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Tantalum(V) Catalysis of PerborateOxidation of Iodide Ion

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Abstract : Tantalum(V) catalyzesperborate oxidation of iodide ion in acidic solution, being 1.6 order with respect to the oxidant, first order in the catalyst, inhibited by H^+ and displays Michaelis-Menten kinetics on the reductant. In aqueous solution perborate generates hydrogen peroxide and the kinetic results reveal formation of oxodiperoxotantalum(V)-iodide ion complex.

Key words:Kinetics,mechanism,hydrogen peroxide.

Introduction

Sodium perborate is a cheap,non-toxic, large scale industrial chemical used primarily in detergents and as a mild oxidant. It is a convenient source of hydrogen peroxide¹, commercially, industrially and also in the laboratory. In acidic solution it oxidizes iodide ion and we have reported the kinetics and mechanism of the oxidation². Zirconium(IV)³, molybdenum(VI)⁴, tungsten(VI)⁵ and iron(III)⁶ form peroxo species with hydrogen peroxide and catalyze the oxidation. The catalyzed oxidations are independent of acidity of the medium, while the zirconium(IV) catalyzed oxidation is zero order the others are first order with respect to the oxidant. Here we report Tantalum(V) catalysis of the iodide ion oxidation, and the kinetic study reveals that the Tantalum(V) catalysis is acid inhibited; also the oxidation is apparent 1.6 order with respect to the oxidant.

Experimental

Sodium perborate, NaBO_{3.}4H₂O (Riedel) and KI (Merck), were used as received. Other chemicals were of analytical grade. Methanol AR was purified by the usual procedure. Solution of perborate was prepared afresh and standardized iodometrically. Kinetics of the oxidation in aqueous sulphuric acid at constant temperature was studied under pseudo-first order conditions with a very large excess of iodide ion. The oxidation was followed spectrophotometrically(UVIDEC-340, Jasco) at 460 nm. The pseudo first order rate constant was calculated from the slope of $\ln(A_a$ -A)*versus* time plot by the method of least squares; A and A_a are the absorbance at time t and at the completion of the reaction, respectively.

Results and Discussion

In acidic medium, perborate oxidation of iodide ion is catalyzed by Tantalum(V). At fixed excess $[I^-]_o$ and $[H^+]$ (with sulphuric acid), and fixed[Ta(V)], plots of $\ln(A_{\alpha} - A)$ versus time are linear to more than 80% of

the oxidation with correlation coefficient (r) not less than 0.9992 and standard error of estimate (sd) not larger than 0.046. However, the pseudo-first order rate constant in perborate (k*) increases with increasing initial concentration of perborate (Table 1), indicating the oxidation in the presence of Tantalum(V) is not strictly first order in the oxidant.Also, the oxidation is not second order with respect to perborate.The oxidation in the presence of Tantalum(IV) also gives similar results. Under identical conditions, the rates of oxidation in the presence of Tantalum(IV) are slightly lower than those in the presence of Tantalum(V).Since the oxidation proceeds in absence of catalysts also,the kinetics of the oxidation under identical conditions was studied in absence of catalysts.Theproduct of the specific oxidation rate in perborate and the initial concentration of perborate yields the initial rate of oxidation. The difference in the rates, in the presence and absence of catalysts,gives the rate of Tantalum(V) or Tantalum(IV) catalyzed oxidation:

 $rate_0 = (k^*-k)[perborate]_0$

where rate₀ is the initial rate of Tantalumcatalyzed oxidation and k is the pseudo-first order rate constant (in perborate) for the uncatalyzedoxidation, obtained from the linear plot of $1n(A_{\alpha}-A)$ versus time. The double logarithmic plot of the initial rate in perborate against the initial concentration of perborate is linear with slope of 1.6 and 1.7 for Ta(V) and Ta(IV), respectively (r= 0.995, 0.994, sd=0.070, 0.075 for Tantalum(V) and Tantalum(IV), respectively) pointing out the apparent order with respect to perborate as 1.6-1.7. This type of fractional order may not throw light on the rate law and mechanism. The 1.6-1.7 order is indicative of the following rate law and the kinetic data conform to the rate equation:

