

under which Fe(TPP)(CCl₂) and Fe(TPP)(CBr₂) are completely transformed into Fe(TPP)(CNR)(RNH₂) within a few seconds.^{3,15} Similarly, complex **1** is half-transformed into the hemochrome Fe(TPP)(pyridine)₂, after a ~15 h reaction with 1 M pyridine in benzene at 25 °C, conditions in which Fe(TPP)(CBr₂) is half-transformed after about 2 min.³

Another unique property of complex **1** compared to other Fe^{II}(TPP) pentacoordinated complexes such as Fe(TPP)(C-Cl₂),¹ Fe(TPP)(CS),¹⁶ or Fe(TPP)(C=C(*p*-ClC₆H₄)₂)¹⁷ is its very low binding affinity for various ligands. Oxygen-containing ligands such as CH₃OH or DMF do not bind to complex **1** since its visible spectra in C₆H₆, DMF, or C₆H₆-CH₃OH (90:10) are identical.¹⁸ The addition of pyridine or isopropylamine to complex **1** (in C₆H₆) leads immediately to the formation of new entities characterized respectively by peaks at 418 (ε 3 × 10⁵), 532 (ε 12 × 10³) and 560 nm (ε 11 × 10³), and 418 (ε 2.9 × 10⁵), 535 (ε 12 × 10³) and 561 nm (ε 11 × 10³). Their formation constants at 27 °C are ~75 and 50 L·mol⁻¹, whereas the formation constants of the hexacoordinated complexes Fe(TPP)(CCl₂)(py) or Fe(TPP)(CS)(py) from the corresponding pentacoordinated complexes and pyridine are, respectively 3500¹ and 5600 L·mol⁻¹.¹⁶

All these results are in agreement with the (TPP)FeCFe(TPP) structure for complex **1** involving a central carbon atom hardly accessible to reactants and iron atoms greatly displaced from the mean porphyrin plane and hardly able to bind ligands. Complex **1** would be, to our knowledge, the first example of a transition-metal complex of the type M=C=M¹⁹ involving a formally dicarbenic carbon atom ligand bridging two transition metals.

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Registry No. **1**, 75249-87-5; Fe^{III}(TPP)(Cl), 16456-81-8; Cl₄, 507-25-5.

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 (18) For comparison, the association constants of DMF or alcohols to Fe(TPP)(CCl₂)₂ are ~5 L·mol⁻¹.
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Simple Electrochemical Approach for Determining Rapid Homogeneous Redox Reaction Rate Constants

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We recently have developed a novel electrochemical procedure for measuring rapid irreversible homogeneous redox reaction rates.¹⁻⁵ The method is applied readily to inorganic

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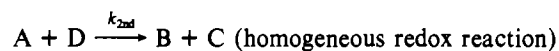
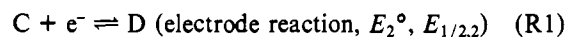
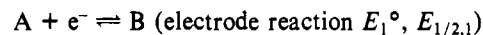
Table I. Diffusion Coefficient Values Determined for Various Relevant Ions with Use of Polarography and Eq 1^a

| ionic species | diffusion coeff, cm ² s ⁻¹ × 10 ⁶ |
|--------------------------------|---|
| Eu(III) | 7.88 |
| RN ₃ ²⁺ | 5.08 |
| RNO ₃ ²⁺ | 5.16 |
| RNCS ²⁺ | 1.46 |
| RONO ²⁺ | 3.40 |
| RNO ₂ ²⁺ | 6.01 |
| RPO ₄ | 1.88 |

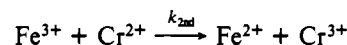
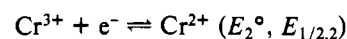
^a Solvent medium was a pH 0.3 aqueous electrolyte containing NaClO₄ and HClO₄ of 1 M ionic strength. R = Co(NH₃)₅³⁺.

and organometallic redox processes. It is applicable to second-order rate constants in the range normally probed by stopped-flow and pulsed radiolysis. We view the electrochemical approach as complementary to these more conventional procedures in most cases, and, with certain systems, it may prove to be the preferred or only method available. The latter remark is based on the fact that the electrochemical approach does not require an absorption or emission spectrum. Consequently, difficulties attending the lack of a spectroscopic response or a complex overlapping multicomponent spectra do not influence the electrochemical procedure. It shares with pulsed radiolysis the advantage over stopped flow that highly air-sensitive compounds are prepared in situ rather than in bulk quantities.

