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Kinetics of Oxidation of Methionine by Chromic Acid in Sulphuric Acid Medium

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Kinetics of oxidation of methionine by chromic acid in sulfuric acid medium has been investigated. The reaction is second order; first order each with respect to [methionine] and [chromic acid]. Iodometric titrations were done for study of rate of reaction. The rate constants (K_2) have been computed by integration method as well as by graphical method.

INTRODUCTION

Kinetics is concerned with the rate of reaction, the influence of various conditions on these rates and mechanisms by which a reaction occurs. The subject of chemical kinetics covers not only reaction rate but also covers a wide range of studies, which includes empirical studies of the effects of concentration, temperature, hydrostatic pressure, pH, catalyst etc. on reactions of various types. It has proved to be the best means of study of various reactions such as oxidation, thermal decomposition, halogenation, hydrogenation, etc. For large-scale production of compounds, it is very essential to know the velocity of the reaction[1].

Oxidation-reduction reactions are those reactions, which involve transfer of electrons from one atom to another. These involve the use of many oxidizing agents. Commonly used oxidizing agents include potassium permanganate, potassium dichromate, hydrogen peroxide, chromic acid, etc[2]. Among the various types of oxidants employed metal ions are widely used in organic chemistry. Chromates, vanadates, manganates, cobaltates and cerrates, arsenates find extensive use as oxidizing agents. Analytical importance or redox reactions is as extenstive as those of acid-base reaction. These are also used in the quantitative analysis of various compounds. The metal ion oxidation studies are important not only from synthetic but also from theoretical and kinetic point of view[3].

Chromic acid acts as a very good oxidizing agent. It readily oxidizes compounds thereby reducing itself. This is clearly visible by the color change exhibited by chromic acid in redox reactions. The change in color depicts change in oxidation number. Chromium exhibits +6, +3 and +2 oxidation states[4]. Change in oxidation number and respective change in color of chromium is shown below in Table-1.

TABLE-1
OXIDATION STATES EXHIBITED BY CHROMIUM

Characteristics	Oxidation state of chromium			
Chromium ions	$Cr_2O_7^{2-}$	Cr^{3+}	Cr^{2+}	CrO_3
Oxidation number	+6	+3	+2	+6
Colour	Orange	Green	Blue	Reddish orange
	Oxidizing	Most stable	Reducing	Oxidizing

Chemically, methionine is α-amino γ-methyl thiobutyric acid. It was discovered as a growth factor from a strain of hemolytic *streptococcus*. This amino acid is an essential constituent of the diet and has lipotropic action similar to that of choline. It facilitates recovery from liver diseases. It also enhances the synthesis of glutathione necessary for the detoxification of the toxic metabolite of paracetamol. It is useful in the treatment of paracetamol poisoning[5]. Like other amino acids, methionine is also susceptible to oxidation. The oxidative enzymes and other oxidizing agents result in oxidative deamination of amino acids to form keto acids and ammonia[6]. It was observed that methionine oxidizes very easily in presence of chromic acid and that it has been possible to obtain satisfactory kinetic results. There is no evidence of any systematic investigation in the literature on the kinetics of oxidation of methionine with chromic acid in sulfuric acid medium. Hence, the present work is undertaken with a view to seek the reaction kinetics and various factors affecting it.

EXPERIMENTAL

Standard solutions of methionine, chromic acid, potassium iodide, and potassium iodate, sodium thiosulfate, sulfuric acid and starch were prepared as per the methods given in Indian Pharmacopoeia[7]. All the chemicals used were of AnalaR grade.

Stoichiometry: Determination of stoichiometry is the stepping-stone for the correct approach towards the mechanistic study of any reaction. The estimation of unreacted chromic acid stabilizes 1 : 4 stoichiometry (methionine : chromic acid) and thus the oxidation is believed to proceed accordingly. All the studies were performed on the basis of this stoichiometry.

Rate Measurements: The kinetics of oxidation of methionine by chromic acid was performed titrimetrically. The unused chromic acid was titrated iodometrically[8] at regular intervals. The kinetics was followed by monitoring the decrease in concentration of chromic acid with time. The order was determined and then the various factors such as rate with respect to concentation of reactants, temperature and pH were determined. All the titrations were performed at 308 ± 1 K.

RESULTS AND DISCUSSION

The oxidation of methionine with chromic acid in sulfuric acid medium was observed feasible. The stoichiometry of the reaction was determined by employing the classic method and was found to be 1 : 4 with respect to amino acid and oxidant. The order of reaction was calculated by integration method and further confirmed by graphical method. The order of reaction was determined at equivalent and non-equivalent concentrations of reactants.

The reaction follows second order kinetics at stoichiometric and non-stoichiometric concentration of reactants. A linear plot between 1/(a – x) *versus* time 't' supports second order kinetics as shown in Fig. 1. The order with respect to [methionine] and [chromic acid] showed first order dependence as is evident by Fig. 2. Moreover, the rate shows increase with increase in [H^+] and temperature. The orders were confirmed by initial rate method and half-life method.

According to Arrhenius, the velocity constant of a chemical process increases exponentially with the temperature for a large number of reactions. It was observed that a plot between log K and 1/T gives a linear relation, which shows that the reaction abides Arrhenius relationship as given in Fig. 3. The slope gives the value of E/2.303 R, from which E, *i.e.*, the activation energy was evaluated. The temperature coefficient of the reaction is 1.478 and the average activation energy calculated from Arrhenius equation and slope of Arrhenius plot is found to be 8.123×10^3 cal K^{-1} mol^{-1}.

