Contribution from the School of Chemistry The University of Western Australia Nedlands. 6009 Western Australia

The Mechanism of Interchange Reactions of Iron(III) in Dimethyl Sulphoxide

D.H. Devia and D.W. Watts

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The kinetic and equilibrium system in dimethyl

$$Fe(DMSO)_6^{3+} + SCN^- = FeSCN(DMSO)_5^{2+} + DMSO$$

sulphoxide (DMSO) has been studied. The results are compared with the analogous data for the aqueous system as a model to study the use of solvent activity coefficients in the diagnosis of mechanism in such interchange reactions at metal centres.

The results confirm a dissociative mechanism. The activation parameters for the anation process are $\Delta H^* = 86$ kJ mol^{-1} and $\Delta S^* = +160$ JK^{-1} mol^{-1}.

Introduction

Parker et.al.[1,2] have clearly shown the value of solvent activity coefficients in establishing the nature of transition states in a great variety of reactions including most recently some reactions of square planar platinium(II) and octahedral cobalt(III) complexes. For the most part Parker has studied the dependence of the rate of bimolecular nucleophilic attack by anionic nucleophiles on a series of substrates in a range of hydroxylic and dipolar aprotic solvents. Because of the much greater chemical potential of small anions in dipolar aprotic solvents compared with hydroxylic solvents, Parker has found that these bimolecular nucleophilic reactions are appreciably faster in aprotic media. Parker has expressed this difference in chemical potential in terms of solvent activity coefficients.

To date, because the majority of reactions studied at octahedral centres are either solvolytic or rate determined by a dissociation rate determining step, little value has been found in using solvent transfer activity coefficients in the discussion of these substitution reactions.

The establishment of the exact nature of the transition state in reactions of the type:

$$M(SOL_1)_6^{n+} + X^- = MX(SOL_1)_5^{(n-1)+} + SOL_1 \qquad (1)$$

where SOL_1 is the solvent medium and X^- an anion is equivocal with some severe complications arising from ion association pre-equilibria, and, when hydroxylic solvents are involved, solvolysis reactions producing both free and coordinated lyate ion. In addition the recent volume of activation work of Swaddle[3] suggests that the chromium(III) system, previously assumed to react by a dissociative mechanism,[4,5] exchanges the solvent water by a bimolecular mechanism.

These difficulties have encouraged us to compare the equilibrium and kinetic properties of reaction (1) in a manner which is not dissimilar from a chemical linear free energy relation but in a manner which, at least to us, appears to be based on less empirical considerations.

Consider the comparison of system (1) with the analogous system (2) in solvent (2):

$$M(SOL_2)_6^{n+} + X^- = MX(SOL_2)_5^{(n-1)+} + SOL_2 \qquad (2)$$

We will define the solvent activity coefficient for the transferable species X^- from solvent (1) to solvent (2), that is

$$\mu^1{}_{X^-} = \mu^2{}_{X^-} + RT\ln{}^2\gamma^1{}_X$$

where we have expressed the change in chemical potential (μ_{X^-}) of the solute (X^-) in a unimolar solution, ideal with respect to Henry's law, on transfer from a solvent (1) to a solvent (2) at a temperature T.

We have for the equilibrium constant from (1) and (2):

$$(K)_1 = \left(\frac{a_{MX(SOL_1)_5^{(n-1)+}}}{a_{M(SOL_1)_6^{n+}}}\right)_1 \frac{1}{(a_{X^-})_1} \quad \text{and} \qquad (3)$$

$$(K)_2 = \left(\frac{a_{MX(SOL_2)_5^{(n-1)+}}}{a_{M(SOL_2)_6^{n+}}}\right)_2 \frac{1}{(a_{X^-})_2} \qquad (4)$$

where $(a_{MX(SOL_1)_5^{(n-1)+}} / a_{M(SOL_1)_6^{n+}})_1$ signifies the value of the property in the solvent (1) etc. and (a_{X^-}) is the activity of X^-.