The method is based on the electrode reaction mechanism



where $E_1^\circ \gg E_2^\circ$ and $E_{1/2,1} \gg E_{1/2,2}$ (E_i° and $E_{1/2,i}$ represent standard potentials and observed dc polarographic half-wave potentials, respectively). A specific example is



Basically, one is dealing with two independent electrode reactions coupled by a homogeneous redox reaction. A classical example of such a mechanism is the so-called catalytic wave,⁶ whose properties have been used for many years to deduce homogeneous redox reaction rate data. However, such processes are infrequently encountered because of the nonthermodynamic requirement that for $E_1^\circ \gg E_2^\circ$ one must have $E_{1/2,1} \ll E_{1/2,2}$ or vice versa. However, Mechanism R1 requires that the order of the observed half-wave potentials be the same as the standard potentials, a condition representing the vast majority of such two-component systems. Although complicated in its derivation, the rate law for the reaction sequence give above¹ predicts that a very simple experimental procedure may be applied to obtain the rate constant for the homogeneous redox reaction. One simply obtains ac polarograms of the more difficultly reduced component (e.g., Cr³⁺) in the absence and presence of the more easily reduced substance (e.g., Fe³⁺). One then plots as a function of the applied dc potential the ratio of the ac current in the presence of the more easily reduced substance over the corresponding current

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in its absence (the "kinetic-nonkinetic" current ratio, R).¹ Provided certain readily accommodated restrictions on the heterogeneous charge-transfer rate¹ are met, a sigmoidal profile is predicted with the current ratio approaching unity at positive dc potentials and a larger limiting value at negative dc potentials.¹⁻⁵ The latter limiting value is recommended for computation of the rate constant for the redox reaction in question. While this example and the data presented below use the ac polarographic response, the theoretical rate law indicates that differential pulse polarography or square wave polarography could be substituted for the ac method without modification of the rate law. Computer programs for these computations are available from the authors on request.

The rate law predictions have been tested experimentally²⁻⁴ and applied to a study of the Eu(II) reduction of some Co(III) pentaammine complexes. Some of the rate constant results from the latter study have been published⁵ and found to be in remarkable agreement with rate data produced by stopped-flow measurements, with one exception. Subsequently, we have synthesized and obtained Eu(II) reduction rate data on additional cobalt(III) pentaammine complexes. For three of these compounds, our literature search suggests that previous rate studies have not been attempted.

The purpose of this note is to present these new data and the foregoing description of the technique used to obtain them.

Experimental Section

Analytical grade reagents and deionized water were used exclusively. All solutions were treated with activated charcoal (12-h stirring) prior to use. A stock solution containing 0.025 M Eu(III) in 0.1 M HClO₄ (Baker and Adamson, Inc.) was prepared by dissolving Eu₂O₃ (99.9% Research Inorganic Chemical Corp.) in a known excess of 60% HClO₄ and diluting to volume. All other Eu(III) solutions were prepared from this stock solution by dilution. Sodium perchlorate solutions were prepared by dilution of a stock solution made from G. F. Smith, Inc. (NaClO₄). Literature recommendations were employed in the preparation of RNO₃²⁺,⁷ RN₃²⁺,⁸ RNO₂²⁺,⁷ RONO²⁺,⁹ RPO₄,¹⁰ and RNCS²⁺,¹¹ where R = Co(NH₃)₅³⁺. Those compounds were prepared as nitrate salts and were added to Eu(III) solutions via a micropipet immediately prior to measurement. The identification and purity of the products were confirmed spectrophotometrically. The spectra of all complexes are in excellent agreement with previously reported data.¹²⁻¹⁴

The polarographic cell was composed of a dropping-mercury working electrode (DME, flow rate = $m = 1.432 \text{ mg s}^{-1}$), a Ag/AgCl (saturated NaCl) reference electrode, and a Pt wire auxiliary electrode. DME drop lives were mechanically controlled with use of an in-house constructed drop-knocker. Voltage pulses activating the drop-knocker originated from a computer-controlled D/A converter.

