Catalytic Effect of 1,4-Dioxane on the Kinetics of the Oxidation of Iodide by Dicyanobis(bipyridine)iron(III) in Water

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Abstract: Dye-sensitized solar cells (DSSCs) are a technically and financially viable alternative to today’s photovoltaic systems using p-n junctions. The two functions are isolated here, which are unlike traditional systems where the semiconductor is thought to perform both light absorption and charge carrier transport. This article discusses the potential use of dicyanobis(bipyridine)iron(III) to oxidize iodide as a sensitizer in DSSCs. However, it is critical to understand the kinetics of this essential process in order to understand the mechanism of electron transport. The oxidation of iodide by dicyanobis(bipyridine)iron(III) in three reaction media was studied: water, 10% media, and 20% media, respectively. The presence of dicyanobis(bipyridine)iron(II). The reaction proceeded with an overall fractional (0.5), first order, and third order in water, 10% media, and 20% media, respectively. The reaction was carried out in a regular laboratory setting, with no special sensitive conditions or the use of expensive materials, making it a cost-effective and practical method. Dicyanobis(bipyridine)iron(III) oxidized iodide in selected media at 0.06 M ionic strength and constant temperature. The reaction was subjected to a spectrophotometric analysis. The data were acquired by measuring the rise in visible absorbance as a function of time after the formation of dicyanobis(bipyridine)iron(II). The reaction proceeded with an overall fractional (0.5), first order, and third order in water, 10% media, and 20% media, respectively. The presence of dicyanobis(bipyridine)iron(III) in either of the reaction media had no effect on the rate. The effect of protons (H+) on the rate constant indicated resistance in water and catalysis in dioxane-water media containing 10–20% dioxane. When the reaction to its maximum, this study discovered the binary solvent media with the highest catalytic efficiency, i.e., 20% v/v 1,4-dioxane-water, which may increase the efficiency of DSSCs without using any expensive material or unusual experimental conditions.

Keywords: photosensitive; sensitizer; 1,4-dioxane-water; dicyanobis(bipyridine)iron(III); oxidation; iodide
1. Introduction

Energy researchers are focusing their efforts on energy harvesting from a range of sources since the ever-increasing human population needs the usage of energy in numerous ways. Fossil fuels and other nonrenewable energy sources are dwindling and will not be replenished in our lifetimes. Carbon-based fossil fuels such as coal, petroleum, and natural gas are nonrenewable energy sources, and they release greenhouse gases (such as carbon dioxide) that cause global warming, posing a severe threat to the earth and humanity. As a result, scientists’ primary attention is on renewable energy-based energy conversion technologies. Solar, wind, hydroelectric, biomass, and geothermal energy are some of the renewable energy resources that our planet has to offer. Solar energy is a significant source of renewable energy that is available 24 h a day, 365 days a year, and it is virtually unlimited in nature. Sunlight-derived radiation can produce heat and light as well as drive photochemical reactions and generate electricity in the case of solar energy. As electricity becomes humanity’s first and the most basic necessity, this amazing energy source may be exploited to convert solar energy to electrical energy, utilizing solar cell technology. Unfortunately, even though solar energy is free, the high costs of conversion and storage limit the technology’s accessibility. As a result of their relatively low cost, easy preparation technique, low toxicity, and ease of processing, dye-sensitized solar cells (DSSCs) have been the subject of extensive research [1–10]. Despite this, due to their high cost, scarcity, and lack of long-term stability, the present DSSC materials have a lot of room for replacement. Existing DSSCs have an efficiency of up to 12% when employing Ru(II) dyes and improving material and structural features, but this is still less than the 20–30% efficiency of solar cells from the first and second generations, such as thin-film solar cells and Si-based solar cells [2,3,9].

The emerging advances and basic concepts for DSSCs must be understood in order to achieve higher solar-to-electricity performance and increase long-term operating stability [4]. DSSCs are built on a semiconductor that is engineered with titanium dioxide (TiO$_2$) nanoparticles coated with a light-sensitive dye. On the surface of TiO$_2$, a metal complex or a dye molecule absorbs the incident photon and acts as a photosensitizer. The excited electrons are subsequently pushed into the TiO$_2$ electrode (conduction band), causing the photosensitizer to be oxidized. The injected electrons in TiO$_2$’s conduction band diffuse between TiO$_2$ nanoparticles, eventually reaching the counter electrode via the circuit. The ground state is regenerated when the oxidized photosensitizer accepts electrons from the mediator or the electrolyte. DSSCs break the two functionalities offered by silicon in a traditional cell architecture. This energy can be stored and used to power electrical device loads. They can generate electricity in low-light environments, such as those found in homes [3]. The cell has colors and transparency due to the structural nature and various color dyes. As a result, DSSCs are applicable to architecture, interior design, mobile devices, and portable power systems [1]. These solar cells outperform their counterparts in a variety of applications, including low-density applications and portable devices [1,8,11,12].

The three subsystems that make the DSSC work are the photoanode with an adsorbed sensitizer such as TiO$_2$ with dye, the electrolyte that functions as an electron mediator, and the catalytic counter electrode. These three subsystems must be improved in order for the DSSC to become more efficient. A cell consisting of a TiO$_2$ electrode, sensitizer/dye, a liquid electrolyte (LiI/0.5 M, I$_2$/0.05 M, and 0.2 M TBP in acetonitrile or 3-methoxypropionitrile), a platinized counter electrode, and polymer-based sealing has been used to achieve a reasonable solar energy conversion efficiency [13–15]. Different advancements were made in the scientific community, and various materials, including photoanode nanomaterials, were synthesized and employed to improve the efficiency of DSSCs. Silver nanoparticles infused titanium dioxide film [16], graphene-based and TiO$_2$–CeO$_2$ photoanodes [17,18], ZnO/TiO$_2$ composite film [19], and Li-ZnO nanoparticles at SnO$_2$ nanocomposite photoanode [20] are some of the recent advances in this field. Meanwhile, there has been a lot of effort put into improving the efficiency of the counter electrode (CE) by using new material(s), nanomaterial(s), and nanocomposite(s) as the counter electrode, or by
using external catalysts for the counter electrode. Counter electrodes made of carbon materials [21], NiO with PEDOT:PSS [22], PdNiCo and PdNiCo-rGO [23], MoS$_2$/PEDOT composite [24], graphite nanoball, graphite nanosheet, and graphite nanofiber as catalytic films on CE [25], platinum with multiwall carbon nanotubes (MWCNT) as a catalytic layer for the reduction of I$_3^-$ [26], and cobalt selenide/graphene composite as the electrocatalyst for CE with a cobalt-based electrolyte [27] were studied.

