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Kinetic and mechanistic studies on the oxidation of hydroxylamine, semicarbazide, and thiosemicarbazide by iron(III) in the presence of triazines

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Abstract In the presence of 3-(2-pyridyl)-5,6-bis(4-phenylsulphonicacid)-1,2,4-triazine disodium salt (PDTS), 3-(4-(4-phenylsulphonic-acid)-2-pyridyl)-5,6-bis(4-phenylsulphonic-acid)-1,2,4-triazine trisodium salt (PPDTS), or 2,4-bis(5,6-bis(4-phenylsulphonic-acid)-1,2,4-triazin-3-yl)pyridine tetra sodium salt (BDTPS), iron(III) oxidizes hydroxylamine to nitrogen gas, semicarbazide to CO_2 and NH_3 and thiosemicarbazide to a disulfide. The corresponding iron product is the 1:3 complex of iron(II) and PDTS, PPDTS, or BDTPS. The kinetics of these reactions was studied by monitoring the iron(II) product by conventional spectrophotometry. The reaction is first order in iron(III). Kinetic evidence was obtained for the formation of 1:1:2 ternary complexes of iron(III), substrate, and sulfonated triazine. Evidence for the ternary intermediate complexes was obtained by ion-exchange studies using ^{59}Fe-labeled iron(III) solutions. The dissociation of the ternary complex is identified as the rate-determining step.

Introduction

Gopala Rao and coworkers found that in the presence of phosphoric acid, the formal redox potential of the Fe(III)/Fe(II) couple decreases while those of the U(VI)/U(IV), Mo(VI)/Mo(V), V(V)/V(IV), V(IV)/V(III), and Cr(VI)/Cr(III) couples increase. The same group estimated uranium(VI) [1], molybdenum [2], and vanadium(IV) [3] by potentiometric methods, titrating against iron(II) in strong phosphoric acid medium. The greater reducing ability of iron(II) in concentrated phosphoric acid solutions is due to the fact that phosphoric acid forms a stronger complex with iron(III) than iron(II). On the other hand, diimines like 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) are known to stabilize iron(II). In the presence of these two diimines, there is an increase in the redox potential of the Fe(III)/Fe(II) couple $[\mathrm{Fe(bpy)}_2^{3+}/\mathrm{Fe(bpy)}_2^{2+}, E = 0.97\ \mathrm{V}, \mathrm{Fe(phen)}_2^{3+}/\ \mathrm{Fe(phen)}_2^{2+}, E = 1.06\ \mathrm{V}]$. Thus, iron(III) acts as a better oxidizing agent in the presence of diimines. The kinetics and mechanism of the oxidation of iron(II) [4], vanadium(IV) [5], cobalt(II)-EDTA [6], water [7], ferrocyanide [8], catechols [9], mercury(I) [10], thiocyanate[11], and titanium(III) [12] by $\mathrm{Fe(bpy)}_2^{3+}$ and $\mathrm{Fe(phen)}_2^{3+}$have been studied. The oxidation of iron(II) by bis-(2,2′,6,2″-terpyridine)iron(III) $\mathrm{Fe(terpy)}_2^{3+}$ was studied by Ford-Smith and Sutin [13]. These reactions are fast and were monitored by stopped-flow spectrophotometry. Conversely, oxidation of H_2O_2, indigo carmine, and aromatic amines by iron(III) is extremely slow. However, in the presence of diimines, the oxidation is sufficiently fast to be monitored by conventional spectrophotometry. Bexandale [14] studied the oxidation of H_2O_2 by iron(III) in the presence of bpy and postulated a 1:2 complex of iron(III) and bpy as the reactive oxidizing species. Subba Rao et al. studied the oxidation of indigo caramine [15], phenols [16], and aromatic amines [17] by iron(III) in the presence of bpy/phen and identified a 1:2 iron(III)–bpy/phen complex as the reactive species of iron(III). Komissarov and Davisov [18] investigated the oxidation of methyl ethyl ketone by iron(III) in the presence of phen and envisaged a similar behavior. Krishna Rao et al. studied the oxidation of hydrazine [19],

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aroylhydrazides [20], and hydroxylamine [21] by iron(III) in the presence of phen and obtained evidence for the formation of a 1:2 complex between iron(III) and phen. Phen and bpy were extensively used in the spectrophotometric determination of iron(II) in the older literature. Systematic studies by Smith and Case have produced a variety of outstanding chromogenic reagents for iron and copper. An important aspect of their studies was the discovery that phenyl substituents in positions *para* to the ferroin nitrogen atoms greatly enhance the molar absorptivities of the metal chelates. Prompted by this principle, Case synthesized many compounds which are sensitive metal chromogenic reagents. 3-((2-pyridyl)-5,6-diphenyl)-1,2,4-triazine, PDT, 3-(4-(4-phenyl-2-pyridyl)-5,6-di-phenyl-1,2,4-triazine, PPDT and 2,4-bis(5,6-bis(4-phenyl)-1,2,4-triazin-3-yl)pyridine BDTP are some such compounds. These compounds are insoluble in water, and therefore, the sulphonated triazines, 3-(2-pyridyl)-5,6-bis(4-phenyl-sulphonicacid)-1,2,4-triazine disodium salt(PDTS), 3-(4-(4-phenylsulphonicacid)-2-pyridyl)-5,6-bis(4-phenylsulphonicacid)-1,2,4-triazine(PPDTS), and 2,4-bis(5,6-bis(4-phenylsulphonic-acid)-1,2,4-triazin-3-yl)pyridine tetra sodium salt(BDTPS) (hereafter referred to generically as tz) are extensively used in the spectrophotometric determination of iron(II) in trace quantities. We have observed that hydroxylamine, semicarbazide (scz), and thiosemicarbazide (tsc) are oxidized by iron(III) in the presence of these sulfonated triazines. The results of kinetic studies on these reactions are presented in this paper.

