, for about 12 hours and was then reweighed. The difference in weight was noted as the amount of tantalite ore undissolved. The percentage of the tantalite ore dissolved was calculated therefrom. This calculation was done for all the concentrations of HCl investigated. The concentration which gave the highest percentage of dissolution, i.e. 12M, was used for the optimization of other parameters such as temperature and particle size. The activation energy was estimated from the Arrhenius plot.

3. Results

(a) Physico-chemical characterization

(i) Moisture content determination

Moisture content determination of the mineral enables us to find out the state of dryness or otherwise of the mineral and enable us to make appropriate correction in the analytical results. Therefore, the result obtained for the moisture content of the ore was 4.9 % ± 0.005.

(ii) Loss of mass on ignition

The average percentage of loss of mass loss on ignition of the oven-dried tantalite ore was approximately 2.8 % ± 0.004. The loss of mass could be accounted for by the possible presence of organic/ decayed substances.

(iii) pH determination

The pH of the tantalite-water suspension was 8.3. This value suggests that the surface of the mineral is basic. This is in support of the predominant chemical form of tantalite, which is oxide.

(b) Elemental analysis by ICP-MS

The elemental analysis of the tantalite ore by ICP-MS technique is summarized in table 1.

(c) Effect of HCl concentration

The effect of HCl concentration on the rate of tantalite ore dissolved has been examined for particle size 0.1mm. The results of fraction of tantalite ore dissolved as a function of contact time at various concentrations of HCl are presented in figure 1.

It is evident from figure 1 that increase in the concentration of HCl is accompanied with increase in the amount of tantalite ore dissolved at various contact time. Concentration of the leachant has a significant effect on the leaching of the tantalite. Therefore, these results showed that the rate of tantalite ore dissolution is controlled by the hydrogen ion concentration. This is in accordance with the work earlier published (Zuo-mei Jin *et al.*, 1984; Feurstenau, *et al.*, 1987; Olanipekun, 2000; Baba, et al., 2003), on a separate studies involving the quantitative leaching of sphalerite and galena by HCl.

(d) Effect of temperature

The effect of temperature on the rate of tantalite dissolution was studied over the temperature ranges of 28 °C-80 °C. Figure 2 shows the variation of the fractions of the tantalite ore dissolved against the contact time at different temperature.

As seen in figure 2, increasing temperature of the system, greatly accelerate the reaction rate and this leads to increase in the amount of tantalite ore dissolved.

(e) Effect of particle diameter

The effect of particle diameter on the dissolution of tantalite ore was investigated in 12M HCl solution at 80 °C, using the three particle size fractions: 0.1 mm, 0.2 mm and 0.3 mm, and at a stirring rate of 270 rpm. The results of these findings are presented in Table 2.

From Table 2, it is apparent that the fraction with the smallest particle size has the highest quantity of tantalite ore being dissolved. This is due to the highest surface area of the smallest particle size fraction.

(f) Effect of stirring speed

The effect of stirring speed on the dissolution of tantalite ore was investigated in 12M HCl solution with the 0.1 mm size fraction of the tantalite ore at 80 °C, using stirring speeds of 0-450 rpm. The results obtained are presented in Table 3.

It is clear from Table 3 that the amount of the tantalite ore dissolved increases with the stirring speed between the range 0-270 rpm. The percentage dissolved appears to be practically constant afterwards. There is no appreciable gain from 270-450 rpm. The dissolution seems to reach a steady state at 270 rpm. Increase in the percentage of tantalite ore dissolved with increasing stirring speed indicates that the dissolution reaction is controlled by diffusion.

4. Discussions

(a) Rates of dissolution analysis.

The rate of tantalite dissolved was analyzed with the shrinking core model, based on the assumption that the ore is a homogenous spherical solid phase (Levenspiel, 1972). However, since the rate of a heterogeneous reaction is directly proportional to the surface area of the reaction solid, kinetic model of such reaction must account for the diminishing surface area of the solid (Zuo-mei Jin *et al.*, 1987).

