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Solvent Effects on Redox Reactions.
2. The Cr(II) Reduction of Tris(pentane-2,4-dionato)cobalt(III) in Water/Acetone Solvent Mixtures

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Abstract

The Cr(II) reduction of Co(ptdn)$_3$ (ptdn = pentane-2,4-dionato) was studied in various acetone/water mixtures. The activation parameters were measured over a temperature range of 25–45 °C and were found to vary in a complex, non-linear fashion. Three pathways for reduction were observed: outer sphere, mono-bridged inner-sphere and di-bridged inner-sphere. Only the di-bridged pathway showed an acid dependence. The results are discussed in terms of the nature of the solvent mixture and its effect on the reactants and the transition state. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ tend to change in such a manner that deviations in $\Delta G^{\ddagger}$ are minimized, although the existence of any isokinetic relationships could not be established. This behavior is compared with that of other redox systems reported to be studied in mixed solvents. Possible reasons for the observation of the di-bridged pathway, which is not observed in water, are presented.

Introduction

Although there is an extensive body of literature on the effect that changing the solvent has on an organic reaction [1] and even on the substitution reactions of coordination compounds [2], very few studies have concentrated on solvent effects on redox reactions between transition metal species [3, 4]. Part of the problem lies in the lability of the metal ions which may be participating in the exchange. For example, the most extensive series of solvent studies performed to date [5–10] have employed Fe(II) as the reducing agent. Both Fe(II) and the Fe(III) product are labile species so that the product criterion for establishing the mechanism of reduction (inner- or outer-sphere) could not be used. A reductant which is capable of distinguishing between an inner- and an outer-sphere mechanism is Cr(II) and we have therefore elected to use this metal ion as the reducing agent in our experiments.

The use of organic solvents in redox studies introduces numerous problems in analysing the results of such efforts which may be subject to a wide variety of interpretations. To circumvent some of the difficulties which may arise in comparing solvent effects on reactions involving different oxidants with Cr(II), we sought a redox process which proceeded simultaneously by both classical mechanisms under identical conditions. Thus, comparisons may be made between the behavior of the inner- and outer-sphere pathways even if the reasons for the changes remain, for the moment at least, obscure.

The model reaction we selected to investigate solvent effects on different pathways was the Cr(II) reduction of Co(ptdn)$_3$ (where ptdn is pentane-2,4-dionato). This system was chosen because it proceeded in water simultaneously by a mono-bridged inner-sphere and an outer-sphere mechanism. In an earlier study in water/dimethylformamide solvent mixtures [11], a third pathway appeared – the di-bridged inner-sphere path. The present work is an extension of this earlier investigation in the sense that we are using the same model reaction in a different solvent system, that is, the Cr(II) reduction of Co(ptdn)$_3$ in water/acetone mixtures. Prior to these series of experiments, there was no information in the literature comparing the behavior of the two classical electron transfer mechanisms as a function of the solvent system employed.

Experimental

Reagents

Tris(pentane-2,4-dionato)cobalt(III), Co(ptdn)$_3$, was obtained from ICN Pharmaceuticals Inc., and was used as received. All reagent solutions were prepared in water which was de-ionized and doubly distilled as described earlier [11]. Spectroscopic grade acetone was obtained from Fisher Scientific Ltd. and was used without further purification.

The lithium salt of trifluoroacetic acid was prepared as described earlier [11]. This salt was dissolved

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in acetone and the solution was standardized by an ion-exchange procedure [11]. A standard solution of trifluoroacetic acid in acetone (~3.0 M) was prepared and standardized titrimetrically. A blank containing a known amount of trifluoroacetic acid in the presence of the same quantity of acetone as was present in the unknown, was similarly analyzed. An aqueous solution of trifluoroacetic acid (~2.8 M) was prepared and analyzed titrimetrically, as well.

Chromium(II) stock solutions were made from chromium pellets (99.99% pure, Ultrex grade, J. T. Baker Chemical Co.) using a standard procedure described earlier [11]. All standard solutions were stored under high purity argon and were handled using standard syringe techniques in an argon atmosphere.

Kinetic Measurements

The rate of reduction of Co(ptdn)$_3$ by Cr(II) was followed using a stopped-flow spectrophotometer (Dionex Model D-110) interfaced to an Explorer II digital oscilloscope (Nicolet Instrument Corporation), and having the temperature controls described previously [11].

All reactions were carried out under pseudo-first order conditions, *i.e.* the reductant was always present in greater than 20-fold excess over the oxidant. The ionic strength in each experiment was controlled to 1.00 M using the standard lithium trifluoroacetate solution.

Product Analyses

In the first series of experiments, approximately equal proportions of Co(ptdn)$_3$ (140 μmol) and Cr(II) (145 μmol) were mixed together in 20 ml of the desired solvent mixture. The proportion of acetone in the aqueous medium varied from 0 to 90% by volume, and the analyses were performed at 25, 35 and 45 °C. In all cases, the acid concentration was controlled to 0.10 M using the standard stock CF_3COOH solutions. Some reaction mixtures were allowed to proceed for 5 half-times and others for 10 half-times. The reaction mixture was diluted to 500 ml with cold distilled water. Air was bubbled through the solution for about five minutes and a cation-exchange column (Dowex 50WX8(200)) was charged with this aerated solution. The excess of acetone was washed from the column using distilled water. Following this, the three products were separated into distinct bands by eluting with a solution of 6.25×10^{-2} M $NaClO_4$ in 1.25×10^{-2} M $HClO_4$. The first band, identified as $[Cr(solv)_2(ptdn)_2]^+$ where solv is water or acetone, was eluted with 6.25×10^{-2} M $NaClO_4$ in 1.25×10^{-2} M $HClO_4$. The second band, $[Cr(solv)_4(ptdn)]^{2+}$, was removed from the column by elution with 0.50 M $NaClO_4$ in 0.10 M $HClO_4$. The final compound, $[Cr(solv)_6]^{3+}$, came off the column by elution with a mixture of 1.0 M $NaClO_4$ in 0.2 M $HClO_4$. The chromate content of each band was estimated using a standard chromate analysis [34].