 $rate_0 = P[perborate]_0^2 / (Q[perborate]_0 + 1)$

where P and Q are constants. Plot of $[oxidant]_0^2/rate_0$ *versus* $[oxidant]_0$ is a straight line with positive y-intercept (Fig. 1: r = 0.984, 0.966, sd = 0.020, 0.028, slope=66.5, 64.0 s, intercept =0.118, 0.171 mol dm⁻³ s for Ta(V) and Ta(IV), respectively). The catalyzed oxidation is first order with respect to the catalysts. The initial rates in perborate increase with increasing concentration of the catalysts (Table 2). Plots of the initial rate of oxidation, k^{*} [perborate]₀ (sum of the initial rates of catalyzed and uncatalyzed oxidations), *versus* (i) [Ta(V)] and (ii) [Ta(IV)] are straight lines (r = 0.997, 0.998, sd = 5.24×10^{-7} , 5.04×10^{-7} , slope = 0.095,0.084 s⁻¹, intercept= 2.12×10^{-6} , 1.79×10^{-6} mol dm⁻³ s⁻¹ for Ta(V) and Ta(IV), respectively).

[Perborate mol dm ⁻³	$k^{-1} = l_0 \times 10^3 k^* \times 10^3 mol dm^{-3} s^{-1}$	$s^{-1}k \times 10^3 s^{-1}$		$rate_0 \times 1$	06	
Ta(V)	Ta(IV)	Ta(V)	Ta(IV)			
0.5	5.70	4.94	2.79	1.46	1.08	
1.0	8.65	7.55	2.51	6.14	5.04	
2.0	10.7	9.20	2.41	16.6	13.6	
3.0	11.6	10.5	2.51	27.2	23.9	
4.0	13.4	12.4	2.93	41.9	37.7	

 a [I⁻]₀=4.0×10⁻²mol dm⁻³,[H⁺] =9.88×10⁻² mol dm⁻³,35⁰C.*[Ta(V)]or[Ta(IV)]=1.0×10⁻⁴mol dm⁻³.

[catalyst]×10 ⁴		k [*] ×10 ³ s ⁻¹ mol o	k [*] [perborate] ₀ ×10 ⁶ dm ⁻³ s ⁻¹	
moram	Ta(V)	Ta(IV)	Ta(V)	Ta(IV)
0	2.51	2.51	2.51	2.51
0.2		3.21		3.21
0.5	6.61	5.57	6.61	5.57
0.8	9.25	8.04	9.25	8.04
1.5	16.7	14.6	16.7	14.6
2.0		18.6		18.6

Table 2. Rate dependence on [Ta(V)] or [Ta(IV)]^a.

^a[perborate]₀= 1.0×10^{-3} mol dm⁻³,[I⁻]₀ = 4.0×10^{-2} mol dm⁻³,[H⁺]= 9.88×10^{-2} mol dm⁻³,35^oC.





Figure 1.Linear variation of [perborate].²/rate₀ with [perborate]₀.



 $10^{2} [I^{-}]_{0} mol dm^{-3}$

Figure 2.Tantalum(V) catalysis: Hanes plot.

The rates of catalyzed oxidations increase with increasing $[\Gamma]_0$ (Table 3) and the dependence of rates on $[\Gamma]_0$ at 25,35 and 45^oC is of Michaelis-Menten type. The double reciprocal plots of the initial rates *versus* $[\Gamma]_0$ and statistically balanced Hanes plots($[\Gamma]_0/rate_0$ *versus* $[\Gamma]_0$) are linear with definite y-intercept (Fig.2. Hanes plots: r=Ta(V): 0.968, 0.987, 0.996; Ta(IV): 0.996, 0.992, 0.962, sd = Ta(V): 652, 524, 253;Ta(IV):697, 671, 1101, slope= Ta(V): 8.13×10⁴, 8.94×10⁴, 8.07×10⁴;Ta(IV): 22.04×10⁴, 14.01×10⁴, 10.73×10⁴ dm³ mol⁻¹ s, intercept = Ta(V): 6082, 3370,1232;Ta(IV): 6690, 3272, 812 s at 25, 35 and 45^oC, respectively).

