Holmes and Kaesz generated a straight line. Aside from the theoretical uncertainties concerning a linear relationship, it does not seem unreasonable to conclude that the Sn–H coupling constants in methyltin derivatives will increase with an increase in the amount of s character in the Sn–C bond.

In Table II, the coupling constants are collected for the systems Lewis base–$(CH_3)_3MCl$, in which M represents tin and lead. In the table, data for tetramethyllead are also included.

The coupling constant data, like the far-infrared data, are consistent with the formation of an addition compound which has structure I. The coupling constant values for the Lewis acids dissolved in the Lewis bases can be taken as those for the addition compounds, $B\cdot(CH_3)_3MCl$. The values indicate an appreciable increase in the s character in the M–C orbitals of the M atom in the addition compound with respect to that of the uncoordinated Lewis acids. It is interesting that the value of the Sn–H coupling constant for the system $(CH_3)_3SnCl\cdot B$ requires (from the plot of Holmes and Kaesz[29]) 33% s character in the tin orbitals which are used for bonding the methyl groups. This distribution of s character can readily be rationalized on the basis of structure I where the methyl groups are bonded by essentially sp^2 hybrids. This result does not appear to be consistent with the other possible structures.

Trimethyltin chloride probably is extensively dissociated to the solvated cation in aqueous solutions. For the unsolvated cation $(CH_3)_3Sn^+$ a planar structure based on the utilization of sp^2 hybridization by the tin atom would be expected. From the line generated by Holmes and Kaesz, the experimental Sn–H coupling constant indicates that the tin atom employs 32% s character in Sn–C bonds. It is likely that the addition compound between water and the trimethyltin cation would possess a structure similar to the isomer depicted in I with two water molecules occupying the axial sites. If any un-ionized trimethyltin chloride exists in the aqueous solutions, it may be hydrated and possess a structure similar to I. In the event that un-ionized trimethyltin chloride does exist in aqueous solutions, the Sn–H coupling constant will be a statistical average of those for the distinct solvated species $(CH_3)_3SnCl\cdot H_2O$ and $(CH_3)_3Sn(H_2O)_2^+$ because of the rapid exchange of Cl^- and H_2O which occurs in the aqueous solutions (only one methyl–proton signal is observable at 31°).

If a plot of the amount of s character in the Pb–C orbitals of methyllead compounds *vs.* the Pb–H coupling constants is constructed in a manner similar to that for the methyltin compounds (by taking as one point the origin and as the other point the coupling constant for tetramethyllead, 62.0 c.p.s., which is assumed to represent 25% s character), obviously a straight line can be generated. From this line for the methyllead compounds, the Pb–H coupling constant for the adduct suggests that 33% s character is incorporated by the lead atom in bonding the methyl groups. For the Lewis base–$(CH_3)_3PbCl$ systems, both the far-infrared spectra and the coupling constant data are then consistent with structure I.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
GEORGETOWN UNIVERSITY, WASHINGTON, D. C.

Reduction Potentials of Some Chromium(III) Complexes[1]

BY JOSEPH H. WALSH AND JOSEPH E. EARLEY

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Polarographic reduction of 1:1 Cr(III) complexes of Y^{-4} (EDTA), F^-, $P_2O_7^{-4}$, PO_4^{-3}, and SCN^- in 0.1 *M* $NaClO_4$ gave two reduction waves for each complex. $E_{1/2}$ of the first wave (Cr(III) → Cr(II)) did not vary when excess ligand was subsitituted for $NaClO_4$. For certain systems stepwise variation of $E_{1/2}$ with pH was observed. This variation is interpreted in terms of protonation of the complexes. The shape of the waves indicated reversible reduction of SCN^- and Y^{-4} complexes and less reversible reduction for other species. Half-wave potentials (−v. *vs.* s.c.e.) characteristic of each species at 25° (water omitted) and the corresponding log slopes (θ) are: Cr^{+3}, 0.810 (1.1); CrF^{+2}, 1.060 (1.4); $CrSCN^{+2}$, 0.880 (1.04); $CrP_2O_7H_{n+1}{}^{n+1}$, 1.16 (1.2); $CrP_2O_7H_{n+1}{}^{n}$, 1.27 (1.2); $CrP_2O_7H_n{}^{1-n}$, 1.42 (1.3); $CrPO_4H_{n+1}{}^{n+1}$, 0.80 (1.5); $CrPO_4H_n{}^{n}$, 1.145 (2.7); CrY^-, 1.250 (1.04); HCrY, 0.905 (1.4). At pH 3.0, $E_{1/2}$ becomes more positive in the order: $P_2O_7^{-4}$, Y^{-4}, F^-, PO_4^{-3}, SCN^-. This variation is discussed in terms of the rate of Cr(II) catalyzed formation of the Cr(III) complexes.