Thus

$$\frac{(K)_1}{(K)_2} = \frac{\left(\frac{a_{MX(SOL_1)_5^{(n-1)+}}}{a_{M(SOL_1)_6^{n+}}}\right)_1}{\left(\frac{a_{MX(SOL_2)_5^{(n-1)+}}}{a_{M(SOL_2)_6^{n+}}}\right)_2} \cdot \frac{(a_{X^-})_2}{(a_{X^-})_1} = {}^2K^1 \qquad (5)$$

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(1) A.J. Parker, *Chem. Rev. 69*, 1 (1969).

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(3) D.R. Stranks and T.W. Swaddle, *J. Am. Chem. Soc., 93*, 2783 (1971).

(4) C. Postmus and E.L. King. *J. Phys Chem. 59*, 1216 (1955).

(5) J.H. Espenson, *Inorg. Chem., 8*, 1554 (1969).

and
$$
{}^2K^1 = \frac{\left(\frac{a_{MX(SOL_1)_5^{(n-1)+}}}{a_{M(SOL_1)_6^{n+}}}\right)_1}{\left(\frac{a_{MX(SOL_2)_5^{(n-1)+}}}{a_{M(SOL_2)_6^{n+}}}\right)_2} \cdot {}^1\gamma^2{}_{X^-} \tag{6}
$$

We note immediately that when the solvent is involved as a coordinated species we cannot simplify this relation in terms of transfer activity coefficients for the complexes because, although they are very similar species, they are certainly not identical.

Now reactions (1) and (2) could be rate determined by either a dissociative unimolecular reaction:

$$
M(SOL)_6^{n+} \rightarrow \underset{\text{(transition state)}}{M(SOL)_5^{n+}} + SOL \tag{7}
$$

or an associative bimolecular mechanism:

$$
M(SOL)_6^{n+} + X^- \rightarrow \underset{\text{(transition state)}}{MX(SOL)_6^{(n-1)+}} \tag{8}
$$

or of course by some path between these extremes which at this stage need not concern us. We will use k_1 for rate constants for the unimolecular process and k_2 for the bimolecular process. We thus expect from the transition state theory:

$$
\frac{(k_1)_1}{(k_1)_2} = \frac{\left(\frac{a^*{}_{M(SOL_1)_5^{n+}}}{a_{M(SOL_1)_6^{n+}}}\right)_1}{\left(\frac{a^*{}_{M(SOL_2)_5^{n+}}}{a_{M(SOL_2)_6^{n+}}}\right)_2} = {}^2k_1{}^1 \tag{9}
$$

and

$$
\frac{(k_2)_1}{(k_2)_2} = \frac{\left(\frac{a^*{}_{MX(SOL_1)_6^{(n-1)+}}}{a_{M(SOL_1)_6^{n+}}}\right)_1}{\left(\frac{a^*{}_{MX(SOL_2)_6^{(n-1)+}}}{a_{M(SOL_2)_6^{n+}}}\right)_2} \cdot \frac{(a_{X^-})_2}{(a_{X^-})_1} = {}^2k_2{}^1 \tag{10}
$$

$$
{}^2k_2{}^1 = \frac{\left(\frac{a^*{}_{MX(SOL_1)_6^{(n-1)+}}}{a_{M(SOL_1)_6^{n+}}}\right)_1}{\left(\frac{a^*{}_{MX(SOL_2)_6^{(n-1)+}}}{a_{M(SOL_2)_6^{n+}}}\right)_2} \cdot {}^1\gamma^2{}_{X^-} \tag{11}
$$

where transition state activities are denoted a*.

If we compare (9) and (11) with (6) we have from (9) that:

$$
\frac{{}^2K^1}{{}^2k_1{}^1} = \frac{(a_{MX(SOL_1)_5^{(n-1)+}})_1}{(a_{MX(SOL_2)_5^{(n-1)+}})_2} \cdot \frac{(a^*{}_{M(SOL_2)_5^{n+}})_2}{(a^*{}_{M(SOL_1)_5^{n+}})_1} \cdot {}^1\gamma^2{}_{X^-} \tag{12}
$$

and from (11) that:

$$
\frac{{}^2K^1}{{}^2k_2{}^1} = \frac{(a_{MX(SOL_1)_5^{(n-1)+}})_1}{(a_{MX(SOL_2)_5^{(n-1)+}})_2} \cdot \frac{(a^*{}_{MX(SOL_2)_6^{(n-1)+}})_2}{(a^*{}_{MX(SOL_1)_6^{(n-1)+}})_1} \tag{13}
$$

