



Anderson type Hexamolybdochromate (III) catalyzed oxidation of acetic acid hydrazide by KBrO_3 in acidic medium

Kadam S.D.* and Gokavi G.S.

Kinetics and Catalysis Laboratory, Department of Chemistry, Shivaji University Kolhapur 416004, India
kadamssanjay123@gmail.com

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Abstract

The kinetic and mechanistic investigation of Anderson type hexamolybdochromate (III) catalyzed oxidation of acetic acid hydrazide by KBrO_3 has been carried out in hydrochloric acid. The order in hydrogen ion was found to be 1.77 due to protonation equilibria of both hexamolybdochromate and hydrazide. Oxidation reaction obeyed first order with respect to bromate, hydrazide and hexamolybdochromate concentrations. The mechanism of reaction involves hydrazide and monoprotonated form of catalyst which is the reactive species in reaction. The initiation of reaction occurs through oxidation of catalyst $\text{H}[\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{2-}$ to $[\text{O}=\text{Cr}^{\text{V}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{3-}$, which then reacts with hydrazide to give product without any intervention of free radical. The oxidized form of catalyst $[\text{O}=\text{Cr}^{\text{V}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{3-}$ was isolated and characterized by FTIR spectra. The effect of ionic strength and dielectric constant of medium on the reaction was also studied. Moreover the thermodynamic parameters E_a , ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger were also calculated to propose mechanism of oxidation reaction.

Keywords: Acetic acid hydrazide, Bromate, Oxidation, Catalysis, Hexamolybdochromate.

Introduction

Hydrazides are the derivatives of hydrazine and carboxylic acids which are used as significant preparatory materials in synthetic organic chemistry¹. These compounds form complexes with transition metals and make them effective reagents for extraction of metal, polymer stabilization and for ion exchange problems. Hydrazides also have various properties like bactericidal, anti-fungal, carcinostatic and also their biological activity increase by complexation with metal ion²⁻⁸. Hence they have many applications in medicine and analytical chemistry². The carbonyl oxygen and the nitrogen of the amino group of the hydrazine moiety of the hydrazide form bidentate ligands with the metal ions⁴. Most oxidant reacts with hydrazides which produce the corresponding acids and also some oxidant convert them into esters, amides or N-N-diacylhydrazines⁹⁻¹¹.

Polyoxomolybdates of the Keggin structure have been utilized as oxidation catalysts for various catalytic oxidations of organic and inorganic compounds and their mechanism was also proposed but less information is available about Anderson type polyoxometalate as a catalyst¹²⁻¹⁹.

The structure of Anderson type polyoxometalates has been described as an isopolyoxometalate which contains a crown of six octahedrons at the sharing edges. The center of structure may or may not be occupied. The structure of polyoxometalate with chromium as hetero atom contains six hydrogen atoms and their positions are considered as the six $-\text{OH}$ groups which bridge the central atom to the molybdenum containing crown octahedrons. Perloff investigated detailed structure of the

heteropoly salt of $\text{Na}_3[\text{CrMo}_6\text{O}_{24}]\cdot 8\text{H}_2\text{O}$ and established that the anion has the same structure as $[\text{TeMo}_6\text{O}_{24}]^{6-}$ anion with an excellent agreement and concluded that hydrogen atoms of salt are bonded to oxygen atoms which is then coordinated to Cr atom²⁰.

Potassium or sodium bromates are stable solids and strong oxidizing reagents used in various organic transformations²¹. The bromate oxidations are mainly yields Br^- ion which is easily handled and recycled thus oxidation by KBrO_3 are naturally caring than metal ion. The oxidative transformations by bromate are generally slow and in presence of a catalyst they proceed with a measurable rate. Hence in the present work in continuation of our interest in polyoxometalate catalyzed reactions, we have used Anderson type hexamolybdochromate (III) as catalyst for oxidation of acetic acid hydrazide by using KBrO_3 to know the probable pathway of its oxidative degradation²²⁻²⁴.

Materials and Methods

Materials and reagents: The solution of acetylhydrazide (Alfa Aesar) was prepared by dissolving requisite amount of it in doubly distilled water. Sodium hexamolybdochromate (III) was prepared by the previously reported method²⁰. The purple colour salt $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]\cdot 8\text{H}_2\text{O}$ was characterized by FTIR using Perkin-Elmer-783 in KBr pellet (Figure 4A). The solution of hexamolybdochromate was prepared by dissolving required amount of it in doubly distilled water. Also the solution of potassium bromate (BDH) prepared in doubly distilled water and then solution was standardized by iodometric titration.

