Monatshefte für Chemie 135, 1489–1502 (2004)
DOI 10.1007/s00706-004-0225-3

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Mechanistic and Spectral Studies of the Ruthenium(III) Catalysed Oxidation of Sulfanilic Acid by Alkaline Hexacyanoferrate(III)

Rahamatalla M. Mulla, Gurubasavaraj C. Hiremath,
and **Sharanappa T. Nandibewoor***

Post-Graduate Department of Studies in Chemistry, Karnatak University,
Dharwad-580 003, India

Received March 17, 2004; accepted (revised) May 25, 2004.

Summary. The kinetics of ruthenium(III) catalysed oxidation of sulfanilic acid (*p*-aminobenzenesulfonic acid) by hexacyanoferrate(III) in alkaline medium at a constant ionic strength of $2.5\,\mathrm{mol\cdot dm^{-3}}$ has been studied spectrophotometrically using a rapid kinetic accessory. The reaction exhibits 2:8 stoichiometry (*SNA*:*HCF*(III)). The reaction showed first order kinetics in [hexacyanoferrate(III)] and [ruthenium(III)] and apparent less than unit order in both sulfanilic acid and alkali concentrations. The reaction rate increases with increasing ionic strength but the relative permittivity (ε_T) of the medium has a negligible effect on the rate of the reaction. Initial addition of reaction products did not affect the rate significantly. A mechanism involving the formation of a complex between sulfanilic acid and hydroxylated species of ruthenium(III) has been proposed. The active species of *HCF*(III) and ruthenium(III) are understood as $[\mathrm{Fe(CN)_6}^{3-}]$ and $[\mathrm{Ru(H_2O)_5OH}]^{2+}$, respectively. The main products were identified by IR, NMR, and mass spectral studies. The reaction constants involved in the different steps of mechanism are calculated. The activation parameters with respect to the slow step of the mechanism are computed and discussed and thermodynamic quantities are also calculated.

Keywords. Sulfanilic acid; Hexacyanoferrate(III); Ruthenium(III); Catalysis.

Introduction

Hexacyanoferrate(III) (*HCF*(III)) has been widely used to oxidise numerous organic and inorganic compounds in alkaline media. It has been suggested that in alkaline media the hexacyanoferrate(III) ion simply acts as an electron abstracting reagent in redox reactions [1, 2]. However, *Speakman* and *Waters* [3] have suggested different paths of oxidation of aldehydes, ketones, and nitroparaffins.

---

* Corresponding author. E-mail: stnandibewoor@yahoo.com

Singh and co-workers, [4, 5] while discussing the oxidations of formaldehyde, acetone, and ethyl methyl ketone, have suggested that the oxidation takes place *via* an electron transfer process resulting in the formation of a free radical intermediate.

Sulfanilic acid (*p*-aminobenzenesulfonic acid) (*SNA*) is an important and interesting compound, which finds a number of applications in the syntheses of organic dyes [6]. The amide of sulfanilic acid (sulfanilamide) and certain related substituted amides are of considerable medical importance as the sulfa drugs. Although they have been supplanted to a wide extent by antibiotics such as penicillin, terramycin, chloromycetin, and aureomycin, the sulfa drugs still have their medical uses, and make up a considerable portion of the output of the pharmaceutical industry [7]. Several studies have been reported on the oxidation of sulfanilic acid by other oxidants such as peroxomonophosphoric acid [8], periodate [9], H_2O_2 [10], Ce(IV) [11], persulfate [12], and peroxy disulfate [13].

Several research groups have identified different products by different oxidants for sulfanilic acid [8–13]. Thus, it becomes important to study sulfanilic acid because of its biological significance and reactivity towards different oxidants.

Ruthenium(III) acts as an efficient catalyst in many redox reactions, particularly in an alkaline medium [14]. The catalysis mechanism can be quite complicated due to the formation of different intermediate complexes, free radicals, and different oxidation states of ruthenium. The kinetics of fast reactions between ruthenate(VII), RuO_4^-, and manganate(VI), *i.e.* MnO_4^{2-}, have been studied [15]. The reaction is presumed to proceed *via* an outer-sphere mechanism. The uncatalysed reaction between sulfanilic acid and *HCF*(III) in an alkaline medium has also been studied previously [16]. A tiny amount of ruthenium(III) is sufficient to catalyse the reaction and a variety of mechanisms is possible. In view of lack of literature on the title reaction, we have selected sulfanilic acid as substrate for this study and its oxidation in presence of ruthenium(III) is studied to understand the possible species of oxidant and ruthenium(III). The present study deals with the title reaction to investigate the redox chemistry of *HCF*(III) in such media, and to arrive at a suitable mechanism.

Results and Discussion

Reaction Orders

As the hexacyanoferrate(III) oxidation of sulfanilic acid in alkaline medium proceeds with a measurable rate in the absence of ruthenium(III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions, so $k_C = k_T - k_U$. Hence the reaction orders have been determined from the slopes of log k_C *versus* log concentration plots by varying the concentrations of reductant, Ru(III), and alkali in turn while keeping the others constant.

The oxidant, *HCF*(III), concentration was varied in the range of 1.0×10^{-4} to $1.0\times10^{-3}\,mol\,dm^{-3}$ and the linearity of a plot of log absorbance *versus* time

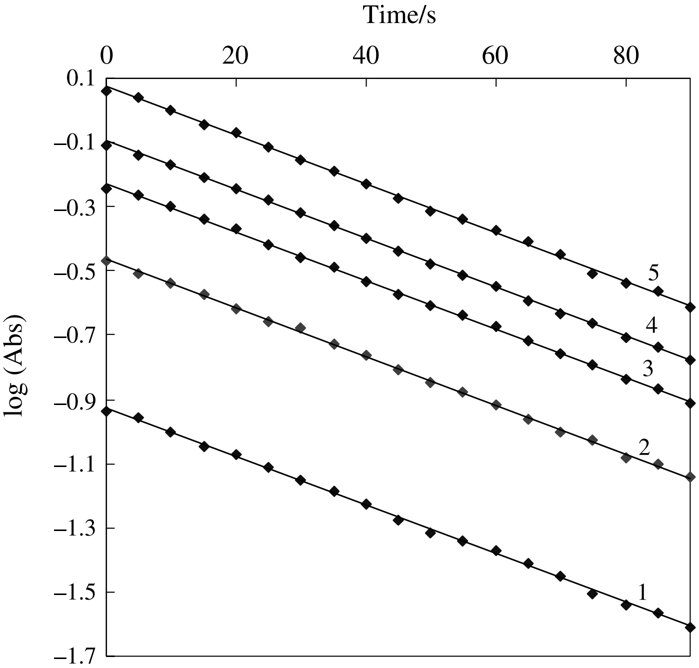


Fig. 1. First order plots of Ru(III) catalysed oxidation of sulfanilic acid by *HCF*(III) in aqueous alkaline medium at 25°C; [*HCF*(III)]×10^4 (mol dm^{-3}); (1) 1.0; (2) 3.0; (3) 5.0; (4) 7.0; (5) 10

