

Mechanism of positive iodine reactions: Kinetics of oxidation of semicarbazide by iodamine-T, iodine monochloride and iodine

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Abstract. Kinetics of oxidation of semicarbazide (SC) by iodamine-T (IAT), iodine monochloride and aqueous iodine has been studied in aqueous perchloric acid medium. The rate laws followed by the oxidation of SC were determined. The rates decreased slightly with increase in ionic strength of the medium in IAT and ICl oxidations, while the reverse trend was observed with I₂. Decrease in dielectric constant of the medium increased the rates with IAT and ICl, while it decreased the rate in I₂ oxidations. Addition of the reduced product, *p*-toluene-sulphonamide had no effect on the rate with IAT. Addition of I⁻ had slight negative and positive effects on the rates of oxidations with IAT and ICl, respectively, but the negative effect was considerable in I₂ oxidations. Mechanisms consistent with the observed rate laws have been proposed and discussed. Rate determining steps have been identified and their coefficients calculated. These constants were used to predict the rate constants from the deduced rate laws as [SC], [H⁺] and [I⁻] varied. Reasonable agreement between the calculated constants and experimental values provide support for the suggested mechanisms.

Keywords. Kinetics of oxidation; semicarbazide; iodamine-T; iodine monochloride; positive iodine.

1. Introduction

The present investigation is a part of our kinetic and mechanistic studies with positive halogen in general and positive iodine in particular (Gowda and Sherigara 1986; Gowda and Rao 1986, 1987; Gowda and Bhat 1987). We report herein the kinetics of oxidation of semicarbazide by iodamine-T, iodine monochloride and aqueous iodine in aqueous perchloric acid medium.

2. Materials and methods

Iodamine-T (RNIK, N-Iodo-N-potassio-*p*-toluenesulphonamide, where R = CH₃C₆H₄SO₂) was prepared by the iodination of *p*-toluene-sulphonamide

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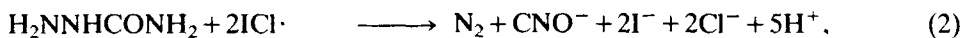
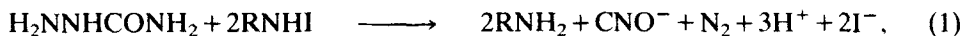
(PTS) in 10% aqueous potassium hydroxide solution (Pillai and Indrasenan 1980). The purity of iodamine-T was checked by recording its IR and NMR spectra and iodometric estimation of the amount of active iodine present in it. Analytical grade (E Merck) samples of iodine monochloride and iodine were used. Stock solutions ($\sim 0.1 \text{ mol dm}^{-3}$) of iodamine-T (in 0.1 mol dm^{-3} aqueous potassium hydroxide solution), iodine monochloride (aqueous) and iodine (in aqueous potassium iodide solution) were prepared, standardized by the iodometric method and stored in dark coloured bottles. Aqueous stock solutions ($\sim 0.1 \text{ mol dm}^{-3}$) of semicarbazide hydrochloride (SC, E Merck) were used. While varying $[\text{H}^+]$, the H^+ present in the substrate were taken into account and studies were made at constant $[\text{Cl}^-]$. The ionic strength of the medium was kept at 0.3 mol dm^{-3} using concentrated solution of sodium perchlorate (E Merck). All other reagents used were of analytical grade.

3. Kinetic measurements

The kinetic studies were made in glass-stoppered pyrex boiling tubes under pseudo-first-order conditions with $[\text{SC}] \gg [\text{oxidant}]$ (5 to 20-fold excess). The reactions were initiated by the rapid addition of requisite amounts of oxidant solution thermally equilibrated at a desired temperature, to a mixture containing known amounts of SC, perchloric acid and sodium perchlorate solutions, and water (to maintain total volume constant), pre-equilibrated at the same temperature. The progress of the reactions was monitored for at least two half-lives by iodometric estimation of unreacted oxidant at regular intervals of time. The pseudo-first-order rate constants (k_{obs}) were computed by the method of least squares and were reproducible within $\pm 4\%$.

