tilled over phosphorus(V) oxide, methanol was distilled from magnesium, and thiophene-free benzene was distilled from calcium hydride.

Apparatus.—The temperatures of samples and reagents were maintained constant with a Sargent S-8405 bath rated at ±0.01°. Lower temperatures required the use of a cooling coil through which Freon was passed. A Haak thermostat and pump (Model F) were used to circulate thermostated water through jacketed cells in the Cary 14 spectrophotometer. While most measurements were made in solutions prepared by routine mixing and delivery to the cell, the more rapid rates were measured by use of a spring syringe of the type described by Gordon.[8] The kind assistance of Dr. Gordon in duplicating the syringe is greatly appreciated. Spectral scans and rate measurements were recorded on the Cary 14 spectrophotometer.

Procedures for Rate Measurements.—All solutions and cells were equilibrated at reaction temperature prior to initiation of reactions. Manual mixing techniques permitted first measurements to be made some 10–20 sec after mixing. Time was recorded on a Kodak timer and chart speed of 5 in./min (Cary 14) was used. The use of the spring syringe permitted measurements to be made during the first few seconds of reaction as well. Our techniques are detailed elsewhere.[7,9]

(8) G. Gordon, *J. Sci. Instr.*, **41**, 480 (1964).
(9) E. L. Blinn and D. H. Busch, *J. Am. Chem. Soc.*, in press.

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Substitution Reactions of Metallic Complexes of β,β′,β″-Triaminotriethylamine. III. Kinetics of Solvolysis of cis-Dibromo(triaminotriethylamine)cobalt(III) Cation in Nonaqueous Solvents

BY STANLEY K. MADAN AND JOSEPH PEONE, JR.

In a recent article we described the kinetics of aquation of the cis-dibromo(triaminotriethylamine)cobalt-(III) cation.[1] This report describes the solvolysis of this cation in dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylformamide (NMF), and formamide, and presents a comparison of these solvents and water as solvolytic reagents. Furthermore, the paucity of kinetic data on reactions of transition metal complexes in nonaqueous solvents prompted us to undertake this investigation.[2,3] Recently, Asperger, *et al.*,[4] Langford,[5,6] and others[7,8]

(1) Part II: S. K. Madan and J. Peone, Jr., *Inorg. Chem.*, **6**, 463 (1967).
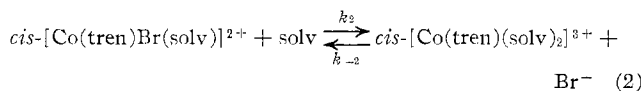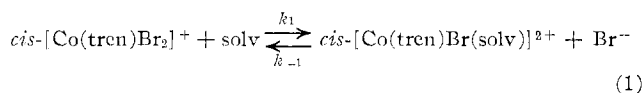(2) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).
(3) D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. C. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 125.
(4) S. Asperger, M. Orhanovic, M. Pribanic, and V. Reic, *J. Chem. Soc.*, 589 (1966).
(5) C. H. Langford and P. Langford, *Inorg. Chem.*, **2**, 300 (1963).

have studied the solvolytic reaction of the trans- and cis-[Co(en)$_2$Cl$_2$]$^+$ cations in nonaqueous solvents. A correlation of the dielectric strengths of the solvents with "k" values has been made by Asperger and co-workers.[4]

For the four solvents mentioned above, forward reaction 1 is considerably faster than forward reaction 2, so that no serious interference is caused by reaction 2 in the study of reaction 1. Under the conditions of the

$$cis\text{-}[Co(tren)Br_2]^+ + solv \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} cis\text{-}[Co(tren)Br(solv)]^{2+} + Br^-$$

(1)

$$cis\text{-}[Co(tren)Br(solv)]^{2+} + solv \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} cis\text{-}[Co(tren)(solv)_2]^{3+} +$$

$$Br^- \quad (2)$$

experiment reported here, equilibrium was not observed for the four solvents in reaction 1 and for N-methylformamide and formamide in reaction 2.

Experimental Section

Reagents. (a) Complex cis-[Co(tren)Br$_2$]Br.—The synthesis of this compound has been reported previously.[1]

(b) **Salts.**—The salts Mg(ClO$_4$)$_2$ and NaCl were anhydrous reagent grade quality.

(c) **Solvents.**—The solvents were Fisher Certified reagents and no attempt was made at further purification. Langford and Langford[5] reported equivalent kinetic results with Fisher Certified reagent DMF and specially purified DMF refluxed over BaO and distilled at reduced pressure. No attempts were made to isolate solvent-substituted products of cis-[Co(tren)Br$_2$]$^+$.