Experimental

A 1.0×10^{-1} mol dm^{-3} ferric nitrate solution (Merck "pro analysi") was prepared by dissolving the requisite quantity in distilled water. This solution was standardized against EDTA using variamine blue as indicator [22]. A 2.0×10^{-1} mol dm^{-3} solution of hydroxylamine was prepared by dissolving the requisite quantity of hydroxylamine sulfate (BDH, AnalaR) in distilled water. A calculated amount of $Ba(NO_3)_2$ was added to this solution to precipitate sulfate ion as $BaSO_4$. The precipitate was removed by filtration and the hydroxylamine content of the filtrate estimated by a bromatometric method [23]. 1.0×10^{-1} mol dm^{-3} solutions of scz and tscz were prepared by dissolving the requisite quantities of semicarbazide hydrochloride and thiosemicarbazide (Merck "pro analysi") in distilled water and standardized iodometrically [24]. PDTS, PPDTS, and BDTPS received from GFS Chemicals Inc., USA, were used as such without any further purification. 1.0×10^{-2} mol dm^{-3} solutions of tz were prepared by dissolving the requisite quantities in water and stored in amber-colored bottles. A 2.0 mol dm^{-3} solution of $NaNO_3$ (Merck "pro analysi") was prepared in distilled water. The strength of this solution was checked by passing 5.0 ml aliquots through a Dowex-50W-X8 cation exchange resin column (H^+ form) and estimating the resultant H^+ ions after thoroughly washing the resin bed with distilled water.

A sample of ^{59}Fe (as ferric chloride in HCl $t_{1/2}$ = 45 days and emits two γ-rays of 1.10 and 1.29 MeV) obtained from Bhabha Atomic Research Centre, Mumbai, was used to label iron(III) solutions.

Equipment

A Shimadzu 1800 UV–visible spectrophotometer fitted with a UV-240A Cell Positioner having a six cell holder in which the temperature was controlled to ±0.1 °C by Peltier effect was used to record the absorption spectra and monitor the reaction kinetics. An Orion Ionalyser/901 was used for pH measurements. The slow reactions were followed in CPS running mode and relatively fast reactions monitored in command chain mode using suitable software. Gamma activity measurements were taken with single channel analyzer SC 800 (ECIL) in conjunction with a 3″ well-type NaI (Tl) crystal (Nuclear Chicago).

Product analysis

A solution containing substrate NH_2OH, tz (PDTS/PPDTS/BDTPS), and HNO_3 was prepared in a 25-ml volumetric flask and to this the requisite volume of iron(III) nitrate solution was added. After a few minutes, a colorless and odorless gas which extinguished a burning splint was evolved. This gas did not respond to the test for N_2O. From these observations, it was inferred that this gaseous product is nitrogen. The requisite volume of 1.0×10^{-3} mol dm^{-3} iron(III) nitrate solution was added to a mixture of scz, tz, and nitric acid. A colorless and odorless gas which extinguished a burning splint and turned lime water milky was evolved. This product solution on heating with NaOH gave ammonia, which formed a reddish brown precipitate with Nessler's reagent. Hence, it is concluded that CO_2 and NH_3 are the products of the oxidation of scz by iron(III) in the presence of tz. This procedure was repeated using tscz instead of semicarbazide. The results did not suggest the formation of CO_2 and NH_3; however, a sulfurous odor was noticed. This suggests the formation of a disulfide. The product solution was extracted with ether, and the ethereal layer was washed with 0.1 mol dm^{-3} HNO_3 and allowed to stand until the ether had evaporated. Elemental analysis of this solid residue by sodium fusion method gave positive tests for N and sulfur, further supporting the formation of a disulfide product.

The formation of free radical intermediates was tested by using acrylonitrile. These tests were performed by taking requisite quantities of the substrate, triazine, HNO_3, and acrylonitrile in the lower limb of a Thunberg tube and iron(III) in its upper limb. The tube was evacuated and then tilted to mix the contents of the two limbs. In the case of oxidation of scz by iron(III) in the presence of all three sulfonated triazines, the formation of a precipitate was observed. Precipitate formation was not observed with NH_2OH or tscz.

Known amounts of NH_2OH/scz/tscz, PDTS, HNO_3 and iron(III) nitrate were taken in an amber colored 25-ml volumetric flask and the contents were made up to the mark with distilled water. The reaction mixture was left for sufficient time for the reaction to complete. All three substrates give a magenta-colored product. The visible absorption spectra of the products exhibit a single peak at 562 nm with a ε value of 28,000 ± 200 [based on the concentration of iron(III) taken] and these values agree well with that of $Fe(PDTS)_3^{4-}$ (27,900 at 562 nm [25]). This indicates that iron(III) is quantitatively reduced to iron(II). Similarly, the visible absorption spectra of the products in the presence of PPDTS and BDTPS show peaks at 563 and 565 nm, respectively, and these values correspond to those of $Fe(PPDTS)_3^{7-}$ and $Fe(BDTPS)_3^{10-}$. The ε values of the products obtained in the presence of PPDTS and BDTPS are 30,700 ± 200 and 32,200 ± 180 respectively, [ε values of $Fe(PPDTS)_3^{7-}$ and $Fe(BDTPS)_3^{10-}$ are 30,700 and 32,200 [26], respectively].

Stoichiometry

To determine the stoichiometry of these reactions, known amounts of substrates (NH_2OH, scz, or tscz), triazine, and nitric acid were taken and a known excess of iron(III) nitrate was added to the mixture. The reaction was allowed to go to completion, indicated by the constancy of absorbance values. The amount of iron(II) formed was evaluated from the absorbance values and ε values of the corresponding iron(II) complex. From these values, the amount of iron(III) reacted was computed. These results suggest that stoichiometric ratio of [Fe(III)]:[substrate] is 1:1 for all three substrates, namely NH_2OH, scz, and tscz. The overall reactions can be represented by the following equations:

$$\begin{aligned} &2Fe^{3+} + 6HL^{(n-1)-} + 2NH_2OH \\ &\quad \rightarrow 2FeL_3^{(3n-2)-} + N_2 + 2H_2O + 8H^+ \end{aligned} \tag{1}$$

$$\begin{aligned} &2Fe^{3+} + 6HL^{(n-1)-} + 2N_3H_5CO + 2H_2O \\ &\quad \rightarrow 2FeL_3^{(3n-2)-} + 4NH_3 + N_2 + 2CO_2 + 8H^+ \end{aligned} \tag{2}$$

$$\begin{aligned} &2Fe^{3+} + 6HL^{(n-1)-} + 2N_3H_5CS \\ &\quad \rightarrow 2FeL_3^{(3n-2)-} + 8H^+ + (H_2NN = C(NH_2)S)_2 \end{aligned} \tag{3}$$

where $HL^{(n-1)-}$ stands for monoprotonated PDTS, PPDTS, and BDTPS and $n = 2$, 3, and 4 for PDTS, PPDTS, and BDTPS, respectively.

