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Copper(II) Catalyzed Oxidation of Aliphatic Thiols (Thioglycolic Acid and 2-Mercaptoethanol) by Heteroleptic Co(III)-Bound Superoxo Complex

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In aqueous acid media (0.02-0.06 M), two aliphatic thiols (RSH) *viz.* thioglycolic acid (TGA) and mercapto ethanol (MERCAP) were oxidized by heteroleptic metal bound superoxo complex, $[(dien)(en)Co^{III}(O_2)Co^{III}(en)(dien)]^{5+}$ (**1**) (en = ethylenediamine, $NH_2CH_2CH_2NH_2$ and dien = diethylenetriamime, $NH_2(CH_2)_2NH(CH_2)_2NH_2$) to the corresponding disulphides. Complex **1** is reduced to its corresponding peroxo complex, $[(dien)(en)Co^{III}(O_2)Co^{III}(en)(dien)]^{4+}$ (**2**) in these reactions. The oxidation of both thiols were dramatically catalyzed by the presence of Cu^{2+} ion. The observed rate constant k_o was found to be proportional to $[RSH]^2$ and $[Cu]_T^2$ (where $[Cu]_T$ is the analytical concentration of Cu^{2+}). The rate of reaction decreases with increasing ionic strength (I) of the reaction media and k_o is also proportional to $[H^+]^{2-}$. The experimental observation suggests that a 1:2 anionic complex formed between Cu^{2+} and RSH participates in the redox cycle.

Keywords: Thiols, Thioglycolic acid, Mercapto ethanol, Superoxide, Redox reaction, Kinetics.

INTRODUCTION

Thiols are ubiquitously distributed in aerobic life forms and have multifaceted functions, including a pivotal role in antioxidant activity [1-7]. Among them aliphatic thiols are susceptible to oxidation by many oxidizing agents and lead to disulphides, sulphoxide and so forth, depending on the thermodynamic strength of the oxidant [8-13]. Thioredoxins are small proteins that demonstrate a wide range of redox activities in plants and animals, all involving their two redox active sulfhydryl groups. In biological systems, thiols are oxidized by flavins, cytochromes and dehydroascorbic acid to control the cellular redox potential and prevent oxidative damage [14-16]. Often trace metal ions, particularly Cu^{2+} ion, catalyze such reactions [17,18]. Even ubiquitous Cu^{2+} ions present as impurities in the solution affect the redox kinetics of these thiol molecules [19].

The present work deals with the Cu(II)-catalyzed oxidation of two thiols, *viz.* thioglycolic acid (TGA, $HSCH_2COOH$) and 2-mercaptoethanol (MERCAP, $HSCH_2CH_2OH$) (a paradigm for aliphatic thiols), in aqueous acidic media with heteroleptic cobalt(III) bound superoxide complex, $[(en)(dien)Co^{III}(O_2)Co^{III}(en)(dien)](ClO_4)_5$ (**1**, en = $NH_2CH_2CH_2NH_2$ and dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$). Even in presence of externally small amount of added Cu^{2+} ions (0.1-9.0 μM), the oxidation reactions for the thiols are overwhelmingly fast in comparison to the uncatalyzed path, details kinetics of which was reported earlier [20].

EXPERIMENTAL

Cobalt(II) nitrate, ethylenediamine, diethylenetriamine, 2-mercaptoethanol, thioglycolic acid, sodium perchlorate, and copper(II) acetate were procured from Sigma-Aldrich, USA and used without further purification. All the experimental solutions were prepared with freshly fetched Milli Q-water. Deuterium oxide (Aldrich) and perchloric acid (Merck) were also used without further purification while the latter was standardized following standard methods [21].

Preparation of complex 1: The complex, μ-superoxo-[*bis*(ethylenediamine)*bis*(diethylenetriamime)dicobalt(III)] perchlorate, $[(en)(dien)Co^{III}(O_2)Co^{III}(en)(dien)](ClO_4)_5$ (**1**) was synthesized from cobalt(II) nitrate following the literature procedure [22]. Complex **1** shows the characteristic UV-VIS absorption bands at 471 and 708 nm (Fig. 1) and the value of molar extinction coefficient, ε at 708 nm (ε in $mol^{-1}\ dm^3\ cm^{-1}$; found 1171; reported 1210 [22]) suggests a more than 96%

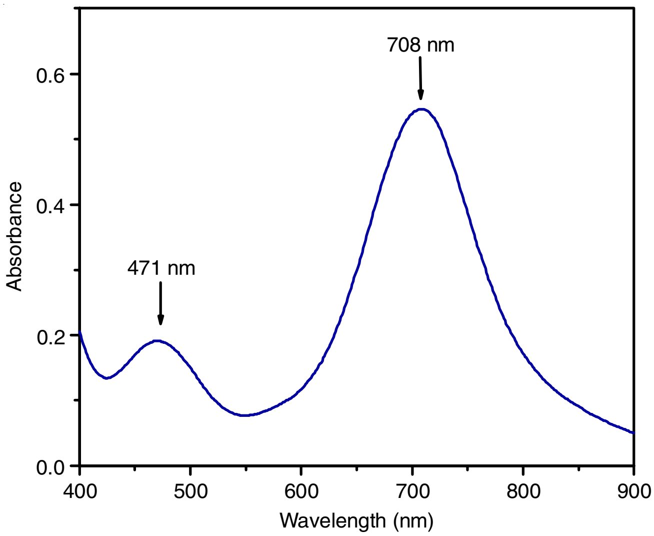

Fig. 1. Complex **1** (0.5 mM) shows two characteristic absorbance values at 471 and 708 nm in aqueous-acid media

