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Influence of the decomposition of *Tris*(2,2-bipyridine)iron(II) and (III) on the reduction of *Tris*(2,2-bipyridine)iron(III) by hydrazine in aqueous acidic medium: a kinetic study

Ali A. G. A. Al Mahdi[1,2] · **Mohammed A. Hussein**[1,2] · **Eleanor Fourie**[1] ·
Jannie C. Swarts[1] · **C. Robert Dennis**[1]

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Abstract The reduction of *tris*(2,2-bipyridine)iron(III) by hydrazine in aqueous acidic medium exhibits first-order kinetics in both $\mathrm{Fe^{III}(bipy)_3^{3+}}$ and hydrazine. Saturation kinetics, consistent with reactant association prior to the redox step, has been observed. Because this reaction takes place while both the reactant, $\mathrm{Fe^{III}(bipy)_3^{3+}}$, and the reduced product, $\mathrm{Fe^{II}(bipy)_3^{2+}}$, decompose, a study of the irreversible decomposition of $\mathrm{Fe^{II}(bipy)_3^{2+}}$ and $\mathrm{Fe^{III}(bipy)_3^{3+}}$ has also been performed. The decomposition rate of the $\mathrm{Fe^{II}(bipy)_3^{2+}}$ and $\mathrm{Fe^{III}(bipy)_3^{3+}}$ species is, respectively, at least ca. 50- and ca. 40-fold slower than the N_2H_4-induced reduction of *tris*(2,2-bipyridine)iron(III) ($k_2 = 2.1\ \mathrm{M^{-1}s^{-1}}$ at $[\mathrm{H^+}] = 0.0273$ M, $\mu = 1.0$ M and $T = 25.0 \pm 0.1$ °C) under comparable conditions. An increase in $[\mathrm{H^+}]$ of the reaction medium has a decreasing effect on the rate of the $\mathrm{Fe^{III}(bipy)_3^{3+}}$ reduction with hydrazine. A kinetically determined K_{a1} value for the dissociation of $N_2H_6^{2+}$ has been obtained as $K_{a1} = 0.16 \pm 0.01$ M ($\mathrm{p}K_{a1} = 0.80$) at $\mu = 1.0$ M. $N_2H_5^+$ was found to be the more reactive hydrazine species in aqueous acidic medium. Activation parameters, applicable to the utilized experimental conditions for the hydrazine-induced reduction of $\mathrm{Fe^{III}(bipy)_3^{3+,}}$ have been determined as $\Delta H^\ddagger = 54 \pm 2\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^\ddagger = -102 \pm 6\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

Introduction

The benefits of substitution-inert one-electron transfer complexes, such as $\mathrm{Mo(CN)_8^{n-}}$, $\mathrm{W(CN)_8^{n-}}$ and $\mathrm{Fe(CN)_6^{n-}}$ ($n = 3$ or 4), in studying the kinetics of multi-electron transfer reactions are widely appreciated [1–3]. They react predominantly via an outer-sphere electron transfer mechanism.

The hydrazinium ion, $N_2H_5^+$, is known [4] to be a more powerful reducing agent than $N_2H_6^{2+}$ in relatively strong aqueous acidic medium, while in aqueous alkaline medium, neutral hydrazine, N_2H_4, is considered a stronger reducing agent than $N_2H_5^+$. It has been shown that the in the hydrazine-induced reduction of $\mathrm{Fe(CN)_6^{3-}}$, $\mathrm{W(CN)_8^{3-}}$, $\mathrm{Mo(CN)_8^{3-}}$ [5, 6], $\mathrm{Ir(Cl)_6^{2-}}$ [7] and the tyrosil radical of the R2 fragment of ribonucleotide reductase [8] in the pH range of $2 < \mathrm{pH} < 10$, N_2H_4 rather than $N_2H_5^+$ is the reactive hydrazine species. In contrast, in the relatively stronger acidity range $0.1 < [\mathrm{H^+}] < 0.3\ \mathrm{mol\ dm^{-3}}$, $N_2H_5^+$ was found to reduce $\mathrm{Fe^{III}(phen)_3^{3+}}$ much faster than $N_2H_6^{2+}$ [9]. In all of these studies, the previously detected [10, 11] radical cation, $N_2H_4^{\bullet +}$, is a reaction intermediate species. Nitrogen gas (N_2) has been suggested as the nitrogen product in all the studies mentioned above. In fact, Stanbury [12] concluded that substitution-inert one-electron oxidants uniformly yield N_2(g) as the sole nitrogen reaction product for reductions with hydrazine. In support of this, N_2(g) was proved to be a reaction product by mass spectroscopy in the reduction of $\mathrm{Fe^{III}(phen)_3^{3+}}$ by hydrazine [9].

Although *tris*(2,2-bipyridine)iron(III) is a strong one-electron oxidant ($E° = 1.06$ V in 0.1 M acid solution [13]), the kinetics of $\mathrm{Fe^{III}(bipy)_3^{3+}}$ reduction by hydrazine

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✉ C. Robert Dennis
Denniscr@ufs.ac.za

[1] Chemistry Department, University of the Free State, P.O. Box 339, Bloemfontein 9300, Republic of South Africa

[2] Present Address: Chemistry Department, University of Khartoum, Khartoum, Sudan

has never been explored. Only kinetic studies of the reduction of $Fe^{III}(bipy)_3^{3+}$ by hydroxide ions [14, 15], cobaloxime ($Co(dmgBF_2)_2(H_2O)_2$) [16] and nitropentacyanocobaltate(III) [17] have been reported. These reactions were found to be first order in both oxidizing and reducing agents. Irreversible decomposition of $Fe^{II}(bipy)_3^{2+}$ [18, 19] and $Fe^{III}(bipy)_3^{3+}$ could cause a major interference and could be of primary importance in systems involving $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ [14–17]. Basolo [18] qualitatively showed that at low [H_2SO_4], the decomposition rate of $Fe^{II}(bipy)_3^{2+}$ increases with increasing [H^+] and reaches a constant rate at $[H^+] > 1.0$ M (H_2SO_4). It was also established that increasing the temperature of reaction mixtures increases the decomposition rate of $Fe^{II}(bipy)_3^{2+}$.

The $Fe^{III}(bipy)_3^{3+}$ complex is frequently used for colorimetric detection of iron. However, the iron to be analyzed must be present as Fe^{2+} [20] before bipy will complex with it. This implies that before iron can be determined colorimetrically in any sample, a reduction of any Fe^{3+} present is necessary to allow formation of the $Fe^{II}(bipy)_3^{2+}$ complex. After the formation of $Fe^{II}(bipy)_3^{2+}$, it must be reoxidized to $Fe^{III}(bipy)_3^{3+}$ for the iron colorimetric analysis [20]. $Fe^{III}(bipy)_3^{3+}$ is known to catalyze self-oscillation in polymer chains as a result of the Belousov–Zhabotinsky reaction [21]. These and other applications make knowledge about the stability and redox processes not only of $Fe^{II}(bipy)_3^{2+}$ [18], but also of $Fe^{III}(bipy)_3^{3+}$, important.