4. Stoichiometry and product analysis

The stoichiometries of SC-iodamine-T/ICl and I_2 reactions were determined by allowing the reaction mixtures containing SC and oxidant in different ratios to proceed to completion at 303 K at different $[\text{H}^+]$. The presence of cyanate in the reaction mixtures was detected by standard tests (Feigl 1958; Van Nostrand 1976). *p*-Toluenesulphonamide (PTS), the reduction 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



5. Results

The kinetics of oxidation of semicarbazide (SC) by iodamine-T, iodine monochloride and aqueous iodine in aqueous perchloric acid medium were investigated at

several initial concentrations of the reactants and HClO_4 ($0.001\text{--}0.10 \text{ mol dm}^{-3}$) (tables 1–3). At constant $[\text{HClO}_4]$ with several-fold excess of the substrate (5 to 20 times), 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 $[\text{oxidant}]_0$, establishing first-order kinetics in $[\text{oxidant}]$.

The kinetic orders in $[\text{SC}]$ and $[\text{H}^+]$ were evaluated from the log-log plots of rate constants (k_{obs}) versus $[\text{SC}]$ or $[\text{H}^+]$. At constant $[\text{oxidant}]$ and $[\text{SC}]$, the rates increased with increase in $[\text{HClO}_4]$ with varying fractional order dependencies (table 3). At constant $[\text{oxidant}]$ and $[\text{HClO}_4]$, the rates increased with increase in $[\text{SC}]$ for ICl and I_2 oxidations (tables 1 and 3) and was independent of $[\text{SC}]$ with IAT.

The rates decreased slightly with increase in ionic strength of the medium in IAT and ICl oxidations, while the reverse trend was observed with I_2 (table 2). Decrease in dielectric constant of the medium by altering the solvent composition with methanol increased the rates with IAT and ICl, while it decreased the rate in I_2 oxidations. Addition of the reduced product of IAT, *p*-toluenesulphonamide, had no significant effect on the rate of oxidation with that oxidant. But the addition of I^- had slight negative and positive effects on the rates of IAT and ICl oxidations respectively and the effect was significant with I_2 .

Table 1. Pseudo-first-order rate constants (k_{obs}) for the oxidation of semicarbazide (SC) by iodamine-T, iodine monochloride and aqueous iodine in perchloric acid medium at 273 K ($\mu = 0.3 \text{ mol dm}^{-3}$).

[X] (mol dm^{-3})			$10^4 k_{\text{obs}}$ (s^{-1})		
$10^3 [\text{oxidant}]_0$	$10^2 [\text{SC}]_0$	$10^3 [\text{HClO}_4]$	IAT ^a	ICl ⁻	I_2
0.2	2.0	2.0	10.8	15.0	14.1
0.5	2.0	2.0	11.2	14.8	14.8
1.0	2.0	2.0	11.2	14.7	14.8
2.0	2.0	2.0	11.5	14.7	14.8
3.0	2.0	2.0	11.4	14.7	14.9
1.0	0.5	2.0	11.0	4.8	6.9
1.0	1.0	2.0	11.2	8.1	10.2
1.0	2.0	2.0	11.2	14.8	14.8
1.0	4.0	2.0	11.3	26.3	19.4
1.0	5.0	2.0	-	30.2	21.9
1.0	6.0	2.0	11.5	-	-
1.0	2.0	0.5	-	-	7.1
1.0	2.0	0.8	-	8.1	-
1.0	2.0	1.0	-	9.3	10.9
1.0	2.0	2.0	-	14.8	14.8
1.0	2.0	5.0	-	23.9	23.0
1.0	2.0	10.0	-	33.1	-
1.0	2.0	15.0	8.3	-	-
1.0	2.0	20.0	11.2	-	-
1.0	2.0	40.0	21.3	-	-
1.0	2.0	80.0	37.2	-	-
1.0	2.0	100.0	50.1	-	-

^a $10^3 [\text{H}^+] = 20.0 \text{ mol dm}^{-3}$ in IAT oxidations during $[\text{SC}]$ and $[\text{IAT}]$ variations; temperature 303 K.

