CHAPTER III

EFFECT OF SULPHATE ION ON THE REACTION

BETWEEN THALLIUM(III) & URANIUM(IV):

ANALYSIS OF THE REPORTED DATA

The reaction between thallium(III) and uranium(iv) has been studied in detail by A.C. Harkness and J.Halpern in perchloric acid.[1] The main reactive species being free thallium (III) and uranium (IV) and the rate depends inversely on hydrogen ion due to activated complexes formed in the rate determining steps. The reaction was also found to be inhibited by chloride ion and catalysed by sulphate ion. Thallium(III) forms highly stable chlorocomplexes than thallium(I). The high stability of thallium(III) chlorocomplexes[2] reduces the redox potential of the couple. Tl(III)/Tl(I) considerably[3] thus making the chlorocomplexes of thallium(III) less reactive. Therefore the inhibition by added chloride ion may be due to the conversion of more reactive free thallium(III) into less reactive thallium(III) chloro-complexes.

The catalysis by the added sulphate was also explained due to the more reactive sulphato complexes of thallium(III). Since thallium(III) forms number of stable complexes with sulphate and bisulphate ions we found it necessary to know which of these is taking part in the mechanism. Therefore, in order to have a probable mechanism of thallium(III)-uranium(iv) reaction

in presence of added sulphate the reported data of A.C. Harkness and J. Halpern was analysed in this chapter.

In their study, the authors have found that the reaction remains second order throughout, including effect of chloride and sulphate ions. They have also used perchloric acid of concentration 2.83 mol dm^{-3} while studying the effect of sulphate with maximum sulphate concentration of 0.014 mol dm^{-3}. Under such conditions of high hydrogen ion concentration it was calculated and found from the reported equilibrium constants[4] that virutually all the sulphate will be in the bisulphate form. Therefore, in the following discussion we are considering only bisulphate complexes of thallium(III) and the concentration of sulphate is taken as that of bisulphate. The order with respect to bisulphate was determined from log (rate constant) vs log (concentration) plot and was found to be 0.6 (Table III(i)) (Figure III(i)).

The mechanism of thallium(III)-uranium(IV) reaction in presence of sulphate may be considered as consisting of two paths occurring simultaneously, the uncatalysed path and the catalysed path due to sulphate. Accordingly the rate will also be sum of the two rates. The rate law in absence of sulphate derived from the mechanism

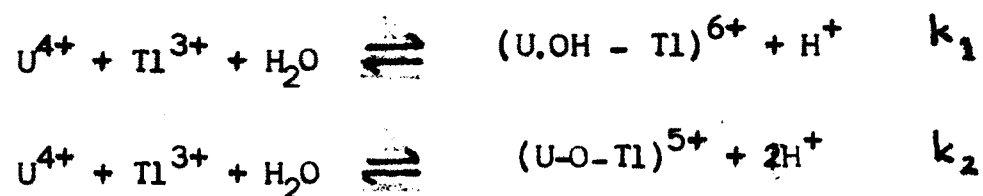Table III(i) : Order with respect to bisulphate ion

$[HSO_4^-]$ $mol\ dm^{-3}$	$k^* \times 10^2$ $mol^{-1}dm^3 s^{-1}$	$-log\ [HSO_4^-]$	$-\ log\ k$
0.0017	1.83	2.7695	1.7375
0.0035	2.65	2.4559	1.5767
0.0052	3.40	2.2839	1.4685
0.0070	3.83	2.1549	1.4168
0.0087	4.88	2.0605	1.3116
0.0113	5.62	1.9469	1.2502
0.0140	6.02	1.8538	1.2204

