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Cu(II) catalyzed oxidation of mercaptoacetic acid by methylene blue in acidic medium: Influence of solvent and morphology

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ABSTRACT

Kinetic studies on the Cu(II) catalyzed oxidation of mercaptoacetic acid (thioglycolic acid, TGA) by the model electron receptor methylene blue in acidic medium show that the reaction follows a second order kinetics in TGA. The order in methylene blue is unity but at higher [TGA], the order is 3/4. The rate shows an inverse relationship with [H⁺] and a second order dependence on [Cu(II)]. The reaction conforms to Arrhenius behavior in aqueous medium but resorts to anti-Arrhenius behavior in aqueous methanol and in aqueous acetone media. The reaction involves the in situ participation of nanoparticles which has been confirmed by SEM, XRD, and FTIR techniques. In aqueous medium, cauliflower shaped nanoparticles (44.21–74.33 nm) are obtained but in the presence of acetone and methanol, nanogranules (38.96–70.73 nm) and nanodisks (47.30–72.16 nm), respectively, are produced at 35°C as revealed by SEM images and XRD data. The reaction is characterized by the participation of two transition states in aqueous acetone medium and the kinetics of the reaction, especially the temperature dependence, is governed by the adsorption of methylene blue on copper nanoparticles as influenced by morphology inter alia dielectric constant of the reaction medium.

ARTICLE HISTORY

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KEYWORDS

Oxidation; kinetics; mercaptoacetic acid; methylene blue; nanocatalysis; anti-Arrhenius behavior

GRAPHICAL ABSTRACT



Introduction

Sulfhydryl substrates are known to play an important role in the regulation of biochemical processes such as respiration and cell division, and the sulfur cycle is regarded to be as indispensable as the nitrogen and carbon cycles are in living systems.

The oxidation of thiols to disulfides is of paramount importance in providing stability to the protein structures and RSH/RSSR couples are important in maintaining the redox potential at biological sites.¹ Methylene blue (MB), the oxidant employed presently is a phenothiazine dye that has been widely used as a photosensitizer in photodynamic therapy, e.g., in the treatment of tumor and hepatitis C.² Due to the capability of changing their oxidation states, transition metal ions often act as promoters of free radical reactions³ and also act as catalysts involving nanocatalysis in some cases. This has motivated us to investigate the oxidation of some sulfhydryl molecules by the model electron receptor MB in the presence of metal ions such as Cu(II) and Ru(III).⁴⁻⁸ The sulfhydryl compounds act as reducing agents as well as the capping reagents in the synthesis of nanoparticles^{9,10} and it seems that this has a bearing on Cu(II)-catalyzed oxidation of mercaptoacetic acid (thioglycolic acid, TGA) by MB in acidic medium reported presently. The reaction exhibits anti-Arrhenius behavior in the presence of non-aqueous solvents such as methanol

CONTACT K. K. Mishra kkmishra.chem@gmail.com Department of Chemistry, Rani Durgavati University, Jabalpur, India Supplemental data for this article can be accessed on the publisher's website at http://dx.doi.org/10.1080/10426507.2015.1085039.

Table 1. Effect of variation of [TGA] on the rate constant [MB] = 2.0×10^{-5} M; [HCI] = 0.1 M; [CuSO₄] = 2.0×10^{-6} M; I = 0.1 M; Temp. = 35° C.

$[\text{TGA}]\times 10^3 \text{ M}$	$k_1 imes 10^4 \ { m s}^{-1}$	$k_{\rm 3/4} imes 10^5 { m M}^{1/4} { m s}^{-1}$
2.0	1.3	
3.0	3.5	
4.0	7.2	
4.4	8.9	
5.0	12.5	
6.0		10.85

Table 2. Effect of variation of initial concentration of methylene blue [TGA] = 3.0×10^{-3} M; [HCI] = 0.1 M; [CuSO₄] = 2.0×10^{-6} M; l = 0.1 M; Temp = 35° C.