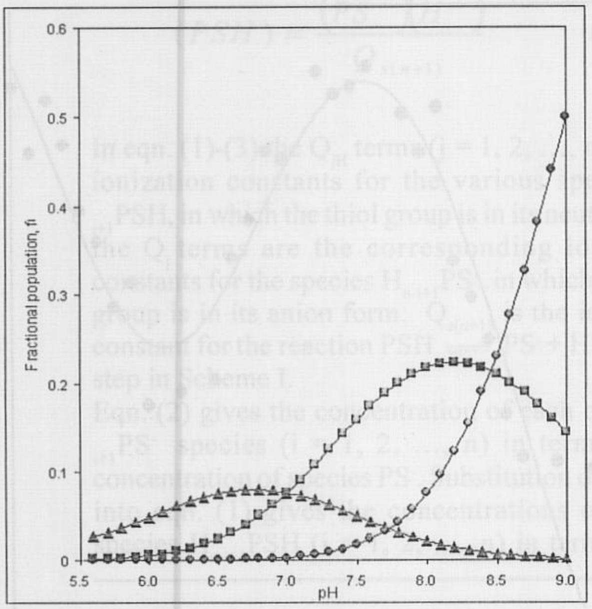
Table 1: Elemental analysis result by ICP-MS.

Element	Fe	Ca	P	Mg	Ti	Al	Na	K	S	Mn	Nb	Ta	Mo	Cu
Concentration	24.9^{a}	0.01^{a}	0.019^{a}	0.11^{a}	14.03^{a}	0.12^{a}	0.09^{a}	0.02^{a}	12.39^{a}	2.39^{a}	4963.2^{b}	29.87^{a}	0.8^{b}	37.8^{b}

Element	Pb	Zn	Ag	Ni	Co	As	U	Au	Th	Sr	Cd	Sb	Bi	V
Concentration	0.11^{a}	419^{b}	5.2^{b}	8.9^{b}	40^{b}	187^{b}	15.8^{b}	20.2^{b}	61.9^{b}	2.0^{b}	0.8^{b}	205^{b}	0.4^{b}	157^{b}

Element	La	Cr	Ba	W	Zr	Ce	Sn	Y	Be	Sc	Li	Rb	Hf
Concentration	177.4^{b}	90.6^{b}	11.0^{b}	65.4^{b}	46.7^{b}	349^{b}	75.1^{b}	17.6^{b}	0.01^{b}	14.0^{b}	4.4^{b}	1.1^{b}	7.3^{b}

a = concentration expressed in %, b = concentration expressed in ppm



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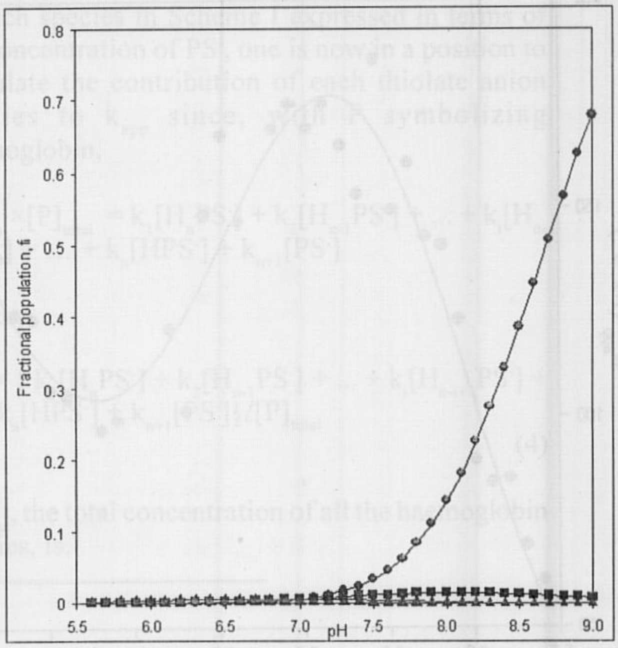

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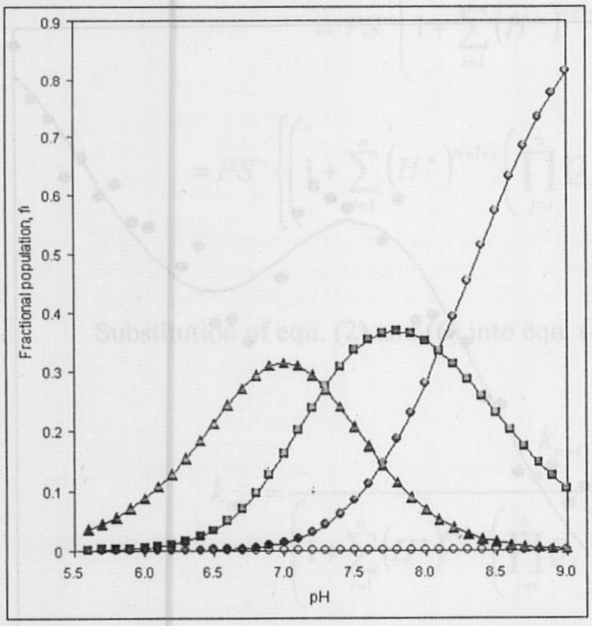

