Monatshefte für Chemie 106, 813—822 (1975)

Electrochemical Studies of Potassium Ferrate(VI)

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With 1 Figure

(Received April 9, 1975)

The electrochemical reduction of potassium ferrate(VI) in 6*N*-KOH occurs in three steps, at approximately + 0.3, — 0.7, and — 1.4 V vs. Hg/HgO, 6*N*-KOH. The first reduction appears as a voltammetric wave on a platinum electrode and the second two are observed as polarographic waves with a dropping mercury electrode. Controlled potential coulometric, voltammetric, and chronopotentiometric studies indicate the reduction proceeds stepwise first to iron(III), then to iron(II) and finally to iron(0).

Introduction

Electrochemical methods have been reported recently for the synthesis[1] and the analysis[2] of ferrate(VI). *Becarud*[3] studied the reduction of potassium ferrate in 10*N*-KOH at a dropping mercury electrode and at a rotating platinum electrode. In the present work the reduction of potassium ferrate was studied by d.c. voltammetry, controlled potential coulometry, and chronopotentiometry using both mercury and platinum electrodes.

Experimental

Potassium ferrate(VI) was prepared by the method of *Thompson* and coworkers[4, 5] except that centrifugation was used in place of all but the final filtration step. The potassium ferrate was analyzed by the method of *Schreyer* et al.[6] and was found to be 97.8% pure.

All polarograms were recorded using either a Sargent Polarograph

Model XXI or a Chemtrix Single-Sweep Polarographic Analyzer System, Model SSP-3.

The polarographic cell consisted of a 100 ml beaker containing the solution to be analyzed. Two H-salt bridges with sintered glass frit ends and containing 6*N*-KOH were used to provide electrical contact between the polarographic cell, an intermediate beaker containing 6*N*-KOH, and the Hg/HgO, 6*N*-KOH reference electrode. When a saturated calomel reference electrode was used, the H-salt bridge contained saturated KCl between the reference electrode and the intermediate beaker. The mercury—mercuric oxide electrode was prepared as described by *Ives* and *Janz*[7]. Its potential as measured against a saturated calomel electrode was found to be — 0.202 V. All potentials were measured relative to this electrode unless otherwise specified.

The chronopotentiometric electrolysis cell had a 1.13 cm^2 area mercury pool or a 1.26 cm^2 area platinum foil cathode with a platinum foil anode isolated by a sintered glass frit.

KOH solution was first deaerated in the polarographic or chronopotentiometric cell by passing N_2 through the solution for 15 minutes and brought to 25 °C in a constant temperature water bath prior to the preparation of the potassium ferrate solution. The potassium ferrate solution was then added to the cell, the solution was deaerated for an additional one minute, and finally the polarogram or chronopotentiogram was recorded.

For controlled potential coulometric studies, a Sargent-Slomin Electrolytic Analyzer was used as the variable potential source. The potential of the working electrode versus the Hg/HgO, 6*N*-KOH reference electrode was monitored by a Heath Vacuum Tube Voltmeter Model EUW 24. The current passing through the electrolysis cell was monitored by a Weston Analyzer Model 980.

For controlled potential coulometry, a 15.9 cm^2 mercury pool cathode was used. The quantity of electricity consumed in the electrolysis was measured with a titration coulometer[8] placed in series in the electrolysis circuit.

20 ml of 6*N*-KOH solution was deaerated in the coulometric cell for 15 minutes prior to the preparation of the potassium ferrate solution. Pre-electrolysis of the KOH solution was carried out by applying — 1.50 V versus Hg/HgO, 6*N*-KOH to the mercury pool electrode until the current decreased to 1 mA. Residual currents of approximately 0.3, 0.7, and 1.0 mA were found for the potentials of — 0.15, — 1.15, and — 1.45 V versus Hg/HgO, 6*N*-KOH, resp. After placing the potassium ferrate in solution, N_2 was again passed through the solution for an additional one minute. The titration coulometer was connected in the circuit and the electrolysis was started. The variable auto-transformer of the potential source was adjusted as needed throughout the electrolysis to keep the working electrode potential at the desired potential versus the reference electrode. The electrolysis was stopped when the current decayed to the residual current.