In the second series of product studies, the acid dependence of the reaction was investigated at 25 °C in all solvent mixtures.

Spectral Measurements

All electronic spectra of reaction products and chromium(II) solvated species were obtained on a Perkin-Elmer Model 330 UV–VIS–NIR Spectrophotometer.

Results

The rates of reduction of Co(ptdn)$_3$ by Cr(II) (at 0.10 M $[H^+]$ and $\mu = 1.00$ M) were measured at various acetone/water mixtures. The overall rate constants are listed in Table I; these were decomposed into three pathways – mono-bridged inner-sphere, di-bridged inner-sphere and outer-sphere – using the product analysis results of Table II. The component rate constants derived in this fashion are collected in Table I; their dependence as a function of the mole fraction of acetone present in the reaction medium at 25 °C is shown graphically in Fig. 1. The mono-bridged inner-sphere pathway shows an increase in rate until a maximum is reached at about a mole fraction of 0.35 acetone, then a decrease in velocity ensues as the proportion of acetone in the medium is further increased. The other two pathways, the outer-sphere and di-bridged inner-sphere paths show a fairly steady increase in rate as the proportion of acetone increases although a levelling off occurs at $\chi_{acetone} = 0.35$ (where χ is mole fraction).

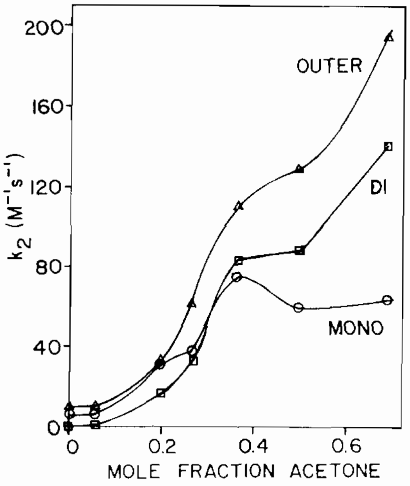


Fig. 1. Rate dependence of each pathway on mole fraction of acetone in the reaction mixture at $[H^+] = 0.10$ and $\mu = 1.00$ M (CF_3COOLi).

TABLE I. Kinetic Data for the Cr(II) Reduction of [Co(ptdn)$_3$] in Acetone/Water Mixtures at [H$^+$] = 0.10 M and μ = 1.00 M (CF$_3$COOLi)

Mole fraction acetone	Temperature[a] (°C)	[Co(III)][b] $\times 10^4$ (M)	[Cr(II)][b] $\times 10^2$ (M)	k_{overall} (M^{-1} s^{-1})	k_{MONO}[c] (M^{-1} s^{-1})	k_{DI}[d] (M^{-1} s^{-1})	k_{OUTER}[e] (M^{-1} s^{-1})
0.056	25.0	7.04	2.82	17.4	6.26	0.957	10.1
		7.04	2.82	17.6	6.34	0.968	10.2
		7.03	2.81	17.6	6.34	0.968	10.2
		7.03	2.81	18.1	6.52	0.996	10.5
		6.96	1.39	16.4	5.90	0.902	9.51
		6.96	13.9	18.1	6.52	0.996	10.5
	35.0	7.03	2.81	34.6	13.5	2.66	17.6
		7.03	2.81	34.6	13.5	2.66	17.6
		7.03	2.81	34.4	13.4	2.65	17.5
	45.0	7.03	2.81	61.9	26.9	5.00	28.1
		7.03	2.81	61.9	27.2	5.57	28.5
		7.03	2.81	61.1	26.9	5.50	28.1
0.197	25.0	7.04	1.41	81.6	31.3	16.9	33.5
		7.04	2.82	78.0	29.9	16.1	32.0
		7.04	2.82	79.3	30.4	16.4	32.5
		7.04	2.82	80.6	30.9	16.7	33.0
		7.04	5.64	84.7	32.4	17.5	34.7
		7.05	7.07	85.2	32.6	17.6	34.9
	35.0	7.04	2.82	137	56.2	32.9	48.0
		7.04	2.82	140	57.4	33.6	49.0
		7.04	2.82	133	54.5	31.9	46.6
	45.0	7.04	2.82	266	112	66.5	85.1
		7.04	2.82	252	106	63.0	80.6
		7.04	2.82	267	112	66.8	85.4
0.269	25.0	7.04	2.82	112	38.1	33.2	60.7
0.364	25.0	7.03	2.81	268	75.0	83.0	110
		7.03	2.81	275	77.0	85.3	113
		7.03	2.81	270	75.6	83.7	111
	35.0	7.03	2.81	550	149	193	204
		7.03	2.81	563	152	197	209
		7.03	2.81	538	145	188	200
	45.0	7.03	2.81	952	295	352	305
		7.03	2.81	990	307	366	317
		7.03	2.81	952	295	352	305
0.495	25.0	6.92	2.80	275	58.9	88.3	128
		6.92	2.80	280	59.9	89.9	130
	35.0	6.92	2.80	481	89.9	159	232
		6.92	2.80	471	88.1	155	227
		6.92	2.80	495	92.6	163	239
	45.0	6.92	2.80	952	175	308	468
		6.92	2.80	990	182	321	487
		6.92	2.80	971	179	314	478
0.687	25.0	7.06	1.42	396	63.4	150	194
		7.06	1.42	383	61.3	146	188
		7.06	1.42	371	53.4	141	182
	35.0	7.06	1.42	618	86.5	210	321
		7.06	1.42	642	89.9	218	334
		7.06	1.42	642	89.9	218	334