Chromium(II) has been shown[2] to be a catalyst for the formation of Cr(III) complexes, the rate of the reaction

$$\mathrm{Cr(III)} + \mathrm{L} + \mathrm{Cr(II)} \leftrightharpoons \mathrm{Cr(III)L} + \mathrm{Cr(II)}$$

depending on the nature of the ligand. The reaction is analogous to certain Co(III)–Cr(II) reactions[3] and is considered to involve an OH^- (or H_2O) bridging group which links two Cr atoms during an electron

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[1] Taken from a portion of a Ph.D. thesis submitted (1963) to the Graduate School of Georgetown University by Br. Joseph H. Walsh, S.M., presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., April, 1962.

[2] J. B. Hunt and J. E. Earley, *J. Am. Chem. Soc.*, **82**, 5312 (1960).

[3] (a) H. Taube, *ibid.*, **77**, 4481 (1955); (b) J. E. Earley and J. H. Gorbitz, *J. Inorg. Nucl. Chem.*, **25**, 306 (1963); (c) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

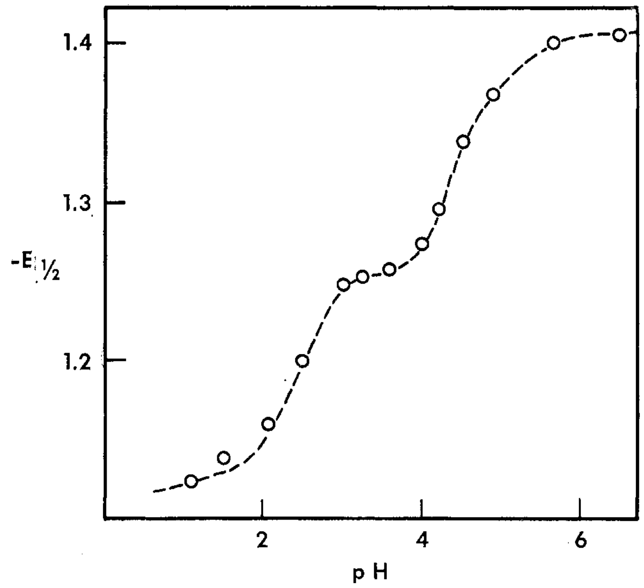

Fig. 1.—Variation of half-wave potential with pH for 1:1 pyrophosphato–Cr(III) complexes at 25° in 0.10 M $NaClO_4$ (0.002% gelatin).

transfer. Taube[3a] has suggested that the effect of nonbridging ligands on the rate of electron transfer in these reactions results from stabilization of one oxidation state by coordination. Such stabilization would be measured by $Cr(III)L + e^- \leftrightharpoons Cr(II)L$ potentials. Under appropriate conditions other factors, such as coulombic effects, would also be expected to be significant in determining the rate of oxidation.

The present study of polarographic reductions of certain Cr(III) complexes was undertaken to determine whether there is a relationship between the potentials characteristic of these electrode reactions and the rates of the bulk phase reactions studied.[2]

Ion-exchange techniques made it possible to study definite Cr(III) species containing one ligand group and up to five water molecules. It seems that this type of species has not been studied polarographically, although Tanaka,[4a] *et al.*, have recently published a study of related complexes. A valuable review by Vlček has appeared after the submission of this paper.[4b]

Experimental

Polarographic measurements were carried out at 25 ± 0.1° using an H cell of standard design and saturated calomel reference electrode. All voltages listed are *vs.* s.c.e. The mercury electrode had a drop time of 2.50 sec. in 0.10 M $NaClO_4$, at a potential of −1.00 v. Polarograms were obtained using a conventional circuit and a Varian Model 11 recorder. Spectra were studied with a Beckman DK-2 at 25 ± 2°, using aqueous $NaClO_4$ (0.10 M) as solvent. Analyses were carried out using a Beckman DU.

