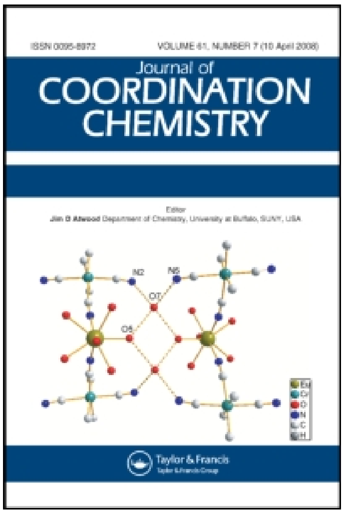

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INTERACTION OF SULFUR(IV)-OXIDES WITH ETHYLENEDIAMINE-TETRAACETATORUTHENATE(III) IN AQUEOUS SOLUTION

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The reaction between $[Ru^{III}(edta)(H_2O)]^-$ (edta = ethylenediaminetetraacetate) with sulfite has been investigated. Formation of a stable diamagnetic $Ru^{II}(edta)(SO_3)^{4-}$ complex as an end product of the reaction was evidenced by epr and electrochemical observations. Experimental results further demonstrate the formation of a μ-oxo intermediate $[Ru^{III}(edta)\text{-}O\text{-}Ru^{III}(edta)]^{4-}$ species in a rapid, sulfite-independent step. Results are discussed with reference to data reported for Fe^{III}(edta)-catalysed auto-oxidation of sulfur(IV) oxides in aqueous solution.

KEYWORDS: Ruthenium, edta, sulfite, kinetics, electrochemistry

INTRODUCTION

We have been engaged in exploring Ru(III)-edta (edta = ethylenediaminetetraacetate)—catalysed oxidation of organic substrates.[1–5] Earlier, we reported the oxidation of PPh_3,[1] $(CH_3)_2S$,[2] aliphatic amines,[3] unsaturated and saturated hydrocarbons,[4,5] catalysed by $Ru^{III}(edta)(H_2O)^-$. In the present study we have selected sulfite as substrate for the following reasons.

Metal ion and metal complex catalysed oxidation of sulfur(IV) oxides is very important particularly in reference to atmospheric auto-oxidation prcesses and pollution control. A number of schemes is known for the oxidation of sulfur(IV) oxides by transition metal and metal complexes.[6–10] However, a series of very recent reports[11,12] on the Fe(III) and $Fe^{III}(edta)(H_2O)^-$ catalysed auto-oxidation of sulfur(IV) oxides in aqueous solution stimulated us to study the interaction between $Ru^{III}(edta)(H_2O)^-$ and SO_3^{2-}. Our goal was to establish the mechanism of the reaction and to compare experimental results with those reported for Fe^{III}-$(edta)(H_2O)^-$. In this paper, we describe experimental results concerning spectrophotometric, kinetic, electrochemical and EPR studies of the interaction of $Ru^{III}(edta)(H_2O)^-$ with sulfite in aqueous solution.

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EXPERIMENTAL

K[Ru^{III}(Hedta)Cl] was prepared by following a published procedure.[13] All other chemicals used were of A.R. grade. Doubly distilled water was used.

Absorption spectra were recorded on a Shimadzu 160 spectrophometer coupled with a TCC 240A temperature controller. Electrochemical studies (cyclic voltammetry) were performed using PAR-175 electrochemical equipment. A glassy carbon working electrode and a saturated calomel electrode were used. Controlled potential electrolysis was carried out using PAR 173 potentiostat equipped with a current integrator (PAR 179). A coulometric cell consisting of a mercury pool as working electrode, a platinum wire as counter electrode (separated from main solution by a glass frit) and SCE as reference electrode was used for constant potential electrolysis. EPR spectra of frozen solutions (at 77K) were recorded on a Bruker Scientific X-band spectrometer (ESP-300) using a field (100 kHz) modulator; magnetic field was calibrated with an ERO 35M NMR gaussmeter with DPPH as field marker ($g = 2.0036$).

Kinetics of interaction of Ru^{III}(edta)(H$_2$O)$^-$ with sulfite were studied spectrophotometrically using a HI-TECH stopped-flow spectrophotometer coupled with Apple IIe data analyser. The slow reactions were studied spectrophotometically using conventional mixing techniques. All solutions for kinetic experiments were pre-equilibrated at the experimental temperature before mixing. Rate constant data measured in the presence of excess sulfite (20–50 times) were reproducible within ± 6%.

