Kinetics of basic hydrolysis of tris (1,10-phenanthroline) iron(11) in Triton X 100/hexanol/water reverse micelles in cyclohexane

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Abstract

The kinetic study of dissociation of the complex tris (1,10-phenanthroline) iron(11) in the presence of OH\(^{-}\) ion has been carried out in the water pools of non-ionic reverse micelles of Triton X 100, hexanol in cyclohexane. The reaction shows completely different kinetic features at low and high \(W\) values. The pseudo first order rate constant (\(k_{obsv}\)) varies linearly with the effective concentration of sodium hydroxide in the water pool (\([\text{OH}^{-}]_e\)) at high values of \(W\) (\(W = 14.0\) and 10.6), on decreasing \(W\), the \(k_{obsv}\) versus \([\text{OH}^{-}]_e\) plots concave upwards showing higher order dependence of \(k_{obsv}\) on \([\text{OH}^{-}]_e\). The kinetics has been accounted for by a mechanism involving intermediate ion-pair formation between oppositely charged ions. The significant increase in rate in reverse micellar media as compared to aqueous media is due to the lower micropolarity of the waterpools in this reverse micellar medium, which facilitates the ion-pair formation between oppositely charged ions.

Keywords: Triton X 100; Reverse micelles; Basic hydrolysis; Tris (1,10-phenanthroline) iron(11); Water pools

1. Introduction

Reverse micelles consists of micropools of water lined by a monolayer of a surfactant, all dispersed in an apolar solvent. The water present in a reverse micelle is referred to as ‘water pool’ [1–3]. Reverse micellar system is optically transparent and the change in the system can be followed by different spectroscopic methods. The parameters, such as waterpool size, nature and concentration of surfactant, can be easily varied. The surfactant solubilized water provides a medium with unique properties [4] for reactions involving polar substrates. The use of reverse micelles as new reaction media has been in forefront of research in recent times. The rates of a large number of organic and inorganic reactions are affected by reverse micelles [5–12].

Kumar and Balasubramanium [13–15] first characterized the reverse micelles of Triton X 100, \(n\)-hexanol and water in cyclohexane by using NMR relaxation, ESR spin probe and fluorescence probe methods. The study of microenvironment of the above system by using absorption probes [16] has established that at low values of water to surfactant molar ratio (\(W\)), water is used up in solvation of ethylene oxide groups at the interface. As \(W\) is progressively increased, water is also involved in secondary hydration and free water begins to appear at \(W > 5.3\). The reverse micelles of Triton X 100 have been used as a medium for synthesis of nanoparticles, such as CdS [17], TiO\(_2\) [18], BaSO\(_4\) [19] and copper [20]. However kinetics of chemical reactions have seldom been studied in this reverse micellar system. Recently, the kinetics of aquation of the complex Fe ([(Phen)]\(^{2+}\)) has been studied in this medium [12].

It has been reported that water pools in the reverse micellar systems have much lower micropolarity [4], which can influence kinetic features. The lower micropolarity conditions enhances the ion-pair formation and reactions which involve the intermediate formation of ion pairs between reactant ions may provide a kinetic basis for understanding the
nature of entrapped water in the reverse micelles. With this objective the kinetics of basic hydrolysis of the Fe(III) complex was investigated in the Triton X 100 reverse micellar system and the results are suggestive of the low micropolarity of the water pools of this system as compared to bulk water.

2. Materials and method

Triton X 100 was purchased from S.D. Fine Chemicals, Mumbai. The Triton X 100 was cleared of any low-boiling impurities by exposure to vacuum for 3 h at 70 °C, following the procedure given by Kumar and Balasubramaniam [13].

All chemicals used were of analytical reagent grade. Cyclohexane was distilled before use. Solutions were prepared in deionised and double distilled water. Tris (1,10-phenanthroline) iron(II) complex was prepared by mixing stoichiometric amounts (1:3) of ferrous ammonium sulphate (Qualigens) and 1,10-phenanthroline (BDH Anal R) to get 0.02 mol dm$^{-3}$ in water.

Stock solutions of sodium hydroxide (0.05–0.3 mol dm$^{-3}$) were freshly prepared by using (Qualigens Anal R) sample of sodium hydroxide and were standardized against standard oxalic acid solutions. The ionic strength was maintained constant at 0.15 with respect to sodium nitrate (Qualigens) solution (0.05–0.3 mol dm$^{-3}$). Sodium nitrate has been found to have no effect on rate of dissociation of the complex [21]. The ionic strength was maintained constant at 0.15 with respect to water pool, throughout the investigation.