Electronic Absorption Spectra.—The spectra in the visible and near-visible region of the various species were obtained with a Cary Model 14 recording spectrophotometer. Approximately millimolar solutions in the appropriate solvent were scanned in matched cells of 1-cm light path.

Kinetic Measurements. (a) **Spectrophotometric Procedure.**—The change in absorbance was followed with time, and the wavelength chosen for the study of the reaction was one at which a substantial absorption difference occurs between reactant and product. For instance, this difference between the dibromo complex and the monosolvated bromo complex occurs at 420 mμ. This wavelength was therefore the one used in the study of reaction 1. Reaction 1 was also followed at 670 mμ to confirm the assumption that no other unexpected side reactions were complicating the reaction. Measurements were made on the same Cary Model 14 described above. The temperature was controlled to within ±0.05° by circulating thermostated water through the compartment surrounding the cells. The concentration of complex in these runs was 0.6–3 mM. Experimental infinity absorptions were obtained after 10 half-lives. As reported in an earlier work,[1] the concentration of the complex can be obtained from A_∞ values of the monosolvated species after t_∞ for reaction 1 (again $k_1 \gg k_2$). Once a Beer's law plot is made on known concentrations at 420 mμ, the concentration of each kinetic run can be measured spectrophotometrically. Results comparable to within 1% were obtained from kinetic runs on solutions whose concentrations were determined by direct weighing of the complex into a known solution volume and with solutions whose concentrations were determined from A_∞.

(b) **Conductometric Procedure.**—The reaction was followed conductometrically. For these measurements an RC-18 Industrial Instruments conductance bridge equipped with a 1000- and 3000-c signal and a cathode ray oscillograph as the null detector

(6) C. H. Langford, *ibid.*, **3**, 228 (1964).
(7) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 2991 (1964).
(8) M. L. Tobe and D. W. Watts, *ibid.*, 4614 (1964).

were used. The conductance cell was immersed in a thermostat kept at 40.0 ± 0.05°. The concentration of the complex was approximately 1 mM.

Results and Discussion

Spectrophotometric data were plotted as log ($A_\infty - A_t$) vs. t where A_∞ was observed at a time corresponding to 10 half-lives and A_t is absorbance at time t. The plots yielded a straight line. The conductometric data were plotted as log ($G_\infty - G_t$) vs. time t, where G_∞ and G_t are conductances in mhos at infinity and at time t, respectively. Data in that form gave a straight line. Results show a relative error of approximately 1.0% between the two procedures. At 40.0° for DMSO and DMF, by the conductometric method, rate constants of 3.19×10^{-3} and 2.40×10^{-3} sec^{-1} were obtained vs. rate constants of 3.20×10^{-3} and 2.40×10^{-3} sec^{-1} at 420 mμ and 3.26×10^{-3} and 2.42×10^{-3} sec^{-1} at 670 mμ, by the spectrophotometric procedure. Table I gives specific rate constants, k_1, for reaction 1 (found by the spectrophotometric procedure) for various solvents at different temperatures.

easily seen that the replacement of the bromide ion at 25.0° by various solvent molecules compared to water is as follows: in NMF (ϵ 182.4) the rate is 11.1 times faster than in water (ϵ 78.5); in formamide (ϵ 109.5) it is the same as in water, while in DMSO (ϵ 46.7) and DMF (ϵ 37.6) it is 36.0 and 66.0 times slower, respectively. The changes in rates in these solvents may be attributed to changes in polarity of the solvents. Generally, the solvent with the larger dielectric constant will facilitate the separation of the charge in the transition state of the S$_N$1-type reactions.[4]

In Table III are given the rates of solvolysis as determined spectrophotometrically in various solvents (DMSO, DMF, NMF, and formamide) under various conditions, complex concentration, temperature, and added electrolyte. In all cases, quadruplicate runs gave straight-line plots whose k_1 values agreed within 3–4%. It is obvious from Table III that in the case of Mg(ClO$_4$)$_2$ in the solvents DMSO and DMF, the rate is independent of initial concentration and ionic strength over the range at which these variables were studied.

TABLE I

RATES OF SOLVOLYSIS OF cis-[Co(tren)Br$_2$]$^+$ IN VARIOUS SOLVENTS

(FIRST-ORDER RATE CONSTANTS IN SEC^{-1})

Solvent	17	20	25	30	Temp, °C 35	40	45	50	55
Formamide	1.19×10^{-2}	1.58×10^{-2}	2.70×10^{-2}	3.82×10^{-2}					
DMSO	...	...	7.65×10^{-4}	9.68×10^{-4}	1.79×10^{-3}	3.20×10^{-3}	4.78×10^{-3}	7.28×10^{-3}	1.40×10^{-2}
DMF	...	...	4.28×10^{-4}	6.27×10^{-4}	1.20×10^{-3}	2.43×10^{-3}	3.64×10^{-3}	6.10×10^{-3}	1.05×10^{-2}
NMF	...	...	2.50×10^{-1}	...	...	...	...	...	...
H$_2$O^a	...	2.32×10^{-2}	2.82×10^{-2}	5.31×10^{-2}	7.88×10^{-2}	9.54×10^{-2}			

^{a} Reported in ref 1.

