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Reduction of Trioxobromate(V)Ion By [Cohedtaoh$_2$]$^-$ in Acid Medium : Kinetics and Mechanism.

***A.D. Onu, J. F. Iyun and S.O. Idris**
Department of Chemistry, Ahmadu Bello University, Zaria.
*** Department of Chemistry, Federal College of Education, Zaria.**
Correspondence author.e-mail:daveonu@gmail.com

Abstract:

The kinetics of the reduction of trioxobromate(V)ion, BrO_3^- *by* $[CoHEDTAOH_2]^-$ *has been studied in aqueous acidic medium at 28* ^0C, $I = 1.0$ *mol* dm^{-3} $(NaClO_4)$ *and* $[H^+] = 7.50x10^{-2}$ *mol* dm^{-3}. *The stoichiometry studies showed that for every mole of the* BrO_3^- , *5 moles of* $[CoHEDTAOH_2]^-$ *was consumed. The stoichiometric equation for the reaction is:* $5[CoHEDTAOH_2]^- + BrO_3^- + 6H^+ \rightarrow 5[CoHEDTAOH_2] + ½ Br_2 + 3H_2O$. *The reaction is first order in both* $[BrO_3^-]$ *and* $[CoHEDTAOH_2^-]$. *The rate of the reaction increased with increase in* $[H^+]$. *A plot of acid dependent rate constants versus* $[H^+]^2$ *is linear and conform to the following equation:* $- [CoHEDTAOH_2^-] / dt = (a + b[H^+]^2) [CoHEDTAOH_2^-] [BrO_3^-]$ *within the acid range* $0.025 \leq [H^+] \leq 0.1$ *moldm*$^{-3}$, $a = 6.0 \times 10^{-5}$ $dm^3mol^{-1}s^{-1}$ *and* $b= 0.146$ $dm^9mol^{-3}s^{-1}$.
Negative salt effect was observed from the rate dependence on ionic strength studies. CH_3COO^- *decreased the rate of the reaction. The outer-sphere mechanism is proposed for the reaction.*

Introduction:

BrO_3^- is a powerful brominating agent for aromatic compounds that contain deactivating substituents (Groweiss, 2000). It is also used in the oxidation of sulfur and vat dyes, for cleaning boilers and as an analytical reagent. It's mixture with sodium bromide is used for dissolving gold from its ores (HSDB, 2003). In the cosmetic industry it is used as neutralizers or oxidizers in hair wave preparations.

BrO_3^- is one of the disinfection by-products formed during the ozonation of water containing bromide. Bromide is naturally present in water and the ozonation of waters containing the bromide ion (Br^-) results in the oxidation of Br^- to hypobromous acid (HOBr) and further oxidation of the hypobromite ion (BrO^-) to BrO_3^- (Downing and Nerenberg, 2007). In humans, intake of BrO_3^- can lead to gastrointestinal symptoms (abdominal pain, nausea, vomiting, and diarrhea), central nervous system depression, renal failure and hearing loss (NTP Report, 2005). It is a suspected human carcinogen (Kurata et al, 1992). It has been shown to cause renal tumors in rats and male mice (DeAngelo et al, 1998). Several studies involving the reduction of bromate by several substrates have been reported (Pujari and Banerjee, 1983; Ayoko et al, 1991; Iyun et al, 1992a; Lohdip et al, 1996; Desai et al, 2002; Chikwana et al, 2004; Bugaje, 2006; Cherkupally and Tumu, 2007). Differing stoichiometries were reported in these works while the oxidation state of $Br^v \rightarrow Br^0$ or $Br^v \rightarrow Br^-$ were established. In this paper the redox reaction of BrO_3^- with $[CoHEDTAOH_2]^-$ complex is reported. It is hoped that the data generated from this work will throw more light on the BrO_3^- reactions.

Experimental:

Materials.

All reagents used were of analar grade. Stock solutions of $[CoHEDTAOH_2]^-$ was prepared according to the method of Mansour (2003), sodium ethanoate and BrO_3^- were prepared by dissolving weighed amount of each and making up to known solution volume with distilled water. The λ_{max} (510 nm) was determined by running the spectrum of the solution of $[CoHEDTAOH_2]^-$ in the wavelength range 380-580 nm . A stock solution of perchloric acid was made by diluting analar grade acid (70 %, specific gravity 1.67) and standardizing titrimetrically. Analar grade sodium perchlorate ($NaClO_4$) was used to maintain the ionic strength.