The production of new dyes and electron mediators, as well as a better understanding of their interactions and the interfacial electron transfer kinetics is critical for future advancement in this field and is currently the focus of the DSSCs community’s scientific efforts [6–8,10,28–36]. In terms of kinetics, efficient cell performance is attained when electron transfer events happen quickly. When choosing materials for DSSCs, a balance between thermodynamics and kinetics must be achieved. Natural dyes [37], zinc porphyrin dye, and Co(II/III)tris(bipyridine)-based redox electrolyte [38], co-sensitization of two metal-free organic dyes and Co(II/III)tris(phenanthroline)-based redox electrolyte [39], Fe(II)-bis(terpyridine) and its cyclometalated analogues [40], Ru(NCS)$_2$ LL$'$, in which L refers to 4,4$'$-dinonyl-2,2$'$-bipyridine and L$'$ stands for 4,4$'$-di(m-X-benzoic acid)-2,2$'$-bipyridine (X = H (RC-73), F (RC-76)) [41], and [Cd$_3$(IBA)$_3$(Cl)$_2$(HCOO)(H$_2$O)]$_n$ as co-sensitizers in N719 sensitized solar cells [42] are some improvements.

One of the most important components in dye-sensitized solar cell devices is the redox mediator, which is also known as a redox shuttle or electrolyte and the solvent used for electrolyte i.e., electrolyte solvent. The efficiency of DSSCs has been determined using a variety of electrolyte solvents, and it has been found that the solvent or medium has a significant impact on the efficiency. A non-nitrile solvent, acetylacetone [43], mixed solvent of tetrahydrofuran (THF) and acetonitrile [44], water and mixture of acetonitrile and ethylene glycol [45], ionic liquids [46], gel-type electrolyte with ionic liquid and liquid-type electrolyte [47], 30 vol% NMP with 70 vol% GBL and 30 vol% NMP with 70 vol% GBL + 0.4 M pyridine [48], sugar-based natural deep eutectic solvents (NADESs) and NADES as a fully natural and bio-renewable dye-sensitized solar cell medium [49] and 1:1 wt% ethylene carbonate (EC) and propylene carbonate (PC) containing iodide/triiodide redox electrolyte [50] have been used.

Despite the fact that the I$^-$/I$_3^-$ redox couple has dominated in recent decades, the volatile nature of the material, complementary absorption with a sensitizer, and the lack of open-circuit potential limit module manufacturing. Metal complexes with changeable oxidation states are viable alternate possibilities as redox shuttles because of the variation in their redox potentials with varied ligands to accommodate diverse sensitizers. In DSSC, polypyridyl liganded Co(III)/(II) redox couples have been widely used, with a system efficiency of 14% [35,51]. Consequently, the transition metal complexes of Fe(III)/(II) with polypyridyl ligands may have the potential to increase the performance of the DSSC if used as a sensitizer to oxidize iodide [13,36,52–65].

Low cost and volatility, non-flammability, and increased environmental compatibility could all be achieved with DSSCs made with water-based electrolytes. If the original goal of DSSCs was to build an artificial photosynthetic system that could convert solar light into power, the inclusion of water as a crucial component could be a huge step ahead in terms of market adoption [66]. In this study, dicyanobis(bipyridine)iron(III) oxidizes iodide in water and dioxane–water media. The kinetics of the reaction was studied to surface the catalytic efficacy of the binary solvent media. Dioxane is entirely miscible with water and is resistant to oxidation by oxidants present throughout the reaction, such as the reactant Fe(III) complex and the products iodine or triiodide. Dicyanobis(bipyridine)iron(III) is an excellent option for use as a sensitizer in DSSCs because of its photosensitive nature. This is a cost-effective and environmentally friendly reaction because it uses readily available reagents such as potassium iodide, potassium nitrate, and 1,4-dioxane, as well as a low-cost transition metal complex of non-harmful Fe(III)/(II) with potential for stability and efficiency improvement of DSSC without the use of costly materials.
2. Results and Discussion

2.1. Kinetic Parameters of Uncatalyzed Reaction in Water

2.1.1. Overall Order of Reaction and the Overall Rate Constant of Uncatalyzed Reaction

The oxidation of iodide by dicyanobis(bipyridine)iron(III) was studied in water. The kinetic parameters such as order of reaction with respect to the reactants and the overall rate constant were determined at 0.06 M ionic strength. The ionic strength was maintained by potassium nitrate (KNO$_3$). The concentration of dicyanobis(bipyridine)iron(III) nitrate was constant at 0.08 mM and that of potassium iodide varied between 0.08 and 4 mM at 293 ± 0.5 K. Linear rate equations of the integration method of various orders as derived and published earlier [36] were implemented on the acquired data to identify the order of reaction with respect to dicyanobis(bipyridine)iron(III). As a result of the most acceptable linear fit R-squared value above other orders, the reaction was observed to undergo the zero order with respect to the concentration of the oxidant; dicyanobis(bipyridine)iron(III) (Equation (1), Figure 1).

$$[A]_t = [A]_0 + \varepsilon \cdot b \cdot k_{obs} \cdot t$$  \hspace{1cm} (1)

The terms $A$, $\varepsilon$, $b$, $k_{obs}$, and $t$ carry usual meanings such as absorbance at time point “$t$” and “0”, molar absorptivity, pathlength of cuvette (1 cm), observed zero-order rate constant, and time in seconds. Here, “$\varepsilon$” corresponds to the value of the molar absorptivity of the product i.e., dicyanobis(bipyridine)iron(II) that was used to monitor the increase in absorbance as a course of time to interpret the kinetics of the reaction. We observed the absorbance at ≥zero time scale, which may be because of the formation of the transition state complex. In the 1 s time scale, the absorbance climbed and then fell quickly, and then, it progressively increased with respect to time until the reaction was completed (Figure 2a,b). The slope of the plot with dimension (s$^{-1}$) is $\varepsilon \cdot b$ (M$^{-1}$ cm$^{-1}$ cm) times bigger than $k_{obs}$ (M s$^{-1}$), with $\varepsilon \cdot b$ having no significant influence on $k_{obs}$ other than the addition of a constant value. Rather than generating a distinct value of $k_{obs}$ by first computing the concentration of dicyanobis(bipyridine)iron(III) and then plotting it against time, we used the entire figure of $\varepsilon \cdot b \cdot k_{obs}$ (s$^{-1}$) by drawing a linear plot between absorbance at time points $t$ versus time scale.
Figure 1. Linear rate equation of integration method for zero-order reaction at 3.2 mM iodide.

\[
y = 1.68 \times 10^{-3}x + 0.0364
\]
\[R^2 = 0.993\]

\[
y = 1.62 \times 10^{-3}x + 0.0564
\]
\[R^2 = 0.992\]

\[
y = 1.62 \times 10^{-3}x + 0.0594
\]
\[R^2 = 0.9950\]

Figure 2. (a) Representative time course graphs at varying concentration of iodide in water. (b) Representative time course graphs at varying ionic strength in 10% (v/v) 1,4-dioxane-water.