The immediate qualitative inference that one is tempted to make on examinin (12), provided ${}^1\gamma^2{}_{X^-}$ is large (which is the case for small anions on transfer from water to dimethyl sulphoxide), is that for a unimolecular mechanism $\frac{{}^2K^1}{{}^2k_1{}^1}$ will be dominated by ${}^1\gamma^2{}_{X^-}$. If one neglects the identity of the coordinated solvent species and considers that a cationic solute will change its activity on solvent transfer only as a result of its charge and size then we have:

$$
\frac{{}^2K^1}{{}^2k_1{}^1} = \frac{{}^2\gamma^1{}_{(n-1)+}}{{}^2\gamma^1{}_{n+}} \cdot {}^1\gamma^2{}_{X^-} \tag{14}
$$

The basis of many of the extrathermodynamic assumptions used in establishing ionic solvent transfer activity coefficients is that very large cations differing by only unit charge will have identical coefficients, thus we could perhaps expect:

$$
\frac{{}^2K^1}{{}^2k_1{}^1} = {}^1\gamma^2{}_{X^-} \tag{15}
$$

Using the same set of assumptions for the model of a bimolecular transition state, that is from equation (13):

$$
\frac{{}^2K^1}{{}^2k_2{}^1} = 1 \tag{16}
$$

The assumption, that one can neglect the identity of the coordinated solvent species and only consider the transfer property of a general charged species of course is not valid when taken in isolation, but above it is not, and the real assumption made is likely to be very reasonable, at least when one limits the use of (15) and (16) as diagnostic tests of mechanism to those systems where ${}^1\gamma^2{}_{X^-}$ is large. The real assumption in reaching (15) is that the difference between:

$$
\frac{(a_{MX(SOL_1)_5^{(n-1)+}})_1}{(a_{MX(SOL_2)_5^{(n-1)+}})_2} \text{ and } {}^2\gamma^1{}_{(n-1)+}
$$

for a single species on transfer will be compensated by the differences between

$$
\frac{(a^*{}_{M(SOL_2)_5^{n+}})_2}{(a^*{}_{M(SOL_1)_5^{n+}})_1} \text{ and } \frac{1}{{}^2\gamma^1{}_{n+}}
$$

or that in similar systems the differences which exist between the values of two sets of successive equilibrium constants will be similar. A similar assumption is inherent in reaching (16). We are admitting then that these is an inherent difference in ground state free energy in the two systems as one replaces (SOL_1) by (SOL_2) but that this differences is also reflected in a compensating difference in the transition state free energy.

In qualitative terms, equation (15) suggests that if the anation reaction is unimolecular a comparison of the way in which the stability constant transfers (${}^2K^1$) and the rate constant transfers (${}^2k_1{}^1$) will show them to differ by a factor ${}^1\gamma^2{}_{X^-}$, while if the reaction is bimolecular the equilibrium constants and, the rate constants will transfer similarly. To a first approximation then ${}^2K^1$ and ${}^2k_2{}^1$ for a bimolecular mechanism will be found to be equal to $^{1}\gamma^{2}_{X^-}$ while $^{2}k^{1}_{1}$ (for a unimolecular model) will be unity showing an independence of rate to solvent transfer. If then $^{1}\gamma^{2}_{X^-}$ is large, as it is for anions on transfer from dipolar aprotic solvents to water, then we have a sensitive insight into mechanism.

The purpose of this paper is to test the value of relationships (15) and (16) in the diagnosis of mechanism for the systems where M^{n+} is Fe^{3+}, $X^- = SCN^-$, and (SOL_1) and (SOL_2) are dimethyl sulphoxide (DMSO) and water, a pair of solvents for which $^{1}\gamma^{2}_{NCS^-}$ is substantial.

The red complexes formed by ferric and thiocyanate ions have been studied by numerous workers[6-10]. The formation of the pentaaquomonoisothiocyanato-iron-(III) complex was studied in detail by Below, Connick and Coppel[8] in aqueous solution and by Weaver[9] at low temperatures using 80% methanol-water mixtures as solvent. Lister and Rivington[7] have done extensive equilibrium studies.