In this study, we first describe the decomposition of the complex ions $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$. After the conditions were identified where these decompositions would least impact on the chemical reduction of $Fe^{III}(bipy)_3^{3+}$ by a suitable reductant, we report on the kinetics and mechanism of the $Fe^{III}(bipy)_3^{3+}$ reduction with hydrazine as a function of acid strength, ionic strength and temperature.

Experimental

Compounds

Tris(2,2-bipyridine)iron(III) perchlorate was synthesized from *tris*(2,2-bipyridine)iron(II) perchlorate by oxidation with lead(IV) oxide, adapting the described procedure for the synthesis of *tris*(1,10-phenantroline)iron(III) perchlorate [22]. The complex was used as a primary standard after recrystallization. Hydrazine solutions were prepared from hydrazine hydrate (Fluka Chemica) and were standardized by potassium iodate [23, 24]. A stock solution of sulfuric acid was prepared and standardized with borax using methyl red as indicator [24] to provide strong acidic conditions during synthesis [25] and kinetic studies. This allowed comparison of the obtained kinetic results of the hydrazine-induced reduction of $Fe^{III}(bipy)_3^{3+}$ with those of the reduction of a similar complex, $Fe^{III}(phen)_3^{3+}$ [9] that was studied before. The free [H^+] in reaction mixtures was calculated by assuming that H_2SO_4 quantitatively dissociates in the first dissociation step to H^+ and HSO_4^- in aqueous solution. For the dissociation of HSO_4^- to H^+ and SO_4^{2-}, the dissociation constant of 1.2×10^{-2} M [24] was utilized. This means that a 0.1 mol dm^{-3} H_2SO_4 solution does not have free [H^+] of 0.2 mol dm^{-3} but rather $[H^+] = 0.1384$ mol dm^{-3}.

Kinetic measurements

Absorbance measurements to obtain extinction coefficients and kinetic data were performed on a Shimadzu 1650 UV–Vis spectrophotometer. Rate data for the decomposition of $Fe^{II}(bipy)_3^{2+}$ have been obtained at 522 nm [$\varepsilon_{522}\{Fe^{II}(bipy)_3^{2+}\} = 8301(57)$ M^{-1} cm^{-1}] and that of $Fe^{III}(bipy)_3^{3+}$ at 610 nm [$\varepsilon_{610}\{Fe^{III}(bipy)_3^{3+}\} = 203(5)$ M^{-1} cm^{-1}]. Kinetic data for the reduction of $Fe^{III}(bipy)_3^{3+}$ by hydrazine under pseudo-first-order conditions at constant ionic strength have been obtained by monitoring the absorbance increase in the product, $Fe^{II}(bipy)_3^{2+}$, at 522 nm. The low extinction coefficient of the $Fe^{III}(bipy)_3^{3+}$ complex at 522 nm [$\varepsilon_{522}\{Fe^{III}(bipy)_3^{3+} = 100(3)$ M^{-1} cm^{-1}] implies that no significant $Fe^{III}(bipy)_3^{3+}$ interference (less than 2 %) was observed while monitoring the formation of $Fe^{II}(bipy)_3^{2+}$ at 522 nm. The purity of the $Fe^{III}(bipy)_3^{3+}$ complex was assessed by comparing our measured extinction coefficient with that reported in the literature [ε_{610}-$\{Fe^{III}(bipy)_3^{3+}\} = 220$ M^{-1} cm^{-1}] [16, 17]. The temperature was controlled to within 0.1 °C by a Shimadzu Peltier system temperature regulator.

Pseudo-first-order reaction rate constants have been obtained by a nonlinear least squares fit of absorbance data to the equation

$$A_t = (A_1 - A_0)\exp(-k_{obsd}t) \quad (1)$$

The value of k_{obsd} was also confirmed with ln-time plots.

Reaction runs have been performed at various temperatures between 20 °C and 35 °C to obtain activation parameters for the reactions. The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been obtained from the linearized Eyring equation (Eq. 2) [26], where k_B and h are the Boltzman and Planck constants, respectively. T and R are the Kelvin temperature and gas constant (8.314 J K^{-1} mol^{-1}), respectively, while

k_2 is the second-order rate constant of the electron transfer reaction.

$$\ln\left(\frac{k_2}{T}\right) = -\left(\frac{\Delta H^{\neq}}{RT}\right) + \left(\frac{\Delta S^{\neq}}{R}\right) + \ln\left(\frac{k_B}{h}\right) \tag{2}$$

A linear plot of ln (k_2/T) versus $1/T$ yielded $\Delta H^{\neq}$ from the slope, $-\Delta H^{\#}/R$, while $\Delta S^{\neq}$ was obtained from the intercept, $-\Delta S^{\#}/R + \ln(k_B/h)$.

Scientist 3.0, a general least square fitting program by Micromath [27] was used for fitting of kinetic data and calculation of parameters.

Results and discussion

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

The reaction profile for the reaction between $Fe^{III}(bipy)_3^{3+}$ and hydrazine shown in Fig. 1 does not resemble a typical pseudo-first-order reaction trace. At the end of the reaction, decomposition of the reduced product, $Fe^{II}(bipy)_3^{2+}$, is responsible for the observed absorbance decrease. Decomposition of the oxidant, $Fe^{III}(bipy)_3^{3+}$, may also contribute to the observed reaction profile in the initial stages of the reaction. These decomposition processes have a direct effect on the determination of the rate of reduction of $Fe^{III}(bipy)_3^{3+}$ by hydrazine.

To determine convenient experimental conditions for the reduction of *tris*(2,2-bipyridine)iron(III) with hydrazine that would at the same time limit interferences by the decomposition of $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ to a minimum, a study of the kinetics of the decomposition of the complex ions $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ was performed first. The decomposition kinetic data of both these complex ions in solution (Table 1; Fig. 2) indicate first-order kinetics. It was found that an increase in the ionic strength of the complex solution for both the complexes $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ has no effect on the decomposition rate (Table 1, entries 11–15). A decrease in the [H^+] of solutions by decreasing the concentration of sulfuric acid (Table 1, entries 1–10), causes a decrease in the rate of decomposition for both the complexes.

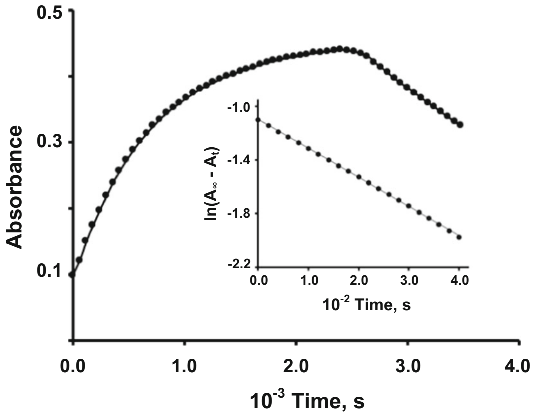


Fig. 1 Reaction profile of the reduction of $Fe^{III}(bipy)_3^{3+}$ by hydrazine at $\lambda = 522$ nm. The decrease in absorbance at the end of the reaction profile is associated with the decomposition of the reaction product, [$Fe^{II}(bipy)_3^{2+}$] *Inset* A ln-time plot from data of approximately the first half-life of the reaction. [$Fe^{III}(bipy)_3^{3+}$] = 0.0003 M; [N_2H_4] = 0.005 M; [H^+] = 0.0692 M; μ(NaCl) = 1.0 M; $T = 25.0 \pm 0.1$ °C. For the calculation of free H^+ content, see "Experimental" section

