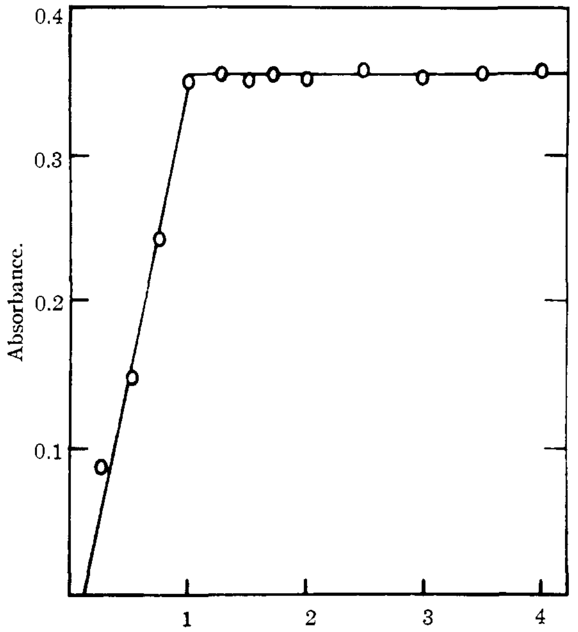

ig. 1.—Molar ratio study: $(Fe^{+++}) = 2.5 \times 10^{-4}$ *M*, λ = 400 mμ.

be the dimer $Fe_2(phen)_2Cl_6$ wherein iron has the more common coördination number of 6.

TABLE I

RESULTS OF PRECIPITATE ANALYSIS

Element	$[Fe(phen)Cl_3]$, % Found	Calcd.
Fe	16.2	16.3
Cl	30.5	31.0

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The Oxidation–Reduction Potentials of Systems Involving the Bivalent and Tervalent Complexes of Iron, Ruthenium and Osmium with 2,2'2''-Terpyridyl

BY F. P. DWYER AND E. C. GYARFAS

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The bis-terpyridyl complexes of iron(III), ruthenium(III) and osmium(III) have not been prepared although the bivalent metal complexes have been known for some time,[1] nor has the potential for the reaction $M(trpy)_2^{++} \rightleftarrows M(trpy)_2^{+++} + e^-$ been determined save for the iron system, for which a single value, −1.10 ± 0.01 v. in 0.1 *f* H_2SO_4, is reported.[2]

The green ions $M(trpy)_2^{+++}$ were found to be much less stable than the corresponding $M(dipy)_3^{+++}$ and rapid reduction occurred in solution except in the presence of at least normal acid. At this acid concentration the iron(II) compound was rapidly destroyed. Whilst the green crystalline perchlorates could be precipitated with sodium perchlorate after oxidation of the bivalent complexes with ceric nitrate, they underwent reduction during filtration and washing. The complex osmium(III) perchlorate, however, was isolated as a pure compound following oxidation with chlorine.

The potentials of the iron and ruthenium systems were determined on solutions that had been exactly half oxidized with ceric ammonium sulfate. The potentials, developed on a smooth platinum electrode, rose rapidly on the addition of the oxidizing agent, and then fell at a variable rate depending on the acid concentration. Since equilibrium is never attained on an electrode under such conditions, the maximum potential was taken as the oxidation–reduction potential, and no attempt was made to extrapolate to zero time. The potential of the osmium system was measured by allowing the electrode to reach equilibrium for 15–20 min. in an initially equimolar solution of the oxidant and reductant, immediately determining the oxidation–reduction ratio spectrophotometrically, and applying the usual correction. The dark brown Os^{II} complex has a strong absorption maximum at 490 mμ and the green Os^{III} complex has a high transmission in this region with an absorption maximum at 650 mμ. Using two 1-cm. cells placed in front of each other, one containing the oxidant with a trace of chlorine, the other with the pure reductant, and a 490 mμ filter a calibration curve for various ratios was prepared. In the range 40–60% reductant this was a straight line and the oxidation–reduction ratio at equilibrium could be readily ascertained.

Although the color changes are favorable: Fe, violet to green; Ru, orange-red to green; Os dark brown to green, the instability of the oxidized form militates against the use of these compounds as oxidation–reduction indicators.