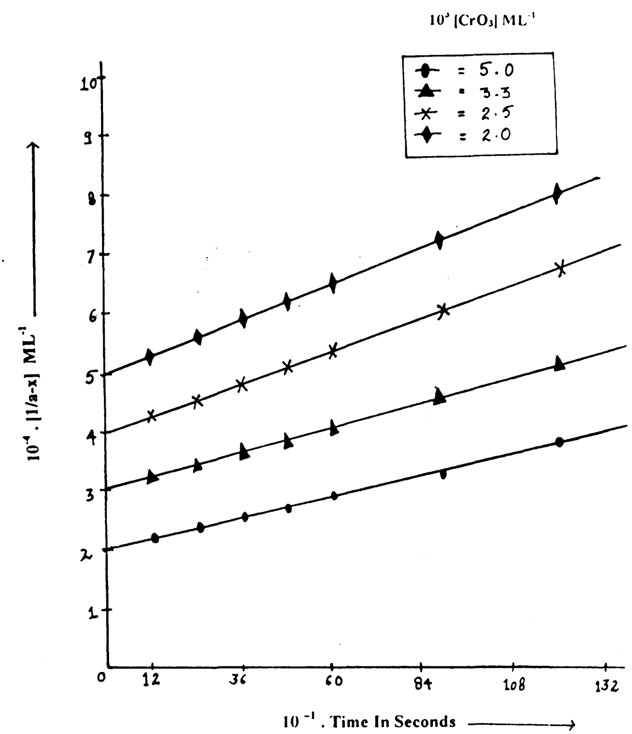

Fig. 1. Order of reaction at equivalent concentration.

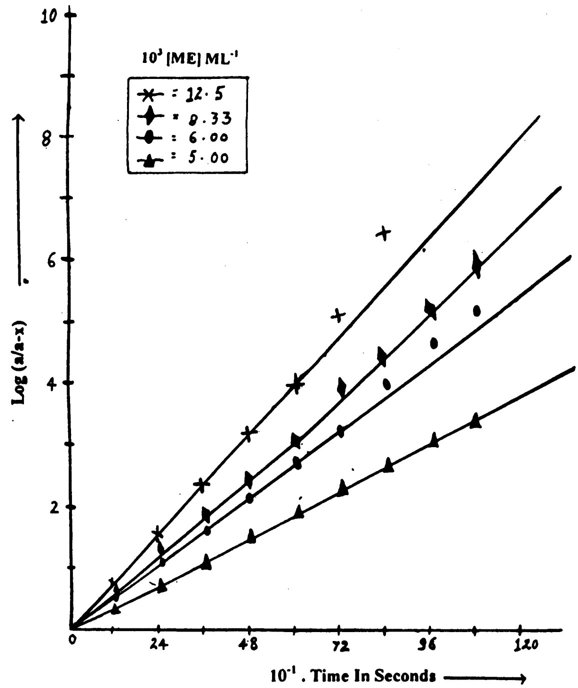

Fig. 2. Order of reaction with respect to substrate.

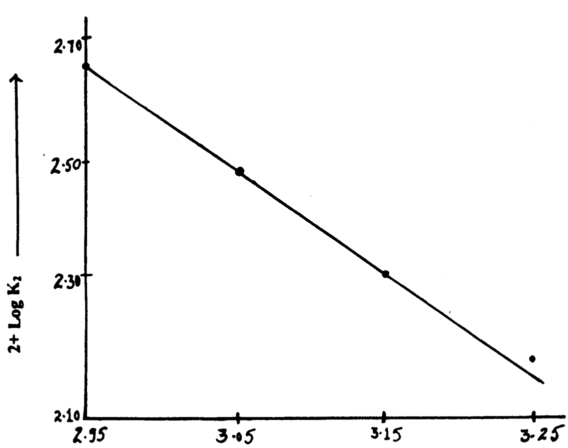

Fig. 3. Arrhenius plot.

Conclusions

The following conclusions can be drawn from the present work under the observed test conditions:

1. The oxidation of methionine with chromic acid in sulfuric acid medium is feasible and chromic acid acts as a reactant and not catalyst but rather an oxidant.
2. The stoichiometry of the reaction between methionine and chromic acid is 1 : 4.
3. The oxidation reaction between methionine and chromic acid is second order kinetics.
4. The order with respect to reactant as well as oxidant is first order.
5. The reaction shows increase in rate when pH increases.
6. The reaction shows positive effect when temperature is increased, *i.e.*, the reaction rate increases on increasing the temperature and it obeys Arrhenius relationship.

REFERENCES

1. C.W. Wood and A.K. Holliday, Physical Chemistry, 3rd Edn., English Language Book Society and Butterworths, London (1973).
2. F.A. Cotton and R.R. Wilkinson, Modern Inorganic Chemistry, 5th Edn., Wiley Interscience Publication (1985).
3. P.L. Soni, Inorganic Chemistry, 17th Edn., Sultan Chand & Sons (1985).
4. B.K. Sharma, Inorganic Chemistry, 4th Edn., Krishna Prakashan (1994).
5. The Merck Index, 11th Edn., Merck & Co. Inc., Rahway, New Jersey (1989).
6. M.N. Chatterjee and Rana Shinde, Textbook of Medical Biochemistry, 1st Edn., Jaypee Brother Medical Publishes Pvt. Ltd. (1984).
7. Indian Pharmacopoeia, 3rd Edn., The Controller of Publications, Ministry of Health and Family Welfare, New Delhi (1985).
8. Vogel, Textbook of Quantitative Inorganic Analysis, 4th Edn., ELBS (1986).

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