Potassium chloride solution was used for adjusting the ionic strength and HCl (BDH) was used to vary H^+ ion concentration. All chemicals were of reagent grade and doubly distilled water was used throughout the work.

Experiment: The kinetic study of oxidation of acetic acid hydrazide by using $KBrO_3$ was carried out under pseudo-first order conditions keeping concentration of acetic acid hydrazide ten times than the concentration of bromate at temperature $28.0 \pm 0.1^\circ C$. To initiate the reaction specified volume of thermostated bromate was rapidly added to the mixture specified volume of thermostated acetic acid hydrazide, hexamolybdochromate, hydrochloric acid, potassium chloride and doubly distilled water. The reaction was monitored by measuring unconsumed $KBrO_3$ by iodometric titration at certain time interval. Then pseudo-first order rate constants ($k_{obs} s^{-1}$) were calculated from the slope of linear graph of $\log [KBrO_3]$ versus time were calculated which up to 90% completion of the reaction. The rate constants are consistent within $\pm 6\%$.

Stoichiometry and reaction product: In 10 ml of 0.6 M hydrochloric acid 40 μM (5.0 mg) of hexamolybdochromate and 3.0 mM (0.222 g), of acethydrazide were dissolved. Then in the above solution 2 mM (0.334 g), potassium bromate was added. The reaction mixture obtained was stirred at $28^\circ C$ for five minutes and kept it in a thermostat for 24 hours to complete the reaction. After 24 hours reaction was complete. Then the reaction mixture was subjected to distillation in order to separate out organic matter. This process was repeated 4-5 times to get sufficient quantity of distillate, which is used for further analysis. The amide derivative of the product, acetic acid was prepared²⁵. The observed physical constant ($83^\circ C$) of amide derivative was found to be in good agreement with those of acetamide²⁵ ($80-82^\circ C$).

Results and Discussion

Effect of oxidant and hydrazide concentrations: The effect of oxidant bromate and hydrazide were studied under pseudo-first-order conditions keeping the [hydrazide] in large excess over [bromate] keeping concentration of catalyst and hydrochloric acid constant at $1.0 \times 10^{-4} M$ and 0.1 M respectively and also at constant temperature and ionic strength of 0.5 M (Table-1). The plots of $\log [BrO_3^-]$ versus time were found to be linear. The values of rate constants were fairly constant as the concentration of both bromate and hydrazide were varied (Table-1). Hence order with respect to hydrazide and oxidant is unity for both of the reactants.

Catalyst concentration effect on the reaction: To study effect of catalyst concentration on the reaction, the reaction was studied by changing its concentration in between 0.5×10^{-4} and $5.0 \times 10^{-4} M$, keeping concentration of hydrazide, bromate and HCl fixed at 0.01 M, 0.001 M and 0.1 M respectively, and also at constant temperature and ionic strength. The reaction shows first order dependence on catalyst concentration since the plot of

$k_{obs} s^{-1}$ against $[H_6Cr^{III} Mo_6O_{24}]^{3-}$ (Figure-1) was found to be linear ($R^2=0.9801$).

Table-1
Effects of variation of acetic acid hydrazide, $KBrO_3$ and HCl concentrations on the rate of reaction

10^2 [acethydrazide] M	10^3 [$KBrO_3$] M	$10[HCl]$ M	$10^3 k_{obs} s^{-1}$
0.5	1.0	1.0	0.88
0.8	1.0	1.0	0.82
1.0	1.0	1.0	0.83
2.5	1.0	1.0	0.84
5.0	1.0	1.0	0.83
1.0	0.4	1.0	0.91
1.0	0.8	1.0	0.88
1.0	1.0	1.0	0.80
1.0	2.0	1.0	0.85
1.0	4.0	1.0	0.91
1.0	1.0	0.4	0.17
1.0	1.0	0.6	0.44
1.0	1.0	0.8	0.78
1.0	1.0	1.0	0.92
1.0	1.0	2.0	3.32
1.0	1.0	3.0	6.59
1.0	1.0	4.0	11.49

$[H_6Cr^{III} Mo_6O_{24}]^{3-} = 1.0 \times 10^{-4} M$ and $I = 0.5 M$

Effect of H^+ ion on the reaction: The effect of H^+ ion on reaction was carried out for identification of reactive species of reactants in the reaction and also to determine order of reaction with respect to H^+ ion concentration. The $[H^+]$ ions was varied between 0.04 M and 0.4 M keeping concentration of substrate, oxidant, catalyst fixed (Table-1). The rate of reaction was accelerates as $[H^+]$ ion increases in solution. Then by plotting graph of $\log k_{obs}$ versus $\log [H^+]$, order in hydrogen ion determined is 1.77.