($r \geq 0.9998$, $S \leq 0.0124$) (Fig. 1) up to 85% completion of the reaction indicates the order in [*HCF*(III)] as unity. This was also confirmed by variation of [*HCF*(III)], which did not result in any change of the pseudo-first order rate constants, k_C (Table 1). The substrate, sulfanilic acid, concentration was varied in the range of 2.0×10^{-3} to 2.0×10^{-2} mol dm^{-3} at 25°C keeping all other reactants' concentrations and conditions constant including the ruthenium(III) catalyst. The k_C values increased with increase in concentration of sulfanilic acid indicating an apparent less than unit order dependence on [sulfanilic acid] (Table 1).

The ruthenium(III) concentration was varied from 1.0×10^{-6} to 1.0×10^{-5} mol dm^{-3}, at constant concentrations of hexacyanoferrate(III), sulfanilic acid, and alkali and constant ionic strength. The order in [Ru(III)] was found to be unity (Table 1) from the linearity of the plot of log k_C *versus* log [Ru(III)] ($r \geq 0.9996$, $S \leq 0.0122$). The effect of alkali on the reaction has been studied at constant concentrations of sulfanilic acid, *HCF*(III), and ruthenium(III) and a constant ionic strength of 2.5 mol dm^{-3}. The rate constants increased with increasing [alkali] and the order was found to be less than unity (Table 1).

Effect of Ionic Strength and Solvent Polarity

The effect of ionic strength was studied by varying the sodium perchlorate concentration. The ionic strength of the reaction medium was varied from 0.90 to 3.0 mol dm^{-3} at constant concentrations of *HCF*(III), sulfanilic acid, ruthenium(III), and alkali. It was found that the rate constant increased with increasing

Table 1. Effect of variation of [*HCF*(III)], [*SNA*], [Ru(III)], and [OH$^-$] on Ru(III) catalysed oxidation of sulfanilic acid (*SNA*) by *HCF*(III) in aqueous alkaline medium at 25°C and $I = 2.5$ mol dm^{-3}

[*HCF*(III)]$\times 10^4$/ mol dm^{-3}	[*SNA*]$\times 10^3$/ mol dm^{-3}	[Ru(III)]$\times 10^6$/ mol dm^{-3}	[OH$^-$]$\times 10^1$/ mol dm^{-3}	$k_T \times 10^2$/ s^{-1}	$k_U \times 10^3$/ s^{-1}	$k_C \times 10^2$/s^{-1}	
						Found	Calc.
1.0	10	10	9.0	2.23	4.72	1.76	1.75
3.0	10	10	9.0	2.24	4.75	1.77	1.75
5.0	10	10	9.0	2.22	4.79	1.74	1.75
7.0	10	10	9.0	2.24	4.76	1.76	1.75
10	10	10	9.0	2.22	4.71	1.75	1.75
5.0	2.0	10	9.0	0.69	1.76	0.51	0.49
5.0	6.0	10	9.0	1.66	3.76	1.28	1.22
5.0	10	10	9.0	2.22	4.79	1.74	1.75
5.0	15	10	9.0	2.79	5.62	2.23	2.24
5.0	20	10	9.0	3.55	6.85	2.86	2.60
5.0	10	1.0	9.0	0.65	4.79	0.17	0.17
5.0	10	3.0	9.0	1.00	4.79	0.52	0.53
5.0	10	5.0	9.0	1.36	4.79	0.88	0.88
5.0	10	7.0	9.0	1.72	4.79	1.24	1.23
5.0	10	10	9.0	2.22	4.79	1.74	1.75
5.0	10	10	1.5	0.74	0.85	0.65	0.65
5.0	10	10	5.0	1.56	2.39	1.32	1.38
5.0	10	10	9.0	2.22	4.79	1.74	1.75
5.0	10	10	12	2.60	6.61	1.94	1.92
5.0	10	10	15	2.93	8.07	2.12	2.03

concentration of $NaClO_4$ and the plot of log k_C *versus* $I^{1/2}$ was linear with a positive slope ($r \geq 0.998$, $S \leq 0.0167$) (Fig. 2).

The relative permittivity (ε_T) on the rate constant has been studied by varying *t*-butyl alcohol-water content in the reaction mixture with all other conditions being maintained constant including the Ru(III) catalyst. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids [17]. There is no reaction of the solvent with the oxidant under the experimental conditions. It was found that the relative permittivity of the medium has negligible effect on the rate constant (k_C).

Effect of Initially Added Reaction Products

The initially added products, such as *HCF*(II), and disodium salt of 2-ketoazoxybenzene-4,4′-disulfonic acid did not have any significant effect on the rate of the reaction.