* $[U(IV)] = 0.0035\ mol\ dm^{-3}$, $[Tl(III)] = 0.009\ mol\ dm^{-3}$,

$[HClO_4] = 2.83\ mol\ dm^{-3}$, $I = 2.9$ at $25^{o}C$

Figure III (i) Order w.r.t. HSO_4^-

(Conditions as in Table III (i))
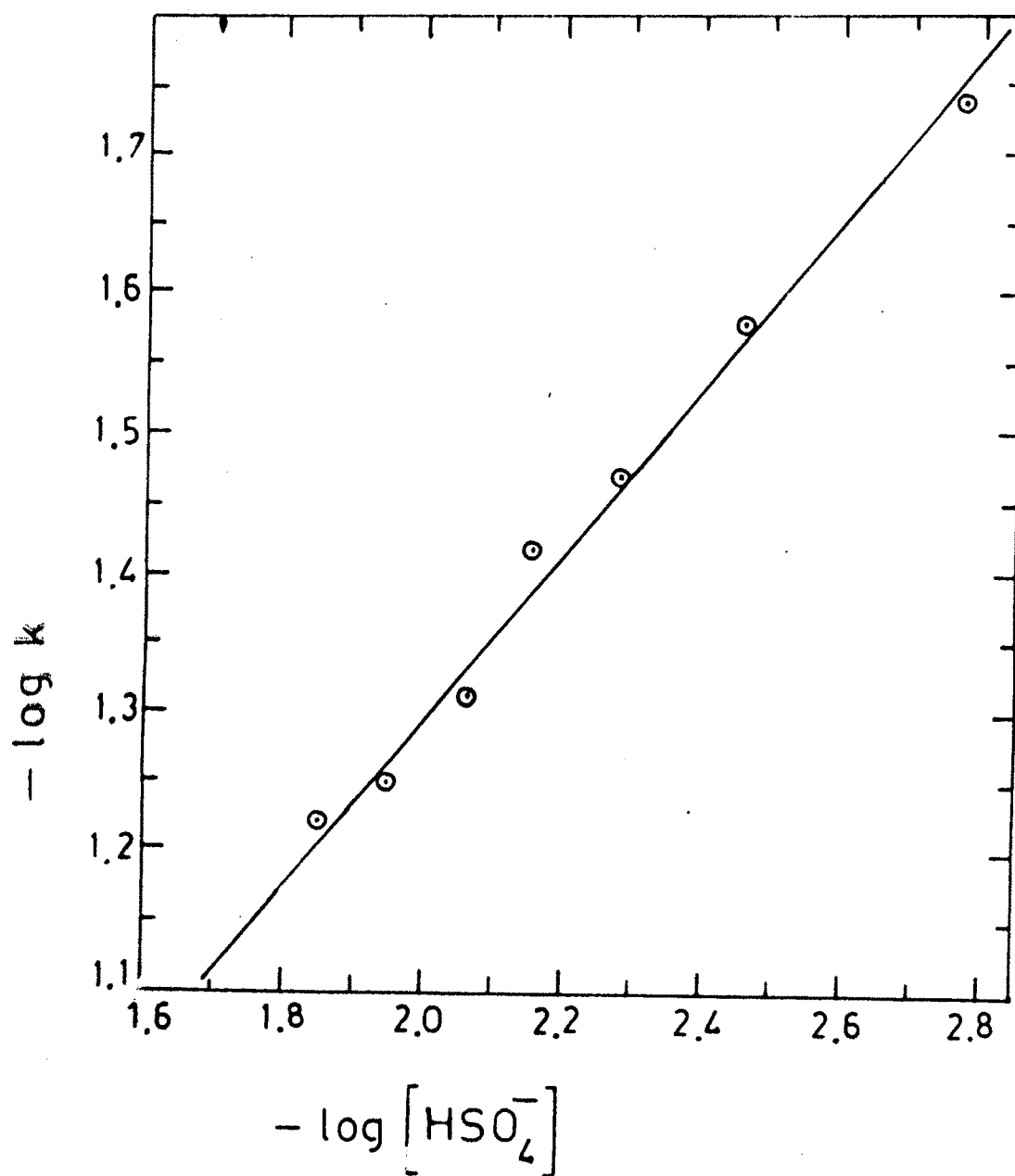
given by A.C. Harkness and J. Halpern as given in Scheme I is represented in equation 1.

