Assignment of Inner- and Outer-sphere Mechanisms to the Vanadium-(II) Reductions of Halogenopenta-amminecobalt(III) Complexes

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Although rate constants (l mol^{-1} s^{-1}) at 25°, I = 2·0M (LiClO$_4$), for the V^{2+} reduction of Co(NH$_3$)$_5$F^{2+} (3·95), Co(NH$_3$)$_5$Cl^{2+} (10·2), Co(NH$_3$)$_5$Br^{2+} (30·0), and Co(NH$_3$)$_5$I^{2+} (127) show a systematic trend, the activation parameters ($\Delta H^\ddagger$ kcal mol^{-1}; $\Delta S^\ddagger$ cal K^{-1} mol^{-1}) indicate a different mechanism for Co(NH$_3$)$_5$F^{2+} (11·1, −18·5) compared with Co(NH$_3$)$_5$Cl^{2+} (7·5, −28·8), Co(NH$_3$)$_5$Br^{2+} (7·2, −27·6), and Co(NH$_3$)$_5$I^{2+} (7·3, −24·6). An inner-sphere substitution-controlled mechanism is proposed for the reduction of Co(NH$_3$)$_5$F^{2+}, whereas Co(NH$_3$)$_5$Cl^{2+}, Co(NH$_3$)$_5$Br^{2+}, and Co(NH$_3$)$_5$I^{2+} react by an outer-sphere mechanism. These assignments are supported by linear free-energy plots using data for the V^{2+}, Cr^{2+}, Ru(NH$_3$)$_6$$^{2+}$, and Cr(bipy)$_3$$^{2+}$ reductions of common oxidants. Reasons for the different behaviour are considered.

VANADIUM(II) reductions of halogenopenta-ammine-cobalt(III) complexes have been investigated previously,[1,2] and although outer-sphere electron-transfer processes have been suggested, the data obtained have not led to a clearcut assignment of mechanism. A particularly noteworthy omission has been the determination of precise activation parameters for these

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[1] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019.

[2] H. Diebler and H. Taube, *Inorg. Chem.*, 1965, **4**, 1029.

reactions. This situation has already been rectified in the case of $Co(NH_3)_5Cl^{2+}$, and recent values obtained at ionic strength I = 2·0M ($\Delta H^{\ddagger}$ = 7·5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −28·8 cal K^{-1} mol^{-1}) [3] are in good agreement with those at I = 1·0M ($\Delta H^{\ddagger}$ = 7·4 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −29·5 cal K^{-1} mol^{-1}).[4] Activation parameters for other reactions in this series are now reported.

RESULTS

The V^{3+} reductions of penta-amminecobalt(III) complexes [5] are slow compared with the corresponding V^{2+} reductions, and V^{3+} products in the present studies have no effect upon the rate processes investigated. Absorbance changes and kinetic data are consistent with 1 : 1 stoicheiometries, and reactions may be represented by (1) for an inner-sphere, or (2) for an outer-sphere reaction.

$$V^{2+} + Co(NH_3)_5X^{2+} \xrightarrow{H^+} VX^{2+} + Co^{2+} + 5NH_4^+ \quad (1)$$

$$V^{2+} + Co(NH_3)_5X^{2+} \xrightarrow{H^+} V^{3+} + X^- + Co^{2+} + 5NH_4^+ \quad (2)$$

The V^{2+} *Reduction of* $Co(NH_3)_5F^{2+}$.—The reaction was monitored at the 509 nm peak position of $Co(NH_3)_5F^{2+}$ (ε = 44 l mol^{-1} cm^{-1}), using a recording spectrophotometer. Second-order reaction conditions were used with first the cobalt(III) complex and then the V^{2+} reactant in excess. Second-order plots were generally linear to ⩾80% reaction, thus indicating a first-order dependence on both [V^{2+}] and [$Co(NH_3)_5F^{2+}$]. There was no dependence on hydrogen-ion concentration, [H^+] = 0·01—1·0M. Second-order rate constants, k_F, at temperatures 2·5—45·0° are listed in Table 1. The data were computed using a non-linear least-squares programme [6] with weighting factor $1/k_F^2$ to give the best k_F value (at 25°), and activation parameters $\Delta H_F^{\ddagger}$ and $\Delta S_F^{\ddagger}$ as listed in Table 4. An experiment with V^{2+} in eight-fold excess of $Co(NH_3)_5F^{2+}$ was carried out using stopped-flow spectrophotometry. The reaction was monitored at λ = 509 and 300 nm. At both wavelengths the observed rates indicated the same single rate process, and there was no evidence at λ = 300 nm for the build-up of VF^{2+} as an intermediate.

