

Kinetics of Oxidation of Thiosemicarbazide by Iodamine-T, Iodine Monochloride & Iodine in Acid Medium

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Received 13 October 1986; rerevised 1 February 1988; accepted 7 March 1988

Kinetics of oxidation of thiosemicarbazide (TSC) by iodamine-T, iodine monochloride and iodine have been studied in perchloric acid medium. The reaction is first order in [oxidant] and fractional order in [TSC] for all these systems. With iodamine-T, the rate is inverse first order (at $[\text{HClO}_4] = 0.02\text{-}0.2 \text{ mol dm}^{-3}$) and inverse fractional order (at $[\text{HClO}_4] = 0.2\text{-}2.0 \text{ mol dm}^{-3}$) in $[\text{H}^+]$. However in the case of ICl and I_2 , the reaction is inverse fractional order in $[\text{H}^+]$ over the entire $[\text{H}^+]$ range. Increase in ionic strength of medium slightly decreases the rate in all the cases, whereas decrease in dielectric constant of the medium increases the rate in the case of ICl and I_2 oxidations. All oxidations studied follow Michaelis-Menten type mechanism. Rate laws in accordance with the proposed reaction pathways have been deduced. The rate constants predicted from the rate laws are in good agreement with the experimental values.

As a part of our broad program on the use of positive halogens as oxidants in the study of kinetics and mechanism of oxidation of organic substrates, specially thiosemicarbazide (TSC), we report herein the hitherto unreported kinetics and mechanism of oxidation of thiosemicarbazide by iodamine-T, iodine monochloride and iodine in aqueous perchloric acid medium.

Materials and Methods

Iodine and iodine monochloride used were of AR grade. Iodamine-T (N-iodo-potassium-*p*-toluenesulphonamide, RNIK where $\text{R} = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$) was prepared by the iodination of *p*-toluenesulphonamide (PTS) in 10% aq. potassium hydroxide solution and its purity checked by spectral data and estimating the amount of active iodine present in it iodometrically. Stock solutions ($\sim 0.1 \text{ mol dm}^{-3}$) of iodine (in aqueous potassium iodide solution), iodine monochloride (aqueous) and iodamine-T (in 0.1 mol dm^{-3} aqueous potassium hydroxide) were prepared, standardised by iodometric method and stored in dark coloured bottles. Thiosemicarbazide, TSC (E Merck) were recrystallised from hot water and its aqueous stock solution ($\sim 0.1 \text{ mol dm}^{-3}$) was used.

The ionic strength of the reaction medium was maintained at 0.5 mol dm^{-3} with sodium perchlorate (E Merck). All other materials and reagents employed were of accepted grades of purity.

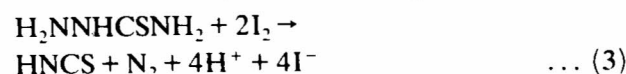
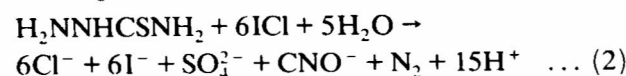
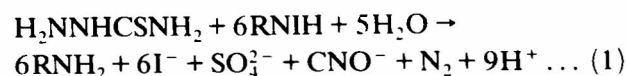
Kinetic measurements

The kinetic runs were carried out under pseudo-first order conditions using (5 to 40-fold excess) of

[TSC] over [oxidant]. The reactions were initiated by the quick addition of measured amounts of oxidant solution, thermally equilibrated at a desired temperature, to a mixture containing requisite amounts of TSC, perchloric acid and sodium perchlorate solutions and water, pre-equilibrated at the same temperature. The progress of the reactions were monitored for two half-lives by iodometric estimation of unreacted oxidant at regular intervals of time. The pseudo-first order rate constants computed by the method of least squares were reproducible within $\pm 3\%$.

Stoichiometry and product analysis

The stoichiometries of TSC-iodamine-T, TSC-ICl and TSC- I_2 reactions were determined by allowing the reactions to go to completion at different [TSC]/[oxidant] ratios and $[\text{H}^+]$ ($0.01\text{-}2.0 \text{ mol dm}^{-3}$). The presence of sulphate and cyanate in the reaction products in iodamine-T and ICl oxidations were detected by standard tests. Further the sulphate was quantitatively determined by gravimetric method (yield: $93 \pm 3\%$). *p*-Toluenesulphonamide (PTS), the reduced product of iodamine-T was detected by paper chromatography using benzyl alcohol saturated with water as solvent and 0.5% vanillin in 1% HCl in ether as spray reagent ($R_f = 0.91$). The observed stoichiometries can be represented by Eqs (1-3).