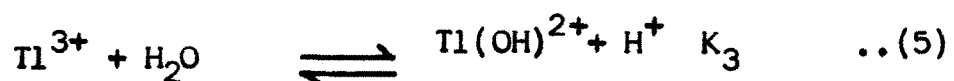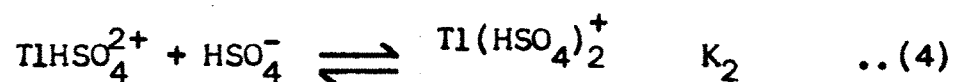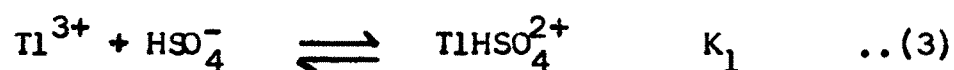$$U^{4+} + Tl^{3+} + H_2O \rightleftharpoons (U.OH - Tl)^{6+} + H^+ \qquad k_1$$

$$U^{4+} + Tl^{3+} + H_2O \rightleftharpoons (U-O-Tl)^{5+} + 2H^+ \qquad k_2$$

<u>Scheme-I</u>

$$\frac{-d[U(IV)]}{dt} = \frac{(k_1[H^+] + k_3)\ [U(IV)][Tl(III)]}{([H^+]+K_U)\ ([H^+] + K_{Tl})} \quad \ldots(1)$$

where K_U and K_{Tl} are the hydrolysis constants of uranium(IV) and thallium(III) respectively. The second order rate, constant denoted as k_{uncat}, is as given in equation (2).

$$k_{uncat} = \frac{k_1[H^+] + k_2}{([H^+]+K_U)([H^+]+K_{Tl})} \qquad \ldots \quad (2)$$

The acceleration of the reaction in presence of sulphate may be visualized due to the complex formation between bisulphate ion and the reactants thallium(III) and uranium(IV). Uranium(IV) forms sulphate complexes with very low stability constants[5] and under the present conditions the concentrations of such

complexes will be negligibly small. On the other hand thallium(III) form two complexes[6] with bisulphate as represented in equilibria 3 & 4 along with hydrolysis of thallium(III) in equation 5. The values of equilibrium constants

$$Tl^{3+} + HSO_4^- \rightleftharpoons TlHSO_4^{2+} \qquad K_1 \qquad ..(3)$$

$$TlHSO_4^{2+} + HSO_4^- \rightleftharpoons Tl(HSO_4)_2^+ \qquad K_2 \qquad ..(4)$$

$$Tl^{3+} + H_2O \rightleftharpoons Tl(OH)^{2+} + H^+ \quad K_3 \qquad ..(5)$$

are 16.98, 7.76[5] and 0.073[1] for the equilibria 3, 4 & 5 respectively. The concentrations of the thallium(III) species can be calculated from *equation 6*

$$[Tl(III)]_T = [Tl(III)]_f \left(1 + \beta_1 [HSO_4^-] + \beta_2 [HSO_4^-]^2 + \frac{K_3}{[H^+]} \right) ..(6)$$

where $[Tl(III)]_T$ and $[Tl(III)]_f$ are total and free thallium(III) concentrations β_1 β_2 are cumulative stability constants of equilibria 3 & 4 respectively. The calculated concentrations of different thallium(III) species along with the rate constants are given in table III(ii). The data of table III(ii) are also used to obtain plot of rate constant, $[TlHSO_4]^{2+}$ against $[HSO_4^-]$ (Figure III(ii)). From the data of table III(ii) and Figure III(ii) it

Table III(ii) : Effect of bisulphate ion on the second order rate constant and on the concentrations of different thallium(III) species.

$[HSO_4^-]$ mol dm^{-3}	$[Tl^{3+}]$x10^3 mol dm^{-3}	$[TlOH^{2+}]$x10^4 mol dm^{-3}	$[TlHSO_4^{2+}]$x10^4 mol dm^{-3}	$[Tl(HSO_4)_2^+]$x10^6 mol dm^{-3}	k^*x10^2 mol^{-1}dm^{3}s^{-1}
0.0017	8.53	2.20	2.46	3.25	1.83
0.0035	8.28	2.13	4.92	13.37	2.65
0.0052	8.05	2.07	7.10	28.13	3.40
0.0070	7.82	2.02	9.29	50.58	3.83
0.0087	7.60	1.96	11.28	75.93	4.88
0.0113	7.29	1.88	13.98	122.9	5.62
0.0140	6.98	1.80	16.59	180.6	6.02

* $[U(IV)]$ = 0.0035 mol dm^{-3}, $[Tl(III)]$ = 0.009 mol dm^{-3},

$[HClO_4]$ = 2.83 mol dm^{-3},   I = 2.9   at 25°C.

