Electron-transfer Reactions of Cobaloximes: Kinetics and Mechanisms of the Vanadium(II) Reduction of Diammine-, Amminebromo-, and Amminechloro-bis(dimethylglyoximato)cobalt(III)

By **Reginald H. Prince** * and **Michael G. Segal**, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The kinetics of the title reactions have been studied and their activation parameters and rate laws at 25 °C determined. It is concluded from these that the monohalogeno-complexes react by an outer-sphere mechanism while the reaction of the diammine complex is a substitution-controlled inner-sphere process. It is suggested that the reaction of Cr^{2+}(aq) with the latter complex proceeds also by an inner-sphere mechanism.

BIS(DIMETHYLGLYOXIMATO) complexes of cobalt, known as cobaloximes, have been the subject of much interest in recent years. The pseudo-macrocycle formed by the two α-dioxime ligands linked by strong hydrogen bonds confers unusual properties on a Co^{III} ion, both thermodynamic, in stabilising cobalt–carbon bonds,[1] and kinetic in labilising the complexes towards substitution of the axial ligands.[2,3] We have investigated the kinetics of electron-transfer reactions of certain of the simple cobaloximes; such reactions of other Co^{III} complexes have been studied in great detail,[4-6] but these studies have in nearly all cases been limited to tetra- and penta-ammine complexes. Very few complexes of macrocyclic ligands have been investigated.[7] Some electron-transfer kinetics involving Co^{II} cobaloximes as reductants have been studied,[8] and inner-sphere electron transfer has been observed in a few cases between Co^{II} and Co^{III} cobaloximes.[9,10] Other than the reactions of alkyl cobaloximes with Cr^{2+}(aq),[11,12] there has as yet been no systematic investigation of the reactions of cobaloximes with other inorganic reducing agents.

The reductions of diamminebis(dimethylglyoximato)-cobalt(III), $[Co(Hdmg)_2(NH_3)_2]^+$ (Hdmg = the mono-anion of dimethylglyoxime), by Cr^{2+}(aq) and V^{2+}(aq) were studied first to determine whether the oxime functions could act as bridges in an inner-sphere mechanism. Product analysis is generally the most satisfactory test for this mechanism, but, in the absence of a positive result from this test, the ratio of the rate constants for vanadium and chromium reductions, and the activation parameters for the vanadium reaction, can provide evidence for either inner- or outer-sphere reaction: Toppen and Linck [13] have shown that when both reagents reduce a given ion by an outer-sphere path the ratio of rate constants is approximately constant, independent of the nature of the oxidant; most inner-sphere reactions of V^{2+}(aq) are believed to have as the rate-determining step the formation of the precursor complex, and they therefore have rate constants and activation parameters similar to those of substitution reactions at V^{2+}(aq),[6,14] and show little variation with changes in the oxidant. The kinetics of reduction of the monohalogeno-complexes $[Co(Hdmg)_2(NH_3)X]$ (X = Cl or Br) were further studied to provide a comparison with the above reactions, and also to investigate the effects of the pseudo-macrocycle on electron-transfer reactions in which it does not, apparently, play a direct part in binding the reducing agent.

EXPERIMENTAL

Reagents.—The salt $[Co(Hdmg)_2(NH_3)_2][ClO_4]$ was prepared by precipitation from aqueous solution of the chloride salt with sodium perchlorate, and washed with water, ethanol, and diethyl ether before drying under vacuum. Microanalysis showed that no further purification was necessary. The chloride salt was synthesised from $CoCl_2,6H_2O$ and H_2dmg in the usual manner.[15] The complexes $[Co(Hdmg)_3(NH_3)Cl]$ [16] and $[Co(Hdmg)_2(NH_3)Br]$ [17] were synthesised from the corresponding penta-amminehalogenocobalt halides, and recrystallised from water and 6% aqueous acetic acid [18] respectively.

Solutions of V^V in perchloric acid were prepared [19] and analysed for vanadium [20] by standard methods; analysis for $[H^+]$ by two literature methods [19,21] gave consistent results. Vanadium(II) was prepared by reduction of these stock solutions with 2% zinc amalgam, shortly before use, and stored over the amalgam, under nitrogen, for periods of 2 h at most. This reduction is quantitative,[19] as was verified by titration with $KMnO_4$ after treatment with an excess of V^V solution.