The activation parameters for reaction 1 were calculated from a linear Arrhenius plot of log k_1 vs. $1/T$ over the range of temperatures shown in Table I. The activation parameters for each solvent studied are given in Table II. Activation parameters for the aquation

TABLE II

ACTIVATION PARAMETERS FOR
cis-[Co(tren)Br$_2$]$^+$ IN VARIOUS SOLVENTS

Solvent	ΔH^*, kcal mole^{-1}	ΔF^*, kcal mole^{-1}	ΔS^*, cal deg^{-1} mole^{-1}
DMSO	17.9 ± 1.0	21.6 ± 1.0	-12.0 ± 2.0
DMF	22.1 ± 0.9	21.9 ± 0.9	~ 0
Formamide	10.1 ± 0.9	19.5 ± 0.9	-32.0 ± 2.0
H$_2$O^a	15.1 ± 1.0	19.5 ± 1.0	-14.8 ± 2.0

^{a} Obtained from ref 1.

reaction are also included for comparison. The values of entropies of activation found for reaction 1 in DMSO, formamide, and water agree with values reported for similar reactions,[5] whereas for DMF we find a difference which we are unable to explain at the present time (Table II). It has been shown that the electron donor halo anions promote aquation by facilitating dissociation (S$_N$1 mechanism).[2,9,10] This dissociation process is affected by different properties of the solvent. Upon examination of the data, it is

It is clear that the chloride ion in a concentration 1–5 times that of the initial complex has no effect on the solvolysis reactions in DMSO and DMF. However, when the chloride ion concentration is 10–50 times that of initial complex, it accelerates the solvolysis reaction. Although the limited data available in this study cannot confirm it, we believe that in these media the less solvated chloride ion[11] probably becomes a reactant, thereby producing the increase in the rate of solvolysis.

In Figure 1 are given the visible spectroscopic features of the cis-[Co(tren)Br$_2$]$^+$ cation in various nonaqueous solvents. The visible spectra show small shifts in the absorption maxima to longer or shorter wavelengths in these solvents for the cobalt(III)–tren complexes. Generally, there is a close similarity in character and shape to those of the cis isomers of other tetramine compounds in aqueous media.[1] Based on this evidence, the monodentate ligands (DMSO, DMF, NMF, and formamide) in these tren complexes can be assigned a cis configuration (Figure 1).

Tobe and coworkers[10,12] have reported on the steric course of a large number of octahedral aquation reactions. In every case, the aquation of cis complexes appears to be stereospecific, and only the cis isomer of

(9) M. L. Tobe, *Sci. Progr.* (London), **48**, 483 (1960).

(10) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

(11) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(12) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

TABLE III

RATES OF SOLVOLYSIS OF cis-[Co(tren)Br₂]⁺ IN NONAQUEOUS SOLVENTS UNDER VARIOUS CONDITIONS (420 mμ)

[Complex], mM	Solvent	Temp, °C	Added electrolyte	Ionic strength, M	k_1, sec⁻¹
0.58[a]	DMSO	40.0	None	5.8×10^{-4}	3.20×10^{-3}
0.96	DMSO	40.0	None	9.6×10^{-4}	3.29×10^{-3}
3.20	DMSO	55.0	None	3.2×10^{-3}	1.37×10^{-2}
0.65	DMSO	55.0	None	6.5×10^{-4}	1.40×10^{-2}
3.30[b]	DMF	40.0	None	3.3×10^{-3}	2.40×10^{-3}
1.20	DMF	40.0	None	1.2×10^{-3}	2.43×10^{-3}
3.40	DMF	55.0	None	3.4×10^{-3}	1.07×10^{-2}
1.50	DMF	55.0	None	1.5×10^{-3}	1.05×10^{-2}
1.50[c]	NMF	25.0	None	1.5×10^{-3}	2.50×10^{-1}
2.00[d]	Formamide	25.0	None	2.0×10^{-3}	2.70×10^{-2}
1.00	DMSO	40.0	0.02 M Mg(ClO₄)₂	6.0×10^{-2}	3.10×10^{-3}
1.00	DMSO	40.0	0.10 M Mg(ClO₄)₂	3.0×10^{-1}	3.16×10^{-3}
1.00	DMSO	40.0	0.20 M Mg(ClO₄)₂	6.0×10^{-1}	3.35×10^{-3}
1.00	DMSO	40.0	0.005 M NaCl	6.0×10^{-3}	3.38×10^{-3}
1.00	DMSO	40.0	0.05 M NaCl	5.0×10^{-2}	5.10×10^{-3}
1.00	DMF	40.0	0.02 M Mg(ClO₄)₂	6.0×10^{-2}	2.35×10^{-3}
1.00	DMF	40.0	0.10 M Mg(ClO₄)₂	3.0×10^{-1}	2.38×10^{-3}
1.00	DMF	40.0	0.001 M NaCl	2.0×10^{-3}	2.50×10^{-3}
1.00	DMF	40.0	0.01 M NaCl	6.0×10^{-2}	4.25×10^{-3}