$[MB] \times 10^5 M$	$k_{\rm 1} imes 10^4 { m s}^{-1}$	$k_2 {\rm M}^{-1} {\rm s}^{-1}$
0.5	4.1	
1.0	3.4	
2.0	3.5	
2.5		13.43
3.0		11.30
3.5		10.36

and acetone which is ascribed to the influence of morphology of Cu nanoparticles on the rate of reaction.

were also verified by van't Hoff differential and graphical methods (Figure 1). The statistical treatment of kinetic data also confirms this conclusion.

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Results and discussion

Stoichiometry and the reaction products

The principal reactants interact in a molar ratio of 2:1 forming the end products disulfide and dihydromethylene blue as was determined spectrophotometrically. It was experimentally observed that MB is completely reduced to give dihydromethylene blue (leucobase, H₂MB) showing maximum absorbance at 257 nm¹¹ whereas the formation of the disulfide RSSR was qualitatively demonstrated by recording the FTIR spectra of the reaction mixture after completion of reaction which shows the characteristic S–S linkage near 443.6 cm⁻¹.¹² Therefore, the chemical reaction is represented as:

$$2RSH + MB \longrightarrow RSSR + H_2MB$$

Kinetic features of the reaction

The order of reaction in MB was determined by employing the Ostwald isolation method¹³ and the runs with 200- to 500-fold excess [TGA] over [MB] were followed. At low concentrations of mercaptoacetic acid (TGA) (ca. $\leq 5.0 \times 10^{-3}$ M), the order of reaction in MB is 1 but at higher concentrations, the order changes from 1 to 3/4 as shown in Table 1. These conclusions



Figure 1. Plot of log(*a*−*x*) versus time *t* at different [TGA]. [TGA] = 2.0×10^{-3} M (♠), 3.0 × 10⁻³ M (■), 4.0 × 10⁻³ M (**x**), 4.4 × 10⁻³ M (♠), 5.0 × 10⁻³ M, (✦) [HCI] = 0.1 M, [Cu(II)] = 2.0×10^{-6} M; [MB] = 2.0×10^{-5} M, Temp. = 35° C.

The values of the rate constant $k_{3/4}$ were calculated (Table S1) by using the equation for nth order rate constant¹⁴ and substituting n = 3/4 where n gives the order in MB (Equation SI). The order of reaction in TGA is 2 as verified by drawing plots between the logarithm of the rate constant and [TGA] which give a straight line with a slope equal to 2.4.

The rate constant remains almost unchanged on increasing the initial concentration of MB. However, the reaction shows a first-order kinetics in MB at low [MB] while the order changes from 1 to 2 on increasing [MB] beyond 2.0×10^{-5} M (Table 2).

The rate decreases linearly with increasing the concentration of hydrogen ions, which influences the kinetics in MB in a complex manner (Table S2). The plots of log $k_{3/4}$ against log [H⁺] give a straight line with a negative slope (0.80) (Figure 2).

The ionic strength of the system was maintained at a fixed level (ca. 0.35M) in these variations by adding the requisite amount of KCl to the reaction system. Incidentally, the relation between the rate constant and $[H^+]$ in the oxidation of thiols is generally found to be complex.¹⁵ The rate increases on increasing the concentration of KCl and NaCl, while it remains almost unaffected on adding K₂SO₄ to the reaction mixture. The rate constant decreases, however, on addition of KNO₃ and attains a limiting value at higher concentrations (ca. > 0.10M). The ionic strength was also calculated in terms of molality but on calculating the former on the basis of Debye-Hückel limiting law,¹⁶ a



Figure 2. A plot of log $k_{3/4}$ versus log [HCI] [TGA] = 3.0×10^{-3} M; [MB] = 2.0×10^{-5} M; [CuSO₄] = 2.0×10^{-6} M; l = 0.1M; Temp. = 35° C.



Figure 3. A plot of logk₁ versus log $[CuSO_4]$. $[TGA] = 3.0 \times 10^{-3}$ M; $[MB] = 2.0 \times 10^{-5}$ M; [HCI] = 0.1 M; I = 0.1M; Temp. = 35° C.

negligible difference of 6.17×10^{-3} was noticed in the value of the activity coefficient. The rate increases on increasing the concentration of Cu(II) and the order with respect to the catalyst is nearly 2. The plots of log k_1 against log [CuSO₄] give a straight line with a slope of 1.8 (Figure 3).