A mechanism for the decomposition of $Fe^{II}(bipy)_3^{2+}$ has been suggested by Basolo and co-workers [18], and their mechanism is mutually consistent with the results of Tachiyashiki and Yamatera [19]. Our present results for the $Fe^{II}(bipy)_3^{2+}$ decomposition are in agreement with the results of these two research groups, although an additional equilibrium involving protonation of an intermediate species has been identified and quantified in the proposed decomposition mechanism (Scheme 1). New in this scheme is the acid equilibrium involving the k'_3 and k'_{-3} steps. The quantification of the acid dependence of the decomposition enabled us to solve all the other rate constants, k'_1, k'_{-1}, k'_2, k'_3, k'_{-3} and k'_4 as well as the equilibrium constant K'_a in the decomposition mechanism of $Fe^{II}(bipy)_3^{2+}$ (values are shown in Scheme 1). This was not possible before. Previously, except for k'_1, only the ratios k'_2/k'_{-1}, k'_3/k'_{-1} and $-\left(\frac{k'_{-1}+k'_2}{k'_3}\right)$ could be obtained (Table 2) [19]. No similar data were available before for the decomposition of $Fe^{III}(bipy)_3^{3+}$, which were also obtained in this study.

According to the originally proposed decomposition mechanism for $Fe^{II}(bipy)_3^{2+}$ (i.e., by ignoring the k'_{-3} step in the mechanism), with application of the steady-state approximation, a rate law (Eq. 3) for the observed decomposition was derived [18, 19] as

$$R' = \frac{k'_1\left(k'_2 + k'_3[H^+]\right)}{k'_{-1} + k'_2 + k'_3[H^+]}\left[Fe^{n}(bipy)_3^{n+}\right] \tag{3}$$

with

$$\frac{k'_1\left(k'_2 + k'_3[H^+]\right)}{k'_{-1} + k'_2 + k'_3[H^+]} = k'_{dec,obsd} \tag{4}$$

A quantitative fit of the kinetic data of Table 1 to Eq. (4) to resolve values for k'_{-1}, k'_2 and k'_3 is not possible. Failure to do this is probably due to activity effects of nonideal solutions which cannot be taken into account [19]. However, when [H^+] is sufficiently low, the term $k'_3[H^+]$ in Eq. (4) becomes negligibly small and the value of $k'_{dec,obsd}$ will be equal to the limiting value described by Eq. (5).

Table 1 Reaction conditions and observed decomposition rate constants for $Fe^{II}(bipy)_3^{2+}$ ($\lambda = 522$ nm) and $Fe^{III}(bipy)_3^{3+}$ ($\lambda = 620$ nm) complexes; $[Fe^{II}(bipy)_3^{2+}] = 1.0 \times 10^{-4}$ M; $[Fe^{III}(bipy)_3^{3+}] = 3.0 \times 10^{-3}$ M

Entry	Common temp (°C)	$Fe^{II}(bipy)_3^{2+}$ results			$Fe^{III}(bipy)_3^{3+}$ results		
		$[H^+]$ (M)[a]	μ (M)[b]	$10^4 k'_{obsd}$ (s^{-1})	$[H^+]$ (M)[a]	μ (M)[b]	$10^4 k'_{obsd}$ (s^{-1})
1	20.0	0.572	1.000	3.5 (4)	0.572	2.000	2.95 (4)
2	20.0	0.463	1.000	3.2 (2)	0.463	2.000	2.67 (5)
3	20.0	0.354	1.000	2.80 (3)	0.354	2.000	2.47 (4)
4	20.0	0.243	1.000	2.40 (2)	0.299	2.000	2.32 (3)
5	20.0	0.187	1.000	2.08 (2)	0.243	2.000	2.09 (3)
6	20.0	0.129	1.000	1.73 (2)	0.129	2.000	1.64 (3)
7	20.0	0.0692	1.000	1.26 (7)	0.0692	2.000	1.31 (3)
8	20.0	0.0306	1.000	0.912 (3)	0.0273	2.000	0.98 (3)
9	20.0	0.0165	1.000	0.731 (2)	0.0165	2.000	0.81 (2)
10	20.0	0.0088	1.000	0.574 (2)	0.0088	2.000	0.78 (2)
11	20.0	0.0692	1.000	1.33 (5)	0.572	2.000	2.7 (4)
12	20.0	0.0692	0.700	1.26 (3)	0.572	1.700	2.7 (2)
13	20.0	0.0692	0.500	1.20 (5)	0.572	1.500	2.7 (3)
14	20.0	0.0692	0.300	1.23 (4)	0.572	1.300	2.6 (2)
15	20.0	0.0692	0.100	1.21 (2)	0.572	1.100	2.6 (1)
16	35.0	0.0692	1.000	8.99 (4)	0.572	2.000	12.8 (4)
17	30.0	0.0692	1.000	5.21 (4)	0.572	2.000	8.0 (2)
18	27.0	0.0692	1.000	3.45 (1)	0.572	2.000	5.6 (1)
19	25.0	0.0692	1.000	2.57 (7)	0.572	2.000	4.5 (1)
20	23.0	0.0692	1.000	1.98 (5)	0.572	2.000	3.8 (2)
21	20.0	0.0692	1.000	1.32 (4)	0.572	2.000	3.0 (7)
22	17.0	0.0692	1.000	0.853 (5)	0.572	2.000	0.70 (8)
23	15.0	0.0692	1.000	0.570 (2)	0.572	2.000	0.41 (4)

[a] H^+ source = H_2SO_4, for the calculation of free $[H^+]$, see "Experimental" section

[b] Controlled by NaCl

$$k'_{dec,lim} = \left(\frac{k'_1 k'_2}{k'_{-1} + k'_2}\right) \tag{5}$$

The expression for $k'_{dec,obsd}$ (Eq. 4) can be linearized (Eq. 6):

$$k'_{dec,obsd} = k'_1 - \left(\frac{k'_{-1} + k'_2}{k'_3}\right)\left(\frac{k'_{dec,obsd} - k'_{dec,lim}}{[H^+]}\right) \tag{6}$$

A plot of $k'_{dec,obsd}$ versus $\frac{k'_{dec,obsd} - k'_{dec,lim}}{[H^+]}$ for the variation of $[H^+]$ should be a straight line with gradient, $m = -\left(\frac{k'_{-1}+k'_2}{k'_3}\right)$, and the intercept yields a value for k'_1 (Fig. 3).

Values for $-\left(\frac{k'_{-1}+k'_2}{k'_3}\right)$ and k'_1 as well as the calculated values for the ratios k'_2/k'_{-1} and k'_3/k'_{-1} for the decomposition of both $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ in aqueous solution are given in Table 2. The values obtained for the $Fe^{II}(bipy)_3^{2+}$ decomposition are in agreement with values calculated by Tachiyashiki and Yamatera [19]. Similar data for the decomposition of $Fe^{III}(bipy)_3^{3+}$ are also reported in Table 2 for the first time. To separate k'_{-1}, k'_2 and k'_3, an evaluation of the $[H^+]$ dependency of the decompositions was necessary.