Two mechanisms have been considered, firstly the associative mechanism:

$$Fe(OH_2)_6^{3+} + SCN^- \rightarrow (Fe(SCN)(OH_2)_6^{2+})^* \rightarrow Fe(SCN)(H_2O)_5^{2+} + H_2O$$

involving a seven coordinate intermediate and secondly a dissociative mechanism:

$$Fe(OH_2)_6^{3+} \rightarrow (Fe(OH_2)_5^{3+})^* + H_2O$$

$$(Fe(OH_2)_5^{3+}) + SCN^- \rightarrow Fe(SCN)(OH_2)_5^{2+}$$

This second mechanism requires that the entering thiocyanate competes with water molecules for the intermediate. The rate of thiocyanate entry will be limited to something like the water exchange rate in the free complex ion and the thiocyanate entry rate will be thiocyanate ion concentration dependant while this concentration affects the standing concentration of ion associated aggregates of the type $Fe(OH_2)_6^{3+} \cdot (SCN^-)$, since only thiocyanate ions in the inner solvation sphere of the complex can be expected to compete with the solvent for entry into the coordination sphere. Thiocyanate entry is base catalysed through hydroxo-species and these results are complicated by the existence of binuclear species.

The results in methanol[10] show an increased rate of anion entry which has been correlated with the lower dielectric constant of methanol which increases the electrostatic interaction of the thiocyanate ion with the complex, or with the lower dipole moment of methanol which leads to weaker ferric methanol bonds.

Less work has been done on the ferric system in DMSO although Langford and Chung[11] have studied the DMSO exchange rate by proton magnetic resonance procedures and Wada, Yoshizawa and Sakamoto[12] have determined both the first and second stability constants for thiocyanate complexation incidental to following Fe^{2+}–Fe^{3+} electron exchange in DMSO.

Experimental Section

Ferric perchlorate from the Kanto Chemical Company was used. The solutions in DMSO were found to contain insignificant chloride and the effects of trace water were evaluated by the deliberate addition of controlled amounts (see later). Stock solutions of iron(III) were analyzed by the Zimmerman-Reinhardt method[13]. Sodium thiocyanate was recrystallized from ethanol and standardized against silver nitrate. The ionic strength of solutions was controlled by the addition of Unilab AR sodium perchlorate. Ajax technical grade DMSO was purified as previously[14].

A Durrum Stopped-Flow Spectrophotometer was used for all rate measurements following checks that mixing was complete in 2 milliseconds. The reacting solutions were thermostatted to ± 0.1°C. In most kinetic studies, following Below, Connick and Coppel[8], the ferric ion concentration (10^{-3}dm^{-3}mol) was held in large excess of the thiocyanate concentration (*ca.* 10^{-5}dm^{-3}mol) to avoid the formation of complexes containing more than one thiocyanate ligand. This procedure effectively controlled the ionic strength as the thiocyanate concentration was varied. All optical densities were measured at 460 nm. The summated errors in the constants were estimated at ± 2.5% and the rate constants were found to be reproducible to ± 1.5%.

The equilibrium measurements were made at ferric concentrations of 5×10^{-3}dm^{-3}mol and thiocyanate ion concentrations from 5×10^{-5}dm^{-3}mol — 3×10^{-4}dm^{-3}mol. All optical density measurements (at 460 nm) were made in 1 cm. quartz cells in a thermostatted cell block of a Perkin Elmer 450 Spectrophotometer. The transmission results were treated by a modification of the methods of Rabinowitch and Stockmayer[15] yielding concentration based equilibrium constants. The extinction coefficient of the $[Fe(SCN)(DMSO)_5]^{2+}$ species was found to be 2970 at 460 nm. In all these measurements the ionic strength was controlled at 3.58×10^{-2}dm^{-3}mol using sodium perchlorate.

Results

Table I shows the first order rate constants for $[FeSCN(DMSO)_5]^{2+}$ formation from $[Fe(DMSO)_6]^{3+}$ over a range of thiocyanate ion concentrations but at constant ionic strength. These results show the reproducibility achieved. The results in Table II show the dependence of the rate constants for the same reaction on ionic strength for constant reagent concentrations. The results give a linear log k *v.* $\sqrt{I}$ plot of slope −1.72 which compares unfavourably with a slope of −6.4 predicted for bimolecular reaction between ferric and thiocyanate ions.

