

Kinetic Study on the Photo-oxidation of Oxalate Ion by Iodine

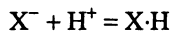
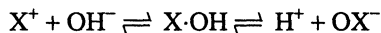
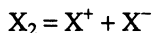
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The kinetics of photo-oxidation of oxalate ion in acidic medium by aquo iodine has been investigated at 297 K. The reaction follows identical kinetics and obeys the rate law, rate = $k[(\text{COO})_2^{2-}][\text{I}_2][\text{H}^+]^x$ where x is less than unity. Addition of Cl^- in the form of HCl has no effect on the reaction rate, whereas the reaction product, Γ has appreciable influence on the reaction rate. Variation of ionic strength and dielectric constant of the medium and the rate of reaction have been studied.

Key Words: Kinetic, Photo-oxidation, Oxalate ion, Iodine.

INTRODUCTION

The chemistry of halides has attracted the attention of many investigators on account of their diverse behaviour. They are the source of halonium cations and hypohalite species. When a halogen is hydrolysed the molecule breaks up into positive and negative ions. Hydroxyl and hydrogen ions react with halonium cations and halide ions; they form hypohalous acid and halo acid¹ respectively.



Hypohalous acid dissociates into X^+ and OH^- and H^+ and OX^- . Hypohalous acids are treated as good oxidants. They are very sensitive in presence of light radiation, hence they are photochemically^{2,3} reactive reagents.

The reaction between iodine and oxalic acid has been found to be photosensitive. The latest work on photochemical study of the metal complex and iodide ion has aroused our interest to carry out a detailed study on the kinetics of photochemical reaction of oxalate ion and aquo iodine⁴.

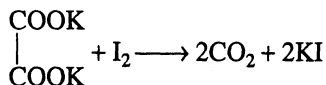
EXPERIMENTAL

Iodine, potassium oxalate and other chemicals used were of BDH/AR/SM/GR grade. Doubly distilled water was used to prepare all solutions. The requisite amounts of potassium oxalate and iodine solutions were taken in the reaction

flask at desired temperature. Requisite amount of iodine was mixed with potassium oxalate solution and the mixture was kept before the light radiation. The kinetics of the reaction followed by the estimation of unreacted iodine were estimated from time to time.

Stoichiometry and Product Analysis

Reaction mixtures containing varying compositions of iodine and potassium oxalate were kept at 297 K in presence of $1 \times 10^{-1} \text{ mol dm}^{-3}$ concentration of HCl. It was observed that 1 mol of oxlate consumes 1 mol of iodine.



RESULTS AND DISCUSSION

Order with respect to oxidant: The rate of oxidation reaction is first order with respect to I_2 in all the cases studied. It has been found that the first order rate constant decreases with increasing I_2 concentration. The results are presented in Table 1 (Fig. 1).

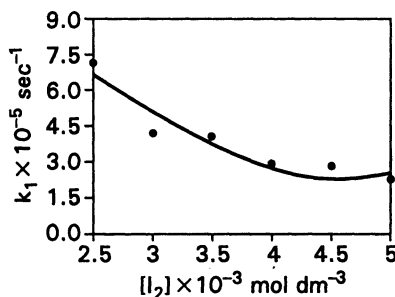


Fig. 1.

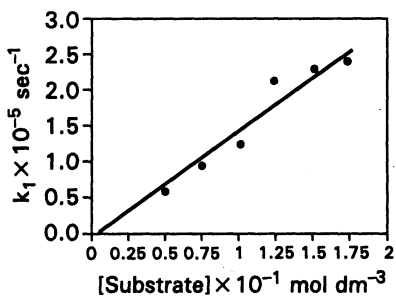


Fig. 2

Order with Respect to Substrate: The plot of rate constant against concentrations of potassium oxalate⁵ gives a straight line passing through the origin, thus showing that the order of reaction with respect to oxalate is one. The results are shown in Table-1 (Fig. 2).

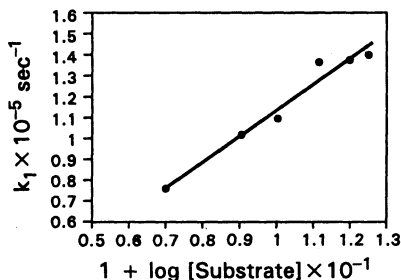


Fig. 3.