Stoichiometry

The stoichiometry of the $[CoHEDTAOH_2]^-$ - BrO_3^- reaction was determined by spectrophotometric titration using the mole ratio method. The $[CoHEDTAOH_2^-]$ was kept constant at $5.0x10^{-3}$ mol dm^{-3} while that of

$[BrO_3^-]$ ion was varied from (2.0-100.0) $x10^{-4}$ mol dm^{-3} at $I = 0.5$ mol dm^{-3} ($NaClO_4$) and $[H^+] = 0.05$ mol dm^{-3}. The reactions were allowed to go to completion and the absorbances of the solutions were taken at 510 nm. The stoichiometry was determined from the plot of absorbance versus the mole ratio BrO_3^- $/[CoHEDTAOH_2]^-$.

Kinetics

The wavelength of maximum absorption, λ_{max} of $[CoHEDTAOH_2]^-$ was determined to be 510 nm using Spectronic 20 colorimeter. The rate of the reaction of $[CoHEDTAOH_2]^-$ with BrO_3^- ion was studied at this λ_{max} by observing the change in absorbance of $[CoHEDTAOH_2]^-$ with time. All the kinetic measurements were carried out under pseudo-first order condition with $[BrO_3^-]$ in large excess over $[CoHEDTAOH_2^-]$ at 28 ^0C and 1.0 mol dm^{-3} ($NaClO_4$) ionic strength. The plots of log $(A_\infty - A_t)$ versus time were made. From the gradient of the plots the pseudo-first order rate constants k_1 were determined as given by the equation:

$$\log(A_t - A_\infty) = -\frac{k_1 t}{2.303} + \log(A_0 - A_\infty) \qquad (1)$$

The second order rate constants k_2, were obtained from k_1 as $k_1/[BrO_3^-]$. The results are presented in Table 1.

Results/Discussion

Stoichiometry

The analysis of the plot of absorbance versus mole ratio $BrO_3^-/[CoHEDTAOH_2]^-$gave a ratio of 5:1. On the basis of the stoichiometry the over all equation for the reaction is

$$5\ [CoHEDTAOH_2]^- + BrO_3^- + 6H^+ \rightarrow 5[CoHEDTAOH_2] + 1/2Br_2 + 3H_2O \qquad (2)$$

The stoichiometry of 5:1 obtained in this reaction is similar to those obtained for reactions of BrO_3^- with $[Co(cedta)]^{2-}$ (Pujari and Banerjee, 1983), $[CoW_{12}O_{10}]^{6-}$ (Ayoko et al, 1991) Methylene blue (Iyun and Asala, 1994), Acetaldehyde (Lohdip et al,1996) and diaquotetrakis(2,2'-bipyridine)-μ-oxo-diRuthenium(III) ion(Iyun et al, 1992b) but differs from 6:1(reductant/oxidant) obtained from bromate –[$Co(II)EDTA]^{2-}$ reaction (Bugage, 2006) . Other stoichiometries reported for the reaction of the oxidant with non- one electron transfer reductants includes reaction with urea and L-ascorbic acid (Iyun et al, 1992a), Catechol (Iyun, 1990), Guanylthiourea, (Chikwana et al, 2004) that obtained 3:1, 5:2 and 8:5 (reductanct/oxidant) respectively. The bromine product obtained is in agreement with previous result (Pujari and Banerjee, 1983) and this conforms to a change in oxidation state from $Br^v \rightarrow Br^0$. It is reasonable to accept Br_2 as product of the reaction since under the experimental condition any Br^- formed would have reacted with the excess BrO_3^- to form bromine according to the equation:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

High stoichiometry is to be expected for reaction involving bromate ion being a multi-electron oxidant (Sarathi et al, 2005).

Order of reaction

The pseudo-first order plots of log $(A_\infty - A_t)$ versus time for the reaction were linear for about 70 % of the reaction (A_t and A_∞ are the absorbance of the complex at time t and the end of the reaction respectively).The linearity of the plot indicates that the reaction is first order with respect to $[CoHEDTAOH_2^-]$. From the slopes of the plots, the pseudo-first order rate constants (k_1) were obtained. Analysis of the plot of log k_1 versus log $[BrO_3^-]$ (Fig.1) gave slope of 1.04 showing that the reaction is first order in $[BrO_3^-]$.The reaction is therefore second order overall. The rate law for the reaction is:

$$-\frac{d[CoHEDTAOH_2^-]}{dt} = k_2[CoHEDTAOH_2^-][BrO_3^-] \qquad (3)$$

$$k_2 = (14.85 \pm 0.66) \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$$

Similar overall order of reaction has been reported for BrO_3^- reactions (Lohdip et al, 1996; Iyun et al, 1992a&b; Ayoko et al, 1991).

