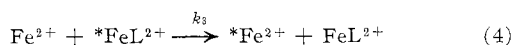
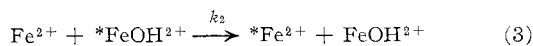
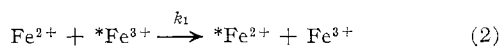


Figure 1.—Plot of $\log [(y_0 - y_\infty)/(y - y_\infty)]$ vs. time in seconds. Ionic strength 0.50 M , $[\text{Fe}^{2+}] = 5.00 \times 10^{-4} M$, $[\text{Fe}^{3+}] = 5.00 \times 10^{-4} F$; \square , $[\text{H}^+] = 0.025 M$, $[\text{L}^-] = 1.56 \times 10^{-14} M$; \circ , $[\text{H}^+] = 0.500 M$, $[\text{L}^-] = 0$; Δ , $[\text{H}^+] = 0.029 M$, $[\text{L}^-] = 0$.

At high hydrogen ion concentration ($\text{pH} < 2$) and low concentration of Fe^{3+} , the species $\text{Fe}(\text{OH})_2^{2+}$ and $\text{Fe}_2(\text{OH})_2^{4+}$ may be neglected. Under the experimental conditions, the calculated concentration of unprotonated ligand species $[\text{L}^-]$ was $\approx 10^{-14} M$, which corresponds to the value of $[\text{FeL}^{2+}]/[\text{FeL}_2^{2+}] = \beta_1[\text{L}^-]/\beta_2[\text{L}^-]^2 \approx 1/(5 \times 10^{-3})$. Hence, only the following electron-exchange reactions need be considered



where L^- represents an 8-quinolinolate ion. The overall rate of the reaction may then be expressed

$$R = k_1[\text{Fe}^{2+}][\text{Fe}^{3+}] + k_2[\text{Fe}^{2+}][\text{FeOH}^{2+}] + k_3[\text{Fe}^{2+}][\text{FeL}^{2+}] \quad (5)$$

The above equation may be rewritten

$$R = k_1[\text{Fe}^{2+}][\text{Fe}^{3+}] + k_2[\text{Fe}^{2+}][\text{Fe}^{3+}] \frac{K_h}{[\text{H}^+]} + k_3[\text{Fe}^{2+}][\text{Fe}^{3+}]\beta_1[\text{L}^-] = ab \left[\frac{k_1 + k_2 K_h [\text{H}^+]^{-1} + k_3 \beta_1 [\text{L}^-]}{1 + K_h [\text{H}^+]^{-1} + \beta_1 [\text{L}^-]} \right] \quad (6)$$

where $K_h = 1.82 \times 10^{-3} M$,⁹ and β , the over-all formation constant of the complex ML^{2+} , is $2.76 \times 10^{13} M^{-1}$.⁶

The concentration of unprotonated ligand species L^- may be calculated from

$$H_T = L_T + C \quad (7)$$

$$H_T = 2[\text{H}_2\text{L}^+] + [\text{HL}] + [\text{H}^+]$$

where H_T is the analytical concentration of titratable hydrogen, L_T the analytical concentration of total ligand, and C the concentration of HClO_4 added. Equation 7 may be rewritten in terms of the acid dissociation constants

$$H_T = [\text{L}^-] \left\{ \frac{2[\text{H}^+]^2}{K^{\text{H}_1} K^{\text{H}_2}} + \frac{[\text{H}^+]}{K^{\text{H}_2}} \right\} + [\text{H}^+] \quad (8)$$

where K^{H_1} and K^{H_2} are the stoichiometric dissociation constants of 8-quinolinol. The apparent rate constant k may be recognized as the factor in brackets in eq 6.

(9) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

In order to use 6 for the calculation of k_1 , k_2 , and k_3 , it was necessary to carry out exchange reactions at various pH values with and without the ligand species. In the absence of ligand, $[\text{FeL}^{2+}] = 0$, and at moderately high pH (≈ 2) the concentration of FeOH^{2+} is relatively high. Previous work¹⁰ has shown that $k_2 \gg k_1$; under these conditions $R = k_2[\text{Fe}^{2+}][\text{Fe}^{3+}] \cdot K_h[\text{H}^+]^{-1}$, and k_2 can be evaluated. Once k_2 is evaluated, k_1 may be calculated from the data obtained at a higher hydrogen ion concentration, correcting for the small contribution due to the presence of FeOH^{2+} . The values of k_1 and k_2 were obtained at several hydrogen ion concentrations ranging from 0.500 to 0.02 M . The results of this investigation are given in Table I. The values of these two rate constants agree reasonably well with those reported by Fukushima and Reynolds.¹¹