[a] k_1 at 670 mμ for DMSO = 3.26×10^{-3} sec⁻¹. [b] k_1 at 670 mμ for DMF = 2.42×10^{-3} sec⁻¹. [c] $k_2 = 6.8 \times 10^{-5}$ sec⁻¹. [d] $k_2 = 6.3 \times 10^{-5}$ sec⁻¹.
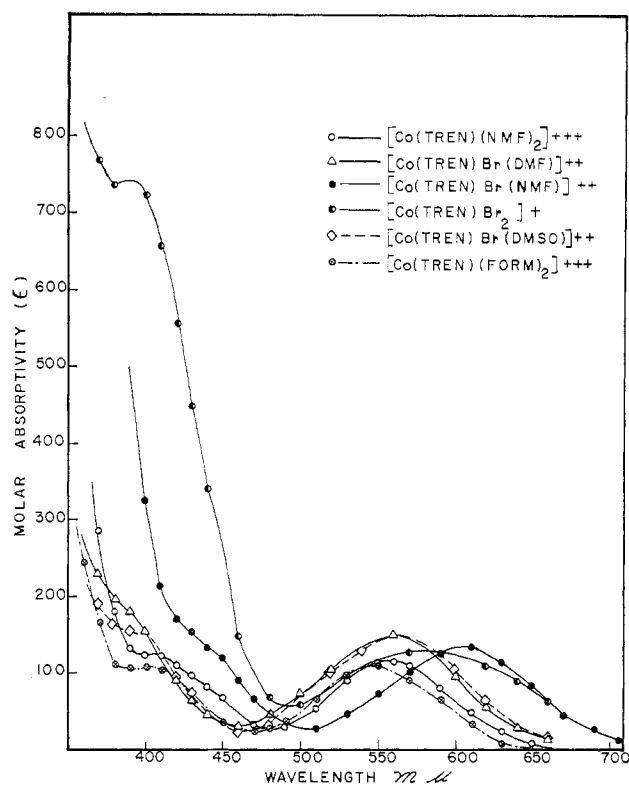

Figure 1.—Visible spectra of cis-[Co(tren)Br₂]⁺, cis-[Co(tren)-Br(solv)]²⁺ (where solv = DMF, NMF, or DMSO), and cis-[Co(tren)(solv)₂]³⁺ (where solv = NMF or formamide).

the product is formed. Quinn and Garner[13] have reported similar results for cis isomers of chromium(III) complexes. The solvolysis product in the present study must assume cis configuration because the steric property of the dibromo(triaminotriethylamine)cobalt-(III) cation is fixed, since the tertiary nitrogen atom must be *trans* to bromo or a solvent molecule. The electronic absorption spectra certainly indicate a cis

configuration for various species (Figure 1). Therefore, it is quite reasonable to assume that the stereospecific rule for cis complexes in this case is also followed.

Langford[6] observed a significant decrease in the solvolysis rates in DMSO and DMF, as compared to the aquation rate of the trans-[Co(en)₂Cl₂]⁺ cation. This observation is consistent with results obtained in the present study for cis-[Co(tren)Br₂]⁺. Furthermore, a comparison of the relative solvolysis rates (aquation rate 1.0) at 35° of trans-[Co(en)₂Cl₂]⁺ in DMSO (0.31) and DMF (0.05) and of cis-[Co(tren)-Br₂]⁺ in DMSO (0.022) and DMF (0.015) seems to support the notion that solvolysis in nonaqueous, coordinating solvents is not basically different from solvolysis in water. The rates are altered but only moderately.[6]

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The Magnetic Susceptibilities of Erbium–Tellurium Intermediate Phases[1]

BY J. HOGGINS AND H. STEINFINK

The Er–Te system contains an intermediate stoichiometric compound ErTe₃ and a second intermediate phase which displays a solid solubility range

(13) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).