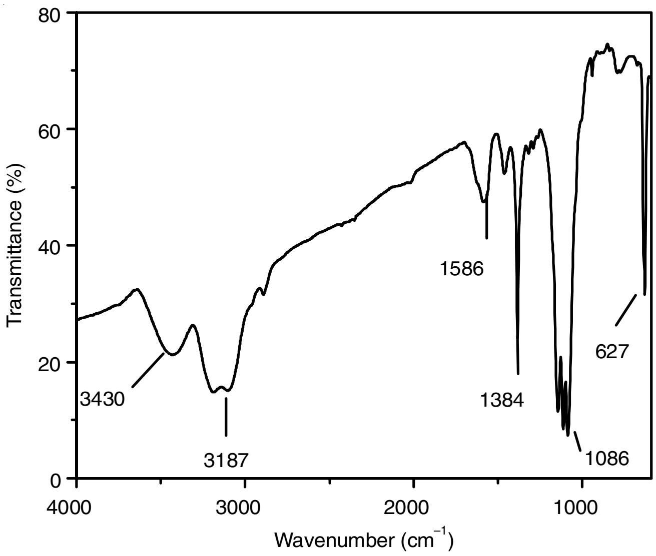

Fig. 2. FTIR spectra of complex **1**

purity of complex **1**. Complex **1** has also been subjected to FTIR spectroscopy (Fig. 2), which exhibit the peak at 1086 cm^{-1} (s) confirm the presence of the bridging superoxo group [23]. In FTIR, mainly due to the ligands 'en' and 'dien' are always difficult to ascribe as their characteristic M–N (M = Co^{3+}) stretching frequencies lie in the fingerprint region and are strongly coupled with other skeletal modes [24].

Instrumentation: The UV-VIS absorbance of reaction mixture and the respective kinetic studies for the title reactions were monitored *in situ* in a thermostatted cell housing (CPS-240A, ± 0.1 ºC) of Shimadzu (UV-1700) spectrophotometer. Fourier Transform Infrared (FTIR) spectrometry and mass spectrometry data were recorded in Perkin-Elmer (L1600300) FTIR spectrometer and micro-mass Q-TOF spectrometer (Waters) with an electro-spray ionization source, respectively. Acid solutions were standardized by pH metric titration in Metrohm 736-GP Titrino instrument and the pH of the reacting solutions during the stoichiometric titration was determined with a Toshniwal pH-meter (CL-54, India).

Kinetic measurements: The uncatalyzed oxidation of TGA and MERCAP by complex **1** is already reported [20]. The uncatalyzed slow oxidation of TGA and MERCAP by complex **1** is readily achieved when Cu^{2+} ion added in the reaction media to catalyze the reaction. In comparison to the uncatalyzed reactions, the extent of catalysis using Cu^{2+} ions even as low as ~ 10^{-6} M can be perceived from the representative absorbance *vs*. time as shown in Fig. 3. Kinetics for the Cu^{2+} catalyzed reactions between complex **1** and TGA (or MERCAP) were studied following the decrease in the absorbance value of the reaction solution at 708 nm where only complex **1** but no other

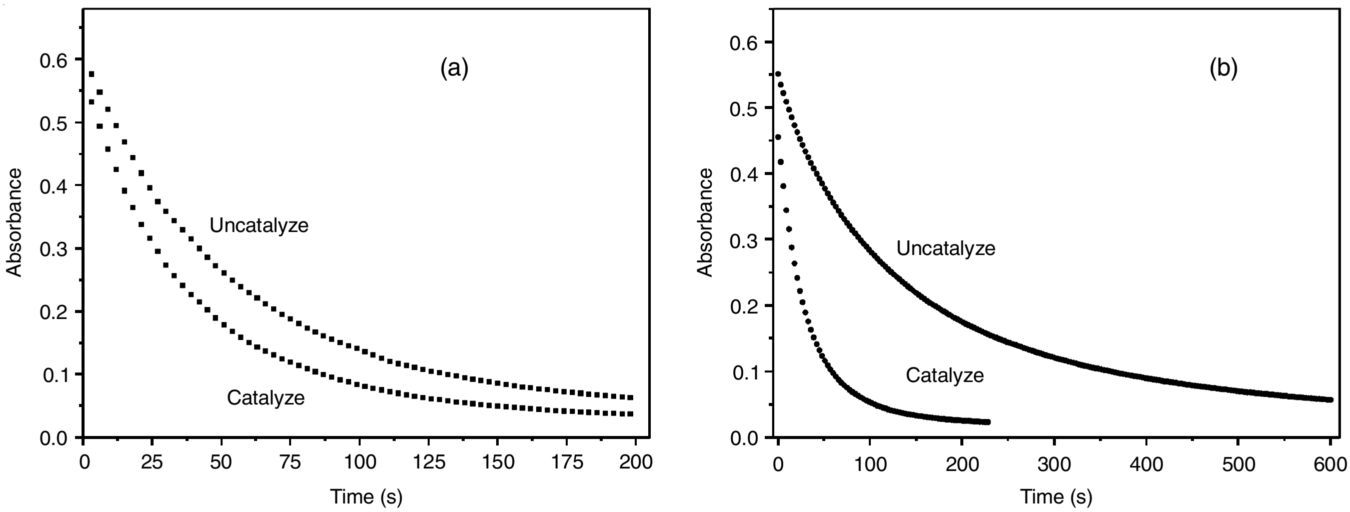

Fig. 3. Plot of absorbance *versus* time for uncatalyzed and Cu(II) catalyzed oxidation of TGA (a) and MERCAP (b) at 708 nm Conditions for uncatalyzed oxidation of TGA: [**1**] = 0.5 mM; [TGA] = 5.0 mM; [H$^+$] = 0.05 M; I = 0.5 M; T = 20.0 ± 0.1 °C and for catalyzed oxidation of TGA: [**1**] = 0.5 mM; [TGA] = 5.0 mM; [Cu^{2+}] = 0.1 × 10^{-6} M; [H$^+$] = 0.05 M; I = 0.5 M; T = 20.0 ± 0.1 ºC Conditions for uncatalyzed oxidation of MERCAP: [**1**] = 0.5 mM; [MERCAP] = 20.0 mM; [H$^+$] = 0.05 M; I = 0.5 M; T = 25.0 ± 0.1 ºC and for catalyzed oxidation of MERCAP: [**1**] = 0.5 mM; [MERCAP] = 20.0 mM; [Cu^{2+}] = 3.0 × 10^{-6} M; [H$^+$] = 0.05 M; I = 0.5 M; T = 25.0 ± 0.1 ºC