RESULTS AND DISCUSSION

Before describing the experimental results we recapitulate the aqueous chemistry of Ru(III)-edta and S(IV) oxides in aqueous solution, and acid dissociation equilibria of aqueous SO_2 at different pH values. K[Ru^{III}(Hedta)Cl] is rapidly aquated to give a neutral [Ru^{III}(Hedta)(H$_2$O)] species at low pH (< 2).[14] The complex is pentacoordinate in aqueous solution and the sixth position is occupied by a water molecule[14] at low pH or by a hydroxide ion at high pH. The Ru^{III}(Hedta)(H$_2$O) complex shows two pKa values which are associated with the following acid dissociation equilibria.

$$\mathrm{Ru^{III}(Hedta)(H_2O)} \underset{(\mathrm{p}K_1 = 2.4^{14})}{\overset{K_1}{\rightleftharpoons}} \mathrm{Ru^{III}(edta)(H_2O)^-} + \mathrm{H^+} \tag{1}$$

$$\mathrm{Ru^{III}(edta)(H_2O)^-} \underset{(\mathrm{p}K_2 = 7.6^{14})}{\overset{K_2}{\rightleftharpoons}} \mathrm{Ru^{III}(edta)(OH)^{2-}} + \mathrm{H^+} \tag{2}$$

The most reactive species towards substitution is [Ru^{III}(edta)(H$_2$O)$^-$, which exists predominantly in the pH range 4.5–6.5.[14]

Sulfur(IV) oxides dissolve readily in water to produce sulfurous acid. The characteristic acid dissociation equilibria of H_2SO_3 are outlined in (*3*) and (*4*).

$$\mathrm{H_2SO_3} \underset{(\mathrm{p}K_3 = 1.9^{15})}{\overset{K_3}{\rightleftharpoons}} \mathrm{HSO_3^-} + \mathrm{H^+} \tag{3}$$

$$HSO_3^- \underset{(pK_4 = 6.3^{15})}{\overset{K_4}{\rightleftharpoons}} SO_3^{2-} + H^+ \qquad (4)$$

Upon addition of sulfite to an aqueous solution of the Ru(III)-edta complex causes an immediate colour change from pale-yellow to marron. The change associated with the formation of the maroon species is shown in Figure 1. The formation of maroon species can be observed only in fairly concentrated solutions (not less than 1×10^{-2}M) of Ru(III)-edta in the presence of at least ten times excess sulfite. Stopped-flow kinetic measurements (at 547 nm) showed that good kinetic traces can only be obtained at high pH (> 8), and the rate of formation of the maroon species did not show any dependence on sulfite concentration (0.2 – 0.5 M) at constant pH (8.5). On the basis of earlier results reported for thio-ligand substitution[16] of $Ru^{III}(edta)(H_2O)^-$, it was expected that if the maroon species is an S-bound sulfito complex of Ru(III)-edta, it would show a sulfite concentration dependence of observed rate constant. However, this apparent anamoly in kinetic observations can be explained if the above reaction is considered as a reaction of Ru(III)-edta complex itself at high pH as outlined below.

$$2Ru^{III}(edta)(OH)^{2-} \rightleftharpoons [Ru^{III}(edta)\text{-}O\text{-}Ru^{III}edta)]^{4-} + H_2O \qquad (5)$$

The value of log K determined spectrometrically is 2.26 at 35° C.

In order to check the pertinence of (5), a concentrated solution (2×10^{-2}M) of Ru(III)-edta was mixed with water (0.5M KCl) at pH 8.5. The resulting solution