Table 2. Effect of varying ionic strength or dielectric constant of the medium and [products] on the rates of oxidation of semicarbazide by iodamine-T, iodine monochloride and aqueous iodine at 273 K.

μ (mol dm ⁻³)	$10^4 k_{\text{obs}} (\text{s}^{-1})$		
	Iodamine-T ^a	ICl ^b	I ₂
0.053	12.1	15.9	12.4
0.1	11.8	15.1	12.9
0.3	11.2	14.8	14.8
0.5	10.9	14.2	15.2
% Methanol			
0	11.2	14.8	14.8
10	11.5	14.9	13.7
20	11.9	15.4	12.9
40	12.1	15.9	11.8
10^3 [PTS] (mol dm ⁻³)			
0	11.2	-	-
0.1	11.1	-	-
0.5	11.0	-	-
10.0	10.8	-	-
10 [KI] (mol dm ⁻³)			
0 (0.06)	11.2	14.8	-
1.0 (0.16)	10.9	14.9	28.0
5.0 (0.56)	10.5	15.4	19.8
10.0 (1.06)	10.1	15.9	14.8
- (2.06)	-	-	10.4

^a 10^3 [oxidant]₀ = $50[\text{H}^+] = 50[\text{SC}]_0 = 1.0 \text{ mol dm}^{-3}$,

$\mu = 0.3 \text{ mol dm}^{-3}$ (except during its variations);

^b Same as ^a but $10^3[\text{H}^+] = 2.0 \text{ mol dm}^{-3}$.

The rates of oxidations were measured at different temperatures and the activation parameters were computed from the Arrhenius plots (table 3).

6. Discussion

Iodamine-T (RNIK where R = CH₃C₆H₄SO₂) is analogous to chloramine-T (Bishop and Jennings 1958; Campbell and Johnson 1978; Gowda and Mahadevappa 1983), bromamine-T and bromamine-B (Hardy and Johnston 1973) in aqueous solutions. The following equilibria may exist (Pillai and Indrasenan 1980) in its acid solutions.

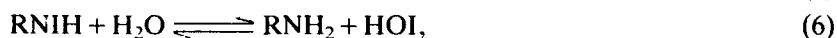
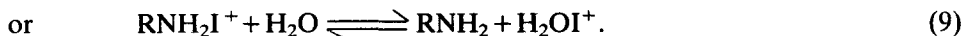
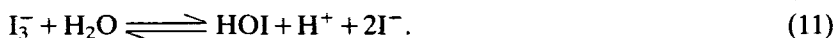
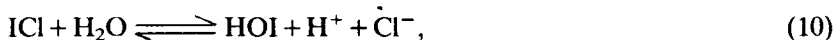


Table 3. Observed kinetic orders and activation parameters for the oxidation of semicarbazide by iodamine-T, iodine monochloride and iodine.

Observed orders in	IAT	ICl	I ₂
[oxidant]	1	1	1
[SC]	0	0.84	0.6
[H ⁺]	0.9	0.6	0.5
[I ⁻]	-	-	-0.35
<i>Parameters</i>			
log A	9.3	11.5	11.8
E _a (kJ mol ⁻¹)	71.3	70.8	76.5
ΔH [‡] (kJ mol ⁻¹)	68.8	68.4	74.0
ΔS [‡] (JK ⁻¹)	-16.0	-5.8	-4.4
ΔG [‡] (kJ mol ⁻¹)	73.6	69.6	75.2



Iodine monochloride may also undergo hydrolysis to give HOI,

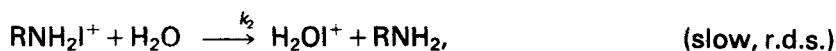


Therefore the probable reactive species in acid solutions of the oxidants are RNHI, HOI, RNH₂I⁺ and H₂OI⁺.

7. Mechanism of oxidation

7.1 With iodamine-T

The kinetics of reaction are first order in [IAT], nearly first order in [H⁺] and zero order in [S] and the observed negligible effects of the reaction products may be explained by scheme 1 and the rate law (12).