The method of making solution meant that the

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Table I. First Order Rate Constants for the Reaction $Fe(DMSO)_6^{3+} + SCN^- \rightarrow [FeSCN(DMSO)_5]^{2+} + DMSO$ at 25° and on Ionic Strength of $5.95 \times 10^{-3} dm^{-3} mol$.

$[Fe(DMSO)_6^{3+}]$ $dm^{-3}mol$	$[SCN^-]$ $dm^{-3}mol.$	k s^{-1}	$t_{1/2}$ s
0.99×10^{-3}	5.10×10^{-5}	0.86	0.80
»	5.10×10^{-5}	0.85	0.81
»	$5.1\text{-}0 \times 10^{-5}$	0.87	0.79
0.99×10^{-3}	10.2×10^{-5}	0.86	0.80
»	10.2×10^{-5}	0.88	0.78
»	10.2×10^{-5}	0.88	0.78
»	10.2×10^{-5}	0.87	0.79
0.99×10^{-3}	15.3×10^{-5}	0.89	0.78
»	15.3×10^{-5}	0.91	0.76
»	15.3×10^{-5}	0.89	0.78
»	15.3×10^{-5}	0.89	0.78

Table II. Dependence of First Order Rate Constant for $[FeSCN(DMSO)_5]^{2+}$ Formation on Ionic Strength (I) at 25° $[Fe(DMSO)_6^{3+}] = 0.99 \times 10^{-3} dm^{-3} mol$ and $[SCN-] = 5.095 \times 10^{-5} dm^{-3} mol$.

$I \times 10^3$ $dm^{-3}mol$	k s^{-1}
5.952	0.86
7.085	0.83
10.22	0.78
16.62	0.71
20.88	0.66

Table III. Dependence of First Order Rate Constants for $[FeSCN(DMSO)_5]^{3+}$ Formation on Temperature. $[Fe(DMSO)_6^{3+}] = 0.99 \times 10^{-3} dm^{-3} mol$ and $[SCN^-] = 5.09 \times 10^{-5} dm^{-3} mol$. $I = 5.95 \times 10^{-3} dm^{-3} mol$.

Temperature	k s^{-1}
23.2°	0.82
25.0°	0.86
27.8°	1.14
29.5°	1.51
30.0°	1.55
34.1°	2.35

Table IV. Dependence of the First Order Rate Constant [a] for $[FeSCN(DMSO)_5]^{2+}$ Formation on $Fe(DMSO)_6^{3+}$ Concentration at 25° and Ionic Strength of $7.2 \times 10^{-3} dm^{-3} mol$.

$10^4[Fe(DMSO)_6^{3+}]$ $dm^{-3}mol.$	k s^{-1}	1/k s	$\frac{10^{-3}}{[Fe^{3+}]}$ dm^3mol^{-1}
1.19	.102	9.8	8.90
1.62	.140	7.1	6.18
2.39	.207	4.83	4.19
4.77	.431	2.32	2.10
7.16	.73	1.37	1.40
9.54	.86	1.16	1.05
11.9	1.38	0.72	0.84

[a] Determined here, because $[Fe(DMSO)_6^{3+}]$ is not in great excess over $[SCN^-]$, from second order constants.

DMSO solutions of $[Fe(DMSO)_6]^{3+}$ inevitably contained about 0.2% water. It was shown that water concentration up to 1% had no effect on the substitution kinetics although amounts greater than this had appreciable and to some extent erratic consequences.

The rate data collected in Table III measured over a range of temperatures, constant reagent concentrations and constant ionic strength yields an activaion energy (ΔH^*) of 86 kJ mol^{-1} and an activation entropy (ΔS^*) of 160 $JK^{-1}mol^{-1}$.

Table IV shows data on the dependence of the same rate constant on $[Fe(DMSO)_6^{3+}]$. Here because the $[Fe(DMSO)_6^{3+}]$ is not greater than $[SCN^-]$ in all cases we have determined second order rate constants.

