



Kinetic and Mechanism of Oxidation of Oxalic Acid by Cerium (IV)

Dr. Ammar J. Mohammed

Biochemical Engineering Dept./Al-khwarizmi Engineering College/ University of Baghdad

Abstract:

Kinetic and mechanism studies of the oxidation of oxalic acid by Cerium sulphate have been carried out in acid medium sulphuric acid. The uv- vis. Spectrophotometric technique was used to follow up the reaction and the selected wavelength to be followed was 320 nm. The kinetic study showed that the order of reaction is first order in Ce(IV) and fractional in oxalic acid. The effect of using different concentration of sulphuric acid on the rate of the reaction has been studied and it was found that the rate decreased with increasing the acid concentration. Classical organic tests were used to identify the product of the oxidation reaction, the product was just bubbles of CO₂.

Keyword: Cerium(IV), Kinetics, Oxidation, Oxalic Acid.

Introduction:

Cerium element is considered as one of the most spread lanthanides elements. It has numerous oxidation cases (+4, +3, +2) [1]. Ce(IV) ion is considered as one of important oxidants, since its reduction potential was found in sulphuric acid solutions of normality (1-8)N equal 1.44 V. this potential value is different according to the difference of acidic media which contains [2]. Ce(IV) solution in acidic media is a stable for long time and is not influenced by light and increasing temperatures for short time [3]. Therefore the Ce(IV) solution in acidic media is considered as ideal oxidant in oxidation reaction. Thus Ce(IV) solution in acidic media had region been used as oxidant to oxidize many organic Compounds [4-7], such as carboxylic acids [8]. But there was no results reported for oxidation of dicarboxylic acid by Ce(IV) except malonic acid [9]. Ce(IV) ion in sulphuric acid solution gives absorption peak in ultra violet at 320nm in which Ce(IV) ion consumption can be followed up.

Experimental:

1- **Materials:** Cerium (IV) sulphate supplied by Riedel-deHean of 96% purity, oxalic acid supplied by Fluka of 99% purity, sulphuric acid supplied by BDH of 98% purity and double distilled water had been used.

Method: The reaction was followed up throughout consuming the concentration of Ce(IV) ion through tracing decreasing absorption of Ce(IV) ion in ultra violet absorption area at wavelength (320)nm. The reaction was carried out by adding 2.5 ml of Ce(IV) solution of different concentrations in quartz cell (1×1)cm and adding 100 µl of different concentrations oxalic acid solutions. The absorption was recorded directly after mixing the materials quickly. Then, the absorption was determined in successive intervals. The reaction was carried out in different acidic media of sulphuric acid, as shown in **Table (1)**.

Results and Discussion:

1- Kinetic measurement:

The kinetic of oxidation of oxalic acid by Ce(IV) was studied under 25C° in different concentrations acid media of sulphuric acid and by using different concentrations of the reacting materials. The kinetic study showed that the reaction was pseudo first order under condition $[Ce(IV)] \ll [Oxalic\ acid]$ by using the absorption as function for the concentration in first order equation:

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - kt$$

where A_∞ , A_0 , A_t are absorption at the end of reaction, absorption before reaction started, and absorption at particular time respectively. The results showed that the values of rate constant for the first order remained constant at changing the concentration of Ce(IV) with constant of other parameters, as it is shown in **Table (1)**, **Fig.1**. This indicates that the reaction is first order with respect to Ce(IV).

Rate constant of first order was found it increase by increasing concentration of oxalic acid at constant of other parameters, as it shown in **Table (1)** and **Fig.2**. To find out order of reaction with respect to oxalic acid, log of observed rate constant (k_{obs}) was plotted against log of oxalic acid concentration as shown in **Fig.3**.

The relation was linear with a slope 0.66, this value represents order of reaction with respect of oxalic acid.

Kinetic study showed that the first order rate constant decrease by increasing of sulphuric acid concentration, as it is shown in **Table (1)** and **Fig.4**.

Log observed rate constant (k_{obs}) was plotted against log (H_2SO_4), as it is shown in **Fig.5**. The relation was linear with a slope-1.03, this value represents the effect of sulphuric acid concentration on the rate of reaction.

The relation was linear with a slope 0.66, this value represents order of reaction with respect of oxalic acid. Kinetic study showed that the first order rate constant decrease by increasing of sulphuric acid concentration, as it is shown in **Table (1)** and **Fig.4**.

