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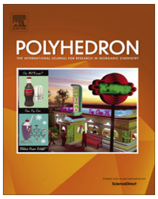

A kinetic study of the oxidation of hydrazine by tris(1,10-phenanthroline)iron(III) in acidic medium

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ABSTRACT

The oxidation of hydrazine by tris(1,10-phenanthroline)iron(III) in acidic medium shows first order kinetics in the oxidant, Fe^{III}(phen)$_3^{3+}$. With respect to N_2H_4 saturation kinetics, consistent with reactant association (small *k*-values) prior to the redox step, has been observed. Irreversible decomposition of Fe^{II}(phen)$_3^{2+}$ and Fe^{III}(phen)$_3^{3+}$ cause unwanted interference in the latter stages of the reaction. An increase of [H$^+$] has a decreasing effect on the rate of the N_2H_4 oxidation by Fe^{III}(phen)$_3^{3+}$ and a value of $K_{a1} = 0.42 \pm 0.05$ M (p$K_{a1} = 0.38$) at $\mu = 1.0$ M with $N_2H_5^+$ the more reactive species has been obtained. Activation parameters, applicable to the specific experimental conditions, for the oxidation of hydrazine by Fe^{III}(phen)$_3^{3+}$ have been determined as $\Delta H^{\ddagger} = 69 \pm 6$ kJ mol^{-1} and $\Delta S^{\ddagger} = -53 \pm 20$ J K^{-1} mol^{-1}. A study of the decomposition of Fe^{II}(phen)$_3^{2+}$ and Fe^{III}(phen)$_3^{3+}$ have also been performed to quantify the effect of these decomposition reactions on the oxidation rate of the hydrazine. The rate of decomposition of the Fe^{II}(phen)$_3^{2+}$ and Fe^{III}(phen)$_3^{3+}$ are *ca* 50 and 75 fold slower than the N_2H_4 induced reduction of the tris(1,10-phenanthroline)iron(III).

1. Introduction

The hydrazinium ion is known to be a very powerful reducing agent [1]. The oxidation of hydrazine by several oxidizing agents in both alkaline and acidic medium has been the subject of a considerable amount of studies. The oxidation of hydrazine by Mo(CN)$_8^{3-}$, W(CN)$_8^{3-}$ and Fe(CN)$_6^{3-}$ [2,3] suggested that N_2H_4 is the reactive species in alkaline medium. The oxidation of hydrazine by hexachloroiridate(IV) [4], studied over a wide pH range (pH 1–10), yielded N_2(g) as a reaction product and N_2H_4 was considered the reactive hydrazine species in the proposed reaction mechanism. In several studies in an acidic medium of [H$^+$] > 0.01 M, the hydrazinium ion, $N_2H_5^+$ (pK_a = 7.98 [5]) was considered as the reactive species [6–11]. Stanbury [5] concluded, after analysis of the work done by Higginson and co-workers [12], that substitution inert one-electron oxidants uniformly yield N_2(g) as the sole nitrogen reaction product during oxidation of hydrazine.

Several kinetic studies on the reduction of Fe(phen)$_3^{3+}$ have been reported [13–18]. Studies involving Fe(phen)$_3^{3+}$ can be misleading, if it is assumed when Fe^{3+} and 1,10-phenanthroline are mixed in a 1:3 ratio, Fe(phen)$_3^{3+}$ is formed. This, however, is not the case. Such studies merely study the reactivity of the aquated Fe^{3+} species in the presence of 1,10-phenanthroline [19]. Authentic tris(1,10-phenanthroline)iron(III) can only be obtained by the oxidation of Fe(phen)$_3^{2+}$ [20].

Fe(phen)$_3^{3+}$ is a strong one-electron oxidant [20] (E^0 = 1.14 V [21]). Irreversible decomposition of Fe(phen)$_3^{2+}$ and Fe(phen)$_3^{3+}$ could be a major source of unwanted interference, and are of primary importance in systems involving these cations [13,14,20]. The decomposition (or dissociation) of these complexes have been studied [22,23]. It was established that the decomposition of Fe(phen)$_3^{2+}$ is independent of [H$^+$] while for Fe(phen)$_3^{3+}$ it is [H$^+$] dependent. Variation of the ionic strength of the reaction mixture causes the decomposition rate of both species to decrease with an increase in the ionic strength. It was also established that increasing temperature of the reaction mixture enhances the rate of decomposition for both Fe(phen)$_3^{2+}$ and Fe(phen)$_3^{3+}$.