Scheme 1

$$-\frac{d[\text{IAT}]}{dt} = \frac{K_1 k_2 [\text{RNHI}]_0 [\text{H}^+] [\text{H}_2\text{O}]}{1 + K_1 [\text{H}^+]}, \quad (12)$$

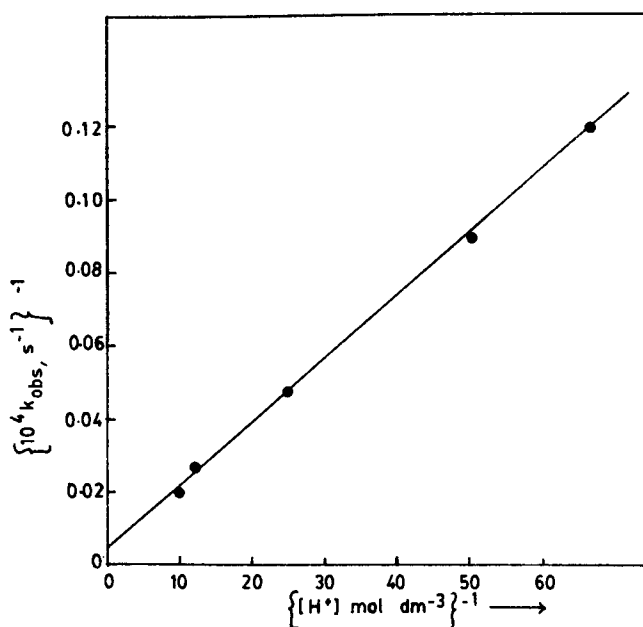


Figure 1. Plot of $1/k_{\text{obs}}$ versus $1/[H^+]$. $10^3[\text{IAT}] = 50[\text{SC}] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 303 K.

Applying the steady state hypothesis to the intermediate X, we have

$$[X] = \frac{k_3[\text{ICl}]_0[\text{S}][\text{H}^+]}{k_{-3} + k_4 + k_3[\text{S}][\text{H}^+]}, \quad (15)$$

where $[\text{ICl}] = [\text{ICl}]_0 - X$ and $[\text{S}]_0 \approx [\text{S}]$.

If one makes the assumption that k_4 is negligible as compared to the other terms in the denominator then (15) becomes

$$[X] = \frac{k_3[\text{ICl}]_0[\text{S}][\text{H}^+]}{k_{-3} + k_3[\text{S}][\text{H}^+]} = \frac{K_3[\text{ICl}]_0[\text{S}][\text{H}^+]}{1 + K_3[\text{S}][\text{H}^+]}, \quad (16)$$

where $K_3 = k_3/k_{-3}$.

The rate of the reaction is then given by

$$-\frac{d[\text{ICl}]}{dt} = \frac{K_3 k_4 [\text{ICl}]_0 [\text{S}][\text{H}^+]}{1 + K_3 [\text{S}][\text{H}^+]}. \quad (17)$$

The rate law (17) may also be written as

$$-\frac{1}{[\text{ICl}]} \frac{d[\text{ICl}]}{dt} = \frac{K_3 k_4 [\text{S}][\text{H}^+]}{1 + K_3 [\text{S}][\text{H}^+]}. \quad (18)$$

If we now make a further assumption that

$$-\frac{1}{[\text{ICl}]} \frac{d[\text{ICl}]}{dt} = -\frac{d \ln [\text{ICl}]}{dt} = k_{\text{obs}},$$

then the rate law given below (19) explains the kinetic results.

$$k_{\text{obs}} = \frac{K_3 k_4 [\text{S}][\text{H}^+]}{1 + K_3 [\text{S}][\text{H}^+]}, \quad (19)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_3 k_4 [\text{S}][\text{H}^+]} + \frac{1}{k_4}. \quad (20)$$

The plots of $1/k_{\text{obs}}$ versus $1/[\text{S}]$ and $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ were linear with finite intercepts on the ordinate (figure 2) in conformity with rate law (20). The two sets of K_3 and k_4 were calculated from the slopes and intercepts of the plots. The constants K_3 and k_4 computed from one plot were used to predict the rate constants as the other is varied and vice versa. The predicted values compared with the experimental rate constants are shown in table 4. Reasonable agreements between the two sets provide additional support to the suggested mechanism. Activation parameters were calculated from the Arrhenius plots by measuring rates at different temperatures.