Test for Free Radicals

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 1 hour under nitrogen atmosphere. On dilution

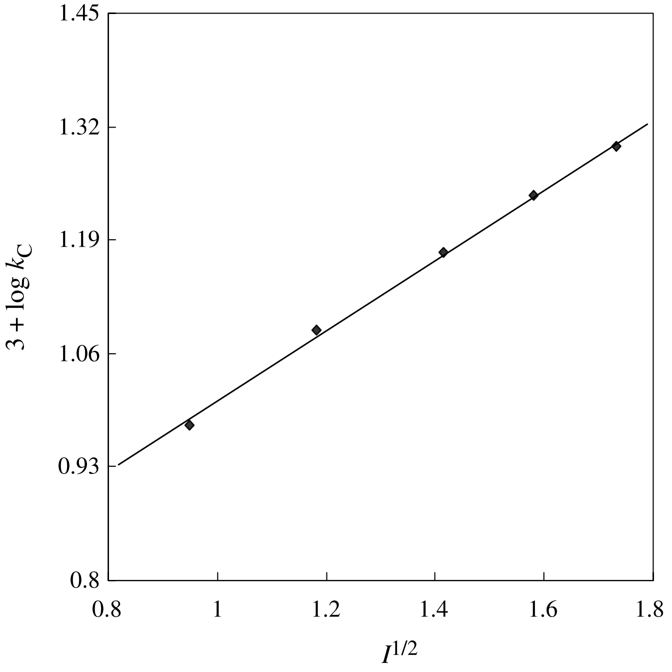


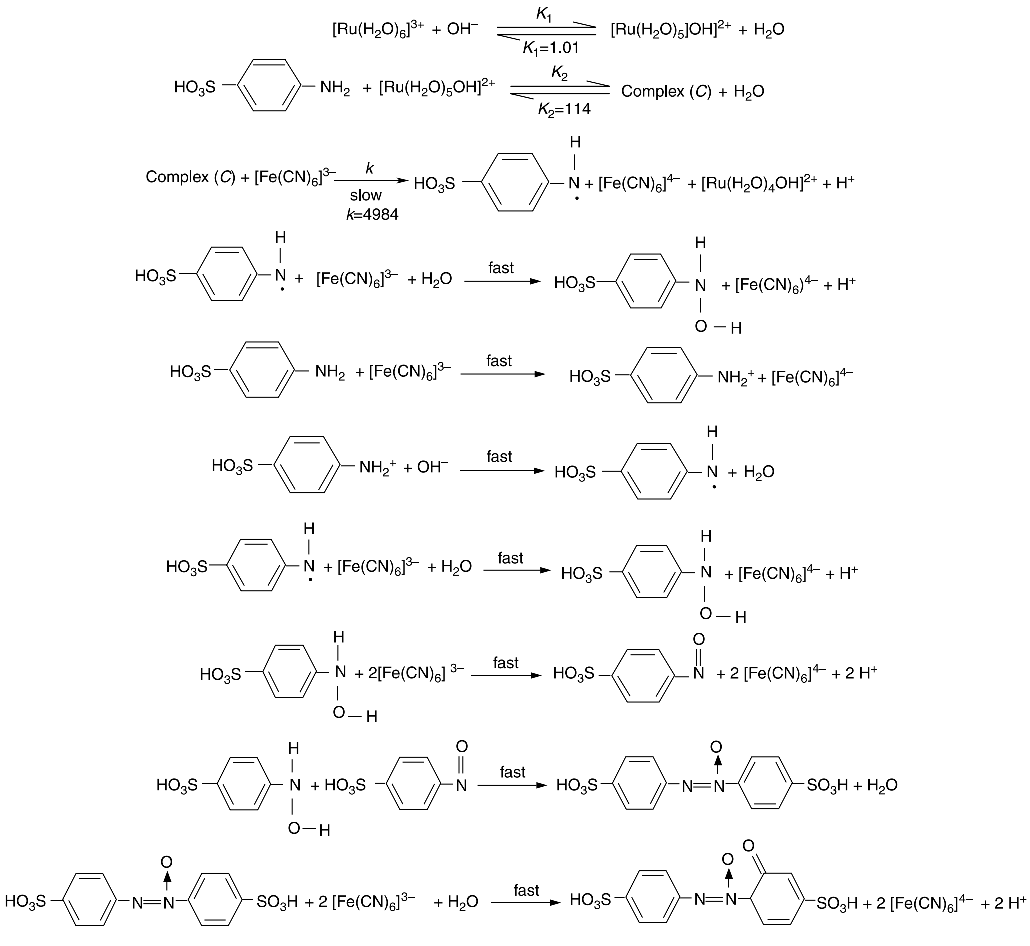
Fig. 2. Plot of $\log k_C$ *versus* $I^{1/2}$; $[HCF(\text{III})] = 5.0\times10^{-4}$, $[SNA] = 10\times10^{-3}$, $[\text{Ru(III)}] = 1.0\times10^{-5}$, and $[\text{OH}^-] = 0.90\,\text{mol dm}^{-3}$ (sodium perchlorate was used to change the ionic strength of the solution)

with methanol, a white precipitate of polymer was formed. This indicates the intervention of free radicals in the reaction. The blank experiment of either *HCF*(III) and ruthenium(III) or *SNA* and ruthenium(III) alone with acrylonitrile did not induce polymerization under the same conditions as those which induce polymerization with reaction mixtures. Initially added acrylonitrile decreases the rate indicating the free radical intervention. This fact was reported previously [18].

Effect of Temperature

The rate of reaction was measured at different temperatures under varying [*SNA*]. The rate of reaction increased with increasing temperature. The rate constants, *k*, of the slow step of Scheme 1 were obtained from the intercept of the plot of $[\text{Ru(III)}]/k_C$ *versus* $1/[SNA]$ ($r \geq 0.9996$, $S \leq 0.0141$) (Fig. 3) and used to calculate the activation parameters. The values of $k\times10^{-3}$ ($\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$) were 4.98, 6.23, 7.73, 9.54, and 12.2 at 298, 303, 308, 313, and 318 K, respectively. From the plot of $\log k$ *versus* $1/T$ ($r \geq 0.9989$, $S \leq 0.0135$) with least square analysis, the activation parameters, E_a, $\log A$, $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ are calculated as 35 ± 2, 8.8 ± 0.4, 33 ± 2, kJ mol^{-1}, $-16 \pm 0.8\,\text{JK}^{-1}\,\text{mol}^{-1}$, and $37 \pm 1.8\,\text{kJ mol}^{-1}$ (for the uncatalysed reaction [16] the values are 60 ± 3, 8.4 ± 0.4, $58 \pm 3\,\text{kJ mol}^{-1}$, $-93 \pm 3\,\text{JK}^{-1}\,\text{mol}^{-1}$, and $86 \pm 4\,\text{kJ mol}^{-1}$).