Figure III(ii) : Plot of TlHSO₄²⁺ , k against HSO₄⁻ (conditions as in Table III(ii))
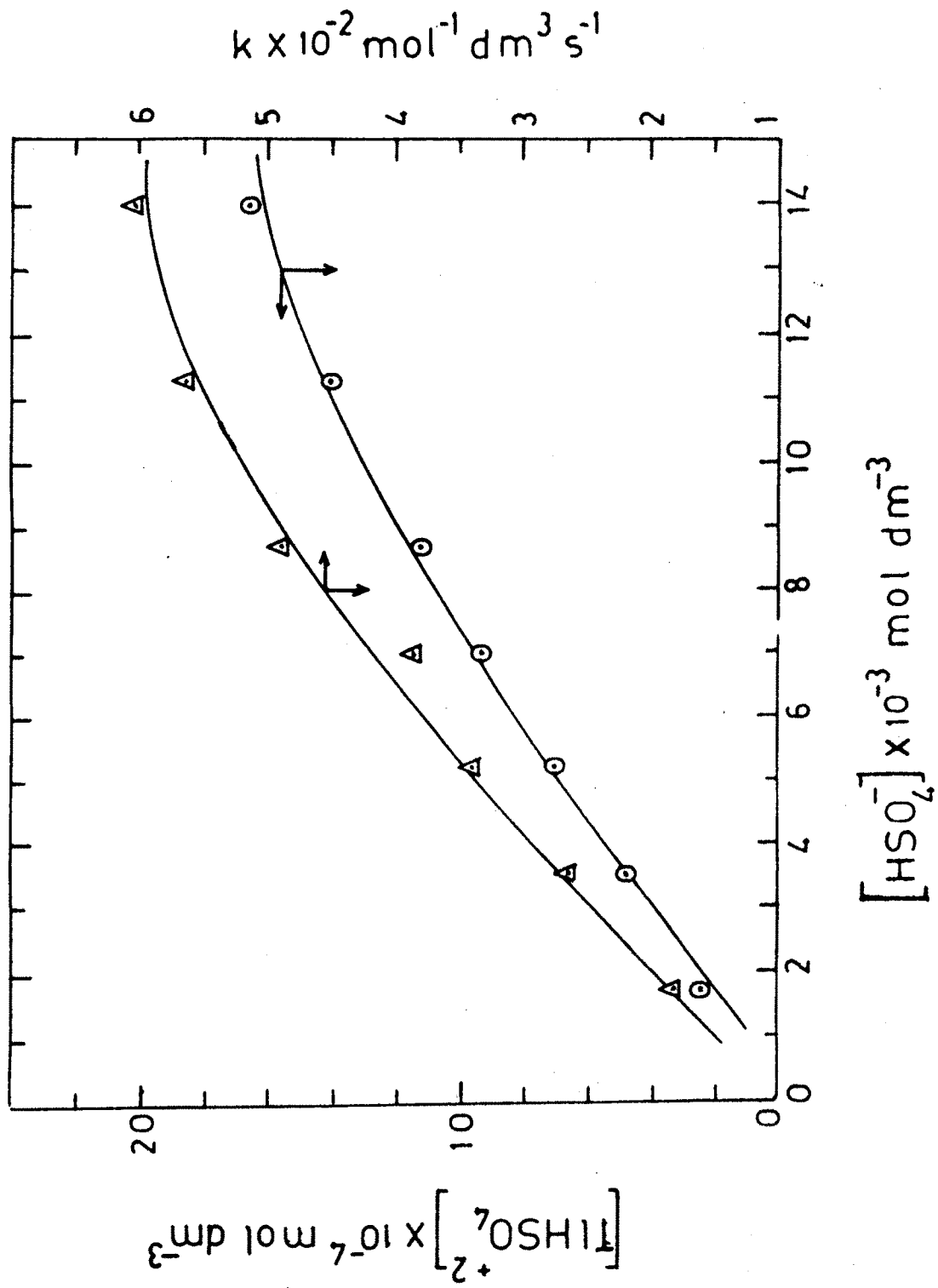
can be seen that there is a rough parallel between $[TlHSO_4^{2+}]$ and rate constant as bisulphate concentration is varied. Therefore monobisulphate complex of thallium (III) can be reasonably taken as main active species under the conditions of reaction.