The equilibrium results treated by a Rabinowitch-Stockmayer plot gave a concentration based equilibrium constant for the reaction of 3.35×10^3 at 25°

$$Fe(DMSO)_6^{3+} + SCN^- = [FeSCN(DMSO)_5]^{2+}$$

and $I = 3.58 \times 10^{-2} dm^{3-} mol$. Assuming, at these low concentrations, that the Debye-Hückel Limiting Law will give a reasonable approximation to ionic activity coefficients the corrected thermodynamic equilibrium constant under these same conditions is 5.0×10^4-dm^3mol^{-1}.

Discussion

The work of Below, Connick and Coppel[8] on the reaction between feric and thiocyanate in aqueous solution has been mentioned earlier. They find it difficult to decide between the associative and dissociative models for the transition state. It is argued that in principle the entropies of activation can be used to distinguish between the models. The entropy of activation for a seven-coordinated activated complex would be expected to be appreciably more negative than for the five-coordinated activated complex, because an additional water molecule is bonded in the former. The difference may be as great as 33 $JK^{-1}mol^{-1}$. The observed entropy of activation -21 ± 21 $JK^{-1}mol^{-1}$ could be taken as evidence for the associative mechanism. However the uncertainties in the entropies and in the estimated values expected for the two models is great and little reliance can be placed on such arguments.

In the present solvent system the entropy of activation is 160 $JK^{-1}mol^{-1}$ which is a large positive value with a good degree of reliability and on the basis of the above argument supports a dissociative mechanism.

Before relationships (15) and (16) can be checked against the experimental results for ${}^2K^1$, ${}^2k_1{}^1$ and ${}^2k_2{}^1$ a decision must be made concerning the appropriate ionic strengths at which to compare the values of $(K)_1$ and $(K)_2$, $(k_1)_1$ and $(k_1)_2$ and $(k_2)_1$ and $(k_2)_2$ as determined in the two solvents. There is no doubt that the most appropriate is to measure all these equilibrium and rate constants as a function of ionic strength and to extrapolate to infinite dilution. However not all the aqueous data is available in this form and we have compared our data in DMSO, which has been studied over a range of ionic strengths, with the aqueous data measured at that ionic strength which yields identical Debye Hückel activity coefficients under the conditions of the measurement. In this way we believe specific differences between the systems will be reflected in the compared data, while activity differences from solution non-ideality derived from long range electrical forces will be allowed for, in that they will be comparable in the sets of data for each solvent.

On this basis ${}^{2}K^{1} = 10^{2.5}$ based on $(K)_1 = 172$ dm^3mol^{-1} in water at an ionic strength of 0.286 dm^3 mol at 25° (i.e. $\gamma_\pm = 0.25$) and $(K)_2 = 5.4 \times 10^4$ dm^3mol^{-1} in water at an ionic strength of $3.58 \times 10^{-2}dm^{-3}mol$ at 25° (i.e. $\gamma_\pm = 0.25$). The kinetic data has been compared for $\gamma_\pm = 0.704$ (i.e. ionic strength of $1 \times 10^{-2}dm^{-3}mol$ in water and $2.29 \times$ $\times$ $10^{-3}dm^{-3}mol$ in DMSO) and at 25°C yields ${}^{2}k_2{}^{1} =$ $= {}^{2}k_1{}^{1} = 10^{-1.25}$.

The first and most important observation is that ${}^{2}K^{1}$ ($10^{2.5}$) is extremely close to the accepted value of ${}^{1}\gamma^{2}{}_{SCN}$ which is $10^{2.6}$ which clearly supports the idea that the dominant term in the determination of the change in the equilibrium constant with solvent is the variation in the activity of the anion. This observation leads to the totally justifiable conclusion that if the anation reaction is bimolecular in nature then ${}^{2}k_2{}^{1}$ will also be of the order $10^{2.6}$ or that the anation reaction will be $10^{2.6}$ faster in DMSO, since as in (16) ${}^{2}K^{1}$ / ${}^{2}k_2{}^{1}$ should be unity.

The observation is that the reaction is slower in DMSO than in water which is incompatible with a bimolecular mechanism. This is shown by the values of ${}^{2}k_2{}^{1}$and ${}^{2}k_1{}^{1}$. This observation of a slower rate for reaction rates determined by the breaking of a metal-DMSO bond is consistent with rates in related systems which have correlated with M-SOL bonds decreasing in strength in the order SOL = DMSO>DMF> >DMA$\simeq H_2O$[16].

