Kinetic and Mechanism of Oxidation of Formic acid by Cerium (IV)

Rawaa Hussein Ali
Biochemistry Dept. , college of medicine , University of Baghdad.

Abstract:

Kinetic and mechanism studies of the oxidation of Formic acid(FA) by Cerium sulphate have been carried out in acid medium of 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(0.66) in FA. 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 was used to identify the product of the oxidation reaction, the product was just bubbles of CO_2.

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

الخلاصة:

تم دراسة حركية وميكانيكية اكسدة حامض الفورميك 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(٠,٦٦) بالنسبة لحامض الفورميك .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 الكاربون.

Introduction:

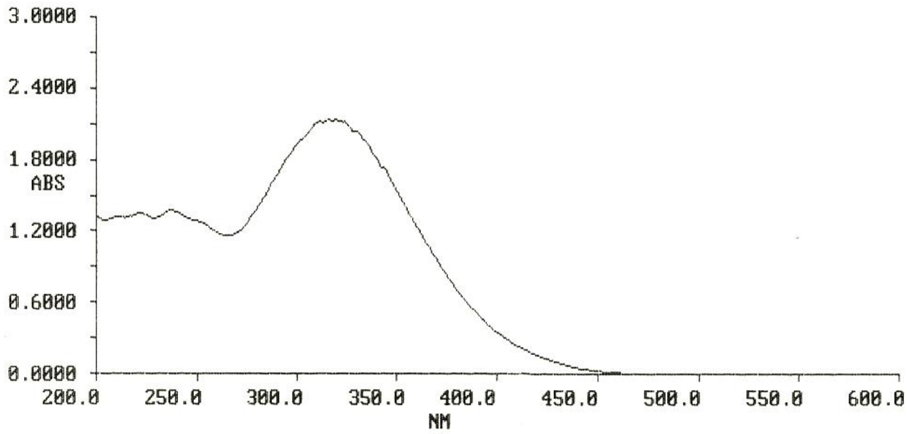
Cerium element is considered as one of the most spread lanthanides elements. It has numerous oxidation cases (+4, +3, +2)[J.E.Huheey 1972] .Ce(IV) ion is considered as one of important oxidantes, since its reduction potential was found in sulphuric acid solutions of normality (1-8)N equal 1.44 V. this potential value is different according to the difference of acidic media which contains[F.A.Cotton1988] . Ce(IV) solution in acidic media is a stable for long time and is not influenced by light and increasing temperatures for short time [G.Nagy 1996] . 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 [R.Dayal 1972 ,R.G. Varma 1983 , T. Tzedakis 1992 , D.C.Bilehal 2003 , B.Neumann 1997 , A. P. Savanur 2009 , Katafias 2006 , F.G Anand 2012] and inorganic[Katafias 2006 , K. A. Thabaj 2006] . But there was no results reported for oxidation of formic acid by Ce(IV) .Ce(IV) ion in sulphuric acid solution gives absorption peak in ultra violate 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, Formic acid supplied by Fluka of 99% purity, sulphuric acid supplied by BDH of 98% purity and double distillated water had been used.

2-Method: The reaction was followed up throughout consuming the concentration of Ce(IV) ion through tracing decreasing absorption of Ce(IV) ion in ultra violate absorption area at wavelength (320)nm as shown in Figure (1) . The reaction wascarried 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 Formic 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).



Figure(1) Adsorption of Ce(IV) in acidic media of H_2SO_4

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

[Ce(IV)]/M	[Formic]/M	$[H_2SO_4]$/M	K_{obs}/min^{-1}
$0.3125*10^{-4}$ $0.625*10^{-4}$ $1.25*10^{-4}$ $2.5*10^{-4}$ $5*10^{-4}$	$3.8*10^{-2}$	0.125	1.410 1.420 1.420 1.350 1.410
$1.25*10^{-4}$	$0.24*10^{-2}$ $0.48*10^{-2}$ $0.96*10^{-2}$ $1.9*10^{-2}$ $3.8*10^{-2}$	0.125	0.276 0.396 0.768 1.188 1.420
$1.25*10^{-4}$	$3.8*10^{-2}$	0.125 0.250 0.500 1.000	1.420 0.726 0.360 0.166

Results and Discussion:

1- **Kinetic measurement:**

The kinetic of oxidation of Formic 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)]<<[Formic acid] by using the absorption as function for the concentration in first order equation:

$$In(A_t - A_\infty) = In(A_o - A_\infty) - kt \text{ ....(1)}$$

where A_∞, A_o and 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), Figure(2). 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 Formic acid at constant of other parameters, as it shown in Table (1) . To find out order of reaction with respect to Formic acid, log (observed rate constant $\mathbf{k_{obs}}$) was plotted against log (Formic acid) concentration as shown in Figure(3).
The relation was linear with a slope 0.66, this value represents order of reaction with respect of Formic acid.