Effect of $[H^+]$

The influence of $[H^+]$ ion on the rate was investigated using perchloric acid in the range $0.025 \leq [H^+] \leq 0.1$ mol dm^{-3} while the $[CoHEDTAOH_2^-]$ and $[BrO_3^-]$ were kept constant with T= 28 ^0C and I = 1.0 mol dm^{-3} ($NaClO_4$). The results on Table 2 show that the rate of the reaction increased with increase in $[H^+]$ in the range investigated. The plot of k_2 versus $[H^+]^2$ was linear with intercept (Fig.2). The acid dependent rate constant can be represented as

$$k_2 = a + b\,[H^+]^2 \qquad (4)$$

The overall rate equation in the acid range investigated is

$$-\frac{d[CoHEDTAOH_2^-]}{dt} = (a + b[H^+]^2)[CoHEDTAOH_2^-][BrO_3^-] \quad (5)$$

Acid dependence of this nature indicates that there are two parallel reaction pathways; one which depends on acid and the other which is acid-independent (Gupta and Gupta, 1984). In acid solution, bromate establishes the following equilibria

$$BrO_3^- + H^+ \rightleftharpoons HBrO_3$$

$$HBrO_3 + H^+ \rightleftharpoons H_2BrO_3^+$$

The nature of acid dependence or lack of it has therefore been used to suggest the possible reactant bromate species in solution. Second – order acid-dependence has been ascribed to the presence of $H_2BrO_3^+$ and BrO_3^- species (Ayoko et at, 1991 and ref. within) while first-order acid-dependence was used to suggest BrO_3^- and $HBrO_3$ as the likely bromated species (Lohdip et al, 1996 and ref. wthin). The result obtained in this study suggests that both BrO_3^- and $H_2BrO_3^+$ are the reactive species. This result is similar with result commonly obtained for bromate reactions. The addition of proton to oxy-anion is thought to labilize the oxygen by converting it from the oxide form to water enroute the hydroxide form (Birk, 1973 in Iyun et al, 1992b). Thus, protonating an oxide in an oxy-anion should facilitate the scission of the oxygen-central atom bond.

Effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigated in the range I = 1.0 – 2.0 mol dm^{-3} $NaClO_4$, while the concentration of other reagents were kept constant.

Ionic strength dependence studies show a general trend of decrease in reaction rate with increase in ionic strength of the reaction medium (Table 3). The plots of log k_2 versus $\sqrt{I}$ was linear (Fig. 3). Decrease in reaction rate with increase in ionic strength of the medium is generally believed to occur when reaction involves oppositely charged ions (Atkins and dePaula, 2002). Since the $[CoHEDTAOH_2]^-$ ion is negatively charged, it is reasonable to accept the $H_2BrO_3^+$ as a likely reactive specie of the bromate ion in this reaction as suggested by the nature of acid-dependence studies.

Effect of added ion

The concentration of all other reactions were kept constant at

I =1.0 mol dm^{-3} ($NaClO_4$). The effect of added anion on the rate of the reactions was investigated for $[CH_3COO^-]$ = (1.0-5.0) x10^{-2} mol dm^{-3}. The CH_3COO^- was observed to decrease the reaction rate (Table 4). Decrease of the reaction by the added anion shows that the added ion has hindered the approach of the reactant species in a simple collision process. The observed decrease in reaction rate by the added anion in effect suggests that the reactant species are not linked together in the activated complex.

