

# Kinetics and Mechanism of Oxidation of Ibuprofen (IBUP) Chromium(III) Complex by Periodate

Hammed M. Abou Elnader<sup>1</sup>, Hamada E. Ali<sup>1</sup>, Essam A.Gomaa<sup>1</sup>, A.A. El.Bindary<sup>2</sup>

<sup>(1)</sup>Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

<sup>(2)</sup>Chemistry Department, Faculty of Science, Damietta University, Damietta 34517, Egypt

**ABSTRACT** —The kinetics of oxidation of binary complex  $[Cr^{III}(IBUP)(H_2O)_4]^{+2}$  to Cr(VI) by periodate has been investigated spectrophotometrically at 356nm under pseudo first order reaction conditions in aqueous medium over (20- 40)°C range, pH (1.2-2.4), and  $I=0.4 \text{ moldm}^{-3}$ , first order reaction depend on  $[IO_4^-]$  and Cr(III), reaction rate increased by pH increasing and it undergoes with the following rate law:  $\text{Rate}=(k_5 K_5 + \{k_6 K_6 K_2\}) [Cr^{III}(IBUP)(H_2O)_4]^{+2} [H_5O_6][H^+]$ , oxidation of  $[Cr^{III}(IBUP)(H_2O)_4]^{+2}$  is going to coordinated with water molecule by Ibuprofen. This approved electron transfers proceeds by inner sphere mechanism via coordination of  $IO_4^-$  to Cr(III).

**Keywords:** Kinetics; Oxidation; Ibuprofen chromium (III) complex; periodate.

## INTRODUCTION:

Chromium metal oxidation from trivalent to hexavalent states environmental very important because Chromium (VI) compounds is highly toxic and Chromium (VI) compounds is potent toxic and carcinogenic products.

Highly absorbing of Chromium (VI) products by cells and reducing to trivalent form chromium (III) or other oxidation states chromium(V) and chromium(IV), was supposed that it makes advertising biological effects to chromium (VI) compounds. (A. Barnhart, J., 1999).

Periodate  $[IO_4^-]$  play an important role in different biological determination by its oxidation effects. (M. P. Woodward et al., 1985 and Cotton FA., 1997) Periodate is a stronger oxidant in acid medium than in alkaline medium, (V.Y. Kukushkin et al., 1999) Periodate solutions decomposed photo chemically if exposed to day light due to formation of ozone forms, so it recommended to put in dark places (E.A. Burton et al., 2011).

Physical chemistry of oximes with metal complexes is very important in medicine field reactions behaviors (B.G. Malmstrom., 1993 and A.Y Kassim et al., 1987).

## EXPERIMENTAL

### Materials and solutions

Used chemicals in this study from Analar (BDH, fisher scientific, sigma) or of reagent specify and some used without changing in properties.

Preparation of complex done by [0.1 M] in smallest amount of solution by mixing chromium (III) nitrate with that of IBUP ligand by a concentration ratio 1:1.20 % excess ligand was added to ensure complete formation of the complex. Heating of mixture done by using water bath until dark violet solution was appeared.

Preparation of buffer solution from citric acid, and disodium hydrogen orthophosphate solution of known concentration, ionic strength adjusted by  $NaNO_3$  solution in buffer solution.

Distilled water was used in solutions preparation. A stock solution of  $NaIO_4$  was prepared by accurate weighing and wrapped in aluminum foil to avoid photochemical decomposition (Custot, J.-L et al., 1999).

A UV-1100 spectrophotometer chromtech was used in this investigation. All reactants were thermally equilibrated for 20 min in an automatic circulation thermostat with an electrically thermo stated (assistant) compartment was used to monitor the reaction, thoroughly mixed and quickly transferred to a thermostat cell. The reaction was followed over the 356-375 nm wavelength range the choice of the wavelength depended on the pH as the product peak is pH dependent.