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Table 1—Effect of [Reactants] on the Rate of Oxidation of Thiosemicarbazide by Iodamine-T in Perchloric Acid Medium at 303K ($\mu = 0.5 \text{ mol dm}^{-3}$)

$10 [\text{HClO}_4]$ (mol dm^{-3})	$10^4 k_{\text{obs}}^a$ (s^{-1})	$10^3 [\text{Iodamine-T}]_0$ (mol dm^{-3})	$10^2 [\text{TSC}]_0$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$ at $10 [\text{HClO}_4] = (\text{mol dm}^{-3})$				
				0.05	0.1	0.2	0.5	1.0
0.2	21.6	0.5	2.0	7.5	—	2.1	—	—
0.3	12.0	1.0	2.0	7.5	—	2.2	—	—
0.5	7.5	2.0	2.0	7.5	—	2.1	—	—
0.75	4.5	4.0	2.0	7.4	—	2.1	—	—
1.0	3.2	1.0	0.5	4.1	2.0	1.7	0.92	0.71
1.5	2.5	1.0	1.0	5.2	2.6	1.9	1.1	0.78
2.0	2.0	1.0	2.0	7.5	3.2	2.1	1.2	0.80
3.0	1.4	1.0	4.0	9.2	3.8	2.2	1.3	0.85
5.0	1.2	1.0	6.0	12.3	—	2.6	—	—
10.0	0.8							
20.0	0.53							

^a $10^3 [\text{iodamine-T}]_0 = 1.0 \text{ mol dm}^{-3}$, $10^2 [\text{TSC}]_0 = 2.0 \text{ mol dm}^{-3}$.

Table 2—Pseudo-first Order Rate Constants for the Oxidation of Thiosemicarbazide (TSC) by Iodine Monochloride and Iodine in Perchloric Acid Medium at 303K

$[\mu = 0.5 \text{ mol dm}^{-3}]$			$10^4 k_{\text{obs}} (\text{s}^{-1})$	
$10^3 [\text{ICl or I}_2]$ (mol dm^{-3})	$10^2 [\text{TSC}]_0$ (mol dm^{-3})	$10 [\text{HClO}_4]$ (mol dm^{-3})	ICl	I ₂
0.5	2.0	1.0	2.6	3.8
0.75	2.0	1.0	2.7	—
1.0	2.0	1.0	2.6	3.8
2.0	2.0	1.0	2.6	3.9
3.0	2.0	1.0	—	4.1
4.0	2.0	1.0	2.6	—
1.0	0.5	1.0	1.9	—
1.0	0.8	1.0	2.0	3.4
1.0	1.0	1.0	2.1	3.5
1.0	4.0	1.0	3.1	4.2
1.0	6.0	1.0	3.5	4.6
1.0	2.0	0.1	15.4	—
1.0	2.0	0.2	8.9	9.3
1.0	2.0	0.5	4.1	5.4
1.0	2.0	1.5	1.8	3.3
1.0	2.0	2.0	1.5	2.7

^a $[\text{KI}] = 0.02 \text{ mol dm}^{-3}$.

Under the experimental conditions employed HNCS produced would be around $0.0005 \text{ mol dm}^{-3}$. It was observed that HNCS produced in reaction 3 did not get oxidised by I₂ at these concentrations.

Results

Kinetics of oxidations of TSC by iodamine-T, iodine monochloride and aqueous iodine were studied at several initial [TSC] and [oxidant] over a wide