reagents absorb. A time-resolved UV-VIS spectral change for the Cu(II) catalyzed reaction mixture containing complex **1** and TGA is shown in Fig. 4. Similar the UV-VIS spectral changes for the reaction between complex **1** and MERCAP is shown in Fig. 5. All the kinetic experiments were performed in the presence of excess of thiol concentration over [**1**] ($[T_{Thiol}]/[\mathbf{1}] \geq 10$; $[T_{Thiol}]$ denotes the analytical concentration of respective thiol molecules, either TGA or MERCAP) and a non-linear least-square fit to the absorbance *vs*. time data (Fig. 6a-b for TGA and MERCAP, respectively) yields the observed pseudo first-order rate constant (k_o). Each of the kinetics for this study was performed for at least three times and the reported k_o values for this work are the average of the best three nearly equal values.

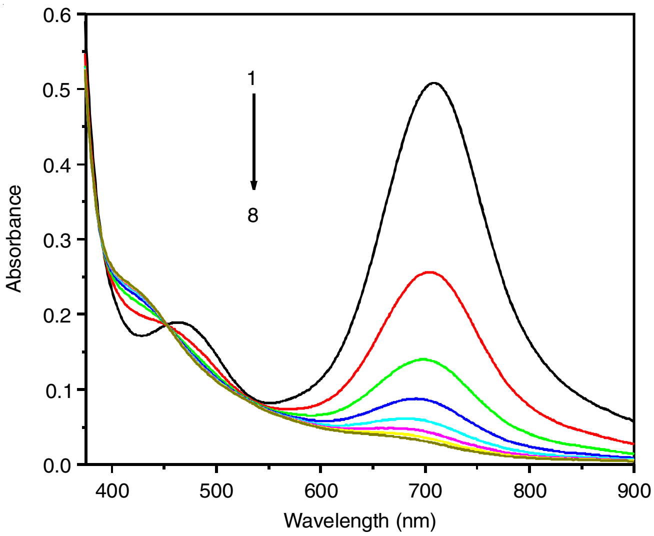

Fig. 4. Spectral changes of complex **1** on reaction with TGA at an interval of 10 s. Condition: [**1**] = 0.5 mM; [TGA] = 5.0 mM; [Cu(II)] = 1.0 × 10^{-7} M; [H^+] = 0.05 M; I = 0.5 M; T = 15.0 ± 0.1 ºC

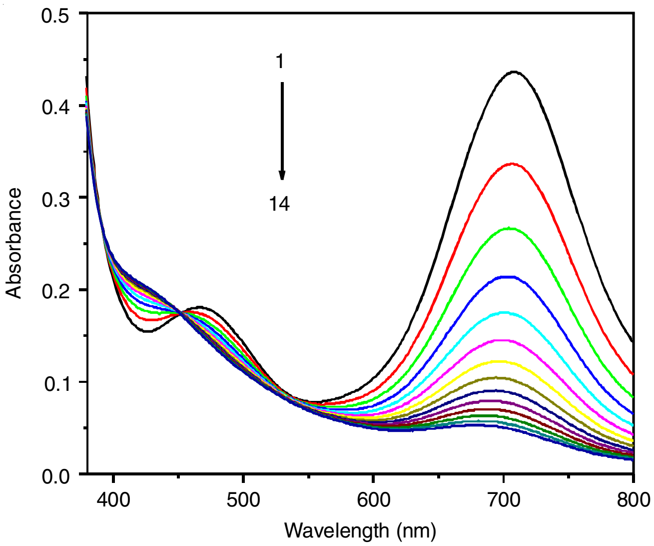

Fig. 5. Spectral change of the absorbance of the reaction mixture recorded at an interval of 30 s for the reaction of MERCAP and complex **1**. Condition: [**1**] = 0.5 mM; [MERCAP] = 10.0 mM; [Cu^{2+}] = 3.0 × 10^{-6} M; [H^+] = 0.5 M; I = 0.5 M; T = 25.0 ± 0.1 °C

The catalyzed oxidations were studied in aqueous acid perchlorate media ([H^+] = 0.02-0.06 M) at constant media ionic strength (I, maintained by $NaClO_4$) over the temperature range of 288-313 K. A large excess of [RSH] over [**1**] was maintained in all the kinetic runs to ensure the pseudo first-order condition. To catalyze the oxidations of TGA and MERCAP by complex **1**, Cu^{2+} ions were added in the reaction media. The analytical concentration of Cu^{2+} ions in the reaction mixture, $[Cu]_T$ was maintained over the range of (0.1-9.0) × 10^{-6} M. All the reagent solutions necessary for the study were prepared with freshly fetched Milli-Q water, which has a resistance of 16.6 MΩ and thus assumed to be devoid of any significant amount of metal ions. The absence of any metal ion can catalyze the title reactions was further ensured from the independent kinetic runs with and without a metal-ion chelating agent dipicolinic acid (dpa). The fact that the observed rate constant values for both kinetics are nearly equal ensures the absence of any metal ions in the Milli-Q water.

