

A. C. POLAROGRAPHIC STUDY OF SOME PENTAAMMINECOBALT(III) COMPLEXES ON A DROPPING MERCURY ELECTRODE IN AQUEOUS ACID PERCHLORATE SOLUTION*

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The totally irreversible one-electron polarographic reduction of the hexa- and some of the pentaamminecobalt(III) complex ions on a DME in an aqueous acid perchlorate solution has been investigated by a.c. polarography. The standard heterogeneous charge-transfer rate constant k_s has turned out to be too small to be determined accurately by this method. No alternative method seems readily available at present to remedy this.

The totally irreversible one-electron polarographic reduction of a variety of substitution-inert penta- and tetraamminecobalt(III) complexes on a DME was investigated by Vlček^{1,2} by d.c. polarography. Evaluation of the standard heterogeneous charge-transfer rate constant k_s was not feasible on the basis of the d.c. polarographic result alone due to the lack of the data of the corresponding standard equilibrium redox potential E^0 . In a previous report³, the present author demonstrated that the application of the a.c. polarographic technique enables a crude comparison of the k_s -value of the polarographic reduction of a series of related substitution-inert chromium(III) complexes provided k_s is not too small altogether. To test the applicability and limitation of the a.c. polarographic technique in the study of substitution-inert metal complexes, the pentaamminecobalt(III) complex series has been investigated in the present work.

EXPERIMENTAL

The description of the polarographic measuring device and procedure was given elsewhere⁴. Hexaammine- and monochloropentaamminecobalt(III) perchlorates were prepared by recrystallization of commercial salts from aqueous perchloric acid solution. Monoaquo-, monofluoro-, monoacetato-, mononitrato- and monosulfatopentaammine-cobalt(III) perchlorates were

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prepared by standard procedures⁵. The spectra of all prepared complexes in the visible range were found to agree with the previously reported values⁵. As those metal complexes undergo an aquation process in aqueous solutions, all polarographic test solution were freshly prepared before each run.

RESULTS

Experimental results are shown in the figures. Results of the d.c. polarographic measurements are consistent with Vlček's results¹, except for the monosulfatopentaammine Co(III) complex. Transfer coefficients of the cathodic process are about 0.5 to 0.6 throughout the series (the chloro and sulfato complexes excluded, Fig. 1), indicating that the irreversibility is primarily induced by a slow charge-transfer step:

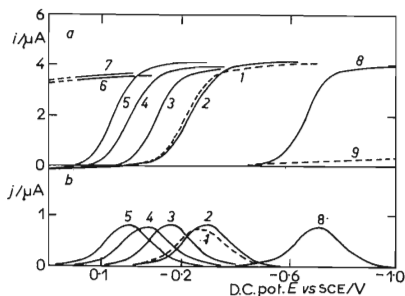
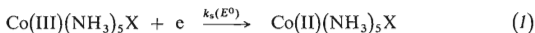
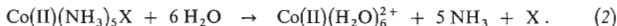


FIG. 1

D.C. *a*) and A.C. (in-phase component); *b*) Polarograms of the Hexa- and Some Pentaamminecobalt(III) Complexes

1 mM solutions of cobalt(III) perchlorates: 1 hexaamine (extrapolated from 0.4 mM); 2 monofluoropentaammine; 3 monoacetato-pentaammine; 4 monoaquopentaammine; 5 mononitratopentaammine; 6 monosulfato-pentaammine; 7 monochloropentaammine; 8 europium(III) perchlorate as pilon ion; 9 0.14M-HClO₄-1.26M-NaClO₄ aqueous solution (supporting electrolyte). C.c. current (plots of the average value during a drop period); D.c. current (plots of the maximum value in rms during a drop period); a.c. cell voltage 10 mV rms; a.c. frequency 40 Hz; measured at constant mercury column height of 42 cm; mercury flow rate of 2.43 mg s⁻¹; drop life time of 3.90 s at $E = -0.5$ V vs s.c.e. in the supporting electrolyte; 25°C; nitrogen-saturated.

rather than by a subsequent fast irreversible chemical decomposition¹¹ (aquation) of the electrolysis product $\text{Co(II)(NH}_3)_4\text{X}$ to an electroinactive form Co^{2+}