The V^{2+} *Reduction of* $Co(NH_3)_5Br^{2+}$.—The rate of disappearance of the complex at the 551 nm peak position (ε = 53·9 l mol^{-1} cm^{-1}) was studied under pseudo-first-order conditions (20—80 fold excess of [V^{2+}]), using the stopped-flow spectrophotometer. First-order plots of log ($OD_t - OD_\infty$) against time were linear to ⩾90% completion. The reduction is first order in both reactants, and the rate is independent of [H^+] in the range 0·4—1·6M. Rate constants, k_{Br}, at temperatures 15—45° are listed in Table 2. Data were computed as before, and the rate constant at 25° and activation parameters are listed in Table 4.

The V^{2+} *Reduction of* $Co(NH_3)_5I^{2+}$.—The complex is known to undergo an internal redox reaction between iodide and cobalt(III).[7] To minimize any possible effects of this decomposition the sample was used within 24 h of preparation. As a further precaution the V^{2+} reduction was monitored at λ = 380 nm as well as the peak position λ = 580 nm (ε = 79·4 l mol^{-1} cm^{-1}). The stopped-flow method was used. At both wavelengths the observed rate processes were in agreement, and first-order plots were linear to ⩾85%. The reduction was again first-order in both reactants and no [H^+] dependence was observed in the range 0·1—1·9M. Second-order rate constants, k_I, are given in Table 3. The data were computed as before and relevant kinetic parameters are shown in Table 4.

TABLE 1

Rate constants for the V^{2+} reduction of $Co(NH_3)_5F^{2+}$, I = 2·0M ($LiClO_4$); λ = 509 nm

Temp. °C	[H^+] M	10^3[V^{2+}] M	10^3[$Co(NH_3)_5F^{2+}$] M	k_F l mol^{-1} s^{-1}
2·5	0·026	1·76	2·76	0·775
5·0	0·026	1·72	2·78	0·965
5·4	0·026	6·74	3·40	0·97
5·4	0·038	6·80	3·00	0·99
5·4	0·049	13·20	3·05	1·04
5·4	0·105	13·90	2·70	0·96
5·4	0·562	7·30	3·13	1·03
5·4	0·575	14·10	2·30	1·03
15·0	0·026	6·70	3·40	2·07
15·0	0·050	13·20	3·00	1·92
15·0	0·083	6·45	2·50	1·90
15·0	0·105	14·00	2·70	1·99
15·0	0·561	7·15	2·61	1·90
15·0	0·575	13·20	2·21	1·88
25·0	0·004	0·59	1·06	4·15
25·0	0·011	1·10	1·52	4·05
25·0	0·040	1·35	2·23	3·75
25·0	0·061	12·40	2·10	4·00
25·0	0·061	12·50	2·15	3·80
25·0	0·065	8·25	1·0	3·91 [a]
25·0	0·065	8·25	1·0	3·59 [b]
25·0	0·071	1·51	1·21	3·97
25·0	0·082	0·71	1·78	4·10
25·0	0·148	12·60	2·24	3·85
25·0	0·148	12·55	2·20	3·85
25·0	0·148	12·50	2·15	3·90
25·0	0·367	1·35	2·23	3·90
25·0	0·671	1·30	1·55	4·20
25·0	1·012	12·55	2·20	4·10
35·0	0·013	1·29	2·05	7·50
35·0	0·017	2·00	2·00	7·75
35·0	0·034	7·18	0·53	7·80
35·0	0·041	7·05	2·00	7·70
35·0	0·102	0·85	1·75	7·95
35·0	0·107	2·12	2·12	7·65
35·0	0·121	4·56	0·77	7·40
35·0	0·129	7·05	2·00	7·75
45·0	0·013	1·62	1·95	13·75
45·0	0·025	1·46	2·78	13·95
45·0	0·025	1·42	2·76	13·75
45·0	0·025	1·66	2·80	13·75
45·0	0·040	6·15	0·91	13·45
45·0	0·103	0·98	2·06	13·70
45·0	0·107	2·09	2·09	13·50
45·0	0·122	4·70	1·08	13·50
45·0	0·129	6·05	0·77	13·90

[a] Using stopped flow, λ = 300 nm. [b] Using stopped flow λ = 509 nm.