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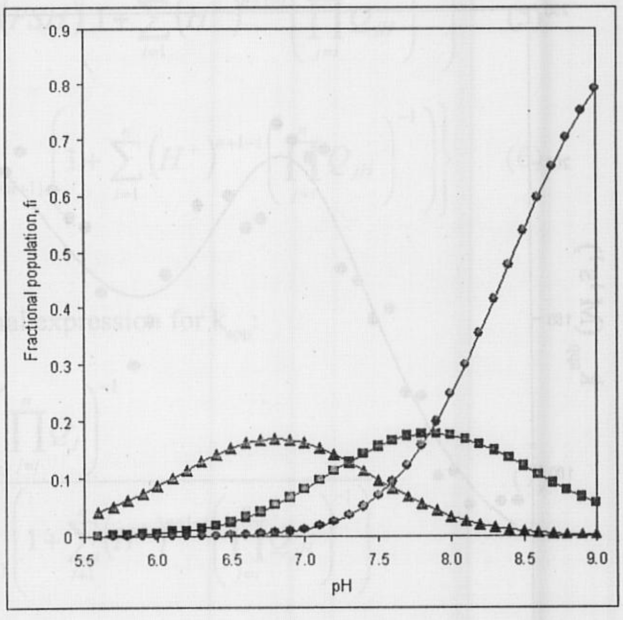

(d)

Figure 3a: Fractional population, f_i ($i = 1\text{-}3$), of species $H_{n-i+1}PS^-$ ($n = 2$) as a function of pH (compare with eqn. 9). carbonmonoxyhaemoglobin Conditions as in Fig 1. (▲ - H_2PS^-; ■ - HPS^-; ● - PS^-).

Figure 3b: Fractional population, f_i ($i = 1\text{-}3$), of species $H_{n-i+1}PS^-$ ($n = 2$) as a function of pH (compare with eqn. 9) for oxyhaemoglobin. Conditions as in Fig 1. (▲ - H_2PS^-; ■ - HPS^-; ● - PS^-).

Figure 3c. Fractional population, f_i ($i = 1\text{-}3$), of species $H_{n-i+1}PS^-$ ($n = 3$) as a function of pH (compare with eqn. 9) for aquomethaemoglobin. Conditions as in Fig 1. O, H_3PS^-; (▲ - H_2PS^-; ■- HPS^-; ● - PS^-).

Figure 3d: . Fractional population, f_i ($i = 1\text{-}3$), of species $H_{n-i+1}PS^-$ ($n = 2$) as a function of pH (compare with eqn. 9) for azidomethaemoglobin. Conditions as in Fig 1. (▲ - H_2PS^-; ■ - HPS^-; ● - PS^-).

advantage of the observation (Okonjo *et al.*, 1995; Okonjo *et al.*, 1996) that it is the positively charged groups at the organic phosphate binding site of haemoglobin that are electrostatically linked to CysF9[93]^2. In human haemoglobin these groups are only four in number, namely, ValNA1[1]^2, HisNA2[2]^2, HisH21[143]^2 and LysEF6[82]^2 (Arnone, 1972; Arnone and Perutz, 1974). Of these four, LysEF6[82]^2 is not ionisable in the pH range 5.6 to 9 in which the data in Fig. 2 were gathered, because its pK_a is ca 10.5. It was therefore not taken into consideration in the analyses. In addition to this, the NA2[2]^2 position in horse haemoglobin is occupied by glutamine residue, not by a histidine (Matsuda *et al.*, 1980). The glutamine residue is uncharged and unionizable. Consequently, the value of n in Scheme I and eqn. (7) is 2 for the horse haemoglobin derivatives other than the aquomet derivative. For aquomethemoglobin the value of n is 3 because the ionization of the water molecule at the 6th coordination position of the ferric iron atom is also linked electrostatically to CysF9[93]^2 [Okonjo *et al.*, 1995; Okonjo *et al.*, 1996].