The order of reaction with respect to the reductant, i.e., iodide was identified by determining the value of the slope \(e \cdot b \cdot k_{obs}\) at a fixed 0.08 mM oxidant and varying the concentration of iodide ion within the range between 1 and 50 times over the oxidant. The plot between the concentration of iodide ion on the x-coordinate and \(e \cdot b \cdot k_{obs}\) on the y-coordinate yields an increasing curvature that indicates that the reaction does not follow zero and first order with respect to the reductant (Figure 3a). If it would have been zero order with respect to the iodide, then all the values of \(e \cdot b \cdot k_{obs}\) should have been constant at different concentration of iodide. Similarly, if the order of reaction is supposed to be first, then a linear fit with an acceptable \(R^2\) value should have been obtained, passing through the origin of the plot. We did not observe any such result (Figure 3a). When we implemented fractional (0.5) and second-order models, we obtained curves passing through the origin, respectively (blue curves in Figure 3b,c). The reaction was fractional (0.5) order in iodide (red linear fit, Figure 3b) between 1 and 30 times its concentration ratio over the oxidant i.e., dicyanobis(bipyridine)iron(III), while from 30 to 50 times its concentration ratio over the oxidant, the reaction underwent second order with respect to the iodide (red linear fit, Figure 3c). In both cases, the linear fit passes...
through the origin and yields a very promising value of $R^2$, which confirms that the reaction follows complex kinetics corresponding to the excess concentration of iodide over dicyanobis(bipyridine)iron(III). Consequently, the oxidation of iodide follows an overall fractional (0.5) order in water within the concentration range from 0.08 to 2.4 mM of iodide at constant 0.08 mM of dicyanobis(bipyridine)iron(III) that oxidized iodide. Meanwhile, the redox reaction follows an overall second order at 30–50 times excess concentration of iodide over a fixed 0.08 mM concentration of dicyanobis(bipyridine)iron(III). In both phases of the reaction, the rate of the oxidation of iodide was observed independent of concentration of dicyanobis(bipyridine)iron(III) in water that yielded zero order in oxidant. The overall fractional (0.5) order rate constant ($c-b-k$) and overall second-order rate constant ($c-b-k'$) were determined from the slope of the plots as $2.11 \times 10^{-2} \text{ M}^{-0.5} \text{ s}^{-1}$ and $1.68 \times 10^{2} \text{ M}^{-2} \text{ s}^{-1}$, respectively. The conventional dimensions of the fractional (0.5) and second-order rate constants are $\text{M}^{0.5} \text{ s}^{-1}$ and $\text{M}^{-1} \text{ s}^{-1}$, respectively. However, in our case, the dimensions are different because of the multiplication of $c-b$ to the fractional and second-order rate constants according the resulting Equations (19) and (20) obtained by Equations (2)–(18).

Conventionally, we assume the rate of any reaction at the beginning of the study considering the reactants and products of the reaction as follows.

$$2 \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2 \right]^+ + 2I^- \rightarrow 2 \left[ \text{Fe}^{\text{II}}(\text{bpy})_2(\text{CN})_2 \right] + I_2$$

(2)

$$\text{Rate} = k \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right] [I^-]$$

(3)

At pseudo-first order condition such as $[I^-] >> > > \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]$

$$\text{Rate} = k_{\text{obs}} \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]$$

(4)

The rate in Equation (4) can also be written in terms of the formation of dicyanobis(bipyridine)iron(II). There is a 1:1 ratio of electron acceptance between the redox couple as follows.

$$\left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2 \right]^+ + \tau \leftrightarrow \left[ \text{Fe}^{\text{II}}(\text{bpy})_2(\text{CN})_2 \right]$$

(5)

The molar concentration of the reduction or consumption of dicyanobis(bipyridine)iron(III) yields the same molar concentration of the product i.e., dicyanobis(bipyridine)iron(II). Consequently, the concentration ratio between dicyanobis(bipyridine)iron(III)/(II) is equal. However, Equation (4) can be rearranged into Equation (7).

$$\frac{d \left[ \text{Fe}^{\text{II}}(\text{bpy})_2(\text{CN})_2 \right]}{dt} = k_{\text{obs}} \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]$$

(6)

$$\frac{d \left[ \text{Fe}^{\text{II}}(\text{bpy})_2(\text{CN})_2 \right]}{ \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]} = k_{\text{obs}} \text{dt}$$

(7)

If absorbance is monitored as a time course graph rather than concentration, Equations (8)–(10) are produced as the consequent equations after integration, solution, and application of the Beer-Lambert law. If the change in concentration is observed over time, Equation (8) shows the rate of reaction in terms of molar concentration ($[\text{Fe}^{\text{II}}(\text{bpy})_2(\text{CN})_2]$), and Equations (9) and (10) show the rate in terms of rise in absorbance ($A$) over time.

$$\ln \left[ \frac{\left[ \text{Fe}^{\text{II}}(\text{bpy})_2(\text{CN})_2 \right]}{[\text{A}]_0} \right] = k_{\text{obs}} t$$

(8)

$$\ln \left[ \frac{[A]_t}{[A]_0} \right] = k_{\text{obs}} t$$

(9)
\[
\ln[A]_t = \ln[A]_0 + k_{obs} \cdot t \tag{10}
\]

Equations (8)–(10) are the typical integrated rate equations of linear regression for first-order reaction under pseudo-first-order condition. These equations help to identify the order of reaction with respect to the reactant that is maintained at low concentration where \( k_{obs} \) is the observed pseudo-first-order rate constant with dimension \( \text{s}^{-1} \). Then, the value of \( k_{obs} \) is used to identify the order of reaction with respect to the other reactant that was maintained at excess concentration during the implementation of the pseudo-first-order condition. For a typical first-order reaction, Equation (11) is used in such circumstances.

\[
k_{obs} = k [I^-] \tag{11}
\]

**Figure 3.** Cont.
The linear Equation (11) is used to get the value of the overall rate constant \((k)\), which is the reaction’s second-order rate constant. When plotted between \(k_{\text{obs}}\) and the molar concentration of iodide on y and x coordinates, the linear line should pass through the origin and provide a slope with dimensions M\(^{-1}\) s\(^{-1}\). Similarly, for iodide oxidation in this study, zero, fractional, and second orders were identified with respect to dicyano(bpyridine)iron(III), iodide at moderate concentration, and iodide at quite high concentration, using Equations (1), (12) and (13).

