Inorganica Chimica Acta, 40 (1980) 273–276
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Effect of D_2O on the Rate and Activation Parameters of the Dissociation of Tris-(2,2'Bipyridine) and Tris-(1,10-Phenanthroline)Fe(II) Complexes in HCl

SAROJA RAMAN

Department of Soil Science & Agricultural Chemistry, A. P. Agricultural University, Hyderabad-500 030, India

Received December 17, 1979

The rates of dissociation of tris(2,2'-bipyridine)-Fe(II) and tris-(1,10-phenanthroline)Fe(II) complexes are lower in D_2O at 1.0, 0.1 and 0.01 N HCl, by about 10–20%. Gibb's free energy of activation in all the cases is higher in D_2O. Differences in enthalpy and entropy of activation are insignificant. However, the variation of rate with the percentage of D_2O, and the applicability of Barclay–Butler relationship between $(\Delta H^{\ddagger})_{H_2O\to D_2O}$ and $(\Delta S^{\ddagger})_{H_2O\to D_2O}$ strongly suggest that the differences in rates are primarily due to differences in the free energy of solvation of the initial and transition states in H_2O and D_2O.

Introduction

It is well established that addition of salts and solvents bring about serious alterations in the structure of water. The regions and the amounts of order and disorder prevailing under normal conditions in pure water, are subject to distortion, the magnitude of which depends on the nature and quantities of substances added. Monovalent cations like Na^+, K^+, Cs^+, Rb^+, etc. are structure breakers while Li^+ and the tetraalkylammonium ions (higher than methyl) are structure makers. These effects have already been exhaustively reviewed [1–4].

It has been shown that changes in the structure of water by added salts or solvents may alter the kinetics and activation parameters of several reactions. The nature and the extent of this effect depends primarily on the conditions prevailing around the initial state of the reactants and the transition state complex, particularly when the role of water is crucial. The effect of added salts on the activation parameters in the acid catalysed dissociation of tris-5-nitrophenanthroline Fe(II) complex and 2,2'-bipyridine Fe(II) complex have been reported earlier [5, 6]. Divalent metal cations also effect the rate of dissociation of tris bipyridine and tris phenanthroline Fe(II) complex [7].

D_2O, while retaining several of the general properties of water, is a unique solvent, because of its enhanced structure and on account of the profound differences in the O–D and O–H bonds, arising mainly out of the mass effect of the two isotopes. Thus there is a definite solvent effect of D_2O in the kinetics of several reactions. The most useful and important effect is exhibited for reactions which involve a protonation equilibrium in the kinetics or the breaking or formation of an O–H/O–D bond [8, 9]. It has been possible to categorically establish the mechanism of several reactions on the basis of this alone. The kinetic course of reactions where such processes are not present may be affected by the increased structure of D_2O and/or by its lower basicity just as in the case of added salts, especially if water molecules take up an intimate role in the transition complex. The present investigation deals with the kinetics of tris 2,2'-bipyridine, and tris 1,10-phenanthroline Fe(II) cations in about 98% D_2O.

Materials and Methods

All reagents were of AR grade. All solutions were made in D_2O of isotope purity > 99.9%, supplied by the Bhabba Atomic Research Centre, Trombay, India. The complexes were formed by mixing stoichiometric proportions of ferrous ammonium sulphate and the ligand. The dissociations of all the three complexes were studied spectrophotometrically in 1.0 N, 0.1 N and 0.01 N HCl as first order reactions till at least 2 half lives for the slow runs and to practically completion for the others. Dissociation of tris phenanthroline Fe(II) in 0.01 N HCl was reversible at very early stages and hence only the first 5 minute data (where reverse rate was insignificant) was used for estimating rates. The activation parameters were calculated from the effect of temperature on the rate constants, using the transition state theory.