[I ⁻] ₀ ×10 ² mol dm ⁻³		k*×1	$0^3 s^{-1}$	$k \times 10^3 s^{-1}$	rate ₀ mol di	×10 ⁶ m ⁻³ s ⁻¹
		Ta(V)	Ta(IV)		Ta(V)	Ta(IV)
25° C	1.0	2.03	1.73	0.56	1.47	1.17
	2.0	3.30		0.87	2.43	
	3.0	4.51	3.33	1.09	3.42	2.24
	4.0	6.11	3.77	1.35	4.76	2.42
	6.0		4.81	1.69		3.14
	8.0	8.33	5.42	2.10	6.23	3.32
	10.0		6.02	2.57		3.45
35 ⁰ C	1.0	3.26	2.79	0.88	2.38	1.91
	2.0	4.90		1.35	3.55	
	3.0	6.59	5.72	1.88	4.71	3.84
	4.0	8.65	7.55	2.51	6.14	5.04
	6.0	10.6	8.69	3.30	7.28	5.39
	8.0	12.2	9.71	4.26	7.94	5.45
	10.0	13.1	11.0	5.33	7.72	5.66
45°C	1.0	5.97	5.37	1.25	4.72	4.12
	2.0	9.63	7.80	2.42	6.94	5.38
	3.0	11.7	10.9	3.29	8.42	7.59
	4.0	14.0	13.0	4.24	9.71	8.77
	6.0	15.3	15.8	5.92	9.38	9.87
	8.0	17.6	17.0	7.50	10.1	9.48
	10.0	20.1	16.7	9.13	11.0	7.60

Table 3.Rate dependence on [I⁻]_{0.}

 a^{-3} [perborate]₀=1.0×10⁻³ mol dm⁻³, [H⁺]=9.88×10⁻² mol dm⁻³.*[catalyst]=1.0×10⁻⁴ mol dm⁻³

The tantalum(V) and tantalum(IV) catalyzed oxidations are inhibited by hydrogen ion of the medium (Table 4). Plots of (i) rate₀*versus* 1/[H⁺] and (ii) 1/rate₀*versus* [H⁺] are non-linear. On the other hand, there exists a linear relationship between the reciprocal of the initial rate of tantalumcatalyzed oxidation and [H⁺]² of the medium. Plot of 1/rate₀*versus*[H⁺]² is a straight line with a small y-intercept (r=Ta(V): 0.975, 0.998, 0.9996; Ta(IV): 0.997, 0.997, 0.992, sd= Ta(V): 7.16×10⁴, 1.43×10⁴, 3.47×10³; Ta(IV): 3.77×10⁴, 1.98×10⁴, 1.43×10⁴, slope= Ta(V): 1.49×10⁷, 1.18×10⁷, 5.70×10⁶; Ta(IV): 3.20×10⁷, 1.58×10⁷, 6.99×10⁶ dm⁹ mol⁻³ s, intercept= Ta(V): 9.82×10⁴, 4.38×10⁴, 4.49×10⁴; Ta(IV): 8.49×10⁴, 4.93×10⁴, 3.68×10⁴ dm³mol⁻¹s at 25,35 and 45⁰C, respectively). At high acidity, the ionic strength of the medium, varied with potassium nitrate, has little influence on the oxidation rates. But at low acidity the rate increases with increasing ionic strength(Table 5).

The rate of oxidation increases with decreasing dielectric constant of the medium, decreased by the addition of methanol(Table6). Under identical conditions, in the absence and in the presence of Tantalum(V) or Tantalum(IV), the rates of perborate and hydrogen peroxide oxidations are almost equal (Table7). Boric acid and borate fail to influence the rates oxidation by perborate as well as hydrogen peroxide(Table 8). Initial addition of vinyl monomer acrylonitrile to the reaction solution does not decrease the oxidation rate. Also, the

reaction mixture, when the oxidation is in progress, fails to initiate polymerization of the vinyl monomer. The reaction solution does not give ESR signal (Bruker X-band) and hence the reaction is not through one electron transfer.

Table 4.Rate dependence on acidity^a.