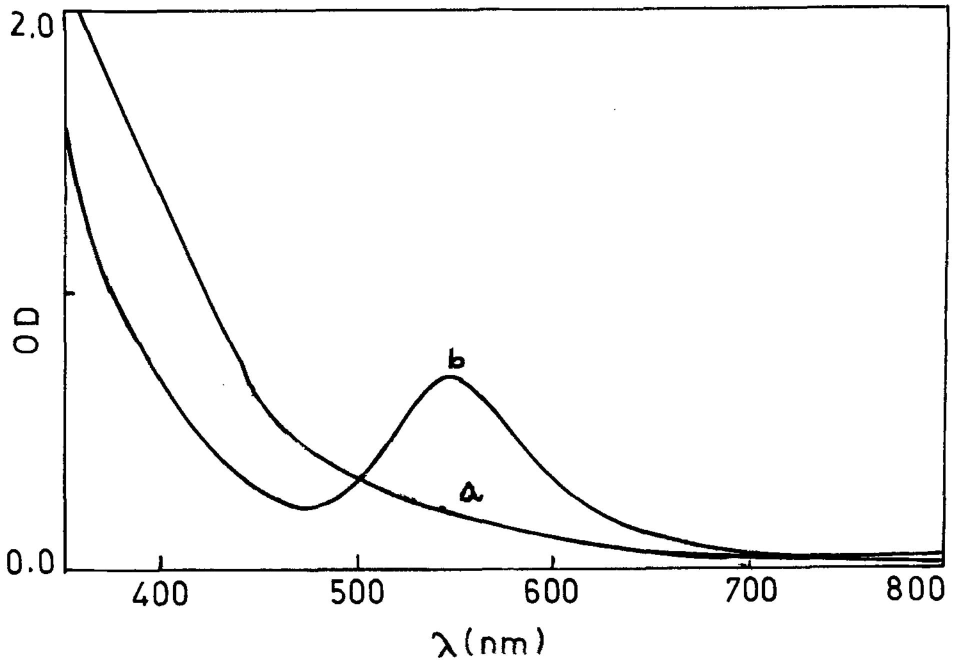

Figure 1 Spectroscopic changes observed during the reaction of Ru^{III}-edta with sulfite, (a) initially, (b) 100 sec after addition of sulfite; $[Ru^{III}] = 2 \times 10^{-2}$M, $[S^{IV}] = 0.5$ M

gave a similar spectrum to that of Figure 1 and analysis of kinetic traces so obtained gave data (k_{obs} = 0.03 s^{-1} at 25°C) in close agreement with those obtained in the presence of sulfite (Table 1). Moreover, no kinetic traces were obtained at a complex concentration of less than 2 x 10^{-2}M. At this stage, it is understood that formation of the maroon μ-oxo dimer is due to the effect of the pH of the sulfite solution (pH values of the sulfite solutions (0.2–0.5M) fall in the range 8.0–9.5). Additional evidence in favour of the μ-oxo dimer was obtained by resonance Raman studies. The Raman spectrum of the maroon solution exhibits a band at 555 cm^{-1} (Fig. 2) due to Ru^{III}-o-Ru^{III} symmetric stretching. A typical M-O-M stretch at 400–450 cm^{-1} was reported for Fe(III)-O-Fe-(III) μ-oxo complexes.[17] The increase by 100 cm^{-1} in our case may be due to better overlapping of ruthenium-oxygen orbitals. Rate and activation parameters for the formation of the dimer determined by temperature dependance studies of observed rate constants are summarised in Table 1. In the presence of excess sulfite, the marooon colour developed did not persist for a long period and gradually changed to give a pale yellow solution which was epr inactive. EPR spectra of the Ru(III)-edta complex (frozen solution at 77K) both in the absence and presence of excess sulfite are shown in Figure 3. The spectrum of Ru(III)-edta alone has characteristic features g_1 = 2.393, g_2 = 2.345, g_3 = 1.765. Upon addition of sulfite, the band intensities decrease (Fig. 3a-c) and after 1/2 h the system becomes epr inactive, indicating the formation of a diamagnetic ruthenium(II) complex.

Cyclic voltammograms of Ru(III)-edta show a pair of reversible cathodic and anodic waves (Fig. 4a) associated with the Ru^{3+}/Ru^{2+} redox couple ($E_{1/2}$ = −0.24V *vs* SCE).[14] Figure 4b shows cyclic voltammogram of the epr inactive solution obtained by reacting Ru(III)-edta with excess sulfite. It is seen that the anodic peak (Epa) observed at −0.19V in the cyclic voltammogram of Ru(III)-edta complex practically disappears and a new irreversible peak at 0.34V is developed (marked as E'pa in Figure 4(b)). This new peak is assigned to electrochemical oxidation of S-bound $Ru^{II}(edta)(SO_3)^{4-}$ (hereafter designated as Ru^{II}-S). The basis for the assignment is the earlier report of electrochemical studies of $[Ru(NH_3)_5(dmso)]^{3+/2+}$ complexes,[8] in which the Ru^{3+}/Ru^{2+} couple for the Ru-S isomer was found to be more positive than that of Ru^{III}-O isomer. It can be understood that O-bound complexes are expected to show similar properties to those of aquo-complexes and Ru^{II}-S isomers, stabilised due to strong π-interations with the coordinated sulfur atom of S-oxide ligands, are consequently oxidised at higher potentials. Recently, very similar electrochemical observations were reported by Toma *et al.*[19] $Ru^{II}(edta)(dmso)^{2-}$ was found to be extremely stable (K = 77 × $10^9 M^{-1}$) in comparison with its ruthenium(III) analogue (K = 1.8M^{-1}). By contrast,

Table 1 Rate and activation parameters for the formation of the μ-oxo-dimer $[Ru^{III}(edta)]_2O^{4-}$ complex[a].

