

Use of aqueous DMSO in resolving 'proton ambiguity' in the formation of monocomplexes of iron(III)

G KRISHNAMOORTHY* and B S PRABHANANDA

Chemical Physics Group, Tata Institute of Fundamental Research, Bombay 400 005, India

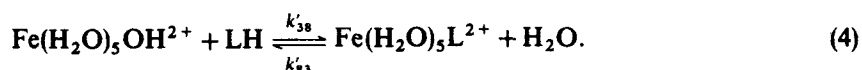
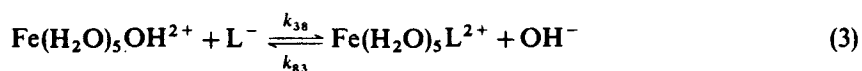
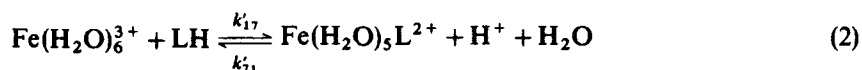
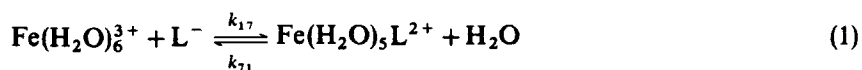
MS received 17 November 1984

Abstract. The formation of FeL^{2+} ($\text{L}^- = \text{N}_3^-, \text{SCN}^-$) in H_2O -dimethylsulphoxide (DMSO) mixtures was studied by equilibrium, stopped flow and temperature jump observations. The acid dissociation constants associated with LH and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and the formation constants associated with FeL^{2+} were determined at various solvent compositions. In kinetic studies, the solvent composition dependence of the overall equilibration rate was explained in terms of equations predicted by a reaction scheme which includes DMSO coordinated species. Analysis of results on the basis of these equations identified $\text{Fe} \cdot \text{OH}^{2+} \cdot \text{HN}_3$ and $\text{Fe}^{3+} \cdot \text{SCN}^-$ as the dominant transition states contributing to pH-independent paths of formation of FeL^{2+} in the cases of N_3^- and SCN^- respectively. Thus, the results which support the Eigen-Tamm-Wilkins mechanism have resolved the mechanistic ambiguity in the pH-independent paths of formation of FeL^{2+} . It is also shown that we cannot neglect species such as $\text{FeOH} \cdot \text{HN}_3^{2+}$, $\text{Fe} \cdot \text{OH} \cdot \text{N}_3^-$ and $\text{Fe} \cdot \text{HN}_3^{3+}$ while accounting for the kinetic behaviour.

Keywords. Proton ambiguity; iron(III) complexes; aqueous DMSO; temperature jump; stopped flow.

1. Introduction

When a molecule in the protonated state reacts with a second molecule in the unprotonated state in aqueous solutions, the pH dependence of the observed equilibrium and of the kinetic parameters does not indicate which of the two molecules was protonated before the formation of the transition state or as a constituent of the transition state (Frost and Pearson 1961; Espenson and Dustin 1969; Accasina *et al* 1967; Calvaruso *et al* 1978; Cavasino 1968). For example, the possible paths of formation of $\text{Fe}(\text{H}_2\text{O})_5\text{L}^{2+}$ from $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and the unidentate ligand L^- are as follows:



* To whom all correspondence should be addressed.

In kinetic experiments, such as temperature jump or stopped flow studies, the time constant τ associated with the exponential change in concentration is given by (Calvaruso *et al* 1978; Cavasino 1968)

$$1/\tau B = k_{17} + (k'_{38} K_H)/K_{LH} + (k_{38} K_H)/[H^+] + (k'_{17}[H^+])/K_{LH} \quad (5)$$