The influence of the dielectric constant was studied by adding varying volumes of methanol to the system and it was observed that the rate initially increases on decreasing the dielectric constant of the medium but subsequent variations in the dielectric constant did not influence the rate (Table 3). The rate is not affected on adding dithiodiglycolic acid (disulfide) externally to the reaction system. The addition of leucobase (H₂MB) slightly retards the rate at higher concentrations and leads to zero-order kinetics in MB (Table S3). In order to account for the kinetic influence of the Sn/HCl couple used to reduce MB; identical blank runs were made by adding the solution of tin dissolved in HCl so that an equal amount of the metal could be added to the reaction system.

It was found that the rate attains a limiting value at lower dielectric constant ($D \le 75.0$). Thus the runs were made at different temperatures in aqueous and aqueous methanol media. The rate constants are summarized in Table 4.

The reaction adheres to Arrhenius behavior in aqueous medium but exhibits anti-Arrhenius behavior in aqueous methanol medium where the rate constant remains unaffected on varying the temperature. The energy of activation, entropy of activation and free energy of activation in aqueous medium are found to be 34.8 kJ mol⁻¹, -199.9 JK⁻¹mol⁻¹, and 96.3 kJ mol⁻¹ respectively. In order to verify this and to study the influence of the dielectric constant on the temperature dependence of the reaction, acetone was introduced to the system. It

Table 3. Rate constant at different dielectric constant [TGA] = 3.0×10^{-3} ; [MB] = 2.0×10^{-5} M; [CuSO₄] = 2.0×10^{-6} M; [HCI] = 0.1 M; [/] = 0.1 M; Temp = 35° C.

D	$k_1 imes 10^4 { m s}^{-1}$
79.9	3.5
77.4	3.4
75.0	5.0
72.7	5.2
70.2	5.9
67.6	5.6
65.4	5.5

Table 4. Rate constants at different temperatures in aqueous and aqueous methanol (30%v/v) media [TGA] = 3.0×10^{-3} M; [MB] = 2.0×10^{-5} M; [HCI] = 0.1 M; [CuSO₄] = 2.0×10^{-6} M; I = 0.1 M.

Medium $k_1 \times 10^4 \text{ s}^{-1}$	$k_{3/2} \times 10^2 \mathrm{M}^{-1} \mathrm{s}^{-1}$	(B) Aqueous methanol Temperature (K)	Medium $k_1 \times 10^4 \text{ s}^{-1}$
	4.5	293	5.9
2.3		298	6.1
2.9		308	5.8
3.5			
4.5			
	Medium $k_1 \times 10^4 \text{ s}^{-1}$ 2.3 2.9 3.5 4.5	Medium $k_{3/2} \times k_1 \times 10^4 \text{ s}^{-1} 10^2 \text{ M}^{-1} \text{ s}^{-1}$ 4.5 2.3 2.9 3.5 4.5	$\begin{array}{c} \text{(B) Aqueous methanol} \\ \text{Medium } k_{3/2} \times \\ k_1 \times 10^4 \text{ s}^{-1} 10^2 \text{ M}^{-1} \text{ s}^{-1} \end{array} \begin{array}{c} \text{(B) Aqueous methanol} \\ \text{Temperature (K)} \\ \text{Temperature (K)} \\ 2.9 \\ 2.9 \\ 3.08 \\ 3.5 \\ 4.5 \end{array}$

Temperature in Kelvin (K).

is found that anti-Arrhenius behavior is more pronounced in aqueous acetone medium (36% v/v) (Table 5) where the rate constant decreases on increasing the temperature.