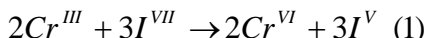
Reaction pH measured by Chertsey (7065), pH-meter. Pseudo-first-order conditions were maintained in all runs by the presence of a large excess (> 10-fold) of  $IO_4^-$ .

Ionic strength fixed by NaNO<sub>3</sub> solution. reaction pH fixed by using buffer solution from citric acid and disodium hydrogen orthophosphate.

## Results and Discussion

IR absorption spectrum in (Figure 1) of the oxidation products indicate that the chromium(III) peak band intensity decreased from peak (2) at 3573.14cm<sup>-1</sup> to peak (10) at 1375.66 cm<sup>-1</sup> corresponds to chromium(VI).

The oxidation kinetics of  $[Cr^{III}(IBUP)(H_2O)].nH_2O$  by periodate carried out over the (1.2-2.4) pH range, [0.2-0.7]M ionic strength and (20-40)°C over arrange of complex and periodate concentrations. Experiments were carried out varying the  $[IO_4^-]:[Cr^{III}(IBUP)(H_2O)].nH_2O$  ratios, with the concentration of  $[Cr^{III}(IBUP)(H_2O)].nH_2O$  was always a twice of  $[IO_4^-]$ . The study indicates that about two moles of  $[Cr^{III}(IBUP)(H_2O)].nH_2O$  were consumed for every 3 moles of  $IO_4^-$ , where the ratio of iodine (VII) to chromium (VI) initially present was  $1.50 \pm 0.1$ . Through the pH range applied, Chromium (III) complex not oxidize by  $IO_4^-$ , so stoichiometry the reaction can supposed by the following equation:



ln(A $\infty$ -At) versus time drawings showed linearity about 95%, where at and A $\infty$  are absorbance at time (t) and infinity ( $\infty$ ), respectively. From the drawings Pseudo-first order rate constants, k<sub>obs</sub>, obtained from the slopes of these drawings, are (0.17783,0.173444,0.17775,0.16888,0.17854,0.17767)

corresponding to the complex concentrations (0.5 m, 1 m, 1.5 m, 1.75 m, 2 m, 2.2 m) respectively and this showed in fig. (3). table (1).

Showed that k<sub>obs</sub> was unaffected

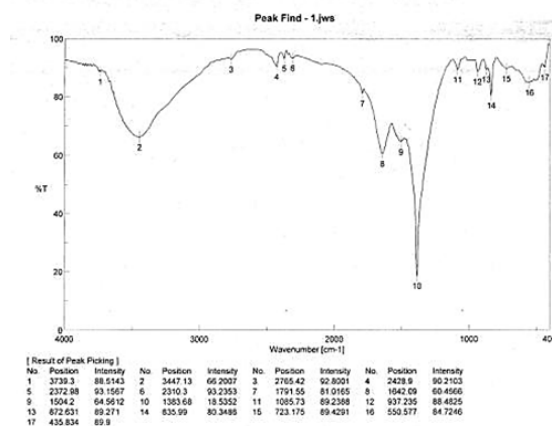
when chromium(III)-complex concentration changed at fixed periodate concentration, this proven that first order dependence on the complex concentration that illustrated by the following equation:

$$d[Cr^{VI}]/dt = K_{obs} [Cr^{III}]_T \quad (2)$$

Where  $[Cr^{III}]_T$  is the total chromium(III) concentration present. At fixed  $[H^+]$  and ionic Strength, (1/ k<sub>obs</sub>) varies linearly with 1/  $[IO_4^-]$  at different temperatures (Figure 5), and reaction kinetics illustrated by the following equation:

$$K_{obs} = a[IO_4^-] / (1 + b[IO_4^-]) \quad (3)$$

Constants (a) and (b) were obtained from the slope and intercept as  $0.005 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  and  $5.76 \text{ mol}^{-1} \text{ dm}^3$ , respectively at 30°C,  $[I] = 0.4 \text{ mol dm}^{-3}$  and pH = 2.4 drawings of k<sub>obs</sub> versus  $[IO_4^-]$  at different pH values (1.6-2.4) (Figure



show that the reaction rate increased with pH increasing (Table II).