3. Preparation of reverse micellar system and initiation of the reaction

Triton X 100 was mixed with hexanol in the ratio 4:1 (v/v) to form a blend. This blend was then dissolved in cyclohexane to obtain Triton X 100/hexanol/cyclohexane system of fixed Triton X 100 concentration.

Since all the reactants in the reaction carried out are ionic they can exist only in the water pool, and not in the oil phase, and this concentration effect on rate due to confinement of the reactants in the small volume of the water pool has been separated from the overall kinetics by dividing the overall concentration of sodium hydroxide ([OH$^{-}$]$_o$), by the volume fraction ($f$) of solubilized water ($f'=v$olume of water/total volume of the system), which is equal to the effective concentration of sodium hydroxide[OH$^{-}$]$_e$. The rate data was analyzed by taking this effective concentration in the water pool.

To study the rate of basic hydrolysis, all solutions were kept at constant temperature for 1 h. Small quantities of the stock aqueous solutions of sodium hydroxide and sodium nitrate (0.02–0.2 cm$^3$) were added to 5 cm$^3$ of Triton X 100 solution taken in a 25 ml volumetric flask. The overall concentration of sodium hydroxide ([OH$^{-}$]$_o$) in 5 cm$^3$ of Triton X 100 solution, was varied between 0.4 × 10$^{-3}$ and 8.0 × 10$^{-3}$ mol dm$^{-3}$. A known volume (0.02 cm$^3$) of the complex tris (1,10-phenanthroline) iron(I) was added in the end to initiate the reaction. These mixtures were shaken to obtain a transparent solution that can be regarded as reverse micellar system [22]. The molar ratio of water to Triton X 100 (W) was varied in the range 4.0–14.0. The concentration of Triton X 100 used (0.174–0.322) is far greater than CMC [12] (2.2 × 10$^{-3}$ mol dm$^{-3}$) of Triton X 100 reverse micelles in cyclohexane, showing that micellization is complete under the experimental condition.

The reactions were monitored by measuring the absorbance of the complex at suitable time intervals at $\lambda_{max} = 510$ nm ($\epsilon = 11,000$ dm$^3$ mol$^{-1}$ cm$^{-1}$) with a Milton Roy (spectronic 1201) spectrophotometer using a 1 cm stoppered cell inside a thermostatted cell compartment.

The reaction was carried out under the condition [OH$^{-}$]$_o$ ≫ [Fe (Phen)$_3$]$^{2+}$ in order to keep the experimental results fit the pseudo first order rate equations. Concentrations have been chosen such that Beer’s law is strictly followed. Pseudo first order rate constants were obtained from the slopes of log (absorbance) versus time plot. The standard error in determination of kinetic data was less than 5%.

4. Results and discussion

4.1. Effect of variation of sodium hydroxide concentration on rate

The kinetic study was carried out keeping the concentration of the complex [Fe (Phen)$_3$]$^{2+}$ very small compared to that of sodium hydroxide thus isolating [Fe (Phen)$_3$]$^{2+}$. A plot of log $A_t$ ($A_t$ being absorbance at time $t$) versus time $t$ has been found to be linear (Fig. 1) for 95% of the reaction showing first order kinetics with respect to tris (1,10-phenanthroline) iron(II) complex under the condition [OH$^{-}$]$_o$ ≫ [Fe (Phen)$_3$]$^{2+}$. The study was carried out at different initial concentrations of sodium hydroxide keeping the concentrations of [Fe (Phen)$_3$]$^{2+}$, Triton X 100 and W fixed. The pseudo first order rate constants $k_{obs}$, obtained from the slopes of log $A_t$ versus time plots are presented in Tables 1 and 2.
We observe from Tables 1 and 2 that values of \( k_{\text{obs}} \) increase with increase in concentration of sodium hydroxide.

An analysis of concentration effect of \( \text{OH}^- \) on rate has shown that for low spin iron(II) complexes containing ligands, such as 2,2′-bipyridyl (bipy), 1,10-phenanthroline (Phen) or their derivatives, the rate data fit into the empirical equation [23]:

\[
k_{\text{obs}} = (p + q[\text{OH}^-]^0 + r[\text{OH}^-]^2 + s[\text{OH}^-]^3 + \ldots)
\]

Here, \( p \) is the rate of dissociation of the complex in the absence of \( \text{OH}^- \).

