

[CONTRIBUTION NO. 185 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Spectrophotometric Investigations of Some Complexes of Ruthenium. III. The Ruthenium-Dithiooxamide System¹

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The ruthenium(IV)-dithiooxamide system has been studied spectrophotometrically. It was found that both Ru(III) and Ru(IV) form the same blue-green complexes, $\text{Ru}[\text{SC}(\text{NH})\text{CSNH}_2]^{+2}$ and $\text{Ru}[\text{SC}(\text{NH})\text{CSNH}_2]_3$. The formation constants of these complexes were evaluated at unit ionic strength.

The reaction of ruthenium(III) and ruthenium(IV) with dithiooxamide in acetic acid to form a blue-green color has been developed into a colorimetric method for the analysis of ruthenium.³⁻⁹ Although the reaction has been used in a colorimetric procedure, none of the investigators has reported any study of the nature of the reaction to determine the formulas and stability constants of the complexes involved.

Preliminary investigation of the ruthenium-dithiooxamide reaction suggested that, as in the thiocyanate⁷ and thiourea⁸ reactions, the Ru(IV) was being reduced to Ru(III) at the expense of the complexing agent. Therefore the method of interpretation of spectrophotometric data was that presented in the previous papers.^{7,8}

Experimental

Absorption Measurements.—A Cary automatic recording spectrophotometer was used for all the optical density measurements. Matched silica cells of 5.00-cm. optical length were used. The results are expressed in terms of optical density, D , defined by the relationship, $D = \log_{10} (I_0/I)$ where I_0 and I are the incident and transmitted light intensities, respectively.

Materials.—The preparation and standardization of the $\text{Ru}(\text{ClO}_4)_4$ solution have been given in a previous paper.⁷ Dithiooxamide, Eastman Kodak Co. Organic Chemical 4394, was weighed out directly to provide solutions of the desired concentrations. Since it is only slightly soluble in cold water, the solvent used was a mixture of water, perchloric acid and acetic acid. The LiClO_4 and HClO_4 were from G. Frederick Smith Chemical Co., while the acetic acid was from Mallinckrodt Chemical Works. These were purified, recrystallized and standardized as necessary by standard procedures. Particular care was taken to avoid iron contamination.

Technique.—As reported previously,⁸ it was found that heating was necessary to attain equilibrium within a reasonable length of time. A minimum period of heating of 30 min. in a boiling water-bath was required to produce equilibrium. No decomposition of the complex was noted even when heating periods as long as two hours were investigated. In this study all solutions were heated exactly 45.0 min. in a boiling water-bath, and then cooled in ice until the temperature of the solution reached $25 \pm 1^\circ$. Immediately after preparation, each solution was scanned as quickly as possible on the spectrophotometer. It was determined on the Cary that the colored solution, after preparation, was stable for at least two days at room temperature.

In the determination of the formulas and stability constants, in all solutions, the ruthenium concentration was maintained constant at $2.793 \times 10^{-3} M$, the perchloric acid constant at 0.127 M , the acetic acid constant at 50%, and the ionic strength constant at 1.0. Solutions were prepared by mixing necessary quantities of a solution of ruthenium(IV) perchlorate and a freshly prepared solution of dithiooxamide to give the final desired concentrations. Equilibrium was attained by the previously described heating and cooling procedure. More than sixty solutions which contained ratios of dithiooxamide to ruthenium from 360 to 1 were so prepared and scanned.

Discussion

A typical constant wave length plot of the optical density as a function of the dithiooxamide to ruthenium ratio is given in Fig. 1. This shows clearly that the optical density of the solution does not change for ratios of dithiooxamide to ruthenium greater than 140 (the line labeled d_3 in Fig. 1).

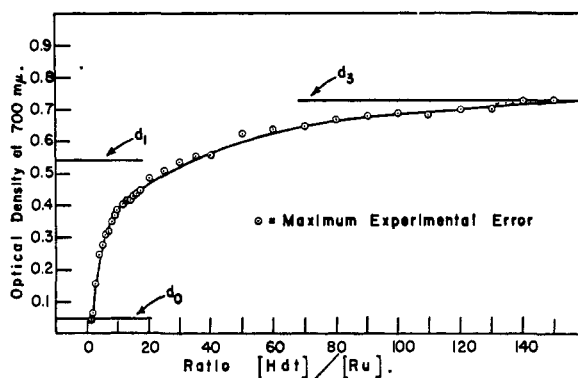


Fig. 1.—Optical densities at 700 $m\mu$ of various solutions with excess dithiooxamide present: $[\text{Ru}] = 2.793 \times 10^{-3} M$; $[\text{HClO}_4] = 0.127 M$; $[\text{HOAc}] = 50\%$; $\mu = 1.0$; cell length = 5.00 cm.; circles, experimental points; curve⁸ calculated on the basis of $\text{Ru}(\text{dt})_1^{+2}$ and $\text{Ru}(\text{dt})_3$.