To eliminate the effect of any product from the internal redox reaction a check run was performed with a sample 1 week old. Spectrophotometric analysis indicated that the sample was only 90% pure, however, a plot of log ($OD_t - OD_\infty$) against time was 95% linear and gave a rate constant in agreement with other values. It is concluded that any impurities present do not interfere with the observed reaction.

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[3] R. S. Taylor, R. N. F. Thorneley, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 856.

[4] K. W. Hicks, D. L. Toppen, and R. G. Linck, *Inorg. Chem.* 1972, **11**, 310.

[5] See for example O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, 1969, **91**, 1313.

[6] Los Alamos Report LA2367 (1959) and addenda by R. H. Moore and R. K. Ziegler.

[7] A. Haim and H. Taube, *J. Amer. Chem. Soc.*, 1963, **85**, 495.

DISCUSSION

Rate constants obtained previously at 25° for the V^{2+} reduction of halogenopenta-amminecobalt(III) complexes [1,2] are in satisfactory agreement with the present data. A steady increase is observed for the complexes, fluoro < chloro < bromo < iodo, and different mechanisms are not immediately apparent. Activation parameters reported by Candlin *et al.*[1] from limited rate-constant data are not in satisfactory agreement with those determined in this study, Table 4. The activation parameters now determined clearly indicate the possibility of a different mechanism for the fluoro-complex, which has activation parameters as required for a substitution-controlled process. Vanadium(II) reductions of mononuclear cobalt(III) complexes which appear to fall into this category are summarized in Table 5.

TABLE 2

Rate constants for the V^{2+} reduction of $Co(NH_3)_5Br^{2+}$, $I = 2{\cdot}0$M ($LiClO_4$); λ = 551 nm. Number of runs which have been averaged indicated in parentheses

Temp. °C	[H^+] M	10^2[V^{2+}] M	10^3[$Co(NH_3)_5Br^{2+}$] M	k_{Br} l mol^{-1} s^{-1}
15·0	0·44	3·97	1·00	19·1 (3)
	1·28	3·89	1·00	19·0 (3)
25·0	0·44	3·86	1·00	31·1 (3)
	1·28	3·88	1·00	30·9 (3)
35·0	0·80	3·99	0·50	42·6 (3)
	0·80	3·99	2·00	44·4 (3)
	0·80	3·99	1·00	46·6 (1)
	0·80	1·20	1·00	48·3 (2)
	0·80	4·55	1·00	46·8 (3)
	0·45	3·82	1·00	44·2 (3)
	1·60	3·98	1·00	43·5 (3)
45·0	0·44	3·97	1·00	71·0 (3)
	0·80	0·46	1·00	69·7 (3)
	1·28	3·87	1·00	71·1 (3)

TABLE 3

Rate constants for the V^{2+} reduction of $Co(NH_3)_5I^{2+}$, $I = 2{\cdot}0$M ($LiClO_4$). All runs monitored at 380 and 580 nm peak positions for $Co(NH_3)_5I^{2+}$. Number of runs which have been averaged indicated in parentheses

Temp. °C	[H^+] M	10^2[V^{2+}] M	10^3[$Co(NH_3)I^{2+}$] M	k_I l mol^{-1} s^{-1}
3·6	0·20	3·61	1·00	47·9 (2)
	1·20	3·61	1·00	45·4 (2)
15·0	0·20	2·64	1·00	80·3 (4)
	1·20	2·64	1·00	79·2 (2)
25·0	1·00	1·12	1·00	119 (4)
	1·00	6·59	1·00	133 (3)
	1·00	2·83	1·00	133 (4)
	1·00	2·83	0·50	134 (3)
	1·00	2·83	2·50	127 (2)
	1·00	1·12	1·00	114 (3)
	0·10	2·87	1·00	131 (3)
	0·30	2·87	1·00	126 (4)
	1·93	3·10	1·00	126 (3)
35·0	0·20	2·61	1·00	194 (2)
	1·20	2·61	1·00	211 (4)

The rate constant for the vanadium(II) reduction of $Co(NH_3)_5I^{2+}$ is too high for substitution into the vanadium(II) co-ordination sphere to occur prior to electron transfer,[8] which necessarily excludes an inner-sphere mechanism. The activation parameters for the V^{2+} reductions of $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and $Co(NH_3)_5I^{2+}$ suggest that all three reactions may be assigned to the outer-sphere category. We now look for further evidence to substantiate this assignment.