(continued)

Table I. *(continued)*

Mole fraction acetone	Temperature[a] (°C)	[Co(III)][b] ×10^4 (M)	[Cr(II)][b] ×10^2 (M)	$k_{overall}$ (M^{-1} s^{-1})	k_{MONO}[c] (M^{-1} s^{-1})	k_{DI}[d] (M^{-1} s^{-1})	k_{OUTER}[e] (M^{-1} s^{-1})
	45.0	7.06	1.42	986	98.6	365	522
		7.06	1.42	1017	102	376	539
		7.06	1.42	1038	104	384	550

[a] The temperature was controlled to ±0.1 °C or better. [b] All concentrations are initial values in molar units. [c] This is the rate constant for the mono-bridged pathway. It is obtained by multiplying the overall rate constant with the percentage of mono-bridged product produced. [d] This is the rate constant for the di-bridged pathway. It is obtained by multiplying the overall rate constant with the percentage of di-bridged product produced. [e] This is the rate constant for the outer-sphere path. It is obtained by taking the difference between the overall rate constant and the sum of the rate constants for the inner-sphere pathways.

TABLE II. Product Analysis Data for the Cr(II) Reduction of [Co(ptdn)$_3$] in Acetone/Water Mixtures at [H^+] = 0.10 M (CF_3COOH)

Mole fraction acetone	Temperature[a] (°C)	Cr(II)[b] used (μmol)	[Co(ptdn)$_3$][b] used (μmol)	[Cr(sol)$_4$(ptdn)]$^{2+}$ recovered (μmol)	[Cr(sol)$_2$(ptdn)]$^+$ recovered (μmol)	MONO[c] path (%)	DI[d] path (%)	OUTER[e] path (%)
0.056	25.0	142	141	53.2	7.70	37.7	5.46	56.8
		142	141	49.2	7.95	34.0	5.64	59.5
	35.0	142	141	56.6	11.1	40.1	7.87	52.0
		146	141	61.0	10.5	43.3	7.45	49.3
	45.0	142	141	6.48	14.0	46.0	9.93	44.1
		146	143	60.6	14.3	42.4	10.0	47.6
		146	142	63.2	12.8	44.5	9.01	46.5
0.197	25.0	147	141	54.1	29.3	38.4	20.8	40.8
		147	141	54.2	29.0	38.4	20.6	41.0
		147	141	53.7	29.2	38.1	20.7	41.2
	35.0	147	141	55.8	31.9	39.6	22.6	37.8
		147	142	58.2	34.9	41.0	24.6	34.4
		147	140	57.9	34.0	41.4	24.3	34.3
	45.0	147	142	57.1	35.2	40.2	24.8	35.0
		147	141	60.7	36.6	43.0	26.0	31.0
		147	140	61.2	35.9	43.7	25.6	30.7
0.297	25.0	147	142	48.3	42.1	34.0	29.6	54.2
0.364	25.0	144	142	44.9	45.0	31.6	31.7	36.7
		147	143	37.9	46.7	26.5	32.7	40.8
	35.0	145	141	40.2	45.5	28.5	32.3	39.2
		146	141	40.6	48.0	28.8	34.0	37.2
		145	140	40.8	48.3	29.1	34.5	36.4
	45.0	142	141	44.9	45.9	31.8	32.6	35.6
		145	140	47.3	46.0	33.7	32.8	33.5
		145	139	46.0	49.5	33.0	35.5	31.5
0.495	25.0	141	144	26.6	41.2	18.9	29.3	51.8
		141	144	29.8	44.5	21.1	31.5	47.4
	35.0	141	144	27.2	45.8	19.2	32.4	48.4
		142	144	25.6	47.6	18.1	33.6	48.3
		141	144	30.4	47.5	21.6	33.7	44.7

(continued)

TABLE II. *(continued)*

Mole fraction acetone	Temperature[a] (°C)	Cr(II)[b] used (μmol)	$[Co(ptdn)_3]$[b] used (μmol)	$[Cr(sol)_4(ptdn)]^{2+}$ recovered (μmol)	$[Cr(sol)_2(ptdn)]^+$ recovered (μmol)	MONO[c] path (%)	DI[d] path (%)	OUTER[e] path (%)
	45.0	144	140	25.9	46.5	18.5	33.1	48.4
		144	141	26.3	44.7	18.7	31.7	49.6
		144	141	25.2	45.5	17.9	32.4	49.7
0.687	25.0	145	141	24.9	50.3	17.7	35.7	46.6
		144	141	25.8	44.8	18.3	31.8	49.9
	35.0	145	141	19.6	47.0	13.9	33.3	52.8
		145	141	19.6	49.5	13.9	35.1	51.0
		145	141	20.3	48.3	14.4	34.3	51.3
	45.0	145	141	13.3	53.4	9.43	37.9	52.7
		145	140	13.5	52.4	9.64	37.4	53.0

[a] The temperature was controlled to ±0.1 °C or better. [b] All concentrations are initial values in molar units. [c] This is the percentage of the reaction which proceeded by the mono-bridged transition state based on the moles of $[Cr(solv)_4(ptdn)]^{2+}$ recovered per mole of $[Coen(ptdn)_2]^+$ used. [d] This is the percentage of the reaction which proceeded by the di-bridged transition state based on moles of $[Cr(solv)_2(ptdn)_2)]^+$ recovered per moles of $[Coen(ptdn)_2]^+$ used. [e] This is the percentage of the reaction which proceeded by the outer-sphere pathway. It is obtained by taking the difference between 100% and the total percentage of the inner-sphere products.