The Eyring plot between $\log (kh/KT)$ (where k and K denote the rate constant and Boltzmann constant, respectively) and 1/Tfor the reaction studied in aqueous medium is found to be linear (Figure 4a) but these plots for aqueous acetone medium are nonlinear (Figure 4b) and the two linear segments on extrapolation intersect at a particular temperature (T_{inv}) . These segments correspond to low temperature and high temperature zones,¹⁷ and $T_{\rm inv}$ was found to be 303 K for the reaction in aqueous acetone medium. According to Gypser et al., this indicates two transition states for the reaction.¹⁸ At temperatures below T_{inv} , ΔH^* is found to be -89.5 kJ mol⁻¹ while for a higher temperature zone, its value is $-25.1 \text{ kJ mol}^{-1}$. The activation entropy ΔS^* for the corresponding medium is found to be -604 JK⁻¹ mol⁻¹ at 20°C and $-391.2 \text{ JK}^{-1} \text{ mol}^{-1}$ at 35°C. In aqueous acetone medium, it is evident that a larger negative value of ΔH^* for the reaction at lower temperature compensates a larger negative value of ΔS^* making the process more favorable under these conditions.¹⁷ A larger negative value of ΔS^* also indicates the prominence of adsorption at 20°C.

The FTIR spectra of TGA (Figure S1a) and the reaction mixture after completion of the reaction suggest the participation of S-H stretch (2500 cm⁻¹), C-H stretch for aliphatic compounds near 2850–3000 cm⁻¹, symmetric COOH stretch (1400 cm⁻¹) and asymmetric COOH stretch (1700 cm⁻¹).^{19,20} The spectra of the reaction system recorded after completion of the reaction also show that the S-H stretching vibration which occurs near 2500 cm⁻¹ is feebly present in aqueous and aqueous methanol media but is absent in aqueous acetone medium (Figure S1.bd) indicating a specific involvement of the sulfhydryl group under these conditions. Moreover, a larger negative ΔS^* in aqueous acetone medium implies that at lower temperature, perhaps adsorption of MB on a reacting species occurs while at higher temperature, desorption is favored leading to a retardation in rate.

Table 5. Rate constant obtained at different temperatures in aqueous-acetone medium (36%v/v) [TGA] = 1.6×10^{-3} M; [MB] = 2.0×10^{-5} M; [HCI] = 2.0×10^{-2} M; [KCI] = 0.1 M; [CuSO₄] = 2.0×10^{-5} M; I = 0.12 M.

Temperature (K)	$k_{\rm 1} imes 10^3 { m s}^{-1}$
293 298	2.2
303	0.70
308 313	0.58 0.49



Figure 4. The Eyring plot between log(kh/KT) and 1/T for reaction system in (a) aqueous medium and (b) aqueous acetone medium (36% (v/v)).

Reaction scheme

The kinetic results suggest that Cu(II) interacts with TGA leading to deprotonation of the substrate molecule to form complexes with varying compositions,^{21,22} represented as C_1 and C_2 , respectively (Equations 1 and 2).

$$Cu(II) + RSH \stackrel{K_1}{\rightleftharpoons} [Cu^{II}(RS^-)]^+ + H^+$$
(1)

$$[\operatorname{Cu}^{\mathrm{II}}(\mathrm{RS}^{-})]^{+} + \mathrm{RSH} \stackrel{K_{2}}{\rightleftharpoons} [\operatorname{Cu}^{\mathrm{II}}(\mathrm{RS}^{-})_{2}] + \mathrm{H}^{+} \qquad (2)$$

A hypsochromic shift from 222 nm in methanol to 204 nm in aqueous medium in the UV spectra of the Cu(II)-TGA system (Figure S2a and b) confirms the formation of species like C_2 which is expected to be less polar than the reactants. It is very likely that an electron is transferred in situ from one of the ligated thiolate anions to the central Cu^{II} metal ion to form [Cu^I(RS⁻)] (C₃) and a thiyl radical as reported earlier.²¹ (Equation 3).

$$[\operatorname{Cu}^{\mathrm{II}}(\mathrm{RS}^{-})_{2}] \xrightarrow{k'_{1}} [\operatorname{Cu}^{\mathrm{I}}(\mathrm{RS}^{-})] + \mathrm{RS}^{\cdot}$$
(3)