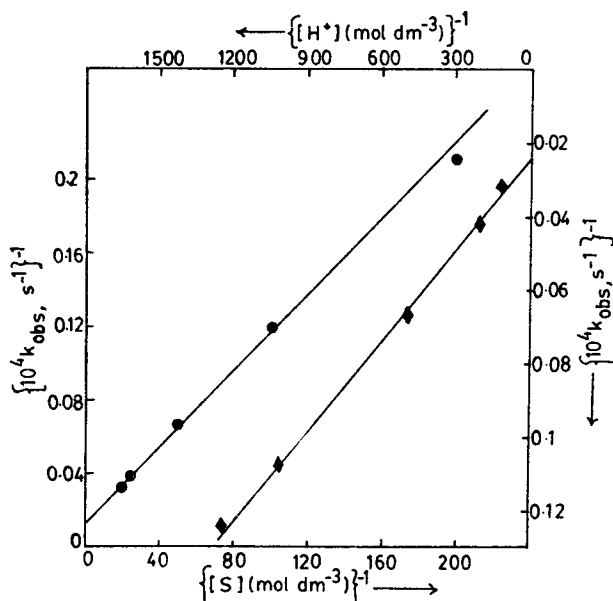


Figure 2. ● Plot of $1/k_{\text{obs}}$ versus $1/[\text{S}]$. $10^3[\text{ICl}] = 500[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 273 K. ◆ Plot of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$. $10^3[\text{ICl}] = 50[\text{SC}] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 273 K.

Table 4. Predicted and the experimental rate constants for the oxidation of semicarbazide by ICl and I₂.

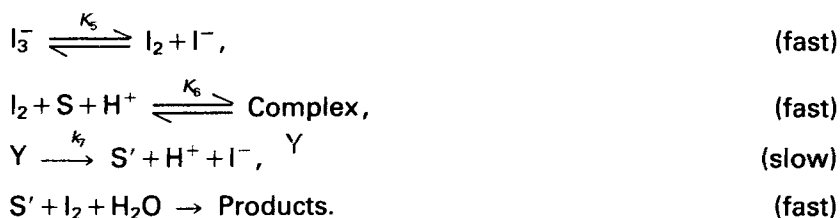
10 ² [S] (mol dm ⁻³)	10 ⁴ k (s ⁻¹)			
	ICl		I ₂	
	Cal ^a	Obs	Cal ^b	Obs
0.5	5.1	4.8	5.9	6.9
1.0	9.1	8.1	9.8	10.2
2.0	15.1	14.8	14.8	14.8
4.0	24.4	26.3	19.8	19.4
5.0	28.8	30.2	21.2	21.9
10 ³ [HClO ₄] (mol dm ⁻³)				
0.5	-	-	5.9	7.1
0.8	7.8	8.1	-	-
1.0	9.4	9.3	9.8	10.9
2.0	15.2	14.8	14.8	14.8
5.0	26.1	23.9	21.2	23.0
10.0	35.3	33.1	-	-
10[I ⁻] (mol dm ⁻³)				
0.16	-	-	25.6	28.0
0.56	-	-	19.3	19.1
1.06	-	-	14.8	14.8
2.06	-	-	10.1	10.4

^aFrom (20); ^bfrom (23) and (24).

The detailed mechanism of oxidation of semicarbazide by ICl is similar to that in scheme 2.

7.3 With iodine

The kinetics observed in iodine oxidations were similar to the ones with iodine monochloride (table 1), but the variation in ionic strength or solvent composition of the medium had different effects in ICl and I₂ oxidations (table 2). The rate decreased with increase in ionic strength of the medium and increased with decrease in dielectric constant of the medium in ICl oxidations. The trend was exactly the opposite with iodine, probably indicating the operation of a slightly different mechanism in I₂ oxidations. The observed results in this case can be explained through scheme 4.