4.2. Effect of variation of \( W \)

The variation of water to surfactant molar ratio (\( W \)) has considerable effect on rate. At constant surfactant concentration, the \( k_{\text{obs}} \) values decrease with increase in \( W \). The reaction shows completely different kinetic features at low and high values of \( W \).

4.2.1. At high values of \( W (W = 14.0) \)

A plot of pseudo first order rate constant, \( k_{\text{obs}} \) versus \([\text{OH}^-]_e \) (Fig. 2) gives a straight line with an intercept, showing that the higher terms in equation (1) are negligible.

Equation (1) now takes the form:

\[
k_{\text{obs}} = p + q[\text{OH}^-]_e
\]

Fig. 2. Plot of \( k_{\text{obs}} \) vs. \([\text{OH}^-]_e \). TX 100 = 0.322 mol dm\(^{-3}\), \( W = 14.0 \), ionic strength = 0.15 and temperature = 26 °C.
The values of \( p \) and \( q \) obtained from intercepts and slopes of linear plots of \( k_{obs} \) versus \([\text{OH}^-]_c\) are presented in Table 1. Here, \( p \) represents the rate constant of the \( \text{OH}^- \) independent path, which has been found to be closed to the experimentally determined rate of dissociation \( (k_{1exp}) \) of the complex in absence of \( \text{OH}^- \) (Table 1), under similar experimental conditions.

The effect of variation of concentration of the surfactant on the rate of reaction was studied and as can be seen from Table 1 the variation of surfactant concentration \((0.174 - 0.322 \, \text{mol dm}^{-3})\) at this high \( W \) value does not have any significant effect on rate. Since the increase in surfactant concentration at constant \( W \) increases the interfacial area, this shows that at this high \( W \) value the reaction is taking place mainly in the waterpool and not on the micellar surface, so there is no specific effect of Triton X 100 on rate.

4.2.2. At \( W = 4.0 \)

The values of \( k_{1exp} \) at different values of \([\text{OH}^-]_c\) at \( W = 4.0 \). \( k_{1exp} \) values in Table 2 are the experimentally determined rates of dissociation of the complex in absence of \( \text{OH}^- \) at \( W = 4.0 \). The rate increases with increase in \([\text{OH}^-]_c\), but the plot of \( k_{obs} \) versus \([\text{OH}^-]_c\) deviates from linearity (Fig. 3) and the curves concave upwards showing that there is a higher order dependence of \( \text{OH}^- \) on the rate of dissociation of the complex.

Moreover, at \( W = 4.0 \), the pseudo first order rate constant \( k_{obs} \) increases with increase in concentration of the surfactant from \(0.174\) to \(0.322 \, \text{M}\) (Fig. 3), at fixed ionic strength and \([\text{OH}^-]_c\). The reactants being ionic cannot exist in the bulk organic phase; the reaction can take place either in the waterpool or on the micellar interface. It is known [24] that at constant \( W \) the increase in surfactant concentration results in increase in the micellar concentration and hence the area of the interface, but there is no change in the micellar composition or other properties. The increase in rate with surfactant concentration shows that at this low value of \( W \), the reaction is taking place on the micellar interface, between

bound \([\text{Fe (Phen)}]^{2+}\) and \(\text{OH}^-\). But it has been shown earlier [12,21] that binding constant of \([\text{Fe (Phen)}]^{2+}\) and \(\text{OH}^-\) on the surface of neutral micelle like Triton X 100 are low in magnitude, hence the complete binding of reactants to the interface does not take place and at \( W = 4 \), the reactants are also present in the waterpool, thus the reaction takes place partly on the micellar interface and partly in the waterpool.

On increasing \( W \), the reactants are displaced into the waterpool and at \( W = 14 \), the reaction takes place mainly in the water pool, where there is no surfactant effect on rate. The acceleration by the micellar surface may be due to the special properties of water like lower micropolarity that hydrates the micelle which helps in ion-pair formation between oppositely charged reactants or catalysis by the material of the micelle.

Fig. 4 shows the plot of \( k_{obs} \) versus \([\text{OH}^-]_c\) at different values of \( W \), the surfactant concentration in each case is \(0.322\), ionic strength is \(0.15\) and temperature is \(26^\circ\)C. As can be seen from the figure, the \( k_{obs} \) versus \([\text{OH}^-]_c\) plots are linear at \( W = 14.0 \) and \(10.6\) but as \( W \) is reduced, the plots deviate from linearity, \( k_{obs} \) now increases much more rapidly with \([\text{OH}^-]_c\), and the higher terms in equation (1) become important.