This behavior contrasts with that shown in water/dimethylformamide mixtures, since, in these solutions, the mono-bridged inner-sphere and outer-sphere paths showed a similar response to increasing organic content in the medium, but the di-bridged pathway reacted in a different fashion [11].

Activation parameters derived for each of the three pathways are collected in Table III. The changes which occur in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as the mole fraction of acetone is increased, for each pathway, are presented graphically in Figs. 2 and 3, respectively. For both inner-sphere paths, extrema are reached at about $\chi_{acetone} = 0.06$ and 0.35. In the presence of added dimethylformamide, the outer-sphere path showed the smallest response [11] whereas in the acetone/water mixtures, both the outer-sphere and di-bridged inner-sphere paths show large changes in $\Delta S^{\ddagger}$ as the medium changes (Fig. 3).

The acid dependencies of the three pathways were measured at 25 °C and the results obtained are presented in Tables IV and V. As was true also in water/dimethylformamide solvent mixtures, there

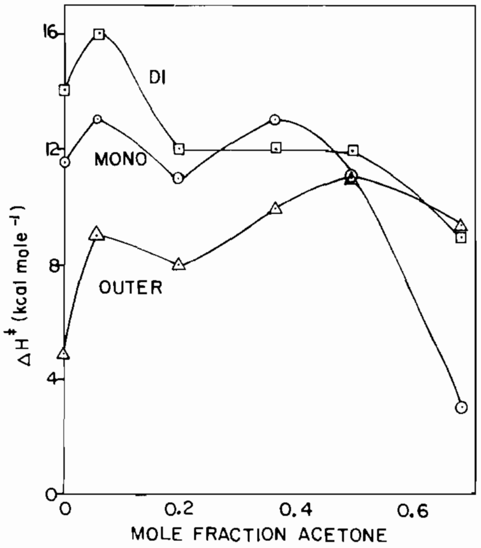


Fig. 2. Dependence of $\Delta H^{\ddagger}$ for each pathway on mole fraction of acetone.

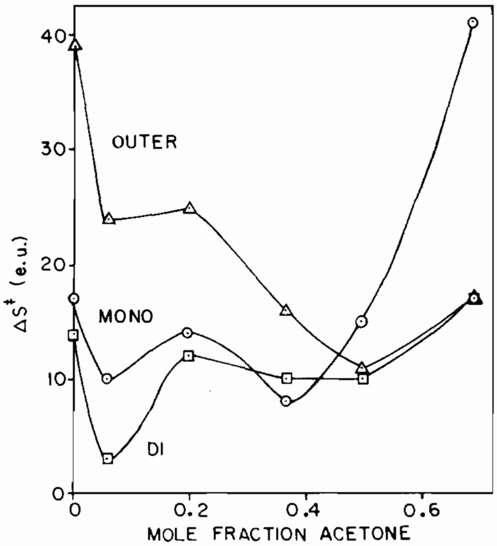


Fig. 3. Dependence of $\Delta S^{\ddagger}$ for each pathway on mole fraction of acetone.

TABLE III. Summary of Rate Constants and Activation Parameters[a] for the Cr(II) Reduction of $[Co(ptdn)_3]$ in Acetone/Water Mixtures at $[H^+] = 0.1$ M and $\mu = 1.00$ M (CF_3COOLi)

Mole fraction acetone	Pathways	k 25 °C $(M^{-1}\ s^{-1})$	$\Delta H^{\ddagger}$ $(kcal\ mol^{-1})$	$\Delta S^{\ddagger}$ (e.u.)
0.000	Mono	4.01	11.5 ± 0.7	−17 ± 2
	Di	0.346	14 ± 1	−14 ± 3
	Outer	4.42	4.9 ± 0.6	−39 ± 2
0.057	Mono	6.4 ± 0.1	13 ± 1	−10 ± 4
	Di	0.99 ± 0.01	16 ± 1	−3 ± 3
	Outer	10.3 ± 0.1	9.0 ± 0.8	−24 ± 3
0.197	Mono	30.9 ± 0.3	11 ± 1	−14 ± 4
	Di	16.8 ± 0.2	12 ± 2	−12 ± 3
	Outer	32.9 ± 0.5	8 ± 2	−25 ± 5
0.364	Mono	78 ± 2	13 ± 1	−8 ± 4
	Di	91 ± 2	12 ± 1	−10 ± 4
	Outer	109 ± 3	10 ± 2	−16 ± 5
0.495	Mono	53 ± 2	11 ± 2	−15 ± 5
	Di	83 ± 1	11.9 ± 0.9	−10 ± 3
	Outer	131 ± 4	11 ± 1	−11 ± 5
0.687	Mono	71 ± 1	3 ± 1	−41 ± 4
	Di	129 ± 3	9 ± 1	−17 ± 4
	Outer	187 ± 2	9.4 ± 0.8	−17 ± 3

[a] The activation parameters were calculated on an IBM 3032 computer using a least-squares programme. The errors reported are standard deviations.