- **At moderate concentration of iodide:**

  \[
  \text{Rate} = k \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]^0 [\text{I}^-]^{0.5}.
  \]  
  \hspace{1cm} (12)

- **At fairly high concentration of iodide:**

  \[
  \text{Rate} = k t \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]^0 [\text{I}^-]^2.
  \]  
  \hspace{1cm} (13)

Equations (18)–(20) are obtained by applying the pseudo-first-order condition i.e., \([\text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+] << [\text{I}^-]\), integration, the Beer-Lambert law, and then solving Equations (12) and (13).

\[
\frac{d}{dt} \left[ \text{Fe}^{\text{II}}(\text{bpy})_2(\text{CN})_2 \right] = k \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]^0 [\text{I}^-]^{0.5}
\]  
(14)

\[
\frac{d}{dt} \left[ \text{Fe}^{\text{II}}(\text{bpy})_2(\text{CN})_2 \right] = k \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]^0 [\text{I}^-]^2
\]  
(15)

Since \( \left[ \text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2^+ \right]^0 = 1 \)
\[
\frac{d\left[\text{Fe}^\text{II}(\text{bpy})_2(\text{CN})_2\right]}{dt} = k_{\text{obs}}
\]
(16)

\[
\left[\text{Fe}^\text{II}(\text{bpy})_2(\text{CN})_2\right] = \left[\text{Fe}^\text{II}(\text{bpy})_2(\text{CN})_2\right]_0 + k_{\text{obs}} \cdot t
\]
(17)

In terms of increase in absorbance upon the formation of dicyanobis(bipyridine)iron(II), Equation (17) becomes Equation (18).

\[
\frac{1}{\varepsilon \cdot b} \cdot (\left[A\right]_t - \left[A\right]_0) = k_{\text{obs}} \cdot t
\]
(18)

Equations (1) and (18) are equivalent if \(\varepsilon \cdot b\) in the denominator and the negative value of \([A]_0\) on the left-hand side of Equation (18) are rearranged to the numerator and positive value of \([A]_0\) on the right-hand side. This rearrangement yields Equation (1), which we used to determine the value of \(\varepsilon \cdot b \cdot k_{\text{obs}}\) in \(\text{s}^{-1}\) at different concentrations of iodide in water. The values of the slope \(\varepsilon \cdot b \cdot k_{\text{obs}}\) at different and excess concentrations of iodide were plotted against the molar concentration of iodide to obtain a linear plot passing through the origin. The linear fit of the plot helped to identify the order of reaction with respect to the iodide ion at moderate and high concentration range, and the slope yielded the overall rate constant of the reaction according to Equations (19) and (20).

\[
\varepsilon \cdot b \cdot k_{\text{obs}} = \varepsilon \cdot b \cdot k \cdot [\text{I}^-]^{0.5}
\]
(19)

\[
\varepsilon \cdot b \cdot k_{\text{obs}} = \varepsilon \cdot b \cdot k \cdot [\text{I}^-]^2
\]
(20)

2.1.2. Active Reactants of the Rate-Determining Step of Uncatalyzed Reaction

Iodide is very well known to produce triiodide ion, protonated iodide, and protonated triiodide molecules. However, dicyanobis(bipyridine)iron(III) is a substitution inert outer-sphere oxidant that does not produce any other corresponding species, including its protonation, which is impossible under the experimental conditions we employed herein this study. The following equilibria may exist in the reaction vessel (Equations (21)–(23)).

\[
\text{I}^- + \text{I}_2 \rightleftharpoons \frac{K_1}{K_2} \text{I}_3^-
\]
(21)

\[
\text{H}^+ + \text{I}^- \rightleftharpoons \frac{K_1}{K_2} \text{HI}
\]
(22)

\[
\text{H}^+ + \text{I}_3^- \rightleftharpoons \frac{K_1}{K_2} \text{HI}_3
\]
(23)

To identify the active reactant among iodide, triiodide, protonated iodide, and protonated triiodide, the effect of variation in the concentration of protons was studied on the observed zero-order rate constant. The equilibrium between iodide and protonated iodide may hardly be possible because the dissociation constant of HI is very high. In order to rectify our results, the kinetics of the reaction was probed at increasing concentrations of nitric acid (HNO\textsubscript{3}) within the range from neutral pH (i.e., without the addition of nitric acid) to 0.1 M nitric acid. The experimental conditions such as the concentration of oxidant (0.08 mM) and reductant (0.8 mM) were constant at 0.11 M ionic strength and 290 ± 0.5 K to draw the results of the effect of protons on the rate constant. The ionic strength was maintained by potassium nitrate (KNO\textsubscript{3}). The value of \(\varepsilon \cdot b \cdot k_{\text{obs}}\) declined gradually as the concentration of protons increased up to 0.01 M H\textsuperscript{+} (HNO\textsubscript{3}); then, it increased at 0.1 M H\textsuperscript{+} (HNO\textsubscript{3}). The results show that the unprotonated iodide or triiodide ion controls the slow-step of the reaction by donating an electron to dicyanobis(bipyrididine)iron(III) (Figure 4a). Therefore, the protonation of these species reduced their concentration in the vicinity and reduced the value of the rate constant, consequently. Here, it is worthwhile to consider that the dissociation constant of HI is known to be fairly high. If iodide is expected to be the active reactant among iodide and triiodide ions that leads the slow-step of the reaction, then increasing the concentration of protons (H\textsuperscript{+}) in the reaction mixture to 0.1 M HNO\textsubscript{3}...
should have reduced the rate of reaction and/or the rate constant. Since the concentration of protons increases, the equilibrium (22) moves forward, motivating the protonation of iodide to form HI, which should result in a drop in the concentration of rate-controlling iodide and, as a result, a fall in the rate constant’s value. However, our findings show that adding nitric acid to the reaction vessel lowered the rate of the reaction to some extent, and adding excess nitric acid (0.1 M) increased it. The findings pinpoint the active species in the rate-determining step of iodide oxidation by dicyanobis(bipyridine)iron(III) in water as triiodide (I$_3^-$) ion (Equations (24) and (25)) rather than iodide. Iodide was oxidized by dicyanobis(bipyridine)iron(III) in the fast-step of the reaction (Equation (2)), which resulted in iodine that interacted with iodide in the vicinity to create triiodide ions (Equation (21)). These triiodide ions were involved in the reaction’s rate-determining step. Since HI$_3$ is a weak acid in comparison to HI, the equilibrium (23) is expected to have a low dissociation constant. At 0.01 M H$^+$ ions, the reaction (Equation (23)) maintained equilibrium, and further protonated triiodide production appeared to be halted. As a result, additional protons did not diminish the concentration of maximum accessible triiodide ion in the reaction vessel; rather, interionic repulsive forces between the same charge carriers, such as cations, supported the interaction between triiodide ion and dicyanobis(bipyridine)iron(III) in the slow-step of the reaction (Equations (24) and (25)). Using NOx as an oxidant, the oxidation of triiodide ion has previously been described [67]. The oxidation of iodide and triiodide occurs when the concentration of HNO$_3$ exceeds 1 N, according to the same study and yields iodine as the product of the reaction (Equation (24)).