TABLE 4

Summary of data for the V^{2+} reduction of halogenopenta-amminecobalt(III) complexes, $I = 2{\cdot}0$M ($LiClO_4$)

Oxidant	k (25°) l mol^{-1} s^{-1}	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal K^{-1} mol^{-1}
$Co(NH_3)_5F^{2+}$	3·95	11·1 ± 0·1	−18·5 ± 0·2
$Co(NH_3)_5Cl^{2+}$ [a,b]	10·2	7·5 ± 0·15	−28·8 ± 0·5
$Co(NH_3)_5Br^{2+}$ [c]	30·0	7·2 ± 0·2	−27·6 ± 0·7
$Co(NH_3)_5I^{2+}$ [d]	127·0	7·26 ± 0·25	−24·6 ± 0·8

[a] From ref. 3. [b] Data obtained at $I = 1{\cdot}0$M ($LiClO_4$), k (25°) = 7·6 l mol^{-1} s^{-1}, $\Delta H^‡ = 7{\cdot}4 \pm 0{\cdot}5$ kcal mol^{-1}, and $\Delta S^‡ = -29{\cdot}5 \pm 3{\cdot}0$ cal K^{-1} mol^{-1}, see ref. 4. [c] Candlin *et al.*, ref. 1, report values $\Delta H^‡ = 9{\cdot}1$ kcal mol^{-1} and $\Delta S^‡ = -22$ cal K^{-1} mol^{-1}. [d] Candlin *et al.*, ref. 1, report values $\Delta H^‡ = 4{\cdot}6$ kcal mol^{-1} and $\Delta S^‡ = -32$ cal K^{-1} mol^{-1}.

TABLE 5

Kinetic data for V^{2+} reductions of penta-amminecobalt(III) complexes, $Co(NH_3)_5X^{n+}$, which are possibly of the V^{2+}-substitution controlled type

Complex	k (25°) l mol^{-1} s^{-1}	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal K^{-1} mol^{-1}	Ref.
$Co(NH_3)_5N_3^{2+}$ [a]	13	11·7	−14	1
$Co(NH_3)_5SO_4^{+}$ [b]	25·5	11·6	−13·1	*c*
$Co(NH_3)_5C_2O_4^{+}$	45·3			*d*
$Co(NH_3)_5C_2O_4H^{2+}$	12·5	12·2	−13	*d*
$Co(NH_3)_5$(glyoxalate)$^{2+}$	8·2	11·0	−17	*d*
$Co(NH_3)_5$(pyruvate)$^{2+}$	10·2	11·6	−15	*d*
$Co(NH_3)_5$(Me_3-pyruvate)$^{2+}$	2·1	11·9	−17	*d*
$Co(NH_3)_5$(oxamate)$^{2+}$	20·7	11·6	−14	*d*
$Co(NH_3)_5(HCO_2)^{2+}$ [e]	3·6	13·9	−13	*f*
$Co(NH_3)_5(MeCO_2)^{2+}$	1·2	11·6	−19	*f*

[a] The V^{2+} reduction of related azido-cobalt(III) complexes are also substitution controlled, (ref. 4). [b] The V^{2+} reduction of μ-amido-μ-selenato- and μ-amido-μ-phosphato-bis[tetra-amminecobalt(III)] complexes are substitution controlled [see *e.g.* M. Green, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 509], and mononuclear selenato- and phosphato-complexes probably react in a similar manner. [c] R. S. Taylor, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 277. [d] H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1. [e] The V^{2+} reduction of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^{+}$ are substitution controlled, T. J. Przystas and A. Haim, *Inorg. Chem.*, 1972, **11**, 1018. [f] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1971, **10**, 1983.

Guenther and Linck [9] have previously assigned outer-sphere mechanisms to the vanadium(II) reduction of a series of chlorocobalt(III) complexes, including $Co(NH_3)_5Cl^{2+}$. The basis of this assignment was the linearity of a plot of log k_V against log k_{Fe}, where k_V and k_{Fe} are rate constants for vanadium(II) and iron(II) reductions of common chlorocobalt(III) oxidants. Some

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[8] See for example N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 225; K. Kustin and J. Swinehart, *Progr. in Inorg. Chem.*, 1970, **13**, 107.

[9] P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, 1969, **91**, 3769.

of the vanadium(II) reductions are too fast for inner-sphere electron transfer to occur, and one at least of the iron(II) reactions is known to be inner sphere because the product $FeCl^{2+}$ has been detected.[10] The linearity of the plot suggests that vanadium(II) reactions are all outer sphere, and those of iron(II) are all inner sphere with a chloride ligand occupying a similar position relative to oxidant and reductant at the time of electron transfer.