It may be pointed out here that Cu^+ ion in presence of excess RS⁻ ion leads to the formation of species $[Cu^I(RS^-)]^{23}$ and although Cu(I) is not stable in aqueous solutions,²⁴ a number of stable cationic and anionic Cu(I) complexes are reported to be stable under such conditions.^{25, 26} In fact, Cu(I)-glutathione complexes are known to be the intermediates in cellular metabolism and storage of Cu(I).²⁷

The complex C_3 may be oxidized by protonated methylene blue (MBH⁺) to produce the complex C_1 along with the half-reduced MB radical (HM·) as given by Equations 4 and 5.

$$MB + H^+ \stackrel{\kappa_3}{\rightleftharpoons} MBH^+ \tag{4}$$

$$[\operatorname{Cu}^{\mathrm{I}}(\mathrm{RS}^{-})] + \mathrm{MBH}^{+} \xrightarrow{K_{2}^{\prime}} [\operatorname{Cu}^{\mathrm{II}}(\mathrm{RS}^{-})]^{+} + \mathrm{HM}^{\cdot} \quad (5)$$

The half-reduced MB radical subsequently interacts with the substrate molecule RSH to give the end products *viz.*, leucobase and the disulfide (Equations 6 and 7).

c. . .

$$HM^{\cdot} + RSH \xrightarrow{k'_3} H_2MB + RS^{\cdot}$$
(6)

$$2RS^{-} \xrightarrow{rast} RSSR$$
 (7)

Looking to the possibility of adsorption of MB as explained earlier and since a thiol itself is a reducing agent it can reduce metal ions to nanoparticles⁹ and in some cases, metal ion catalysis is associated with the participation of nanoparticles; such a possibility in the present case was checked under these conditions by recording SEM images and XRD spectra of the reaction system after completion of the reaction. These studies suggest the participation of Cu nanoparticles which may be formed by the involvement of species C_3 during the course of reaction as shown below.

$$[\operatorname{Cu}^{\mathrm{I}}(\operatorname{RS}^{-})] \xrightarrow{k_{4}} \operatorname{Cu}(0) + \operatorname{RS}^{\cdot}$$
(8)

Thus, on presuming step (5) as the rate determining step and assuming steady state for C_3 and substituting $[C_1]$, $[C_2]$ and $[MBH^+]$ from the respective equilibria; the following rate expression is obtained (for complete derivation of the rate expression, please see supporting information Equation SII):

$$-\frac{d[MB]}{dt} = \frac{k_1' k_2' K_1 K_2 K_3 [Cu(II)] [RSH]^2 [MB]}{[H^+] (k_2' K_3 [MB] [H^+] + k_4')}$$
(9)

If $k'_4 > k'_2 K_3$ [MB] [H⁺]; the rate is given as

$$-\frac{d[MB]}{dt} = \frac{k_1' k_2' K_1 K_2 K_3 [Cu(II)] [RSH]^2 [MB]}{k_4' [H^+]}$$
(10)

Equations (9) and (10) explain a second order kinetics in TGA (RSH) and a first-order and fractional order kinetics in MB as well as an inverse relationship of rate with $[H^+]$. The rate expression, however, does not explain the second-order kinetics behavior in Cu(II) which may perhaps be attributed to the participation of copper nanoparticles in the reaction system. From Equation (10), the pseudo first order rate constant (k_{obs}) will be given as

$$k_{obs} = \frac{k'_1 k'_2 K_1 K_2 K_3 [\text{Cu(II)}][\text{RSH}]^2}{k'_4 [\text{H}^+]}$$
(11)

$$\frac{1}{k_{obs}} = \frac{k'_4[\mathrm{H}^+]}{k'_1 k'_2 K_1 K_2 K_3 [\mathrm{Cu}(\mathrm{II})] [\mathrm{RSH}]^2}$$
(12)

It is thus evident that a plot of $1/k_{obs}$ against $1/[RSH]^2$ should give a straight line passing through the origin as has been



Figure 5 A plot of $1/k_{obs}$ against $1/[RSH]^2$.

observed (Figure 5). From Equation (12)

Slope =
$$\frac{k'_4[\mathrm{H}^+]}{k'_1k'_2K_1K_2K_3[\mathrm{Cu}(\mathrm{II})]}$$
 (13)

From Figure 5, the slope = 0.025 and since $K_1 = 10^9$ and $K_3 = 0.6$,^{28,29} the value of $\frac{k'_1k'_2K_2}{k'_*}$ is found to be 3.33×10^{-3} .