Temperature, °C	k_{obs}, s^{-1}	ΔH≠ (kJ/mol)	Δ S≠ (J/deg mol)
25	0.03		
30	0.05		
35	0.07	62 ± 3	-65 ± 9
45	0.16		

[a] $[Ru^{III}]$ = 2 × 10^{-2}M, $[S^{IV}]$ = 0.5M, pH = 8.5.

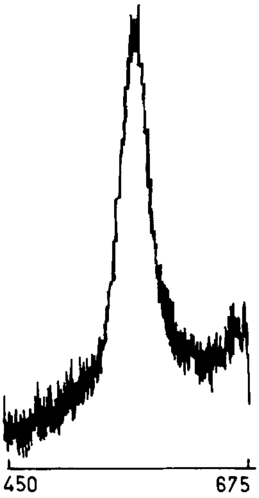

Figure 2 Resonance Raman spectrum of the μ-oxo complex.

$Ru^{II}(edta)(H_2O)^{2-}$ was found to be more reactive (k = 43 ± 6 $M^{-1}s^{-1}$) towards substitution with dmso, than the ruthenium(III)-aquo complex (k = 11 ± 3$M^{-1}s^{-1}$). By comparing our results with those of Toma *et al.*[19], it can be reasonably assumed that the S-bound $Ru^{II}(edta)(SO_3)^{4-}$ complex is responsible for

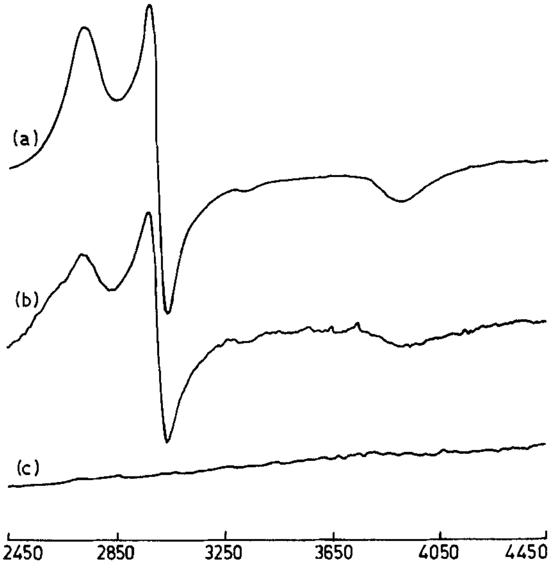

Figure 3 EPR changes observed during the reaction of Ru(III)-edta with sulfite, (a) before adding sulfite, (b) 5 mins after addition of sulfite, and (c) 30 mins after addition. All spectra were recorded at 77K.

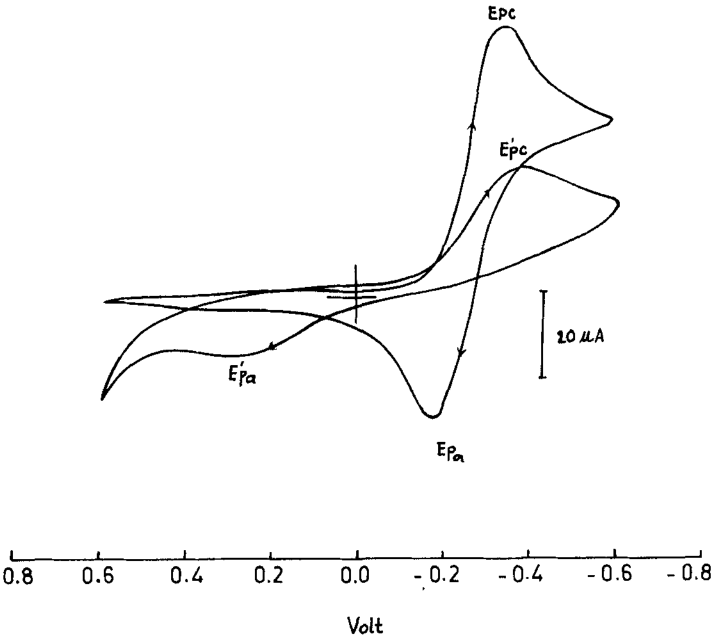

Figure 4 Cyclic voltammogram of (a) $Ru^{III}(edta)(H_2O)^-$ and (b) $Ru^{II}(edta)(SO_3)^{4-}$ complexes in H_2O; scan rate 100 mVs^{-1}, reference electrode SCE, supporting electrolyte KCl.