Kinetic procedure

Requisite volumes of HNO_3, tz, substrate, and $NaNO_3$ solutions were taken in an amber-colored 25-ml volumetric flask, and the contents were diluted with distilled water such that the total volume after the addition of iron(III) solution was 10 ml. The volumetric flask was suspended in a water bath kept at the experimental temperature for sufficient time to allow the reaction mixture to attain temperature equilibrium. Then, a known volume of iron(III) solution, which was also equilibrated at the experimental temperature was added. The contents were thoroughly mixed, and a portion of this solution was transferred quickly to the spectrophotometer. The absorbance values at different time intervals were recorded at 562, 563, and 565 nm for PDTS, PPDTS, or BDTPS, respectively, using CPS recording or command chain mode depending on the rate of the reaction. In all these experiments, a solution containing all the reactants except the substrate was used as the blank. The absorbance at infinite time, A_∞, was obtained by allowing the reaction mixtures to stand for sufficient time for the reactions to complete. The pseudo-first-order rate constants were evaluated from plots of time, t versus $\log(A_\infty - A_t)$ where A_t is the absorbance at time t, computed using an MS Excel worksheet. About 25 % of the kinetic runs were performed in duplicate. The rate constants were reproducible to within ±5 %.

Results and discussion

The reactions were carried out under pseudo-first-order conditions isolating the oxidant, that is, [substrate] (and [tz]) $\gg$ [Fe(III)]. Plots of $\log(A_\infty - A_t)$ versus time were linear up to more than 80 % completion of the reactions, indicating first-order behavior with respect to iron(III). Kinetic runs were performed varying the concentration of iron(III) at $[tz] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[substrate] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1 \times 10^{-2}$ mol dm^{-3}, and $\mu = 1.0 \times 10^{-1}$ mol dm^{-3} at 30 °C (substrate = NH_2OH, scz, or tscz), and k_{obs} values were evaluated. In all the systems, the k_{obs} values are independent of the initial concentration of iron(III), see supplementary table S1, further confirming first-order dependence on oxidant. The reactions were carried out varying the concentration of substrate keeping the concentrations of iron(III), tz, hydrogen ion, and ionic strength constant. The rate of these reactions increased with [substrate], see supplementary table S2. Plots of $1/k_{obs}$ against

1/[substrate] were linear with positive intercepts on the ordinate, indicating the formation of 1:1 complexes between iron(III) and each substrate. The plots of $1/k_{obs}$ against $1/[NH_2OH]$ in the presence of PDTS are shown in Fig. 1.

For the plots of $1/k_{obs}$ against 1/[scz] and $1/k_{obs}$ against 1/[tscz], see supplementary figures S3 and S4. The reactions were also performed at different concentrations of tz and fixed concentrations of oxidant, substrate, hydrogen ion, and ionic strength. The rate data show that the rate of the reaction increases with [tz], see supplementary table S5. Plots of reciprocal of k_{obs} versus reciprocal of $[tz]^2$ were also linear with positive intercepts on the rate axis, supplementary figure S6, suggesting the formation of 1:2 complexes of iron(III) and tz. Hydrogen ion has a decelerating effect on these redox processes. The plots of $1/k_{obs}$ versus $1/[tz]^2$ for the Fe(III)-NH_2OH-PDTS system are shown in Fig. 2.

The plots of $1/k_{obs}$ versus $[tz]^2$ for the other systems are given in supplementary figure S7. The reactions were carried out at different initial concentrations of hydrogen ion with the concentrations of all other reactants constant, supplementary table S8. Ionic strength has no influence on the reaction rates in all these systems, see supplementary table S9, indicating that the rate-determining step is between ions of opposite charge. Representative kinetic data for the PDTS system are given in Table 1 and that for PPDTS and BDTPS in Table 2.

The oxidation of NH_2OH, scz, and tscz by iron(III) in the presence of all three sulfonated triazines is first order in iron(III). The plots of $1/k_{obs}$ versus 1/[substrate] and $1/k_{obs}$ versus $1/[tz]^2$ were linear with positive intercepts on the x-axis. This suggests that the substrates form 1:1 complexes with iron(III), while the three tz species form 1:2 complexes with the oxidant. Hydrogen ion decelerates the reaction, and ionic strength has no effect on the rate. The reaction mixtures did not initiate polymerization of acrylonitrile for the NH_2OH and tscz oxidations, whereas polymerization was noticed in the oxidation of scz.

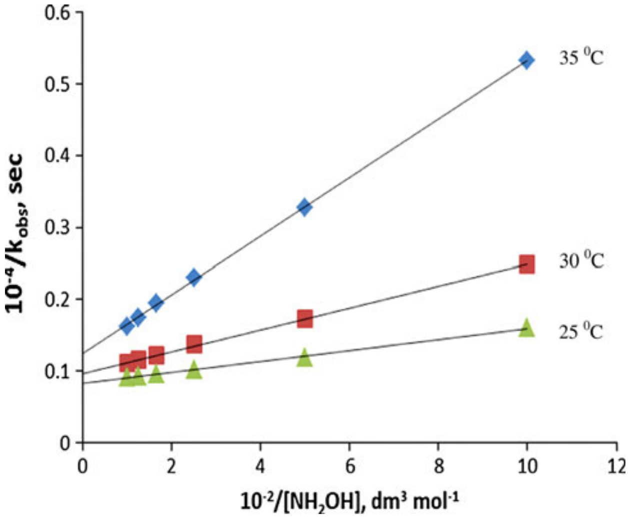

Fig. 1 Effect of $[NH_2OH]$ on the reaction rate in the oxidation of NH_2OH by Fe(III) in the presence of PDTS at $[Fe(III)] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[PDTS] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H+] = 2.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.1$