Distilled water that had been passed through a mixed bed ion-exchange column was used throughout. Sodium salts of ligands were analytical grade and were used without further purification. The supporting electrolyte was 0.10 M $NaClO_4$, which was prepared by neutralizing $HClO_4$ with NaOH. Gelatin was prepared daily for use as maximum suppressor.

Hexaaquochromium(III) perchlorate was prepared by reduction of CrO_3 with formic acid in $HClO_4$ medium. The product was recrystallized twice from dilute $HClO_4$ and once from water.

Chromium analyses were made spectrophotometrically after decomposition of the complexes by heating in alkaline media followed by peroxide oxidation.

Chromium(II) solutions prepared by reducing Cr(III) with amalgamated zinc in aqueous $HClO_4$ were stored in a flask equipped with a rubber serum cap and dispensed with a hypodermic syringe.

Complexes of Cr(III) with 1:1 ligand to metal ratio were prepared in the following manner. Equimolar amounts of hexaaquochromium(III) perchlorate and ligand were mixed in dilute $HClO_4$. After carefully adjusting the pH to 2.5 by slow addition of dilute NaOH with constant stirring, the solution was placed in a 25-ml. flask equipped with a rubber serum cap and deaerated with oxygen-free nitrogen. Chromium(II) was injected into the Cr(III)–ligand solution to catalyze the formation of the Cr(III) complex. After standing for 2 hr., the solution was exposed to air and placed on a 20-cm. column of 100–200 mesh Dowex 50 cation-exchange resin, hereafter referred to as the cation column.

Chromium(III) polymer formed by air oxidation of Cr(II), and also uncomplexed Cr(III), remained at the top of the cation column while the Cr(III) complexes moved down the column at various rates. $CrSCN^{+2}$ and also CrF^{+2} were eluted from the cation column with 1.0 M $HClO_4$ after the column had been washed with 0.10 M acid. The effectiveness of this separation for the first ion has been shown previously.[5]

$Cr(Y)H_2O$ (Y^{-4} = ethylenedinitrilotetraacetate) was eluted from the cation column with distilled water.

The 1:1 phosphato Cr(III) and 1:1 pyrophosphato Cr(III) complexes were also eluted from the cation column with 1.0 M $HClO_4$, excess phosphate being removed from the effluent by a 20-cm. column of Amberlite IRA-CG anion-exchange resin (hereafter referred to as the anion column). The removal was shown to be effective by ^{32}P tracer experiments. Phosphorus analyses were made colorimetrically at 660 mμ as phosphomolybdate[6] after decomposition of the complex by base. Pyrophosphate was converted to the orthophosphate by heating with 10 M $HClO_4$ prior to analysis. The analytical results confirmed the 1:1 composition in both cases.

Results

Solutions containing complexes with 1:1 ligand to metal ratio as the only Cr(III) species were subjected to polarographic reduction shortly after preparation (25°, N_2 atmosphere, 0.1 M $NaClO_4$, 0.002% gelatin, no buffers). No significant hydrolytic decomposition was observed in the experiments reported below although the presence of uncomplexed Cr(III) was readily detectable polarographically and was observed if solutions of the complexes were allowed to stand for several hours.

Two well-defined waves were observed when each of the complexes was separately reduced at the dropping mercury electrode. The first wave is ascribed to the reduction of the Cr(III) complex to a Cr(II) species (*vide infra*). The second wave was complicated by reduction of hydrogen ion. The following refers to the first wave.

In all cases investigated, plots of eq. 1 were linear.

$$\log \frac{i_d - i}{i} = 0.059\theta E \qquad (1)$$

A value of θ close to unity was taken as a provisional

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(4) (a) N. Tanaka, E. Itabashi, and E. Kyuno, *Bull. Chem. Soc. Japan*, **36**, 917 (1963); (b) A. A. Vlček, *Progr. Inorg. Chem.*, **5**, 216 (1963).

(5) E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952).

(6) C. H. Fiske and Y. Subbarow, *J. Biol. Chem.*, **66**, 375 (1925).