2- Stoichiometry:

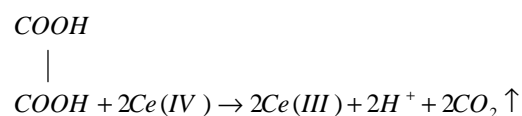
Stoichiometric measurements, by iodometric titration, showed that each mole of oxalic acid reacts with 2 moles of Ce(IV).

3-Identification of product:

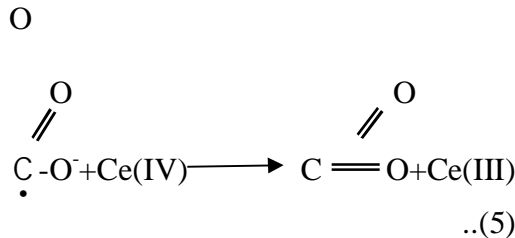
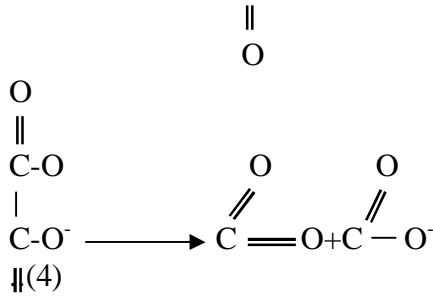
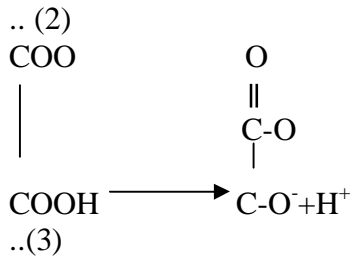
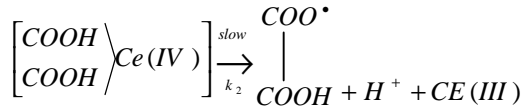
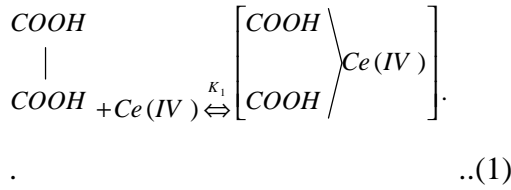
Literature showed that the product of oxidation of malonic acid⁽⁹⁾, methyl malonic acid⁽¹⁰⁾ and glyoxylic acid⁽¹²⁾ by Ce(IV) was formic acid with release of CO₂. In this research, CO₂ release was only observed, and the product of oxidation was not carboxylic acid, no change observed when adding sodium bicarbonate to oxidation product. Thus as it is expected the oxidation product of oxalic acid by Ce(IV) was just CO₂.

4-Mechanism suggested and concluding law of rate reaction:

Depending on kinetic measurements, stoichiometric measurements and identification of product, general equation for reaction was suggested as follows:



The following is the mechanism suggested for reaction:



Basing on earlier explanation, law of reaction rate was found out as follow:

$$-\frac{d\text{Ce(IV)}}{dt} = \frac{K_1 k_2 [\text{Ce(IV)}][\text{Oxalic acid}]}{1 + K_1 [\text{Oxalic acid}]} \quad \dots(6)$$

Supposing that the reaction was first order:

$$-\frac{d[\text{Ce(IV)}]}{dt} = k_{obs} [\text{Ce(IV)}] \quad \dots(7)$$

Compare (6) with (7):

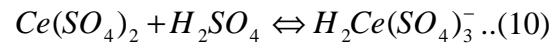
$$k_{obs} = \frac{K_1 k_2 [\text{Oxalic acid}]}{1 + K_1 [\text{Oxalic acid}]} \quad \dots(8)$$

$$\frac{1}{k_{obs}} = \frac{1}{K_1 k_2 [\text{Oxalic acid}]} + \frac{1}{k_2} \quad \dots(9)$$

With using Michaleis Menten plot as shown in **Fig.6**, the plot gave linear relation, this proved correctness of the law of reaction rate and mechanism suggested.