$$2I^- \rightarrow 3I_2 + 2e$$ (24)

$$2[Fe^{III}(bpy)_2(CN)_2]^+ + 2I^- + 2e \rightarrow 2[Fe^{II}(bpy)_2(CN)_2] + 3I_2 + 2e$$ (25)

A straight line was drawn by plotting the reciprocal of rate constant ($\epsilon \cdot b \cdot k_{obs}$) on the $y$-axis against the fractional (0.25) power of protons concentration ($1 \times 10^{-7}$–0.01 M) on the $x$-axis (Figure 4b). The slope of the figure is equivalent to the value of the proton-dependent inverse fractional order rate constant ($2.59 \times 10^3$ M$^{-0.25}$ s), whereas the intercept displays the reciprocal of the proton-independent observed rate constant. The findings confirmed triiodide as the active species in the rate-limiting stage of the redox process.

For further rectification of the results, the effect of ionic strength on the observed zero-order rate constant was studied. Equation (26) is the formulation of the transition state theory of reactions in solution that correlates the rate constant with the ionic strength.

$$\text{log } k = \text{log } k_0 + 1.02z_Az_B\sqrt{\mu}$$ (26)

The intercept of the plot determines the value of the rate constant at zero ionic strength according to Equation (26). This is a theoretical value that illustrates the effect of the dielectric constant or medium of the reaction on the rate constant, excluding the effect of existing ions in the vicinity. The slope of the plot helps to identify the active participants of the reaction that form the transition state complex while the reaction medium is water. Here, 1.02 is a constant value for water at 25 °C and $z_Az_B$ are the charges on the reactants that form the transition state complex. From the value of the slope of the plot, we can determine the interaction between the ions or molecules that lead the reaction mechanism. While the reactants carry opposite electrical charges, we should have obtained a negative value of the slope with a corresponding multiplication product of the charges on the reactants $z_Az_B$ as the magnitude of the slope in water. When the similar charge carriers form the transition state complex and lead the reaction mechanism, the positive value of the slope should have been obtained with the corresponding magnitude of the multiplication product of the electrical charges. However, the transition state complex formation between ion-molecule and or molecule-molecule yields a zero value of the slope with no effect of ionic strength on the rate constant.
protons did not diminish the concentration of maximum accessible triiodide ion in the reaction vessel; rather, interionic repulsive forces between the same charge carriers, such as cations, supported the interaction between triiodide ion and dicyano-bis(bipyridine)iron(III) in the slow-step of the reaction (Equations (24) and (25)). Using NO\textsubscript{x} as an oxidant, the oxidation of triiodide ion has previously been described [67]. The oxidation of iodide and triiodide occurs when the concentration of HNO\textsubscript{3} exceeds 1 N, according to the same study and yields iodine as the product of the reaction (Equation (24)).

\[
2I^- \rightarrow 3 I^+ + 2 e^- 
\]  

(24)

\[
2 \text{Fe}\textsubscript{bpy}(CN)\textsubscript{2}^+ + 2 I^- + 2 e^- \rightarrow 2 \text{Fe}\textsubscript{bpy}(CN)\textsubscript{2}^+ + 3 I^+ + 2 e^- 
\]  

(25)

A straight line was drawn by plotting the reciprocal of rate constant (ɛ \cdot b \cdot k_{obs}) on the y-axis against the fractional (0.25) power of protons concentration (1 \times 10^{-7}–0.01 M) on the x-axis (Figure 4b). The slope of the figure is equivalent to the value of the proton-dependent inverse fractional order rate constant (2.59 \times 10^3 M^{-0.25} s), whereas the intercept displays the reciprocal of the proton-independent observed rate constant. The findings confirmed triiodide as the active species in the rate-limiting stage of the redox process.

If we carefully review our results, we observe that the primary reactant i.e., iodide ion, was not involved in the rate-determining step (Equation (25)); rather, it led the fast-step of the reaction (Equation (2)). It formed triiodide ion upon reaction with iodine, and the equilibrium was established between iodide and triiodide ions (Equation (21)) in the reaction mixture. Essentially, iodine was the limiting reactant, which controlled the overall reaction mechanism by producing triiodide ion. The production of triiodide ion depended upon the concentration of iodine that was produced during the reaction and the equilibrium constant (K\textsubscript{1}). Then, the triiodide ion interacted with dicyanobis(bipyridine)iron(III) during the slow-step of the reaction. As a result, we conclude that because iodide was not involved in the rate-determining step, iodine was the reactant that formed the transition state complex with dicyanobis(bipyridine)iron(III) and subsequently led the reaction mechanism by creating triiodide ion following interaction with iodide. However, the reaction should not show any effect of variation in the ionic strength on the rate constant because of the interaction between monopositive oxidant and neutral iodine. We rearranged Equa-

![Figure 4. (a) Plot illustrating the rate constant as a function of rising proton concentration. (b) Inverse fractional (0.25) order plot with respect to proton (H\textsuperscript{+}).](image)
tion (26) to Equation (27) for the kinetic parameters of our investigation in order to confirm our findings.