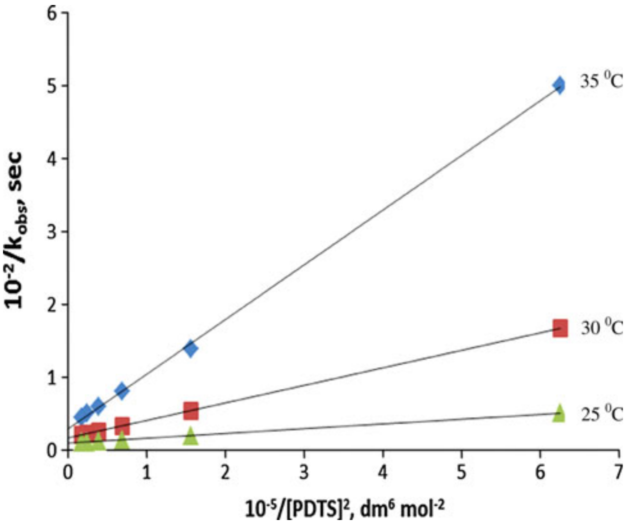

Fig. 2 Effect of [PDTS] on the rate of the reaction in the oxidation of NH_2OH by Fe(III) in the presence of PDTS at $[Fe(III)] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[NH_2OH] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H+] = 2.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.1$

Olson and Simonson [27] concluded from their spectrophotometric studies that iron(III) exists mainly as Fe^{3+} at 10^{-4} mol dm^{-3} concentrations in slightly acid solutions. Anipindi [28] determined the protonation constants of PDTS and PPDTS as 3.032 and 3.165, respectively, at 25 °C. In the present studies, we have determined the protonation constant of BDTPS as 2.762 also at 25 °C by potentiometry. The species distribution using these protonation constants indicates that at pH ~ 2.0, more than 95 % of PDTS, PPDTS, and BDTPS exist in monoprotonated forms. The protonation constants of NH_2OH [29], scz [30], and tscz [31] are high, and hence the protonated form of the substrate is the predominant species. However, the unprotonated form of the substrate is considered as the reactive species because of its greater nucleophilicity over the protonated form. A mechanism is proposed to explain all the experimental results considering the formation of a ternary intermediate complex of iron(III), NH_2OH, and tz in two steps, as follows:

$$\text{sub} + H^+ \overset{K_1}{\rightleftharpoons} \text{subH}^+ \tag{4}$$

$$Fe^{3+} + 2Htz^+ \overset{K_2}{\rightleftharpoons} \underset{C_1}{Fe^{III}(tz)_2} + 2H^+ \tag{5}$$

$$C_1 + \text{sub} \overset{K_3}{\rightleftharpoons} \underset{C_2}{Fe^{III}(tz)_2(\text{sub})} \tag{6}$$

The dissociation of this intermediate ternary complex occurs in a slow step to give $Fe^{II}(tz)_2$ and the reduced form of the substrate [sub(red)];

Table 1 k_{obs} values for iron(III)-NH_2OH reactions in the presence of PDTS at 30 °C

[Fe(III)] × 10^5 mol dm^{-3}	[NH_2OH] × 10^3 (mol dm^{-3})	[PDTS] × 10^3 (mol dm^{-3})	[H^+] × 10^2 (mol dm^{-3})	μ	10^3 × k_{obs} (s^{-1})
2.0	1.0	1.0	2.0	0.1	4.00
3.0	1.0	1.0	2.0	0.1	3.92
4.0	1.0	1.0	2.0	0.1	4.20
5.0	1.0	1.0	2.0	0.1	4.08
6.0	1.0	1.0	2.0	0.1	4.25
4.0	2.0	1.0	2.0	0.1	5.81
4.0	4.0	1.0	2.0	0.1	7.29
4.0	6.0	1.0	2.0	0.1	8.20
4.0	8.0	1.0	2.0	0.1	8.70
4.0	10.0	1.0	2.0	0.1	9.02
4.0	1.0	0.4	2.0	0.1	0.60
4.0	1.0	0.8	2.0	0.1	1.84
4.0	1.0	1.2	2.0	0.1	2.99
4.0	1.0	1.6	2.0	0.1	3.83
4.0	1.0	2.0	2.0	0.1	4.41
4.0	1.0	2.4	2.0	0.1	4.80
4.0	1.0	1.0	1.0	0.1	6.18
4.0	1.0	1.0	2.0	0.1	2.48
4.0	1.0	1.0	3.0	0.1	1.00
4.0	1.0	1.0	4.0	0.1	0.47
4.0	1.0	1.0	5.0	0.1	0.25
4.0	1.0	1.0	6.0	0.1	0.15
4.0	1.0	1.0	2.0	0.1	4.03
4.0	1.0	1.0	2.0	0.2	3.98
4.0	1.0	1.0	2.0	0.3	3.95
4.0	1.0	1.0	2.0	0.4	4.08
4.0	1.0	1.0	2.0	0.6	4.12
4.0	1.0	1.0	2.0	0.8	4.06

$$C_2 \xrightarrow[k_1]{\text{Slow}} Fe^{II}(tz)_2 + H^+ + \text{sub(red)} \tag{7}$$

The iron(II) species $Fe^{II}(tz)_2$ reacts with another mole of Htz to give $Fe^{II}(tz)_3$ in a series of fast steps, while the reduced form of the substrate rapidly rearranges to give the final products.