for the reaction schemes shown in (1)–(4). K_H and K_{LH} are dissociation constants for the protonation equilibria $Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5OH^{2+}$ and $L^- \rightleftharpoons LH$ respectively. B depends on the equilibrium concentrations of the reactants and the formation constant $K_S (= k_{17}/k_{71})$ (the expression for B is given in §3). Paths (1) and (4) contribute to the pH independent part of $1/\tau B$. Thus a study of the pH dependence of $1/\tau B$ in aqueous solutions cannot tell us the relative magnitudes of these two contributions. There have been some attempts to remove such proton ambiguities (Accasina *et al* 1967; Calvaruso *et al* 1978). In this paper, we show that a preferred answer to this problem could be obtained for the kinetics of formation of $Fe(H_2O)_5L^{2+}$ ($L^- = N_3^-, SCN^-$) by a study in H_2O -DMSO mixtures (DMSO = dimethylsulphoxide). This has been possible due to the ability of H_2O -DMSO mixtures to alter K_H/K_{LH} without significantly affecting the rate constants (Krishnamoorthy and Prabhananda 1981). The presence of DMSO undoubtedly increases the complexity of the system. However, our analysis of the kinetic data shows that this complexity can be accounted for by additional terms in the expression for the kinetic parameters.

2. Experimental

The spectrophotometric titrations were carried out using a Cary 17D spectrophotometer. T -jump relaxations were studied using a home-made instrument (Prabhananda 1977). The kinetic spectrophotometer of the T -jump instrument was also used for monitoring the concentration changes in stopped flow experiments. The driving syringes, ratio drive mechanism, mixing chamber and observation chamber assembly of the stopped flow set up had been obtained from Hi-Tech (England). A pneumatic drive made in our laboratory was used for driving the syringes. The metal ion concentration was sufficiently small such that the change in the transmitted light due to complex formation could be directly related to concentration changes in stopped flow experiments. The stopped flow experiments were carried out at sufficiently high ligand concentration (or buffered) such that it could be treated as a constant. The stopped flow traces obtained under such conditions were single exponentials with time constants τ . These were determined by the procedure described elsewhere (Prabhananda 1978). Chemicals used and the preparation of reaction mixtures are described in our earlier papers (Krishnamoorthy and Prabhananda 1981; Prabhananda 1978). The ionic strength was regulated at $\mu = 1.0$ using $NaClO_4$. Observations were made at $25^\circ C$ and $pH = -\log [H^+]$ was used in the evaluation of pH dependent quantities. The K_{LH} associated with N_3^- were determined for convenient solvent mixtures by monitoring the pH as a function of the volume of a strong acid (HCl) added in preparing the solutions. In the case of the ligand SCN^- , the extent of change in K_{LH} with solvent composition was estimated by monitoring the change in absorbance of thiocyanate solutions at 250 nm (Morgan *et al* 1965). The metal ligand complex formation constants were estimated by using optical density (OD) vs $OD/[L^-]$ plots (Krishnamoorthy and Prabhananda 1981).

3. Results and discussion

The general reaction scheme for the formation of $\text{Fe}(\text{H}_2\text{O})_5\text{L}^{2+}$ in H_2O -DMSO mixtures is shown in figure 1. Coordination of water molecules is not depicted in order to reduce the complexity. Reactions (1)–(4) correspond to the boxed region of figure 1. Various equilibrium constants used in this work are defined in the figure. Analysis of kinetic data to elucidate the dominant pH-independent path (5) requires the knowledge of equilibrium constants K_{H} , K_{LH} and K_{S} .

3.1 Acid dissociation constants K_{H} and K_{LH} :

The acid dissociation constants K_{H} associated with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ in various H_2O -DMSO mixtures were determined in our previous work (table 1 in Krishnamoorthy and Prabhananda 1981). These can be related to the mole fraction of DMSO, f , by a linear equation

$$pK_{\text{H}} = (1-f)pK_{\text{H}}^{\text{O}} + fpK_{\text{H}}^{\text{I}} \quad (6)$$

with $pK_{\text{H}}^{\text{O}} = 2.53$ and $pK_{\text{H}}^{\text{I}} = 19.9$. Similarly the acid dissociation constants K_{LH} associated with the ligands in H_2O -DMSO mixtures fit the equation

$$pK_{\text{LH}} = (1-f)pK_{\text{LH}}^{\text{O}} + fpK_{\text{LH}}^{\text{I}} \quad (7)$$

with $pK_{\text{LH}}^{\text{O}} = 4.15$ and $pK_{\text{LH}}^{\text{I}} = 7.5$ for N_3^- and $pK_{\text{LH}}^{\text{O}} = -1.85$ and $pK_{\text{LH}}^{\text{I}} = 3.5$ for