TABLE IV. Kinetic Data on the Cr(II) Reduction of $[Co(ptdn)_3]$ in Acetone/Water Mixtures at 25.0 °C and $\mu = 1.00$ M (CF_3COOLi)[a] at Various Acidities

Mole fraction acetone	$[H^+]$ M	[Co(III)][b] $\times 10^4$ (M)	[Cr(II)][b] $\times 10^2$ (M)	$k_{overall}$ $(M^{-1}\ s^{-1})$	k_{MONO}[c] $(M^{-1}\ s^{-1})$	k_{DI}[d] $(M^{-1}\ s^{-1})$	k_{OUTER}[e] $(M^{-1}\ s^{-1})$
0.057	0.05	7.03	2.81	17.4	7.53	1.51	8.36
	0.10	VAR[f]	VAR[f]	17.5	6.69	0.968	9.94
	0.30	7.03	2.81	15.2	6.37	0.654	8.18
	0.50	7.03	2.81	13.9	6.19	0.307	7.40
	0.80	7.03	2.81	11.0	5.23	0.212	5.56
0.197	0.05	7.06	2.82	81.9	33.9	19.7	28.3
	0.10	VAR[f]	VAR[f]	81.6	31.2	16.9	33.5
	0.20	7.06	2.82	74.5	32.5	9.12	37.7
	0.30	7.06	2.82	71.2	33.7	6.57	30.9
	0.40	7.06	2.82	63.0	30.3	4.64	28.1
	0.50	7.06	2.82	58.5	30.5	3.69	24.3
0.495	0.10	7.06	2.83	340	82.3	121	136
	0.40	7.06	2.81	280	69.7	41.4	169
	0.60	7.06	2.81	250	70.8	24.8	154
	0.80	7.06	2.81	224	74.8	15.9	133
0.687	0.10	7.06	1.42	396	70.1	141	184
	0.40	7.06	1.42	558	89.3	90.4	378

(continued)

TABLE IV. *(continued)*

Mole fraction acetone	$[H^+]$ M	$[Co(III)]^b$ $\times 10^4$ (M)	$[Cr(II)]^b$ $\times 10^2$ (M)	$k_{overall}$ $(M^{-1}\,s^{-1})$	$k_{MONO}{}^c$ $(M^{-1}\,s^{-1})$	$k_{DI}{}^d$ $(M^{-1}\,s^{-1})$	$k_{OUTER}{}^e$ $(M^{-1}\,s^{-1})$
0.687	0.60	7.06	1.42	610	101	64.7	444
	0.80	7.06	1.42	678	145	54.3	479

[a] The temperature was controlled to ±0.1 °C or better. [b] Concentrations are initial values in molar units. [c] This is the rate constant for the mono-bridged pathway. It is obtained by multiplying the overall rate constant with the percentage of mono-bridged product produced. [d] This is the rate constant for the di-bridged pathway. It is obtained by multiplying the overall rate constant with the percentage of di-bridged product produced. [e] This is the rate constant for the outer-sphere path. It is obtained by taking the difference between the overall rate constant and the sum of the rate constants for the inner-sphere pathways. [f] Several runs at different concentrations were performed. The results quoted are averaged values.

TABLE V. Product Analysis Data for the Cr(II) Reduction of $[Co(ptdn)_3]$ in Acetone/Water Mixtures at Various Acidities at 25.0 °C[a]

Mole fraction acetone	$[H^+]$	[Cr(II)] used (μmol)	$[Co(ptdn)_3]$ used (μmol)	$[Cr(solv)_4(ptdn)]^{2+}$ recovered (μmol)	$[Cr(solv)_2(ptdn)_2]^+$ recovered (μmol)	MONO[c] path (%)	DI[d] path (%)	OUTER[e] path (%)
0.056	0.06	146	140	60.6	12.2	43.3	8.69	48.0
	0.10	VAR[f]	VAR[f]	41	7.8	36.3	5.55	58.2
	0.30	145	140	58.6	6.03	41.9	4.30	53.8
	0.50	145	140	62.3	3.09	44.5	2.21	53.3
	0.80	145	142	67.5	2.74	47.5	1.93	50.6
0.197	0.05	145	141	58.3	33.8	41.4	24.0	34.6
	0.10	VAR[f]	VAR[f]	54.0	29.2	38.2	20.7	41.1
	0.20	145	140	61.3	16.1	43.6	11.5	44.9
	0.30	146	140	66.9	13.0	47.4	9.22	43.4
	0.40	145	140	67.3	10.3	48.1	7.36	44.5
	0.50	145	140	68.4	7.56	48.8	5.40	45.8
0.495	0.10	145	141	34.1	50.3	24.2	35.7	40.1
	0.40	145	143	35.6	21.2	24.9	14.8	60.3
	0.60	145	142	40.2	14.1	28.3	9.93	61.8
	0.80	145	141	46.1	9.80	33.4	7.10	59.5
0.687	0.10	VAR	VAR	23 ± 2	54 ± 3	16.0	37.9	46.1
	0.40	145	143	22.9	23.1	16.0	16.2	67.8
	0.60	145	141	23.4	15.0	16.6	10.6	72.8
	0.80	145	138	30.3	11.3	21.5	8.01	70.5