$$\log(\varepsilon \cdot b \cdot k_{\text{obs}}) = \log \varepsilon \cdot b \cdot (k_{\text{obs}})_0 + 1.02z_B \sqrt{\mu}$$  \hspace{1cm} (27)

To determine the effect of ionic strength on $\varepsilon \cdot b \cdot k_{\text{obs}}$, the time course graph was obtained at different values of the ionic strength by keeping other experimental parameters constant. The concentration of oxidant and reductant were fixed at 0.08 mM and 0.8 mM, respectively. The reaction was probed at $289 \pm 0.5$ K in aqueous medium, and the ionic strength was increased from 0.005 to 0.37 M by adding potassium nitrate to the reaction mixture. The graph was plotted between the $\log_{10}(\varepsilon \cdot b \cdot k_{\text{obs}})$ (i.e., determined at each value of the ionic strength) and the square root of the value of ionic strength according to Equation (27). The results are illustrated in Figure 5. We did not observe any effect of variation in the ionic strength on the observed rate constant, which confirmed that the transition state complex was formed between monopositive dicyanobis(bipyridine)iron(III) i.e., [Fe$^\text{III}$$(\text{bpy})_2(\text{CN})_2]^+$, and neutral iodine (I$_2$).

![Figure 5. Plot of the effect of ionic strength on the observed rate constant.](image)

2.1.3. Thermodynamic Parameters of Activation

The thermodynamic parameters of activation were determined for the uncatalyzed oxidation of iodide by dicyanobis(bipyridine)iron(III) in water. The temperature was varied and the time course graph was probed at each temperature by keeping all other experimental parameters constant. The concentrations of the oxidant, reductant, and ionic strength were maintained constant at 0.08 mM, 0.8 mM, and 0.06 M, respectively. The ionic strength was preserved by adding potassium nitrate to the reaction mixture. The value of the observed zero-order rate constant ($\varepsilon \cdot b \cdot k_{\text{obs}}$) was evaluated at each temperature, and the thermodynamic parameters of activation were determined by applying Arrhenius and Eyring Equations (28), (29) and (30), respectively.

$$k = A e^{-\frac{E_a}{R T}}$$  \hspace{1cm} (28)

$$k = \frac{k k_B T}{\hbar} e^{-\frac{\Delta H^\#}{R T}} e^{\frac{\Delta S^\#}{R}}$$  \hspace{1cm} (29)

or,

$$k = \frac{k k_B T}{\hbar} e^{-\frac{\Delta H^\#}{R T}} e^{\frac{\Delta S^\#}{R}}$$  \hspace{1cm} (30)

In Equations (28)–(30), $k$, $A$, $E_a$, $R$, $T$, $k_B$, $h$, $\Delta H^\#$ and $\Delta S^\#$ have conventional meanings such as rate constant, pre-exponential factor, activation energy, universal gas constant,
Kelvin temperature, transmission coefficient (generally taken to be mathematical figure ‘1’), Boltzmann constant, Planck’s constant, enthalpy change of activation, and entropy change of activation, respectively. Equations (28) and (30) can be rearranged to linear Equations (31) and (34), respectively, to draw plots and to estimate the activation parameters. The values of b (path length of quartz cuvette) and $\varepsilon$ (molar absorptivity of [Fe$^{II}$(bpy)$_2$(CN)$_2$] in water) are 1 cm and $\approx 4388$ M$^{-1}$ cm$^{-1}$, respectively.

$$\ln(\varepsilon \cdot b \cdot k_{obs}) = \ln(\varepsilon \cdot b \cdot A) - \frac{E_a}{R \cdot T}$$  \hspace{1cm} (31)

$$\frac{\varepsilon \cdot b \cdot k_{obs}}{T} = \frac{\varepsilon \cdot b \cdot k_B}{h} e^{-\frac{\Delta H^\#}{R} e^{\frac{\Delta S^\#}{R}}}$$  \hspace{1cm} (32)

$$\ln \frac{\varepsilon \cdot b \cdot k_{obs}}{T} = \ln \frac{\varepsilon \cdot b \cdot k_B}{h} + \frac{\Delta S^\#}{R} - \frac{\Delta H^\#}{RT}$$  \hspace{1cm} (33)

$$\ln \frac{\varepsilon \cdot b \cdot k_{obs}}{T} = 32.146 + \frac{\Delta S^\#}{R} - \frac{\Delta H^\#}{R} \cdot \frac{1}{T}$$  \hspace{1cm} (34)

A plot of $\ln(\varepsilon \cdot b \cdot k_{obs})$ was drawn against $1/T$ that yielded intercept and slope with 99% linear fit ($R^2$ value 0.99), as shown in Figure 6a. The values of A (24.62 M s$^{-1}$) and $E_a$ (46.23 kJ mol$^{-1}$) were calculated from the intercept and the slope of the plot, respectively. Meanwhile, a linear plot between $\ln(\varepsilon \cdot b \cdot k_{obs}/T)$ and $1/T$ helped to calculate $\Delta S^\#$ ($-226.5$ J mol$^{-1}$ K$^{-1}$) and $\Delta H^\#$ (43.76 kJ mol$^{-1}$) from the intercept and the slope of the plot, respectively (Figure 6b). The Gibbs free energy of activation ($\Delta G^\#$) was also determined by using Equation (35) and found 111.26 kJ mol$^{-1}$ at 25 °C.

$$\Delta G^\# = \Delta H^\# - T \Delta S^\#$$  \hspace{1cm} (35)
2.2.1. Overall Order of Reaction and the Overall Rate Constant of Catalyzed Reaction

Similar to the uncatalyzed reaction, the catalyzed reaction followed zero order with respect to dicyanobis(bipyridine)iron(III) in 10–20% dioxane-water. The catalysis was observed upon the addition of 1,4-dioxane to water. The order of reaction with respect to iodide was identified to be first and third in 10% (v/v) 1,4-dioxane–water and 20% (v/v) 1,4-dioxane–water. For the uncatalyzed reaction, all the experimental parameters were maintained and/or varied in water. However, for the catalyzed reaction, the entire process, including the concentration of constant and varying experimental parameters, was identical to that of the uncatalyzed reaction, albeit in media containing 10% and 20% 1,4-dioxane–water rather than water. As a result, the experimental parameters will not be provided in the next section, and only the results or outcomes will be presented and discussed.