In order to gain new insights in the electron transfer properties of Fe(phen)$_3^{3+}$ while taking into account the decomposition of both Fe(phen)$_3^{3+}$ and Fe(phen)$_3^{2+}$, we decided to focus our attention on the hydrazine/Fe^{III}(phen)$_3^{3+}$ redox system. Since hydrazine is a well-known reducing agent, the study of the oxidation of hydrazine by Fe(phen)$_3^{3+}$ can complement the knowledge and characteristics of both hydrazine and the Fe^{III}(phen)$_3^{3+}$ complex. In this study we report the rate and mechanism of the reduction of Fe(phen)$_3^{3+}$ with hydrazine as a function of [H$^+$], ionic strength and temperature while allowing for the decomposition of Fe(phen)$_3^{3+}$ and the reaction product, Fe(phen)$_3^{2+}$.

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2. Experimental

2.1. Compounds

Tris(1,10-phenanthroline)iron(III) perchlorate was prepared from tris(1,10-phenanthroline)iron(II) perchlorate by oxidation with lead(IV) oxide, as described by Subramaniam and co-workers [18] and was used as primary standard after re-crystallization. Hydrazine solutions were prepared from hydrazine hydrate obtained from Fluka Chemika and were standardized by potassium iodate [24,25]. A stock solution of dilute sulfuric acid has been prepared and standardized with borax using methyl red as indicator [25]. Sulfuric acid was used as a recent report by Lente and co-workers [20] indicated that during the synthesis of tris(1,10-phenanthroline)iron(II) and -iron(III) sulfuric acid is beneficial. They also indicated that meaningful experiments with tris(1,10-phenanthroline)iron(III) are limited to acidic solutions. The free [H^+] was calculated by assuming that H_2SO_4 dissociates in the first dissociation step quantitatively to H^+ and HSO_4^- in aqueous solution. For the second dissociation of HSO_4^- to H^+ and SO_4^{2-} the acid dissociation constant of 1.2×10^{-2} M [25] was considered. This implies, for example, that a solution with total concentration of 0.05 M H_2SO_4 has free [H^+] of 0.0692 M and not 0.1 M. All other reagents were analytical grade and redistilled water was used throughout.

2.2. Kinetic measurement

Kinetic data for the decomposition of the $Fe(phen)_3^{3+}$ complex have been obtained at 590 nm (ε [λ_{590}{$Fe^{III}(phen)_3^{3+}$}] = 670(16) M^{-1} cm^{-1}; ε [λ_{605}{$Fe^{III}(phen)_3^{3+}$}] = 847(18) M^{-1} cm^{-1}) and that of the $Fe^{II}(phen)_3^{2+}$ complex at 510 nm (ε [λ_{510}{$Fe^{II}(phen)_3^{2+}$}] = 9672(12) M^{-1} cm^{-1}) on a Shimadzu 1650 UV–Vis spectrophotometer. Kinetic data for the hydrazine oxidation by $Fe^{III}(phen)_3^{3+}$ under pseudo first order conditions were obtained at constant ionic strength (NaCl), by monitoring the absorbance increase of the formation of the product, $Fe^{II}(phen)_3^{2+}$, at 510 nm. The low extinction coefficient of the $Fe(phen)_3^{3+}$ complex at 510 nm (ε [λ_{510}-{$Fe^{III}(phen)_3^{3+}$}] = 295(8) M^{-1} cm^{-1}) implies no significant $Fe(phen)_3^{3+}$ interference (less than 2.5%) was observed when monitoring $Fe^{II}(phen)_3^{2+}$ formation at 510 nm. $Fe(phen)_3^{3+}$ complex purity was assessed by noting that our measured extinction coefficients duplicated those reported in literature (ε [λ_{510}{$Fe^{III}(phen)_3^{3+}$}] = 300 M^{-1} cm^{-1} [13] and ε [λ_{600}{$Fe^{III}(phen)_3^{3+}$}] = 843(16) M^{-1} cm^{-1} [20]), almost exactly. The temperature was controlled to within 0.1 °C by a Shimadzu Peltier temperature regulator. Reaction rate constants were determined by a non-linear least squares fit of absorbance data to the equation:

$$A_t = (A_1 - A_0)\mathrm{Exp}(-k_{obsd}t) \qquad (1)$$

Due to the decomposition of $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$ the absorbance of approximately the first half-life of the reaction for the oxidation of hydrazine by $Fe(phen)_3^{3+}$, where the decomposition is negligibly small, were used for the data fitting. The value of k_{obsd} was also confirmed with ln-time plots of approximately the first half-life data.