[a] The temperature was controlled to 0.1 °C or better. [b] Concentrations are initial values in molar units. [c] This is the percentage of the reaction which proceeded by the mono-bridged transition based on the moles of $[Cr(solv)_4(ptdn)]^{2+}$ recovered per mole of $[Co(ptdn)_3]$ used. [d] This is the percentage of the reaction which proceeded by the di-bridged transition state based on moles of $[Cr(solv)_2(ptdn)_2)]^+$ recovered per moles of $[Co(ptdn)_3]$ used. [e] This is the percentage of the reaction which proceeded by the outer sphere pathway. It is obtained by taking the difference between 100 per cent and the total percentage of the inner-sphere products. [f] Several runs at different concentrations were performed. The results quoted are averaged values.

was no effect on the rate that could be ascribed to the acidity of the medium, for either the mono-bridged inner-sphere or the outer-sphere pathways. However, the k_{obs} for the di-bridged rate contained a term inverse in hydrogen ion concentration. This effect was observed in all water/acetone mixtures studied.

From these results, the rate law for the mono-bridged and outer-sphere routes, at a particular acetone/water ratio, in both cases is

$$-\frac{d[Co(ptdn)_3]}{dt} = k_2[Co(ptdn)_3][Cr(II)] \qquad (1)$$

whereas the rate law for the di-bridged path is of the form

$$-\frac{d[Co(ptdn)_3]}{dt} = k_{DI}[Co(ptdn)_3][Cr(II)][H^+]^{-1} \quad (2)$$

When the plots of $1/k_{DI}$ *versus* $[H^+]$ were examined, the intercepts were found to be zero within the error limits of the experiment. Therefore, the values of the slopes listed in Table VI were obtained by constraining the computer generated least-squares lines to go through the origin.

TABLE VI. Values of k_{DI} Calculated from the Slopes of the Lines Obtained by Plotting $1/k_{obs}$ *versus* $[H^+]$ [a]

Mole fraction acetone	$1/k_{DI}K_a$ (s)[b,c]
0.057	6.4 ± 0.4
0.197	0.55 ± 0.01
0.495	0.071 ± 0.005
0.687	0.027 ± 0.004

[a] Data for plots given in Table IV. [b] Lines were constrained to pass through the origin. [c] Errors listed are computer estimated standard errors.

We have attempted to measure the pK_a of Co(ptdn)$_3$ in water but have not succeeded because it is almost completely insoluble. The fact that it *is* soluble in acidic water implies that its solubility arises from the protonation of one (or more) of the chelate rings, thus rendering the molecule charged and therefore soluble.

Numerous attempts were made to determine the ratio of acetone to water ligands in the final products. All of these failed due to the lability of at least one of the acetone ligands coordinated to Cr(III), *i.e.* it was impossible to measure the primary product distribution of this reaction. The ratio of acetone molecules to water molecules in the final product is highly dependent on the amount of time spent on the ion-exchange column which is a difficult variable to control. The spectra of large numbers of products were examined; they were similar but rarely identical, either to each other or to the spectra of the same chromium–pentane-2,4-dionato complexes prepared in pure water. Peaks shifted by 5–10 nm and extinction coefficients varied by 10–15% but not in any systematic fashion. Our inability to determine the primary product distribution of the non-bridging ligands is unfortunate but does not affect the conclusions reached in this study. All of our results were based on determinations of the total chromium content of each band. For example, the first band obtained always contained Cr(ptdn)$_2^+$ (whatever its remaining two ligands were) and its spectrum was always similar to that of the same compound obtained in a purely aqueous environment [33].

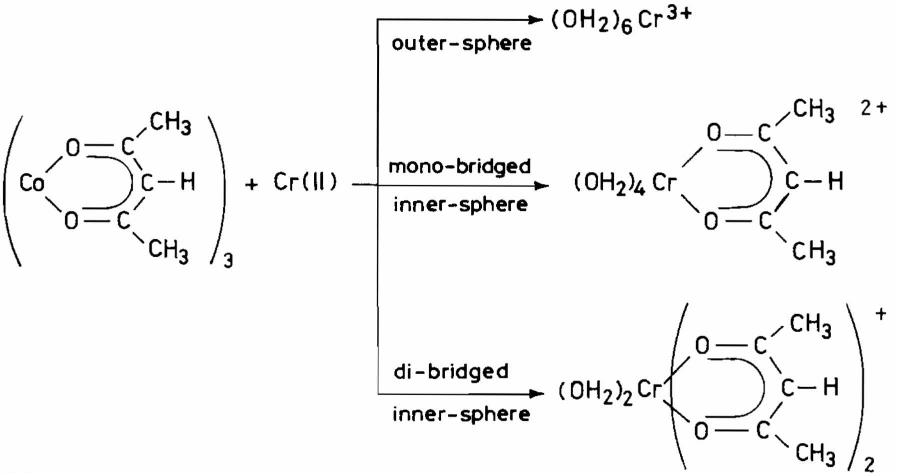
The variable results obtained in the spectral studies can probably be attributed to a *trans*-labilizing effect introduced by the pentane-2,4-dione ligand. Such a phenomenon has been observed earlier in chromium(III) chemistry. For example, nitrate [12], sulfite [13, 14], carbonate [15], nitrite [16], acetate [17, 18], and ethylenediamine [19, 20] are all ligands which are known to labilize the chromium(III) ion towards substitution.

Our studies indicate that the distribution of pentane-2,4-dione ligands in the final products are not substantially affected by the presence of excess Cr(III) since the product ratio was the same (to within 3–7%) after a reaction time of 5 or 10 half-times. Also, employing various Cr(II) to Co(III) ratios in the product studies produced essentially no differences in the final results. The tendency for slow attack of Cr(II) on Cr(III) complexes of the pentane-2,4-dione ligand in purely aqueous solutions has been established earlier [33].