The rate law for this mechanism is derived as follows:

$$[\mathrm{Fe(III)}]_t = [\mathrm{Fe}^{3+}]_e + [\mathrm{C}_1]_e + [\mathrm{C}_2]_e \tag{8}$$

$$= \frac{[\mathrm{C}_1]_e[\mathrm{H}^+]_e^2}{K_2[\mathrm{Htz}]_e^2} + [\mathrm{C}_1]_e + [\mathrm{C}_2]_e \tag{9}$$

$$= \frac{[\mathrm{C}_2]_e[\mathrm{H}^+]_e^2}{K_2K_3[\mathrm{Htz}]_e^2[\mathrm{sub}]_e} + \frac{[\mathrm{C}_2]_e}{K_3[\mathrm{sub}]_e} + [\mathrm{C}_2]_e \tag{10}$$

$$= [\mathrm{C}_2]_e\left\{\frac{[\mathrm{H}^+]_e^2 + K_2[\mathrm{Htz}]_e^2 + K_2K_3[\mathrm{Htz}]_e^2[\mathrm{sub}]_e}{K_2K_3[\mathrm{Htz}]_e^2[\mathrm{sub}]_e}\right\} \tag{11}$$

$$[\mathrm{C}_2]_e = \frac{K_2K_3[\mathrm{Fe(III)}]_t[\mathrm{Htz}]_e^2[\mathrm{sub}]_e}{[\mathrm{H}^+]_e^2 + K_2[\mathrm{Htz}]_e^2 + K_2K_3[\mathrm{Htz}]_e^2[\mathrm{sub}]_e} \tag{12}$$

Replacing [Htz] by [tz] and $[H^+]_e$ by $[H^+]$ where [tz] and $[H^+]$ are the initial concentrations of tz and H^+, respectively,

$$[\mathrm{C}_2]_e = \frac{K_2K_3[\mathrm{Fe(III)}]_t[\mathrm{tz}]^2[\mathrm{sub}]_e}{[\mathrm{H}^+]^2 + K_2[\mathrm{tz}]^2 + K_2K_3[\mathrm{tz}]^2[\mathrm{sub}]_e} \tag{13}$$

$$[\mathrm{sub}]_t = [\mathrm{sub}]_e + [\mathrm{sub}^+]_e = [\mathrm{sub}]_e\{1 + k_1[\mathrm{H}^+]_e\} \tag{14}$$

Since the protonation constant of hydroxylamine, scz, and tscz are very high, $K_1[H^+] \gg 1$. Hence, Eq. 14 can be written as

$$[\mathrm{sub}]_e = [\mathrm{sub}]_t / k_1[\mathrm{H}^+]_e \tag{15}$$

$$\text{Rate} = k_1[\mathrm{C}_2] = \frac{k_1K_2K_3[\mathrm{Fe(III)}]_t + [\mathrm{tz}]^2[\mathrm{sub}]_e}{[\mathrm{H}^+]^2 + K_2[\mathrm{tz}]^2 + K_2K_3[\mathrm{tz}]^2[\mathrm{sub}]_e} \tag{16}$$

Table 2 k_{obs} values for iron(III)-NH_2OH reactions in the presence of PPDTS and BDTPS at 30 °C

[Fe(III)] × 10^5 (mol dm^{-3})	[NH_2OH] × 10^3 (mol dm^{-3})	[tz] × 10^3 (mol dm^{-3})	[H^+] × 10^2 (mol dm^{-3})	μ	10^4 × k_{obs} (s^{-1})	
					PPDTS	BDTPS
2.0	1.0	0.5	2.0	0.1	3.03	23.51
3.0	1.0	0.5	2.0	0.1	2.86	24.26
4.0	1.0	0.5	2.0	0.1	2.61	25.73
5.0	1.0	0.5	2.0	0.1	2.83	26.85
6.0	1.0	0.5	2.0	0.1	3.07	27.52
2.0	2.0	0.5	2.0	0.1	2.04	3.01
2.0	4.0	0.5	2.0	0.1	2.77	5.38
2.0	6.0	0.5	2.0	0.1	3.05	7.30
2.0	8.0	0.5	2.0	0.1	3.31	8.85
2.0	10.0	1.0	2.0	0.1	3.42	10.16
2.0	12.0	0.5	2.0	0.1	3.57	11.28
2.0	1.0	0.2	2.0	0.1	0.55	0.63
2.0	1.0	0.4	2.0	0.1	2.08	1.66
2.0	1.0	0.6	2.0	0.1	3.90	2.32
2.0	1.0	0.8	2.0	0.1	7.58	2.72
2.0	1.0	1.0	2.0	0.1	9.25	3.03
2.0	1.0	1.2	2.0	0.1	10.30	3.22
2.0	1.0	0.5	1.0	0.1	30.00	14.83
2.0	1.0	0.5	2.0	0.1	13.52	3.85
2.0	1.0	0.5	3.0	0.1	5.64	1.28
2.0	1.0	0.5	4.0	0.1	2.63	0.56
2.0	1.0	0.5	5.0	0.1	1.42	0.29
2.0	1.0	0.5	6.0	0.1	0.85	0.17
2.0	1.0	0.5	2.0	0.1	1.43	25.45
2.0	1.0	0.5	2.0	0.2	1.35	25.10
2.0	1.0	0.5	2.0	0.3	1.39	24.28
2.0	1.0	0.5	2.0	0.4	1.51	23.23
2.0	1.0	0.5	2.0	0.6	1.46	26.07
2.0	1.0	0.5	2.0	0.8	1.37	24.84

Substituting the value of $[sub]_e$ in the above equation and replacing $[sub]_e$ and $[H^+]_e$ by [sub] and [H^+], respectively

$$\text{Rate} = \frac{k_1K_2K_3[\text{Fe(III)}]_t{+}[\text{tz}]^2[\text{sub}]_e}{K_1[\text{H}^+]^3 + K_1K_2[\text{H}^+][\text{tz}]^2 + K_2K_3[\text{tz}]^2[\text{sub}]_e} \tag{17}$$

This rate law satisfactorily explains all the experimental observations. The pseudo-first-order rate constant, k_{obs}, is given by

$$k_{obs} = \frac{k_1K_2K_3[\text{tz}]^2[\text{sub}]}{K_1[\text{H}^+]^3 + K_1K_2[\text{H}^+][\text{tz}]^2 + K_2K_3[\text{tz}]^2[\text{sub}]} \tag{18}$$

This equation on rearrangement gives

$$\frac{1}{k_{obs}} = \frac{K_1[\text{H}^+]^3}{k_1K_2K_3[\text{tz}]^2[\text{sub}]} + \frac{K_1[\text{H}^+]}{k_1K_3[\text{sub}]} + \frac{1}{k_1} \tag{19}$$