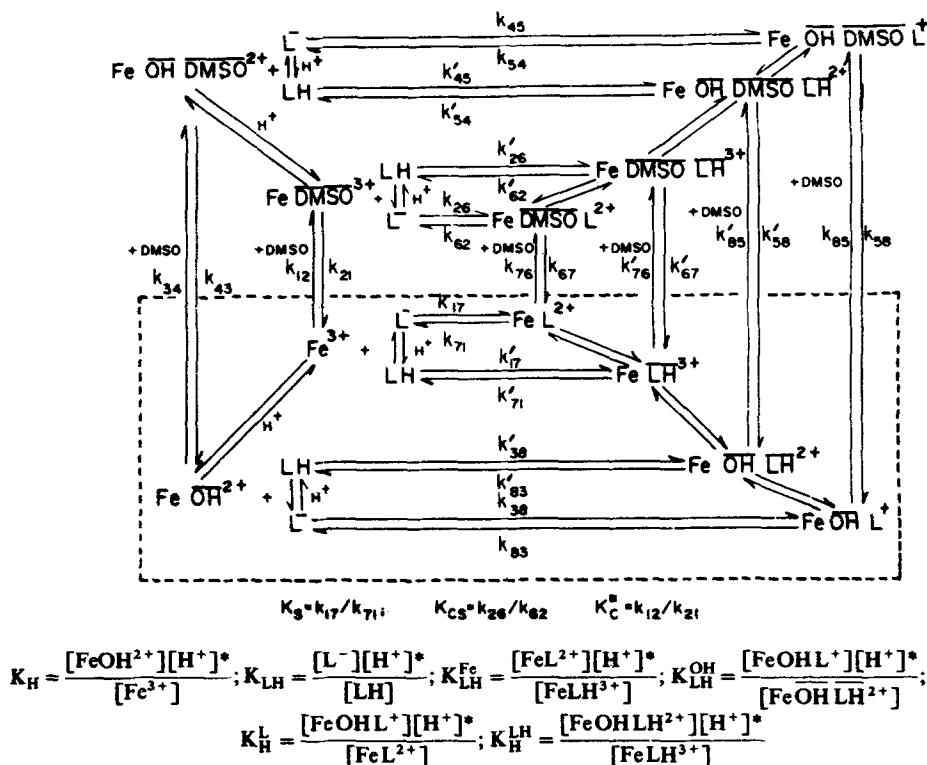


Figure 1. A reaction scheme which accounts for the kinetics of the formation of Fe(III) complexes in aqueous DMSO. Number of coordinated water molecules = 6 – number of coordinated ligands explicitly written in the figure.

SCN⁻. Changes in K_{LH} for the ligand SCN⁻ were estimated from the pH dependent changes of absorbance at 250 nm with the reasonable assumption that the extinction coefficient does not change significantly with the solvent composition in H₂O-DMSO mixtures.

3.2 The formation constant K_s

The constant $K_s (= k_{17}/k_{71})$ associated with the formation of FeL²⁺ (neglecting the water molecules for simplicity) at various H₂O-DMSO mixtures are obtained from the slopes of plots of optical density (OD) vs OD/[L⁻]. In the case of SCN⁻, K_s values are given in column 4 of table 1 of our earlier work (Krishnamoorthy and Prabhananda 1981). (Terms involving K_{CS} are neglected since analysis of OD vs OD/[L⁻] plots show that $K_{CS} < 0.1 K_s$.) For the ligand N₃⁻, values of K_{LH} and concentrations of HN₃ were used to calculate [N₃⁻] at different pH values. In this case (N₃⁻), the slopes $1/K_s^*$ obtained in various H₂O-DMSO mixtures could be fitted to the following equation

$$1/K_s^* = (1 + K_C^* \gamma [\text{DMSO}])/K_s \quad (8)$$

with $K_C^* = 3 \text{ M}^{-1}$ and $K_s = 1.67 \times 10^4 \text{ M}^{-1}$. γ is the activity coefficient of DMSO (Lam and Benoit 1974). This value of K_C^* is comparable to that determined from temperature-jump experiments (Krishnamoorthy and Prabhananda 1981). Also analysis suggests that $K_{CS} \ll K_s$.