Results and Discussion

A) Polarography and Voltammetry

At a platinum wire electrode, the half-wave potential for the reduction of $1.52 \times 10^{-4} M$-ferrate in 6*N*-KOH was + 0.32 Volt using the

Sargent Polarograph and + 0.28 V using fast sweep voltammetry with the Chemtrix Polarograph. Although *Becarud*[3] reported a second reduction wave of potassium ferrate in $10N$-KOH at a rotating platinum electrode, this was not observed in the present study.

Polarographic studies of the reduction of $2–5 \times 10^{-4} M$-potassium ferrate in $6N$-KOH at a dropping mercury electrode showed waves with halfwave potentials of > 0, -0.68, -0.82, -1.43 V versus Hg/HgO, $6N$-KOH, resp.

The first reduction process at the d.m.e. occurs at potentials greater than those at which the electrode is oxidized. The two intermediate reduction waves appear as two waves merged together, and the final wave is well-defined; the two intermediate waves are initially a single wave that separates into two close waves upon standing (see time study below). The wave height ratios were calculated for the initial wave, the combined intermediate waves, and the final wave, with average values of 3.00 : 1.45 : 1.93. These values are approximately what is expected for a 3, 1, 2 electron change, although the combined intermediate waves are somewhat high. The n-values of the separate intermediate waves calculated from log-plots were inconclusive (0.9 to 1.5). The calculated n-value of the final reduction wave obtained from log-plots was close to the value of a two-electron change (average 1.85).

Diffusion coefficients were calculated using the *Ilković* equation, assuming an n-value of 3 for the initial reduction. The average value was 0.590×10^{-5} cm^2/sec, with an average deviation of 0.018×10^{-5} cm^2/sec.

Plots of the net diffusion currents of the initial, combined intermediate, and final waves (measured at -0.10, $-0{,}92$, and -1.50 V versus Hg/HgO, $6N$-KOH, resp.) as a function of concentration resulted in linear calibration curves for 0 to $5 \times 10^{-4} M$-potassium ferrate.

A polarographic study was made of the stability $7.08 \times 10^{-4} M$-potassium ferrate in $6N$-KOH. The polarograms of the solution immediately after preparation indicate the reduction occurs in three steps: one reduction occurs in the potential region more positive than the anodic oxidation of mercury, the intermediate reduction wave occurs at -0.84 V and is drawn out, and the final reduction wave occurs at -1.46 V and is well-defined. After 24 hours, the intermediate wave consisted of two distinct well-defined waves at -0.81 and -1.09 V, resp. The same general shape of polarograms was obtained at 48, 72, and 120 hours after the initial preparation of the potassium ferrate solution. Decomposition of the potassium ferrate was indicated by the change of color from a dark red solution immediately after preparation through a pink solution after 24 hours to a colorless solution after 72 hours. Along with the decrease of intensity of the color, a precipitate of ferric oxide was noted.

The half-wave potentials of the reduction waves increased slightly in the more negative direction for the intermediate reduction waves and remained constant for the final wave as the solution grew older. Fig. 1 is a plot of the wave height versus time for the initial, the two intermediate, and the final reduction waves of potassium ferrate in 6*N*-KOH. Wave height ratios were not conclusive.