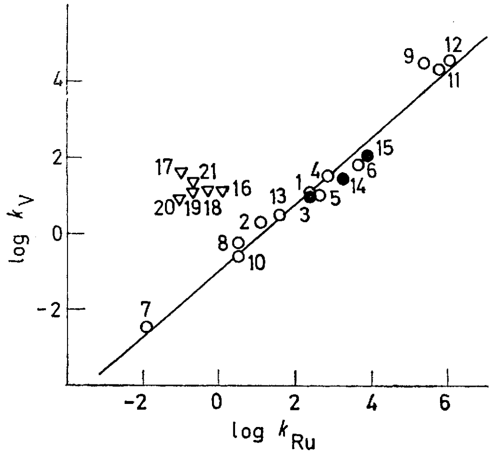

FIGURE 1 Rate constants for V^{2+} and $Ru(NH_3)_6^{2+}$ reductions of common oxidants. All the reductions with $Ru(NH_3)_6^{2+}$ are outer sphere. Points marked (○, ●) indicate outer-sphere V^{2+} reductions, and points marked ▽ indicate inner-sphere V^{2+} reductions: 1, *cis*-$Co(en)_2(H_2O)Cl^{2+}$; 2, *cis*-$Co(en)_2(NH_3)Cl^{2+}$; 3, *cis*-$Co(en)_2(NH_2CH_2C_6H_5)Cl^{2+}$; 4, *cis*-$Co(en)_2(C_5H_5N)Cl^{2+}$; 5, *cis*-$Co(en)_2Cl_2^+$; 6, *trans*-$Co(en)_2Cl_2^+$; 7, $Co(NH_3)_6^{3+}$; 8, $Co(NH_3)_5H_2O^{3+}$; 9, $Co(C_2O_4)_3^{3-}$; 10, *trans*-Co(1,4-diene)$(NH_3)_2^{3+}$; 11, *trans*-Co(1,4-diene)Br_2^+; 12, Co(tetra)Br_2^+; 13, $Co(NH_3)_5Cl^{2+}$; 14, $Co(NH_3)_5Br^{2+}$; 15, $Co(NH_3)_5I^{2+}$; 16, $Co(NH_3)_5N_3^{2+}$; 17, $Co(NH_3)_5(C_2O_4)^+$; 18, $Co(NH_3)_5(C_2O_4H)^{2+}$; 19, $Co(NH_3)_5$(pyruvate)$^{2+}$; 20, $Co(NH_3)_5$(glyoxalate)$^{2+}$; 21, $Co(NH_3)_5$(oxamate)$^{2+}$. Data taken from refs. 1, 3, 9, 11, 13, 14 and the following: R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, 1968, **90**, 6364; H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1; D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, 1972, **94**, 394; T. J. Meyer and H. Taube, *Inorg. Chem.*, 1968, **7**, 2369; and B. Grossman and A. Haim, *J. Amer. Chem. Soc.*, 1971, **93**, 6490.

A correlation of this sort is generally only to be expected when both reductants operate by the same mechanism, and that mechanism is of the outer-sphere class. The comparison of V^{2+} and Fe^{2+} reductions along these lines is not strictly valid, since it is concluded that the vanadium(II) reductions are outer sphere, and those of iron(II) are inner sphere. However, the reasonable assumption that precursor complexes for both series of reactions will be subject to similar influences justifies the comparison. The use of theories developed for weak adiabatic electron transfer reactions is not applicable to inner-sphere reactions, where bonds are formed and broken. Nevertheless if the same bonds are formed and broken in every case there should justifiably be a correlation of some sort.

Hexa-ammineruthenium(II) exhibits substitution inert properties and reacts by an outer-sphere mechanism,[11] and for this reason serves as an excellent standard by which to compare other reductants. Vanadium(II), on the other hand, although the most inert of 2+ ions in the first transition series is a much more labile ion.[12] Vanadium(II) reductions of for example $Co(NH_3)_6^{3+}$ [13] and $Co(NH_3)_5H_2O^{3+}$ [14] are firmly established as outer-sphere processes. It is noteworthy that these and the vanadium(II) reductions of chlorocobalt(III) complexes when compared with hexa-ammineruthenium(II) reduction of the same oxidants, indicate a linear relationship (see Figure 1). Points for the reductions of $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and $Co(NH_3)_5I^{2+}$ also lie on this line, which again is consistent with an outer-sphere assignment. The points indicated in Figure 1 for outer-sphere reactions give a least-squares fit, with equal weighting, to equation (3). Points believed to

$$\log k_V = 0{\cdot}89 \log k_{Ru} - 0{\cdot}95 \qquad (3)$$

represent inner-sphere reactions do not lie on the line and have not been included in equation (3).