It seems that Cu nanoparticles (Equation 8) are oxidized by MBH⁺ to give Cu(II):

$$Cu(0) + MBH^{+} + H^{+} \longrightarrow Cu(II) + H_2MB$$
(14)

In spite of the participation of copper nanoparticles, the reaction system remains homogeneous because the particles are an order of magnitude smaller than the wavelength of visible light as explained by El-Sayed in nanocatalysis.³⁰ Incidentally, the reaction represented by Equation (14) has been shown to occur by Lopez-Quintela and coworkers in the reduction of MB by hydrazine catalyzed by size-selected Cu nanoclusters.³¹

SEM images of the reaction system recorded in aqueous medium after completion of the reaction reveal the participation of cauliflower shaped nanoparticles at 35°C (Figure 6a). The size of the particles as determined by XRD analysis in aqueous medium was found to vary between 44.21 and 74.33 nm (Figure S3) while in aqueous methanol medium (30%v/v) the particle size was found in the range 47.30–72.16 nm at 35°C

(Figure S4). The morphology of the nanoparticles changed to nanodisks in aqueous methanol as shown by SEM images of the reaction system (Figure 6b). Incidentally, the aggregation of suspended metal oxide and oxyhydroxide nanoparticles is reported to change drastically as a function of solvent properties such as dielectric constant and coordinative ability.³²

This is again revealed in the present case because in aqueous acetone medium (36%v/v), nanogranules are obtained at 35°C whereas nanowires are obtained at 20°C (Figures 7a and 7b). XRD analysis of the reaction mixture in aqueous acetone medium showed that the size of the particles varied between 39.96 and 70.33 nm at 25°C and lay in the range of 66.81-105.21 nm at 40°C (Figure S5a and S5b and Table S4). It clearly demonstrates that the temperature dependence of the reaction is governed by the dielectric constant of the medium as well as by the morphology of nanoparticles. It may be mentioned here that the morphology of ZnO nanoparticles is reported to be influenced by solvents such as acetone, water and ethanol.³³ In the present case also, the solvents appear to exert a specific influence on the morphology of the Cu nanoparticles. The reaction rate is highly influenced by the morphology of the nanoparticles as illustrated by the fact that in aqueous acetone medium the nanowires obtained at 20°C were catalytically more active than nanogranules obtained at higher temperatures. This contention is also supported by the observations of Suib et al. on the influence of different morphologies of ZnO nanoparticles on their photocatalytic activity.34

The extent of adsorption decreases on increasing the polarity of the reaction medium³⁵ and in view of this it seems that aqueous methanol plays an intermediary role between water and aqueous acetone. These conclusions are also confirmed by comparing the values of Gibbs free energy ΔG^* which is found to be 87.5 kJmol⁻¹ at 20°C and 95.5 kJmol⁻¹ at 35°C in aqueous acetone medium indicating the prominence of adsorption at lower temperature. In aqueous methanol medium, however, the values of ΔH^* and ΔS^* seem to counterbalance each other to nullify the influence of temperature on the rate of reaction.

These explanations justify the mechanistic approach advanced presently and also highlight the complex chemistry of sulfhydryl substrates vis-à-vis the nature of metal ion acting as a catalyst, the nature of the reaction medium and temperature.



Figure 6. SEM images of the reaction system at 35°C (a) in aqueous medium (b) in aqueous methanol medium (30%v/v).



Figure 7. SEM image of reaction system in aqueous acetone (36%v/v) medium at (a) 35°C and (b) 20°C.