Ionic strength effect on the reaction: The reagent grade potassium chloride was used to study effect of the ionic strength

on the rate of reaction. As ionic strength varied from 0.05 M to 0.5 M the value observed rate constant also increases shows the reaction between similar kinds of charged ions.

Effect of dielectric constant of medium: The percentage of acetonitrile was varied between 10 and 40 % v/v to understand effect of dielectric constant of medium on the reaction. The rate of reaction increases as the percentage of acetonitrile increases in the reaction mixture. Then from the dielectric constant values of pure solvents, the dielectric constant values of reaction mixtures were determined. Also the plot of $\log k_{\text{obs}}$ versus $1/D$ was found to be linear with positive slope (Figure-2).

Effect of temperature: The reaction was studied at different five temperatures in between 20 and 40°C to study temperature effect on the oxidation reaction. The observed value of pseudo-first order rate constants (k_{obs}) for different five temperatures was $3.5 \times 10^{-4} \text{ s}^{-1}$, $6.3 \times 10^{-4} \text{ s}^{-1}$, $8.8 \times 10^{-4} \text{ s}^{-1}$, $1.28 \times 10^{-3} \text{ s}^{-1}$ and $2.9 \times 10^{-3} \text{ s}^{-1}$ respectively. The thermodynamic activation parameters are evaluated as $E_a = 81.61 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 79.61 \text{ kJ mol}^{-1}$, $\Delta G^\ddagger = 91.32 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -38.85 \text{ JK}^{-1} \text{ mol}^{-1}$.

Test for free radical intervention: The rate of reaction was unaffected by added acrylonitrile and also no formation precipitation observed due to polymerization by added acrylonitrile which confirms no any intervention of free radical in the reaction.

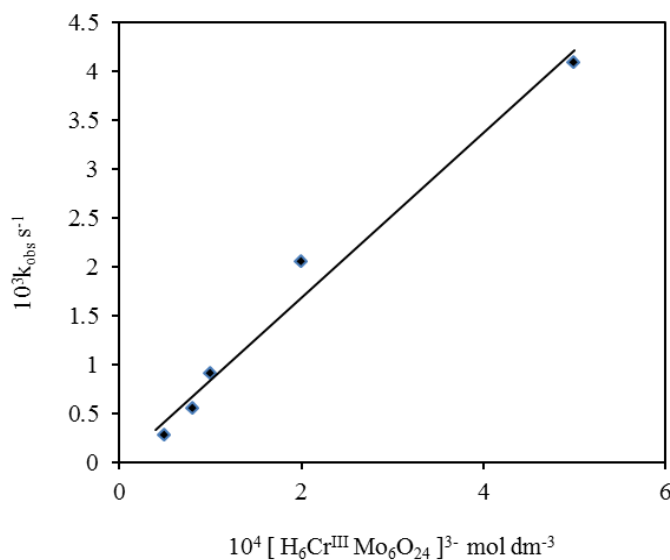


Figure-1
Effect of concentration of $[\text{H}_6\text{Cr}^{\text{III}} \text{Mo}_6\text{O}_{24}]^{3-}$ on the rate of reaction

Discussion: Oxidation reaction of inorganic substrates like V^{IV} and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ by bromate have been studied along with their stoichiometry predicts either Br_2 or HOBr as the product of reduction of bromate^{26, 27}. The oxidation potential of HOBr and Br_2 were respectively 1.34 and 1.07 V indicating that the

substrate, acetylhydrazide was easily oxidized into acid by HOBr and Br_2 in acidic medium. Therefore, in order to confirm the end product of the oxidant, either bromide ion or bromine, the reaction was studied in H_2SO_4 medium instead of HCl solution.