It is possible to carry out a similar plot of log k_V against log $k_{Cr'}$, where $k_{Cr'}$ represents the rate constant for outer-sphere reduction by $Cr(bipy)_3^{2+}$ [1,15] (see Figure 2). The best least-squares fit is given by equation (4).

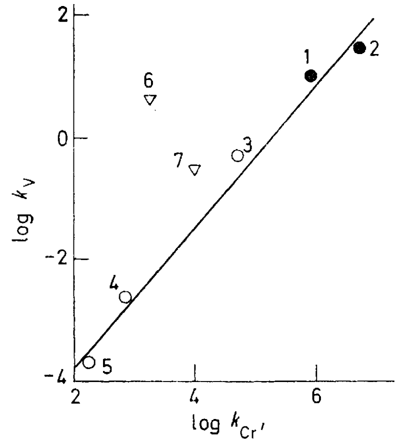

FIGURE 2 Rate constants for V^{2+} and $Cr(bipy)_3^{2+}$ reduction of common oxidants. All the reductions of $Cr(bipy)_3^{2+}$ are outer-sphere. Points marked (○, ●) indicate outer-sphere V^{2+} reductions, and points marked ▽ indicate inner-sphere vanadium(II) reductions: 1, $Co(NH_3)_5Cl^{2+}$; 2, $Co(NH_3)_5Br^{2+}$; 3, $Co(NH_3)_5H_2O^{3+}$; 4, $Co(NH_3)_6^{3+}$; 5, $Co(en)_3^{3+}$; 6, $Co(NH_3)_5F^{2+}$; 7, $Co(NH_3)_5NCS^{2+}$

$$\log k_V = 1{\cdot}18 \log k_{Cr'} - 6{\cdot}1 \qquad (4)$$

The rate constant for reduction of $Co(NH_3)_5I^{2+}$ by

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[10] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 1966, **88**, 5343.

[11] J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, 1964, **86**, 1686.

[12] M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, 1969, **51**, 289.

[13] A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 793.

[14] P. Dodel and H. Taube, *Z. phys. Chem. (Frankfurt)*, 1965, **44**, 92.

[15] A. Zwickel and H. Taube, *Discuss. Faraday Soc.*, 1960, **29**, 42.

$Cr(bipy)_3^{2+}$ has not been measured, possibly because the reaction is too rapid. However, the remaining halogenopenta-amminecobalt(III) complexes have been studied. As required by the outer-sphere assignment both $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ lie on this line and the point for $Co(NH_3)_5F^{2+}$ lies well off. An interesting feature of this latter plot is that rate constants for reduction of $Co(NH_3)_5NCS^{2+}$ ($k_V = 0{\cdot}3$ l mol^{-1} s^{-1}, $k_{Cr'} = 1{\cdot}0 \times 10^4$ l mol^{-1} s^{-1}) give a point which lies close to the line. Accordingly inner- and outer-sphere contributions are possible in the case of the V^{2+} reduction.

Finally, we refer to a plot of rate constants log k_V against log k_{Cr}, where the latter is for outer-sphere reactions of hexa-aquochromium(II). Toppen and Linck[16] have observed that k_{Cr}/k_V is of similar magnitude for the chromium(II) and vanadium(II) reductions of a wide range of oxidants including ions of different metals, providing an outer-sphere mechanism holds. This relationship has been well substantiated for cobalt(III) complexes.[17] The Cr^{2+} reductions of all four halogenopenta-ammine complexes are known to be inner sphere,[18] and when rate constants are plotted against those for the now established outer-sphere V^{2+} reductions the points lie well away from the line, as predicted. The use of free-energy correlations such as this provides an important tool not only for establishing a series of outer-sphere reactions, but also for further verifying inner-sphere processes. Rosseinsky[19] has recently extended the approach to a consideration of factors which determine the gradients of such plots.

Although the V^{2+} reduction of $Co(NH_3)_5F^{2+}$ is inner-sphere substitution controlled VF^{2+} was not detected as an intermediate. Two factors are probably responsible for this. First, even at 300 nm absorption bands for VF^{2+} are probably not strong, and secondly, under the conditions of $[H^+]$ used in these experiments protonation of the fluoride ligand probably results in a rapid dissociation.