Variation of $[H^+]$ during the decomposition of both $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ (Table 1, entries 1–10) clearly indicates a protonation equilibrium. The amended mechanism we propose, Scheme 1, makes provision for this previously unaccounted protonation equilibrium in the k'_3 and k'_{-3} steps.

A nonlinear least squares fit of the $[H^+]$ variation data in Table 1 and Fig. 4 to Eq. (7) [28]

$$k'_{obsd} = \frac{k'_4[H^+] + k'_2 K'_{a1}}{[H^+] + K'_{a1}} \tag{7}$$

applied to the k'_2 and k'_4 reaction steps and the equilibrium step involving K'_a and k'_3/k'_{-3} of Scheme 1 (normally one would use the notations k_A, k_{HA} and K_a [28] for these steps and equilibrium, but we chose to use the notations of Scheme 1 so as not to lead to confusion with our data obtained later for the reduction of $Fe^{III}(bipy)_3^{3+}$ with hydrazine), yields $k'_4 = k_{HA} = (5.7 \pm 0.2) \times 10^{-4}\ s^{-1}$, $k'_2 = k_A = (5.3 \pm 0.3) \times 10^{-5}\ s^{-1}$ and $k'_3/k'_{-3} = K'_a =$

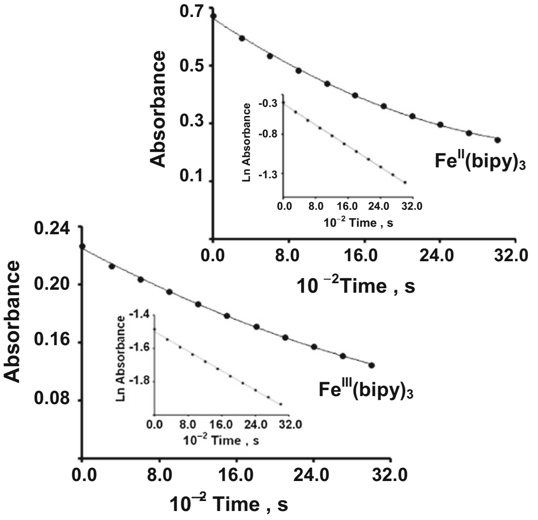


Fig. 2 Reaction trace of the decomposition at 30.0 ± 0.1 °C of $Fe^{III}(bipy)_3^{3+}$ ($[Fe^{III}(bipy)_3^{3+}] = 0.003$ M; $[H^+] = 0.572$ M; μ(NaCl) = 2.0 M; $\lambda = 610$ nm) and $Fe^{II}(bipy)_3^{2+}$ ($[Fe^{II}(bipy)_3^{2+}] = 0.0001$ M; μ(NaCl) = 1.0 M; $[H^+] = 0.0692$ M; $\lambda = 522$ nm). *Insets* A ln-time plot of the data. [Note that the concentration of $Fe^{III}(bipy)_3^{3+}$ is more than ten times higher than that of $Fe^{II}(bipy)_3^{2+}$] to observe the data on the same timescale

Table 2 Rate constant ratios as per Eq. (6) under limiting $[H^+]$ of the decomposition rate of *tris*(2,2-bipyridine)iron(II)

Rate constant ratio	$Fe^{II}(bipy)_3^{2+}$	$Fe^{III}(bipy)_3^{3+}$
$-(k'_{-1} + k'_2)/k'_3$ [a]	-0.57 ± 0.04	-0.46 ± 0.02
k'_1/s^{-1} [b]	$6.22 \pm 0.02 \times 10^{-4}$	$4.6 \pm 0.1 \times 10^{-4}$
k'_2/k'_{-1} [c]	0.133	0.214
k'_3/k'_{-1} [c]	1.99	2.64

($[Fe^{II}(bipy)_3^{2+}] = 0.0001$ M; μ(NaCl) = 1.0 M; $T = 20.0 \pm 0.1$ °C; $\lambda = 522$ nm) and *tris*(2,2-bipyridine)iron(III) ($[Fe^{III}(bipy)_3^{3+}] = 0.003$ M; μ(NaCl) = 2.0 M; $T = 25.0 \pm 0.1$ °C; $\lambda = 610$ nm) in aqueous solution

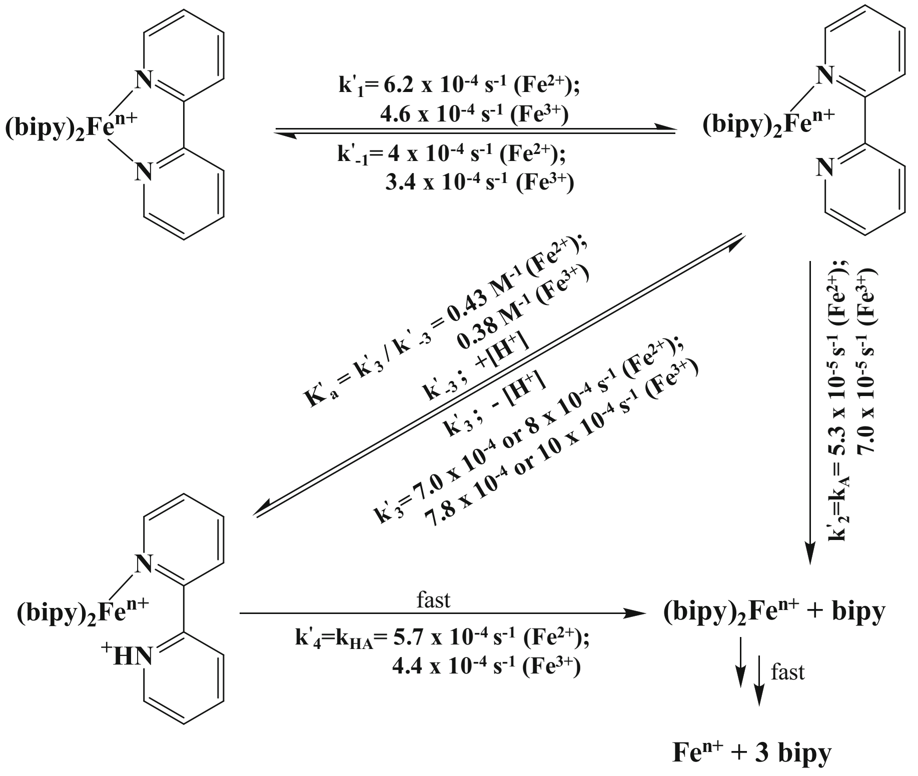
[a] The slope of a graph of data applied to Eq. (6)

[b] The *y*-intercept of a graph of data applied to Eq. (6)

[c] Calculated from Eq. (5) and the slopes obtained in Fig. 3

0.43 ± 0.03 M ($pK_a = 0.37$) for the $Fe^{II}(bipy)_3^{2+}$ complex. For the $Fe^{III}(bipy)_3^{3+}$ complex, values of $k'_4 = k_{HA} = (4.4 \pm 0.2) \times 10^{-4}\ s^{-1}$, $k'_2 = k_A = (7.0 \pm 0.3) \times 10^{-5}\ s^{-1}$ and $k'_3/k'_{-3} = K'_a = 0.38 \pm 0.04$ M ($pK_a = 0.42$) were obtained.