This incompatibility with a bimolecular mechanism is also reflected in the dependence of the rate constants on ionic strength which in DMSO yields a log k v. $\sqrt{I}$ plot of slope –1.72 compared with the predicted –6.40. This prediction is identical to the slope predicted for the dissociative model of Eigen[17] and Langford and Chung[11]. It is clear that simple Debye Hückel theory is inadequate in these systems and further the significantly lower dependence of rate constant appears to be typical of this class of reaction. A similar set of data for the entry of SCN^-, N_3^- and Cl^- into $Cr(DMSO)_5{}^{3+}$ in DMSO shows this small dependence of rate on ionic strength[18].

The dissociative model of Langford and Chung[11]:

$$Fe(DSO)_6{}^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe(DMSO)_5{}^{3+} + DMSO$$

$$SCN^- + Fe(DMSO)_5{}^{3+} \xrightarrow{k_2} FeSCN(DMSO)_5{}^{2+}$$

$$SCN^- + Fe(DMSO)_6{}^{3+} \overset{K_{IP}}{\rightleftarrows} Fe(DMSO)_6{}^{3+} \ldots\ldots SCN^-$$

$$Fe(DMSO)_6{}^{3+} \ldots\ldots SCN^- \xrightarrow{k_3} FeSCN(DMSO)_5{}^{2+} + DMSO$$

where the rate constants (k) and the ion association constant (K_{IP}) are defined as shown, yields, if $[SCN^-]_F$ and $[SCN^-]_T$ are free and total unreacted thiocyanate concentrations that where γ^{3+} etc are molar

$$\frac{d[PRODUCT]}{dt} = \frac{k_1k_2[SCN^-]_F[Fe^{3+}]}{k_{-1}+k_2[SCN^-]_F} + k_3K_{IP}[Fe^{3+}][SCN^-]_F\frac{\gamma^{3+}\gamma^-}{\gamma^{2+}} \qquad (17)$$

activity coefficients of species of charge +3 etc, and for convenience $[Fe^{3+}]$ is used for $[Fe(DMSO)_6{}^{3+}]$.

In order to further test the dissociative model some data (Table IV) was obtained as a function of $[Fe^{3+}]$ where $[Fe^{3+}]$ is not in excess of $[SCN^-]_T$. Here second order rate constants were determined because the data confirmed rate dependence on both reactants and thus that K_{IP} was of such a value that ion pairing was incomplete. Under these conditions equation (17) predicts an experimental second order constant (k^*_{expt}) which rearranges to give an effective

$$k^*_{expt} = \frac{k_3K_{IP}\dfrac{\gamma^{3+}\gamma^-}{\gamma^{2+}}}{1+K_{IP}(\dfrac{\gamma^{3+}\gamma^-}{\gamma^{2+}})[Fe^{3+}]} \qquad (18)$$

initial (t=O) first order rate constant $k_{expt} = k^*_{expt}$ $[F^{3+}]_{t=o}$ in the relation:

$$\frac{1}{k_{expt}} = \frac{1}{k_3} + \frac{1}{k_3K_{IP}\dfrac{\gamma^{3+}\gamma^-}{\gamma^{2+}}} \cdot \frac{1}{[Fe^{3+}]_{t=0}}$$

The figure shows a plot of ($1/k_{expt}$) against $1/[Fe^{3+}]_{t=o}$ which yields from the intercept a value of $k_3=50\ s^{-1}$ and a value of $(K_{IP}\gamma^{3+}\gamma^-/\gamma^{2+})$ from the inter-