3.3 Kinetic studies and evaluation of dominant pathways

The experimentally observed time dependence of the concentration in temperature-jump and stopped flow observation can be written as follows:

$$\frac{d}{dt} \{ [\text{FeL}^{2+}]_{\text{eq}} - [\text{FeL}^{2+}] \} = -k \{ [\text{FeL}^{2+}]_{\text{eq}} - [\text{FeL}^{2+}] \}, \quad (9)$$

where $[\text{FeL}^{2+}]_{\text{eq}}$ is the concentration at equilibrium. From the time constant associated with the exponential change, we get the relaxation rate $k (= 1/\tau)$. The observed dependence of τ on [DMSO] and pH can be explained in terms of equations obtained for the reaction scheme given in figure 1. For this scheme, the relaxation rate $1/\tau$ for the slowest step (9) is given by

$$1/\tau B = X + k_{38} K_H / [\text{H}^+]^* + k'_{17} [\text{H}^+]^* / K_{LH} + K_s \gamma [\text{DMSO}] \{ k_{85} K_H^L / [\text{H}^+]^* + k'_{76} [\text{H}^+]^* / K_{LH}^{\text{Fe}} \}. \quad (10)$$

The fast steps are similar to those mentioned earlier (Krishnamoorthy and Prabhananda 1981).

$$X = k_{17} + k'_{38} K_H / K_{LH} + K_s \gamma [\text{DMSO}] \{ k_{76} + k'_{85} K_H^L / K_{LH}^{\text{OH}} \} \quad (11)$$

$$B \simeq [\text{L}^-] / \{ (1 + K_H / [\text{H}^+]^*) (1 + K_C^* \gamma [\text{DMSO}]) \} + 1/K_s, \quad (12)$$

neglecting small terms. The origin of proton ambiguity lies in our inability to identify the dominant terms of X from a pH dependent study.

N₃⁻: Table 1 gives the typical values of τ obtained in the stopped flow experiments on the formation of FeN₃²⁺. The dependence of $1/\tau B$ on $[\text{H}^+]^*$ in different solvent mixtures (figure 2) could be analysed as follows:

$$1/\tau B = X + Y[\text{H}^+]^* + Y'/[\text{H}^+]^*, \quad (13)$$

Table 1. Observed and calculated relaxation times τ for the stopped flow experiments on the formation of FeN_3^{2+} in aqueous DMSO at 25°C and $\mu = 1.0$, $[\text{Fe}^{2+}] = 1.0 \times 10^{-4}$ M and $[\text{N}_3^-] + [\text{HN}_3] = 4 \times 10^{-2}$ M.

Mole fraction of DMSO $f = 0.0$			Mole fraction of DMSO $f = 0.06$		
pH	Observed ^a τ m sec	Calculated τ m sec	pH	Observed ^a τ m sec	Calculated ^b τ m sec
2.00	13.0	13.2	2.00	55.3	56.0
1.86	14.8	16.1	1.85	66.0	67.1
1.66	21.3	21.2	1.66	75.4	80.4
1.50	25.8	26.1	1.51	86.0	88.7
1.36	29.8	30.3	1.36	98.0	94.0
1.23	34.3	34.6	1.23	89.4	95.5
1.10	39.3	38.6	1.14	86.4	94.8
0.95	46.0	42.8	1.01	83.0	91.4

^a The error in the value of τ is less than 5%.

^b Calculated using the constants given in the text and considering only the terms which have been shown to be dominant in the text.