By utilizing k'_2 obtained from the acid dependence of $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ and substituting this in the equations yielding the values for k'_2/k'_{-1} and k'_3/k'_{-1} from Table 2, the rate constants k'_{-1} and k'_3 could also be calculated, see Scheme 1 for the values. The proposed decomposition mechanism that is shown in Scheme 1 also contains all determinable rate constants. To independently verify these rate constants and those from the $[H^+]$ study,



Scheme 1 Reaction mechanism for the decomposition of *tris*(2,2-bipyridine)iron(II) and iron(III), adapted from Ref. [18]. For k'_3 values, the first value was obtained utilizing Eq. (4) in Table 2 ($k'_3/k'_{-1} = 1.79$, with $k'_{-1} = k'_2/0.133$, the 3rd eq. in Table 2; and k'_2 obtained from the $[H^+]$ dependence of the reaction), while the second value was obtained from the gradient of the graphs shown in Fig. 4 [Eq. (1) in Table 2]. The obtained values are mutually consistent, lending credibility to the data treatment method

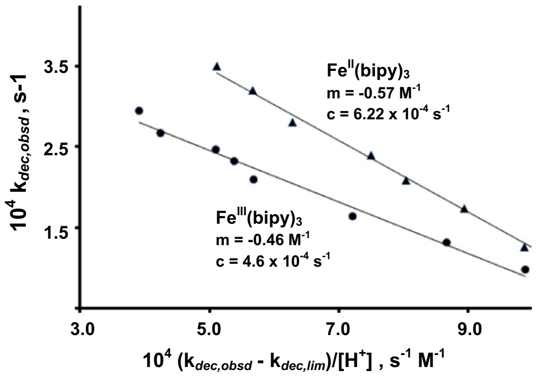


Fig. 3 Relationship between $k_{\mathrm{dec,obsd}}$ and $\frac{k_{\mathrm{dec,obsd}}-k_{\mathrm{dec,lim}}}{[\mathrm{H}^+]}$ at 20.0 ± 0.1 °C for the decomposition of $\mathrm{Fe^{II}(bipy)_3^{3+}}$ (*triangular points*: $[\mathrm{Fe^{II}(bipy)_3^{2+}}] = 0.0001$ M; $\mu(\mathrm{NaCl}) = 1.0$ M; $\lambda = 522$ nm) and $\mathrm{Fe^{III}(bipy)_3^{3+}}$ (*circular points*: $[\mathrm{Fe^{III}(bipy)_3^{3+}}] = 0.003$ M; $\mu(\mathrm{NaCl}) = 2.0$ M; $\lambda = 610$ nm)

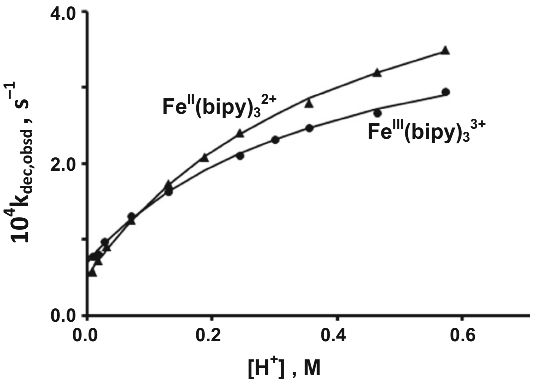


Fig. 4 Relationship between $k_{\mathrm{dec,obsd}}$ and $[\mathrm{H}^+]$ at 20.0 ± 0.1 °C for the decomposition of $\mathrm{Fe^{II}(bipy)_3^{2+}}$ (*triangular points*; $\lambda = 522$ nm; $[\mathrm{Fe^{II}(bipy)_3^{2+}}] = 1.0 \times 10^{-4}$ M; $\mu(\mathrm{NaCl}) = 1.0$ M) and $\mathrm{Fe^{III}(bipy)_3^{3+}}$ (*circular points*; $\lambda = 610$ nm; $[\mathrm{Fe^{III}(bipy)_3^{3+}}] = 3 \times 10^{-3}$ M; $\mu(\mathrm{NaCl}) = 2.0$ M). For the calculation of free H^+ content, see "Experimental" section

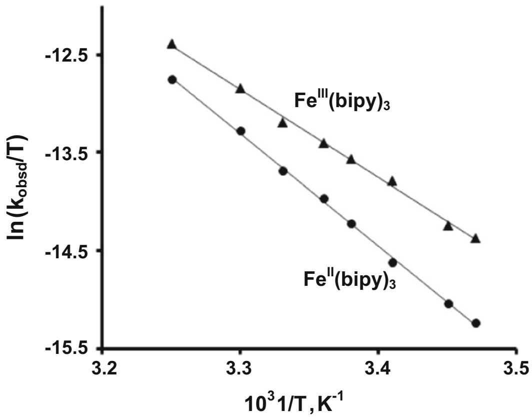


Fig. 5 Relationship between $\ln(k_{\mathrm{obsd}}/T)$ and $1/T$ from the linearized Eyring equation for the decomposition of $\mathrm{Fe^{II}(bipy)_3^{2+}}$ (*circular points*) and $\mathrm{Fe^{III}(bipy)_3^{3+}}$ (*triangular points*). ($[\mathrm{Fe^{II}(bipy)_3^{2+}}] = 0.0001$ M; free $[\mathrm{H}^+] = 0.0692$ M; $\mu(\mathrm{NaCl}) = 1.0$ M), and $[\mathrm{Fe^{III}(bipy)_3^{3+}}] = 0.003$ M; free $[\mathrm{H}^+] = 0.572$ M; $\mu(\mathrm{NaCl}) = 2.0$ M)

the obtained rate constants were substituted into the expression $-\left(\frac{k'_{-1}+k'_2}{k'_3}\right)$, the gradient in Fig. 3, of Table 2. The values obtained this way (−0.64 for $\mathrm{Fe^{II}(bipy)_3^{2+}}$ and −0.54 for $\mathrm{Fe^{III}(bipy)_3^{3+}}$) were mutually consistent with the experimental values reported in Table 2 (−0.57 and −0.46, respectively).