5-Effect of sulphuric acid on reaction rate:

Literature showed that $\text{H}_2\text{Ce}(\text{SO}_4)_3^-$ was active species resulted from solving Ce(IV) in sulfuric acid (11):



$$K^* = \frac{[\text{H}_2\text{Ce}(\text{SO}_4)_3^-]}{[\text{Ce}(\text{SO}_4)_2][\text{H}_2\text{SO}_4]} \quad \dots(11)$$

$$[\text{Ce}(\text{SO}_4)_2] = \frac{[\text{H}_2\text{Ce}(\text{SO}_4)_3^-]}{K^* [\text{H}_2\text{SO}_4]} \quad \dots(12)$$

Substituting $\text{Ce}(\text{SO}_4)_2$ from (12) to (6)

$$-\frac{d[\text{Ce(IV)}]}{dt} = \frac{K_1 k_2 [\text{H}_2\text{Ce}(\text{SO}_4)_3^-] [\text{Oxalic acid}]}{K^* (1 + K_1 [\text{Oxalic acid}]) [\text{H}_2\text{SO}_4]} \quad \dots(13)$$

The last equation that clarifies the negative effect of sulfuric acid on reaction rate agrees with experimental results.

References:

1. J.E.Huheey, "Inorganic Chemistry", Harper-Row (1972).
2. F.A.Cotton; G.Wilkinson, "Advanced Inorganic Chemistry", Jhon Wiley. 4th ed, (1988).
3. G.Nagy; E.Koros; N. Of tedal; K.Tjelfhat; P. Ruoff, "Effect of temperature in Cerium-ion catalyzed bromate-driven oscillators", *Chemical physics Letters*, 250 (1996) 255-260.
4. R.Dayal; G.V.Bakore, "Kinetics of the oxidation of mandelic acid by Cerium (IV) sulphate", *J.Indian Chem. Soc.*, 49 (11), (1972) 1093-1095.
5. R.G. Varma; R.L. Yadav, "Ceric – Cerium oxidation of ortho-cersol", *J. Indian Chem. Soc.*, LX (1983) 554-556.
6. T. Tzedakis; A.J. Savall, " Ceric sulphate oxidation of p-methoxytoluene: Kinetics and reaction results", *Ind. Eng. Chem. Res.*, 31(11), (1992) 2475-2483.
7. D.C.Bilehal; R.M.Kulkarni; S.T. Nandibewoor, "Kinetics of oxidation of pyridylmethylphiny-benzimidazole by Cerium (IV) in an aqueous perchloric acid medium", *Turk. J. Chem.*, 27(2003) 695-702.
8. B.Singh; P.Kumar; R.K.Shukla; B.Krishna, "Kinetics of Ce(IV) oxidation of 3-Bromo propionic acid in aqueous nitric acid Solution", *J.Indian Chem.Soc.*, LIV (1977) 378-380.
9. B.Neumann; O.Stenbock; S.C.Muller; N.S.Dalal, "Stoichiometric fingerprinting as an aid in understanding complex reaction : The oxidation of malonic acid by Cerium (IV)", *J.Phys. Chem*, 101 (1997) 2743-2745.
10. P.O.Kvernberg; E.W.Hansen; B.Pedersen; A.Rasmussen; P.Ruoff; "Oxidation of methylmalonic acid by Cerium (IV). Evidence for parallel reaction pathways", *J.Phys. Chem. A*, 101 (1997) 2327-2331.
11. P.K.Saxena; B.Singh; R.K.Shuka; B.Krishna, "Kinetics of Ce(IV) oxidation of diethy ketone in sulphuric acid solutions", *J.Indian Chem. Soc.*, LV(1978) 56-59.
12. B.Neuman; O.S.Stefan; S.C.Muller; N.S.Dalal, "Oxidation of glyoxylic acid by Cerium (IV)", *J.Phys. Chem.*, 100(1996) 12342-12348.
- 13.

Table (1)The values of concentration of reactors and rate constant

$10^4[\text{Ce(IV)}]/\text{M}$	$10^2[\text{Oxalic}]/\text{M}$	$[\text{H}_2\text{SO}_4]/\text{M}$	$\text{K}_{\text{obs}}/\text{min}^{-1}$
0.3125 0.625 1.25 2.5 5	3.8	0.125	1.41 1.42 1.42 1.35 1.41
1.25	0.24 0.48 0.96 1.9 3.8	0.125	0.276 0.396 0.768 1.188 1.42
1.25	3.8	0.125 0.25 0.5 1	1.42 0.726 0.36 0.166