TABLE I
ANALYTICAL AND KINETIC DATA ON IRON(II)-IRON(III)
EXCHANGE REACTIONS AT 25° ($\mu = 0.50 M$)

$10^4 a$, M	$10^4 b$, M	$[\text{H}^+]$, M	$10^3 L_T$, M	$10^{14} [\text{L}^-]$, M	$t_{1/2}$, sec	k , $M^{-1} \text{sec}^{-1}$
4.00	5.00	0.500	0.00	0.00	35.5	19.5
5.00	5.00	0.0295	0.00	0.00	3.77	181.4
4.00	5.00	0.355	0.00	0.00	5.44	151.1
4.00	5.00	0.0201	4.02	2.32	2.31	334.0
5.00	5.00	0.0251	4.02	1.51	2.56	276.0

$$k_1 = 8.35 M^{-1} \text{sec}^{-1}, k_2 = 3020 M^{-1} \text{sec}^{-1}, k_3 = 450 M^{-1} \text{sec}^{-1}$$

The rate constant k_3 was obtained by similar measurements in the presence of ligand, using the values of k_1 and k_2 to solve eq 6.

Acknowledgment.—We wish to thank the research board of Marshall University for the financial support which covered part of the expenses of this study. Our sincere thanks are due to Mr. J. B. Fodor for his assistance in the experimental setup.

(10) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).
(11) S. Fukushima and W. L. Reynolds, *Talanta*, **11**, 283 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN

On the Rapid Electron Exchange between Ruthenate and Perruthenate Ions in Basic Solutions

BY E. V. LUOMA AND C. H. BRUBAKER, JR.

Received April 18, 1966

Sheppard and Wahl¹ and others^{2,3} have studied the rate of electron exchange between manganate and permanganate ions in aqueous solutions, and the present work was undertaken in an effort to extend the information available on outer-sphere electron-transfer processes and to attempt to test further the theory of

(1) J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957).
(2) O. E. Myers and J. C. Sheppard, *ibid.*, **83**, 4739 (1961).
(3) A. D. Britt and W. M. Yen, *ibid.*, **83**, 4516 (1961).

Marcus.⁴ We find, however, that the exchange between ruthenate and perruthenate is too rapid to measure by the techniques available to us.

Experimental Section

Reagents.—Analytical and Reagent grade chemicals were used throughout. Sodium hydroxide solutions were prepared by diluting saturated solutions, after sodium carbonate was removed by decantation.

A stock solution of ruthenium(III) was prepared by fusing ruthenium metal with KOH and KNO₃ at 600° and dissolving the fused mass in aqueous sulfuric acid. The solution was evaporated until SO₃ fumes were observed. During the evaporation, several portions of aqueous HCl were added to destroy the excess nitrate. The final solution was then diluted with water and H₂SO₄ to make a stock of Ru(III) in 3 M H₂SO₄.

Perruthenate was prepared by oxidizing the Ru(III) with sodium bismuthate in the 3 M H₂SO₄. The RuO₄ vapor, thus produced, was carried in a stream of air into 1.0 M NaOH where it decomposed to give RuO₄⁻. The conversion to RuO₄⁻ is taken to be complete when the ratio of the absorbancies at 465 and 385 mμ reaches 0.121.^{5,6} A lower ratio indicates RuO₄ is still present; a higher ratio shows the presence of RuO₄²⁻. The RuO₄⁻ solutions decompose slowly⁵⁻⁷ to form RuO₄²⁻; consequently, all of the RuO₄⁻ solutions, which we used, contained some RuO₄²⁻.

Ruthenate solutions were prepared by passing the RuO₄ directly into 2.0 M NaOH and then heating at about 70° until the ratio of the absorbancies at 465 to 385 mμ reached 2.07, corresponding to pure ruthenate.⁵ These stocks were then diluted and stored in an ice bath. They proved stable, as long as the hydroxide ion concentration exceeded 0.1 M.

Concentrations of the ruthenate and perruthenate in stocks and other solutions were determined spectrophotometrically. The following molar absorptivities were used: for RuO₄⁻, 2150 at 385 mμ and 260 at 465 mμ; for RuO₄²⁻, 840 at 385 mμ and 1740 at 465 mμ. The molar absorptivities are determined in this work and are in substantial agreement with those of Larsen and Ross.⁵

The ¹⁰⁶Ru tracer was obtained as ruthenium-106–rhodium-106, carrier free, from Oak Ridge National Laboratory as RuCl₃ in 6 N HCl. It was added to one sample of Ru(III) in 3 M H₂SO₄ before the BiO₃⁻ oxidation.