The decomposition of both the complexes, $\mathrm{Fe^{II}(bipy)_3^{2+}}$ and $\mathrm{Fe^{III}(bipy)_3^{3+}}$, in aqueous solution is enhanced by an increase in the temperature of the complex ion solution (Table 1, entries 16–23). From the linearized Eyring equation (Eq. 2; Fig. 5), the activation parameters for $\mathrm{Fe^{II}(bipy)_3^{2+}}$, under the experimental conditions in Table 1, have been determined as $\Delta H^{\neq} = 102 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = 30 \pm 7$ J K^{-1} mol^{-1} at $\mu = 1.0$ M (NaCl). The activation parameters for $\mathrm{Fe^{III}(bipy)_3^{3+}}$ have been determined as $\Delta H^{\neq} = 77 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = 58 \pm 5$ J K^{-1} mol^{-1} at $\mu = 2.0$ M (NaCl). The small size of these $\Delta H^{\neq}$ values ($\Delta H^{\neq} \leq 102$ kJ mol^{-1} for both complexes) are consistent with only one rate-determining decomposition step, shown in Scheme 1 as k'_2. All other components of the decomposition are at least one order of magnitude faster than k'_2, as in the case, for example, with k'_4. Consistent with this conclusion are the positive $\Delta S^{\neq}$ values of both complexes. Any positive $\Delta S^{\neq}$ value is consistent with bond breaking. The rate-determining step in Scheme 1, k'_2, consists of bond breaking between Fe^{n+} and a "half-bonded" bipy ligand.

The decomposition results of $\mathrm{Fe^{II}(bipy)_3^{2+}}$ and $\mathrm{Fe^{III}(bipy)_3^{3+}}$ indicated that convenient experimental conditions for the reduction of *tris*(2,2-bipyridine)iron(III) with hydrazine that would minimize the influence of decomposition of $\mathrm{Fe^{II}(bipy)_3^{2+}}$ and $\mathrm{Fe^{III}(bipy)_3^{3+}}$ on this redox process, are low $[\mathrm{H}^+]$ and relatively low reaction temperatures. We therefore chose the general experimental conditions for the redox reaction between $\mathrm{Fe^{III}(bipy)_3^{3+}}$ and hydrazine as $[\mathrm{H}^+] = 0.0237$ M and a temperature of 25.0 ± 0.1 °C.

Reduction of $\mathrm{Fe^{III}(bipy)_3^{3+}}$

The reduction of $\mathrm{Fe^{III}(bipy)_3^{3+}}$ with hydrazine has been followed by monitoring the formation of $\mathrm{Fe^{II}(bipy)_3^{2+}}$ at 522 nm [$\varepsilon_{522}\{\mathrm{Fe^{II}(bipy)_3^{2+}}\} = 8301(57)$ M^{-1} cm^{-1}] under pseudo-first-order conditions, with $[\mathrm{N_2H_4}]$ at least a factor

Table 3 Observed rate constants for the oxidation of hydrazine by $Fe^{III}(bipy)_3^{3+}$

Reaction entry	$[N_2H_4]$ (M)	$[H^+]$ (M)[a]	μ (M)[b]	Temp. (°C)	$10^2k'_{obsd}$ (s^{-1})
1	0.0020	0.0273	1.00	25.0	0.44 (2)
2	0.0030	0.0273	1.00	25.0	0.60 (7)
3	0.0050[c]	0.0273	1.00	25.0	0.95 (8)
4	0.0080	0.0273	1.00	25.0	1.47 (9)
5	0.010	0.0273	1.00	25.0	1.72 (7)
6	0.015	0.0273	1.00	25.0	2.31 (8)
7	0.020	0.0273	1.00	25.0	2.40 (7)
8	0.005	0.0088	1.00	25.0	1.11 (4)
9	0.005	0.0273	1.00	25.0	1.02 (4)
10	0.005	0.0373	1.00	25.0	0.96 (5)
11	0.005	0.0567	1.00	25.0	0.87 (4)
12	0.005	0.0692	1.00	25.0	0.83 (4)
13	0.005	0.129	1.00	25.0	0.68 (5)
14	0.005	0.187	1.00	25.0	0.58 (5)
15	0.005	0.296	1.00	25.0	0.45 (2)
16	0.005	0.0273	0.10	25.0	0.85 (5)
17	0.005	0.0273	0.30	25.0	0.92 (6)
18	0.005	0.0273	0.50	25.0	1.01 (9)
19	0.005	0.0273	0.70	25.0	0.89 (7)
20	0.005	0.0273	1.00	25.0	0.91 (7)
21	0.005	0.0273	1.00	35.0	2.30 (9)
22	0.005	0.0273	1.00	33.0	1.89 (8)
23	0.005	0.0273	1.00	30.0	1.58 (9)
24	0.005	0.0273	1.00	27.0	1.25 (5)
25	0.005	0.0273	1.00	25.0	1.03 (3)
26	0.005	0.0273	1.00	23.0	0.96 (6)
27	0.005	0.0273	1.00	20.0	0.71 (7)
28	0.005	0.0273	1.00	17.0	0.62 (5)

$[Fe^{III}(bipy)_3^{3+}] = 0.0003$ M, $\lambda = 522$ nm

[a] H^+ source = H_2SO_4, for calculation of free $[H^+]$, see "Experimental" section

[b] Controlled with NaCl

[c] This reaction was repeated with $[Fe^{III}(bipy)_3^{3+}] = 0.0001$ and 0.001 M. Rate constants were 0.0101 and 0.0103 s^{-1}, respectively (i.e., constant)

of 10 larger than $[Fe^{III}(bipy)_3^{3+}]$. Results are summarized in Table 3. Due to the decomposition of the complexes $Fe^{III}(bipy)_3^{3+}$ and $Fe^{II}(bipy)_3^{2+}$ in solution, albeit at least 40 times slower than the rate of electron transfer, only rate data processed up to the first half-life of the reaction were utilized. The decomposition of $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ may be considered as insignificant up to this point. To explain this, from the decomposition results of $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ (Table 1), at the chosen reaction conditions of [H] = 0.0273 M and 25.0 ± 0.1 °C, half-lives for the decompositions were calculated as 8.5×10^3 s and 6.7×10^3 s, respectively. Since the slowest pseudo-first-order hydrazine-induced reduction of $Fe^{III}(bipy)_3^{3+}$ resulted in $k = 0.44 \times 10^{-2}\ s^{-1}$ (Table 3, entry 1) with a half-life of 157 s, it is reasonable to assume that during the first half-life of the redox reaction, the decomposition of $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ can be neglected.

Linear $\ln(A_\infty - A_t)$ versus time plots indicate that the reaction is first order in the complex ion $Fe^{III}(bipy)_3^{3+}$. The ionic strength of the reaction medium does not have an effect on the oxidation reaction rate (Table 3, entries 16–20). Pseudo-first-order reaction rate constants, k_{obsd}, for the variation of $[N_2H_4]$ in the reaction mixture give a nonlinear dependence on $[N_2H_4]$ (Table 3, entries 1–7; Fig. 6). This is consistent with a reaction mechanism involving saturation kinetics [29], Eqs. (8) and (9).