The rate of reaction is independent on ionic strength when varied between (I=0.2,0.3,0.4,0.5,0.6,0.7) corresponding to (0.17684,0.169825,0.188356,0.188964,0.179984,0.183345) respectively and that illustrated in fig. (6).

Figure (1): IR absorption of chromium (III) with (IBUP) ligand.

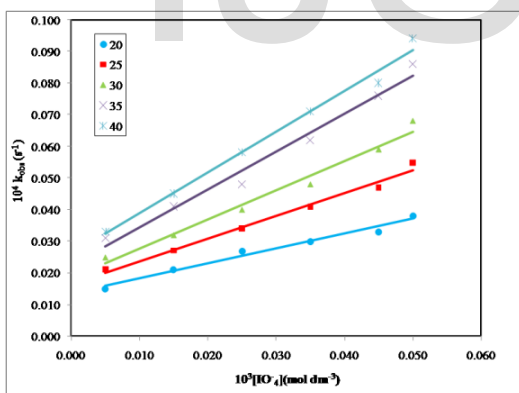


Figure (2): Variation of k<sub>obs</sub> with different concentrations of periodate at different temp.

Table (I): k<sub>obs</sub> with different concentrations of complex at temp.=30°C, pH = 1.9 and I = 0.4 mol dm<sup>-3</sup>

Tim(m)	0.5ml comp.	1ml comp.	1.5ml comp.	1.75ml comp.	2ml comp.	2.2ml comp
1	0.7762	1.5861	1.4787	2.0148	2.2548	3.7584
2	0.7826	1.4440	1.6457	2.6455	2.6051	3.1485
3	1.1224	1.5454	1.8457	2.7845	2.8845	3.2154
4	1.2372	1.5874	1.8998	2.8945	2.9878	3.2948
5	1.4684	1.9844	2.1234	2.8999	3.9848	3.4845
6	1.6770	2.2458	2.5487	2.8978	3.1458	3.6485
7	2.8388	2.4544	2.5845	2.9458	3.2548	4.7845
8	2.8248	2.4888	2.7124	3.2587	3.3344	4.9485
9	2.4498	2.4998	2.9784	3.2587	3.5899	4.9889
10	2.5589	2.6525	2.9999	3.4578	3.8948	4.9968
11	2.6458	2.8545	3.3458	3.6587	3.9998	4.9969
12	2.7896	3.3548	3.4878	3.7587	4.2455	4.9989
13	3.8785	3.3999	3.4999	3.9458	4.3548	4.9999
14	3.4548	3.4548	3.5487	4.3584	4.5848	5.0125
15	3.1458	3.6894	3.9658	4.3333	4.7485	5.2654

16	3.4586	3.9485	4.1487	4.5849	4.9458	5.4878
17	3.5846	3.9946	4.3945	4.7845	5.1254	5.4578
18	4.4586	4.2548	4.4878	4.9888	5.4578	5.6428
19	4.9458	4.5487	4.9247	5.5845	5.7584	6.9845
Slope	0.17783	0.173444	0.17775	0.16888	0.17854	0.17767

30	0.485
35	0.862
40	0.964

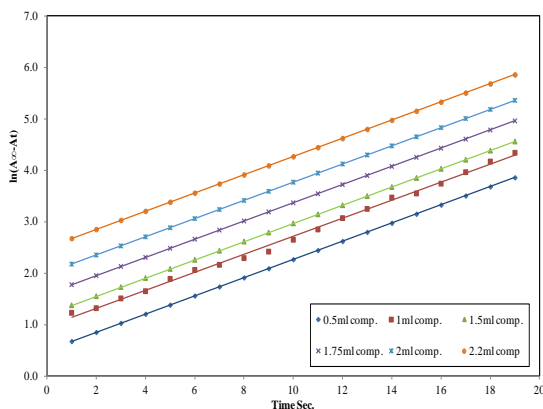


Figure (3):  $k_{obs}$  with different concentrations of complex at temp.=30 °C, pH = 1.9 and I = 0.4 mol dm<sup>-3</sup>