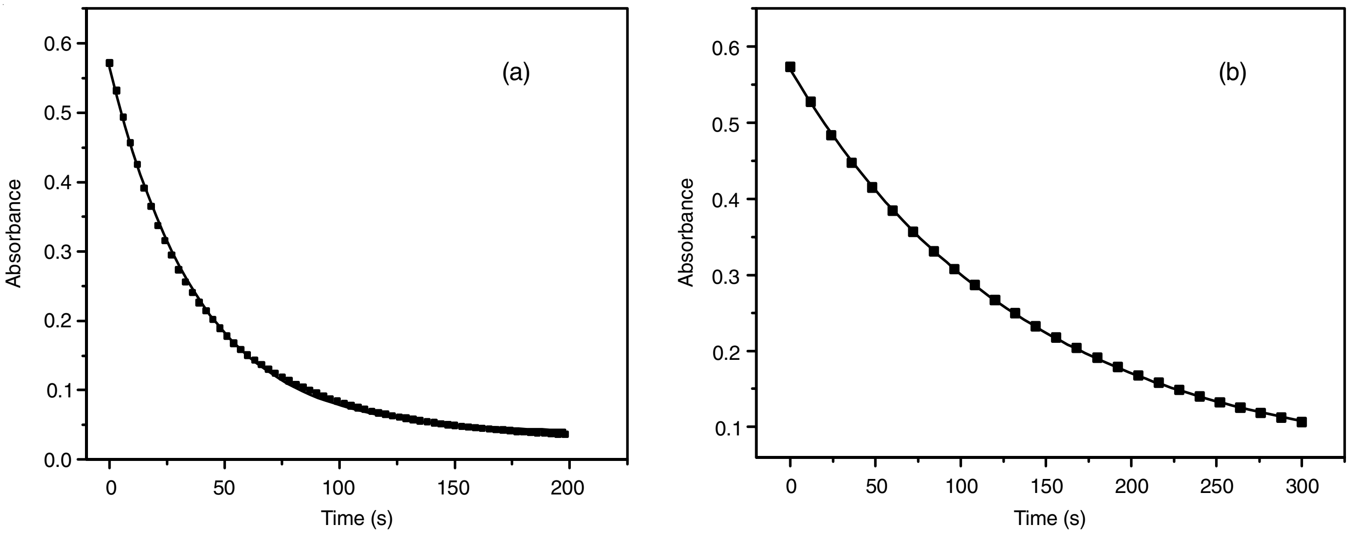

Fig. 6. Kinetic profile for the reduction of complex **1** by RSH at 708 nm

(a) Condition: [**1**] = 0.5 mM; [TGA] = 5.0 mM; [Cu^{2+}] = 0.1 × 10^{-6} M; [H^+] = 0.05 M; I = 0.5 M; T = 20.0 ± 0.1 °C

(b) Condition: [**1**] = 0.5 mM; [MERCAP] = 10.0 mM; [Cu^{2+}] = 3.0 × 10^{-6} M; [H^+] = 0.05 M; I = 0.5 M; T = 25.0 ± 0.1 ºC

RESULTS AND DISCUSSION

Products from the reaction: The metal-bound superoxo complex **1** is known to be an one electron oxidant and on reaction the complex $[(en)(dien)Co^{III}(O_2)Co^{III}(en)(dien)]^{5+}$ (**1**) is reduced to its corresponding peroxo complex, $[(en)(dien)Co^{III}(O_2)Co^{III}(en)(dien)]^{4+}$ (**2**). On the other hand, thiol molecules (RSH; for TGA, R = $-CH_2COOH$ and for MERCAP, R = $-CH_2CH_3OH$), which are one electron-reductants were oxidized to the corresponding disulfides (RSSR). The previous work on uncatalyzed oxidation of TGA and MERCAP by complex **1** showed that the same reaction products were produced [20]. The evidences for the formation of disulphide compounds from TGA and MERCAP can be found from the corresponding ^{1}H NMR and mass spectrum of the reaction products, which show the requisite responses of disulphide molecules from MERCAP and TGA [20].

Variation of k_o with [TGA] and [MERCAP]: The observed rate constant, k_o values for the uncatalyzed reaction do not increase linearly with the increase in [TGA] and [MERCAP] (Fig. 7). The k_o values rather increases sharply with increase in [TGA] and [MERCAP] and forms an upward curvature indicating higher than linear dependences in these reductant concentrations. Indeed, k_o *versus* $[TGA]^2$ or $[MARCAP]^2$ plots were linear passing through the origin (Table-1).

Variation of k_o with $[Cu]_T$: Most of the transition metal ions like copper, iron, zinc or mercury form complexes with molecules having thiol group [25-38]. The formation of metal-thiol complex, particularly with copper ion has been found to accelerate the oxidation of thiol molecules and indeed with the increasing $[Cu^{2+}]$ the k_o values increases very rapidly (Fig. 8, inset). For the catalyzed oxidation, k_o values are only proportional to $[Cu]_T^2$ (Fig. 8) and the intercepts values of $(1.96 \pm 0.3) \times 10^{-2}\ s^{-1}$ ($r^2 = 0.998$) and $(0.57 \pm 0.2) \times 10^{-2}\ s^{-1}$ ($r^2 = 0.995$)