ac polarographic measurements were performed with use of on-line computerized data acquisition and FFT-assisted data processing with instrumentation whose characteristics have been described.¹⁵ Most rate constant calculations used data obtained at 108 Hz. Measurement steps used in obtaining the homogeneous redox reaction rate data are given above. Electroactive species concentrations and Eu(III) concentrations were $5 \times 10^{-3} \text{ M}$ in all cases except for the (isothiocyanato)pentaammine case where it was 10^{-3} M . DME drop lives (τ) were 5 s in all cases. Diffusion coefficient and homogeneous rate constant calculations assume one electron transfer for both homogeneous and heterogeneous charge-transfer steps. With regard to the homogeneous process, one electron transfer has not been firmly es-

Table II. Second-Order Rate Constants for the Eu(II) Reduction of Some Cobalt(III) Pentaammine Complexes^d

| Co(III) complex | $k_{2nd},^e \text{ M}^{-1} \text{ s}^{-1}$ | Co(III) complex | $k_{2nd},^e \text{ M}^{-1} \text{ s}^{-1}$ |
|-------------------------------|--|--------------------------------|--|
| RN ₃ ²⁺ | 1.9×10^2 ^b 1.5×10^2 (18 °C) ^b 2.4×10^2 (31.7 °C) ^b 3.5×10^2 ^a 1.6×10^2 (pH 1) ^a 1.3×10^2 (pH 1.5) ^a | RNO ₃ ²⁺ | 1.0×10^2 ^b 1.2×10^2 ^a |
| | | RNCS ²⁺ | 10^c 30^a |
| | | RPO ₄ | 29^a |
| | | RNO ₂ ²⁺ | 43^a |
| | | RONO ²⁺ | 58^a |

^a This work. ^b Reference 12. ^c Reference 13. ^d Unless noted otherwise, 25 °C, pH 0.3, and unity ionic strength mixture of NaClO₄ and HClO₄ represent measurement conditions. ^e Rate constant uncertainties approximately 2-4 units at second significant figure for data from this work.

established, to our knowledge, for the three previously uninvestigated compounds RPO₄, RNO₂²⁺, and RONO²⁺.

Results

It has been pointed out² that diffusion coefficient magnitudes must be known with good accuracy to obtain accurate estimates of the homogeneous redox reaction rate constant with the method invoked here. Consequently, diffusion coefficients were measured for all relevant species with use of observed dc polarographic limiting currents and the Koutecky-Levich expanding sphere equation^{16,17} (eq 1), where D_0 and C_0^* are

$$i_d = nFAC_0^*(7D_0/3\pi\tau)^{1/2}[1 + 39.6(D_0^{1/2}\tau^{1/6}/m^{1/3})] \quad (1)$$

the oxidized form diffusion coefficient and bulk concentration, respectively, and other symbols either are defined above or have their usual significance. Results are given in Table I for the species involved in this study.

A compilation of second-order rate constants for the Eu(II) reduction of the cobalt(III) pentaammine complexes listed in Table I is given in Table II.

Discussion

The rate constants listed in Table II (first three entries) indicate that excellent to reasonable agreement with results produced by the stopped-flow method are produced by the electrochemical method described above. When combined with previously published data,⁵ it is clear that the electrochemical method is accurate when applied to moderately facile redox processes. Subsequent investigation¹⁸ suggest that *optimum* conditions for the electrochemical method correspond to reaction *half-lives* between 10^{-2} and 1 s. Useful, but less accurate, rate constant measurements are possible with half-lives as long as 10 s and as short as 10^{-3} s. Because one is dealing with second-order reactions, concentration and measurement time manipulation permits one to probe a reasonably extensive range of rate constants (approximately $10 \text{ M}^{-1} \text{ s}^{-1} \leq k_{2nd} \leq 10^5 \text{ M}^{-1} \text{ s}^{-1}$).

As stated above, the purpose of this brief presentation is to indicate the existence of a new, widely applicable electrochemical method for probing homogeneous redox reactions of inorganic complexes and to present some illustrative data. We trust that the foregoing remarks have accomplished this end.

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Registry No. Eu³⁺, 22541-18-0; RN₃²⁺, 14403-83-9; RNO₃²⁺, 15077-47-1; RNCS²⁺, 14970-18-4; RONO²⁺, 16633-04-8; RNO₂²⁺, 14482-68-9; RPO₄, 15612-03-0; Eu²⁺, 16910-54-6.

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