the anodic peak at 0.34V. Also, in this case, the absence of a corresponding cathodic peak indicates the extremely unstable nature of $[Ru^{III}(edta)(SO_3)]^{-3}$; once it forms by oxidation of Ru^{II}-S it undergoes rapid hydrolysis to give $Ru^{III}(edta)(OH)^{2-}$ which is reduced at negative potentials, −0.3V, (E'_{pc}) as seen in Figure 4(b). Further, in the presence of excess sulfite, the observed anodic peak (E'_{pa}) in Figure 4(a) is not seen because of the formation of $Ru^{II}(edta)(SO_3)^{4-}$ within the time scale of cyclic voltammetry at slow scan rates (100 mVs^{-1}). The overall electrochemical properties of the system are summarised in the following scheme.

$$\begin{tikzcd}
Ru^{II}(edta)(SO_3)^{4-} \arrow[r, "-e", "0.34V"'] & Ru^{III}(edta)(SO_3)^{3-} \arrow[d, "H_2O/OH^-", "\text{fast}"'] \\
Ru^{II}(edta)(OH)^{3-} \arrow[u, "\text{fast}", "SO_3^{2-}"'] & Ru^{III}(edta)(OH)^{2-} \arrow[l, "+e"', "-0.3V"]
\end{tikzcd}$$

Scheme I

At this stage, it is understood that the epr and electrochemical studies go some way towards explaining the formation of a stable $Ru^{II}(edta)(SO_3)^{4-}$ complex in the reacting system. Additional evidence in favour of $Ru^{II}(edta)(SO_3)^{4-}$ formation was obtained by the interaction of the Ru(II)-edta complex (produced in solution by constant potential electrolysis of Ru(III)-edta at −0.4V under an inert atmosphere) and sulfite in which no maroon colour was developed and the resulting solution was also epr inactive. However, we could not isolate $Ru^{II}(edta)(SO_3)^{4-}$ in the presence of a large excess of sulfite.

In order to elucidate the mechanism of formation of $Ru^{II}(edta)(SO_3)^{4-}$, we have carried out a series of spectroscopic and kinetic measurements both in the absence and presence of molecular 0_2. In both the cases $Ru^{II}(edta)(SO_3)^{4-}$ so formed is not oxygen sensitive and the formation of $Ru^{II}(edta)(SO_3)^{4-}$ is controlled by the equilibrium in (*5*). Based on the above experimental observations a probable mechanism is proposed (Scheme II) for the formation of $Ru^{II}(edta)(SO_3)^{4-}$ and the concomitant disappearance of the maroon colour in the reaction mixture.

$$Ru^{III}(edta)(OH)^{2-} + SO_3^{2-} \longrightarrow Ru^{II}(edta)(OH)^{3-} + SO_3^{-} \qquad (6)$$

$$Ru^{III}(edta)(OH)^{2-} + SO_3^{-} \xrightarrow{OH^-} Ru^{II}(edta)(OH)^{3-} + HSO_4^{-} \qquad (7)$$

$$Ru^{II}(edta)(OH)^{3-} + SO_3^{2-} \longrightarrow Ru^{II}(edta)(SO_3)^{4-} + OH^{-} \qquad (8)$$

$$HSO_4^{-} + OH^{-} \longrightarrow SO_4^{2-} + H_2O \qquad (9)$$

Scheme II

In the above suggested mechanism it is believed that a series of electron-transfer steps are involved. However, we have not shown them categorically as we are not sure of the nature (inner-sphere or outer-sphere) of these steps. The proposed mechanism is to some extent based on one proposed for Fe(III)-edta catalysed oxidation of sulfite.[12] Notwithstanding the mechanistic details of the reaction, the experimentally found end-products $Ru^{II}(edta)(SO_3)^{4-}$ and SO_4^{2-} (determined by $HCl/BaCl_2$ test) are in good agreement with the proposed mechanism. The rate and corresponding activation parameters (determined by temperature dependence studies of observed rate constants) for the formation of $Ru^{II}(edta)(SO_3)^{4-}$ are summarised in Table 2. From Scheme II, one may consider the reaction as a reduction of Ru(III)-edta complex by sulfite at high pH and it could have been studied at low complex concentration. In practice, however, formation of $Ru^{II}(edta)(SO_3)^{4-}$ could not be followed spectrophotometrically due to absence of any substantial difference in the spectra of reactant Ru(III)-edta and product $Ru^{II}(edta)\ SO_3)^{4-}$ complexes. Therefore, formation of $Ru^{II}(edta)(SO_4)^{4-}$ was studied by following the shift of equilibrium (*5*). The kinetic parameters k'_{obs} include contributions from all the electron transfer steps including predissociation of μ-oxo dimer complex.