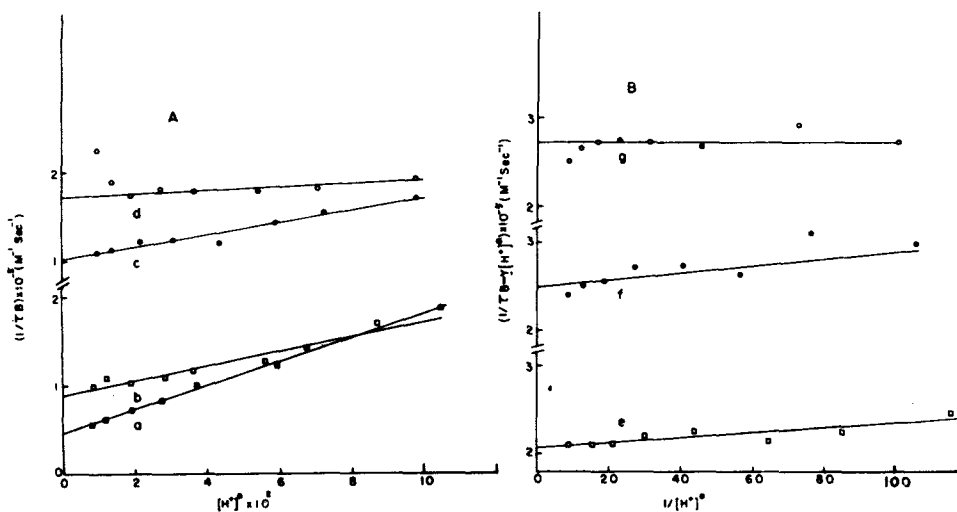


Figure 2. Dependence of $1/\tau B$ on $[\text{H}^+]$ * in aqueous DMSO with mole fraction of DMSO $f = 0.108$ (a) 0.079 (b) 0.060 (c), 0.043 (d), 0.019 (e), 0.008 (f) and 0.0 (g) in the stopped flow experiments on the formation of FeN_3^{2+} at 25°C and $\mu = 1.0$. See text for the evaluation of Y used in plotting figure 2B.

which has the same form as (10). When the mole fraction of DMSO is large (figure 2A), the term involving Y' is negligible. Table 2 gives X the pH independent part of $1/\tau B$ obtained by the least square analysis of typical data. The decrease in X with increasing $[\text{DMSO}]$ suggests that the second term of (11) [reaction path (4)] could be the dominant term of X . However, such a conclusion would be valid only if the rate constants (11) are

Table 2. Equilibrium and kinetic parameters for the formation of FeN_3^+ in DMSO-water mixtures at 25°C and $\mu = 1.0$. Calculated X and Y obtained using (14) and (15) respectively with the constants given in the text. Observed values are for a typical set of data.

Mole fraction of DMSO f	K_H/K_{LH}	$K_S\gamma[\text{DMSO}] \times 10^{-3}$	$Y \times 10^{-6} (\text{sec}^{-1})$		$X \times 10^{-5} (\text{M}^{-1} \text{sec}^{-1})$	
			Observed ^a	Calculated	Observed ^a	Calculated
0.0	42.0	0.0	—	0.056	2.72 ± 0.02 $(2.54 \pm 0.13)^b$	2.70
0.0079	36.2	0.423	—	0.096	2.48 ± 0.09	2.75
0.019	22.5	1.04	—	0.16	2.07 ± 0.04	2.10
0.043	10.1	2.47	0.17 ± 0.05	0.32	1.73 ± 0.03	1.39
0.060	5.8	3.58	0.68 ± 0.06	0.52	1.02 ± 0.03	1.03
0.079	3.2	4.82	0.84 ± 0.05	0.76	0.85 ± 0.02 $(0.99 \pm 0.03)^b$	0.76
0.108	1.2	7.15	1.34 ± 0.04	1.36	0.46 ± 0.02	0.51

^a Determined from the slopes and intercepts of figure 2. The errors given correspond to those obtained by the least square analysis of a particular set of data.

^b From the temperature jump experiments.

insensitive to the solvent composition. The analysis given below does show that the rate constants do not vary significantly with solvent composition. The values of X corresponding to seven solvent mixtures could be fitted to a linear equation with only three constants b_1 , b_2 and b_3 quite well.

$$X = b_1 K_H/K_{LH} + b_2 K_S\gamma[\text{DMSO}] + b_3 K_S\gamma[\text{DMSO}] \cdot K_H/K_{LH}. \quad (14)$$

The four values of Y (table 2) could be fitted to a linear equation with only two constants, b_4 and b_5 .

$$Y = b_4 + b_5 K_S\gamma[\text{DMSO}]/K_{LH}. \quad (15)$$

In figure 2B we have used Y extrapolated with the help of (15).