Discussion

The redox reaction between Co(ptdn)$_3$ and Cr(II) in aqueous solution proceeded partly by the mono-bridged inner-sphere and partly by an outer-sphere route, in aqueous solution [21]. If dimethylformamide is added to the reaction mixture, a second inner-sphere pathway derived from a double-bridged attack of Cr(II) on two different pentane-2,4-dione rings of Co(ptdn)$_3$, becomes energetically feasible. In acetone, this redox reaction similarly proceeds by the three parallel routes (Scheme 1).

In aqueous solution chemistry, it is well-known that an important aspect of the activation process is the reorganization of the solvent molecules surrounding the reacting species as they come together to form the activated complex [22]. For outer-sphere electron transfer reactions, this may even be the energetically dominant term in calculating $\Delta G^{\ddagger}$ and all theories treating this problem, the most well-known of which is Marcus theory [23], explicitly treat this problem. It should not be surprising, then, that such solvent reorganizations will be markedly affected by the addition of a co-solvent to the aqueous solution. In fact, it is very evident that the action of the non-aqueous component of the mixture is more than that of a simple diluent of water or modifier of its dielectric properties. In order to understand the complex patterns of the type shown in Figs. 1–3, it is necessary to investigate how reactants and transition states are affected when a co-solvent is added to the reacting system in water. There are three possible effects to be considered, then. First of all, Cr(II) is a labile reactant and it may have either acetone or water in its first coordination sphere. Its chemical potential will differ depending on



Scheme 1.

its ligands and this will affect its rate of reaction with the substrate, $Co(ptdn)_3$ as well as the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of the process. Second, one must consider the solvent preferences of each of the individual reactants, Cr(II) and $Co(ptdn)_3$, in their respective ground states. There may also be huge changes in the preferred solvent structure of one or both of the reactants in forming the transition state. Finally, one must consider the water/acetone interactions themselves as striking changes may occur in the properties of the reactants from modifications of normal water–water interactions as a result of the presence of the co-solvent; this is an indirect effect which can be extremely important, even dominant, as we shall demonstrate.

Burgess [22] has classified solvent mixtures according to their thermodynamic properties, in particular, their molar excess functions. These excess functions express the extent to which the properties of a given mixture differ from those of the corresponding ideal mixture at the same temperature and pressure. Aqueous mixtures for which $[TS^E] > [H^E]$, *i.e.* the entropy of mixing is the dominant term, are called 'typically aqueous' solvent systems. Examples of this class include acetone/water and ethanol/water mixtures. The properties of typically aqueous mixtures are particularly sensitive to the mole fraction of the non-aqueous component, χ. At low mole fractions, a typically aqueous solvent promotes a water 'structure-forming' action. As more co-solvent is added, at some point χ_1, there is a maximum of hydrogen bonds between water molecules and after this point, there is insufficient water present to maintain a three-dimensional hydrogen-bonded network of water molecules. After χ_1 is passed, there are localized attempts to create a water hydrogen-bonded network which is increasingly defeated as the concentration of co-solvent is increased. The effect of maximum structure-breaking or solvent disorder is reached at some mole fraction, χ_2. These two values of mole fraction, that is χ_1 and χ_2, depend both on co-solvent and temperature. At 298 °C, they are approximately 0.06 and 0.35, respectively, for acetone [22]. An inspection of Fig. 1 shows a strong response of the rate constant at 298 °C at a mole fraction of 0.35 for the mono-bridged inner-sphere path and a more general levelling off of the rate at this value of χ for the other two pathways. Only the di-bridged path shows a response to the first critical value of χ_1 at 0.06. There is, in fact, no appreciable rate of the di-bridged path until $\chi_1 = 0.06$. Thus, we can speculate that the presence of a water sheath around the activated complex effectively prevents a di-bridged transition state from forming. Recall that this pathway was not observed at all in a purely aqueous environment [21]. Only after the critical mole fraction, χ_1, is reached, can the double-bridged transition state form. After this point, the three-dimensional properties of the water network are lost and the Cr(II) may orient itself properly with respect to the substrate to utilize this pathway.

Inspection of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Figs. 2 and 3) both show a relatively strong response to the first critical value of the mole fraction, 0.06. The enthalpy increases for all three pathways and the entropy decreases. This implies that the co-solvent, acetone, is beginning to play an important role in the solvation of the activated complex at this point and a more ordered transition state is now possible compared to that formed in pure water. However, the enthalpy expended in reaching this state is correspondingly greater, as well.

Burgess [22] has noted that $\Delta G^{\ddagger}$ is generally a well-behaved function, that is, it usually changes smoothly and gradually as the solvent composition changes. This behavior contrasts markedly with those of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$; these quantities often vary in what may appear to be an erratic manner but usually change in such a way as to minimize changes in $\Delta G^{\ddagger}$. For each of the two co-solvents we have investigated

TABLE VII. Ranges of $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ Values for Redox Reactions in Mixed Solvents