Procedures.—In experiments in which RuO₄⁻ was separated from the exchanging mixture, RuO₄⁻ solutions were added to RuO₄²⁻ (both in 0.1 M NaOH), at 0°, and the mixture was stirred mechanically. A quench solution consisting of 4.00 ml of 0.1 M tetraphenylarsonium chloride in 0.1 M NaOH and 5.00 ml of 0.01 M perrhenate (ReO₄⁻, nonisotopic carrier) was added. The precipitate was filtered with suction, and the supernatant liquid was reserved for counting. When it had been learned that exchange was very rapid, several experiments were carried out with the quench solution added before the RuO₄⁻ and the solution was stirred vigorously during the addition.

In an effort to determine that the fast exchange was not due to separation-induced exchange, a second series of experiments was carried out, in which RuO₄²⁻ was precipitated. In these experiments RuO₄²⁻ was added to stirred RuO₄⁻ at 0° in 0.1 M NaOH. A quench solution was prepared with 4.00 ml of saturated Ba(OH)₂ plus 5.00 ml of 0.01 M Na₂SO₄ and was added rapidly to the exchange mixture. The BaRuO₄ was filtered off, and the filtrate was reserved for counting.

Samples of the various supernatant liquids (2.00 ml) were placed in 1-dram, screw-cap vials and were counted in an integral, well-type scintillation counter. The energetic γ rays (0.51–2.4 Mev) from the ¹⁰⁶Rh daughter were counted after the

solutions reached radioactive equilibrium (a few minutes is required).

Results and Discussion

In all experiments conducted, even those with the quench added before the reagents were mixed, complete exchange was observed in the time of mixing and separating, which is estimated to be 5–15 sec for precipitation and another 10–40 sec for the filtration. Thus, the exchange must be complete in less than 5 sec, if there is no exchange between the precipitates and the supernatant liquids.

Table I gives the concentrations of reactants which were used.

TABLE I
CONCENTRATIONS OF RuO₄⁻, RuO₄²⁻, AND OH⁻ IN THE EXCHANGE STUDIES AT 0°. ALL SOLUTIONS SHOW COMPLETE EXCHANGE IN TIME OF MIXING AND SEPARATION

10 ⁶ [RuO ₄ ²⁻], M	10 ⁶ [RuO ₄ ⁻], M	[OH ⁻], M
2.5	4.9	0.1 ^a
2.8	2.95	0.1 ^b

^a (C₆H₅)₄AsRuO₄ separation. ^b BaRuO₄ separation.

Sheppard and Wahl¹ were able to measure half-lives as short as 0.25 sec in the MnO₄⁻–MnO₂²⁻ exchange by similar experimental procedures. Thus, we may estimate a second-order rate constant >3.3 × 10⁴ M⁻¹ sec⁻¹ if we assume 0.25 sec as a lower limit, and 1.7 × 10³ if we assume 5 sec as a lower limit.

Separation-induced exchange cannot be ruled out, but two methods of separation were tested and Sheppard and Wahl¹ found little induced exchange in the tetraphenylarsonium chloride method.

Electron spin resonance measurements were made on solutions of 2.0 × 10⁻² M RuO₄²⁻ in 2.0 M NaOH and 1.0 × 10⁻² M RuO₄⁻ in 1.0 M NaOH, in the hope that suitable signals could be detected for following the exchange by line broadening. A very weak signal, probably peroxide, was found in the perruthenate, and no other signal was detected.

Acknowledgment.—The authors thank the U. S. Atomic Energy Commission, which supported this work under AT(11-1)-1001. E. V. L. thanks The Dow Chemical Co. for fellowship aid during 1965.

CONTRIBUTION FROM THE INORGANIC CHEMISTRY LABORATORY, UNIVERSITY OF OXFORD, OXFORD, ENGLAND

Ultraviolet Spectra of Some First Transition Series Pseudohalide Complexes

By P. DAY

Received May 2, 1966

The π–π* transitions of many conjugated ligands are very little modified by complex formation, but the spectra of thiocyanate complexes usually contain intense absorption bands at much lower energies than the free anion. In certain cases (*e.g.*, iron(III)) these are

(4) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **26**, 867, 872 (1957); **43**, 789 (1965); *J. Phys. Chem.*, **67**, 853 (1963).

(5) R. P. Larsen and L. E. Ross, *Anal. Chem.*, **31**, 176 (1959).

(6) G. Nowogrocki and G. Tridot, *Bull. Soc. Chim. France*, 684 (1965).

(7) A. Carrington and M. C. R. Symons, *J. Chem. Soc.*, 284 (1960).