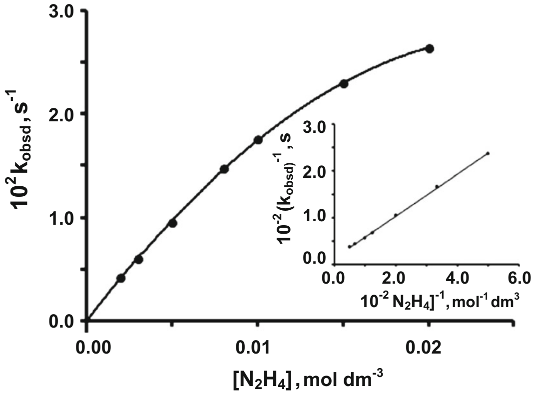


Fig. 6 Dependence of k_{obsd} on $[N_2H_4]$. A linear reciprocal plot (*inset*), consistent with saturation kinetic behavior from Eq. (11), is obtained. $[Fe^{III}(bipy)_3^{3+}] = 0.0003$ M; $\mu(NaCl) = 1.0$ M; free $[H^+] = 0.0692$ M; $T = 25.0 \pm 0.1$ °C

$$Fe^{III}(bipy)_3^{3+} + N_2H_4^{3+} \overset{K_{ass}}{\rightleftharpoons} [Fe^{III}(bipy)_3 \cdot N_2H_4]^{3+} \tag{8}$$

$$[Fe^{III}(bipy)_3{\cdot}N_2H_4] \xrightarrow{k_2} Fe^{II}(bipy)_3^{2+} + N_2H_4^{\bullet+} \tag{9}$$

The radical cation intermediate, $N_2H_4^{\bullet+}$, has previously been proposed as an intermediate in the oxidation of hydrazine in several studies, and its detection has been described [7, 10, 11].

The saturation rate dependence at constant $[H^+]$ from Eqs. (8) and (9) can be derived as [29]:

$$k_{obsd} = k_2K_{ass}[N_2H_4]/(1 + K_{ass}[N_2H_4]) \tag{10}$$

The reciprocal equation,

$$\frac{1}{k_{obsd}} = \frac{1}{k_2K_{ass}} \cdot \frac{1}{[N_2H_4]} + \frac{1}{k_2} \tag{11}$$

implies that a plot of ($1/k_{obsd}$ vs. $1/[N_2H_4]$) should be linear with slope = $1/k_2K_{ass}$ and y-intercept = $1/k_2$. This dependence between k_{obsd}^{-1} and $[N_2H_4]^{-1}$ was observed (inset Fig. 6), and a nonlinear least squares fit of the variation data of $[N_2H_4]$ (Table 3) to Eq. (10) yielded $K_{ass} = 38 \pm 4$ M^{-1} and the redox step rate constant, $k_2 = 0.046 \pm 0.004$ s^{-1}. The initial slope in the curve of Fig. 6 is $k_2K_{ass} = 1.8 \pm 0.2$ $M^{-1}s^{-1}$. In terms of N_2H_4 oxidation with $Fe^{III}(phen)_3^{3+}$, the redox rate constant was found to be $k_2 = 0.041 \pm 0.001$ s^{-1}, and the value of K_{ass} was 55 ± 6 $M^{-1}s^{-1}$ [9].

Results in Table 3 (entries 8–15) indicate a decrease in reaction rate with an increase in hydrogen ion concentration. This indicates that a protonated hydrazine species should be involved in the reaction mechanism. Two protonated hydrazine species are known (Eqs. 12, 13).

$$N_2H_6{}^{2+} \overset{K_{a1}}{\rightleftharpoons} N_2H_5{}^+ + H^+ \tag{12}$$

$$N_2H_5{}^+ \overset{K_{a2}}{\rightleftharpoons} N_2H_4 + H^+ \tag{13}$$

Hydrazine is a weak base, and $N_2H_5^+$ has a pK_{a2} of 7.89 [12, 30–32]. The lowest experimental $[H^+]$ used, 0.0088 M (Table 3, entry 8), is high enough that N_2H_4 as reactive species is not possible under the conditions used, as 99.9 % of the added hydrazine in the reaction mixture will be present as the hydrazinium ion, $N_2H_5^+$. This means that Eq. (13) will not have a noticeable effect on the redox reaction rate under the experimental conditions reported in Table 3. With respect to Eq. (12), several K_{a1} values for $N_2H_6^{2+}$ have been reported [12, 30], but the value of $K_{a1} = 0.57$ M reported by Zhongjiang and Margerum [30] stands out as the most reliable. By applying $K_{a1} = 0.57$ M to Eq. (12), it can be calculated that ± 8 % of the added hydrazine will be present as $N_2H_6^{2+}$ and ± 92 % will be $N_2H_5^+$ at $[H^+] = 0.0088$, the lowest $[H^+]$ used. The decrease in the reaction rate with increase in $[H^+]$ suggests that $N_2H_6^{2+}$ is less reactive in the reduction of $Fe^{III}(bipy)_3^{3+}$ than the $N_2H_5^+$ species.

From Eq (12), two hydrazine species can therefore be involved in the reduction of $Fe^{III}(bipy)_3^{3+}$ as per Eqs. (14) and (15).

$$\begin{tikzcd}
N_2H_6{}^{2+} + Fe^{III}(bipy)_3{}^{3+} \arrow[r, "k_1"] \arrow[d, shift left, "K_{a1}"] & Fe^{II}(bipy)_3{}^{2+} + N_2H_4{}^{\bullet+} + 2H^+ \\
N_2H_5{}^{+} + Fe^{III}(bipy)_3{}^{3+} \arrow[r, "k_2"] \arrow[u, shift left] & Fe^{II}(bipy)_3{}^{2+} + N_2H_4{}^{\bullet+} + H^+
\end{tikzcd} \tag{14, 15}$$

A nonlinear least squares fit of the kinetic data for the variation of $[H^+]$ in the reaction mixture (Table 3; Fig. 7) to Eq. (7) [28] yielded $k_1 = (8 \pm 2) \times 10^{-4}$ s^{-1},

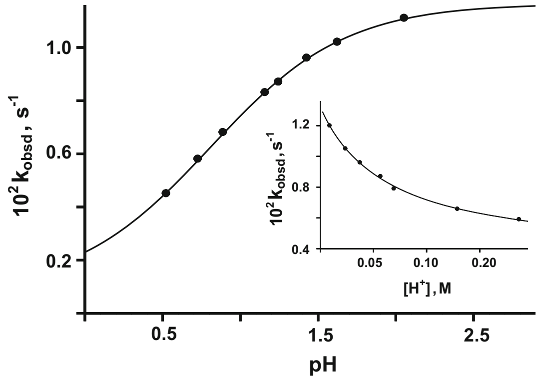


Fig. 7 Relationship between k_{obsd} and pH and in the *inset*, $[H^+]$, for the reduction of $Fe^{III}(bipy)_3^{3+}$ by N_2H_4. $[Fe^{III}(bipy)_3^{3+}] = 0.0003$ M; $[N_2H_4] = 0.005$ M; $\mu(NaCl) = 1.0$ M; $T = 25.0 \pm 0.1$ °C. For the calculation of free $[H^+]$, see "Experimental" section

$k_2 = (1.17 \pm 0.01) \times 10^{-2}$ s^{-1} and a kinetically determined equilibrium constant, $K_{a1} = 0.16 \pm 0.01$ M^{-1} (p$K_{a1} = 0.80$) at $\mu = 1.0$ M (NaCl) for equilibrium 12. This acid dissociation constant is in the same order of magnitude as the literature value previously reported by Margerum and co-workers ($K_{a1} = 0.57 \pm 0.05$ M, p$K_a = 0.24$ [30]) and is also mutually consistent with the value obtained during the oxidation of hydrazine by $Fe^{III}(phen)_3^{3+}$ ($K_{a1} = 0.42 \pm 0.05$ M, p$K_a = 0.38$ [9]). The value obtained for $k_{HA} = (8 \pm 2) \times 10^{-4}$ s^{-1} could be considered as zero within an error of 4σ(I).