[H ⁺]×10 ² mol dm ⁻³		k *× 1	$10^3 \mathrm{s}^{-1}$	k× 10 ³ s ⁻¹	$rate_0 \times 10^6$ mol dm ⁻³ s ⁻¹		
		Ta(V) Ta(IV)			Ta(V)	Ta(IV)	
$25^{\circ} \mathrm{C}$	0.88		17.5	0.61		16.9	
	1.88		15.3	0.68		14.6	
	3.88		9.20	0.83		8.37	
	6.88		4.62	1.01		3.61	
	9.88	6.11	3.77	1.35	4.76	2.42	
	14.9	3.46	2.59	.40	2.06	1.19	
	19.9	3.06	2.34	1.58	1.51	0.76	
35°C	0.88	31.2	28.2	1.39	29.8	26.8	
	1.88		27.7	1.54		26.1	
	3.88	19.1	14.0	1.77	17.4	12.2	
	6.88	11.9	9.29	2.05	9.84	7.24	
	9.88	8.65	7.55	2.51	6.14	5.04	
	14.9	5.76	5.03	2.69	3.07	2.33	
	19.9	5.20	4.70	3.18	2.02	1.52	
45°C	0.88		44.7	2.81		41.9	
	1.88		34.8	3.12		31.7	
	3.88	23.5	26.1	3.33	20.1	22.7	
	6.88	17.4	16.5	3.88	13.5	12.6	
	9.88	14.0	13.0	4.24	9.71	8.77	
	14.9	7.95	9.60	4.86	3.09	4.74	
	19.9	9.43	9.07	5.72	3.71	3.35	

 $a^{\text{a}}[\text{perborate}]_{0}=1.0\times10^{-3}\text{mol dm}^{-3}, [\Gamma]_{0}=4.0\times10^{-2}\text{mol dm}^{-3}$. *[catalyst]=1.0×10⁻⁴mol dm⁻³.

Table 5.Influence of ionic strength(μ)^a.

$\mu \times 10^2$ mol dm ⁻³	[H ⁺]×10 ² mol dm ⁻³	$k^* \times 10^3 \mathrm{s}^{-1}$		$k^* \times 10^3 s^{-1}$	$rate_0 \times 10^6$ mol dm ⁻³ s ⁻¹		
		Ta(V)	Ta(IV)		Ta(V)	Ta(IV)	
0.56	0.88	31.2	28.2	1.39	29.8	26.8	
1.56	0.88	41.7	30.2	1.35	40.3	28.9	
2.56	0.88	43.6	32.8	1.50	42.1	31.3	
2.66	14.9	5.76	5.02	2.69	3.07	2.33	
3.66	14.9	5.86	4.96	2.68	3.18	2.28	
4.66	14.9	5.81	4.96	2.83	2.98	2.13	

 a^{a} [perborate]₀=1.0×10⁻³mol dm⁻³,[I⁻]₀=4.0×10⁻²mol dm⁻³,35⁰C. *[catalyst]=1.0×10⁻⁴mol dm⁻³.

Mechanism of catalysis:

In crystalline state perborate exists as a dimericperoxo salt with water of hydration, but in solution affords hydrogen peroxide[1]. In acidic medium, even in the presence of excess of boric $acid([H_3BO_3]_0 \text{ or } [NaBO_2]_0 = 1.0 \times 10^{-2} \text{mol } dm^{-3})$, calculation of the relative concentrations of perboric acid and perborate([(HO)_2BOOH]/[H_2 O_2] and [(HO)_3BOOH^-]/[H_2O_2]) using the equilibrium constants reported already^{1,7} shows that they are non-existent. Almost the same rates of oxidation by perborate and hydrogen peroxide, under identical conditions, supports the proposition that the reactive species of perborate is hydrogen peroxide. The tantalumcatalyzed oxidation is first order with respect to tantalum. Separate experiment showsthatperborateinacid solution oxidizes tantalum(IV) to tantalum(V).

D	MeOH- H ₂ O	[H ⁺]×10 ² mol dm ⁻³	$k^* \times 10^3 s^{-1}$		k×10 ³ s ⁻¹	rate _d mol d	o×10 ⁶ m ⁻³ s ⁻¹
	%(v/v)	morum	Ta(V)	Ta(IV)		Ta(V)	Ta(IV)
78.5	0-100	0.88	31.2	28.2	1.39	29.8	26.8
73.9	10-90	0.88	45.2	40.9	1.12	44.1	39.8
69.3	20-80	0.88		43.8	1.00		42.8
64.8	30-70	0.88		49.8	0.82		49.0
78.5	0-100	14.9	5.76	5.02	2.69	3.07	2.33
73.9	10-90	14.9	6.14	6.14	2.53	3.61	3.61
69.3	20-80	14.9	7.46	6.32	2.63	4.83	3.69
64.8	30-70	14.9	8.58	6.68	2.16	6.42	4.52

Table 6.Influence of dielectric constant(D) of the medium^a

^a[perborate]₀= 1.0×10^{-3} mol dm⁻³, [I⁻]₀= 4.0×10^{-2} mol dm⁻³, 35^{0} C. *[catalyst]= 1.0×10^{-4} mol dm⁻³.