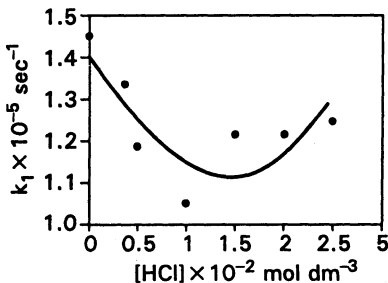


Fig. 4

Furthermore the plot of $\log k_1$ vs. \log [potassium oxalate] (Fig. 3) gives a straight line with unit slope value. This represents first order with respect to substrate, *i.e.*, oxalate ion.

Effect of HCl concentration: The reaction was studied at different initial concentrations of hydrochloric acid (0.25×10^{-2} to 2.5×10^{-2} mol dm⁻³). It has been observed that the reaction rate is more or less constant with increase of concentration of the acid. This indicates the formation of polyhalide salts. (Table-1, Fig. 4).

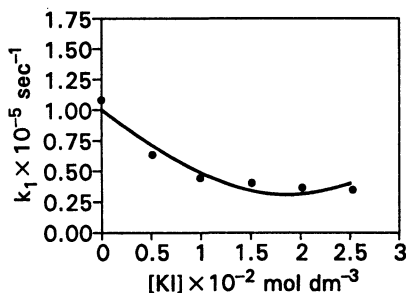


Fig. 5

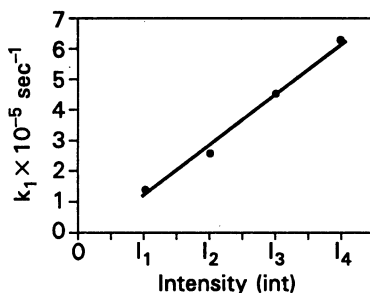


Fig. 6

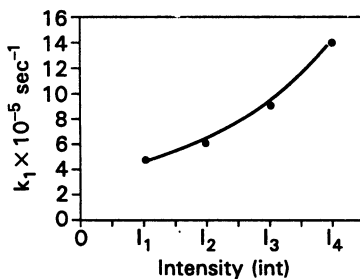


Fig. 7

Effect of I⁻ concentration: The reaction was studied at different initial concentrations of potassium iodide (0.5×10^{-2} to 2.5×10^{-2} mol dm⁻³). It has been observed that the reaction rate decreases with increase in concentration of potassium iodide. This indicates (Table-1) the formation of more complex polyhalide ions and thus it inhibits electron transfer (Fig. 5).

Effect of ionic strength: The effect of ionic strength was studied by the addition of sodium perchlorate and it was observed that there is no change in the reaction rate.

The role of sensitizer: It has been studied by the addition of sensitizer Hg(OAc)₂ to the reaction system. It was observed (Table-1) that the reaction rate increases appreciably with increase of Hg(OAc)₂ concentration.

Effect of intensity of radiation

Visible light: The reaction was studied at different intensities (I₁, I₂, I₃, I₄) of visible light; the reaction rate increases with the increase of intensity (Table-2).

Fig. 6 shows that the rate constant increases directly with increase in intensity of visible light.

Ultraviolet light: The reaction was studied at different intensities (I_1, I_2, I_3, I_4) of UV; the reaction rate increases with the increase of intensity (Table-2, Fig. 7).

TABLE-1

VARIOUS KINETIC ORDERS IN PHOTO-OXIDATION OF OXALATE ION BY IODINE

$[I_2] \times 10^{-2}$ (mol dm ⁻³)	$[(COOK)_2] \times 10^{-1}$ (mol dm ⁻³)	$[HCl] \times 10^{-1}$ (mol dm ⁻³)	$[KI] \times 10^{-2}$ (mol dm ⁻³)	$[Hg(OAc)_2] \times 10^{-4}$ (mol dm ⁻³)	$k_1 \times 10^{-5}$ (sec ⁻¹)
0.25	5	1	—	—	7.08
0.30	5	1	—	—	4.07
0.35	5	1	—	—	3.50
0.40	5	1	—	—	2.53
0.45	5	1	—	—	2.38
0.50	5	1	—	—	2.03
1.00	5	1	—	—	1.04
1	0.00	1	—	—	0.02
1	0.50	1	—	—	0.56
1	0.75	1	—	—	0.95
1	1.00	1	—	—	1.23
1	1.25	1	—	—	2.06
1	1.50	1	—	—	2.21
1	1.75	1	—	—	2.38
1	5	1	0.00	—	1.05
1	5	1	0.50	—	0.62
1	5	1	1.00	—	0.41
1	5	1	1.50	—	0.32
1	5	1	2.00	—	0.30
1	5	1	2.50	—	0.28
1	5	0.00	—	—	1.44
1	5	0.25	—	—	1.33
1	5	0.50	—	—	1.19
1	5	1.00	—	—	1.05
1	5	1.50	—	—	1.21
1	5	2.00	—	—	1.21
1	5	2.50	—	—	1.24
1	5	1	—	0.00	1.04
1	5	1	—	1.25	1.33
1	5	1	—	2.25	1.38
1	5	1	—	5.00	5.05
1	5	1	—	7.50	3.20
1	5	1	—	10.00	6.22