Variation of the concentrations each of the oxidant (*HCF*(III)), catalyst (ruthenium(III)), substrate (*SNA*), and alkali, while keeping the others constant showed that the reaction exhibits first-order in oxidant and ruthenium(III) and less than unit



Scheme 1

order in substrate and alkali concentrations (Table 1). The reaction between *HCF*(III) and *SNA*, in alkaline medium in presence of ruthenium(III) has a stoichiometry of 2:8. No effect of added products was observed.

It is interesting to identify the probable ruthenium(III) chloride species in the alkaline medium. In the present study it is quite probable that the species $[Ru(H_2O)_5OH]^{2+}$ might assume the general form $[Ru(III)(OH)_x]^{3-x}$. The value of x would always be less than six because there are no definite reports of any hexahydroxo species of ruthenium. The remainder of the coordination sphere will be filled by water molecules. Hence under the conditions $[OH^-] \gg [Ru(III)]$, ruthenium(III) is mainly present [19] as the hydroxylated species, $[Ru(H_2O)_5OH]^{2+}$. Increase in rate with increase in $[OH^-]$ indicates the presence of the hydroxylated species of ruthenium(III) as a reactive species, which is shown by the following equilibrium (1) in accordance with earlier work [20].

$$[Ru(H_2O)_6]^{3+} + OH^- \rightleftharpoons [Ru(H_2O)_5OH^{2+} + H_2O \qquad (1)$$

Based on the experimental results, a mechanism can be proposed for which all the observed orders in each constituent such as [oxidant], [catalyst], [reduc-

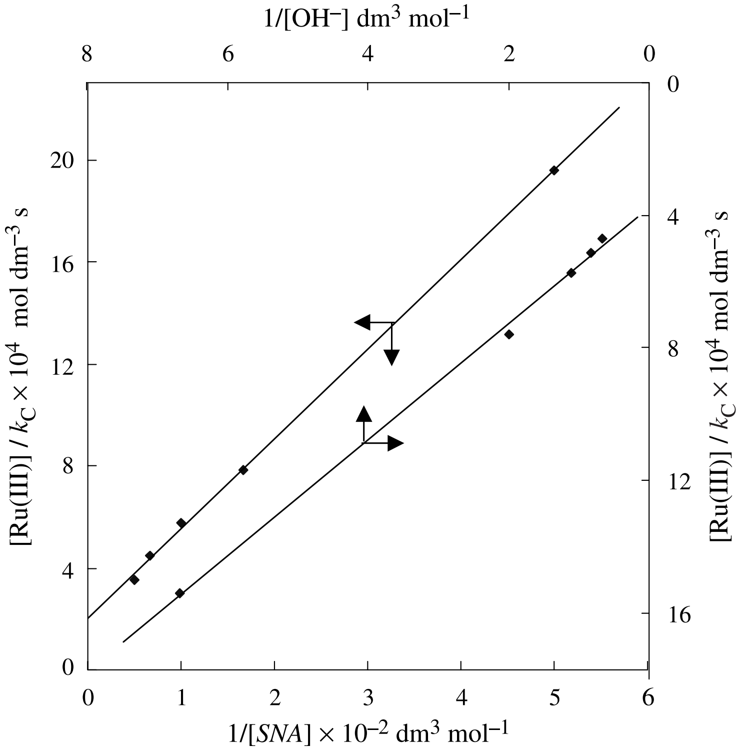
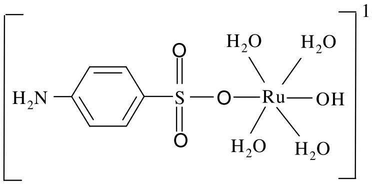


Fig. 3. Verification of rate law (3) in the form of (4) (conditions as given in Table 1)

tant], and [OH^-] may be well accommodated. Oxidation of sulfanilic acid by hexacyanoferrate(III) in presence of ruthenium(III) in NaOH media is a non-complementary reaction with oxidant undergoing eight equivalent changes. In most of the oxidation reactions, hexacyanoferrate(III) resembles Cu(II), which involves free radical formation and rapidly oxidises it [21–23]. In the present study, the oxidation reaction proceeds via formation of a complex (*C*) between *SNA* and the hydroxylated ruthenium(III) species. Such a complex (*C*) formation between substrate and catalyst, which is also supported by the observed fractional order in [sulfanilic acid], has also been observed previously [24]. The complex (*C*) decomposes in presence of oxidant in a slow step to form a free radical derived from *SNA*, hexacyanoferrate(II), and regeneration of catalyst, ruthenium(III). The free radical further reacts with one *HCF*(III) in aqueous media in a fast step to give another intermediate product, hydroxylamine benzene sulfonic acid, and *HCF*(II). The hydroxylamine benzene sulfonic acid so formed further reacts with two *HCF*(III) in a fast step to give nitrosobenzene sulfonic acid and *HCF*(II). Another molecule of *SNA* reacts with two *HCF*(III) in fast steps to give hydroxylamine benzene sulfonic acid as intermediate product and *HCF*(II). The two intermediate products, namely nitrosobenzene sulfonic acid and hydroxylamine benzene sulfonic acid, rearrange themselves in a fast step to azoxybenzene-4,4′-disulfonic acid as another intermediate product, which in presence of two *HCF*(III) undergoes further oxidation to the final products, 1,2-dihydro-2-oxoazoxybenzene-4,4′-disulfonic acid and hexycyanoferrate(II) (*HCF*(II)), satisfying the stoichiometric observations. The results can be accommodated by Scheme 1.

Probable structure of complex (*C*) =



Spectral evidence for the proposed catalyst-substrate complex was obtained from the UV-V is spectra of sulfanilic acid and a mixture of ruthenium(III) and sulfanilic acid. A hypsochromic shift, λ_{max}, of *ca.* 7 nm from 344 to 337 nm is observed together with hyperchromicity at 337 nm. Further the formation of complex (*C*) is also proved kinetically by the non-zero intercept of the plot of $[\mathrm{Ru(III)}]/k_C$ *versus* 1/[sulfanilic acid] ($r \geq 0.9996$, $S \leq 0.0141$) (Fig. 3).