According to Eq. 19, plots of 1/k_{obs} versus 1/$[tz]^2$ should be linear with positive slopes and positive intercepts on the ordinate. However, the dependence of rate on hydrogen ion concentration is not simple. Rearrangement of Eq. 19 gives

$$(1/k_{obs} - 1/k_1)\frac{1}{\text{H}^+} = \frac{K_1[\text{H}^+]^2}{k_1K_2K_3[\text{tz}]^2[\text{sub}]} + \frac{K_1}{k_1K_3[\text{sub}]} \tag{20}$$

According to Eq. 20, the plot of ($1/k_{obs}-1/k_1$)/[H^+] versus $[H^+]^2$ should be linear with positive intercept on the ordinate. Such plots were obtained in the oxidation of NH_2OH by iron(III) in the presence of PDTS and PPDTS and also for the oxidation of scz and tscz in the presence of PDTS, see supplementary figure S8. The intercept of the plot of 1/k_{obs} versus 1/[sub] is equal to 1/k_1 and hence the k_1 values were evaluated from the intercepts of these plots. The slope and intercept of the plot of ($1/k_{obs} - 1/k_1$)/[H^+] versus $[H^+]^2$ give $K_1/k_1K_2K_3[tz]^2[sub]$ and $K_1/k_1K_3[sub]$, respectively. Taking the literature [32] values of K_a, the K_1 ($1/K_a$) values for NH_2OH [(1.14, 1.52, and 1.86) × 10^{-6} dm^3 mol^{-1} at 25, 30, and 35 °C, respectively], scz [(5.43, 3.28, and 1.40) × 10^{-1} dm^3 mol^{-1} at 25, 30, and 35 °C,

Table 3 Equilibrium and specific rate constants for Fe(III)–subtrate–PDTS and Fe(III)-NH_2OH-PPDTS reactions at 30 °C

System	K_2	K_3 ($dm^3\ mol^{-1}$)	k_1 ($dm^3\ mol^{-1}, s^{-1}$)
Fe(III)-NH_2OH-PDTS	1.10×10^2	4.58×10^{-5}	1.01×10^{-3}
Fe(III)-NH_2OH-PPDTS	3.05×10^2	9.17×10^{-5}	4.15×10^{-3}
Fe(III)-scz-PDTS	0.33	1.32×10^{-4}	1.45×10^{-3}
Fe(III)-tscz-PDTS	0.48×10^{-3}	1.87×10^{-3}	30.30×10^{-3}

respectively], and tscz [(4.92, 4.77, and 4.64) × 10^{-1} $dm^3\ mol^{-1}$ at 25, 30, and 35 °C, respectively] and from the slopes and intercepts of the plots of $(1/k_{obs}-1/k_1)/[H^+]$ versus $[H^+]^2$, the values of K_2 and K_3 were computed and the values of k_1, K_1 and K_2 at 30 °C are presented in Table 3. For these values at 25 and 35 °C, see supplementary Table S9.

For the other systems, that is, oxidation of scz and tscz by iron(III) in the presence of PPDTS and iron(III) oxidation of all three substrates in the presence of BDTPS, plots of $(1/k_{obs}-1/k_1)[H^+]$ versus $[H^+]^2$ were not linear. Hence, a slightly different mechanism involving that the formation of a ternary intermediate complex of iron(III), substrate, and tz in a single equilibrium step is proposed and the rate law derived as follows:

$$Fe^{3+} + 2Htz + sub \overset{K_4}{\rightleftharpoons} \underset{C_3}{Fe^{III}(tz)_2(sub)^{5-}} + 2H^+ \tag{21}$$

$$C_3 \xrightarrow[k_2]{Slow} Fe^{II}(tz)_3 + H^+ + sub(red) \tag{22}$$

The rate law for this mechanism is derived as below:

$$[Fe(III)]_t = [Fe^{3+}]_e + [C_3]_e \tag{23}$$

$$= \frac{[C_3]_e[H^+]_e^2}{K_4[Htz]_e^2[sub]_e} + [C_3]_e \tag{24}$$

$$= [C_3]_e\left\{\frac{[H^+]_e^2 + K_4[Htz]_e^2[sub]_e}{K_4[Htz]_e^2[sub]_e}\right\} \tag{25}$$

$$[C_3]_e = \frac{K_4[Fe(III)]_t[Htz]_e^2[sub]_e}{[H^+]_e^2 + K_4[Htz]_e^2[sub]_e} \tag{26}$$

On substituting the value of $[sub]_e$ from Eqs. 14 and 26 transforms to

$$[C_3]_e = \frac{K_4[Fe(III)]_t[Htz]_e^2[sub]_t}{K_1[H^+]^3 + K_4[Htz]_e^2[sub]_t} \tag{27}$$

Replacing $[Htz^+]_e$ by [tz}, $[H^+]_e$ by $[H^+]$, and [sub] where [sub], $[H^+]$, and [sub] are the initial concentrations of tz, H^+, and sub, respectively,

$$[C_3]_e = \frac{K_4[Fe(III)]_t[tz]^2[sub]}{K_1[H^+]^3 + K_4[tz]^2[sub]} \tag{28}$$

The rate of the reaction can other be expressed as

$$Rate = k_2[C_3]_e = \frac{k_2K_4[Fe(III)]_t[tz]^2[sub]}{K_1[H^+]^3 + K_4[tz]^2[sub]} \tag{29}$$

The pseudo-first-order rate constant, k_{obs}, is given by

$$k_{obs} = \frac{k_2K_4[tz]^2[sub]}{K_1[H^+]^3 + K_4[tz]^2[sub]} \tag{30}$$

or

$$\frac{1}{k_{obs}} = \frac{K_1[H^+]^3}{K_4k_2[tz]^2[sub]} + \frac{1}{k_2} \tag{31}$$

Equation 31 stipulates that plots of $1/k_{obs}$ versus 1/[sub] and $1/k_{obs}$ versus $1/[tz]^2$ should be linear with the same magnitude of intercept on the $1/k_{obs}$ axis. Plots of $1/k_{obs}$ versus $[H^+]^3$ should also be straight lines with positive intercept on the ordinate, of the same magnitude as the above plots. The experimental results are in consonance with these requirements for the iron(III)-scz-PPDTS, iron(III)-tscz-PPDTS, and all the three iron(III)–substrate–BDTPS systems. The values of the specific rate constants k_2 were evaluated from the intercept of the plot of $1/k_{obs}$ versus $[H^+]^3$. Using the literature values of K_1 and from the slope of this plot, the values of K_4 were calculated. The values of specific rate constant k_1 and the equilibrium constant K_4 at 30 °C are given in Table 4. These values at 25 and 35 °C are available in supplementary Table S10.