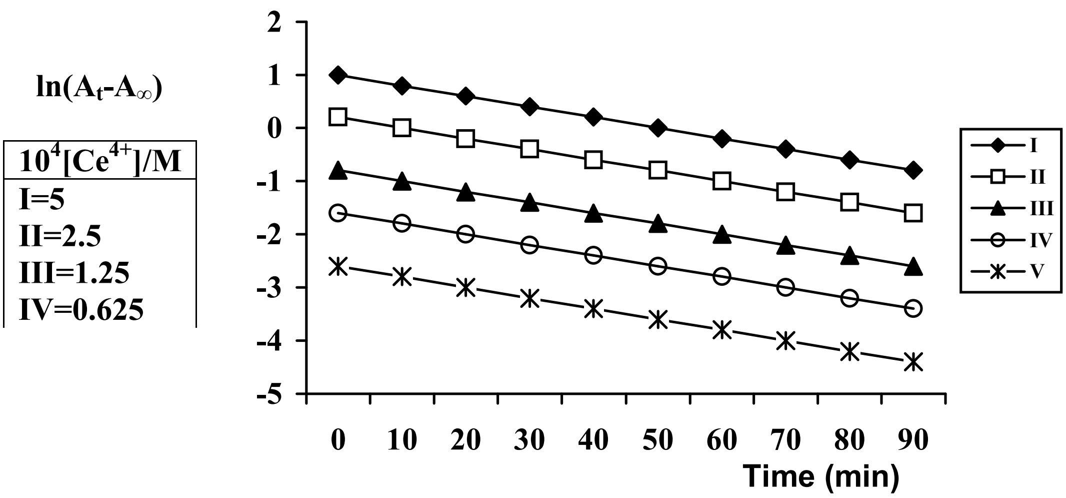


Figure (2) the relation of first order reaction to find the rate constant

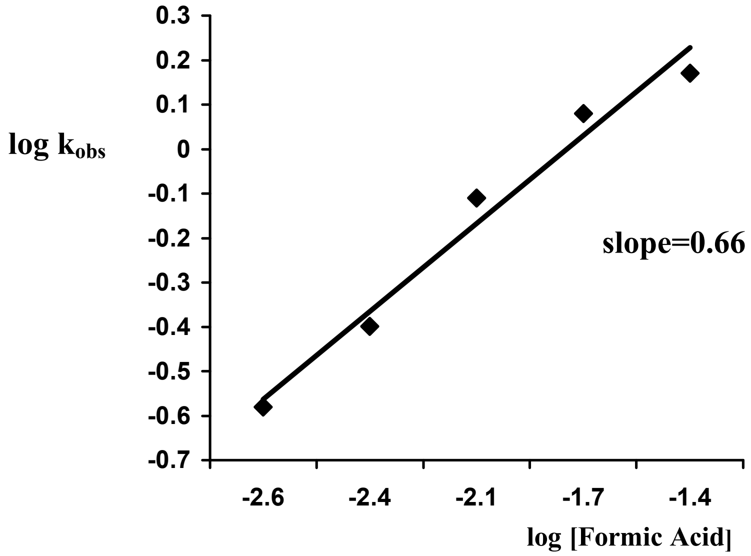


Figure (3) the relation between log(observed rate constant) and log concentration of Formic acid to find

Kinetic study showed that the first order rate constant decrease by increasing of sulphuric acid concentration, as it's shown in Table (1) . Log (observed rate constant **k_{obs}**) was plotted against log [H_2SO_4], as it's shown in Figure(4). The relation was linear with a slope -1.03, this value represents the effect of sulphuric acid concentration on the rate of reaction.