All solutions were prepared in deionised distilled water and deaerated with nitrogen. The acidity and ionic strength were adjusted by the addition of AnalaR grade $NaClO_4$ and $HClO_4$ solutions to the oxidant solutions;

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[1] See, for example, G. N. Schrauzer, *Accounts Chem. Res.*, 1968, **1**, 97.

[2] D. N. Hague and J. Halpern, *Inorg. Chem.*, 1967, **6**, 2059.

[3] These reactions have been studied in great detail by Ablov and his co-workers: see, for example, N. M. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1145 and refs. therein.

[4] A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 153.

[5] H. Taube and E. S. Gould, *Accounts Chem. Res.*, 1969, **2**, 321.

[6] R. G. Linck, *Reaction Mechanisms in Inorg. Chem.*, 1972, **9**, 303.

[7] D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, 1972, **11**, 2361.

[8] A. Adin and J. H. Espenson, *Inorg. Chem.*, 1970, **11**, 686.

[9] L. G. Marzilli, R. C. Stewart, L. A. Epps, and J. B. Allen, *J. Amer. Chem. Soc.*, 1973, **95**, 5796.

[10] L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, 1972, **11**, 2050.

[11] J. H. Espenson and J. S. Schveima, *J. Amer. Chem. Soc.*, 1973, **95**, 4468.

[12] R. H. Prince and M. G. Segal, *Nature*, 1974, **249**, 246.

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

[14] N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 225.

[15] *Gmelins Handbuch der Chemie*, **B58**, 729.

[16] L. A. Tchugaev, *Ber.*, 1906, **39**, 2692.

[17] L. A. Tchugaev, *Ber.*, 1907, **40**, 3498.

[18] L. Cambi and C. Coriselli, *Gazzetta*, 1936, **66**, 81.

[19] T. J. Przystas and A. Haim, *Inorg. Chem.*, 1972, **11**, 1016.

[20] L. A. Sarver and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1931, **53**, 2906.

[21] C. Hwang and A. Haim, *Inorg. Chem.*, 1970, **9**, 500.

these were made up on the day of their use, to minimise aquation of the complexes.

Kinetic Measurements.—All reactions were carried out in 1 cm quartz cells; the oxidant solution (1 cm^3) was placed in the cell, which was then flushed with nitrogen and sealed with a serum cap before placing in a specially constructed, thermostatted, cell holder in the cell compartment of a Gilford 240 u.v.–visible spectrophotometer. The reductant solution was placed in the thermostat bath and given time to equilibrate. The reductant solution (1 cm^3) was then injected into the cell and the reagents mixed before returning to the spectrophotometer. Using this technique, the first absorbance reading could be taken within *ca.* 6 s of the start of reaction. Readings were recorded automatically at preset time intervals on an electronic data logger.[22] All reactions were carried out under pseudo-first-order conditions, with at least a 20-fold excess of reductant, and were monitored for at least three half-lives (see below). For each reagent used, some sample runs were allowed to proceed to 'infinity' to verify that they obeyed first-order kinetics throughout. The disappearance of the cobaloximes was monitored at 280 nm in all cases, at which wavelength the difference in absorbance between the reagents and products is approximately maximised.

Stoicheiometry.—The stoicheiometry of the reactions was determined by measurement of the Co^{II} produced on addition of a known amount of reductant to excess of cobaloxime; Co^{II} released was determined spectrophotometrically as the tetrachloro-complex.[23] The ratio Co^{II} produced : V^{II} added was in the range 0·8—1·0 : 1 in all the reactions studied, indicating the expected 1 : 1 stoicheiometry.

Analysis of Results.—Between 40 and 80 readings of absorbance, on an arbitrary scale, were recorded permanently on punched tape for each run, with an equal number of further readings for the 'infinity' measurements. The data were then analysed by the program GILFIRST on the University's I.B.M. 370 computer, using the Guggenheim method.[24] (Full details of the apparatus and programs have been published elsewhere.[22]) For those reactions where the rate constants observed were dependent on $[H^+]$, a simple least-squares program was used to fit the best straight line to the observed data; no significant differences appeared when the points were weighted according to the standard deviations of the mean values. The activation parameters were calculated using the program DELTACP (for which our thanks are due to Dr. M. V. Twigg of this laboratory), in which the data points are weighted according to their standard deviations.