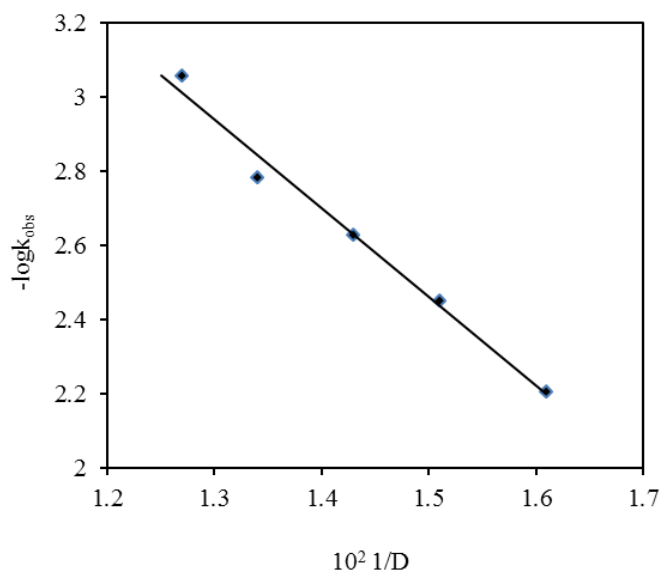
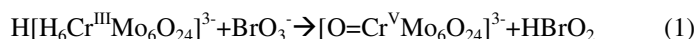


Figure-2
Effect of dielectric constant on the rate of reaction

After completion of the reaction, silver nitrate was added to the reaction mixture which gives precipitate of silver bromide confirming one of the products of oxidation that is bromide ion. Moreover no bromine was liberated either during the product analysis or at the time of kinetic measurements of reaction which duly confirmed the product of oxidation as bromide ion. From kinetic results, reaction shows first order with respect to oxidant and hydrazide concentration, as the values of k_{obs} are fairly constants for both of them (Table-1). The graph of k_{obs} versus $[\text{H}_6\text{Cr}^{\text{III}} \text{Mo}_6\text{O}_{24}]^{3-}$ is linear ($R^2 = 0.977$), indicating first order with respect to catalyst concentration. Since uncatalysed reaction does not proceed under the investigational condition, catalytic reaction initiates with the interaction between catalyst and oxidant. The catalyst used in the present investigation is a hexamolybdochromate and its structure is not suitable for the formation of a complex with substrate hydrazide because the Cr^{III} atom is covered by the six molybdate. Hence the catalyst acts as an inert redox catalyst. As a result oxidation reaction initiates with the oxidation of the $\text{H}[\text{H}_6\text{Cr}^{\text{III}} \text{Mo}_6\text{O}_{24}]^{3-}$ to $[\text{O}=\text{Cr}^{\text{V}} \text{Mo}_6\text{O}_{24}]^{3-}$ by bromate in a prior fast step, which then oxidises the substrate. In acidic solutions, the stable oxidation states of chromium are Cr^{VI} and Cr^{III} . Intervention of either Cr^{V} or Cr^{IV} is predicted in most of the oxidations of Cr^{III} by various oxidizing agents and these are stabilized in presence of ligands like 2-ethyl-2-hydroxy butyric acid²⁸. The former is a two-electron oxidant whereas the later is a one-electron oxidant. In absence of stabilizing ligands like 2-ethyl-2-hydroxybutyric acid the oxidation of a substrate by Cr^{IV} , produces Cr^{III} as a result of one-electron change, which leads to the generation of a free

radical. Since, in the present study test for formation of free radical was negative, it was assumed that the oxidized form of the catalyst undergo two-electron change. Therefore, oxidation of molybdochromate by bromate results into the formation of Cr^{V} -molybdate which then absorbs two electrons from the hydrazide without any intervention of free radical. Therefore, for the confirmation of formation of Cr^{V} -molybdate, FTIR spectrum of green compound obtained by treating Cr^{III} -molybdate with bromate in hydrochloric acid that was investigated. The FTIR of the green product obtained shows that the peak corresponding to M-O-M stretching at 651 cm^{-1} (Figure-4A) was splitted into two peaks (Figure-4B) because oxidation state Cr^{III} atom changes to Cr^{V} . There was also a new peak at 829 cm^{-1} corresponding to the $\text{Cr}^{\text{V}}=\text{O}$. Such type of oxidation of Cr^{III} polyoxometalates has also been reported while studying the preparation of chromium substituted heteropolytungstate anions²⁹. Therefore, the Cr^{III} -molybdate under the experimental conditions gets oxidized to Cr^{V} -molybdate according to the Equation 1.