Tantalum(IV) is also oxidized by hydrogen peroxide [8]. In acidic medium tantalum(IV) exists as TaO^{2+} and tantalum(V) as TaO_2^{+9} . The redox potentials of iodine, tantalum(V) (TaO_2^{+}) and hydrogen peroxide in acidic medium are 0.54, 1.0 and 1.77V, respectively. Tantalum(V) oxidizes iodide ion and one of the possible mechanisms of catalysis is oxidation of tantalum(IV) to tantalum(V) by hydrogen peroxide, followed by reduction of tantalum(V) to tantalum(IV) by iodide ion. But, operation of tantalum(IV)/tantalum(V) cycle is unlikely. This inference is from the complex dependence of the oxidation rate on [perborate]₀ and Michaelis-Menten kinetics on iodide ion.

Hydrogen peroxide complexes with tantalum(V). Oxoperoxotantalum(V) $(Ta(O)(O_2)^+)$ and oxodiperoxotantalum(V) $(Ta(O)(O_2)^-)$ are formed in acidic solution¹⁰⁻¹². Tetraperoxotantalum(V) $(Ta(O_2)_4^{-3})$ is formed only in alkaline medium.

The equilibrium constants for the formation of (i) oxoperoxotantalum(V) from TaO_2^+ and hydrogen peroxide and(ii) oxodiperoxotantalum(V) from oxoperoxotantalum(V) and hydrogen peroxide are 3.5×10^4 dm³ mol⁻¹ and 1.3 mol dm⁻³ at 25[°] C, respectively¹¹. These species are formed rapidly. One of the two peroxotantalum(V) species should be the reactive oxidizing species and reactivity of oxodiperoxotantalum(V) is greater than that of oxoperoxotantalum(V). If $TaO(O_2)^+$ were to be the reactive species, contrary to the experimental findings, the specific oxidation rate in perborate should either remain constant or decrease with increasing [perborate]₀. Proposal of $Ta(O)(O_2)^-$ as the reactive oxidizing species accounts for all the observed kinetic results. Scheme 1 is the possible mechanism of catalysis.

Scheme 1

$TaO_2^+ + H_2O_2$	K_1	$Ta(O)(O_2)^+ + H_2O$	
$Ta(O)(O_2)^+ + H_2O_2$		$Ta(O)(O_2)^{-}_2 + 2H^+$	
$Ta(O)(O_2)^2 + \Gamma$	K ₃	$[Ta(O)(O_2)_2 - I]^{2-}$	
$[Ta(O)(O_2)_2 - I]^{2-}$	<u> </u>	$Ta(O)_2(O_2)^- + IO^-$	
$Ta(O)_2(O_2) + H_2O_2$	\rightarrow	$Ta(O)(O_2)^{-}_2 + H_2O$	fast
$IO^{-} + I^{-} + 2H^{+}$	\rightarrow	$I_2 + H_2O$	fast

[oxic × 10 mol	lant] ₀ 3 dm ⁻³	$k^* \times 10^3 s^{-1}$						ra	ate _o × 10 ⁶ r	nol dm ^{.:}	³ s ⁻¹
		Ta	n(V)	Ta(IV)		k×10 ³ s ⁻¹ H ₂ O ₂ NaBO ₃		Ta(V)	Ta(V)		n
[H ⁺]×10 ² mol dm ⁻³		H_2O_2	NaBO ₃	H ₂ O ₂	NaBO ₃			H ₂ O ₂	NaBO ₃	H ₂ O ₂	NaBO ₃
2.0	9.88	11.0	10.7	9.29	9.20	2.24	2.41	17.6	16.6	14.1	13.6
1.0	9.88	8.65	8.65	7.04	7.55	2.21	2.51	6.44	6.14	4.83	5.04
1.0	14.9	5.93	5.76	5.30	5.02	2.72	2.69	3.21	3.07	2.58	2.33

Table 7.Oxidation by hydrogen peroxide^a.