Experimental

Bis-2,2',2''-terpyridylosmium(III) Perchlorate Dihydrate.—A warm aqueous solution of the bivalent complex iodide[1] was treated with dilute perchloric acid and the resulting sparingly soluble perchlorate recrystallized from hot water. The finely divided microcrystalline powder was suspended in ice-water and oxidized by shaking in a current of chlorine. After filtration from traces of unreacted material, the deep green solution was treated with a little 20% sodium perchlorate, the resulting green needles collected, washed with cold 2% perchloric acid, then purified ether containing a trace of chlorine and dried *in vacuo*. The dry substance was stable, but an aqueous solution at *p*H 6 rapidly became brown due to reduction. This behavior is characteristic of the tervalent ion, ruthenium and osmium complexes with dipyridyl and phenanthroline.[3]

Anal. Calcd. for $Os(C_{15}H_{11}N_3)_2(ClO_4)_3 \cdot 2H_2O$: Os, 19.19; N, 8.47. Found: Os, 19.3; N, 8.6.

Oxidation-Reduction Potentials.—The pure perchlorates of the iron(II) and ruthenium(II) complexes[1] in *M*/500 solution containing various concentrations of sulfuric acid were oxidized by the addition of the calculated volume of *N*/100 ceric ammonium sulfate, prepared in sulfuric acid of the same concentration, in the oxidation–reduction assembly previously described.[4] The potential of the saturated calomel half-cell, calibrated against the quinhydrone electrode at *p*H 4 in the same assembly was taken as 0.2423 v. at 25°. The oxidation–reduction mixture of the osmium complexes was prepared initially *M*/2000 with respect to each and $10^{-4}N$ with respect to nitric acid, and subsequently diluted to *M*/4000 with sulfuric acid. Higher

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(1) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 20 (1932).

(2) W. W. Brandt, THIS JOURNAL, **76**, 6215 (1954).

(3) F. P. Dwyer and E. C. Gyarfas, *ibid.*, **74**, 4699 (1952).

(4) G. T. Barnes, F. P. Dwyer and E. C. Gyarfas, *Trans. Faraday Soc.*, **48**, 269 (1952).

concentrations could not be used owing to the sparing solubility of the osmium(II) complex. The potentials found are shown in Table I. The potentials are generally higher than with the corresponding dipyridyl complexes, which in 0.1 *f* acid, for comparison, are, respectively, −1.07,[5] −1.288,[6] −0.856.[7]

TABLE I

Acid concn., *f*	$Fe(trpy)_2^{++}$/ $Fe(trpy)_2^{+++}$, v.	$Ru(trpy)_2^{++}$/ $Ru(trpy)_2^{+++}$, v.	$Os(trpy)_2^{++}$/ $Os(trpy)_2^{+++}$, v.
0.1	−1.076[a]	−1.281[a]	−0.9512[b]
0.2	−1.060	−1.263	−0.9414
0.5	−1.054	−1.219	−0.9250
1.0	−0.927	−1.202	−0.9070
2.0	....	−1.175	−0.8838

[a] ±0.002 v.
[b] ±0.0002 v.

The Standard Potential of the $Os(trpy)_2^{++}/Os(trpy)_2^{+++}$ System.—The potentials of oxidation–reduction mixture above, with the addition of potassium nitrate were measured at various ionic strengths at 25°. The plot of $I^{1/2}$ against E_h corrected, Table II, gave a straight line of slope 16.6 mv./0.1 unit of $I^{1/2}$. This compares with the calculated Debye–Hückel slope of 14.8 mv.[8] By extrapolation to $I = 0$, E_0 was found to be −0.9866 ± 0.0005 v. as compared with the $Os(dipy)_3^{++}/Os(dipy)_3^{+++}$ system[4] −0.8795 v.

TABLE II

$I^{1/2}$	E_h	E_h (cor.)
0.0474	−0.9773	−0.9786
0.0575	−0.9746	−0.9768
0.0652	−0.9726	−0.9759
0.0791	−0.9682	−0.9734
0.0908	−0.9677	−0.9711
0.1013	−0.9657	−0.9700

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(5) F. P. Dwyer and H. H. McKenzie, *J. Proc. Roy. Soc. N. S. W.*, **81**, 93 (1947).

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(8) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 945 (1935).