2.2. Kinetic Parameters of 1,4-Dioxane Catalyzed Reaction

The catalyzed reaction was monitored in the same way as the uncatalyzed reaction. Only the reaction media were different. The catalyzed reaction was studied in two reaction media: i.e., 10% (v/v) 1,4-dioxane–water and 20% (v/v) 1,4-dioxane–water. For the uncatalyzed reaction, all the experimental parameters were maintained and/or varied in water. However, for the catalyzed reaction, the entire process, including the concentration of constant and varying experimental parameters, was identical to that of the uncatalyzed reaction, albeit in media containing 10% and 20% 1,4-dioxane–water rather than water. As a result, the experimental parameters will not be provided in the next section, and only the results or outcomes will be presented and discussed.

Figure 6. (a) Arrhenius plot. (b) Eyring plot.

2.2.1. Overall Order of Reaction and the Overall Rate Constant of Catalyzed Reaction

Similar to the uncatalyzed reaction, the catalyzed reaction followed zero order with respect to dicyanobis(bipyridine)iron(III) in 10–20% dioxane–water. The catalysis was observed upon the addition of 1,4-dioxane to water. The order of reaction with respect to iodide was identified to be first and third in 10% (v/v) 1,4-dioxane–water and 20% (v/v) 1,4-dioxane–water (Figure 7b,c), respectively. The reaction is considered in its maximum rate while the rate of reaction depends upon the third power of a concentration term involved in the rate law. The third power dependence corresponds to the third-order reaction i.e., the maximum rate of a reaction. Our results show that in 10% dioxane–water, the reaction rate is overall fractional (0.5) order in water medium. The slope of the plot produces an overall first-order rate constant (ε·b·k) as 4.438 M⁻¹ s⁻¹ (Figure 7a), according to Equation (36).

\[ \varepsilon \cdot b \cdot k_{obs} = \varepsilon \cdot b \cdot k \ [\text{I}^{-}] \]  

(36)
Figure 7. (a) Plot of first order with respect to iodide in 10% v/v dioxane–water at 293 ± 0.5 K. (b) Plot of first order with respect to iodide in 20% v/v dioxane–water at 284 ± 0.5 K. (c) Third-order plot with respect to iodide in 20% v/v dioxane–water at 284 ± 0.5 K.
However, in 20% dioxane–water, where the reaction followed an overall third-order kinetics, the reaction attained its maximal rate by rapidly completing. According to the data (Figure 7c), the oxidation of iodide by dicyanobis(bipyridine)iron(III) reaches its highest rate in 20% binary solvent system, with an overall rate constant \( \varepsilon \cdot b \cdot k \) \( 2.76 \times 10^5 \text{ M}^{-3} \text{s}^{-1} \) according to Equation (37).

\[
\varepsilon \cdot b \cdot k_{\text{obs}} = \varepsilon \cdot b \cdot k [I^-]^3 
\] (37)

2.2.2. Active Reactants of the Rate-Determining Step of Catalyzed Reaction

The effect of additional protons such as nitric acid was probed on the observed zero-order rate constant by maintaining all the experimental parameters similar to the uncatalyzed reaction in 10% and 20% (v/v) 1,4-dioxane-water rather than 100% water. The results reveal that raising the concentration of protons has a catalytic effect on the rate constant in both binary solvent media (Figure 8a,c). Within the concentration range of externally injected protons (HNO\(_3\)), such as 1 mM to 0.1 M (red data in Figure 8a), the value of \( \varepsilon \cdot b \cdot k_{\text{obs}} \) grew linearly, with an increasing curvature below 1 mM in 10% binary solvent media. The linear plot yields the proton catalyzed rate constant; \( 8.99 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1} \) (slope) and the proton independent rate constant \( 2.69 \times 10^{-4} \text{ s}^{-1} \) (intercept). If we divide \( \text{M}^{-1} \text{s}^{-1} \) by the dimension of \( \varepsilon \cdot b \) (M cm\(^{-1}\)cm), the proton catalytic rate constant can be used to identify the first order in proton (H\(^+\)) throughout the range of 1 mM to 0.1 M. Meanwhile, when the externally injected protons concentration is less than 1 mM, the log–log plot of the rate constant and proton yields a straight line with a 0.076 ‘n’ value, which represents the order of reaction according to Equation (39) (Figure 8b).

\[
\varepsilon \cdot b \cdot k_{\text{obs}} = \varepsilon \cdot b \cdot k \cdot [H^+]^n
\] (38)

\[
\log(\varepsilon \cdot b \cdot k_{\text{obs}}) = \log(\varepsilon \cdot b \cdot k) + n \log[H^+]
\] (39)

In Equations (38) and (39), \( \varepsilon \cdot b \cdot k \) is the multiplication product of \( \varepsilon \cdot b \) with the proton-independent observed zero-order rate constant. We obtained similar results in 20% binary solvent media with a straight line plot between log(\( \varepsilon \cdot b \cdot k_{\text{obs}} \)) and log([H\(^+\)]) with 0.15 ‘n’ value at below 1 mM concentration of externally injected protons (Figure 8d). However, as the concentration of protons increased above 1 mM–0.1 M, the value of the observed zero-order rate constant decreased and became constant at high concentration (Figure 8c). A detailed examination of Figure 8c reveals that the values of the rate constant at 0.01 M and 0.1 M additional proton (H\(^+\)) are nearly identical to the rate constant without any external proton/acid addition. When contrasted to water as a medium, this highlights the strong hydrogen bonding between 1,4-dioxane and water, which aids in achieving equilibrium (23) at low proton concentrations. The reactions of protons’ influence in binary solvent media of 10% and 20% helped to identify the iodide ion as the active reactant of the rate-determining step in both media. Equilibria (21)–(23) lower its concentration in the vicinity. The reaction is catalyzed by the protonation of triiodide to produce HI\(_3\), which eliminates the rate-slowing I\(_3^-\) and supports the interaction between iodide and dicyanobis(bipyridine)iron(III). Up to 0.1 M H\(^+\), a linear fit was observed in 10% binary solvent media, as previously discussed. As a result of the higher volume fraction of 1,4-dioxane to water in 20% binary solvent media, the media have strong and excess hydrogen bonding compared to 10% media. As a result, equilibrium (23) is expected to be established at a concentration of 1 mM, and an excessive addition of protons does not reduce the concentration of rate resisting I\(_3^-\), but it does delay the effective collisions between the monopositive oxidant, dicyanobis(bipyridine)iron(III), and the iodide ion. We found identical values of the observed zero-order rate constant for iodide oxidation in 20% binary solvent media without and with 0.01–0.1 M H\(^+\).
Figure 8. CONT.
For further rectification of the results, the effect of ionic strength on the observed zero-order rate constant was studied in both 10–20% binary solvent media. We proposed iodide as the reactive species that controls the rate-determining step and leads the reaction mechanism. As a result, according to the formulation of the transition state theory (Equation (40)), our results should produce a linear fit with a negative slope. For greater ionic strength values, Equation (40) is employed, where A is the Debye-Hückel constant. Its mathematical value is determined by the solvent/media’s composition and dielectric constant as well as temperature. The dielectric constant is lowered in 10–20% reaction media, and a robust hydrogen bonding network is generated. As a result, the ionic strength we utilized for the uncatalyzed reaction becomes strong in both binary solvent media, making Equation (27) ineffective. Equation (40) is used when the ionic strength is high.