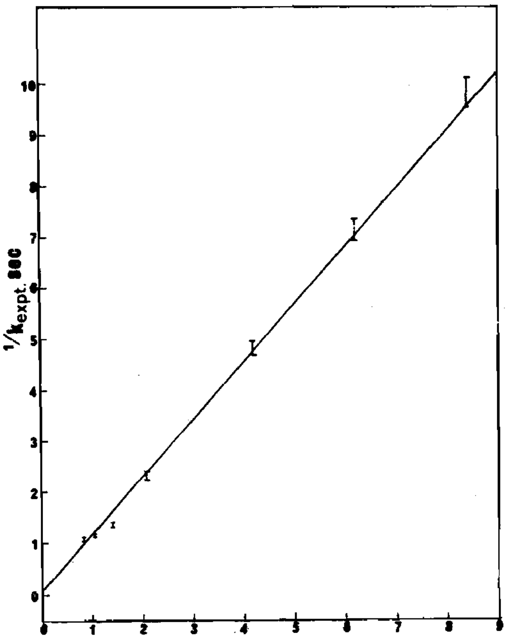

Figure 1. The Dependence of k_{expt} on $[Fe^{3+}]_{t=0}$ at 25° and an Ionic Strength of $7.2\times10^{-3}dm^{-3}mol$.

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(16) D.W. Watts, "Physical Chemistry in Organic Solvent Systems", Plenum Press, London, in press.

(17) M. Eigen and R.G. Wilkins in "Mechanism of Inorganic Reactions", Ed. R.K. Marmann, R.T.M. Fraser and J. Bauman, *Advances in Chemistry series 49, Am. Chem. Soc., Washington, D.C.*, 1965, p. 55.

(18) D.S.T. Lo, Ph.D. Thesis, University of Western Australia.

cept and slope of 20. These values depend on an extrapolation to $1/[Fe^{3+}]_{t=0} = 0$ and this procedure cannot be precise. A reasonable estimate of the possible error would be ± 50%. These figures are however of considerable interest particularly when compared with the recent results of Langford and Chung[11].

These workers measured the exchange of DMSO with $Fe(DMSO)_6^{3+}$, k_1 in our mechanism, and find a value of 50 s^{-1} at 25°. This value based on their estimated limits of accuracy could be as great as 108 s^{-1} and as low as 2 s^{-1} at 25°. Further Langford and Chung calculate a value of our k_3 based on $K_{IP} = 106$, estimated from the Fuoss Theory[19]. It is interesting that with this value at K_{IP} and their concentration, the value of the second order rate constant is not k_3K_{IP} because the denominator in expression (18) cannot be taken as unity. Our experimental value of $(K_{IP}\ \gamma^{3+}\gamma^{-}/\gamma^{2+})$ would allow this approximation and yelds a value of k_3, based on their results, of 33 s^{-1} at an ionic strength of 0.024 $dm^{-3}mol$. Our own data based on the application of relation (18) gives a k_3 value of 43 s^{-1} at an ionic strength of $5.95 \times 10^{-3} dm^{-3}mol$.

These comparisons point to the compatibility of these two investigations and of course with our other evidence must leave little doubt of the validity of the dissociative mode of reactions in this anation reaction.

Perhaps tthe most interesting point lies not in the rates but in the activation parameters. The Langford and Chung values for the solvent exchange are $E_a = 42$ kJ mol^{-1} and $\Delta S^* $ is -46 $JK^{-1}mol^{-1}$ while our results for the thiocyanate interchange reaction yield $\Delta H^* = 86$ kJ mol^{-1} and $\Delta S^* = +160$ $JK^{-1} mol^{-1}$. These results show that while k_1 and k_3 are comparable at 25°C ($k_1 = 50$ s^{-1} and $k_3 = 43$ s^{-1}) they differ widely at 100°C, the temperature at which k_1 was measured, where the respective values would be $k_1 = 1400$ s^{-1} and $k_3 = 36{,}000$ s^{-1}.

While uncertainties exist in both these set of activation parameters (Langford and Chung estimate ± 20% in theirs and our estimate is ± 3% for the anation results) there must be a substantial difference, at least 31 kJ mol^{-1}, in the values of E_a for the two processes. Such results are not incompatible since as we have emphasized before,[16] the free ion and the ion pair are different species and will thus react through different transition states. There is no requirement that the free energy change associated with the ion pairing of a substrate will be reflected in the change induced by this ion pairing in the transition state. These results further emphasize that to make statistical interpretations on the fates of intermediates based on the ratios of k_3 and k_1 as some have been tempted to do is not a fruitful occupation. If the activation parameters are as widely separated as in this system the considerations apply only at one temperature and may prove embarrassing if considered at other temperatures.

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