In order to obtain the various k_i, pQ_i and pQ_{jH} values of Scheme I for the horse haemoglobin data (Fig. 2), a computer analysis was carried out on Equ. (7), using the fitting software of Micro Maths Scientist (Salt Lake City, Utah). The curves through the data points in Fig. 2 are the best-fit curves calculated with the best-fit parameters reported in Table 1 for carbonmonoxy-, oxy-, aquomet- and azidomethaemoglobin. It is seen that the curves through the data points are very good fits to the data. The mean pQ values obtained are: $pQ_1 = 7.21 \pm 0.1$, $pQ_2 = 8.02 \pm 0.2$ and $pQ_{S3} = 8.49 \pm 0.2$. Following the assignments made in the case of human haemoglobins (Okonjo et al., 1995; Okonjo et al., 1996) we assign the pQ_1 of 7.21 to HisH21[143]^2, the pQ_2 of 8.02 to ValNA1[1]^2 and the pQ_{S3} of 8.49 to CysF9[93]^2.

Equation 7 provides an insight into the contribution of each species $H_{n+1-i}PS^-$ to k_{app}. This contribution is equal to the product of k_i, the apparent second order rate constant for the reaction of DTNB with species $H_{n+1-i}PS^-$, and the fractional population, f_i, of this species. Now for species PS^- of Scheme I, i = n+1 and

$$f_{n+1} = \frac{1}{\left(1+\sum_{i=1}^{n}(H^+)^{n+1-i}\left(\prod_{j=i}^{n}Q_j\right)^{-1}\right)+{}^{(H^+)}\!\!\diagup_{Q_{s(n+1)}}\left(1+\sum_{i=1}^{n}(H^+)^{n+1-i}\left(\prod_{j=i}^{n}Q_{jH}\right)^{-1}\right)} \qquad (8)$$

For the other species,

$$f_i = \frac{(H^+)^{n+1-i}\left(\prod_{j=i}^{n}Q_j\right)^{-1}}{\left(1+\sum_{i=1}^{n}(H^+)^{n+1-i}\left(\prod_{j=i}^{n}Q_j\right)^{-1}\right)+{}^{(H^+)}\!\!\diagup_{Q_{s(n+1)}}\left(1+\sum_{i=1}^{n}(H^+)^{n+1-i}\left(\prod_{j=i}^{n}Q_{jH}\right)^{-1}\right)} \qquad (9)$$

It therefore becomes possible to discuss the relative contributions of the various species in Scheme I to the magnitude of k_{app} at different pH values.

Figs. 3a-d show the dependence of f_i on pH for i = 1-3. These curves were calculated with the aid of the Micro Maths Scientist program (Salt Lake City, Utah) using eqn. (9) and the best-fit Q_j and Q_{jH} values reported in Table 1. When n = 2, we have f_1 as the fractional population of H_2PS^-; f_2 as the fractional population of HPS^-; and f_3 as that of PS^-. If n = 3, then f_1, f_2, f_3 and f_4 become the fractional populations of H_3PS^-, H_2PS^-, HPS^- and PS^- respectively. These curves enable us to see the contribution of each species to k_{app} as a function of pH in the different haemoglobin derivatives and provide an explanation for the complex nature of the pH dependence of k_{app}.

4. Conclusion

The analytical equation derived in this paper, eqn. (7), is generally applicable to complex reaction profiles obtained for the reaction of DTNB with protein sulphydryl groups in general, particularly in cases where the number, n, of thiol-linked groups is not known with certainty. The computer analysis of the k_{app} data with eqn. (7) provides a powerful tool for the determination of the number of such groups and of their nature, as gauged from their calculated pK_as.

Table 1: Reaction of Horse haemoglobin with DTNB at an ionic strength of 0.05 mol dm^{-3}. Best - fit parameters used to fit the data in Figs.2a - d [compare with Scheme I and equation (7)]

	Haemoglobin derivatives			
Parameter	oxy	aquomet	carbonmonoxy	azidomet
pQ_{1H}	6.24	6.22	6.17	6.49
pQ_1	7.40	7.15	7.00	7.30
pQ_{2H}	7.00	6.55	7.50	7.28
pQ_2	8.28	7.50	8.46	7.85
$pQ_{s3/s4}$	8.55	8.30	8.84	8.26
k_1 ($M^{-1}s^{-1}$)	553.1	279.21	2046.6	499.89
k_2 ($M^{-1}s^{-1}$)	474.6	1032.3	212.8	161.95
k_3 ($M^{-1}s^{-1}$)	168.3	232.0	227.7	150.71
k_4 ($M^{-1}s^{-1}$)	-	253.5	-	-

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