In the presence of catalyst, the reaction is understood to occur in parallel paths with contribution from the uncatalysed and catalysed paths. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions.

$$\mathrm{Rate_{cat}} = \mathrm{Rate_{total}} - \mathrm{Rate_{uncat}}$$

Scheme 1 leads to the following rate law given in Eq. (2). For details see Appendix.

$$\begin{aligned}\mathrm{Rate_{cat}} &= -\frac{\mathrm{d}[\mathrm{Fe(CN)_6}]^{3-}}{\mathrm{d}t}\\ &= \frac{kK_1K_2[SNA]_T[\mathrm{Fe(CN)_6}]^{3-}[\mathrm{Ru(III)}]_T[\mathrm{OH^-}]_T}{\{1+K_1K_2[\mathrm{Ru(III)}]_T[\mathrm{OH^-}]_T\}\{1+K_1[\mathrm{Ru(III)}]_T\}\{1+K_1[\mathrm{OH^-}]_T+K_1K_2[SNA]_T[\mathrm{OH^-}]_T\}}\end{aligned} \tag{2}$$

The terms $(1+K_1K_2[\mathrm{Ru(III)}]_T[\mathrm{OH^-}]_T)$ and $(1+K_1[\mathrm{Ru(III)}]_T)$ in the denominator of Eq. (2) approximate to unity in view of low concentration of ruthenium(III) used. Therefore Eq. (2) becomes Eq. (3) (omitting the subscripts 'T').

$$\frac{\mathrm{Rate_{cat}}}{[\mathrm{Fe(CN)_6}]^{3-}} = k_C = k_T - k_U = \frac{kK_1K_2[SNA][\mathrm{Ru(III)}][\mathrm{OH^-}]}{1+K_1[\mathrm{OH^-}]+K_1K_2[SNA][\mathrm{OH^-}]} \tag{3}$$

Further, Eq. (3) can be rearranged to Eq. (4), which is suitable for verification of the rate law.

$$\frac{[\mathrm{Ru(III)}]}{k_C} = \frac{1}{kK_1K_2[\mathrm{OH^-}][SNA]} + \frac{1}{kK_2[SNA]} + \frac{1}{k} \tag{4}$$

According to Eq. (4), the plots of $[\mathrm{Ru(III)}]/k_C$ *versus* $1/[SNA]$ ($r \geq 0.9996$, $S \leq 0.0141$) and $[\mathrm{Ru(III)}]/k_C$ *versus* $1/[\mathrm{OH^-}]$ ($r \geq 0.999$, $S \leq 0.0113$) are linear with an intercept supporting the Ru(III)-sulfanilic acid complex, and which is verified in Fig. 3. From the slope and intercept of such plots, the values of

K_1, K_2, and k are calculated as 1.0 ± 0.05, $(1.14 \pm 0.06) \times 10^2\,\mathrm{dm^3\,mol^{-1}}$, and $(4.98 \pm 0.25) \times 10^3\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. The value of K_1 is in agreement with earlier data [25]. Using these K_1, K_2, and k values, the rate constants under different experimental conditions were calculated by Eq. (3) and compared with experimental data. There is a good agreement between them (Table 1).

The effect of increasing ionic strength on the rate explains qualitatively the reaction between two negatively charged ions, as seen in Scheme 1. The effect of solvent on the reaction rate is described elsewhere [26]. The negligible effect of permittivity (ε_T) on the rate of reaction explains that the reaction takes place between an ion and a neutral molecule as given in Scheme 1.

The difference in the activation parameters for the catalysed and uncatalysed reaction explains the catalytic effect on the reaction. The catalyst, Ru(III), forms the complex with sulfanilic acid which shows more reducing property than sulfanilic acid itself. Hence the catalyst, Ru(III), lowers the energy of activation. The negative value of $\Delta S^{\#}$ indicates that the complex (C) is more ordered than the reactants [27]. The observed modest enthalpy of activation and higher rate constant of the slow step (than k_C) indicate that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by earlier work [28]. Scheme 1 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequences of one-electron steps.

The thermodynamic quantities for the first equilibrium step in Scheme 1 can be evaluated as follows. The hydroxyl ion concentration and substrate ion concentration (as in Table 1) was varied at five different temperatures. From the slopes and intercepts, of the plots of $[\mathrm{Ru(III)}]/k_C$ *versus* $1/[\mathrm{OH^-}]$ ($r \geq 0.999$, $S \leq 0.0113$) and $[\mathrm{Ru(III)}]/k_C$ *versus* $1/[SNA]$ ($r \geq 0.9996$, $S \leq 0.0141$) the values of K_1 ($\mathrm{dm^3\,mol^{-1}}$) are calculated at different temperatures and these values are 1.01, 1.18, 1.41, 1.66, and 1.95 at 298, 303, 308, 313, and 318 K, respectively. The *van't Hoff*'s plot was drawn for the variation of K_1 with temperature [*i.e.*, $\log K_1$ *versus* $1/T$ ($r \geq 0.9998$, $S \leq 0.0128$)] and the values of the enthalpy of reaction, ΔH, entropy of reaction, ΔS, and free energy of reaction, ΔG, were calculated as $26 \pm 1\,\mathrm{kJ\,mol^{-1}}$, $88 \pm 4\,\mathrm{JK^{-1}\,mol^{-1}}$, and $-1.10 \pm 0.05\,\mathrm{kJ\,mol^{-1}}$. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reactions preceding the rate determining step are fairly fast and involve little activation energy [29].

Conclusion

The ruthenium(III) catalysed oxidation of sulfanilic acid by hexacyanoferrate(III) in alkaline medium is consistent with product, mechanistic, and kinetic studies. A micro amount of ruthenium(III) is sufficient to catalyse the title reaction with measurable rate.

Experimental

Devices

Since the initial reaction was too fast to be monitored by the usual methods, kinetic measurements were performed on a Peltier Accessory (temperature control) attached Varian CARY 50 Bio UV-Vis

Spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12), Thin layer Chromatography, Nicolet Impact-410 FT IR, ^{1}H NMR by Gemini-200 MHz Spectrometer with operating procedure (DOP-13) (in CF_3COOD), Autospec Electron Impact Mass Spectrometer, and Elementar Vario EL.