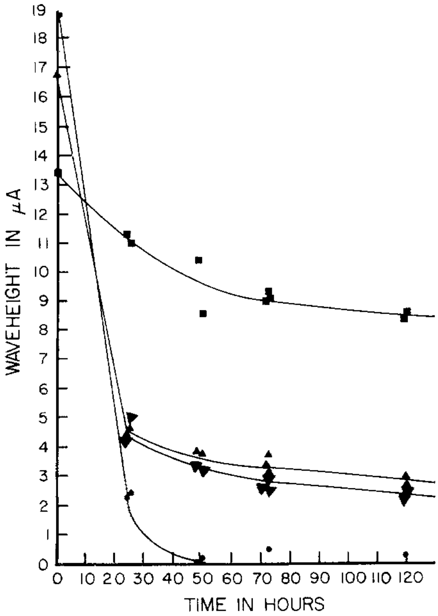

Fig. 1. Wave height versus time for the reduction waves of potassium ferrate(VI) in 6*N*-KOH. ● Initial Wave. ▲ First Intermediate Wave. ▼ Second Intermediate Wave. ■ Final Wave

Ferric sulfate in 5.5*N*-KOH gave polarographic waves with half-wave potentials of — 0.86 and — 1.44 V versus Hg/HgO, 6*N*-KOH, corresponding to reduction to iron(II) followed by reduction to the metal. These are close to the potentials for the initial intermediate and the final reduction waves of potassium ferrate in 6*N*-KOH. The wave height ratio of the two reduction waves was approximately 1 : 1.8. The E versus log $[(i_d—i)/i]$ plots of the first wave were nonlinear, and therefore, no n-values were calculated. This wave was drawn out due to the apparent irreversibility of the reduction. The n-value of the final reduction wave was calculated to be approximately 1.4 from log-plots.

A summary of the half-wave potentials of potassium ferrate and ferric sulfate obtained in this study using different reference electrodes and those obtained by *Becarud*[3] is given in Table 1. All potential values are corrected to the S.H.E. reference electrode for comparison. The half-wave potentials of the two intermediate waves found at the d.m.e. are shown separately.

Since the half-wave potentials of the ferric sulfate compare very closely with those of the intermediate half-wave potentials and final half-wave potential of the potassium ferrate, the first reduction step appears to be the reduction of ferrate(VI) to iron(III).

Table 1. *Comparison of d.c. Polarographic Results of Potassium Ferrate(VI) in 10N*-KOH *and 6N*-KOH *and Ferric Sulfate in 5.5N*-KOH. All Half-Wave Potentials in V Versus S.H.E. Column Headings Indicate Reference Electrode Used to Collect Data

	K_2FeO_4						$Fe_2(SO_4)_3$
	10*N*-KOH[3]		6*N*-KOH				5.5*N*-KOH
	Ag/Ag+; d.m.e.	Ag/Ag+; Pt	S.C.E.; d.m.e.	Hg/HgO, 6*N*-KOH; d.m.e.	S.C.E.; Pt	Hg/HgO, 6*N*-KOH; Pt	Hg/HgO, 6*N*-KOH; d.m.e.
Initial Wave		+ 0.43			+ 0.36	+ 0.36	
Intermediate Wave	— 0.60	— 0.60	— 0.67	— 0.64			— 0.82
			— 0.79	— 0.78			
Final Wave	— 1.20		— 1.41	— 1.39			— 1.40

The potential values listed for the first reduction step are significantly more negative than the standard potential of + 0.72 V versus S.H.E. for the ferrate(VI)—iron(III) couple in alkaline solution[9], indicating an irreversible reduction at the platinum electrode.

B) Controlled Potential Coulometry

Controlled potential coulometry was employed to determine the *n*-values for the different reduction steps of potassium ferrate at the mercury electrode.

Table 2 summarizes the results using stepwise electrolysis to obtain the *n*-values of successive waves. The *n*-values were calculated on the basis of the purity of 98.0 per cent of potassium ferrate and the assumption that the impurity was ferric oxide.