TABLE-II
KINETIC STUDIES OF PHOTO-OXIDATION OF OXALATE ION BY IODINE
AT DIFFERENT INTENSITIES OF VISIBLE AND UV LIGHT

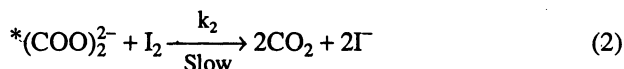
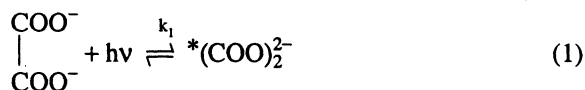
Intensity	$[I_2] \times 10^{-2}$ (mol dm ⁻³)	$[(COOK)_2] \times 10^{-1}$ (mol dm ⁻³)	$[HCl] \times 10^{-1}$ (mol dm ⁻³)	Light	
				Visible	UV
				$k_1 \times 10^{-5}$ (sec ⁻¹)	$k_1 \times 10^{-5}$ (sec ⁻¹)
I ₁	1	5	1	1.05	4.67
I ₂	1	5	1	2.46	6.15
I ₃	1	5	1	4.37	8.90
I ₄	1	5	1	6.17	13.48

Reaction Mechanism

On the basis of experimental results and findings the given probable reaction mechanism has been suggested as follows:

As we know in this case oxidation proceeds by both the paths, *i.e.*, in absence and presence of the sensitizer. Hence we can express:

Case 1. In absence of the sensitizer:



Therefore the rate of the reaction is

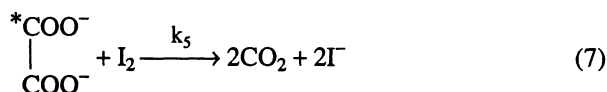
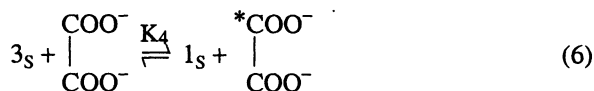
$$\frac{-d[I_2]}{dt} = k_2 [*(\text{COO})_2^{2-}] [I_2] \quad (3)$$

On substitution, we have the equation

$$\frac{-d}{dt} [I_2] = \frac{K_1 k_2 [I_2] [(\text{COO})_2^{2-}] I_n}{1 + K_1 [(\text{COO})_2^{2-}]} \quad (4)$$

I_n = Intensity.

Case 2. In presence of the sensitizer, the reaction scheme is shown by:



Total rate of the reaction can be given by:

$$\frac{-d[I_2]}{dt} = \frac{k_2 K_1 [I_2] [(COO)_2^{2-}] In}{1 + K_1 [(COO)_2^{2-}]} + \frac{k_5 K_4 [I_2] [S] [(COO)_2^{2-}] In}{1 + K_4 [(COO)_2^{2-}]} \quad (8)$$

$$\frac{-d[I_2]}{dt} \frac{1}{[I_2]} = \frac{k_2 K_1 [Oxalate] In}{1 + K_1 [Oxalate]} + \frac{k_5 K_4 [Oxalate] [S] In}{1 + K_4 [Oxalate]} \quad (9)$$

$$i.e., \quad k_{obs} = \frac{k_2 K_1 [Oxalate] In}{1 + K_1 [Oxalate]} + \frac{k_5 K_4 [Oxalate] [S] In}{1 + K_4 [Oxalate]} \quad (10)$$

where, In = intensity.

From eqn. (10) we find that k_{obs} , i.e., observable rate constant is varying with the change of oxalate ion concentration which was actually seen in this case of photochemical oxidation. The term oxalate ion concentration comes in both numerator and denominator [eqn. 10] which shows fractional order with respect to oxalate ion concentration. This is also seen in this oxidation process.

Similarly in eqn. (10) the S term indicates that k_{obs} is directly proportional with sensitizer concentration which is also observed experimentally. Hence experimental results and findings follow the proposed reaction mechanism.

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(Received: 2 May 2003; Accepted: 18 October 2003)

AJC-3179