

Kinetics of Oxidation of Metol by Iodine in different Acids Media

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Summary: The kinetics of oxidation of metol "N-methyl-p-aminophenol sulphate(1:2)" by iodine dissolved in ethanol have been studied in acetic, hydrochloric, sulphuric and perchloric acids media and the oxidation reaction was found to be bimolecular.

The rate of the reaction decreases with increase in the hydrogen ion concentration. The pseudo first order both with respect to metol and iodine has been found to be unity. The effects of concentration, acidity and temperature have been studied. The rate constants of the reaction (k), the pseudo first order rate constants (k₁), the activation parameters are also given and mechanism of the oxidation reaction has been suggested as well as.

Introduction

Kinetics of the oxidation of some organic compounds using iodine as a reagent have been studied in acidic medium. These studies include kinetics of the reaction of iodine with uric acid [1], acetophenones [2], ethyl alcohol [3], ally alcohol [4], acrolein [5], and benzaldehyde [6]. Most of the rates were either independent or inversely proportional to the hydrogen ion concentration.

Up to now there are no kinetics studies on the oxidation reaction of metol "N-methyl-p-aminophenol sulphate (1:2)" while there are many kinetics studies on the quinol [7-9] which is similar to metol in behaviour. In the present investigation, iodine is used for the oxidation of metol in different acids of different concentrations and different temperatures.

Results and Discussion

Stoichiometry

The analysis indicated the stoichiometry



Where H₂W = N-methyl-p-aminophenol

W = N-methyl-p-quinimine.

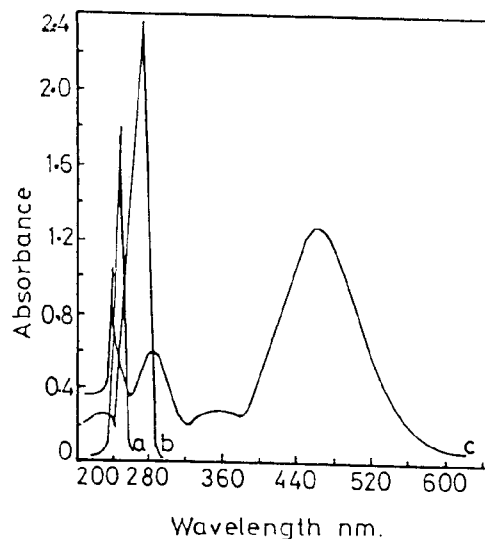


Fig. 1: Selection of the suitable wave length (at 2N HAc and 20°C) for a = 1.75×10^{-3} M KI, b = 0.25×10^{-3} M. Metol and C = 1.75×10^{-3} M I₂

Determination of the overall order

The measurements were carried out at equal variable concentrations of both the reactants, at $\lambda = 460$ nm, in 2N HAc and 27°C. On plotting $\log T_{1/2}$ ($T_{1/2}$ = half - life time which was obtained

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from time absorbance curves) against $\log a$ (a = initial concentration), a straight line of slope equal to $-(n-1)$ should be obtained according to the following equation:

$$\log T_{1/2} = \log \frac{2^{n-1} - 1}{k(n-1)} - (n-1) \log a \quad [12]$$

where n , the overall order, was found to be 2 (Fig. 2).

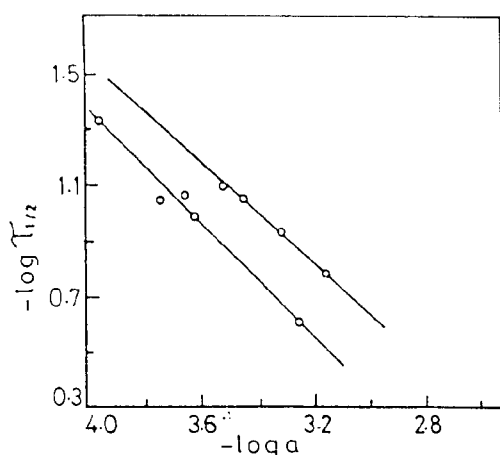


Fig. 2: Determination of the overall order of the reaction (at 2N HAc, 20°C and $\lambda = 460$ nm).