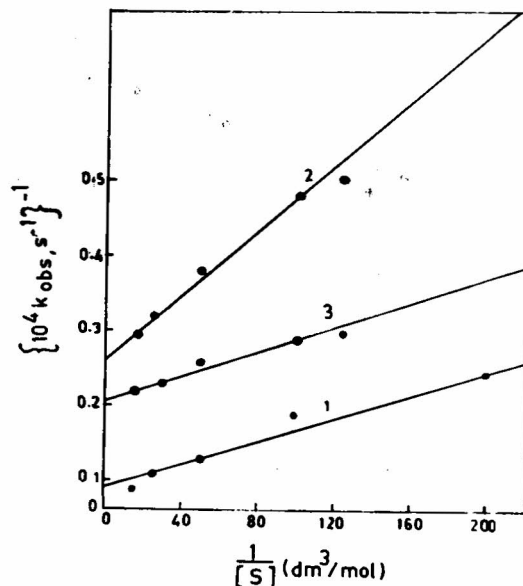


Fig. 1—Plot of $1/k_{\text{obs}}$ versus $1/[\text{S}]$: (1) Iodamine-T (2) ICl (3) I₂ ($10^3 [\text{oxidant}] = 1.0 \text{ mol dm}^{-3}$; $10^2 [\text{HClO}_4] (\text{mol dm}^{-3}) = 5.0$ (iodamine-T), 10.0 (ICl and I₂). $\mu = 0.5 \text{ mol dm}^{-3}$, $10^3 [\text{KI}] = 6.0 \text{ mol dm}^{-3}$ (with I₂), temp. = 303 K).

range of $[\text{HClO}_4]$ (0.01 - 2.0 mol dm^{-3}). At constant $[\text{HClO}_4]$ with several fold excess of TSC (~ 20 times), the plots of $\log [\text{oxidant}]_0/[\text{oxidant}]$ versus time were linear for at least two half-lives with all the oxidants and the pseudo-first order rate constants were unaffected by the changes in $[\text{oxidant}]_0$ (Tables 1 and 2), establishing first order kinetics in $[\text{oxidant}]$ in all the cases.

The orders in [TSC] and $[\text{H}^+]$ were evaluated from the log-log plots of rate constants (k_{obs}) versus [TSC] or $[\text{H}^+]$. At constant $[\text{oxidant}]$ and [TSC], the rates decreased with increase in $[\text{HClO}_4]$ with all the

Table 3—Kinetic Orders and Activation Parameters for the Oxidation of Thiosemicarbazide (TSC) by Iodamine-T, Iodine Monochloride and Iodine

Kinetic orders Observed in	Iodamine-T at $[H^+]$ (mol dm ⁻³)					ICl	I ₂
	0.05	0.1	0.2	0.5	1.0		
[oxidant]	1.0		1.0			1.0	1.0
[TSC]	0.44	0.3	0.2	0.14	0.1	0.25	0.14
[H ⁺]	-1.0		-0.6			-0.85	-0.53
log A	4.3 ± 0.1					11.3 ± 0.2	10.1 ± 0.3
E _a (kJ mol ⁻¹)	42.5 ± 2.1					86.2 ± 3.4	80.8 ± 2.8
ΔH [‡] (kJ mol ⁻¹)	40.2 ± 2.0					83.6 ± 5.0	78.3 ± 2.1
ΔS [‡] (JK ⁻¹)	-38.9 ± 1.9					-6.5 ± 0.3	-12.3 ± 0.3
ΔG [‡] (kJ mol ⁻¹)	50.9 ± 3.0					85.8 ± 5.0	81.7 ± 2.1

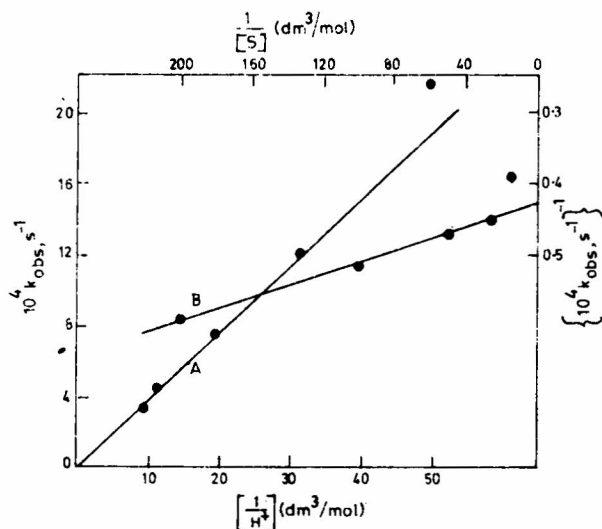


Fig. 2—(A) Plot of k_{obs} versus $1/[H^+]$; (10^3 [iodamine-T] = 1.0 mol dm⁻³, 10^2 [TSC] = 2.0 mol dm⁻³, temp = 303 K; μ = 0.5 mol dm⁻³). (B) Plot of $1/k_{obs}$ versus $1/[S]$ (10^3 [iodamine-T] = 1.0 mol dm⁻³; 10^2 [HClO₄] = 2.0 mol dm⁻³, temp = 303 K; μ = 0.5 mol dm⁻³).