Hence the adsorption spectrum of the last complex is known from experimental data. The absorption spectrum of this complex at various concentrations is given in Fig. 2, from which it may be seen that the complex obeys Beer's law.

The method used to interpret the data was that presented in previous papers.^{7,8} Noting the similarity in the plot of optical density against ratio between the dithiooxamide system, and that of the thiocyanate system,⁷ it seemed reasonable to assume that only one complex was formed. Calculations were made on this assumption, but under no circumstances could the data be fitted adequately. Therefore the assumption that only one complex was present appeared to be erroneous.

(1) Work performed in the Ames Laboratory of the Atomic Energy Commission.

(2) Taken from part of the Ph.D. thesis of Ruth Powers Yaffe, Iowa State College, 1951.

(3) H. Wöbbling, *Ber.*, **67B**, 773 (1934).

(4) H. Wöbbling and B. Steiger, *Mikrochemie*, **15**, 295 (1934).

(5) F. J. Welcher, "Organic Analytical Reagents," Volume 4, D. Van Nostrand Co., Inc., New York, N. Y., 1948.

(6) G. H. Ayres and F. Young, *Anal. Chem.*, **22**, 1281 (1950).

(7) R. P. Yaffe and A. F. Voigt, *This Journal*, **74**, 2500 (1952).

(8) R. P. Yaffe and A. F. Voigt, *ibid.*, **74**, 2608 (1952).

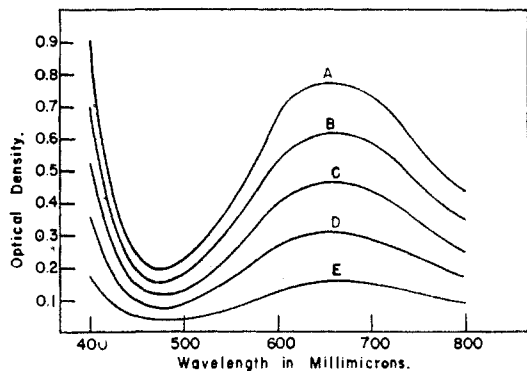
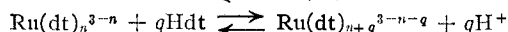
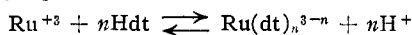


Fig. 2.—Absorption spectra of $\text{Ru}(\text{dt})_3$; $[\text{HClO}_4] = 0.127 M$; $[\text{HOAc}] = 50\%$; $\mu = 1.0$; cell length = 5.00 cm.; A, $[\text{Ru}] = 2.793 \times 10^{-5} M$; B, $[\text{Ru}] = 2.234 \times 10^{-5} M$; C, $[\text{Ru}] = 1.676 \times 10^{-5} M$; D, $[\text{Ru}] = 1.117 \times 10^{-5} M$; E, $[\text{Ru}] = 5.585 \times 10^{-6} M$.

Assuming that two complexes are present, the following equations may be written



where Hdt is used as an abbreviation for dithioöxamide. The non-thermodynamic equilibrium constants then become

$$K_n = \frac{[\text{Ru}(\text{dt})_n^{3-n}][\text{H}^+]^n}{[\text{Ru}^{+3}][\text{Hdt}]^n}$$

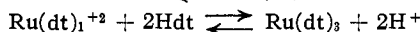
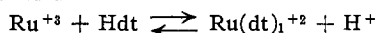
$$K_{n+q} = \frac{[\text{Ru}(\text{dt})_{n+q}^{3-n-q}][\text{H}^+]^q}{[\text{Ru}(\text{dt})_n^{3-n}][\text{Hdt}]^q}$$

By use of the method for two complexes already given,⁸ the following equation may be obtained

$$D = \frac{\frac{d_0[\text{H}^+]^n}{K_n[\text{Hdt}]^n} + d_1 + \frac{K_{n+q}[\text{Hdt}]^q d_3}{[\text{H}^+]^q}}{\frac{[\text{H}^+]^n}{K_n[\text{Hdt}]^n} + 1 + \frac{K_{n+q}[\text{Hdt}]^q}{[\text{H}^+]^q}}$$

where d_0 , d_1 and d_3 are the optical densities of the uncomplexed ruthenium, the first complex, $\text{Ru}(\text{dt})_n^{3-n}$, and the second complex $\text{Ru}(\text{dt})_{n+q}^{3-n-q}$, respectively. This equation was used in a series of successive approximations in the analysis of the system.