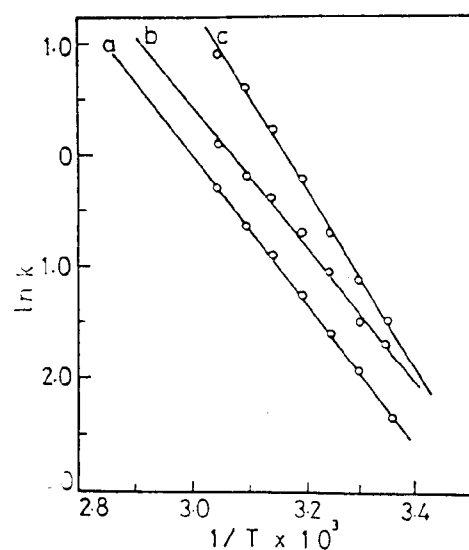


Fig. 3: Temperature effect on the rate reaction (at $\lambda = 460$ nm) for a = 2N HCl, b = 2N HClO₄ and c = 2N H₂SO₄.

Temperature effect

At different temperatures 25, 30, 35, 40, 45, 50 and 55°C; and 2N of each HCl, H₂SO₄, and HClO₄. The determination of the rate constants (at $\lambda = 460$ nm), one can calculate the activation energy (E) and Arrhenius factor (A) by plotting $\ln k$ against $1/T$ with a slope of $-E/R$ and intercept of $\ln A$ (Fig. 3). It was found that the activation energies are 13.84, 17.31, and 12.22 Kcal. mol⁻¹, and the Arrhenius factors are 1.32×10^9 , 9.89×10^{11} and 16.2×10^8 mol⁻¹ s⁻¹ for HCl, H₂SO₄ and HClO₄, respectively.

The other activation parameters were shown in Table 1. Table 2 shows the acidity effect on the reaction, using different acids of different con-

Table 1: The dependence of the rate constant k on the temperature for the (i) 2N HCl, (ii) 2N H₂SO₄ and (iii) 2N HClO₄ (at $\lambda = 460$ nm).

(i) T °C	k ₂ l.mol ⁻¹ .s ⁻¹	-ΔS [‡] cal. deg ⁻¹ .mol ⁻¹	ΔH [‡] Kcal. mol ⁻¹	ΔG [‡] Kcal. mol ⁻¹	-Ln K
25	0.095	16.80	13.83	18.84	31.81
30	0.146	16.84	13.80	18.90	31.39
35	0.205	16.87	13.82	19.01	31.06
40	0.286	16.90	13.84	19.13	30.76
45	0.406	16.93	13.84	19.22	30.41
50	0.51	16.96	13.91	19.39	30.21
55	0.735	16.99	13.89	19.46	29.86

$$A = 1.32 \times 10^9 \text{ l.mol}^{-1} \text{ s}^{-1}; E = 13.84 \text{ Kcal.mol}^{-1}$$

(ii) T °C	k ₂ λmol ⁻¹ .s ⁻¹	-ΔS [‡] cal. deg ⁻¹ .mol ⁻¹	ΔH [‡] Kcal. mol ⁻¹	ΔG [‡] Kcal. mol ⁻¹	-Ln K
25	0.218	3.65	17.26	19.42	32.80
30	0.323	3.68	17.3	19.53	32.44
35	0.50	3.71	17.33	19.60	32.02
40	0.80	3.74	17.32	19.65	31.59
45	1.256	3.78	17.31	19.70	31.17
50	1.86	3.81	17.33	19.76	30.79
55	2.50	3.84	17.41	19.91	30.55

$$A = 9.89 \times 10^{11} \text{ l.mol}^{-1} \text{ s}^{-1}; E = 17.31 \text{ Kcal.mol}^{-1}$$

(iii) T °C	k ₂ λmol ⁻¹ .s ⁻¹	-ΔS [‡] cal. deg ⁻¹ .mol ⁻¹	ΔH [‡] Kcal. mol ⁻¹	ΔG [‡] Kcal. mol ⁻¹	-Ln K
25	0.18	20.98	12.21	18.46	31.18
30	0.22	21.01	12.29	18.66	30.98
35	0.346	21.04	12.22	18.70	30.55
40	0.51	21.07	12.17	18.76	30.17
45	0.71	21.10	12.16	18.87	29.86
50	0.82	21.13	12.26	19.08	29.73
55	1.12	21.17	12.25	19.19	29.45

$$A = 1.62 \times 10^8 \text{ l.mol}^{-1} \text{ s}^{-1}; E = 12.22 \text{ Kcal. mol}^{-1}$$

Table 2: The dependence of the rate constant k on the acidity for the (i) HCl, (ii) H₂SO₄ and (iii) HClO₄ (at 20°C and 460 nm.)