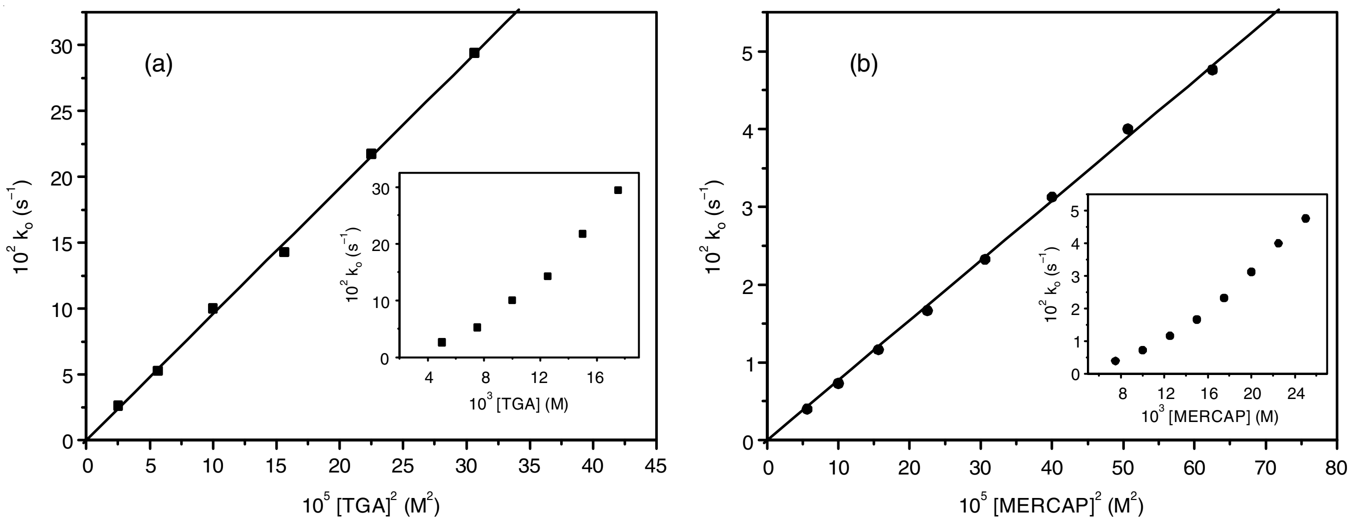

Fig. 7. Variation of k_o with [TGA] (inset) and k_o *vs.* $[TGA]^2$ (a) and [MERCAP] (inset) and k_o *vs.* $[MERCAP]^2$ (b)
Conditions for TGA: [**1**] = 0.5 mM; [Cu(II)] = 1.0×10^{-7} M; $[H^+]$ = 0.05 M; I = 0.5 M; T = 20.0 ± 0.1 ºC
Conditions for MERCAP: [**1**] = 0.5 mM; [Cu(II)] = 3.0×10^{-6} M; $[H^+]$ = 0.05 M; I = 0.5 M; T = 25.0 ± 0.1 ºC

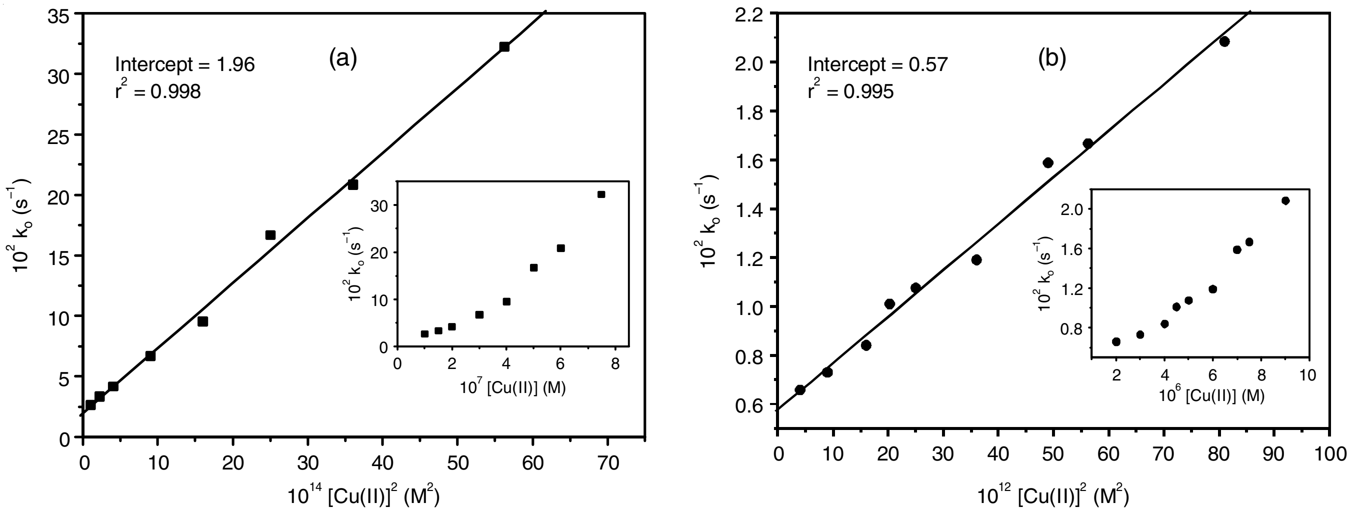

Fig. 8. Variation of k_o with [Cu(II)] (inset) and k_o *vs.* $[Cu(II)]^2$
(a) Conditions: [**1**] = 0.5 mM; [TGA] = 5.0 mM; $[H^+]$ = 0. 05 M; I = 0.5 M; T = 20.0 ± 0.1 ºC
(b) Conditions: [**1**] = 0.5 mM; [MERCAP] = 10 mM; $[H^+]$ = 0. 05 M; I = 0.5 M; T = 25.0 ± 0.1 ºC

TABLE-1
REPRESENTATIVE DATA FOR VARIATION OF k_o WITH DIFFERENT CONDITIONS FOR TGA (AT 20 °C) AND MERCAP (AT 25 °C)