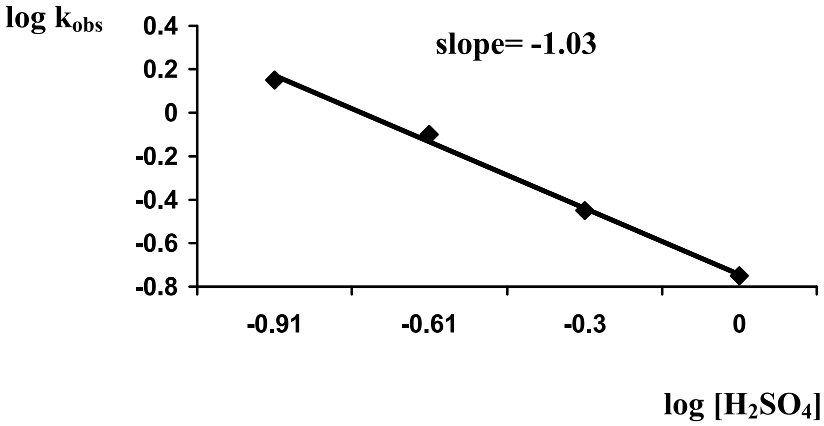


Figure (4) the relation between log(observed rate constant) and log concentration of sulphuric acid to find the order of sulphuric acid.

2- Stoichmetery:
Stoichmetric measurements, by iodometric titration(titrate Na_2 S_2O_3 with unreact KI from reaction between KI and unreacet Ce(IV) , showed that each mole of Formic acid reacts with 2 moles of Ce(IV).

3-Identification of product:
Literature showed that the product of oxidation of malonic acid[B.Neumann 1997] , methyl malonic acid[K. A. Thabaj 2006] and glyoxylic acid[B.Neuman 1996] by Ce(IV) was formic acid with release of CO_2. In this research, Classical organic tests of carboxylic acids was used to identify the product of the oxidation reaction , CO_2release 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 Formic acid by Ce(IV) was just CO_2.

4-Mechanism suggested and concluding law of rate reaction:

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

$$HCOOH + 2Ce(IV) \rightarrow 2Ce(III) + 2H^{+} + CO_2 \uparrow \text{..........(2)}$$

The following is the mechanism suggested for reaction:

$$HCOOH + Ce(IV) \overset{K_1}{\Leftrightarrow} [HCOOH.Ce(IV)]_{complex} \text{.........(3)}$$

$$[HCOOH.Ce(IV)]_{complex} \xrightarrow[k_2]{slow} HCOO^{\bullet} + H^{+} + Ce(III) \text{......(4)}$$

$$HCOO^{\bullet} + Ce(IV) \rightarrow CO_2 + H^{+} + Ce(III) \text{............(5)}$$

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

$$-\frac{dCe(IV)}{dt} = \frac{K_1 k_2 [Ce(IV)][Formicacid]}{1 + K_1[Formicacid]} \text{.............(6)}$$

Supposing that the reaction was first order:

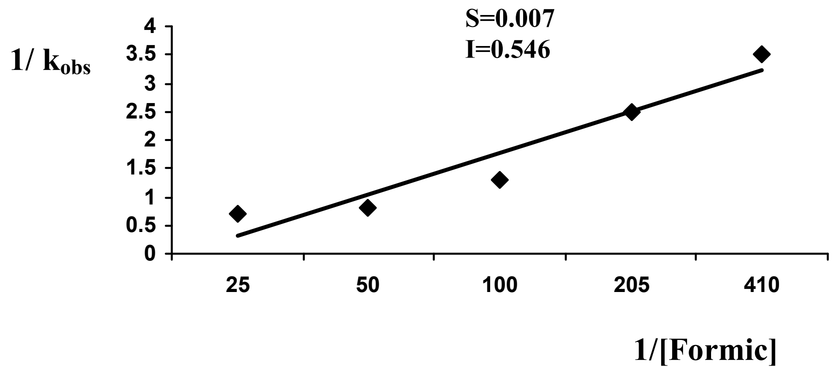
$$-\frac{d[Ce(IV)]}{dt} = k_{obs}[Ce(IV)] \quad \text{............(7)}$$

Compare (6) with (7):

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

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

With using Michaleis Menten plot as shown in Figure(5) , the figure gave linear relation, this proved correctness of the law of reaction rate and mechanism suggested.