The rate of reaction was accelerates as $[\text{H}^+]$ ion increases and the order in hydrogen ion was found to be 1.77, due the involvement of two protonation equilibria. Since in the present investigation, the reaction was studied in acidic condition the protonation of potassium bromate does not take place as it is a strong electrolyte and that exists as BrO_3^- in solution that is a strong acid. Hence order in hydrogen ion concentration 1.77 is due to protonation of hydrazide and catalyst in acidic solution³⁰. The Anderson type polyoxometalates are known to undergo selective protonation at the oxygen atom shared by two Mo atoms³¹. The catalyst prepared is $[\text{H}_6\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ which has three successive protonation among which the monoprotonated form is the reactive species in the present reaction.

The kinetic data obtained satisfactorily explain monoprotonated form of catalyst and protonated form of hydrazide. Hence mechanism of the reaction was summarized on the basis of kinetic results in the Scheme 1 considering protonated forms of the substrate and the catalyst. These are in active form and information with their respective equilibria. According to Scheme 1, oxidation reaction was initiated by the oxidation of $\text{H}[\text{H}_6\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ to $[\text{O}=\text{Cr}^{\text{V}}\text{Mo}_6\text{O}_{24}]^{3-}$ by oxidant in a prior equilibrium, then Cr^{V} -molybdate oxidizes the hydrazide to an intermediate RCONNH, acyl diimide. This type of acyl diimide formation was reported in oxidation of hydrazides by various oxidizing agents¹. The acyl diimide gives acetic acid as a product and another intermediate $\text{HN}=\text{NH}$ due to nucleophilic attack of H_2O on the carbonyl carbon of the acyl diimide. The change in FTIR spectrum of the oxidized catalyst (Figure-4B) is observed as compared to that of the catalyst that supports formation of Cr^{V} . Hence, the interaction between oxygen atom of oxidized form of catalyst and hydrogen atom of the ammonium group of the hydrazide moiety occurs to form probable transition state of reaction (Figure-3).

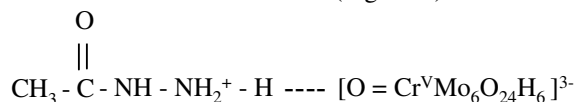


Figure 3
Structure of probable transition state

The reaction between similar kinds of charged ions can be qualitatively explained on the basis of ionic strength effect on the reaction rate. As the content of acetonitrile in the reaction mixture increases the rate of reaction also increases. As the size of probable transition state is large, that is less solvated and become more stable in the medium of higher relative permittivity as observed³². The negative value entropy of activation supports formation of such a transition state (Figure-3).