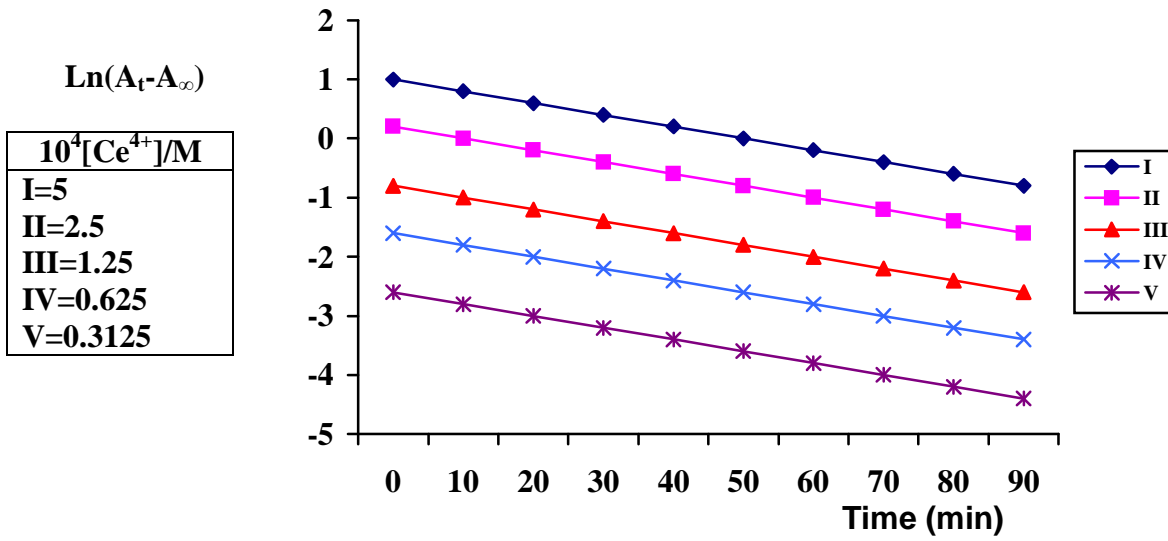


Figure (1)

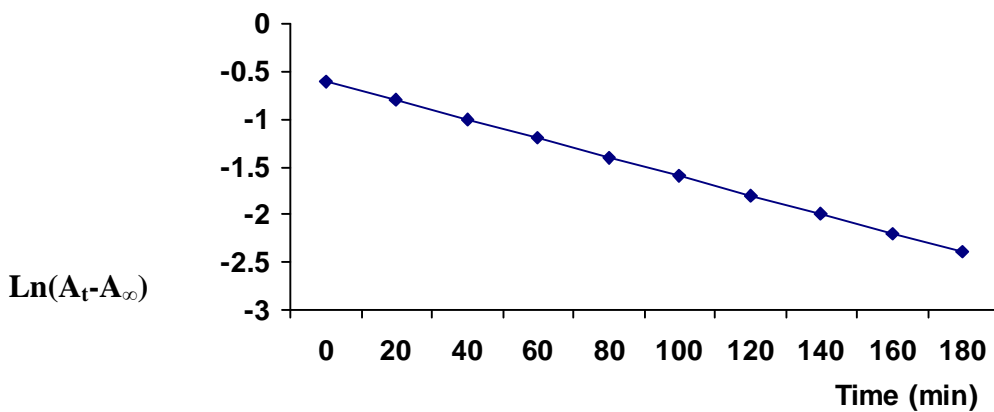
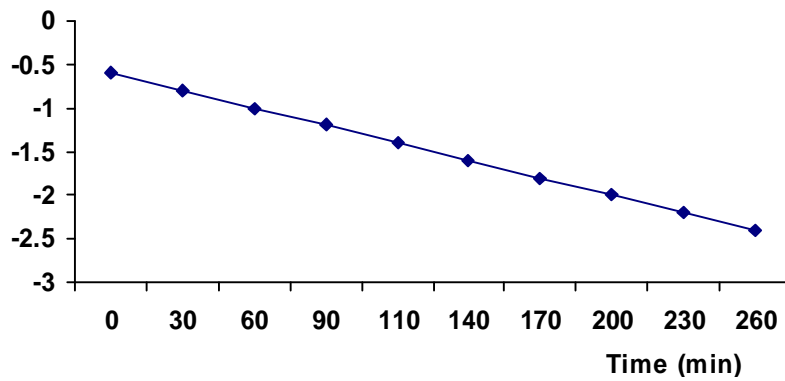
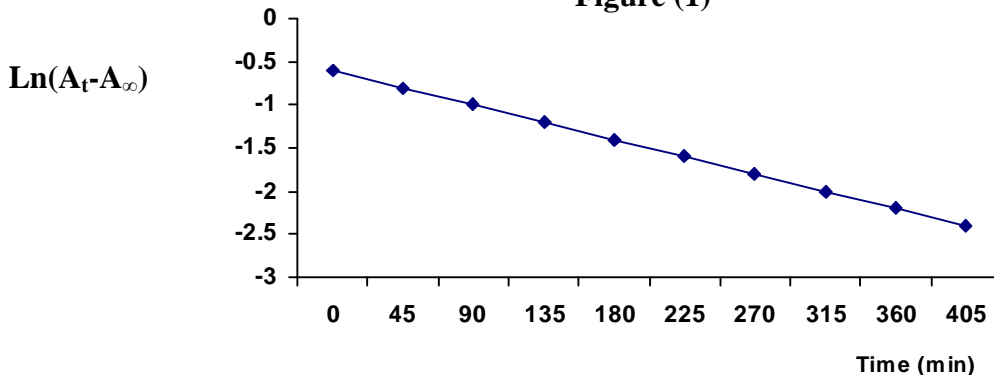