(i) N	k ₂	-ΔS [‡]	ΔH [‡]	ΔG [‡]	-ln K [‡]
0.5	0.126	15.38	13.43	17.94	30.81
1.0	0.105	15.74	13.54	18.15	31.18
1.5	0.086	16.14	13.66	18.39	31.58
2.0	0.056	16.99	13.91	18.89	30.44
2.5	0.047	17.34	14.00	19.08	32.77

(ii) N	k ₂	-ΔS [‡]	ΔH [‡]	ΔG [‡]	-ln K [‡]
0.5	0.208	2.54	17.00	17.74	30.48
1.0	0.190	2.72	17.05	17.85	30.65
1.5	0.167	2.92	17.12	17.99	32.90
2.0	0.136	3.39	17.24	18.23	31.32
2.5	0.097	4.06	17.44	18.63	32.00

(iii) N	k ₂	-ΔS [‡]	ΔH [‡]	ΔG [‡]	-ln K [‡]
0.5	0.15	20.56	12.11	18.13	31.14
1.0	0.13	220.82	12.18	18.28	31.40
1.5	0.08	21.81	12.48	18.87	32.41
2.0	0.02	24.57	13.28	20.48	35.17

centrations. The activation parameters were also listed. Under the pseudo conditions, [Metol] > [I₂] (25 fold), the order of the reaction with respect to I₂ has been found to be unity. Also the order with respect to metol was found to be unity when [I₂] > [metol] (40 fold). Therefore, the overall order of the reaction is two. The calculated k₁ values of pseudo first order reaction has been given Table 3.

Table 3: Determination of the pseudo first order constant (k₁) both with respect to (i) Metol ([I₂]/[Metol]) = 40 (ii) Iodine ([Metol]/[I₂] = 25 (at 30°C, λ = 530 nm and 2N HAc)

(i) [I ₂] x 10 ⁴ M	k ₁ S ⁻¹	k ₁ /[I ₂]
2.42	1x10 ⁻⁴	0.41
3.63	1.15x10 ⁻⁴	0.32
4.84	1.19x10 ⁻⁴	0.25
6.05	2.78x10 ⁻⁴	0.46
7.27	3.33x10 ⁻⁴	0.46
8.48	0.833	982.3

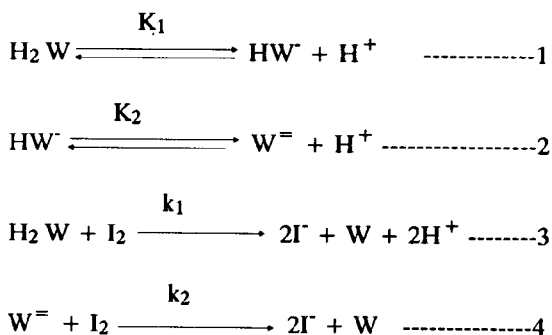
[Metol]/[I₂] = 25, λ = 530 nm, 2N HAc and T = 30°C

(ii) [Metol] x 10 ⁴ M	k ₁ S ⁻¹	k ₁ /[Metol]
0.200	7.88x10 ⁻⁵	3.94
0.263	8.89x10 ⁻⁵	3.38
0.325	7.5x10 ⁻⁵	2.31
0.388	7.78x10 ⁻⁵	2.00
0.463	6.25x10 ⁻⁵	1.35

[I₂]/[Metol] = 40, λ = 460 nm, 2N HAc and T = 30°C

Mechanism of Oxidation

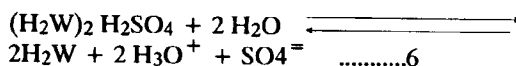
The metol in aqueous solution i.e. at high dielectric constant of medium dissociation (K₁ > K₂) and forms dianion. The reaction sequence is shown as :



On the basis of the above scheme, the final rate expression comes out to be

$$\frac{d[\text{W}]}{dt} = -\frac{d[\text{I}_2]}{dt} = (k_1 + \frac{k_2 K_1 K_2}{[\text{H}^+]^2} [\text{I}_2] [\text{H}_2\text{W}]) - 5$$

H W is largely unionized in acidic solutions



and hence at fixed acid concentration equation 5 becomes:

$$-\frac{d[\text{I}_2]}{dt} = k^* [\text{I}_2] [\text{H}_2\text{W}] \quad \text{....7}$$

$$\text{Where } k^* = (k_1 + \frac{k_2 K_1 K_2}{[\text{H}^+]^2}) \quad \text{..... 8}$$

The derived rate law [7] satisfies our observed first order kinetics both with respect to I₂ and H₂W. i.e. second order with respect to overall reaction.