Table (II): effect of pH on  $k_{obs}$  at  $[Cr^{III}(IBUP)(H_2O)_4]^{+2} = 5 \times 10^{-3}$  mol dm<sup>-3</sup>, I=0.4 mol dm<sup>-3</sup> and T = 30 °C.

$10^3 [IO_4^-]$ mold m <sup>-3</sup>	PH=1.2	PH=1.6	PH=1.9	PH=2.4
	$k_{obs}$	$k_{obs}$	$k_{obs}$	$k_{obs}$
0.005	0.010	0.031	0.038	0.035
0.015	0.031	0.036	0.039	0.045
0.025	0.044	0.049	0.050	0.059
0.035	0.045	0.050	0.053	0.066
0.045	0.051	0.064	0.066	0.093
0.05	0.055	0.074	0.078	0.132

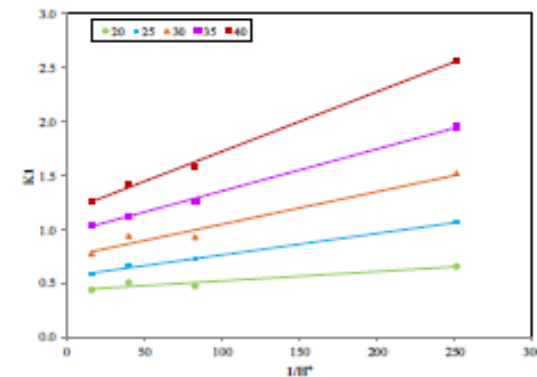


Figure (5): Values of  $k_1$  against  $1 / [H^+]$  at different temperatures.

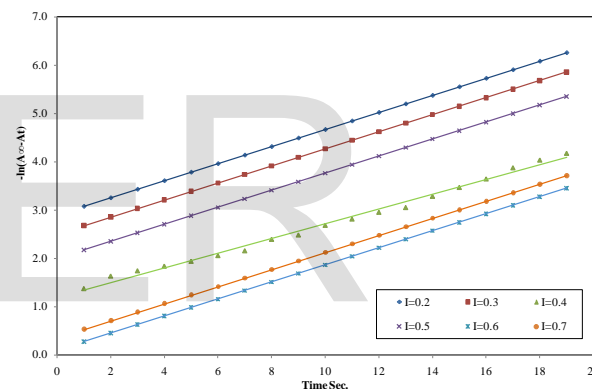


Fig. (6).  $k_{obs}$  with different ionic strength values at temp.=30 °C, pH = 1.9

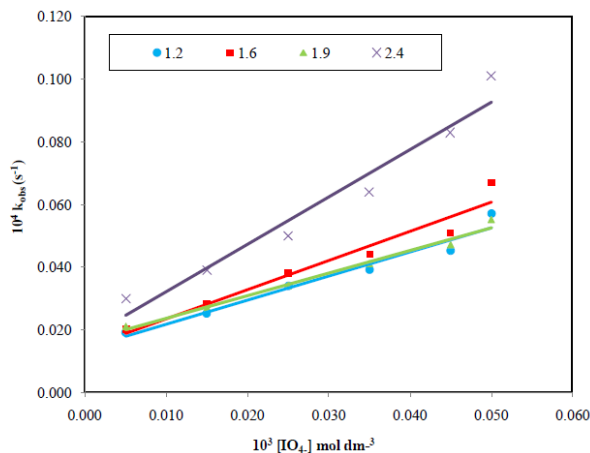


Figure (4): Effect of pH on  $k_{obs}$  at  $[Cr^{III}(IBUP)(H_2O)_4]^{+2} = 5 \times 10^{-3}$  mol dm<sup>-3</sup>, I=0.4 mol dm<sup>-3</sup> and T = 30°C.