Due to the decomposition of $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ in solution, the stoichiometry of the hydrazine-induced reduction of $Fe^{III}(bipy)_3^{3+}$ could not be determined volumetrically. Stanbury [12], however, reported that N_2(g) is the sole nitrogen product of the oxidation of hydrazine by an inert one-electron oxidant. This was confirmed in the kinetic study of the oxidation of hydrazine by $Fe^{III}(phen)_3^{3+}$ [9], where the formation of N_2(g) was confirmed by mass spectrometry.

In this study, utilizing reagent concentrations substantially larger than that for the kinetic experiments, gas bubbles have also been observed forming in the reaction mixtures for the reduction of $Fe^{III}(bipy)_3^{3+}$ with hydrazine. Since $Fe^{III}(bipy)_3^{3+}$, like $Fe^{III}(phen)_3^{3+}$, is also a one-electron oxidant and together with Stanbury's observation [12], it is reasonable to assume that the observed gas bubbles are N_2 gas. N_2(g) as the sole nitrogen reaction product necessitates the following hydrazine redox half-reaction:

$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^- [12, 29] \quad (16)$$

This indicates a consumption rate of 4 mol $Fe^{III}(bipy)_3^{3+}$ for 1 mol N_2H_4. The overall reaction to satisfy such a stoichiometry is

$$4Fe^{III}(bipy)_3^{3+} + N_2H_4 \rightarrow 4Fe^{II}(bipy)_3^{2+} + N_2(g) + 4H^+ \quad (17)$$

This stoichiometry implies Eq. (18), following the rate-determining step Eq. (15) (which is composed of Eqs. 8, 9), represents three consecutive one-electron transfer steps k_3, k_4 and k_5, each faster than the rate-determining step (k_2), Eq. (15), to form the product N_2(g) as explained by Stanbury [7].

$$3Fe^{III}(bipy)_3^{3+} + N_2H_4^{\bullet+} \xrightarrow[\xrightarrow{k_5}]{\xrightarrow{k_3}\;\xrightarrow{k_4}} 3Fe^{II}(bipy)_3^{2+} + N_2(g) + 4H^+ \quad (18)$$

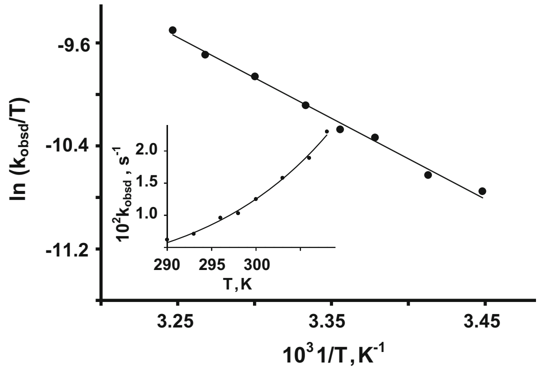


Fig. 8 Linear relationship between ln (k_{obsd}/T) and $1/T$ from the linearized Eyring equation (the *inset* is a direct fit to the Eyring equation) for the electron transfer reaction of $Fe^{III}(bipy)_3^{3+}$ and N_2H_4. Specific reaction conditions are $[Fe^{III}(bipy)_3^{3+}] = 0.0001$ M; $[N_2H_4] = 0.005$ M; free $[H^+] = 0.0692$ M; μ(NaCl) = 1.0 M

Activation parameters for the electron transfer reaction between $Fe^{III}(bipy)_3^{3+}$ and hydrazine applicable to the conditions employed in this study (Table 3) have been obtained by variation of the reaction temperature between 20 °C and 35 °C (Table 3, entries 20–27). Higher temperatures were not possible due to interference of the decomposition of $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ in solution, as it becomes too fast to ignore. The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the specific reaction conditions (Table 3) have been obtained from a nonlinear least squares fit to the linearized Eyring equation (Eq. 2; Fig. 8). This yielded an activation enthalpy, $\Delta H^{\neq} = 54 \pm 2$ kJ mol^{-1}, and an activation entropy, $\Delta S^{\neq} = -102 \pm 6$ J K^{-1} mol^{-1}. These thermodynamic parameters are associated with the fast equilibrium (Eq. 8) and the ensuing rate-determining electron transfer step (Eq. 9), in the overall reduction mechanism of the $Fe^{III}(bipy)_3^{3+}$. The smallness of $\Delta H^{\neq}$ is consistent with only one elementary rate-determining step. The negative value of $\Delta S^{\neq}$ is consistent with this reaction step involving bond formation. This is depicted in Eq. (8), which highlights the fast association between hydrazine and $Fe^{III}(bipy)_3^{3+}$ to form the intermediate transition state, $[Fe^{III}(bipy)_3 \cdot N_2H_4]^{3+}$, prior to the slow electron transfer step (Eq. 9).

The obtained thermodynamic values have been validated by the method of Lente et al. [26] utilizing Eq. (19).

$$\sigma\Delta S^{\neq} = \frac{1}{T_{av}}\sigma\Delta H^{\neq} \quad (19)$$

where $\sigma\Delta S^{\neq}$ and $\sigma\Delta H^{\neq}$ are the standard errors of the activation parameters, and T_{av} is the average temperature (in Kelvin) at which the experiments have been performed.

Conclusion

Under appropriate reaction conditions (relatively low reaction temperatures and high [H$^+$]), the reduction of $Fe^{III}(bipy)_3^{3+}$ with N_2H_4 proceeds fast enough to be independent of any influences of the decomposition of both reactant $Fe^{III}(bipy)_3^{3+}$ and product $Fe^{II}(bipy)_3^{2+}$. The kinetically determined pK_a of $N_2H_5^+$ from the reduction of $Fe^{III}(bipy)_3^{3+}$ with N_2H_4 were mutually consistent with published values. The hitherto unreported quantification of the $[H^+]$ dependence of the decomposition of $Fe^{II}(bipy)_3^{2+}$ and $Fe^{III}(bipy)_3^{3+}$ allowed for the unique determination of all rate constants in the decomposition mechanism. The huge change in the N-binding sphere from $N_2H_5^+$ to $N_2(g)$ in the chemical reduction of $Fe^{III}(bipy)_3^{3+}$ with hydrazine, the slowness of the electron transfer rate ($t_{1/2} = 157$ s if free $[H^+] = 0.0273$ M and $[N_2H_4] = 0.002$ M, entry 1 Table 3) and the formation of a bridged intermediate, $[Fe^{III}(bipy)_3{\cdot}N_2H_5]^{4+}$, are consistent with an inner-sphere electron transfer reaction mechanism [33]. In support of this, the negative $\Delta S^{\neq}$ (-102 ± 6 J K^{-1} mol^{-1}) is consistent with the electron transfer process favouring bond formation (association of reactants) and is thus also indicative of an inner-sphere redox process [34].

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