A careful analysis and comparison of our experimental results to those of reported for $Fe(III)\text{-}edta/SO_3^{2-}$ system[12] reveals the fact that the key factor in the Fe(III)-catalysed oxidation of sulfite is the formation of $Fe^{III}(edta)(SO)_3)^{3-}$ which reacts with O_2 to initiate the catalytic process. In our case, $Ru^{III}(edta)(SO_3)^{3-}$ is extremely

Table 2 Rate and activation parameters [a] for the formation of $Ru^{II}\ (edta)(SO_3)^{4-}$

Temperature, °C	$k_{obs} x 10^3 s^{-1}$	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/deg mol)
25	0.6		
30	1.1		
35	1.9	71 ± 6	-69 ± 19
45	3.9		

[a] Same experimental conditions as given in Table 1.

unstable and undergoes rapid hydrolysis to give corresponding aquo/hydroxo species. We did not obtain any experimental evidences for $Ru^{III}(edta)(SO_3)^{3-}$ in solution. Moreover, $Ru^{II}(edta)(SO_3)^{4-}$ is completely inert and is insensitive to molecular oxygen. The marked difference in stability may be due to the fact that the $3d^5$ system preferentially stabilises the π-acceptor sulfur-oxides.

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References

1. M.M. Taqui Khan, M.R.H. Siddiqui, A. Hussain and M.A. Moiz, *Inorg. Chem.*, **25**, 2765 (1986).
2. M.M. Taqui Khan, H.C. Bajaj and D. Chatterjee, *J. Mol. Catal.*, **71**, 177 (1992).
3. M.M. Taqui Khan, D. Chatterjee, S. Sanalkumar, R.R. Merchant and K.N. Bhatt, *J. Mol. Catal.*, **67**, 317 (1991).
4. M.M. Taqui Khan, R.S. Shukla and A. Prakash Rao, *Inorg. Chem.*, **28**, 452 (1989).
5. M.M. Taqui Khan, D. Chatterjee, R.R. Merchant, P. Paul, S.H.R. Abdi, D. Srinivas, M.A. Moiz, M. Badbhade and K. Venkatasubramanian, *Inorg. Chem.* **31**, 2711 (1992).
6. C.J. Weschler, M.L. Mandich and T.E. Giraedel, *J. Geophys. Res.*, **91**, 5189 (1986).
7. T.E. Graedel, M.L. Mandich and C.J. Weschler, *J. Geophys. Res.*, **91**, 5205 (1986).
8. J. Kraft and R. van Eldik, *Inorg. Chem.*, **28**, 2297 (1989).
9. N. Coichev and R. van Eldik, *Inorg. Chem.*, **30**, 2375 (1991).
10. R. van Eldik, N. Coichev, K.B. Reddy and A. Gerhard, *Ber. Bunsenger. Phys. Chem.*, **96**, 478 (1992).
11. K.B. Reddy and R. van Eldik, *Atmos Environ*, **26a**, 661 (1992).
12. M.D. Ritter and R. van Eldik, *J. Chem. Soc., Dalton. Trans.*, 1037, 1045 (1992).
13. A.A. Diamantis and J.V. Dubrawski, *Inorg. Chem.*, **20**, 1192 (1981).
14. T. Matsubara and C. Cruetz, *Inorg. Chem.*, **18**, 1956 (1979).
15. R. van Eldik and G.M. Harris, *Inorg. Chem.*, **19**, 880 (1980).
16. H.C. Bajaj and R. van Eldik, *Inorg. Chem.*, **27**, 4052 (1988).
17. D.M. Kurtz, Jr, *Chem. Rev.*, **90**, 585 (1990).
18 A. Yeh, N. Scott, and H. Taube, *Inorg. Chem.*, **21**, 2542 (1982).
19. H.E. Toma, and K. Araki, *J. Coord. Chem.*, **24**, 1 (1991).