Michealis-Menten (Michaelis-Menten, 1913) plot gave no intercept. An intercept in enzyme kinetics would have suggested presence of binuclear intermediate. The lack of intercept suggests that the mechanism of the reaction did not involve formation of a bridged intermediate at the activated complex, a factor which should have been in favour of the inner-sphere mechanism. Based on the above results which are in favour of outer-sphere mechanism, the mechanism below is proposed.

$$BrO_3^- + 2H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2BrO_3^+ \quad \text{.......}(6)$$

$$[CoHEDTAOH_2]^- + BrO_3^- \xrightarrow{k_2} [CoHEDTAOH_2] + BrO_3^{2-} \quad \text{.......}(7)$$

$$[CoHEDTAOH_2]^- + H_2BrO_3^+ \xrightarrow{k_3} [CoHEDTAOH_2] + BrO_2 + H_2O \quad \text{.......}(8)$$

$$BrO_3^{2-} + 2H^+ \xrightarrow{fast} BrO_2 + H_2O \quad \text{.......}(9)$$

$$4[CoHEDTAOH_2]^- + BrO_2 \xrightarrow{fast} 4[CoHEDTAOH_2] + BrO_2^{4-} \quad \text{.......}(10)$$

$$BrO_2^{4-} + 4H^+ \xrightarrow{fast} Br + 2H_2O \quad \text{.......}(11)$$

With equation (7) and (8) as rate determining steps and applying steady state approximation, the rate of the reaction is given as:

$$\frac{d[CoHEDTAOH_2^-]}{dt} = \left(k_2 + k_3.\frac{k_1}{k_{-1}}[H^+]^2\right)[CoHEDTAOH_2^-][BrO_3^-] \quad (12)$$

Where k_2 = a and $k_3.\frac{k_1}{k_{-1}} = b$

Table 1.:Pseudo - first and second order rate constants for $[CoHEDTAOH_2]^-$ - BrO_3^- reaction at T = 28 ^{0}C, λ_{max} = 510 nm and$[CoHEDTAOH_2]^-$ =5.0x10^{-3} mol dm^{-3}

$10^2[BrO_3^-]$, mol dm^{-3}	$10^2[H^+]$, mol dm^{-3}	I, mol dm^{-3}	10^6k_1, s^{-1}	10^5k_2, dm^{3}mol^{-1}s^{-1}
30	7.5	1.0	43.83	14.61
40	7.5	1.0	59.22	14.81
60	7.5	1.0	84.85	14.14
80	7.5	1.0	127.40	15.93
90	7.5	1.0	132.75	14.75

Table 2:Effect of [H+] on $[CoHEDTAOH_2]^-$ - BrO_3^- reaction at T = 28 ^{0}C, λ_{max} = 510 nm and$[CoHEDTAOH_2]^-$ =5.0x10^{-3} mol dm^{-3}

$10^2[BrO_3^-]$, mol dm^{-3}	$10^2[H^+]$, mol dm^{-3}	I, mol dm^{-3}	10^6k_1, s^{-1}	10^5k_2, dm^{3}mol^{-1}s^{-1}
80	2.5	1.0	44.17	5.52
80	5.0	1.0	81.60	10.20
80	6.5	1.0	104.40	13.05
80	7.5	1.0	117.60	14.70
80	10.0	1.0	157.92	19.74

Table 3:Effect of ionic strength on $[CoHEDTAOH_2]^-$ - BrO_3^- reaction at T = 28 ^{0}C, λ_{max} = 510 nm and$[CoHEDTAOH_2]^-$ =5.0x10^{-3} mol dm^{-3}

$10^2[BrO_3^-]$, mol dm^{-3}	$10^2[H^+]$, mol dm^{-3}	I, mol dm^{-3}	10^6k_1, s^{-1}	10^5k_2, dm^{3}mol^{-1}s^{-1}
80	7.5	1.0	130.20	16.27
80	7.5	1.2	118.86	14.86
80	7.5	1.8	109.10	13.64
80	7.5	2.00	106.29	13.29

Table 4:Ion dependence rate constant for $[CoHEDTAOH^{2}]^{-}$ - BrO_3^{-} reaction at $[BrO_3^{-}]$ = 0.8 mol dm^{-3}, T = 28 ^{0}C,
$[CoHEDTAOH_2]^{-}$ = 5.0X10^{-3} mol dm^{-3}, λ_{max} = 510 nm
I = 1 mol dm^{-3}($NaClO_4$), and $[H^{+}]$ = 0.075 mol dm^{-3}

$10^{2}[CH_3COO^{-}]$ mol dm^{-3}	$10^{5}k_1$ s^{-1}	$10^{5}k_2$ $dm^{6}mol^{-2}s^{-1}$
10.0	10.56	13.19
25.0	9.03	11.29
50.0	6.58	8.23