Reaction	Solvent system	Range $\Delta H^{\ddagger}$ (kcal mol^{-1})	Range $\Delta G^{\ddagger}$ (kcal mol^{-1})	Reference
$Co(NH_3)_5F^{2+}$ + Cu(I)	Me_2SO/H_2O	8–14	17–19	35
$Co(NH_3)_5(HCOO)^{2+}$ + Cu(I)	Me_2SO/H_2O	12–19	19–21	35
$Co(NH_3)_5F^{2+}$ + Fe(II)	Me_2SO/H_2O	9–14	16–20	6
$Co(NH_3)_5Cl^{2+}$ + Fe(II)	Me_2SO/H_2O	10–22	19–22	6
$Co(NH_3)_5Br^{2+}$ + Fe(II)	Me_2SO/H_2O	12–22	19–22	6
cis-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ + Fe(II)	$EtOH/H_2O$	13–21	24–26	6
$Co(ptdn)_3$ + Cr(II) (inner, mono)	$Acetone/H_2O$	3–13	15–17	[a]
$Co(ptdn)_3$ + Cr(II) (inner, di)	$Acetone/H_2O$	9–16	14–18	[a]
$Co(ptdn)_3$ + Cr(II) (outer)	$Acetone/H_2O$	5–11	14–17	[a]
$Co(ptdn)_3$ + Cr(II) (inner, mono)	DMF/H_2O	9–11	16–17	11
$Co(ptdn)_3$ + Cr(II) (inner, di)	DMF/H_2O	9–16	16–19	11
$Co(ptdn)_3$ + Cr(II) (outer)	DMF/H_2O	5–7	13–17	11
$Co(NH_3)_5N_3^{2+}$ + Fe(II)	Me_2SO/H_2O	14–19	18–20	9

[a] Present work.

for the reaction of Cr(II) and $Co(ptdn)_3$, *i.e.* dimethylsulfoxide [11] and acetone (present work), we have also observed that the free energy of activation remains relatively constant within each set of mixed solvents although it may be partitioned very differently between the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as the proportion of organic to aqueous solvent is varied. This appears to be a general feature of redox reactions in mixed solvents (see Table VII). This does not mean that an isokinetic relationship holds for these systems although such claims have been made erroneously in the past by inorganic chemists [24–28] on the basis of linear plots between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Exner [29–31] has provided a statistical treatment for determining the validity of a possible isokinetic relationship. To use his method, one plots a family of 'transition-state' lines, *i.e.* plots of ln *k versus* $1/T$, of a series of related experiments, such as those carried out in a series of water/organic solvent mixtures reported in the present work. These should intersect at some point which Exner calls β (often referred to as the isokinetic temperature) where

$$\Delta H^{\ddagger} = h_o + \beta \Delta S^{\ddagger}$$

In the special case where all the reactions were carried out at the same set of temperatures and all measurements have the same weight, the least-squares non-linear set of equations arising from the error analysis was solved explicitly [30]. Our results fail the Exner test which implies that either an isokinetic relationship does not exist in the present work or that the data are not sufficiently precise to confirm it. Nevertheless, there is a strong tendency in the results of ourselves and others (Table VII) for $\Delta G^{\ddagger}$ to remain fairly constant as the proportion of organic solvent to water is changed in electron transfer reactions. At the same time, there may be dramatic redistributions in free energy between the entropic and enthalpic parts which are reproducible and well outside the error limits of the experiment. At least one inorganic redox system, reported by Linert and Kudrjawsev [32], for the reaction between a series of Mn(II) oxinates with the $Fe^{II}(Me_2NCHO)_6$ solvate in propylene carbonate and acetonitrile, has survived the Exner statistical treatment, thus confirming the existence of a genuine isokinetic relationship in this system.

In the present work, the outer-sphere and mono-bridged inner-sphere pathways show simple second order kinetics with no acid dependencies (Table IV), as was true also in the earlier studies in dimethylformamide mixtures [11], and again the observed rate constant for the di-bridged path did contain a term inverse in acid concentration although the acid dependence is much more pronounced in the acetone solutions.

This implies that the cobalt exists in both the protonated and unprotonated forms with the latter being the reactive species for di-bridged electron transfer.

$$\begin{array}{rcl} Co(ptdnH)(ptdn)_2^+ & \rightleftharpoons & Co(ptdn)_3 + H^+ \\ & & + \\ & & Cr(II) \\ & & \downarrow \\ & & Cr(ptdn)_2(OH_2)_2^+ \end{array}$$

The observed rate constant derived for this mechanism is

$$k_{obs} = \frac{k_{DI}K_a}{K_a + [H^+]}$$

Assuming that $[H^+] \gg K_a$, then

$$1/k_{obs} = \frac{[H^+]}{k_{DI}K_a}$$

which is consistent with the empirical rate expression given in eqn. (2). The slopes of the lines obtained by plotting $1/k_{obs}$ *versus* $[H^+]$ give $1/k_{DI}K_a$ (see Table VI).

The observation of a hydrogen ion dependence for only one of the inner-sphere paths is rather curious and is probably best explained on electronic grounds. It appears that inner-sphere attack on a protonated ring is disfavored. A mono-bridged transition state requires attack at a single pentane-2,4-dione ring. If a Cr(II) approaches the cobalt complex at a ring which is protonated, it must be at the same time very close to another ring on the same cobalt atom, which is unlikely to simultaneously bear an extra proton. Attack is therefore always possible at an unprotonated ring and no acid dependence is observed. However, for the di-bridged mechanism, the Cr(II) must simultaneously find two unprotonated rings on the same cobalt center for electron transfer to occur. The coulombic barrier presented by a charged cobalt(III) complex coming into contact with a charged chromium(II) species may be too great to allow for the sufficiently long-lived transition state that may be necessary for formation of two bonds between the redox centers. Hence, di-bridged electron transfer is observed only for the unprotonated species.

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