Figure (2)

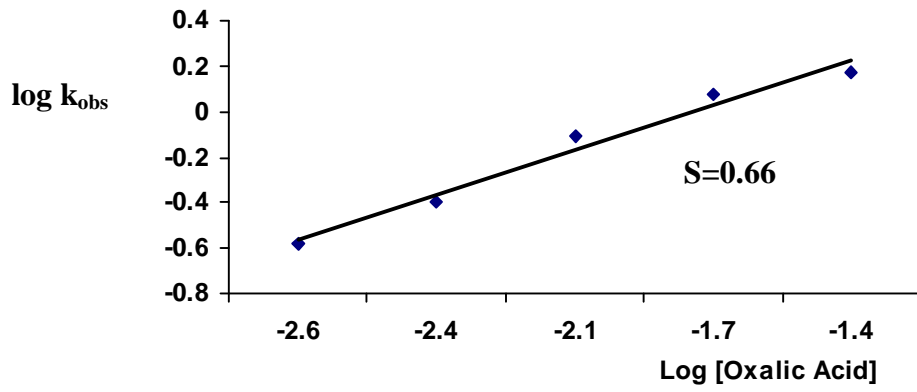
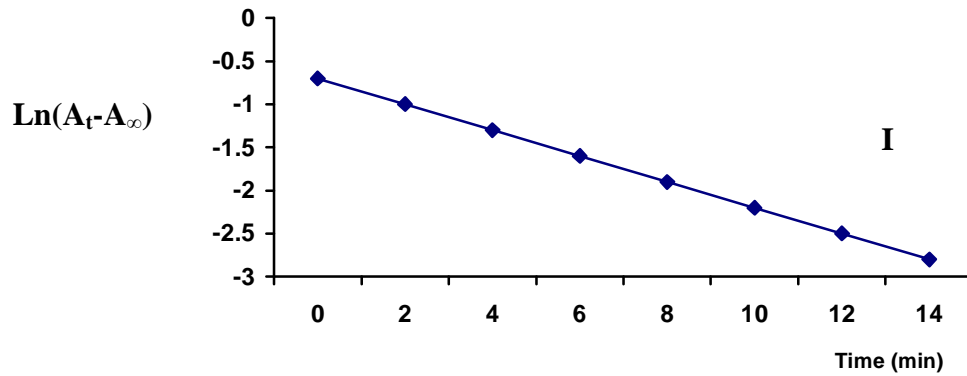
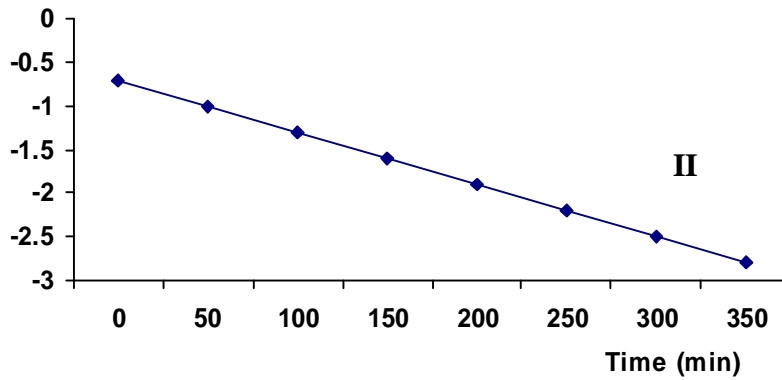


Figure (3)