As all externally adjustable experimental parameters (supporting electrolyte composition, depolarizer concentration, temperature, applied a.c. voltage amplitude and frequency) have been kept constant, and, as all inherent kinetic parameters (α and diffusion coefficients D) other than k_s have by the d.c. measurements turned out to be almost constant throughout the whole complex metal ion series inclusively Eu^{3+} , the a.c. peak current ought to depend on k_s alone³. The k_s -value of $2.5 \cdot 10^{-4} \text{ cm s}^{-1}$ of $\text{Eu}^{3+/2+}$ in 1M- NaClO_4 at 25°C obtained by an earlier independent measurement⁶ is however fairly close to the finite, measureable, k_s -independent a.c. polarographic current limit⁷. As the observed a.c. polarographic peak current height for the metal complexes is not appreciably greater than that of the pilot ion Eu^{3+} , it may be safe to say that the k_s value of the metal complexes is either in the order of $10^{-4} \text{ cm s}^{-1}$ or less at 25°C.

DISCUSSION

The above experimental results have shown that the magnitude of k_s of the one-electron polarographic reduction of the hexa- and pentaamminecobalt(III) complexes is too small to be determined accurately by a.c. polarography under the usual polarographic working condition (room temperature; drop life time 3–7 s).

At present no alternative experimental method seems readily available for us to overcome the difficulty encountered as above. This is discussed in short in the following: The unfavorable ratio of the charge transfer parameter k_s to the diffusional parameter D might probably be improved to some extent by raising the working temperature, and the a.c. polarogram would then acquire a less irreversible character. This presumption is based on the general observation that the apparent heat of activation at the standard equilibrium potential^{8,9} is usually greater than the activation energy of diffusion (the latter being in the range 4–6 Kcal)^{10,11}. In the present case, however, this alternative is seriously handicapped by that some of the pentaammine Co(III) complexes undergoes an aquation process at an appreciable rate even at room temperature.

Timmer and coworkers⁶ described a method to determine even a very small value of k_s by way of a detailed analysis of the (a.c. bridge-measured) complex electrode impedance in function of the applied a.c. cell voltage, frequency and the bulk concentration of the depolarizer ion. This method can not work, however, unless E^0 can be determined with sufficient accuracy by some independent means.

A direct potentiometric determination of E^0 on mercury in the mixture of the hexa- or pentaammine Co(III) complex ion and its redox conjugate seems scarcely possible by the following reasons: by combining the experimental results described in results with the theoretical equation for the a.c. polarographic peak potential^{6,7} expressed in terms of k_s , α , D and others, one can predict that E^0 of the charge-transfer process (1) is very close to the potential of anodic mercury dissolution in an aqueous acid perchlorate medium; an elaborate study of the solution-phase equilibria of the redox conjugates, the corresponding Co(II) ammine complexes, is required prior to the potentiometric determination of E^0 (note that four ligands, NH_3 , X , H_2O and OH^- , are involved); in an aqueous ammoniacal alkaline solution, where the Co(II) ammine complexes are supposed to be stable^{12,13}, the potential of anodic mercury dissolution is more negative than that in an aqueous acid perchlorate solution.

The E^0 -value was reported for the redox couple $\text{Co}(\text{NH}_3)_6^{3+/2+}$ (measured on platinum^{12,14} and $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+/2+}$ (evaluated computationally; related to platinum)¹³. Justification for applying those values obtained on platinum to the present case on mercury is given only on a purely formal basis^{15,16}.

Recently, Ruzic and coworkers¹⁷ made a unique proposal by way of a.c. polarography to evaluate the k_s - and E^0 -values for highly irreversible electrode process, whose E^0 is not obtainable by usual means (*e.g.*, potentiometry), provided one can find a second redox couple of known E^0 whose presence will induce a reversible homogeneous redox process with the original redox couple. This specific requirement is not fulfilled in the present case, as the electrolysis product $\text{Co}(\text{II})(\text{NH}_3)_5\text{X}$ undergoes a fast irreversible chemical decomposition (aquation) according to the equation (2).

Recently, Tanaka and coworkers¹⁸⁻²⁰ proposed a modified potentiostatic method in the study of electrode kinetics. The k_s -value of $1.5 \sim 1.9 \cdot 10^{-3} \text{ cm s}^{-1}$ and the E^0 -value of $-0.241 \sim -0.249 \text{ V vs S.C.E.}$ was reported with some reservation¹⁹ for the one-electron polarographic reduction of the $\text{Co}(\text{NH}_3)_6^{3+}$ ion in an aqueous $0.9\text{M-NaNO}_3 - 0.1\text{M acetate}$ buffer solution at 25°C . The detailed analysis of the lower limit of k_s tractable by this method has at the time of writing been yet unpublished.

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