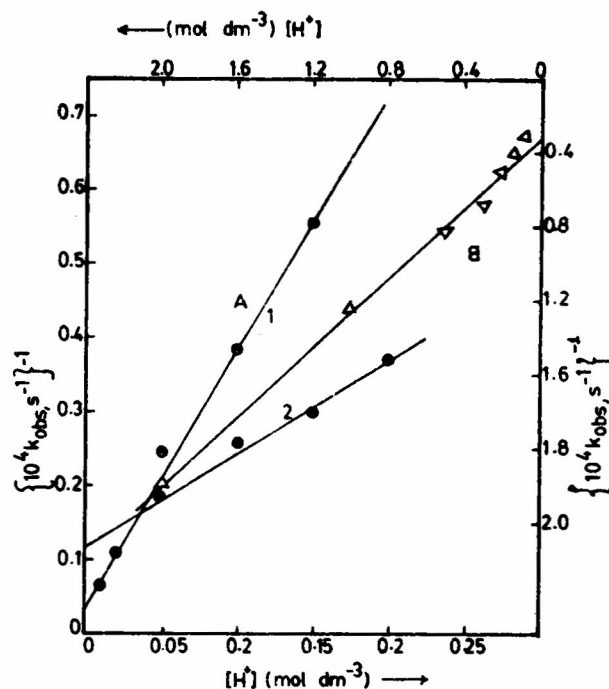


Fig. 3—(A) Plot of $1/k_{obs}$ versus $[H^+]$; (1) ICl (2) I₂, (10^3 [OX] = 1.0 mol dm⁻³; 10^2 [TSC] = 2.0 mol dm⁻³, μ = 0.5 mol dm⁻³; 10^3 [KI] = 6.0 mol dm⁻³ (with I₂); temp = 303K) (B) Plot of $1/k_{obs}$ versus $[H^+]$ (10^3 [iodamine-T] = 1.0 mol dm⁻³; 10^2 [TSC] = 2.0 mol dm⁻³; μ = 0.5 mol dm⁻³; temp = 303K)

oxidants and the plots of $\log k_{obs}$ versus $\log [H^+]$ were linear with varying fractional slopes (Table 3). With iodamine-T there were two ranges. The orders in $[H^+]$ were -1.0 and -0.6 in the $[HClO_4]$ ranges, 0.02-0.2 mol dm⁻³ and 0.2-2.0 mol dm⁻³, respectively. The rates increased with increase in [TSC] with all the oxidants with varying fractional orders (Table 3). Plots of k_{obs} versus $[S]$ were nonlinear in all the cases, attaining limiting values. Double reciprocal plots, $1/k_{obs}$ versus $1/[S]$ were linear (Fig. 1) with all the three oxidants, indicating the operation of Michaelis-Menten type mechanisms in all these systems. Plots of $1/k_{obs}$ versus $[H^+]$ were also linear (Fig. 3) for all the oxidants except with iodamine-T at low $[H^+]$. Under latter conditions, the plot of k_{obs} versus $1/[H^+]$ was linear passing through origin (Fig. 2).

Increase in ionic strength of the reaction medium slightly decreased the rate (Table 4). But decrease in dielectric constant of the medium (by changing the solvent composition with methanol) slightly increased the rate in the case of TSC-ICl and TSC-I₂ systems but it had no effect in the case of TSC-iodamine-T system. Addition of reaction products I⁻, Cl⁻ (with ICl) and PTS (with iodamine-T) had little or no effect on the rate for all these systems.