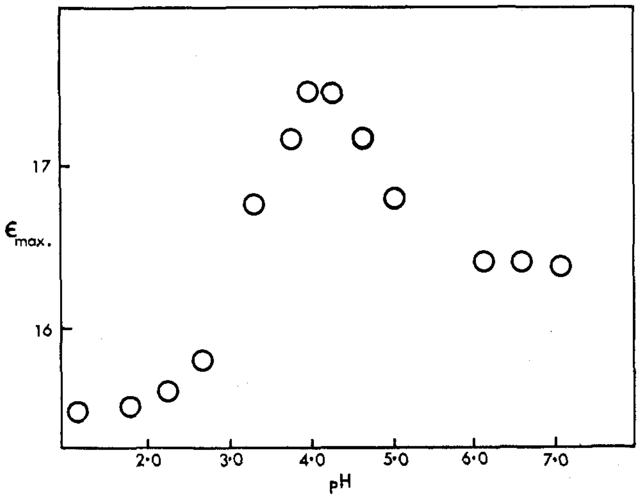

Fig. 2.—Variation of extinction coefficient at 600 mμ with pH for $Cr(III)-P_2O_7$ at 25°, 0.1 N $NaClO_4$.

indication of polarographic reversibility (one-electron change).

Solutions 1.0 mM in $Cr(H_2O)_6{}^{+3}$ were reduced in media of varying pH (1–12). Between pH 2.0 and 4.0, $-E_{1/2}$ was constant at 0.815 v.; at higher pH the wave was displaced to more negative potentials. $-E_{1/2}$ at pH 3.0 was constant at 0.815 ± 0.005 v. for seven determinations in which Cr(III) was varied from 1 to 3 mM. θ was 1.12 at pH 3.0, indicating deviation from polarographic reversibility. The observed value of $E_{1/2}$ is close to previously measured values,[7] but somewhat more positive than other reports.[8] It is possible that the latter study may have involved polymeric and/or complexed species. The Cr(III) salt used in this study had an optical density at 230 mμ which was 26% of that at 260 mμ. This indicates[9] a very small degree of polymerization.

Monothiocyanato Cr(III) ion (1.1 mM) was reduced in media varying from pH 1 to 5. Between pH 2 and 4, $-E_{1/2}$ was 0.875 ± 0.005 v. No change in $E_{1/2}$ occurred when the $NaClO_4$ supporting electrolyte was partially or completely replaced by NaSCN. At pH 3.0 in the absence of NaSCN the reduction gave a θ value of 1.02, indicating polarographic reversibility.

Pecsok and Lingane[10] found that oxidation of Cr(II) in thiocyanate media appears to be irreversible. Departures from reversibility in their labile system may be due to reactions of Cr(II) prior to oxidation. This effect is not present in the reduction of substitution-inert thiocyanato Cr(III) in the absence of excess SCN^-. Since $E_{1/2}$ for this reduction is not dependent on the concentration of excess thiocyanate, it is concluded that the same number of thiocyanate groups are present in the reactant and initial product of the electrode reaction.

Monofluoro Cr(III) ion (0.2–1.0 mM) was reduced in solutions ranging from pH 1 to 5. In several experiments $NaClO_4$ was partially or completely replaced by NaF. For all experiments between pH 2.0 and 3.5, $-E_{1/2}$ was 1.05 ± 0.005. At pH 3.0 θ was 1.39, indicating deviation from reversibility.

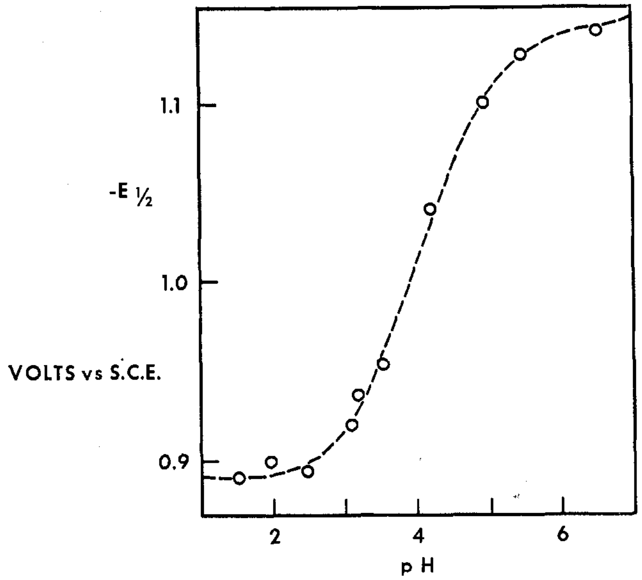

Fig. 3.—Variation of half-wave potential with pH for 1:1 phosphato-Cr(III) complexes at 25° in 0.10 M $NaClO_4$ (0.002% gelatin).