In all cases the term k_2 is used to refer to the observed first-order rate constant divided by the concentration of reductant. Each quoted figure is the mean of three to five runs; the standard deviation of each individual run was less than 2%, and that of the mean of each group of runs less than 6% in almost all cases. The temperatures quoted are accurate to within ±0·2 °C.

RESULTS AND DISCUSSION

Reduction of $[Co(Hdmg)_2(NH_3)_2]^+$.—The results of the reaction of $[Co(Hdmg)_2(NH_3)_2]^+$ with $V^{2+}(aq)$ are given in Table 1. Because of the low solubility of the perchlorate salt, the ionic strength (and hence the possible range of $[H^+]$) was limited to 0·1M.* Perchlorate was used as the anion in most of the experiments, however, since many other anions associate with V^{II} in solution [25] and markedly affect the rates of reactions. In this medium, k_2 is independent of $[V^{2+}]$, and also, apparently, of $[H^+]$. In order to investigate the effect of varying the acidity over a wider range, two experiments were made in chloride media at unit ionic strength. At constant concentration of chloride, any contributions to the observed rate constant due to terms in the rate law in $[Cl^-]$ are constant; thus the change in k_2 with acidity can be attributed to protonation of the cobaloxime at high $[H^+]$.[26] The reduction in rate with increasing acidity is consistent with a mechanism where both protonated and unprotonated forms react, the latter being the more reactive species.

TABLE 1

Reaction of $[Co(Hdmg)_2(NH_3)_2]^+$ with $V^{2+}(aq)$ [a]

θ_c/°C	$10^3[V^{2+}]$/M	$10^2[H^+]$/M	k_2/l mol^{-1} s^{-1}
25·0	4·00	4·80	0·561
25·0	2·00	4·80	0·582
25·0	1·00	4·80	0·536
25·0	1·00	1·20	0·548
25·0	1·00	7·00	0·537
25·0	1·00	9·20	0·529
25·0	1·00	1·20 [b]	1·57
25·0	1·00	99·2 [b]	1·02
15·0	4·00	4·80	0·241
35·0	4·00	4·80	1·32
45·0	4·00	4·80	2·89

[a] $[Co^{III}] \simeq 5 \times 10^{-5}$M; I = 0·10M ($NaClO_4$). [b] I = 1·0M (NaCl–HCl).

The reduction of this cobaloxime by $Cr^{2+}(aq)$ has a rate constant which increases greatly with increasing $[H^+]$.[12] In fact all the reactions we have studied, other than the above reaction, show this behaviour, which is to be expected when the rate-determining step is the electron-transfer process.[12] However, the effects of protonation of the complex on the rate of that process will not be observed if the reaction is of the substitution-controlled type;[6,14] in this case the increase in positive charge on protonation of the cobaloxime might be expected to reduce the observed reaction rate, as is the case here. The activation parameters, taken for the acid-independent path alone (see Table 4), are consistent with the formulation of this reaction as a substitution-controlled inner-sphere process; the very great difference between these parameters and those of the reactions of the amminehalogeno-complexes, which are probably outer sphere (see below), is a further argument to support this formulation.

There is indirect evidence to suggest that the reaction with $Cr^{2+}(aq)$ is also inner sphere, although no direct evidence could be found to show that the oxime ligands were bound to the chromium at any stage.[12] It is

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* 1M = 1 mol dm^{-3}.

[22] S. H. Palmstrøm, Ph.D. Thesis, Cambridge University, 1973.

[23] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 1964, **86**, 1318.

[24] E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

[25] T. J. Przystas and N. Sutin, *J. Amer. Chem. Soc.*, 1973, **95**, 5545.

[26] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 6041.

observed[13] that, when the reduction of a given species by both V^{2+}(aq) and Cr^{2+}(aq) is outer sphere, the ratio of the rate constants obeys quite closely the relation $k_V/k_{Cr} = 50$ irrespective of the nature of the oxidant. For the reduction of $[Co(Hdmg)_2(NH_3)_2]^+$, this ratio is several orders of magnitude lower, *i.e.* the chromium reaction is much faster than this relation would predict for an outer-sphere mechanism. This is only reasonable if the reaction with Cr^{2+} is inner sphere, whatever the mechanism of the reaction with V^{2+}. Moreover, if the vanadium reaction is inner sphere, as we believe, then the chromium reaction is almost certain to be so too, as Cr^{2+}(aq) nearly always reacts *via* an inner-sphere path when a suitable bridging ligand is present.