Acidity effect

As shown from Fig. 4 and Table 2, there is small inverse proportionality to [H⁺], i.e. small slopes, except for HAc, numerous inverse dependence between [H⁺] and the rate constant, this may be due to complex formation (CH COOI) between

iodine and acetic acid. From equation 5, was found a linear dependence on $1/[H^+]^2$ with a non-zero intercept at $1/[H^+]^2 \rightarrow 0$ slight deviation and small slopes. This indicates that the reaction rate is independent of $[H^+]$ with a small component inhibited by H^+ ions (Fig. 4), showing there by that unionized metal $[H_2W]$ plays a dominant role in the rate determining step.

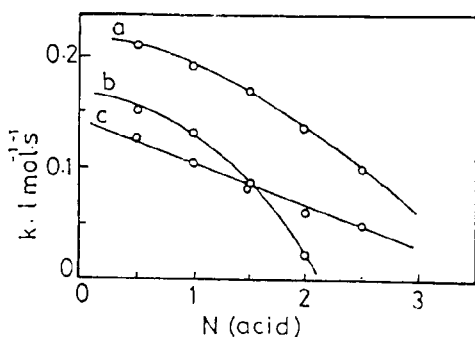


Fig. 4: Acidity effect on the rate reaction (at 20°C and $\lambda = 460$ nm) for a = H_2SO_4 , b = $HClO_4$ and c = HCl .

Activation parameter

The activation parameters have been evaluated from $\ln k$ versus $1/T$ plots. The observed negative entropy of activation (ΔS^\ddagger) is due to solvation of the product which becomes more polar than the reactants leading to decrease in entropy. Use of the value of ΔS^\ddagger has been suggested by Long [13] as a criterion for the role of water in hydrolysis. Small value of ΔS^\ddagger about zero are expected for unimolecular reactions. Larger negative values, generally -15 to -30 eu are expected for bimolecular reactions. Subsequently, our reactions indicate the bimolecular mechanism (Tables 1 and 2). The summarized results in Table 3 show that the reaction rate constant (k_1) decreases gradually with a decrease in the concentration of iodine. The ratios $k_1/[H_2W]$ are uniform confirming the pseudo first-order dependence of the rate on $[metol]$. Fig. 5 shows the pseudo first order with respect to each iodine and metol.

Experimental

The chemicals employed were of highest purity available. Metol (Fluka), potassium iodide

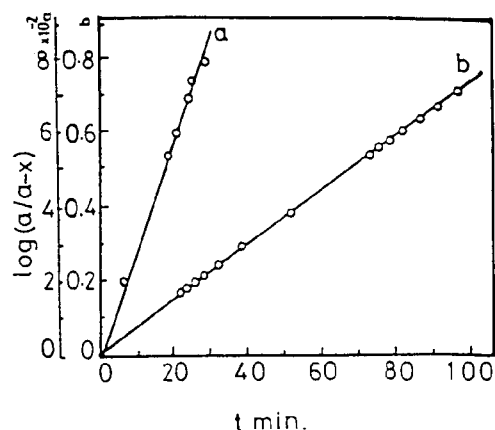


Fig. 5: Determination of the pseudo first order both with respect to:

$$a/Metol [I_2] / [Metol] = 40$$

$$b/Iodine ([Metol]/[I_2]) = 25$$

(at 30°C. $\lambda = 530$ nm and 2N HAc).

(BDH) and iodine (BDH). Bidistilled water was used. Stock solution 0.0134M of metol was prepared and standardized potentiometrically [10]. Stock solution 0.015 M of iodine was prepared by dissolving the appropriate weight in ethanol and standardized by recommended procedure [11]. The $(2.24 - 13.44) \times 10^{-4}$ M solutions of all the above stock solutions were prepared accurately. The absorption spectra of 1.75×10^{-3} M of each iodine and potassium iodide and 0.25×10^{-3} M of metol were scanned in 2N acetic acid medium (Fig. 1). At different temperatures and variable concentrations of different acids, the decrease in iodine absorbances were measured at $\lambda = 460$ nm and at $\lambda = 530$ nm for the colour formation of N-methyl-p-quinoline, at intervals of time using PYE UNICAM SP 1750 recording spectrophotometer.

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