TABLE I

VARIATION OF θ WITH pH FOR MONOPYROPHOSPHATO Cr(III)

pH	θ	pH	θ
1.10	1.22	4.00	1.17
2.05	1.63	4.25	1.10
2.50	1.63	4.50	1.21
3.00	1.42	4.90	1.55
3.25	1.38	5.60	1.33
3.60	1.28	6.50	1.26

The variations of $E_{1/2}$ with pH for the reduction of the 1:1 Cr(III) complexes of pyrophosphate, phosphate, and Y^{-4} are shown in Fig. 1, 3, and 4.

Stepwise variation of a physical property of a solution with change of pH is usually associated with acid–base equilibria involving the substance which determines the property. This is illustrated by (Fig. 2) a spectrophotometric "titration" of monopyrophosphato Cr(III), to which species the data of Fig. 1 also refer.

The positions of the maxima in the absorption spectrum of the monopyrophosphato Cr(III) complex do not change with pH between 1 and 6.5. However, as shown in Fig. 2, the peak intensity changes in a manner consistent with the existence of two acid–base equilibria involving this complex.

On this basis, each of the plateaus in Fig. 1 is believed to correspond to the half-wave potential for reduction of the particular protonated species predominant at the pH of the plateau. The pH of the midpoint of the rising portion of the curve between two plateaus corresponds to the pK of the equilibrium between these forms (see Appendix). The values of θ listed in Table I are consistent with this interpretation.

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[7] (a) J. Elving and B. Zemel, *Can. J. Chem.*, **37**, 247 (1959); (b) I. Korsunov and M. Scennikova, *Z. anal. Chem.*, **4**, 5 (1949).

[8] J. J. Lingane and R. L. Pecsok, *J. Am. Chem. Soc.*, **71**, 425 (1949).

[9] C. Altman and E. L. King, *ibid.*, **83**, 2825 (1961).

[10] R. L. Pecsok and J. J. Lingane, *ibid.*, **72**, 189 (1950).

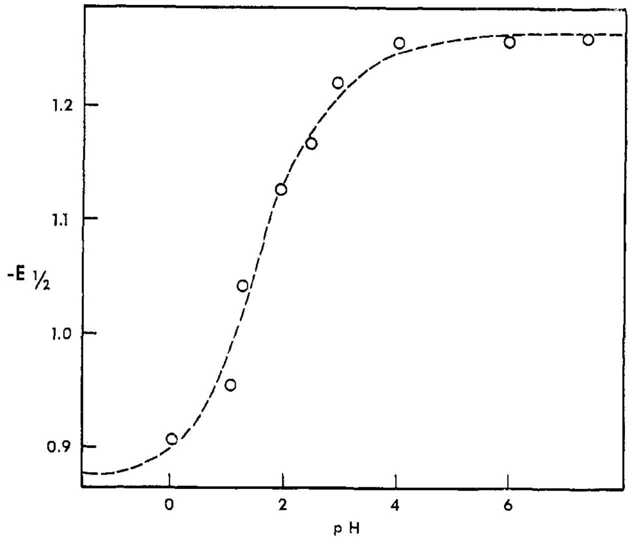

Fig. 4.—Variation of half-wave potential with pH for 1:1 EDTA–Cr(III) complexes at 25° in 0.10 *M* NaClO$_4$ (0.002% gelatin).

TABLE II

VARIATION OF θ WITH pH FOR 1:1 Cr(III) COMPLEXES

(a) Cr(III)–Y		(b) Cr(III)–PO$_4$	
pH	θ	pH	θ
1.10	2.24	1.55	1.46
2.00	1.29	1.96	1.68
2.50	1.29	2.50	1.57
3.00	1.05	3.10	1.60
4.05	1.04	3.50	1.54
6.00	1.10	4.15	1.47
		5.50	2.75
		6.50	2.70

Although at the plateaus reduction occurs with low θ, the waves observed between plateaus are composites of two waves with slightly different $E_{1/2}$; hence the observed waves are drawn out (higher θ).

Since the reduction of the phosphato complex in more basic media and of the Y^{-4} complex in more acidic media involves drawn out waves even at the plateaus (Table II), it is not possible to be certain whether the same or a different rationalization of the $E_{1/2}$ *vs.* pH data is applicable in these cases.