Reduction of the Amminehalogeno-complexes.—Rate constants for the V^{2+}(aq) reduction of $[Co(Hdmg)_2(NH_3)Br]$ under widely varying conditions are shown in Table 2. The reaction was first order in both reagents, as expected, and the rate was virtually independent of ionic strength; the results are thus directly comparable with those discussed above. At 25 °C and $I = 1{\cdot}0$M, the reaction appears to obey the rate law (1), where

$$-d[Co^{III}]/dt = k_0[Co^{III}][V^{2+}] + k_H[Co^{III}][V^{2+}][H^+] \quad (1)$$

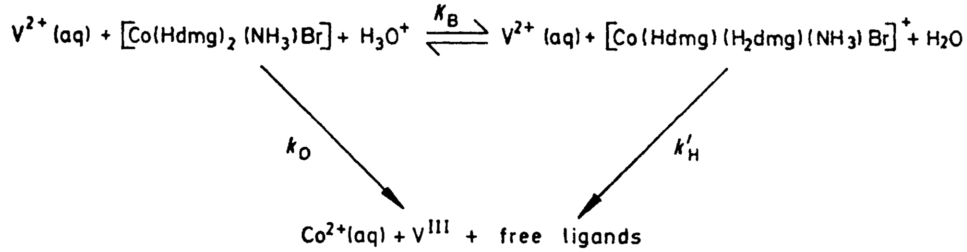
$k_0 = 76{\cdot}1 \pm 1{\cdot}3$ l mol^{-1} s^{-1} and $k_H = 64{\cdot}1 \pm 2{\cdot}2$ l^2 mol^{-2} s^{-1} (see Figure). Some runs were repeated using $LiClO_4$ to maintain the ionic strength; no difference in rate was observed, showing that the dependence of k_2 on $[H^+]$ is genuine and not a specific effect due to Na^+. As we have described,[12] a rate law approximating to this form is expected for the reduction of cobaloximes, where the overall reaction scheme is represented as below and k_H' is greater than k_0.

TABLE 2

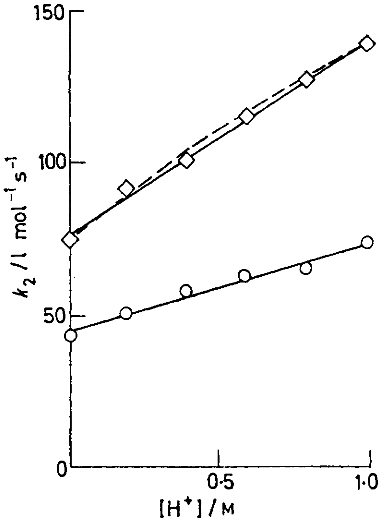
Reaction of $[Co(Hdmg)_2(NH_3)Br]$ with V^{2+}(aq) [a]

θ_c/°C	$10^3[V^{2+}]$/M	$[H^+]$/M	k_2/l mol^{-1} s^{-1}
25·0	0·250 [b, c]	0·012	80·4
25·0	0·500 [b]	0·012	79·5
25·0	1·00 [b]	0·012	82·2
25·0	0·500	0·006	74·5
25·0	0·500	0·194	91·4
25·0	0·500	0·394	101
25·0	0·500	0·594	115
25·0	0·500	0·794	127
25·0	0·500	0·994	139
10·0	0·500	0·006	43·0
15·0	0·500	0·006	51·6
20·0	0·500	0·006	60·3
30·0	0·500	0·006	84·3
35·0	0·500	0·006	106
40·0	0·500	0·006	123

[a] $[Co^{III}] \simeq 2{\cdot}5 \times 10^{-5}$M; $I = 1{\cdot}0$M ($NaClO_4$). [b] $I = 0{\cdot}10$M. [c] $[Co^{III}] = 1{\cdot}25 \times 10^{-5}$M.