Having established that the V^{2+} reduction of $Co(NH_3)_5F^{2+}$ is inner sphere, whereas those of $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and $Co(NH_3)_5I^{2+}$ are outer sphere it is pertinent to ask why this should be so. The Cr^{2+} reduction of halogenopenta-amminecobalt(III) complexes are all demonstrably inner sphere, and there are strong reasons for supposing that the Fe^{2+} [9,10] and Eu^{2+} [1] reductions of $Co(NH_3)_5Cl^{2+}$ are also inner sphere. Why, therefore, is the vanadium(II) reduction of $Co(NH_3)_5Cl^{2+}$ outer sphere? The outer-sphere rate constants for the V^{2+} reductions do not exclude a contribution from an inner-sphere substitution-controlled process. The possibility that one path, either inner sphere or outer sphere, is dominant but not the exclusive pathway for electron transfer has been considered. However it must be stressed that activation-energy plots are strictly linear, and show no curvature as would be expected if two different activation processes were contributing.

It is generally supposed that substitution reactions of 2+ hexa-aquo-ions in the first transition series conform to a dissociative (S_N1) exchange mechanism involving the outer-sphere complex.[20] The experimental evidence is particularly strong and extensive for the Ni^{2+} hexa-aquo-ion.[21] There is a shortage of data for simple straightforward substitution reactions of V^{2+} but the data for many redox reactions which appear to be substitution controlled[8] seem to support an S_N1 process. If the mechanism of substitution at the V^{2+} centre is of the S_N1 type the basicity of the incoming ligand would not be expected to be important, as is apparent from the data in Tables 4 and 5.

Consideration of the thermodynamic stability of possible inner-sphere complexes gives a more credible explanation of the observations. The lifetime of precursor complexes such as $[(H_2O)_5VXCo(NH_3)_5]^{4+}$ ($X^- = F^-$, Cl^-, Br^-, and I^-) will be determined by their stability. Since the rate constants for precursor complex formation are of similar magnitude the thermodynamic stability of the precursor complexes will be reflected in dissociation rates prior to electron transfers. Inner-sphere redox reactions of V^{2+} are represented by equations (5) and (6). When precursor complexes have

$$V(H_2O)_6^{2+} + Co(NH_3)_5X^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(H_2O)_5VXCo(NH_3)_5]^{4+} + H_2O \quad (5)$$

$$[(H_2O)_5VXCo(NH_3)_5]^{4+} \xrightarrow[H^+/H_2O]{k_2} V(H_2O)_5X^{2+} + Co^{2+} + 5NH_4^+ \quad (6)$$

only low thermodynamic stability there may be competition between the rate of dissociation (k_{-1}) and the rate of electron transfer (k_2). With $X^- = Cl^-$, Br^-, and I^-, it appears that the precursor complexes dissociate rapidly before electron transfer occurs (*i.e.* $k_{-1} \gg k_2$) and outer-sphere reduction prevails. With $X^- = F^-$, $k_2 \geqslant k_{-1}$ and dissociation is not effective in restricting inner-sphere electron transfer.

The opposite effect is found when considering reduction of the halogenopenta-ammines by $Co(CN)_5^{3-}$ (in the presence of excess of CN^-). The reduction of $Co(NH_3)_5F^{2+}$ occurs by both inner- and outer-sphere processes whereas with $Co(NH_3)_5Cl^{2+}$ only the inner-sphere pathway is detected.[22] Using the terminology of equations (5) and (6), when $X^- = F^-$ it is concluded that $k_{-1} \approx k_2$ and when $X^- = Cl^-$ it follows that $k_2 \gg k_{-1}$. No information is available for the reactions with $X^- = Br^-$ and I^-.

Thermodynamic stability is often described in terms

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[16] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.

[17] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832.

[18] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

[19] D. R. Rosseinsky, *J.C.S. Chem. Comm.*, 1972, 225.

[20] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, 2nd edn., 1967, p. 154.

[21] R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408.