The catalysed path of the reaction can now be represented as in Scheme II

$$Tl^{3+} + HSO_4^- \rightleftharpoons (TlHSO_4)^{2+} \qquad \beta_1$$

$$(TlHSO_4)^{2+} + U(IV) \longrightarrow TlHSO_4 + U(VI) \qquad k_3$$
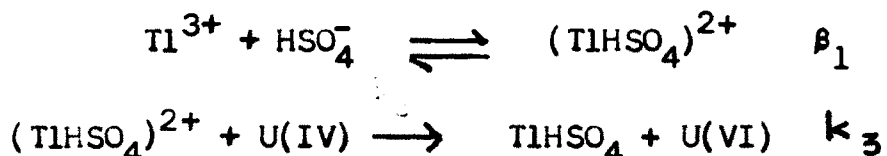
Scheme II

with the rate law as given in equation 7

$$- \frac{d[U(IV)]}{} = \frac{k_3\beta_1[HSO_4^-]\,[Tl(III)]\,[U(IV)]}{1+\beta_1[HSO_4^-] + \beta_2[HSO_4^-]^2 + K_3/[H^+]} \quad ..(7)$$

Therefore, the rate constant for the catalysed path will be :

$$k_{cat} = \frac{k_3\,\beta_1\,[HSO_4^-]}{1+\beta_1[HSO_4^-]+\beta_2[HSO_4^-]^2+K_3/[H^+]} \quad .. (8)$$

Since the total rate constants will be sum of uncatalysed and catalysed, we have

$$k_{Total} = k_{cat} + k_{uncat} \qquad \ldots (9)$$

or

$$k_{cat} = k_{Total} - k_{uncat} \qquad \ldots (10)$$

Equating the equations 8 & 10 we get

$$k_{cat} = k_{total} - k_{uncat} = \frac{k_3\beta_1[HSO_4^-]}{1+\beta_1[HSO_4^-]+\beta_2[HSO_4^-]^2+K_3/[H^+]} \quad \ldots(11)$$

In equation (11) if we assume that the sum of $\beta_2[HSO_4^-]^2$ and $K_3/[H^+]$ is negleted in comparison with other terms we can varify the above equation after rearranging it as given in equation (12) and

$$\frac{1}{k_{cat}} = \frac{1}{k_3\beta_1[HSO_4^-]} + \frac{1}{k_3} \qquad \ldots (12)$$

plotting $\dfrac{1}{k_{cat}}$ Vs $\dfrac{1}{[HSO_4^-]}$. The varification is shown in figure III(iii). The slope and intercept of the straight line are $\dfrac{1}{k_3\beta_1}$ and $\dfrac{1}{k_3}$ respectively. The value of k_3 thus obtained from slope as well as the intercept was found to be 0.0294 $mol^{-1}dm^3sec^{-1}$. Utilising the value of k_3 as 0.0294, k_{cat} values were back calculated and are tabulated in table III(iii). A reasonable aggrement between calculated and experimental values of k_{cat} justifies the proposed mechanism.

Table III(iii) : Data for varification of equation 12 with calculated k_{cal} values.

[HSO$_4^-$] mol dm^{-3}	k^*_{Total}×10^2 mol^{-1}dm^{3}s^{-1}	k_{cat}×10^2 mol dm^{3}s^{-1}	$(k_{cat})^{-1}$	[HSO$_4^-$]$^{-1}$	k_{cat} × 10^2 mol^{-1}dm^{3}s^{-1} (calculated)
0	0.98**	-	-	-	-
0.0017	1.83	0.85	588.23	1176.0	0.80
0.0035	2.65	1.67	285.71	598.8	1.61
0.0052	3.40	2.42	192.31	413.2	2.32
0.0070	3.83	2.85	142.86	350.9	3.04
0.0087	4.88	3.90	114.94	256.4	3.67
0.0113	5.62	4.64	88.49	215.5	4.57
0.0140	6.02	5.04	71.43	198.4	5.42