Results and Discussion

The rates of dissociation for both the complexes in acids of different concentrations in H_2O and D_2O

TABLE I. Rate Constants.[a]

Temperature (K) ±0.2	1.0 *M* HCl		0.1 *M* HCl		0.01 *M* HCl	
	H_2O (R × 10^3 sec^{-1})	D_2O	H_2O (R × 10^3 sec^{-1})	D_2O	H_2O (R × 10^3 sec^{-1})	D_2O
Rate of Dissociation of Tris(2,2'-Bipyridine) Fe(II) Complex in HCl						
303.3	1.7	1.25	0.56	0.38	0.27	0.22
308.5	3.22	2.56	1.07	0.78	0.57	0.47
313.5	6.97	5.5	2.2	1.7	1.3	1.08
318.5	13.8	10.7	4.27	3.3	2.46	2.3
Rate of Dissociation of Tris(1,10-Phenanthroline) Fe(II) Complex in HCl						
303.0	0.16	0.13	0.17	0.15	0.15	0.14
308.0	0.37	0.30	0.37	0.33	0.37	0.33
313.5	0.90	0.74	0.90	0.82	0.91	0.82
318.5	2.0	1.65	2.1	1.80	2.05	1.75
323.0	4.0	3.5	3.9	3.6	4.0	3.40

[a]Rates are averages of at least four runs. The average difference in rates between replicates in most cases was less than ±4%.

TABLE II. Activation Parameters.

Complex	Acid Concentration	$\Delta H^{\ddagger}$ (kcal M^{-1})		$\Delta S^{\ddagger}$ (e.u. M^{-1})	
		H_2O	D_2O	H_2O	D_2O
Tris-2,2'-bipyridine Fe(II)	1.00	27.1 ± 0.5	26.6 ± 0.5	18.0 ± 1.7	15.8 ±1.6
	0.10	25.5 ± 0.4	26.9 ± 0.4	10.7 ± 1.4	14.6 ±1.2
	0.01	27.5 ± 0.6	28.9 ± 0.3	15.8 ± 1.7	20.2 ±1.0
Tris-1,10-phenanthroline Fe(II)	1.00	31.6 ± 0.7	30.9 ± 0.5	28.2 ± 2.1	25.8 ±1.5
	0.10	31.6 ± 0.7	30.9 ± 0.6	28.3 ± 1.8	26.0 ±1.7
	0.01	31.8 ± 0.5	30.9 ± 0.6	29.1 ± 1.5	25.7 ±1.8

are given in Table I. The rates were lower in D_2O. The ratio k_{H_2O}/k_{D_2O} is *ca.* 1.1 to 1.2 for tris bipyridine complex. The activation parameters are given in Table II. It is evident that $\Delta G^{\ddagger}$ is higher in D_2O in all cases. Significance could not be attached to the differences in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, calculated from the dependence of rate on temperature, because the uncertainty of experimental values was comparable with the probable differences in these parameters.

The mechanism of dissociation of these complexes is well established, the rate determining step being proton independent initial breaking of Fe–N bond in the tris bipyridine complex, followed by a proton aided/unaided process. In the case of trisphenanthroline complexes the dissociation is totally proton independent and involves breaking of Fe–N bonds [10, 11]. In either case, the transition state does not involve any bond breaking or making steps involving protons and also the initial and transition states are both divalent. Hence it is reasonable to assume that the differences in rates observed in H_2O and D_2O should arise only as a result of solvent isotope effect on the solvation of the transition state intermediate and the initial state.