Nitrogen was identified as the oxidation product of hydroxylamine. The formation of this product is shown in Eqs. 7 and 22 of the two reaction schemes. The ternary intermediate complexes containing iron(III), NH_2OH, and tz, C_2 or C_3 give $Fe^{II}(tz)_2$ and $NH_2O^{\cdot}$ in the rate-limiting steps:

$$C_2(or\ C_3) \xrightarrow[k_1]{Slow} Fe^{II}(tz)_2 + NH_2O^{\cdot} \tag{32}$$

However, Waters et al. [32] in their studies on the oxidation of hydroxylamine by cerium(IV) also observed the formation of $NH_2O^{\cdot}$ according to the following steps:

Table 4 Equilibrium and specific rate constants for Fe(III)–scz/tscz–PPDTS and Fe(III)–sub–BDTPS reactions at 30 °C

System	$K_4 \times 10^{-4}$ ($dm^3\ mol^{-1}$)	$k_2 \times 10^3$ ($dm^3\ mol^{-1}, s^{-1}$)
Fe(III)-scz-PPDTS	1.53	0.19
Fe(III)-tscz-PPDTS	2.96	0.54
Fe(III)-NH_2OH-BDTPS	0.44	2.50
Fe(III)-scz-BDTPS	0.43	15.15
Fe(III)-tscz-BDTPS	0.50	1.82

$$NH_2O^{\cdot} \xrightarrow{-e} HNO + H^+ \quad (33)$$

$$2HNO \rightarrow N_2O + H_2O \quad (34)$$

This can probably be expected at higher concentrations of oxidant or with strong oxidizing agents. The stoichiometry observed in the present investigations indicates that the steps 33 and 34 do not occur to a significant extent. The formation of free radical ($NH_2O^{\cdot}$) intermediates is postulated in the rate-determining steps, even though the reaction did not induce polymerization of acrylonitrile. Rapid dimerization of the free radicals is probably responsible for this. Gutch and Waters [33] studied the oxidation of NH_2OH by ceric ammonium nitrate and obtained esr evidence for $NH_2O^{\cdot}$ radicals. Bengtsson et al. [34] studied the oxidation of hydroxylamine by iron(III). Their results led to two rate expressions and were consistent with a mechanism dependent on the relative iron(III)-to-hydroxylamine concentrations; an excess of iron(III) gives a stoichiometry of 2:1 for the total reaction and N_2O as the oxidation product, whereas at equal amounts or excess of hydroxylamine, the stoichiometry reduces to 1:1 with N_2 as the main product and involves a dihydroxy species of iron(III), namely $Fe(OH)_2^+$.

In the oxidation of scz, the final products are produced by the decomposition of the ternary intermediate complex, C_2 or C_2, $Fe^{III}(tz)_2(scz)$:

$$Fe^{III}(tz)_2(scz) \xrightarrow{slow} Fe^{II}(tz)_2 + NH_2CONHN^{\cdot}H \quad (35)$$

Polymerization of acrylonitrile by the reaction mixtures gives support to the formation of a free radical intermediate.

$$NH_2CONHN^{\cdot}H + H_2O \xrightarrow{fast} \dot{N}_2H_3 + NH_2COOH \quad (36)$$

The free radical, $NH_2CONH\dot{N}H$, undergoes hydrolytic cleavage giving $\dot{N}_2H_3$ free radical and NH_2COOH (carbamic acid), which being very unstable decomposes to give $\dot{N}_2H_3$ and CO_2. The $\dot{N}_2H_3$ radicals formed undergo dimerization to give N_4H_6, which decomposes giving N_2 and NH_3. In a fast step the oxidation of $\dot{N}_2H_3$ forms N_2H_2 and H^+. The N_2H_2 molecule undergo further decomposition, to give nitrogen gas according to the following fast step:

$$\dot{N}_2H_3 \rightarrow N_2 + 3H^+ + 3e^- \quad (37)$$

However, the observed stoichiometry, [Fe(III)]:[scz] = 1:1, suggests that the contribution from Eq. 37 is not appreciable.

For the Fe(III)-tscz-tz system, formation of the mixed ligand complex, $Fe^{III}(tz)_2(tscz)$, involves coordination of the hydrazinic nitrogen and sulfur of the tscz ligand; however, electron transfer probably takes place preferably from sulfur because of its low electronegativity. The decomposition of $Fe^{III}(tz)_2(tscz)$ in the rate-determining step results in the formation of a thiosemicarbazide free radical intermediate:

$$Fe^{III}(tz)_2(tscz) \xrightarrow{slow} Fe^{II}(tz)_2 + NH_2{-}CS{-}N^{\cdot}{-}NH_2 + H^+ \quad (38)$$

Dimerization of the thiosemicarbazide free radical will give a disulfide; this process is likely to be rapid, which would explain why the reaction mixture did not initiate the polymerization of acrylonitrile. McAuley [35] observed the formation of disulfide in the oxidation of thiomalic acid by iron(III).