The stoichiometry of the N_2H_4 oxidation reaction has been confirmed by identifying $N_2(g)$ (Eq. (5), See introduction, Ref. [5] p. 551) as a reaction product. This was achieved by feeding the gas bubbles that formed during reactions with reagent concentrations substantially larger than that of the experimental kinetic conditions ([$Fe(phen)_3^{3+}$] = 0.002 M and [N_2H_4] = 0.1 M) into a Pfeiffer ThermoStar™ mass spectrometer under an argon atmosphere. N_2 gas was identified on the mass spectra (Fig. 6).

Activation parameters were obtained by performing reactions at various temperatures (Tables 1 and 2, Supplementary information). Temperatures warmer than 35 °C have been avoided because decomposition of the iron complexes becomes too significant to ignore during kinetic work-up of the redox reaction data. The parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, applicable only to the experimental conditions of Tables 1 and 2 (Supplementary information), have been obtained from the linearized Eyring equation (Eq. (2)) where k_B and h are the Boltzman and Planck constants respectively [26]:

$$\ln\left(\frac{k}{T}\right) = -\left(\frac{\Delta H^{\ddagger}}{RT}\right) + \left(\frac{\Delta S^{\ddagger}}{R}\right) + \ln\left(\frac{k_B}{h}\right) \qquad (2)$$

where $\Delta H^{\ddagger}$ can be obtained from the slope, $\frac{-\Delta H^{\ddagger}}{R}$, and $\Delta S^{\ddagger}$ from the intercept,

$$\frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right).$$

The least squares fitting of measured data was carried out by using the general fitting software Micro Math "Scientist" [27].

3. Results and discussion

3.1. Decomposition of $Fe^{n}(phen)_3^{n+}$ (n = 2,3)

The effect of the decomposition of the oxidant, $Fe(phen)_3^{3+}$ and the redox product $Fe(phen)_3^{2+}$, on the reaction profile of the hydrazine induced reduction of $Fe(phen)_3^{3+}$, can be seen in Fig. 1. Due to the decomposition of these complexes in aqueous solution reliable rate data for the oxidation of hydrazine by tris(1,10-phenanthroline)iron(III) could not be calculated from data points for two half lives of the reaction. Hence we first studied the kinetics of the decomposition of $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$ under the conditions used for the oxidation of hydrazine with $Fe(phen)_3^{3+}$.

The results for the decomposition of $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$ (Table 1 in Supporting information and Fig. 2) show that the decomposition of both complexes in solution follows first order kinetics. The decomposition rate of the $Fe(phen)_3^{2+}$ is kinetically independent of [H^+], while the decomposition rate of the $Fe(phen)_3^{3+}$ decreases with an increase in [H^+]. The decomposition of the $Fe(phen)_3^{2+}$ is virtually independent of the ionic strength of the reaction medium, because a decrease of only 11–12% in the rate constant was observed when the ionic strength was increased ten fold (Table 1, Supplementary information). The decomposition rate of the $Fe(phen)_3^{3+}$, however, decreases more significantly with an increase in the ionic strength of the reaction medium. These observations for the decomposition of $Fe(phen)_3^{2+}$ are consistent with a rate law, R = k′[$Fe(phen)_3^{2+}$], while the decomposition of $Fe(phen)_3^{3+}$ adheres to the rate law R = k″[$Fe(phen)_3^{3+}$]. The rate

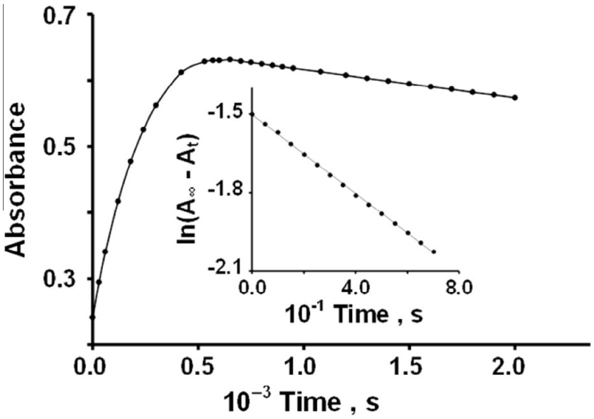

Fig. 1. Reaction profile of the oxidation of hydrazine by $Fe^{III}(phen)_3^{3+}$ at λ = 510 nm, including a ln-time plot of approximately the first half-life used for obtaining k_{obsd}. [$Fe^{III}(phen)_3^{3+}$] = 0.0001 M; [N_2H_4] = 0.002 M; Free [H^+] = 0.0692 M; μ (NaCl) = 1.0 M; T = 20 ± 0.1 °C. For the calculation of free H^+ content, see experimental section.