The differences in the free energy of solvation of cations in H_2O and D_2O have been obtained from ΔG of transfer from H_2O to D_2O. $\Delta G_{H_2O \rightarrow D_2O}$ is +Ve for simple cations and –Ve for large cations like higher tetraalkylammonium cations, involving hydrophobic alkyl chains [12]. In all these cases, however, there is a compensation between ΔH and ΔS of transfer. The rate differences for the dissociation of the cationic complexes in the present study undoubtedly arise from solvation differences in the initial and transition states, with net $\Delta G^{\ddagger}_{D_2O} > \Delta G^{\ddagger}_{H_2O}$ in all cases. But, whether the initial and transition states are individually stabilized or destabilized (whether Fig. 1A or 1B is true) cannot be answered unless

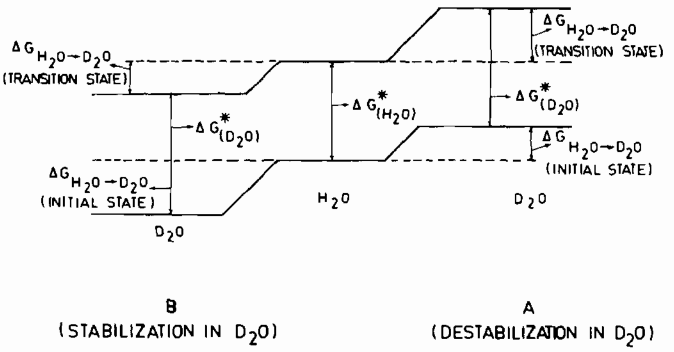

Fig. 1. Change in free energy of initial and transition states on transfer from H_2O to D_2O.

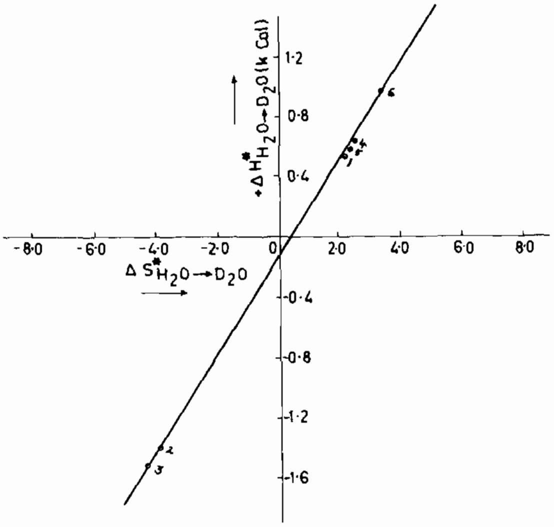

Fig. 2. Barclay–Butler curve for excess enthalpy $(\Delta H^{\ddagger}_{H_2O} \rightarrow D_2O)$ *vs.* excess entropy $(\Delta S^{\ddagger}_{H_2O} \rightarrow D_2O)$ of activation. 1, 2, 3: $Fe(Bipy)_3^{2+}$ 1.0, 0.1 and 0.01 N HCl. 4, 5, 6: $Fe(Ph)_3^{2+}$ in 1.0, 0.1 and 0.1 N HCl.

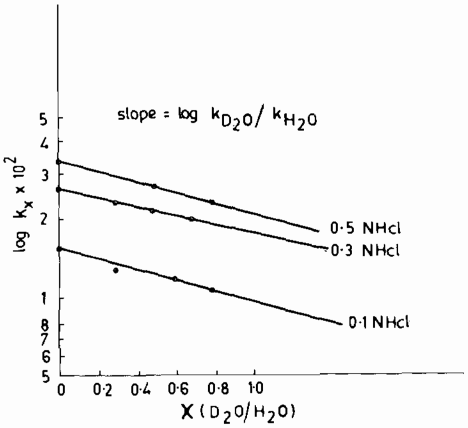

Fig. 3. Rate of dissociation of $Fe(Bipy)_3^{2+}$ in various D_2O–H_2O mixtures.

specific thermodynamic functions for transfer are available for these ions [5]. Intuitively, these complex cations with large hydrophobic aromatic sheath of the ligands, should behave more like higher tetraalkylammonium cations rather than as simple hydrated cations. In any case, the results show that the net difference in ΔG of solvation between the initial and transition states is unfavourable in D_2O.