Materials

All chemicals used were of reagent grade. A standard solution of $Fe(CN)_6{}^{3-}$ was prepared by dissolving the appropriate amounts of $K_3Fe(CN)_6$ (BDH) in doubly distilled water. The solution was standardized iodometrically [30]. Sulfanilic acid (Merck) is not only insoluble in organic solvents, but also nearly insoluble in water and in aqueous acids. Sulfanilic acid is soluble in aqueous bases. Therefore the solution of sulfanilic acid (Merck) was prepared by dissolving an appropriate amount of sample in warm very dilute alkaline solution.

Hexacyanoferrate(II) solution was prepared by dissolving a known amount of $K_4Fe(CN)_6$ (BDH) in water. Sodium hydroxide (Merck) and sodium perchlorate (BDH) were used to provide the required *pH* and to maintain the ionic strength, respectively. The Ru(III) solution was prepared by dissolving a known amount of $RuCl_3$ (s.d.fine-chem) in HCl (0.20 mol dm^{-3}). Hg was added to the Ru(III) solution to reduce any Ru(IV) formed during the preparation of the Ru(III) stock solution which was set aside for 24 h. The Ru(III) concentration was then assayed by *EDTA* titration [31].

Kinetic Measurements

All kinetic measurements were performed under pseudo-first order conditions with excess of sulfanilic acid over *HCF*(III) at a constant ionic strength of 2.5 mol dm^{-3} in alkaline medium. The reaction was initiated by mixing previously thermostatted solutions of hexacyanoferrate(III) and sulfanilic acid which also contained the necessary quantities of Ru(III), NaOH, and $NaClO_4$ to maintain the required alkalinity and ionic strength, respectively. The temperature was kept constant at 25 ± 0.1°C. The course of reaction as a function of time was followed by monitoring the absorbance of hexacyanoferrate(III) at its absorption maximum of 420 nm where the other constituents of the reaction mixture do not absorb significantly. This was carried out in a 1 cm quartz cell of a Peltier Accessory (temperature control), attached to a Varian CARY 50 Bio UV-Vis Spectrophotometer which was connected to a rapid kinetic accessory (HI-TECH SFA-12). The validity of *Beer*'s law for hexacyanoferrate(III) at 420 nm under the reaction conditions had been verified, giving $\varepsilon = 1060 \pm 20\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$. Pseudo first-order rate constants (k_C) were obtained from the plots of log [*HCF*(III)] *versus* time, the plots were linear up to 85% completion of the reaction in alkaline medium and the k_C values were reproducible within ±5%.

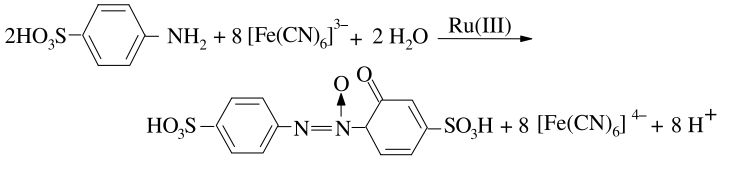
The effect of dissolved O_2 on the rate of reaction was studied by following the reaction under atmospheric conditions and under nitrogen. No significant difference between the results was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used for each experiment.

In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polyethene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.

In the alkaline medium during the progress of the reaction, the colour of the solution changed from yellow to almost colorless, which is verified by titration for *HCF*(II) [32]. Regression analysis of experimental data to obtain the regression coefficient *r* and standard deviation *S* of points from the regression line was performed using a Pentium-IV personal computer.

Stoichiometry and Product Analysis

The reaction mixture containing excessive *HCF*(III) over sulfanilic acid and constant [Ruthenium(III)] were mixed in presence of 0.90 mol dm^{-3} NaOH, adjusted to a constant ionic strength of 2.5 mol dm^{-3}, and allowed to react for about 2 h at 25 ± 0.1°C under nitrogen as gas phase. The remaining *HCF*(III) was then analysed spectrophotometrically. The results indicated that eight moles of *HCF*(III) were consumed by two moles of sulfanilic acid according to Eq. (5).



(5)

The reaction product, the disodium salt of 1,2-dihydro-2-oxoazoxybenzene-4,4′-disulfonic acid, was eluted with ether. A spot test analysis [33] revealed the presence of azo, nitroso, and keto groups. The presence of dye was also confirmed by recording its UV/Vis spectrum [34] and its IR [35] spectrum. IR (KBr) showed bands at $\bar{\nu} = 1128$ and 1079 cm^{-1} for $-C_6H_4SO_3Na$, 1727 cm^{-1} for carbonyl, >C=O, stretching, and 1375 cm^{-1} for −N=N → O stretching. The acidified product of the disodium salt of the ketoazoxy dye (2-hydroxyazoxybenzene-4,4′-disulfonic acid) was further

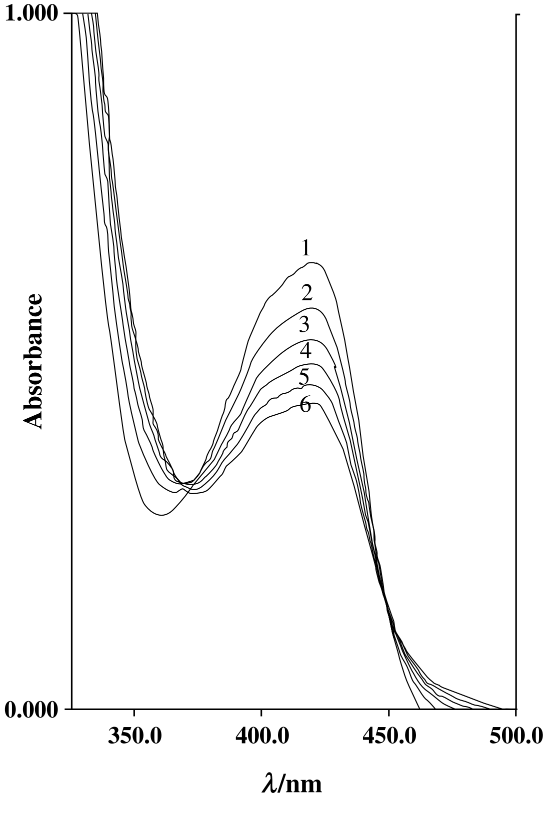
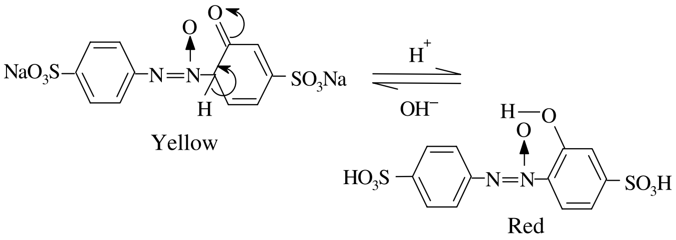