A direct comparison of the magnitudes of k_0 and k_H is not meaningful, since they are in different units. If k_H' can be calculated, however, after determination of K_B, then a quantitative estimate of the effect of protonation of the cobaloxime can be obtained by comparing k_H' and k_0. We tried to determine K_B by spectrophotometric titration; the change in the u.v. spectrum is only very slight, however, on protonation of the complex, and the value of K_B appears so small that only a very approximate result could be obtained, of 0·25 l mol^{-1} (25 °C, $I = 2{\cdot}40$M). (The error in this figure may be as high as ±50%.) Using this figure, we obtain an approximate value of 400 l mol^{-1} s^{-1} for k_H' (see Figure). Thus the protonated cobaloxime reacts some five times faster than the neutral species. There are three ways in which protonation is likely to affect the rate of reaction: by increasing the charge on the complex; by withdrawing electron density from the Co ion; and by opening the pseudo-macrocycle, and hence lowering the Franck–Condon barrier to reduction. Clearly the first effect, which on its own would lower the rate of reaction, is much less significant than either, or both, of the other two.



Reactions of $[Co(Hdmg)_2(NH_3)X]$ with V^{2+}(aq) at 25·0 °C and $I = 1{\cdot}0$M: X = Br (◊) and Cl (○); (——), best straight lines; (— — —), calculated for $K_B = 0{\cdot}25$ l mol^{-1}, $k_H' = 400$ l mol^{-1} s^{-1}, and $k_0 = 74{\cdot}5$ l mol^{-1} s^{-1} (see text)

In view of the great inaccuracy in the derivation of k_H', no attempt was made to determine the activation parameters for this path. However, the magnitude of k_H' indicates that only an outer-sphere mechanism is probable, and k_0 is also great enough to imply that an inner-sphere mechanism for the acid-independent path is unlikely. The activation parameters at $[\mathrm{H}^+] = 0{\cdot}006\mathrm{M}$ were taken to be those of the reaction of the neutral species, as only the k_0 path is significant at this low acidity. The observed parameters (Table 4) are fully consistent with an outer-sphere mechanism. In particular, it has been observed [27] that an activation entropy of the order of -30 cal K^{-1} mol^{-1} is usual for such reactions with $\mathrm{V}^{2+}(\mathrm{aq})$.*

The reaction of $[\mathrm{Co(Hdmg)_2(NH_3)Cl}]$ clearly obeys a similar rate law to that of the bromo-complex (Table 3; Figure). The observed rate constants for the acid-independent and acid-dependent paths were, respectively, $k_0 = 44{\cdot}4 \pm 1{\cdot}3$ l mol^{-1} s^{-1} and $k_\mathrm{H} = 29{\cdot}0 \pm 2{\cdot}2$ l^2 mol^{-2} s^{-1}. The constant K_B could not be determined for this complex, as the change in spectrum in the range $[\mathrm{H}^+] = 0$—$2{\cdot}4\mathrm{M}$ was too slight; so we have no estimate of k_H', unfortunately. Both k_0 and k_H were somewhat less than those of the bromo-complex, so unless there is a considerable decrease in K_B for the chloro-complex both paths follow the ' normal ' order of reactivity of halides.[4,14] The similarity in the activation parameters clearly implies that these halogeno-complexes react by identical outer-sphere mechanisms.

TABLE 3

Reaction of $[\mathrm{Co(Hdmg)_2(NH_3)Cl}]$ with $\mathrm{V}^{2+}(\mathrm{aq})$ *

θ_c/°C	$[\mathrm{H}^+]$/M	k_2/l mol^{-1} s^{-1}
25·0	0·006	43·3
25·0	0·194	50·3
25·0	0·394	58·0
25·0	0·594	62·4
25·0	0·794	65·1
25·0	0·994	73·8
15·0	0·006	30·5
35·0	0·006	61·0
40·0	0·006	71·7

* $[\mathrm{V}^{2+}] = 5{\cdot}00 \times 10^{-4}$, $[\mathrm{Co^{III}}] \simeq 2{\cdot}5 \times 10^{-5}$, $I = 1{\cdot}0\mathrm{M}$ $(\mathrm{NaClO_4})$.

In both cases the halogeno-complexes react faster than the corresponding penta-ammines; [28] our estimate of k_H' for the bromo-species suggests a rate increase for the protonated cobaloxime relative to the penta-ammine of about an order of magnitude. This may be accounted for simply by the lower charge on the cobaloxime; there are a number of other points worthy of note, however. Although the electronic distortion induced by the strong equatorial ligand field could be expected to lower the energy of the Co d_{z^2} orbital, which would lower the overall free energy of the reaction, this is not, apparently, borne out by the electrode potentials: those of simple cobaloximes are generally somewhat negative,[29,30] while the first reduction wave on polarographic reduction of $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ is positive relative to the s.c.e.[31] On this basis, a simple Marcus correlation [32] would predict lower reactivity for the cobaloximes. On the other hand, the change in spin type required in the reduction of the penta-ammine-cobalt(III) complexes [33] may impose an energy barrier not present when the cobaloximes react, since both oxidised and reduced forms are low spin.[34]