Scheme 4

Based on scheme 4, rate law (21) has been deduced.

$$-\frac{d[\text{Iodine}]}{dt} = \frac{K_5 K_6 k_7 [\text{Iodine}]_i [\text{S}] [\text{H}^+]}{[\text{I}^-] + K_5 + K_5 K_6 [\text{S}] [\text{H}^+]} \quad (21)$$

or

$$k_{\text{obs}} = \frac{K_5 K_6 k_7 [\text{S}] [\text{H}^+]}{[\text{I}^-] + K_5 + K_5 K_6 [\text{S}] [\text{H}^+]} \quad (22)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{I}^-] + K_5}{K_5 K_6 k_7 [\text{S}] [\text{H}^+]} + \frac{1}{k_7} \quad (23)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{I}^-]}{K_5 K_6 k_7 [\text{S}] [\text{H}^+]} + \frac{1}{K_6 k_7 [\text{S}] [\text{H}^+]} + \frac{1}{k_7} \quad (24)$$

Plots of $1/k_{\text{obs}}$ versus $1/[\text{S}]$, $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ and $1/k_{\text{obs}}$ versus $[\text{I}^-]$ were linear in accord with rate laws (23) and (24), respectively (figures 3 and 4). Further the plots of k_{obs} versus $[\text{S}]$, k_{obs} versus $[\text{H}^+]$ and k_{obs} versus $1/[\text{I}^-]$ were nonlinear (figures 4 and 5). The constants K_6 and k_7 were calculated from the slope and the intercept of the plot of $1/k_{\text{obs}}$ versus $1/[\text{S}]$ and with the literature value of K_5 (Latimer 1966). ($K_5 = 1.28 \times 10^{-3} \text{ mol dm}^{-3}$; $K_6 = 2.05 \times 10^6$; $k_7 = 2.99 \times 10^{-3} \text{ s}^{-1}$).

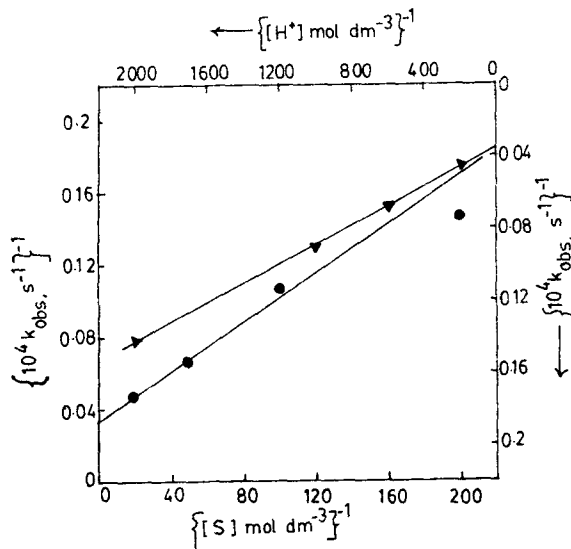


Figure 3. ● Plot of $1/k_{\text{obs}}$ versus $1/[\text{S}]$. $10^3[\text{I}_2] = 500[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 273 K. ▲ Plot of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$. $10^3[\text{I}_2] = 50[\text{SC}] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 273 K.