Fig. 4. Spectroscopic changes occurring in the Ru(III) catalysed oxidation of sulfanilic acid by hexacyanoferrate(III) with $[SNA] = 10 \times 10^{-3}$, $[HCF(III)] = 5.0 \times 10^{-4}$, $[Ru(III)] = 1.0 \times 10^{-5}$, $[OH^-] = 0.90$, and $I = 2.5$ mol dm^{-3} at 25°C; scanning time interval = 30 s



Scheme 2

characterized by ^{1}H NMR, electron impact mass spectroscopy, and CHN and S analysis. ^{1}H NMR showed seven aromatic protons, two protons for SO_3H, and one phenolic proton as multiplet from $\delta = 7.6$–8.8 in CF_3COOH (signal for CF_3COOH at $\delta = 11.5$). The mass spectrum of this compound displayed a peak at $m/z = 372$ after the loss of two hydrogen atoms from its molecular ion of 374. The elemental analysis was in agreement with the molecular formula $C_{12}H_{10}O_8N_2S_2$. The only organic product obtained in the oxidation is 2-hydroxyazoxybenzene-4,4′-disulfonic acid, which is further confirmed by a single spot in TLC and the yield obtained was found to be 75% determined from its acetyl derivative. However, the other product, in alkaline medium is hexacyanoferrate(II), $Fe(CN)_6{}^{4-}$, identified by titration [32]. The spectral changes during the reaction are shown in Fig. 4. It is evident that [*HCF*(III)] decreases at 420 nm.

The product disodium salt of ketoazoxy dye in alkaline medium does not undergo further oxidation under the present kinetic conditions, since the test for possible oxidation products of the ketone, *i.e.* acid and nitrosobenzene, was negative.

Identification of the Ketoazoxy Dye from its UV/Vis Spectrum

When the UV/Vis spectrum was observed at different *pH*, *i.e.* from $pH = 4$–7, no absorption was observed in the visible region but in the UV region at $\lambda_{max} = 278$ nm. The extinction coefficient was found to be $\varepsilon = 174.1\,dm^3\,mol^{-1}\,cm^{-1}$ indicating a $\pi \rightarrow \pi^*$ transition due to the carbonyl chromophore (>C=O). At high H^+ ion concentration absorption was observed in the visible region at $\lambda_{max} = 601.6$ nm, with $\varepsilon = 13.1\,dm^3\,mol^{-1}\,cm^{-1}$ indicating $n \rightarrow \pi^*$ transitions [36]. When we compare the UV/Vis spectrum of azobenzene and azoxybenzene with that of the product ketoazoxy dye, it has been found that for azo dye at $\lambda_{max} = 433$ nm $\varepsilon = 727\,dm^3\,mol^{-1}\,cm^{-1}$, for azoxybenzene at $\lambda_{max} = 322$ nm $\varepsilon = 14700\,dm^3\,mol^{-1}\,cm^{-1}$ in *Me*OH, whereas for ketoazoxybenzene at $\lambda_{max} = 601.6$ nm $\varepsilon = 13.1\,dm^3\,mol^{-1}\,cm^{-1}$ in HCl, indicating a forbidden transition. The shift in λ_{max} value of the product towards longer wavelength may be due to increased conjugation. A carbonyl group (>C=O) extends the conjugation of a chromophore $-N{=}N \rightarrow O$ by resulting in a different absorption maximum with a very low extinction coefficient. The disodium salt of the ketoazoxy dye in acidic medium exists in an enolic form, which is more stable than its keto tautomer due to the change from non-aromatic to aromatic and also due to the formation of an intramolecular hydrogen bond, as shown in Scheme 2.

Appendix

According to Scheme 1

$$\begin{aligned} \text{Rate}_{cat} &= k[\text{Fe(CN)}_6]^{3-}[C] \\ &= kK_1K_2[SNA]_f[\text{Ru(III)}]_f[\text{Fe(CN)}_6]^{3-}[\text{OH}^-]_f \qquad \text{(I)} \end{aligned}$$

The total concentration of sulfanilic acid is given by (subscripts T and f stand for total and free)

$$\begin{aligned}[SNA]_{\mathrm{T}} &= [SNA]_{\mathrm{f}} + [C] \\ &= [SNA]_{\mathrm{f}} + K_2[SNA]_{\mathrm{f}}[\mathrm{Ru(OH)}]^{2+} \\ &= [SNA]_{\mathrm{f}} + K_1K_2[SNA]_{\mathrm{f}}[\mathrm{Ru(III)}])[\mathrm{OH}^-]_{\mathrm{f}} \\ &= [SNA]_{\mathrm{f}}\{1 + K_1K_2[\mathrm{Ru(III)}][\mathrm{OH}^-]_{\mathrm{f}}\}\end{aligned}$$

Therefore,

$$[SNA]_{\mathrm{f}} = \frac{[SNA]_{\mathrm{T}}}{1 + K_1K_2[\mathrm{Ru(III)}][\mathrm{OH}^-]_{\mathrm{f}}} \tag{II}$$

Similarly,

$$[\mathrm{OH}^-]_{\mathrm{f}} = \frac{[\mathrm{OH}^-]_{\mathrm{T}}}{1 + K_1[\mathrm{Ru(III)}]_{\mathrm{f}}} \tag{III}$$

and

$$[\mathrm{Ru(III)}]_{\mathrm{f}} = \frac{[\mathrm{Ru(III)}^-]_{\mathrm{T}}}{1 + K_1[\mathrm{OH}^-]_{\mathrm{f}} + K_1K_2[SNA]_{\mathrm{f}}[\mathrm{OH}^-]_{\mathrm{f}}} \tag{IV}$$

Substituting Eqs. (II), (III), and (IV) in Eq. (I) we get Eq. (2).