TABLE 4

Activation parameters for some reductions by $\mathrm{V}^{2+}(\mathrm{aq})$

Oxidant	$\Delta H^\ddagger$ / kcal mol^{-1}	$\Delta S^\ddagger$ / cal K^{-1} mol^{-1}	Mechanism	Ref.
$[\mathrm{Co(Hdmg)_2(NH_3)_2}]^+$	$14{\cdot}5 \pm 0{\cdot}1$	$-11{\cdot}0 \pm 0{\cdot}4$	I.s.	*a*
$[\mathrm{Co(Hdmg)_2(NH_3)Br}]$	$5{\cdot}67 \pm 0{\cdot}13$	$-31{\cdot}0 \pm 0{\cdot}4$	O.s.	*a*
$[\mathrm{Co(Hdmg)_2(NH_3)Cl}]$	$5{\cdot}40 \pm 0{\cdot}13$	$-32{\cdot}9 \pm 0{\cdot}4$	O.s.	*a*
$[\mathrm{Co(NH_3)_5F}]^{2+}$	$11{\cdot}1 \pm 0{\cdot}1$	$-18{\cdot}5 \pm 0{\cdot}2$	I.s.	*b*
$[\mathrm{Co(NH_3)_5(HC_2O_4)}]^{2+}$	12·2	−13	I.s.	*c*
$[\mathrm{Co(NH_3)_5(HCO_2)}]^{2+}$	13·9	−13	I.s.	*d*
$[\mathrm{Co(NH_3)_4C_2O_4}]^+$	12·3	−9·8	I.s.	*e*
$[\mathrm{Co(NH_3)_5Cl}]^{2+}$	$7{\cdot}5 \pm 0{\cdot}15$	$-28{\cdot}8 \pm 0{\cdot}5$	O.s.	*f*
$[\mathrm{Co(NH_3)_5Br}]^{2+}$	$7{\cdot}2 \pm 0{\cdot}2$	$-27{\cdot}6 \pm 0{\cdot}7$	O.s.	*b*
$[\mathrm{Ru(NH_3)_5Cl}]^{2+}$	3·8	−30	O.s.	*g*
$[\mathrm{Ru(NH_3)_5Br}]^{2+}$	2·8	−34	O.s.	*g*

[a] This work. [b] Ref. 28. [c] H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1. [d] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1971, **10**, 1983. [e] Ref. 21. [f] R. S. Taylor, R. N. F. Thorneley, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 856. [g] Ref. 27.

Endicott and his co-workers [7,35] have discussed the relation between outer-sphere electron-transfer reaction rates and the electrode potentials of a number of $\mathrm{Co^{III}}$ complexes of macrocyclic ligands. At present, accurate $E^\ominus$ values for the cobaloximes that we have used are not available. However, if the observation [7] that the electron-transfer reaction rate is determined almost entirely by $E^\ominus$ and is hardly at all dependent on the ' reorganisational term ' of the oxidant is applicable here, then the rate increase caused by protonation of the oxime may be due mostly to a change in the electrode potential. The decrease in the Franck–Condon barrier to reduction that we expect to accompany the opening of the pseudo-macrocycle would then be largely irrelevant. A polarographic investigation of these cobaloximes may throw further light on this question.

We thank the Royal Society and the S.R.C. for a grant towards the cost of equipment, and the S.R.C. for support (for M. G. S.).

[4/1115 *Received, 7th June*, 1974]

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* 1 cal = 4·184 J.

[27] J. A. Stritar and H. Taube, *Inorg. Chem.*, 1969, **8**, 2281.

[28] M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.

[29] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1966, **88**, 3738.

[30] N. Maki, *Nature*, 1960, **188**, 227.

[31] J. B. Willis, J. B. Friend, and D. P. Mellor, *J. Amer. Chem. Soc.*, 1945, **67**, 1680.

[32] R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155.

[33] See, for example, ref. 4, p. 168.

[34] P. W. Schneider, P. F. Phelan, and J. Halpern, *J. Amer. Chem. Soc.*, 1969, **91**, 77.

[35] D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, 1972, **94**, 394.