\[
\log(\varepsilon \cdot b \cdot k_{\text{obs}}) = \log \varepsilon \cdot b \cdot (k_{\text{obs}})_0 + 2A\varepsilon_{\text{B}} z_{\text{B}} \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \tag{40}
\]

In both reaction media, the plot of \(\log_{10}(\varepsilon \cdot b \cdot k_{\text{obs}})\) versus \(\sqrt{\mu}/1 + \sqrt{\mu}\) produces a straight line with a negative slope value, confirming our hypothesis (Figure 9a,b).
3. Materials and Methods

3.1. Materials and Instrumentation

Without further purification, potassium iodide (Sigma-Aldrich), potassium nitrate (Sigma-Aldrich), 1,4-dioxane (Sigma-Aldrich), and nitric acid (Merck) were used as supplied. The transition metal complex (dicyano bis(bipyridine)iron(III) nitrate) was synthesized, purified, and characterized, as previously reported [30]. Deionized water was used to maintain the aqueous proportion of the media. As a result of the dioxane-water, the quartz cuvettes were used to collect absorbance versus wavelength/time data using the Vernier Go Direct™ SpectroVis plus spectrophotometer + fluorometer. The visible range is covered by the spectrophotometer. The equipment was linked to a laptop via USB, and data were recorded in spectrum/kinetic mode using the Logger Pro 3.15 program. To make 3 mL in a quartz cuvette with a 1 cm path length, disposable syringes were used to combine 1.5 mL of each reactant, such as the oxidant and the reductant.

Figure 9. (a) Plot of the effect of ionic strength on the observed rate constant in 10% v/v dioxane-water at 288 ± 0.5 K. (b) Plot of the effect of ionic strength on the observed rate constant in 20% v/v dioxane-water at 289 ± 0.5 K.
3.2. Kinetic Measurements

The kinetics of the reaction was followed by measuring the increase in absorbance with time at 520.2 nm (water), 533.9 nm (10% v/v 1,4-dioxane-water), and 535.5 nm (20% v/v 1,4-dioxane-water) when dicyanobis(bipyridine)iron(II) was formed. It is worth noting that the oxidant; dicyanobis(bipyridine)iron(III) absorbs at this wavelength as well. As a result of its poor molar absorptivity in comparison to its reduced form, this absorption is relatively low. Consequently, before the start of the reaction, we observed absorbance at zero time. The representative time course graph of the redox reaction is shown in Figure 2a,b.

In all reaction media, the reaction was analyzed at room temperature. To assess the rate dependence upon the reactants in all reaction media at 0.06 M ionic strength (\(\mu\)), the oxidant concentration was kept constant at 0.08 mM and the iodide (reductant) concentration was varied between 0.08 and 4 mM at 1:1, 1:2.5, 1:5, 1:7.5, 1:10, 1:20, 1:30, 1:40, and 1:50 times. During the analysis of the effect of various parameters such as protons, ionic strength, and temperature, the concentration ratio between oxidizing and reducing agents was set at \([\text{Fe}^ {\text{III}}(\text{bpy})_2(\text{CN})_2]^+ \ll < < \Gamma\) such that 1:10, respectively. Nitric acid was used to introduce protons in concentrations of 0 M, 0.01 mM, 0.1 mM, 1 mM, 10 mM, and 100 mM. Ionic strength was varied at 0.005, 0.05, 0.1, 0.15, 0.2, and 0.37. However, the temperature ranged from 10 to 40 °C. Each experiment was repeated three times to ensure that the kinetics was followed precisely. The average of the three readings was used to calculate the rate constant. In all reaction media, the reactants and products were identified by their visible spectra (Figure 10a,c).

![Figure 10. Cont.](image-url)
Figure 10. (a) Visible absorption spectra of reactants and product in water. (b) Visible absorption spectra of reactants and product in 10% v/v 1,4-dioxane-water. (c) Visible absorption spectra of reactants and product in 20% v/v 1,4-dioxane-water.

4. Conclusions

The oxidation of iodide by dicyanobis(bipyridine)iron(III) proceeds through a moderate rate and with a comparatively low value of the rate constant in water. The rate of reaction depends upon the fractional (0.5) power of the concentration term of the iodide ion only. The concentration of the oxidant i.e., dicyanobis(bipyridine)iron(III), has no effect on the rate of reaction. The reaction is led by the formation of iodine and its subsequent conversion to triiodide ion, which reduces dicyanobis(bipyridine)iron(III) by donating electron. As a result of the protonation of triiodide, the rate slows down. However, this reaction is catalyzed by adding a small volume of 1,4-dioxane to water, and the rate achieves its maximal value. If the third power of the concentration terms of the reactants is involved in the rate law, the reaction is considered to be at its full rate. In the oxidation of iodide by dicyanobis(bipyridine)iron(III), the iodide ion is the only species whose concentration determines the rate of reaction. The addition of a small volume fraction of 1,4-dioxane such as 20% to water accelerates the rate of reaction to the third power of iodide ion with a remarkable high value of the third-order rate constant. The 10% volume fraction of 1,4-dioxane to water doubles the rate of reaction by first order in iodide ion that was 0.5 order in water. The 20% volume fraction of 1,4-dioxane to water has the highest catalytic
efficiency in the oxidation of iodide by dicyanobis(bipyridine)iron(III). In the binary solvent media, the iodide ion leads the rate of reaction by participating directly in the rate-limiting step without converting to any other intermediate species. The formation of triiodide ion and its protonation are the rate decelerating and accelerating factors in the binary solvent media, respectively. Concisely, this study identified the environmentally benign and cost-effective procedure to improve the efficiency of the dye-sensitized solar cells.

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