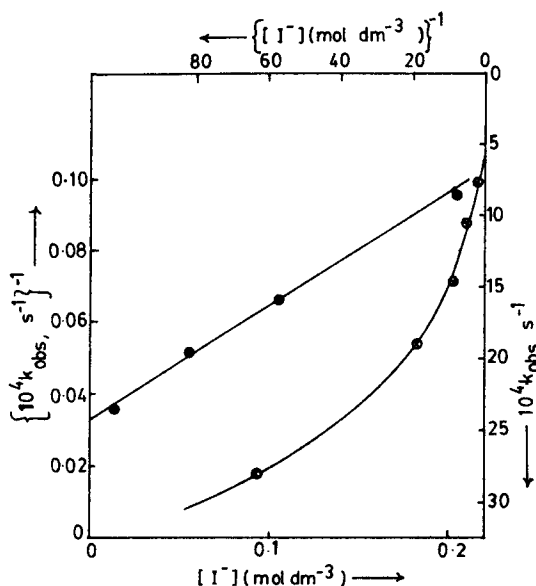


Figure 4. ● Plot of $1/k_{\text{obs}}$ versus $[I^-]$. $10^3[I_2] = 50[SC] = 500[HClO_4] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 273 K. ▲ Plot of k_{obs} versus $1/[I^-]$. $10^3[I_2] = 50[SC] = 500[HClO_4] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 273 K.

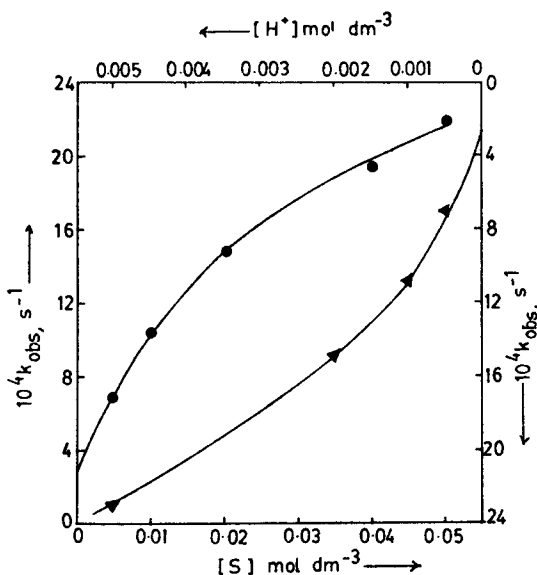


Figure 5. ● Plot of k_{obs} versus $[S]$. $10^3[I_2] = 500[HClO_4] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 273 K. ▲ Plot of k_{obs} versus $[H^+]$. $10^3[I_2] = 50[SC] = 1.0 \text{ mol dm}^{-3}$; $\mu = 0.3 \text{ mol dm}^{-3}$; temperature = 273 K.

These constants are used to predict the rate constants as $[H^+]$ and $[I^-]$ are varied and vice versa. The predicted values compared with the experimental rate constants are shown in table 4. As can be seen there is a reasonable agreement

between the two sets of values, probably justifying the proposed mechanism. Activation parameters were also computed as described earlier (table 3).

The detailed mechanism of oxidation of semicarbazide by I_2 is analogous to that in scheme 2.

The effect of solvent composition on the rates of reactions has been described in well-known monographs (Benson 1960; Amis 1966; Entelis and Tiger 1976; Laidler 1965; Zuman and Patel 1984). The rate constants for ion-dipolar molecule and dipolar molecule-dipolar molecule reactions in a medium of dielectric constant D are given by equations:

$$\log k_D = \log k_\infty + \frac{Ze\mu}{2.303 k_b Tr^2 D}, \quad (25)$$

$$\log k'_D = \log k'_\infty - \frac{2\mu_1\mu_2}{2.303 k_b Tr^3 D}, \quad (26)$$

where the k'_∞ s are rate constants in a medium of infinite dielectric constant, μ 's are the dipole moments of the respective dipolar molecules, Ze is the charge on the ion, r the radii and T the absolute temperature. Equation (25) predicts a linearity between $\log k_D$ and $1/D$ with a positive slope if Ze is positive and a negative slope if Ze is negative, while (26) predicts linearity between $\log k_D$ and $1/D$ with a negative slope. The positive dielectric effects observed in IAT and ICl oxidations conform to the positive ion-dipolar molecule interactions and the negative effect observed in I_2 oxidations is in conformity with dipolar molecule-dipolar molecule interactions. The proposed mechanisms are in accord with the Amis concept (Amis 1966).

Changes in rate with the variation in ionic strength of the medium may be explained by the Quinlan-Amis equation (Quinlan and Amis 1955).

Negative values of ΔS^\ddagger (table 3) may indicate that the transition states are more ordered than the states of the separated reactants.

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