The rates of reactions were measured at different temperatures as functions of [TSC] and $[HClO_4]$ and the rate constants for the rate controlling steps were

Table 4—Effect of Added Reaction Products and Variation in Ionic Strength of the Medium on the Rates of Oxidations of Thiosemicarbazide by Iodamine-T, Iodine Monochloride and Iodine in Perchloric Acid Medium at 303K

μ^a (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹)		
	Iodamine-T	ICl	I ₂
0.07	8.2	—	—
0.10	8.1	—	—
0.12	—	3.5	5.4
0.20	7.8	3.1	5.1
0.50	7.5	2.6	3.8
0.80	—	2.3	—
1.00	7.5	1.9	2.4
$10^2 [\text{KI}]^b$ (mol dm ⁻³)			
0.0	—	2.6	—
0.1	—	2.7	—
0.5	—	—	3.0
0.6	—	2.7	—
1.0	—	2.6	3.5
2.0	—	2.6	3.8
5.0	—	—	5.2
10.0	—	—	6.7

^a 10^3 [oxidant] = 50 [TSC] = 10 [HClO₄] = 1.0 mol dm⁻³.

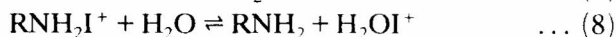
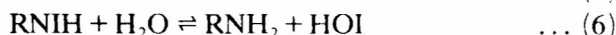
^b Same as (a) and [KI] = 0.02 mol dm⁻³.

^c Same as (a) and $\mu = 0.5$ mol dm⁻³.

calculated at different temperatures from the double reciprocal plots as described under discussion. The constants so computed were used to calculate the activation parameters from the Arrhenius plots, with all the oxidants (Table 3).

Discussion

Iodamine-T (RNIK, where R = CH₃C₆H₄SO₂) is analogous to chloramine-T¹⁻³ and bromamine-B⁴ in aqueous solutions and hence the following equilibria exist in its solutions.

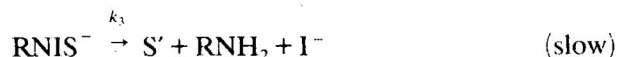
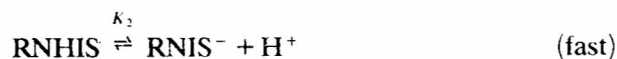
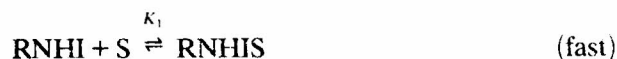


Mechanism of oxidations

(i) With iodamine-T at low [HClO₄]: In this case the order of the reaction was dependent on [H⁺]; it was -1 at low [HClO₄] (0.02 to 0.2 mol dm⁻³) and less than -1 at high [HClO₄] (0.2-2.0 mol dm⁻³).

At low [HClO₄] first order dependence in [iodamine-T], fractional order in [TSC] and inverse first order in [H⁺] and no effect on the rate on the addi-

tion of reaction product, PTS can be accounted for by the mechanism in Scheme 1.



where [RNHI] = [RNIK] and S': HNNCSNH₂

Scheme 1

Rate law (8) was deduced in accordance with Scheme 1.

$$\frac{d[\text{RNIK}]}{dt} = \frac{6k_3K_2K_1[\text{RNHI}]_{\text{tot}}[\text{S}]}{[\text{H}^+](1 + K_1[\text{S}]) + K_1K_2[\text{S}]} \quad \dots (9)$$

or

$$k_{\text{obs}} = \frac{6k_3K_2K_1[\text{S}]}{[\text{H}^+](1 + K_1[\text{S}]) + K_1K_2[\text{S}]} \quad \dots (10)$$

Assuming that [H⁺](1 + K₁[S]) ≫ K₁K₂[S] or K₂ is very small, rate law (10) would be reduced to Eq. (11).

$$k_{\text{obs}} = \frac{6k_3K_2K_1[\text{S}]}{[\text{H}^+](1 + K_1[\text{S}])} \quad \dots (11)$$

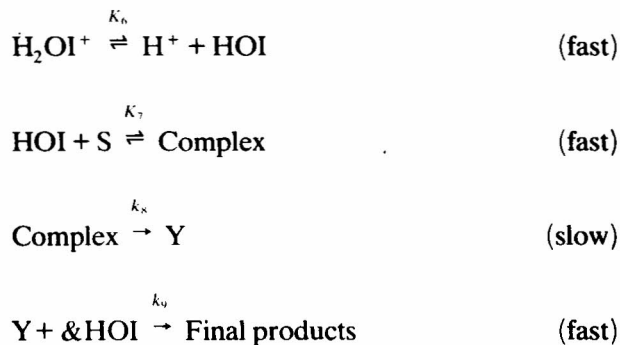
or

$$\frac{1}{k_{\text{obs}}} = \left\{ \frac{1}{6k_3K_2K_1[\text{S}]} + \frac{1}{6K_2k_3} \right\} [\text{H}^+] \quad \dots (12)$$