Complex (mM)	Thiols (mM)		10^7 Cu(II) (M)		$[H^+]$ (M)		Ionic strength (M)		10^2 k_o (s^{-1})	
	TGA	MERCAP	TGA	MERCAP	TGA	MERCAP	TGA	MERCAP	TGA	MERCAP
0.5	5.0	7.5	1	3.0	0.05	0.05	0.5	0.5	2.63	0.40
0.5	7.5	10.0	1	3.0	0.05	0.05	0.5	0.5	5.26	0.73
0.5	10.0	12.5	1	3.0	0.05	0.05	0.5	0.5	10.00	1.16
0.5	12.5	15.0	1	3.0	0.05	0.05	0.5	0.5	14.29	1.67
0.5	15.0	17.5	1	3.0	0.05	0.05	0.5	0.5	21.74	2.33
0.5	17.5	20.0	1	3.0	0.05	0.05	0.5	0.5	29.41	3.13
0.5	5.0	22.5	0	3.0	0.05	0.05	0.5	0.5	1.90	4.00
0.5	5.0	25.0	1	3.0	0.05	0.05	0.5	0.5	2.63	4.76
0.5	5.0	10	1.5	2	0.05	0.05	0.5	0.5	3.33	0.66
0.5	5.0	10	2.0	3	0.05	0.05	0.5	0.5	4.17	0.73
0.5	5.0	10	3.0	4	0.05	0.05	0.5	0.5	6.67	0.84
0.5	5.0	10	4.0	4.5	0.05	0.05	0.5	0.5	9.52	1.01
0.5	5.0	10	5.0	5	0.05	0.05	0.5	0.5	16.67	1.08
0.5	5.0	10	6.0	6	0.05	0.05	0.5	0.5	20.83	1.19
0.5	5.0	10	7.5	7	0.05	0.05	0.5	0.5	32.26	1.59
0.5	5.0	10	1.0	7.5	0.05	0.05	0.25	0.5	3.13	1.67
0.5	5.0	10	1.0	9	0.05	0.05	0.50	0.5	2.63	2.08
0.5	5.0	10	1.0	3.0	0.05	0.05	0.75	0.25	2.22	0.83
0.5	5.0	10	1.0	3.0	0.05	0.05	1.00	0.50	1.85	0.73
0.5	5.0	10	1.0	3.0	0.05	0.05	1.25	0.75	1.56	0.65
0.5	5.0	10	1.0	3.0	0.05	0.05	1.50	1.00	1.33	0.57
0.5	5.0	10	1.0	3.0	0.02	0.05	0.5	1.25	75.19	0.50
0.5	5.0	10	1.0	3.0	0.03	0.05	0.5	1.50	25.00	0.43
0.5	5.0	10	1.0	3.0	0.04	0.05	0.5	0.5	9.09	0.39
0.5	5.0	10	1.0	3.0	0.05	0.05	0.5	0.5	2.63	0.48
0.5	5.0	10	1.0	3.0	0.06	0.05	0.5	0.5	1.82	0.73
0.5	5.0	10	1.0	3.0	0.05	0.05	0.5	0.5	1.92	0.92
0.5	5.0	10	1.0	3.0	0.05	0.05	0.5	0.5	2.63	1.27
0.5	5.0	10	1.0	3.0	0.05	0.02	0.5	0.5	3.45	14.29
0.5	5.0	10	1.0	3.0	0.05	0.03	0.5	0.5	4.00	3.70
0.5	5.0	10	1.0	3.0	0.05	0.04	0.5	0.5	5.00	1.35
0.5	–	10	–	3.0	–	0.05	–	0.5	–	0.73
0.5	–	10	–	3.0	–	0.06	–	0.5	–	0.56

yielded from these linear plots for TGA and MERCAP are in close agreement with the uncatalyzed k_o values (0.59×10^{-2} s^{-1}) and (1.90×10^{-2} s^{-1}), respectively.

Variation of k_o with ionic strength (I): The experimentally observed k_o values, both for TGA and MERCAP decrease linearly with the increase in ionic strength I of the reaction media (Fig. 9), indicating reactions between two oppositely charged reactive species. Since the oxidant species, the superoxo complex **1** is cationic, the reactive reductant species derived from TGA and MERCAP should have negative charge.

Variation of k_o with $[H^+]$ for catalyzed reaction: Fig. 10 shows that for both TGA and MECAP, the observed rate constants (k_o) values decrease with the increase in media $[H^+]$ and attained a saturation over $[H^+] \geq 0.05$ M (inset Fig. 10). When the media acidity is ≤ 0.05 M, it can be seen from Fig. 10 that for the catalyzed oxidation of TGA and MERCAP, k_o values linearly increase with $1/[H^+]^2$. The inverse relationship between the k_o values and the media acidity signifies deprotonated reductants are the reactive species. However, it should be observed that the coordinating ligands 'en' and 'dien' in complex **1** do not participate in the deprotonation equilibrium as such process demands very high media pH [39-43].

Proposed mechanism of Cu^{2+} catalyzed reaction: The mechanism for the catalyzed oxidation of thiol molecules by complex **1** should be proposed in accordance with the facts that k_o is proportional with $[RSH]^2$, $[Cu]_T^2$ and $[H^+]^{2-}$. Moreover, the variation of media ionic strength suggests that cationic complex **1** is reduced by a reactive species that bears negative charges. Based on these observations, the proposed mechanism of the Cu^{2+} catalyzed reaction is shown in eqns. 1-6:

$$Cu^{2+} + RSH \xrightarrow[\text{fast}]{k_1} Cu^+ + RS^\bullet + H^+ \tag{1}$$

$$Cu^+ + RSH \overset{K_1}{\rightleftharpoons} [Cu(I)(RS^-)]^0 + H^+ \tag{2}$$

$$[Cu(I)(RS^-)]^0 + RSH \overset{K_2}{\rightleftharpoons} [Cu(I)(RS^-)_2]^- + H^+ \tag{3}$$