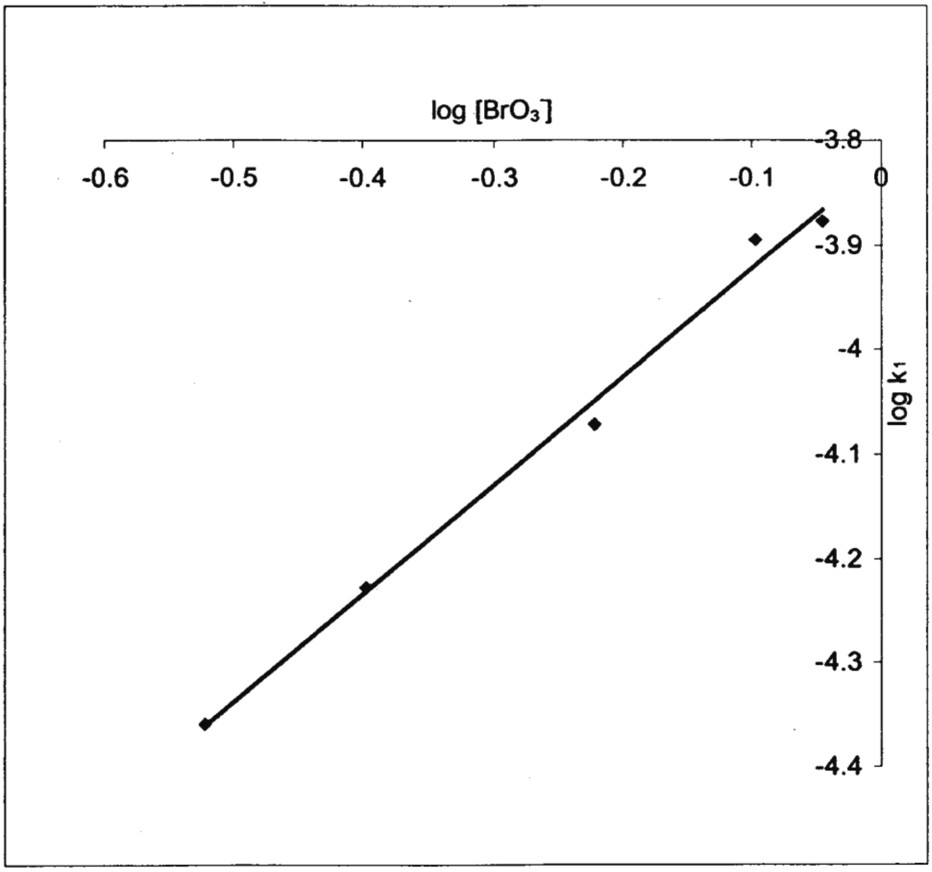

Fig. 1.Plot of log k_1 versus log $[BrO_3^{-}]$ for $[CoHEDTAOH_2]^{-}$ - BrO_3^{-} reaction