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The *cis–trans* Isomerization of $[Co(en)_2Cl_2]Cl$ in 2-Methoxyethanol

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In the course of some work with *cis*-$[Co(en)_2Cl_2]$Cl it was observed that a solution of the salt in 2-methoxyethanol changed in color from purple to green. A study of the absorption spectra of the solutions showed that the color change was due to the rearrangement of the purple *cis*-isomer to the green *trans*-isomer. The kinetics of the reaction could be studied very easily with a spectrophotometer at 530 mμ. The isomerization was found to be followed by a slower reaction between the *trans*-isomer and the solvent to give unknown products.

An attempt was made to follow the reaction polarimetrically, but due to the high optical density of the *cis*-isomer at the NaD wave length it was not possible to obtain sufficiently large rotations for a kinetic study.

Experimental.—The *cis*- and *trans*-$[Co(en)_2Cl_2]$Cl were prepared by the methods given by Bailar in "Inorganic Syntheses," Vol. II. They were washed with alcohol followed by ether, dried at 110°, and stored in a desiccator. The 2-methoxyethanol was Eastman Kodak Co. "Practical Grade." It was dried over anhydrous calcium sulfate and distilled into a dark glass stoppered bottle for storage.

Reagent grade KCl and $KClO_4$ were dried at 110° and used without further treatment. The 2-methoxyethanol solutions of these salts were prepared by shaking the solvent with the appropriate salt for about 10 hours at room temperature and then filtering off the excess solid. These solutions were analyzed by evaporating 5.00-ml. samples and weighing the residue of salt.

Solutions of the complex in the solvent were prepared by mulling the salt with a small amount of liquid. The slurry was then filtered through a sintered glass filter and the concentrated solution was diluted to a convenient concentration. The usual volume of solution used was from 30 to 50 ml. The concentration of the complex was determined colorimetrically at 530 mμ. The value of ϵ_{530} in the equation O.D.$_{530} = \epsilon_{530} \times$ concn. (molar) × path length (cm.) was found to be (83.0 ± 1.6) O.D. units/millimole/cm.[2] This was shown to be valid up to 0.01 *M* solutions.

Optical density was measured with a Beckman DU spectrophotometer. Samples were pipetted from a reaction flask in the constant temperature bath directly into a 1-cm. Corex cell and immediately measured. The time was recorded at the moment the sample was withdrawn from the reaction flask. The entire operation took less than two minutes.

The temperature in the constant temperature bath was found to vary less than ±0.1° about the set temperature.

Because of the subsequent reaction between the solvent and the *trans*-isomer the data could not be treated by the usual simple first order expression. Satisfactorily reproducible results were obtained by plotting the log O.D. against time and drawing a straight line through the initial points. It was found that usually the first four or five points, extending over almost all of the first half-life, were fitted quite well by a straight line, from the slope of which the rate constant was calculated.

Results.—The rate constant for the reaction at 50° is not dependent upon the initial concentration of the complex, the chloride concentration, or the ionic strength of the solutions. This is shown in Table I. The evidence would seem to support an SN1 mechanism for the isomerization.

TABLE I

Concn. (*M*) of *cis*-c. $\times 10^3$	Added salt	Ionic strength	$k \times 10^3$, min.$^{-1}$	Av.
2.92[a]	....	2.92	9.12	
3.52[a]	....	3.52	8.88	
5.12[a]	....	5.12	9.76	
5.71	....	5.71	9.63	$(9.00 \pm 0.73) \times 10^{-3}$ min.$^{-1}$
5.96[a]	....	5.96	9.76	
6.66[a]	....	6.66	7.96	
7.69[a]	....	7.69	9.36	
7.77[a]	....	7.77	7.96	
1.59	$KClO_4$	58.7	9.00	
2.13	$KClO_4$	59.2	9.24	
5.53	$KClO_4$	62.6	9.49	$(9.05 \pm 0.26) \times 10^{-3}$ min.$^{-1}$
6.69	$KClO_4$	63.8	8.89	
9.38	$KClO_4$	66.5	9.12	
11.9	$KClO_4$	69.0	8.77	
3.36	KCl	44.4	9.64	
5.23	KCl	46.2	8.45	$(8.95 \pm 0.62) \times 10^{-3}$ min.$^{-1}$
7.94	KCl	48.9	8.77	

[a] Duplicate runs.

The rate constant was determined at four different temperatures from 30 to 50°. The results are summarized in Table II.

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