The *n*-value of the first reduction wave was somewhat lower than the expected value of three. This was due in part to chemical reduction of some of the potassium ferrate immediately after the addition of the potassium ferrate to the 6*N*-KOH. Evidence of this was the color change of the potassium ferrate solution from red to brown at the mercury-potassium hydroxide interface. Another factor was the decomposition of the potassium ferrate throughout the electrolysis. At the completion of the electrolysis at — 0.15 V versus Hg/HgO, 6*N*-KOH the solution was brown in color.

Table 2. *Controlled Potential Coulometric Results for Reduction of* 98.0% *Pure Potassium Ferrate(VI) in 6N*-KOH

Sample Number	Potential, V vs. Hg/HgO, 6*N*-KOH	*n*
1	— 0.20	2.61
2	— 0.15	2.46
3	— 0.15	2.73
4	— 0.15	2.43
	— 1.15	1.01
	— 1.45	1.53
5	— 0.15	2.65
	— 1.15	0.99
	— 1.45	1.77
6	— 0.15	2.68
	— 1.15	1.00
	— 1.45	1.82

The *n*-value of the intermediate reduction step was found to be very close to the expected value of a one-electron change. At the completion of the electrolysis at — 1.15 V versus Hg/HgO, 6*N*-KOH the solution was dark brown in color.

The *n*-value of the final reduction wave was found to be slightly lower than the expected value of a two-electron change. During the final electrolysis the color of the solution changed from dark brown to black. After the electrolysis at — 1.45 V was completed, the resulting metallic iron particles were attracted to the magnetic stirring bar.

Plots of log current versus time for the controlled-potential coulometric analysis of sample number 6 yielded *n*-values of 2.68, 1.03, and 1.84 for the initial, intermediate, and final reduction waves of potassium ferrate(VI), resp., which compare favorably with the values obtained using the titration coulometer.

C) *Chronopotentiometry*

The chronopotentiometric results for the reduction of potassium ferrate in 6*N*-KOH at a mercury pool electrode are summarized in Table 3. Averages are given for sets of data obtained at different times. The potential at one-fourth the transition time for the first reduction wave is not listed since the reduction occurs at potentials more positive than the oxidation of mercury. The initial potential of the mercury pool was zero Volts versus Hg/HgO, 6*N*-KOH. The potentials at one-fourth the transition times for the intermediate and final reduction waves of potassium ferrate correspond fairly closely to the half-wave potentials of potassium ferrate at the d.m.e. Only one reduction wave was noted for the intermediate reduction of potassium ferrate in 6*N*-KOH with chronopotentiometry at a mercury pool electrode. The relative deviation of measured τ values increased with successive waves as expected because of the accumulation of errors in the determination of consecutive transition times.

The τ ratios in column five are the ratios of τ_1/τ_1, τ_2/τ_1 and τ_3/τ_1, resp., where the transition times are τ_1 for the initial wave, τ_2 for the intermediate wave, and τ_3 for the final wave. If potassium ferrate in 6*N*-KOH is assumed to be reduced in steps of 3, 1, and 2 electrons, one calculates the following theoretical ratios (1): $\tau_2/\tau_1 = 0.778$ and $\tau_3/\tau_1 = 2.22$. The ratio of τ_2/τ_1 in Table 3 appears to be somewhat lower than the expected ratio 0.778 for a 3 and 1 electron change. However, the value of 0.557 is closer to 0.778 than the closest other possible value of $\tau_2/\tau_1 = 1.25$ for a 2, 1, and 3 electron change. The reproducibility of τ_3 determinations was very poor, which led to a wide range of τ_3/τ_1 ratios. At higher currents (0.5 A) the τ_3/τ_1 ratios were lower than the expected ratio of 2.22, while at lower currents (0.09–0.24 A) the ratios were larger than 2.22. The average of τ_3/τ_1 for 50 runs, mostly at about 0.2 A, was 3.42. The uncertainty in this average value prevents a conclusive determination of the number of electrons in this step.