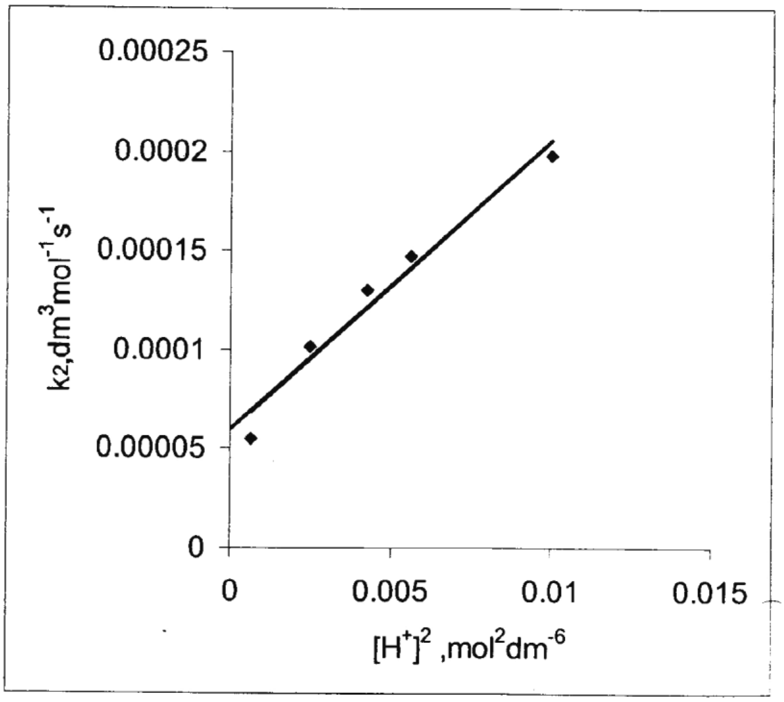

Fig.2. Plot of k_2 versus $[H^+]^2$ for $[CoHEDTAOH_2]^-$ - BrO_3^- reaction

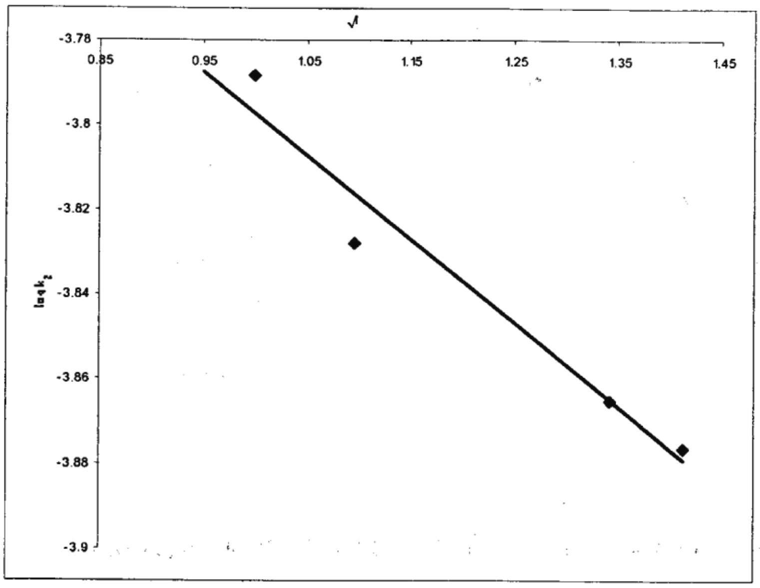

Fig.3. Plot of log k_2 versus $\sqrt{I}$ for $[CoHEDTAOH_2]^-$ - BrO_3^- reaction

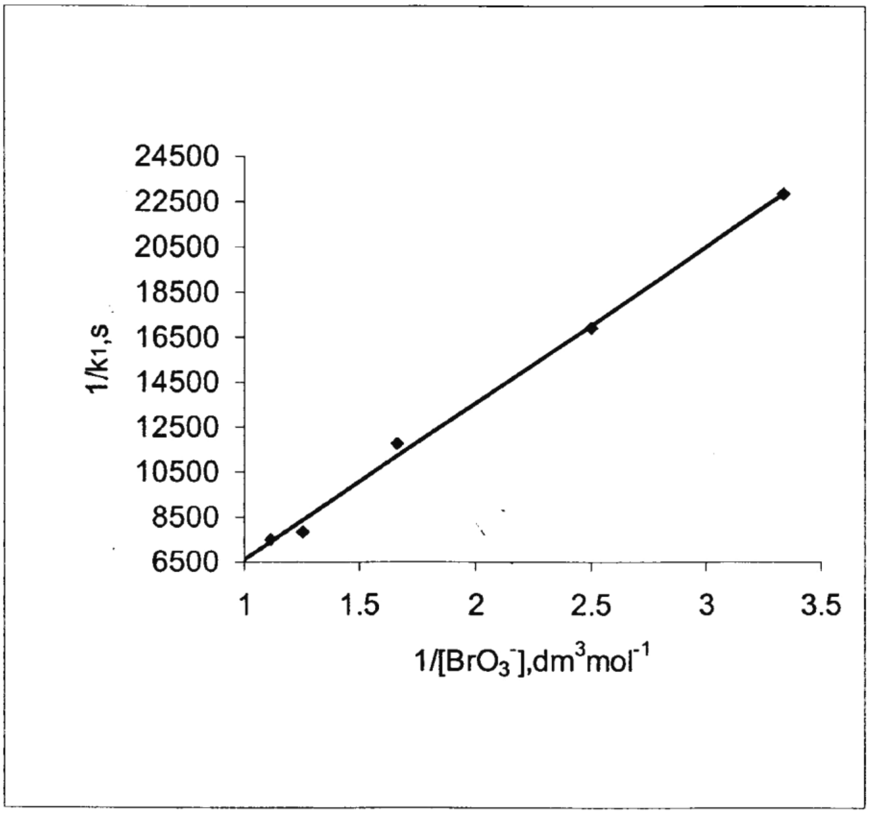

Fig. 4.Michaelis-Menten plot for $[CoHEDTAOH_2]^-$ - BrO_3^- reaction

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