The dashed curves of Fig. 1, 3, and 4 were drawn on the basis of the interpretation used for Fig. 1, using parameters adjusted to give the best fit of the data (Table III). Reactions involving one proton are assumed for simplicity although this is by no means established. It is worthy of note that the data of Fig. 4 are consistent with the values of the acidity constant of the Cr(III)(H$_2$O)Y complex determined by Hamm using a spectrophotometric method (pK = 2.3 at 18°).[11] Also Pecsok and Schaefer[12] have reported the anodic half-wave potential for Cr(II)Y to be −1.24 v. at pH 8, the most acidic pH studied.[12a] This is in accord with the reversible (θ = 1.04) reduction observed for Cr(Y)H$_2$O.

TABLE III

PARAMETERS FOR VARIATION OF $E_{1/2}$ WITH pH FOR 1:1 Cr(III) COMPLEXES

Ligand	$-E_{1/2}$	pK_a
$H_{n+2}P_2O_7^{n-2}$	1.162	2.7
$H_{n+1}P_2O_7^{n-3}$	1.275	4.8
$H_nP_2O_7^{n-4}$	1.420	
$H_{n+1}PO_4^{n-2}$	0.890	4.0
$H_nPO_4^{n-3}$	1.145	
$H_{n-1}Y^{n-3}$	1.25	2.0
H_nY^{n-4}	0.90	

Table IV gives results for measurements at pH 3.0, the pH used in the previous kinetic work.[2]

TABLE IV

DATA FOR Cr(III) COMPLEXES AT pH 3.0, 25°, (1 *M* NaClO$_4$)

Ligand	$-E_{1/2}$, v. *vs.* s.c.e.	θ	$\nu_{max} \times 10^3$, cm.$^{-1}$	Over-voltage,[a] volts
H$_2$O	0.80	1.12	17.4	0.02
SCN$^-$	0.88	1.02	17.4	0.002
PO$_4^{-3}$	1.00	1.46	17.1	0.1
F$^-$	1.02	1.39	17.0	0.03
P$_2$O$_7^{-4}$	1.20	1.13	16.7	0.04
Y^{-4}	1.22	1.07	18.4	0.008

[a] H. Eyring, L. Marker, and T. Kwoh, *J. Phys. Colloid Chem.*, **53**, 1453 (1949). This treatment makes use of the tangent potential, but avoids the objection that E_T varies with concentration by including the slope of the wave at the tangent potential. For most purposes this treatment has been supplanted by later, more rigorous treatments, which, however, are not simply applicable to the specific systems studied here. This treatment is used here to give a rough estimate of overvoltage. The actual numbers are not to be taken seriously, but it seems that the order of magnitude of the values indicates that these reductions are quasi-reversible rather than highly irreversible.

Discussion

Vlček[13] has presented evidence that the rate-determining step in certain reductions of Co(NH$_3$)$_5$X^{+2} involves an internal electronic rearrangement ($d_\epsilon \rightarrow d_\gamma$). It appears that this mechanism is not dominant here since Cr(III) complexes of strong field ligands (Table IV) are more reversibly reduced than those of weak field ligands. Fischerova and Fischer[14] have concluded that the reversible reduction of Cr(SCN)$_6^{-3}$ involves interaction of SCN$^-$ with the electrode. A similar path may be important in the observed reversible reduction of CrSCN^{+2}. It is of interest that the two complexes which are reversibly reduced have charge-transfer bands much nearer the visible than the other complexes.

Many of the reductions studied here are best classified as quasi-reversible. Rough estimates of overpotential (Table IV) indicate that in all cases but one, overvoltage is less than 0.1 v., so that the reactions cannot be discussed as totally irreversible processes.[15] Half-wave potentials for quasi-reversible reductions

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[11] R. Hamm, *J. Am. Chem. Soc.*, **75**, 5670 (1953).

[12] R. Pecsok and W. Schaefer, *ibid.*, **83**, 62 (1961).

[12a] See also R. Pecsok, L. Shields, and W. Schaefer, *Inorg. Chem.*, **3**, 114 (1964).

[13] A. A. Vlček in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan Co., New York, N. Y., 1961, p. 590; *Discussions Faraday Soc.*, **26**, 164 (1958).

[14] E. Fischerova and O. Fischer, *Collection Czechoslov. Chem. Commun.*, **26**, 2570 (1961).