[22] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, 1963, **85**, 2517.

of hard and soft acid and bases.[23] This approach seems particularly appropriate because $V(H_2O)_5^{2+}$ and $Co(CN)_5^{3-}$ would be expected to exhibit different relative stabilities towards halide ligands, since in terms of the ' hard ' and ' soft ' approach $V(H_2O)_5^{2+}$ is a hard acid whereas $Co(CN)_5^{3-}$ is a soft acid. The fluoride ion is classified as a hard base whereas chloride, bromide, and iodide become increasingly softer bases. Consequently the interaction of V^{2+} and F^- is much more favourable than that of V^{2+} and I^-, and the fluoro-complex reacts by an inner-sphere mechanism. The converse is true for $Co(CN)_5^{3-}$, interaction with Cl^- being of the soft acid with soft base type and therefore more favourable than the soft acid–hard base interaction found with $Co(NH_3)_5F^{2+}$ and $Co(CN)_5^{3-}$.

It is possible to estimate a rate constant from Figure 2 for the V^{2+} reduction of $Co(NH_3)_5F^{2+}$ by an outer-sphere mechanism. This value is about 1% of the observed rate constant. Using the same approach (plot of log k_V against log k_{Cr}) an outer-sphere pathway for the Cr^{2+} reduction of $Co(NH_3)_5Cl^{2+}$ accounts for only 0·0001% of the observed rate constant.[24] The latter value once again illustrates how much more favourable inner-sphere reactions are in the case of chromium(II) reductions.

Reductants often have specific properties (related to their substitution and redox activity) which exclude certain mechanistic possibilities. In the case of V^{2+} it is appropriate to consider hard and soft theory for reactions where a precursor complex is formed which can exercise some discrimination to the available mechanisms. Hexa-aquo-chromium(II) does not exhibit such sensitivity to competition between inner- and outer-sphere mechanisms. There are several reasons for this behaviour. Outer-sphere reactions of Cr^{2+} are generally believed to be unfavourable because the Cr^{2+} to Cr^{3+} change is much more demanding in terms of reorganization energy, and whenever possible the inner-sphere pathway is preferable. Also, the greater reducing power of Cr^{2+} compared to V^{2+} will have a more profound effect on the destiny of a precursor complex. With Cr^{2+} an inner-sphere precursor complex will invariably result in inner-sphere electron transfer with $k_2 \gg k_{-1}$. With V^{2+} the choice between dissociation and electron transfer is less obvious, and either possibility may result.

The rates of substitution at V^{2+} and Cr^{2+} centres (*ca.* 10^2 s^{-1} and 10^9 s^{-1} respectively) [20] will restrict possible mechanisms under certain conditions. With powerful oxidants the thermodynamic free-energy change for V^{2+} reductions will be sufficiently great that it lowers the activation free-energy barrier, and outer-sphere redox rates will increase to values which are higher than the substitution rates. In a situation such as this the inner-sphere precursor complex will not have time to form, and outer-sphere reductions must occur. A limitation of this kind is much less likely when Cr^{2+} is the reductant.

EXPERIMENTAL

Vanadium(II) perchlorate solutions were prepared from vanadium(IV) sulphate as described in previous papers from these laboratories. The complexes $Co(NH_3)_5F^{2+}$,[25] $Co(NH_3)_5Br^{2+}$,[26] and $Co(NH_3)_5I^{2+}$ [27] were prepared using procedures available in the literature, and were converted into perchlorate salts. Some care was required in the case of the preparation of $Co(NH_3)_5I^{2+}$ to minimise aquation of the product. Samples were contaminated with as much as 5% of $Co(NH_3)_5H_2O^{3+}$, but this did not affect the kinetics since the latter is much less redox active than $Co(NH_3)_5I^{2+}$. The ionic strength of all reactant solutions was adjusted with lithium perchlorate, which had been recrystallized until free from anionic impurities. A Durrum–Gibson stopped-flow spectrophotometer, and Beckman DK2a and Acta III recording spectrophotometers were used.

Discussions with Dr. H. Diebler at the Max-Planck Institut in Göttingen are gratefully acknowledged. We thank the S.R.C. for a research studentship (to M. R. H.). Part of this work (by R. S. T.) was carried out at the Max-Planck Institute under the tenureship of a Royal Society Fellowship.

[3/1460 *Received*, 12*th July*, 1973]

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[23] See for example ref. 20, p. 23.

[24] M. C. Moore and R. N. Keller, *Inorg. Chem.*, 1971, **10**, 2635.

[25] F. Basolo and R. K. Murmann, *Inorg. Synth.*, 1953, **4**, 171.

[26] H. Diehl, H. Clark, and H. H. Willard, *Inorg. Synth.*, 1939, **1**, 186.

[27] R. G. Yalman, *J. Amer. Chem. Soc.*, 1955, **77**, 3219.