Ln(A_t-A_∞)

[H ₂ SO ₄]/M
I=0.25
II=1
III=0.5



Ln(A_t-A_∞)

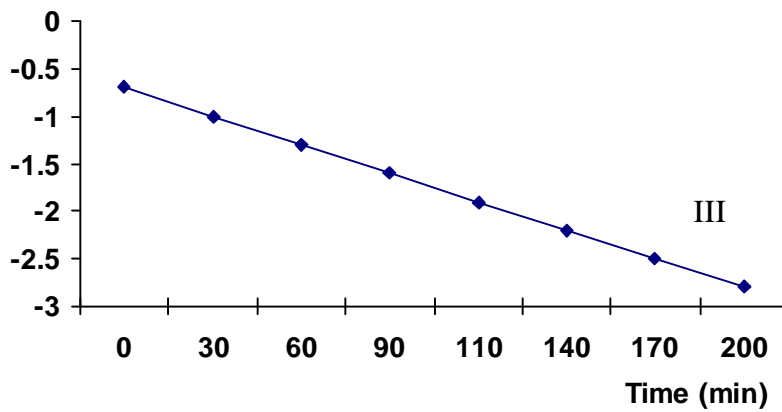


Figure (4)

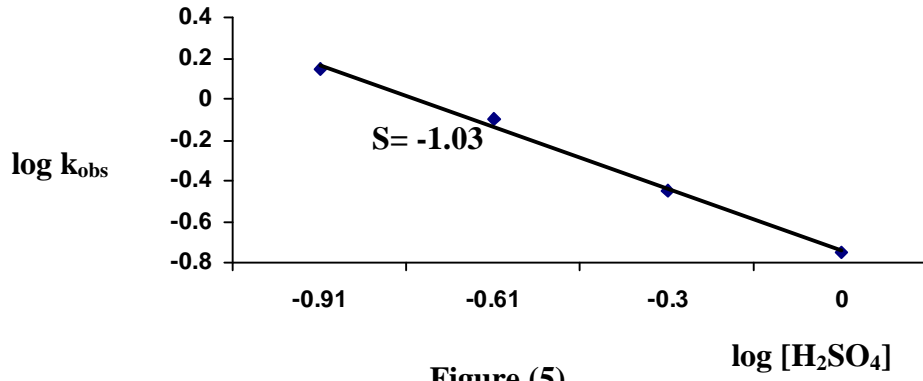


Figure (5)

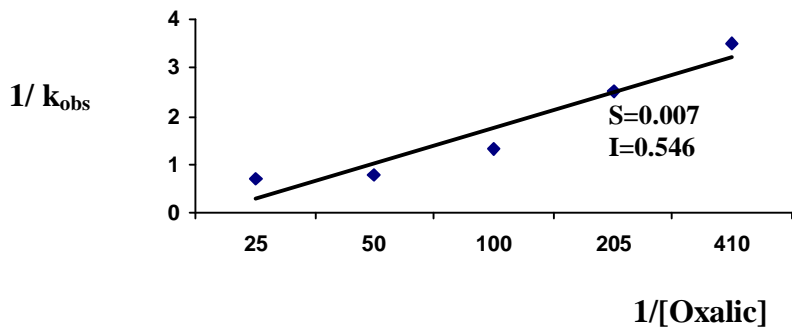


Figure (6)

حركية وميكانيكية اكسدة حامض الاوكزاليك بواسطة السيريوم الرباعي

د.عمار جاسم محمد

قسم هندسة الكيمياء الاحيائية/كلية هندسة الخوارزمي/جامعة بغداد

الخلاصة:

تم دراسة حركية وميكانيكية اكسدة حامض الاوكزاليك في الوسط الحامضي من حامض الكبريتيك . استخدمت تقنية الاشعة فوق البنفسجية- المرئية لمتابعة التفاعل عند الطول الموجي 320 nm . بينت الدراسة الحركية ان التفاعل من المرتبة الاولى بالنسبة للسيريوم الرباعي والمرتبة الكسرية بالنسبة لحامض الاوكزاليك .
تم دراسة تأثير تغيير تركيز حامض الكبريتيك على سرعة التفاعل ووجد ان سرعة التفاعل تقل بزيادة تركيز حامض الكبريتيك تم استخدام الكشوفات العضوية الاولية لتشخيص ناتج الاكسدة ووجد ان ناتج التفاعل هو عبارة عن فقاعات غاز ثاني اوكسيد الكربون.