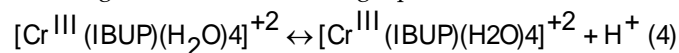
Table (III): Values of  $k_1$  against  $1 / [H^+]$  at different temperatures.

Temperature (°C)	$10^{-3} k_1$ (s <sup>-1</sup> )
20	0.88
25	0.984

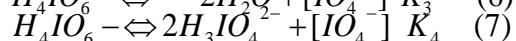
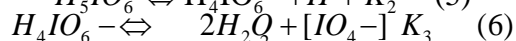
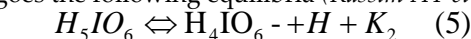
### DISCUSSION:

We propose that the oxidation of  $[Cr(III)-IBUP]$  complex by periodate proceeds via inner sphere mechanism. In acidic medium and take this formula  $[Cr^{III}(IBUP)(H_2O)_4]^{+2}$  according to the above mentioned experimental data and analysis.

$[Cr^{III}(IBUP)(H_2O)_4]^{+2}$  in an aqueous media  
Going to under the following equilibrium:



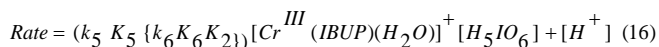
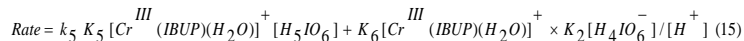
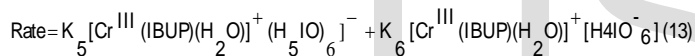
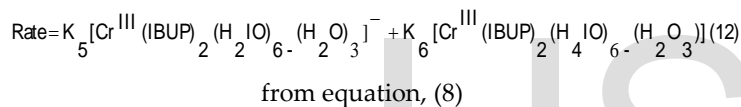
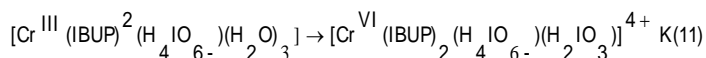
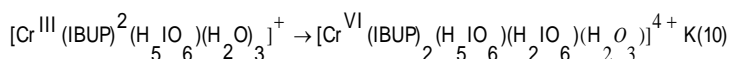
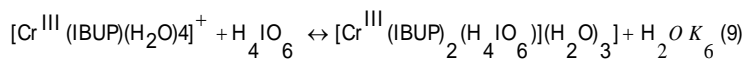
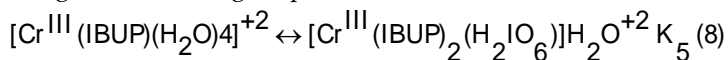
According  $K_1$  value the reactive species is  $[Cr^{III}(IBUP)(H_2O)_4]^{+2}$  at pH range [1.2 –2.4] periodate undergoes the following equilibria (Kassim AY et al., 1977).



The equilibrium constant  $K_2$ ,  $K_3$ , and  $K_4$  are  $[5.1 \times 10^{-4}$ , 40 and  $2.0 \times 10^{-7}]$  respectively. Thus, it may be concluded

that over pH range used periodate will be present as  $H_5IO_6$  and  $H_4IO_6^-$  (Hussein MA et al., 1988).

According to the experimental rate law, the following mechanism is reported, since the reaction rate increased as pH increases, the deprotonated form of the complex is involved in the rate determining step. Also, reaction rate unchanged with increasing of ionic strength. These conditions proven that reaction carried out through charged and uncharged species.



Obtained rate law, equation (16) is identical to the experimental rate law equation (2), confirmed the proven mechanism. Doing in comparison between the two equations showed that:

$$k_5 K_5 = k_2$$

$$k_6 K_6 K_2 = k_3 + k_4$$

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