Since the number of simultaneous equations used are more than the number of terms in (14) and (15), we can have confidence that the dominant variables contributing the X and Y have been included in these equations and the rate constants b_i ($i = 1, 5$) do not vary significantly with solvent composition in aqueous DMSO. All the terms of (13)–(15) are identifiable as the dominant terms of (10) and (11) when we use the following relations:

$$\begin{aligned} b_6 K_H/K_{LH} &= K_H^L/K_{LH}^{\text{OH}} \\ b_7/K_{LH} &= 1/K_{LH}^{\text{Fe}}. \end{aligned} \quad (16)$$

This confirms that figure 1 is a reasonable scheme for our system. (Using microscopic reversibility in figure 1, we find that b_6 and b_7 can be expressed in terms of rate constants of different paths of ligand coordination to the metal and ligand dissociation from the complex.)

Using (14)–(16) and using the estimates of Seewald and Sutin (1963) for k'_{17} ($= b_4 = 4 \text{ M}^{-1} \text{sec}^{-1}$ at $\mu = 1.0$), we obtain by the least square analysis of data $b_1 = b'_{38} = 6.4 \pm 0.2 \times 10^3 \text{ M}^{-1} \text{sec}^{-1}$, $b_2 = k'_{76} = 2.9 \pm 1.2 \text{ M}^{-1} \text{sec}^{-1}$, $b_3 = b_6 k'_{85} = 2.7 \pm 0.3 \text{ M}^{-1} \text{sec}^{-1}$ and $b_5 = b_7 k'_{76} = 5.5 \pm 0.5 \times 10^{-3} \text{ M}^{-1} \text{sec}^{-1}$.

The estimate of k'_{38} obtained here agrees well with that determined by Seewald and Sutin (1963). Tables 1 and 2 include the calculated values τ , X and Y using these estimates.

Changes in the solvent composition in aqueous DMSO undoubtedly changes the free energies of the transition states as well as the reactant pair states. It is reasonable to have a situation when the difference in the free energies of a transition state and a reactant pair state does not change significantly, even though the absolute free energies change with solvent composition. In such a situation the associated bimolecular rate constant would not vary significantly with solvent composition. The constancy of bimolecular rate constants determined above could correspond to such situations.

In the limit of aqueous solutions $\{[\text{DMSO}] \rightarrow 0 \text{ in (11)–(16)}\}$ the dominant term of X is $k'_{38} K_{\text{H}}/K_{\text{LH}}$. The above conclusion regarding the constancy of k'_{38} implies that the free energy difference between the reactant pairs $\text{FeOH}^{2+} + \text{HN}_3$ and the transition state responsible for the dominant term, does not vary significantly with solvent composition in aqueous DMSO. Since the changes in the dielectric constant are small, we can neglect the changes in the electrostatic contributions to the free energy. However, changing the solvent composition in aqueous DMSO would change the solvation energies associated with the hydrogen bonding of the solvent with solute molecules, since DMSO is only a proton acceptor, whereas water can act both as a proton donor and as a proton acceptor. If there is a structural similarity between the constituents of the transition state and a reactant pair, the transition state could form hydrogen bonds with as much facility as it is possible for the reactant pair except for a small steric factor. In such a case, the free energy difference between the reactant pair stated and the transition state would not change much with solvent composition. Such an argument and the above mentioned implication of the constancy of k'_{38} suggest that the dominant transition state contributing to X is of the type $(\text{FeOH}^{2+} \cdot \text{HN}_3)$.

SCN^- : Figure 3 gives $1/\tau B$ against $1/[\text{H}^+]$ * plots obtained for the ligand SCN^- in three typical solvent mixtures. Unlike the above mentioned case of N_3^- , X does not vary with solvent mixture composition in the case of the SCN^- ligand. From (11) we note that this would be the case if the dominant term of X is k_{17} . By arguments similar to the above, we can say that the dominant transition state making this contribution is $(\text{Fe}^{3+} \cdot \text{SCN}^-)$.

The equilibrium and kinetic data of this work and our earlier work (Krishnamoorthy and Prabhananda 1981) can be explained with equations which have dominant terms linear in ligand and DMSO concentrations apart from the constant terms. This suggests that we need not consider species with more than one ligand and one DMSO coordinated to the metal ion. The coordination of a second ligand is known to be much weaker than the first (Laurence 1956). In a study of chromium(III) complexes in aqueous DMSO, Scott *et al* (1969) have suggested the formation of complexes in which more than one DMSO is coordinated. Our results do not rule out the formation of such species in our system. However in the concentration range of our work, the kinetic and equilibrium results are adequately explained by the species shown in figure 1.