The accuracy and reproducibility of chronopotentiometric measurements at the mercury pool were poorer than the polarographic measurements as evidenced by the wide range of diffusion coefficients calculated from τ_1 assuming $n_1 = 3$, to give a relative average deviation of 27.7% compared to 3.05% for the polarographic data. The average value 2.82×10^{-5} cm^2/sec compared to 0.590×10^{-5} cm^2/sec from polarographic data is probably due to the reaction of the ferrate with the mercury pool electrode to form HgO which was subsequently reduced.

Current reversal studies at the mercury pool electrode were carried out. However, reversal of the current at the transition times of each

Table 3. *Chronopotentiometric Results of the Reduction of* 98% *Pure Potassium Ferrate(VI) in* 6*N*-KOH

Electrode	$E_{\tau/4}$ (V vs. Hg/HgO, 6N-KOH)	$i\,\tau^{1/2}/C$ $\left(\frac{\text{amp-sec}^{1/2}}{\text{mole/ml}}\right)$	Average Deviation	τ Ratio	Average Deviation	Diffusion Coefficient, D (cm^2/sec)	Average Deviation
Mercury		1470	193	1.00			
Pool	-0.864*	967	196	0.557	0.24	2.82×10^{-5}	0.78×10^{-5}
	-1.422**	2477	456	3.42	1.29		
Platinum	$+0.223$	618	26	1.00			
Foil	-0.135***	685	62	1.30	0.29	0.367×10^{-5}	0.031×10^{-5}

* Average of 56 runs.
** Average of 50 runs.
*** Average of 17 runs.

of the three reduction waves of potassium ferrate in 6N-KOH resulted in the potential dropping directly to nearly zero Volts versus Hg/HgO, 6N-KOH. This suggests that the reduction processes are either irreversible or the initial reduction product is destroyed by a following reaction.

The chronopotentiometric results for the reduction of potassium ferrate in 6N-KOH at a platinum foil electrode are shown in Table 3. The potential at one-fourth the transition time of the initial reduction wave of approximately $+0.22$ V versus Hg/HgO, 6N-KOH is somewhat less than the half-wave potential of $+0.32$ V at a stationary platinum electrode. The origin of the second chronopotentiometric reduction wave at -0.12 to -0.14 V is unknown. The intermediate wave of $E_{\tau/4}$ of -0.88 to -0.92 V was obtained on several of the chronopotentiograms. The $i\tau^{1/2}/C$ values of the reduction of potassium ferrate at the platinum foil electrode were more precise than those for the mercury pool electrode. Because of the unknown step at -0.12 V, no quantitative conclusion can be drawn from the ratios.

The diffusion coefficient calculated from the platinum foil electrode data gave an average value of 0.367×10^{-5} cm^2/sec with a relative average deviation of 0.031×10^{-5} cm^2/sec (8.4%) compares more favorably with the polarographic results.

Acknowledgement

This work forms part of an investigation of electrochemical processes under Project Themis Contract DAAB07-69-C-0366 with the Department of Defense and taken in part from a thesis submitted by *R. K. Sensmeier* in partial fulfillment of the M.S. degree, University of Kentucky.

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Eigentümer: Österreichische Akademie der Wissenschaften, Dr. Ignaz Seipel-Platz 2, A-1010 Wien. — Herausgeber: Österreichische Akademie der Wissenschaften, Dr. Ignaz Seipel-Platz 2, A-1010 Wien, und Verein Österreichischer Chemiker, Eschenbachgasse 9, A-1010 Wien. — Verlag: Springer-Verlag, Mölkerbastei 5, A-1011 Wien. — Für den Textteil verantwortlich: Prof. Dr. Friedrich Kuffner, Währinger Straße 38, A-1090 Wien. — Für den Anzeigenteil verantwortlich: Bruno Schweder, Mölkerbastei 5, A-1011 Wien. — Druck: Adolf Holzhausens Nachfolger, Kandlgasse 19-21, A-1070 Wien.

Printed in Austria