The experimental observation that the plots of 1/k_{obs} versus 1/[S] and k_{obs} versus 1/[H⁺] are linear with no and finite intercepts, respectively (Figs 1 and 2), is in conformity with rate laws (11) and (12). The ratio of intercept and slope of the latter plot gave K₁ (113.2 mol⁻¹ dm³). The latter and the product 6k₃K₁K₂ have been used to predict the rate constants for the variation of [H⁺]. At 10²[HClO₄] = 2.0, 3.0, 5.0, 7.5 and 10.0 mol dm⁻³, 10⁴k were calculated to be 20.1, 13.4, 8.1, 5.4 and 4.0 s⁻¹ respectively. The corresponding observed values are 21.6, 12.0, 7.5, 4.5 and 3.2 s⁻¹. Reasonable agreement between the predicted the experimental values supports the rate law and hence testifies to the validity of the reaction Scheme 1.

(ii) *With Iodamine-T (at high [HClO₄]), ICl and aqueous iodine*

At high [HClO₄] the rate of oxidation of TSC-iodamine-T system was first order in [iodamine-T], fractional order in [TSC] and inverse fractional order in [H⁺]. Contrary to expectations, the order in [TSC] decreased from 0.5 to 0.1 with increase in [HClO₄] from 0.05 to 1.0 mol dm⁻³ (Table 3). At high [HClO₄] most of the substrate would be present in the protonated form and if RNHI continues to be the reactive species even under these conditions, one would expect a pronounced dependence of rate on [TSC], as protonated species (SH⁺) are difficult to oxidise than the unprotonated form (S). The decrease in dependence of rate on [TSC] with increase in [H⁺] indicates that the reactive oxidising species at high [HClO₄] is different. H₂OI⁺ is likely to be the most probable species under these conditions. It is also evident from the identical kinetics observed with the other two oxidants, viz., ICl and I₂. Therefore, observed kinetics in iodamine-T oxidations at high [HClO₄] (0.1-2.0 mol dm⁻³), and in ICl and aqueous iodine oxidations of TSC may be explained by a common Michaelis-Menten type mechanism shown in Scheme 2.



Scheme 2

Based on Scheme 2 rate law (13) has been deduced.

$$\text{rate} = - \frac{d[\text{oxidant}]}{dt} = k_8[\text{complex}]$$

$$= \frac{6k_8K_7[\text{oxidant}]_r[\text{S}]}{1 + K_6[\text{H}^+] + K_7[\text{S}]} \quad \dots (13)$$

or

$$k_{\text{obs}} = \frac{6k_8K_7[\text{S}]}{1 + K_6[\text{H}^+] + K_7[\text{S}]} \quad \dots (14)$$

or

$$1/k_{\text{obs}} = \frac{1 + K_6[\text{H}^+]}{6k_8K_7[\text{S}]} + \frac{1}{6k_8} \quad \dots (15)$$

The plot of $1/k_{\text{obs}}$ versus $1/[\text{S}]$ was linear for all the three oxidants with slope = $1 + K_6[\text{H}^+]/6k_8K_7$ and intercept = $(1/6k_8)$. The substrate concentrations were varied at different [H⁺] and the slopes of double reciprocal plots (between k_{obs} and [S]) were plotted against [H⁺]. The plots were linear with slopes and intercepts equal to $K_6/6k_8K_7$ and $1/6k_8K_7$. The values of k_8 , K_7 and K_6 were calculated. The activation parameters were computed from k_8 values at different temperatures.

Equation (14) can also be rewritten as Eq. (16) to express the relationship between k_{obs} and [H⁺].

$$\frac{1}{k_{\text{obs}}} = \frac{K_6[\text{H}^+]}{6k_8K_7[\text{S}]} + \frac{1 + K_7[\text{S}]}{6k_8K_7[\text{S}]} \quad \dots (16)$$

Plots between $1/k_{\text{obs}}$ and [H⁺] were linear with intercepts for all the oxidants in conformity with rate law (16) (Fig. 3), thus suggesting the operation of an identical mechanism with all oxidants at high [HClO₄].

References

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