Although the experimental uncertainties in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ preclude rigorous conclusions being drawn, it is significant that the Barclay–Butler linear relationship found for the transfer parameters (ΔH and ΔS) for neutral salts and single ions from H_2O to D_2O is also applicable to the present situation. $(\Delta H^{\ddagger})$-$H_2O \rightarrow D_2O$ is linearly related to $(\Delta S^{\ddagger})_{H_2O \rightarrow D_2O}$ with a slope of ≈300, where $(\Delta H^{\ddagger})_{H_2O \rightarrow D_2O}$ and $(\Delta S^{\ddagger})H_2O \rightarrow D_2O$ are the differences in the enthalpy and entropy of activation respectively for a change in H_2O to D_2O as solvent. The slope is thus very close to that of 298, found for the transfer of neutral salts from H_2O to D_2O [15–17] (Fig. 2).

Earlier work on the rate of dissociation of these complexes in various H_2O–D_2O mixtures shows that $(k_x/k_H) = (k_D/k_H)^x$ where k_x is the rate constant in the D_2O–H_2O mixture, x is the ratio of D_2O to H_2O and k_H and k_D are rate constants in pure H_2O and D_2O [10, 18] (Fig. 3). This is in agreement with solvent isotope effect for reactions involving similar initial and transition states, where rate differences are attributable only to solvation effects [20].

A reference to the qualitative similarity between the present study and the kinetics of solvation of some alkyl halides for which k_{H_2O}/k_{D_2O} is slightly >1, may be of interest. The difference in rates in these cases is attributed to the difference in the vibrational frequencies of the solvating H_2O and D_2O molecules, which arises as a result of the unique structure of water, involving a dynamic equilibrium between bulky H-bonded entities and dense regions with much less degree of H-bonding [19, 20].

References

1 M. J. Blandamer and J. Burgess, *Chem. Soc. Rev., 4,* 55 (1975).
2 T. S. Sarma and J. C. Ahluwalia, *Chem. Soc. Rev., 2,* 203 (1973).
3 'Water, A comprehensive Treatise', Ed. F. Franks, Plenum Press, London, Vol. 3 (1973).
4 M. J. Blandamer, *Quart. Rev., 24,* 169 (1970).
5 M. J. Blandamer, J. Burgess and S. H. Morris, *J. Chem. Soc. Dalton, 16,* 1717 (1974).
6 S. Raman, *J. Inorg. Nucl. Chem., 40,* 1073 (1978).
7 A. P. Chagas, M. Tubino and E. J. S. Vichi, *Inorg. Chim. Acta, 28,* L137 (1978).
8 'Isotope Effects in Chemical Reactions', Ed. C. J. Collins and N. S. Bowman, A.C.S. Monograph, Academic Press (1970).
9 K. B. Wiberg, *Chem. Rev., 55,* 713 (1955).
10 S. Raman, *J. Inorg. Nucl. Chem., 37,* 1747 (1975).
11 'Mechanism of Inorganic Reactions', by F. Basolo and R. G. Pearson, Wiley (1967), p. 218.
12 'Thermodynamics of Ion Hydration', by H. L. Friedman and C. V. Krishnan, in Ref. 3, page 1.
13 J. Burgess and R. H. Prince, *J. Chem. Soc.,* 1772 (1966).
14 G. A. Lawrance and D. R. Stranks, *Inorg. Chem., 16,* 929 (1977).
15 H. S. Frank, *J. Chem. Phys., 13,* 493 (1945).
16 H. S. Frank and M. W. Evans, *J. Chem. Phys., 13,* 507 (1945).
17 R. Lumry and S. Rajender, *Biopolymers, 9,* 1125 (1970).
18 J. Burgess and R. H. Prince, *J. Chem. Soc. A,* 434 (1967).
19 'Water, A Comprehensive Treatise', Ed. F. Franks, Vol. 1, Plenum Press, New York, London (1973).
20 'Origin and Interpretation of Isotope Effects', by E. K. Thornton and E. R. Thornton, in Ref. 8.