Identical pattern was observed for the basic hydrolysis of iron(1) Schiff’s base complexes in aqueous-methanol mixtures [25], the \( k_{obs} \) profile becoming concave upwards at higher methanol content, that is with decreasing polarity of the medium. This has been explained as due to the rate determining hydroxide attack taking place at an intermediate in which hydroxide has already been added to one of the ligand molecules in a fast pre-equilibrium step.

Margerum and Morganthaler [26] investigated the basic hydrolysis of \([\text{Fe (Phen)}]^{2+}\) in aqueous medium and reported that the reaction obeys first order kinetics with respect to

![Fig. 3. Plot of \( k_{obs} \) vs. \([\text{OH}^-]_c\); \( W = 4.0 \), ionic strength = 0.15, temperature = 26°C. TX = 100 = 1 (0.322 mol dm\(^{-3}\)), 2 (0.25 mol dm\(^{-3}\)), and 3 (0.174 mol dm\(^{-3}\)).](image)

![Fig. 4. Plot of \( k_{obs} \) vs. \([\text{OH}^-]_c\) at different values of \( W \); TX 100 = 0.322 mol dm\(^{-3}\), temperature = 26°C, ionic strength = 0.15. \( W = \{1 (4); 2 (6.6); 3 (10.6); 4 (14.0)\}\).](image)
to W ion pairing. This explains the higher rate at water [16,21], with increasing micropolarity and decreased extent of interaction with the metal ligand bond. As fitting the values of $k_{obs}$ in Triton X 100 reverse micelles there is 5.8 times acceleration in $k_{obs}$ of [Fe (Phen)$_3$]$^{2+}$ and first order in OH$^-$ at low [OH$^-$]. At higher concentration of OH$^-$, [OH$^-$]$^2$ and [OH$^-$]$^3$ terms also appear in the rate law. The close approach of the nucleophile and the metal ions are necessary for weakening the metal ligand bond and according to these authors, this is possible in the 1,10-phenanthroline complexes due to formation of inner ion pairs where OH$^-$ replace the water molecules held in the pockets between the planar 1,10-phenanthroline molecules.

Similar trend was also observed in the present investigation in Triton X 100 reverse micelle with much enhanced rate compared to aqueous medium. Margerum [23] reported the values of pseudo first order rate constant ($k_{obs}$) to be $15 \times 10^{-4}$ s$^{-1}$ at ionic strength 0.15 and $[\text{OH}^-]=0.1 \text{mol dm}^{-3}$ in the aqueous medium. In Triton X 100 reverse micellar media, at $W=14$, $[\text{OH}^-]_e=0.1 \text{mol dm}^{-3}$, [Triton X 100] = 0.322 mol dm$^{-3}$, the value of $k_{obs}$ is $86.4 \times 10^{-4}$ s$^{-1}$ (Table 1), and at $W=4$, the $k_{obs}$ value at same $[\text{OH}^-]_e$ and Triton X 100 concentration is $681 \times 10^{-4}$ s$^{-1}$ (Table 2). This shows that in Triton X 100 reverse micelles there is 5.8 times acceleration in rate at $W=14.0$ and 46 times acceleration at $W=4$ as compared to aqueous medium. The micropolarity of water in the water pools of Triton X 100 reverse micelles have been reported [16] to be intermediate between isopropyl alcohol and methanol and much lower than aqueous medium. Lower micropolarity of the Triton X 100 reverse micellar media leads to more extensive ion pairing of the reactants [Fe (Phen)]$^{2+}$ and OH$^-$ than aqueous medium leading to greater rates in the reverse micellar medium.

The kinetics in the water pools of Triton X 100 reverse micelles can be accounted for by the following scheme [26]:

$$
\text{Fe (phen)}^{2+} + \text{OH}^- \rightarrow \text{[Fe (phen) - OH]}^+ + \text{OH}^- \\
\text{products} \hspace{1cm} \text{products}
$$

$$
\text{K}_1 [\text{Fe (phen)}^{2+} + \text{OH}^-] \hspace{1cm} [\text{Fe (phen)}^{2+} + \text{OH}^-] \\
\text{products} \hspace{1cm} \text{products}
$$

All these results clearly point out to the lower micropolarity of water in the water pools of Triton X 100 reverse micelle, resulting in the enhanced ion-pair formation between the oppositely charged ions, thus there is acceleration in rate in the reverse micellar media.

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References