Experimental

Reagents

The samples of mercaptoacetic acid (TGA, RSH) (E. Merck, Germany; assay 80%), MB (E. Merck, Germany) and CuSO₄·5H₂O (Qualigens, AnalaR) were used as such and their solutions were prepared afresh in doubly distilled water by dissolving an exactly weighed quantity of the samples. The solution of TGA was subsequently standardized iodimetrically.36 The solution of MB was stored in the dark to avoid photochemical effects. The solution of CuSO₄·5H₂O (Qualigens, AnalaR) was prepared in doubly distilled water in acidic medium in conformity with the standard procedure.³⁷ The oxidation product viz. the corresponding disulfide was prepared by oxidizing the respective substrate with hydrogen peroxide (30%v/v) and recrystallizing it from ether.³⁸ Dihydromethylene blue was prepared by reducing MB with Sn-HCl couple.³⁹ All reagents were E. Merck's GR grade samples. Doubly distilled water was used throughout these investigations. The Supplemental Materials contain sample spectra of reactions (Figures S1-S4).

Instrumentation

The progress of the reaction was followed on a Thermospectronic Unicam UV-530 spectrophotometer by measuring the depletion in absorbance of MB ($\varepsilon_{\rm max} = 6.76 \times 10^4 \, {\rm M}^{-1} \, {\rm cm}^{-1}$ at 664 nm) with time. Since the rate of reaction was practically unchanged in the presence and in absence of nitrogen under prevailing conditions the inert atmosphere was normally not maintained in these kinetic investigations. The ingredients of the reaction mixture were thermostatted (Julabo, Germany; Model No.F-34E; temperature stability $\pm 0.03^{\circ}$ C) in steam washed reaction vessels (Pyrex, England) coated with Black Japan. The precision of kinetic data are within 5%.

The IR spectra of the samples were recorded on Bruker (Model Alpha-T) and Shimadzu FTIR spectrometers (Model. No.8400 S) using KBr pellets in the range 4000–500 cm⁻¹. SEM images were obtained on a JEOL/EO JSM-6390 Scanning Electron Microscope while XRD spectra were recorded on a PANalytical Empyrean X-ray diffractometer. The wavelength of X-ray used was 1.5418 Å and d-spacing was recorded for different values of 2θ (Bragg angle). The step size (2θ) was 0.06° and the generator setting parameters were 40 mA, 45 kV. The size of the

nanoparticles was calculated from XRD spectra using the Scherrer equation:⁴⁰

$$D = \frac{K.\lambda}{\beta.\cos\theta}$$

where *K* is the shape factor (normally, the value is taken as 0.9), λ is the wavelength of the X-ray used (1.5418 Å), β is the line broadening at half of the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

The reaction mixtures after completion of the reaction were allowed to stand at room temperature, and after evaporation of the solvent the residue was dried and subjected to SEM, XRD, and FTIR analysis. Kinetics were studied by making the runs in presence of a large excess of TGA over MB and by measuring a decrease in absorbance of MB with time at 664 nm at a particular temperature and at a fixed ionic strength. The reaction mixture was thermostatted in steam washed reaction vessel (Pyrex, England) coated with Black Japan and the solution of MB was subsequently added to the reaction system. The aliquots were withdrawn and the concentration of MB was determined at different time intervals by using Thermospectronic Unicam UV-530 Spectrophotometer.

Conclusions

The kinetics of the reaction between mercaptoacetic acid (TGA) and MB in acidic medium catalyzed by Cu(II) are very much influenced by the solvent and a diverse influence has been exerted by water, methanol and acetone vis-à-vis temperature. The reaction adheres to Arrhenius behavior in aqueous medium but in aqueous methanol and aqueous acetone medium an anti-Arrhenius behavior has been noticed. The rate is not influenced on varying the temperature in aqueous methanol medium while in aqueous acetone, the rate decreases on increasing temperature. Our observations confirm the participation and regulatory role of Cu-TGA nanoparticles and entropy controlled adsorption of MB on nanoparticles is found to cause a deviation in reaction path mediated by the solvent and temperature.

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