It is interesting to note that the K_4 values pertaining to the formation of the 1:1:2 ternary complex of iron(III), substrate, and sulfonated triazine are very high (Table 4), indicating that the ternary complexes are fairly stable and hence can be isolated. To isolate these intermediate ternary complexes, an iron(III) nitrite solution labeled with ^{59}Fe was prepared and the reaction mixtures were subjected to ion-exchange studies. Reaction mixtures containing labeled iron(III) (2–4 × 10^{-5} mol dm^{-3}), PPDTS (5.0 × 10^{-4} mol dm^{-3}), scz or tscz (1–2 × 10^{-3} mol dm^{-3}), and HNO_3 (2–3 × 10^{-2} mol dm^{-3}) were prepared. After allowing the reaction mixtures to stand at ambient temperature for above 15 m, the reactions were cooled by adding ice and the cooled solutions were passed through a Dowex 1X8 (200–400 mesh, NO_3^- form) anion exchange resin column. The resin bed was washed with a mixture of PPDTS (5.0 × 10^{-4} mol dm^{-3}) and scz/tscz (1–2 × 10^{-3} mol dm^{-3}) of pH ~ 1.5. The eluates from the column did not show gamma activity, indicating the absence of neutral or cationic species of iron including free Fe^{3+}. The resin bed was then washed with $NaNO_3$ solutions (at pH ~ 1.5) of different concentrations and containing PPDTS (5.0 × 10^{-4} mol dm^{-3}) and scz/tscz (1–2 × 10^{-3} mol dm^{-3}). The presence of scz/tscz and PPDTS in the eluent was to prevent the dissociation of iron(III)–PPDTS–substrate intermediate complexes. The eluents obtained on elution with 3.2 mol dm^{-3} $NaNO_3$ showed gamma activity in the case of both semicarbazide and thiosemicarbazide. For comparison, a solution containing 2.0 × 10^{-3} mol dm^{-3} each *cis*-bisl(oxalate)chromate(III), $Cr(ox)_2(H_2O)_2^-$, and tris(oxalato)chromate(III), $Cr(ox)_3^{3-}$ was passed through a Dowex 1X8 (200–400 mesh, NO_3^- form) anion exchange column. It was noticed $Cr(ox)_2(H_2O)_2^-$ desorbs from the column on elution with 1.0 mol dm^{-3} $NaNO_3$, while elution with 3.0 mol dm^{-3} $NaNO_3$ elutes $Cr(ox)_3^{3-}$ from the resin bed, as established from the visible absorption spectra of the eluates. This indicates that the species separated from the resin bed on elution with 3.2 mol dm^{-3} $NaNO_3$ will have a charge of 3−. A large volume of eluent is required to elute this species completely. The species thus separated slowly turned from colorless to magenta when brought to ambient temperature.

Table 5 Activation parameter for some oxidation reactions of iron(III) in the presence of triazines

Substrate	PDTS		PPDTS		BDTPS	
	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} deg^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} deg^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} deg^{-1})
Hydroxylamine	33	−143	21	−170	70	62
Semicarbazide	56	−123	23	−173	95	32
Thiosemicarbazide	46	−84	26	−153	79	38

The visible absorption spectrum of this magenta species, has $\lambda_{\max}$ at 563 nm, indicating the formation of the final product, iron(II)–PPDTS complex. These results support the formation of ternary intermediate complexes, $\mathrm{Fe^{III}(PPDTS)_2(scz)^{3-}}$ or $\mathrm{Fe^{III}(PPDTS)_2(tscz)^{3-}}$. The magenta species adsorbed at the top of the resin column did not desorb from the resin even on washing the resin bed with 6.0 mol dm^{-3} $NaNO_3$. These results suggest that the magenta species is highly negatively charged. However, on washing the resin bed with 0.05 mol dm^{-3} EDTA (disodium salt) solution (pH ~ 4.0), the magenta color disappeared and the eluents showed gamma activity. We suggest that the intermediates, $\mathrm{Fe^{III}(PPDTS)_2(scz)^{3-}}$ or $\mathrm{Fe^{III}(tscz)(PPDTS)_2^{3-}}$ react with EDTA to give a complex that is more easily desorbed. The gamma activity of these two species separated with 3.2 mol dm^{-3} $NaNO_3$ and 0.5 mol dm^{-3} EDTA solutions accounted for most of the total activity of ^{59}Fe taken. Similar results were obtained for all the reactions carried out in the presence of BDTPS. The reaction mixtures were passed through Dowex 2X8 (NO_3^- form) resin column. The solution that passed through the column did not show any γ-activity, indicating the absence of either neutral or cationic species. The resin bed was washed with the solutions of different concentrations of $Ca(NO_3)_2$ of 2.0 mol dm^{-3} onwards. Eluents obtained on elution with 3.0 mol dm^{-3} $Ca(NO_3)_2$ showed γ-activity. The anionic species eluted could be a highly negative charged iron(III) intermediate, probably $\mathrm{Fe^{III}(scz)(BDTPS)_2^{5-}}$ or $\mathrm{Fe^{III}(tscz)(BDTPS)_2^{5-}}$. Similar results to those obtained in the case of the iron(III)-scz/tscz–PPDTS systems, were obtained on elution with 0.01 mol dm^{-3} EDTA solution (pH ~ 4.0). These results give support to the proposed mechanism and are in consonance with the equilibrium constants obtained from the kinetic data.

$\Delta H^{\#}$ and $\Delta S^{\#}$ values were computed for all these reactions using the specific rate constants k_1/k_2 and are tabulated in Table 5. A comparison of the energies of activation for the oxidation of hydroxylamine, semicarbazide, and thiosemicarbazide by iron(III) in the presence of PDTS, PPDTS, and BDTPS shows that the $\Delta H^{\#}$ values follow the order BDTPS > PDTS > PPDTS.

BDTPS and PPDTS are excepted to form more stable complexes with iron(III)than PDTS, due to their greater π-electron delocalization. On this basis, it is expected that the stability of the intermediate complexes, Fe(III)–PPDTS and Fe(III)–BDTPS, is higher than that of the Fe(III)–PDTS intermediate complexes. Hence, the PDTS systems might be expected to exhibit higher $\Delta H^{\#}$ values than the PPDTS and BDTPS systems. However, the experimental results show that the reactions in the presence of BDTPS exhibit very high $\Delta H^{\#}$ compared to PDTS. Because of the bulky nature of the BDTPS, higher reorganization energy may be required for the formation of the transition state, leading to higher enthalpy values. Between scz and tscz, tscz forms a stronger complex with iron(III) than scz, which is reflected in the enthalpy of the transition state. The entropies of activation $\Delta S^{\#}$ for these reactions also fall in line with this analysis. The $\Delta S^{\#}$ values are the lowest in the PPDTS systems, which indicates that the transition states are more highly ordered compared to the reactions in the presence of PDTS. The very large positive $\Delta S^{\#}$ values noticed for the BDTPS systems indicate that the transition state is highly disordered, which can again also be attributed to steric factors. From these results, it can be concluded that the size and π-electron delocalization ability of the α,α-diimine ligand play a vital role in these reactions.

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