Figure(5) Michaleis Menten plot

5-Effect of sulphuric acid on reaction rate:

Literature showed that $H_2Ce(SO_4)_3^-$ was active species resulted from solving Ce(IV) in sulfuric acid [P.K.Saxena 1978]:

$$Ce(SO_4)_2 + H_2SO_4 \Leftrightarrow H_2Ce(SO_4)_3^- \quad \text{.....(10)}$$

$$K^* = \frac{H_2Ce(SO_4)_3^-}{[Ce(SO_4)_2][H_2SO_4]} \quad \text{..........(11)}$$

$$[Ce(SO_4)_2] = \frac{H_2Ce(SO_4)_3^-}{K^*[H_2SO_4]} \quad \text{..........(12)}$$

Substituting $Ce(SO_4)_2$ from (12) to (6)

$$-\frac{d[Ce(IV)]}{dt}=\frac{K_1k_2[H_2Ce(SO_4)_3^-][Formicacid]}{K*(1+K_1[Formicacid])[H_2SO_4]} \quad \text{........(13)}$$

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

References:

Anand F.G and A. Rashmi ," Kinetuic and Mechanistic Study of Oxidation of Atenolol by Cerium(IV) in Sulphuric Acidic Medium", Inter. Res. J. of Pharmacy ,3(3) ,286-270 ,2012

Bilehal; D.C 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, 695-702,2003.

Cotton; F.A. G.Wilkinson, "Advanced Inorganic Chemistry", Jhon Wiley. 4th ed, (1988).

Dayal; R. G.V.Bakore, "Kinetics of the oxidation of mandelic acid by Cerium (IV) sulphate", J.Indian Chem. Soc., 49 (11), 1093-1095,1972.

Huheey, J.E. "Inorganic Chemistry", Harper-Row (1972).

Katafias ,"Kinetics and mechanism of Bromide ions oxidation by Cerium(IV) in sulphuric soluions reisited", Trans. Met. Chem.,31, 907-911, 2006.

Katafias; P. Kita ; G. Wrzeszcz," Kinetics of the methylene blue oxidation by cerium(IV) in sulphuric acid solutions" , Trans. Met. Chem., 30, 120-126,2006.

Kvernberg; P.O. 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, 2327-2331, 1997.

Nagy; G. E.Koros; N. Of tedal; K.Tjelfhat; P. Ruoff, "Effect of temperature in Cerium-ion catalyzed bromate-driven oscillators", Chemical physics Letters, 250 , 255-260,1996.

Neuman; B. O.S.Stefan; S.C.Muller; N.S.Dalal, "Oxidation of glyoxylic acid by Cerium (IV)", J.Phys. Chem., 100, 12342-12348, 1996.

Neumann B.;O.Stenbock;S.C.Mulle;N.S.Dalal,"Stoichiometric fingerprinting as an aid in understanding complex reaction : The oxidation of malonic acid by Cerium (IV)", J.Phys. Chem, 101 , 2743-2745,1997.

Savanur; A. P. S. T. Nandibewoor; S. A. Chimatadar ,"Manganese(II) catalysed oxidation of glycerol by Cerium(IV) in aqueous sulphric acid medium: a kinetic and mechanism study" , Trans. Met. Chem., 34, 711-718,2009 .

Saxena; P.K. B.Singh; R.K.Shuka; B.Krishna, "Kinetics of Ce(IV) oxidation of diethy ketone in sulphuric acid solutions", J.Indian Chem. Soc., LV, 56-59,1978.

Thabaj; K. A. S. A. Chimatadar; S. T. Nandibeoor ,"Mechanistic study of oxidation of Palladium(II) by Cerium(IV) in aquous acid", Trans. Met. Chem.,31, 186-193, 2006.

Tzedakis; T. A.J. Savall, " Ceric sulphate oxidation of p-methoxytoluene: Kinetics and reaction results", Ind. Eng. Chem. Res., 31(11), 2475-2483,1992.

Varma; R.G. R.L. Yadav, "Ceric – Cerium oxidation of ortho-cersol", J. Indian Chem. Soc., LX , 554-556,1983.