The dependence of various parameters on solvent composition in aqueous DMSO observed in this work has similarities with that reported earlier (Krishnamoorthy and Prabhananda 1981; Buncel and Wilson 1977). It is also gratifying to note that our identification of the dominant transition states are in accordance with the expectations of the Eigen-Tamm-Wilkins mechanism (Eigen and Tamm 1962; Wilkins and Eigen

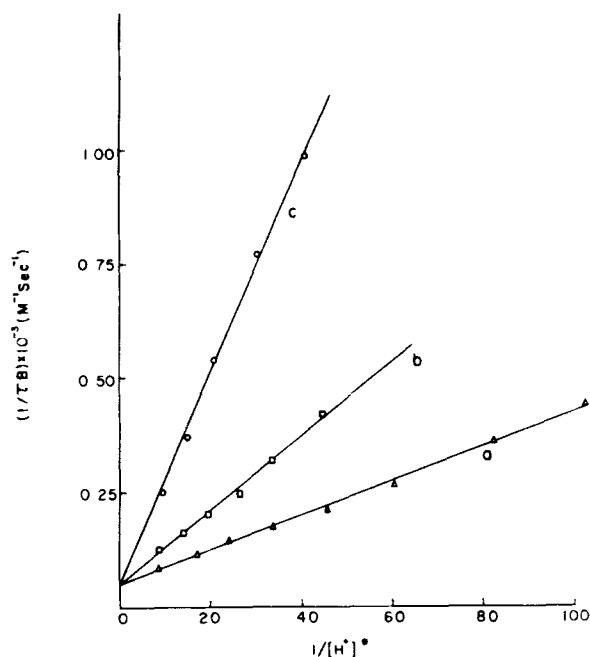


Figure 3. Dependence of $1/\tau B$ on $[H^+]$ * in aqueous DMSO with mole fraction of DMSO $f = 0.079$ (a), 0.043 (b) and 0.0 (c) in the stopped flow experiments on the formation of $FeSCN^{2+}$ at $25^\circ C$ and $\mu = 1.0$.

1965). We note that we cannot neglect species of the type $FeOH \cdot N_3^+$, $FeOH \cdot HN_3^{2+}$, $FeHN_3^{3+}$ and the DMSO coordinated species while accounting for the kinetic behaviour.

References

- Accasina F, Cavasino F P and D'Alessandro S 1967 *J. Phys. Chem.* **71** 2474
 Buncel E and Wilson H 1977 in *Advances in physical organic chemistry* (eds) V Gold and D Bethell (New York: Academic Press) Vol. 14, p. 133
 Calvaruso G, Cavasino F P and Di Dio E 1978 *J. Chem. Soc. Faraday I* **74** 525
 Cavasino F P 1968 *J. Phys. Chem.* **72** 1378
 Eigen M and Tamm K 1962 *Z. Electrochem.* **66** 93, 107
 Espenson J H and Dustin D F 1979 *Inorg. Chem.* **8** 1760
 Frost A A and Pearson R G 1961 in *Kinetics and mechanism* 2nd ed. (New York: Wiley) pp 307-316
 Krishnamoorthy G and Prabhananda 1981 *J. Inorg. Nucl. Chem.* **43** 1267
 Lam S Y and Benoit R L 1974 *Can. J. Chem.* **52** 718
 Laurence G S 1956 *Trans. Faraday Soc.* **52** 236
 Morgan T D B, Stedman G and Whincup P A E 1965 *J. Chem. Soc.* 4813
 Prabhananda B S 1977 Proc. Symp. Fast Reactions, DAE, India, 317
 Prabhananda B S 1978 *J. Inorg. Nucl. Chem.* **40** 525
 Scott L P, Weeks Jr T J, Bracken D E and King E L 1979 *J. Am. Chem. Soc.* **91** 5219
 Sewald D and Sutin N 1963 *Inorg. Chem.* **2** 643
 Wilkins R G and Eigen M 1965 *Adv. Chem. Ser.* **49** 55