$$[Cu(I)(RS^-)_2]^- + Cu^+ \xrightarrow[\text{fast}]{k_2} [Cu(0)(RS^-)_2]^{2-} + Cu^{2+} \tag{4}$$

$$\mathbf{1}^{5+} + [Cu(0)(RS^-)_2]^{2-} \xrightarrow[\text{slow}]{k_c} \mathbf{2}^{4+} + [Cu(I)(RS^-)_2]^- \tag{5}$$

$$2RS^\bullet \xrightarrow{\text{fast}} 2RSSR \tag{6}$$

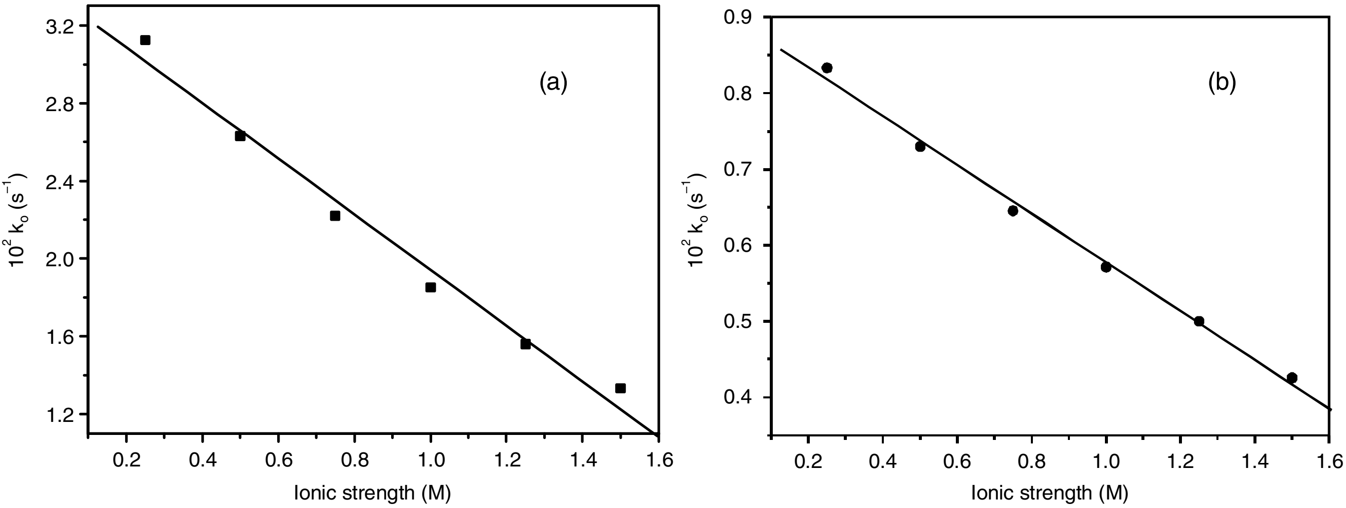

Fig. 9. Variation of k_o with complex **I**

(a) Conditions: [**1**] = 0.5 mM; [TGA] = 5.0 mM; [H^+] = 0.05 M; [Cu(II)] = 1.0×10^{-7} M; T = 20.0 ± 0.1 ºC

(b) Conditions: [**1**] = 0.5 mM; [MERCAP] = 10.0 mM; [H^+] = 0.05 M; [Cu(II)] = 3.0×10^{-6} M; T = 25.0 ± 0.1 ºC

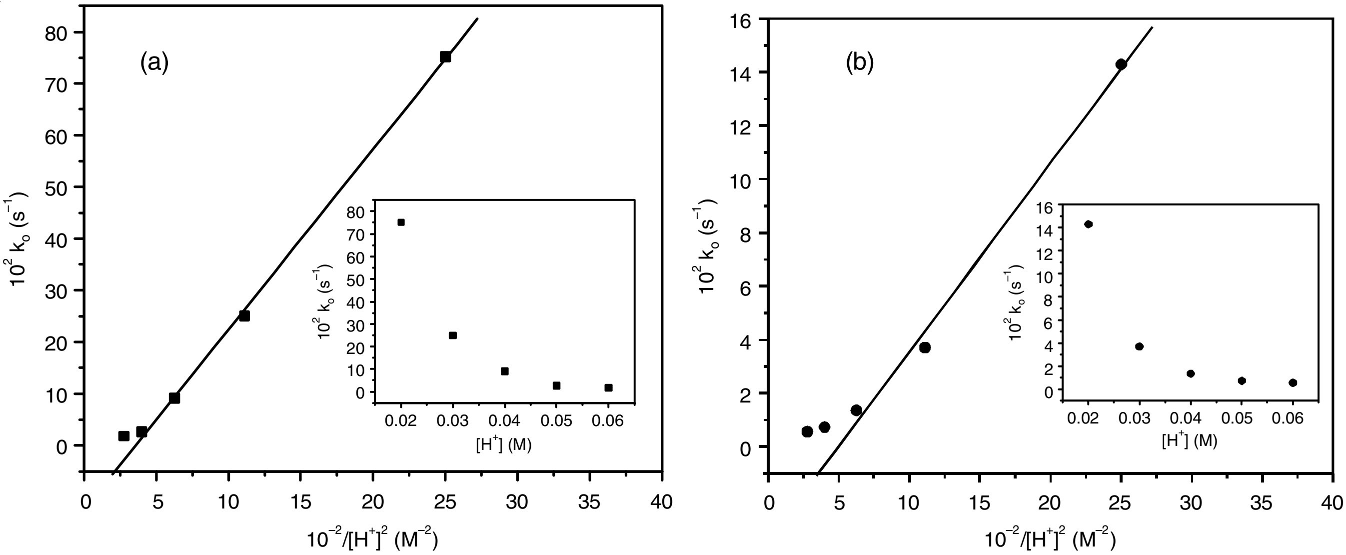

Fig. 10. Variation of k_o with $1/[H^+]^2$

(a) Conditions: [1] = 0.5 mM; [TGA] = 5.0 mM; [Cu(II)] = 1.0×10^{-7} M; I = 0.5 M; T = 20.0 ± 0.1 ºC