^a[Γ]₀= 4.0×10⁻²mol dm⁻³,35^oC.^{*}[catalyst]=1.0×10⁻⁴ mol dm⁻³.

Table 8.Influence of borate and boric acid^a.

[NaBO ₂] ₀ ×10 ² mol dm ⁻³			k [*] ×1			1	rate ₀ × 10 ⁶	mol dm ⁻	³ s ⁻¹		
		Ta(V)		Ta(IV)		$K \times 10^3 \text{s}^{-1}$		Ta(V)		Ta(IV)	
[H ₃ BO ₃] ₀ ×10 ² mol dm ⁻³		H_2O_2	NaBO ₃	H_2O_2	NaBO ₃	H_2O_2N	NaBO3	H_2O_2	NaBO ₃	H ₂ O ₂	NaBO ₃
		8.65	8.65	7.04	7.55	2.21	2.51	6.44	6.14	4.83	5.04
1.0		9.03	9.06	7.13	7.63	2.20	2.37	6.93	6.69	4.93	5.26
	1.0	9.05	8.71	7.53	8.01	2.17	2.41	6.88	6.30	5.36	5.60
			8.35 ^b		8.11 ^b		2.46 ^b		5.89 ^b		5.65 ^b

^a[Γ]₀=4.0×10⁻²mol dm⁻³,[H⁺]=9.88×10⁻² mol dm⁻³,[oxidant]₀=1.0×10⁻³ mol dm⁻³,35⁰C. *[catalyst]=1.0×10⁻⁴ mol dm⁻³. ^b[acrylonitrile]= 1.0×10⁻² mol dm⁻³.

Complex formation between oxidiperoxotantalum(V) and iodide ion accounts for the Michaelis-Menten type dependence of the rate on the reductant concentration. $Ta(O)_2(O_2)$ anion has been identified from partly decomposed diperoxy species¹⁰. The implied rate law is

 $K_1K_2K_3k_4[Ta]_T[I][perborate]^2$

rate=
$$(K_3[I^-]+1)[H^+]^2 + K_1[H^+]^2[perborate] + K_1K_2[perborate]^2)$$

The kinetic study has been made at 0.1 mol dm⁻³ H⁺. Only to determine the rate dependence on [H⁺], the acidity of the medium was lowered to 0.0038 mol dm⁻³ H⁺. Since [perborate]₀«[H⁺] and K₁andK₂ are 3.5×10^4 dm³ mol⁻¹ and 1.3mol dm⁻³, respectively, excluding the results of the investigation of rate -[H⁺] relationship, K₁K₂ [perborate]² may be neglected in comparison with [H⁺] ²+ K₁[H⁺] ²[perborate]¹¹. The complex rate law simplifies to:

 $K_1K_2K_3k_4[Ta]_T[I^-][perborate]^2$

rate=
$$(K_3[\Gamma]+1)[H^+]^2(1 + K_1[perborate])$$

The reduced rate law is in conformity with (i) straight line plot of [perborate]²/ rate₀ versus [perborate]₀ with a positive y-intercept (ii) Hanes plot and (iii) first order dependence of rate on $[Ta]_T$. Explanation for the linear decrease of $\ln(A_{\alpha}-A)$ with reaction time is as follows. The formation constant of oxoperoxotantalum(V) (K₁) at 25^oC is 3.5×10^4 , dm³ mol⁻¹ and [perborate]₀ is 4×10^{-3} to 0.5×10^{-3} mol dm⁻³⁻¹¹. With rough approximation, K₁ [perborate] »1, the simplified rate law further reduces to

 $K_2K_3K_4[Ta]_T[\Gamma]$ [perborate]

rate=

 $(k_3[I]+1)[H^+]^2$

which is in agreement with the linear decrease of $\ln(A_{\alpha}-A)$ with time.Straight line graph of $1/rate_0$ versus $[H^+]^2$ with a small y-intercept is the direct implication of the complex rate equation.Incomplete oxidation of tantalum(IV) to tantalum(V) by hydrogen peroxide is a convincing explanation for the lower rate of tantalum(IV) catalyzed oxidation than tantalum(V). From the plots the kinetic constants are found as:

 $K_3 = 13.4 \text{ dm}^3 \text{ mol}^{-1}$ $k_4 = 1.52 \text{ s}^{-1} \text{ (at } 25^{\circ}\text{C)}$

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