References

[1] Kelson EP, Phengy PP (2000) Int J Chem Kinet **32**: 760

[2] Vovk AI, Muraveva IV, Kukhar VP, Baklan VF (2000) Russ J Gen Chem **70**: 1108

[3] Speakman PT, Waters WA (1955) J Chem Soc 40

[4] Singh VN, Gangwar MC, Saxena BBL, Singh MP (1969) Can J Chem **47**: 1051

[5] Singh VN, Singh MP, Saxena BBL (1970) Indian J Chem **8**: 529

[6] Brewster RQ, McEwen WE (1971) Organic Chemistry, 3rd edn. Prentice-Hall of India, New Delhi

[7] Morrison RT, Boyd RN (2001) Organic Chemistry, 6th edn. Prentice-Hall of India, New Delhi, p 862

[8] Panigrahi GP, Nayak RN (1982) React Kinet Catal Lett **21**: 283

[9] Srivastava SP, Bhattacharjee G, Gupta VK, Satya P (1980) React Kinet Catal Lett **13**: 231; Alexiev AA, Mutaftchiev KL (1985) Mikrochem Acta **2**: 115; Alexiev AA, Mutaftchiev KL (1983) Anal Lett **16**: 769; Caro A, Cortes G, Cerda V (1990) Analyst (London) **115**: 753

[10] Otto M, Werner G (1980) Z Chem **20**: 379

[11] Dziegiec J (1979) Pol J Chem **53**: 1821

[12] Bonchev PR, Aleksiev AA (1970) J Inorg Nucl Chem **32**: 2237

[13] Bonchev PR, Aleksiev AA, Dimitrova B (1969) Talanta **16**: 597

[14] Swarnalaxmi N, Uma V, Sethuram B, Navaneeth Rao T (1987) Indian J Chem **26A**: 592; Chimatadar SA, Kini AK, Nandibewoor ST (2003) Indian J Chem **42A**: 1850; Pol PD, Kathari CP, Nandibewoor ST (2003) Transition Met Chem **28**: 209

[15] Bailar JC, Emeleus HJ, Nyholm RS, Dickenson AF (1975) Comprehensive Inorganic Chemistry, vol 3. Pergamon Press, Oxford p 810

[16] Farokhi SA, Nandibewoor ST (2003) Tetrahedron **59**: 7595

[17] Lide DR (ed) (1992) Hand Book of Chemistry and Physics, 73rd edn. Chemical Rubber Publishing Company, London, p 8–51

[18] Kolthoff IM, Meehan EJ, Carr EM (1953) J Am Chem Soc **75**: 1439; Bhattacharya S, Benerjee P (1996) Bull Chem Soc Jpn **69**: 3475

[19] Nandibewoor ST, Hiremath GA, Timmanagoudar PL (2000) Transition Met Chem **21**: 394; Uma V, Sethuram B, Navaneeth Rao T (1981) React Kinet Catal Lett **18**: 283; Kamble DL, Chougale RB, Nandibewoor ST (1996) Indian J Chem **35A**: 865

[20] Balado AM, Galan BC, Martin FJP (1992) Anals De Quimica **88**: 170; Radhakrishnamurthy PS, Panda HP (1980) Bull Soc Kinet Ind **2**: 6; Cotton FA, Wilkinson G (1966) Advanced Inorganic Chemistry. Wiley, p 153; Timmanagoudar PL, Hiremath GA, Nandibewoor ST (1997) J Indian Chem Soc **74**: 296

[21] Singh MP, Ghosh S (1955) Z Phys Chem (Leipzig) **204**: 1; Singh MP, Ghosh S (1957) Z Phys Chem (Leipzig) **207**: 187, 198

[22] Wiberg KB, Nigh WG (1965) J Am Chem Soc **87**: 3849

[23] Kochi JK, Graybill BM, Kwiz M (1964) J Am Chem Soc **86**: 5257

[24] Langlois S, Broche A (1964) Bull Soc Chim France **61**: 812; Rao SV, Jagannadham V (1985) React Kinet Catal Lett **27**: 239; Upadyaya SK, Agarwal MC (1980) Indian J Chem **19A**: 478; Saxena SD, Gupta KS (1977) J Inorg Nucl Chem **39**: 329

[25] Kini AK, Farookhi SA, Nandibewoor ST (2002) Transition Met Chem **27**: 532

[26] Amis ES (1966) Solvent Effects on Reaction Rates and Mechanisms. Academic Press, New York

[27] Weissberger A (1974) In: Lewis ES (ed) Investigation of Rates and Mechanism of Reactions in Techniques of Chemistry, vol. 4. Wiley, New York, p 421

[28] Martinez M, Pitarque MA, Eldik RV (1996) J Chem Soc Dalton Trans 2665; Sutin N (1966) Ann Rev Phys Chem **17**: 119; Lancaster JM, Murray RS (1971) J Chem Soc A 2755

[29] Rangappa KS, Raghavendra MP, Mahadevappa DS, Channegowda D (1998) J Org Chem **63**: 531

[30] Jeffery GH, Bassett J, Mendham J, Denney RC (1996) Vogel's Text Book of Quantitative Chemical Analysis, 5th edn. ELBS Longman, Essex, UK, p 339

[31] Reddy CS, Vijaykumar T (1995) Indian J Chem **34A**: 615; Sykes AG, Emeleus H (1967) In: Sharpe AG (ed) Advances Inorganic and Radiochemistry, vol. 10. Academic Press, New York, p 321

[32] Ref. No. 30, p 384

[33] Feigl F, Anger V (1975) Spot Tests in Organic Analysis. Elsevier, New York, p 283, 289, 195

[34] Silverstein RM, Clayton BG, Terence CM (1991) Spectrometric Identification of Organic Compounds, 5th edn. Wiley, New York

[35] Bellamy LJ (1958) The IR Spectra of Complex Organic Molecules, 2nd edn. Methuen, London, p 425

[36] Furniss BS, Hannaford AJ, Rogers V, Smith PWG, Tatchell AR (1994) Vogel's Text Book of Practical Organic Chemistry, 5th edn. ELBS, Essex, England; Upadhyay A, Upadhyay K, Nath N (1993) Biophysical Chemistry Principles and Techniques, 1st edn. Himalaya Publishing House, Bombay, India, p 235