(b) Conditions: [1] = 0.5 mM; [MERCAP] = 10.0 mM; [Cu(II)] = 3.0×10^{-6} M; I = 0.5 M; T = 25.0 ± 0.1 ºC

Eqns. 1-6 demonstrate that thiol molecules, TGA and MERCAP (RSH; for TGA, R = $-CH_2COOH$ and for MERCAP, R = $-CH_2CH_2OH$) quickly reduces Cu^{2+} to Cu^+ (eqn. 1), which subsequently reacts with two RSH molecules to form $[Cu(I)(RS^-)_2]^-$ (eqns. 2 and 3). The proposal for such 1:2 complex between Cu^{2+} and RSH is strongly supported by the facts that when under the experimental condition the corresponding Jobs plots were drawn, the points of intersections lie close around the value of 2 for the ratio of $[RSH]/[Cu]_T$ (Fig. 11). This complex $[Cu(I)(RS^-)_2]^-$ reacts fast with Cu^+ and disproportionate to $[Cu(0)(RS^-)_2]^{2-}$ and Cu^{2+} (eqn. 4). The $[Cu(0)(RS^-)_2]^{2-}$ is oxidized by complex **1** to $[Cu(I)(RS^-)_2]^-$ (eqn. 5). Both Cu^{2+} and $[Cu(I)(RS^-)_2]^-$ produced in eqns. 4 and 5 again take part after respectively through eqns. 1 and 4. The thiyl radical produced in eqn. 1 is dimerized to RSSR through eqn. 6, which results in the following expressions:

$$k_o = \{k_cK_1K_2[Cu^{2+}]^2[RSH]^2\}/[H^+]^2 \qquad (7)$$

$$= \{k_cK_1K_2[Cu]_T^2[RSH]^2\}/[H^+]^2 \qquad (8)$$

here it is worth mentioning that the reduction of Cu^{2+} by RSH in eqn. 1 is usually fast and almost quantitative and since the concentration of RSH >> concentration of Cu^{2+}, it is assumed that the analytical concentration of copper, $[Cu]_T = [Cu^{2+}]$. Thus, the final eqn. 8 can be expressed in terms of $[Cu]_T$ instead of $[Cu^{2+}]$.

Conclusion

The oxidation of thioglycolic acid (TGA) and mercapto ethanol (MERCAP) by superoxo complex **1** was rather slow in acid media but is dramatically accelerated by Cu^{2+} ions. The observed rate constant k_o is proportional to $[RSH]^2$, $[Cu]_T^2$ and $[H^+]^{2-}$. The negative slope of the plot of the variation of k_o

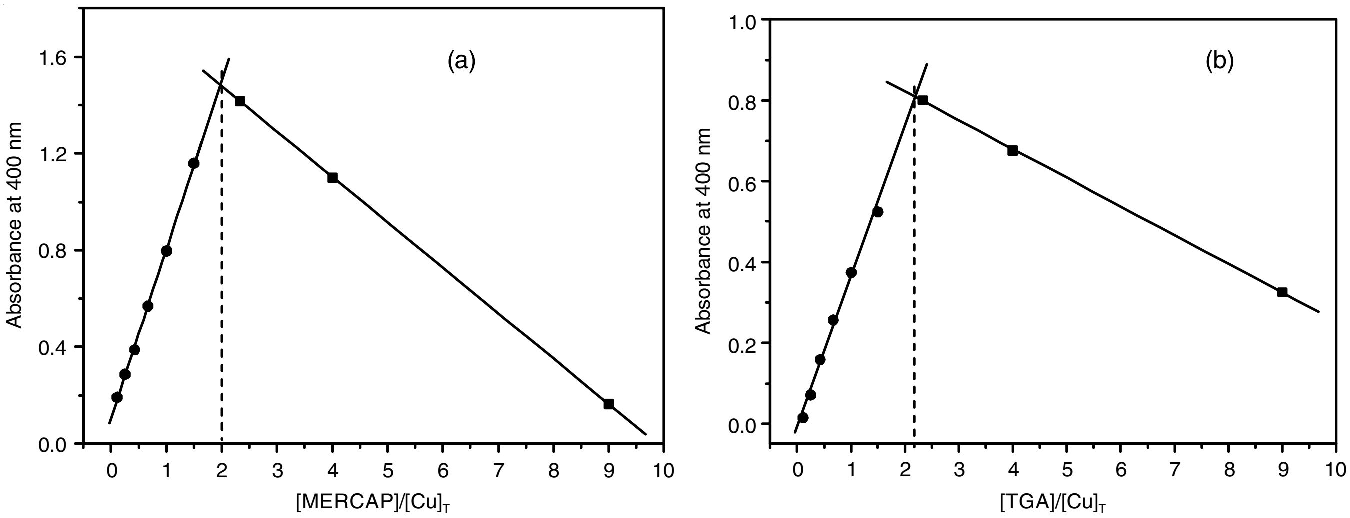

Fig. 11. Job's plot for the variation of Cu^{2+} and MERCAP (a), and Cu^{2+} and TGA (b)

with the media ionic strength shows that the reactive reductant is anionic. The reactive reductant for Cu^{2+} catalyzed reaction is thus assumed to be Cu^{2+} a complex and RSH, namely, $[Cu(0)\text{-}(RS^-)_2]^{2-}$, which reduces the superoxo complex **1** to its corresponding peroxo complex.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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