* [U(IV)] = 0.0035 mol dm^{-3}, [Tl(III)] = 0.009 mol dm^{-3},
[HClO$_4$] = 2.83 mol dm^{-3}, I = 2.9 at 25°C

** Taken as k_{uncat} to obtain k_{cat} values.

Figure III (iii) Plot of K_{cat} against (HSO_4^-)

(Conditions as in Table III (iii))
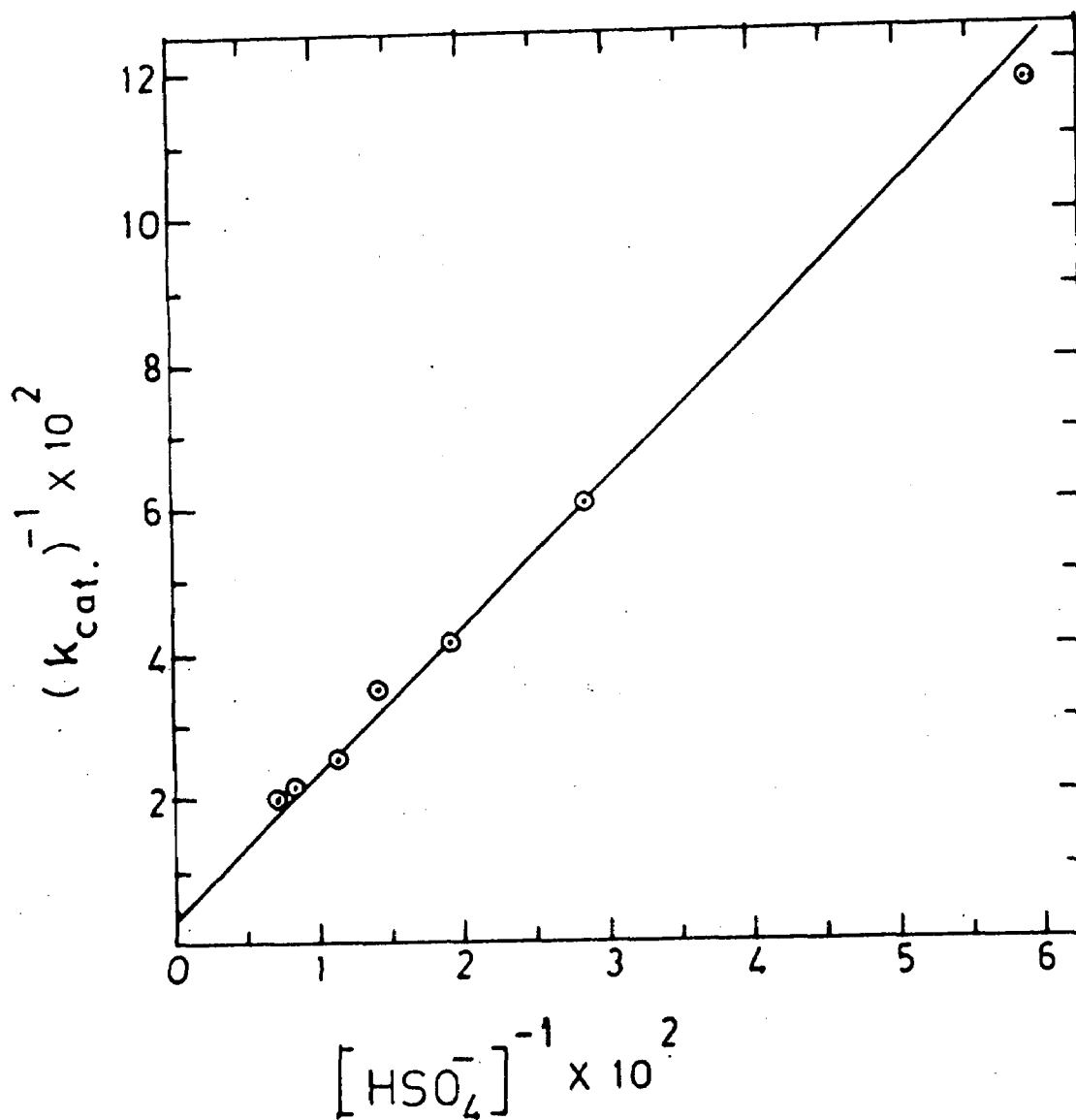
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