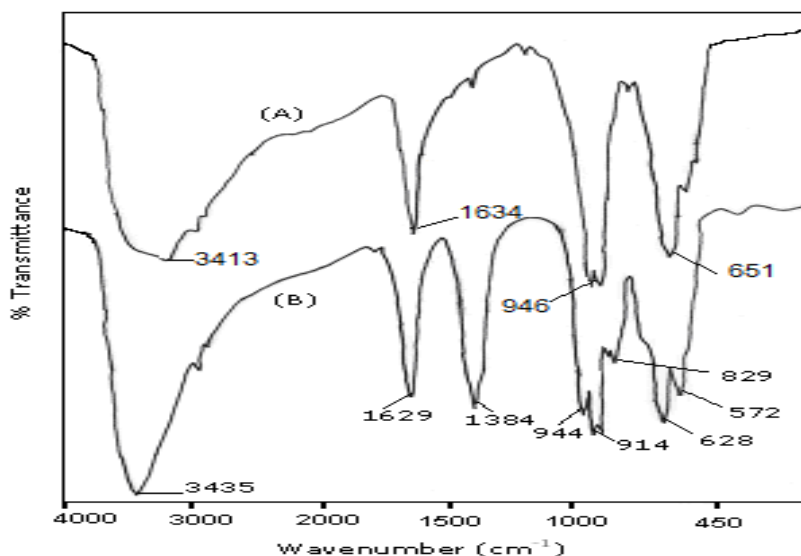
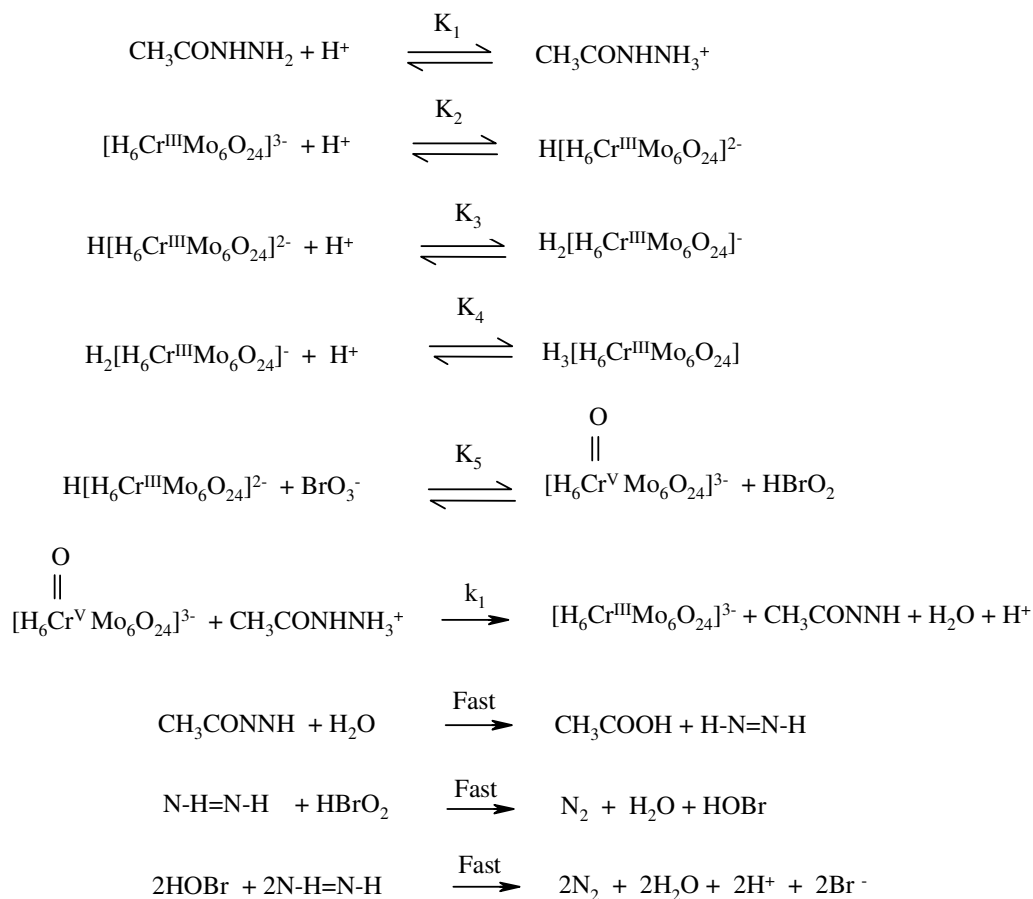


Figure-4
FT-IR Spectra of (A) hexamolybdochromate (III) and (B) hexamolybdochromate (V)



Scheme-1
Mechanism of Reaction

According to scheme-1, rate of reaction is given by Equation-2 and the observed pseudo-first order rate constant is given by Equation-3 as follows,

$$\text{Rate} = \frac{k_1 K_1 K_2 K_5 [\text{H}^+]^2 [\text{CH}_3\text{CONHNH}_2] [\text{BrO}_3^-] [\text{H}_6\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}}{(1 + K_1 [\text{H}^+]) (1 + K_2 [\text{H}^+] + K_2 K_3 [\text{H}^+]^2 + K_2 K_3 K_4 [\text{H}^+]^3)} \quad (2)$$

$$K_{\text{obs}} = \frac{k_1 K_1 K_2 K_5 [\text{H}^+]^2 [\text{H}_6\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}}{(1 + K_1 [\text{H}^+]) (1 + K_2 [\text{H}^+] + K_2 K_3 [\text{H}^+]^2 + K_2 K_3 K_4 [\text{H}^+]^3)} \quad (3)$$

Conclusion

The hexamolybdochromate (III) acts as catalyst for reaction between acethydrazide and KBrO_3 in acidic condition more effective than metal ion. The reaction was initiated by oxidation of catalyst $\text{H}[\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{2-}$ to $[\text{O}=\text{Cr}^{\text{V}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{3-}$ by KBrO_3 , which then reacts with hydrazide to give product without any intervention of free radical. The product of

oxidation is acetic acid. The thermodynamic parameters also have been evaluated for the rate determining step and the plausible mechanism of reaction was proposed. From the kinetic investigation, it is concluded that protonated form of the substrate and the monoprotonated form of catalyst are reactive species in the investigated reaction.

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