[15] *E.g.*, H. Natsuda and Y. Ayabe, *Bull. Chem. Soc. Japan*, **28**, 422 (1955).

do not have precise physical significance. However, when comparing a group of similar reductions, they provide an index of the ease of reduction at the d.m.e., including both kinetic and thermodynamic aspects. The measured values of $E_{1/2}$ are regarded as first approximations to the effective potentials (including overvoltage) of the Cr(III)L + $e^- \leftrightarrows$ Cr(II)L couple. Cr(II)L is considered the product on the basis of the lack of dependence of $E_{1/2}$ on free ligand concentration. It seems that the overvoltages involved at pH 3.0 are small (Table IV). It does not appear likely that more precise values of overvoltage would greatly distort the observed order of $E_{1/2}$ (except for PO_4^{-3}).

The order of the rate of formation of Cr(III) complexes at pH 3 by Cr(II) catalysis was previously[2] found to be $Y^{-4} > P_2O_7^{-4} >> PO_4^{-3} \sim F^- > SCN^-$. $E_{1/2}$ for reduction of the same complexes at pH 3 varies in the order shown below.

$P_2O_7^{-4}$	$\approx$	Y^{-4}	$>$	F^-	$>$	PO_4^{-3}	$>$	SCN^-
−1.24 v.		−1.22 v.		−1.04 v.		−0.92 v.		−0.88 v.

The $P_2O_7^{-4}$ and Y^{-4} complexes are formed most rapidly and reduced least readily. The SCN^- complex is slowly formed and easily reduced, PO_4^{-3} and F^- being intermediate in both experiments. In the case of the Y^{-4} and SCN^- reductions there is no evidence to indicate deviation from reversibility. $E_{1/2}$ values for these two reductions indicate that Y^{-4} has a much greater tendency to stabilize Cr(III) over Cr(II) than has SCN^-. These two systems are in accord with the previously mentioned suggestion that stabilization of valence state is important in the nonbridging ligand effect on the Cr(III)–Cr(II) electron-transfer reaction. The over-all similarity of the two orders also supports this conclusion, although the interchanged positions of PO_4^{-3} and F^- and of $P_2O_7^{-4}$ and Y^{-4} indicate that other factors are of importance.

If coulombic effects were important in the formation of the transition state of the bulk phase reaction, both inversions would be expected, due to the greater negative charge of HPO_4^{-2} relative to F^- and Y^{-4} relative to $H_2P_2O_7^{-2}$.

Acknowledgment.—We are grateful for support from the National Science Foundation and for a grant from the Smith, Kline and French Foundation under which this work was started.

Appendix

Consider the reactions (charges omitted)

$$\begin{tikzcd} A \arrow[r, shift left, "K"] \arrow[d, shift right, "+e"'] & B + H \arrow[l, shift left] \arrow[d, shift right, "+e"'] \\ P \arrow[u, shift right, "E_a"'] & P' \arrow[u, shift right, "E_b"'] \end{tikzcd} \qquad (2)$$

Where $K = BH/A$ (italicized symbols are activities). Let

$$T = A + B + P + P' \approx A + B$$

$$x = A/T;\ 1 - x = B/T$$

If A is reduced at the d.m.e. in the absence of B

$$E = E_a + \frac{RT}{nF}\left\{\frac{i_{da}}{i_a} - 1\right\} \qquad (3)$$

where E_a is the half-wave potential characteristic of A. Similarly, when A is absent

$$E = E_b + \frac{RT}{nF}\left\{\frac{i_{db}}{i_b} - 1\right\} \qquad (4)$$

If E_a and E_b differ by less than 0.2 v. (for reversible waves) then a single elongated wave will be observed when a mixture of A and B is reduced. At the half-wave potential of this elongated wave, if $i_{da} = i_{db} = i_d$, then

$$x\frac{i_a}{i_d} + (1 - x)\frac{i_b}{i_d} = \frac{i}{i_d} = \frac{1}{2} \qquad (5)$$

$$\frac{x}{\exp(nF/RT)(E_{1/2} - E_a) + 1} + \frac{1 - x}{\exp(nF/RT)(E_{1/2} - E_b) + 1} = \frac{1}{2} \qquad (6)$$

When $E_{1/2} = {}^1/_2(E_a + E_b)$, then $x = {}^1/_2$ and $H = K$. When $x = 0$, $E_{1/2} = E_b$; when $x = 1$, $E_{1/2} = E_a$.