It was found that the data would fit only if n is taken as one, and q as two. Thus the equations should be written



The non-thermodynamic equilibrium constants are

$$K_1 = \frac{[\text{Ru}(\text{dt})_1^{+2}][\text{H}^+]}{[\text{Ru}^{+3}][\text{Hdt}]} \text{ and } K_3 = \frac{[\text{Ru}(\text{dt})_3][\text{H}^+]^2}{[\text{Ru}(\text{dt})_1^{+2}][\text{Hdt}]^2}$$

No evidence was found for a two-to-one complex, $\text{Ru}(\text{dt})_2^+$.

Four successive approximations were carried out for the evaluation of K_1 and K_3 . The results of these calculations are summarized in Table I.

TABLE I

SUMMARY OF SUCCESSIVE APPROXIMATIONS TO K_1 AND K_3

Approximation	K_1	K_3
1	1400 ± 400	12000 ± 600
2	990 ± 90	9300 ± 300
3	930 ± 30	8400 ± 300
4	930 ± 30	8300 ± 200

In each approximation, the calculations of both K_1 and K_3 were carried out at 12 different wavelengths at 10-m μ intervals from 640 to 750 m μ and the constants averaged to give the final values.

It should be pointed out that while the precision of the calculations in the dithioöxamide system is as good as in the thiocyanate⁷ and the thiourea⁸ systems, the accuracy is not. One reason for this is that the complexing agent is colored, making it necessary to correct all optical density measurements. Also, the complexes are fairly stable, so that a smaller excess of ligand is necessary to complex the ruthenium. The approximation that the equilibrium concentration of the dithioöxamide is essentially equal to the total analytical concentration then becomes somewhat inaccurate.

Using the final values found for the equilibrium constants K_1 and K_3 , the absorption spectra of the first complex, $\text{Ru}(\text{dt})_1^{+2}$, (Fig. 3) and of the uncomplexed ruthenium were calculated. Even though the solutions contained 50% acetic acid, the absorption spectrum of the uncomplexed ruthenium was essentially that of ruthenium(III) perchlorate and differed from ruthenium(IV) perchlorate sufficiently to justify the conclusion that the ruthenium is in the III state in the complex.

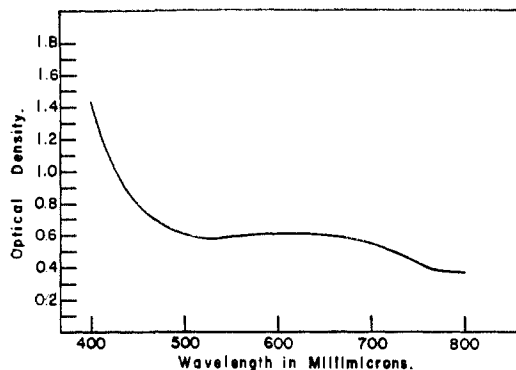


Fig. 3.—Calculated absorption spectrum of $\text{Ru}(\text{dt})_1^{+2}$; $[\text{Ru}] = 2.793 \times 10^{-5} M$; $[\text{HClO}_4] = 0.127 M$; $[\text{HOAc}] = 50\%$; $\mu = 1.0$; cell length = 5.00 cm.

Using the calculated equilibrium constants K_1 and K_3 and the calculated values of d_0 and d_1 , together with the experimental value of d_3 , the optical density curve as a function of dithioöxamide to ruthenium ratio was calculated at 700 m μ . This is the curve drawn through the experimental points in Fig. 1.

To test the acetic acid dependence of the system the procedure was repeated at an acetic acid concentration of 75% instead of 50%. It was found that the reactions themselves are independent of the concentration of acetic acid present, although changing the acetic acid concentration alters the solvation of the ruthenium.

It should be pointed out that all of the equations and equilibrium constants in the ruthenium-dithioöxamide system have been written as a function of the hydrogen ion concentration. To test this dependence, the procedure was repeated at 0.254 M perchloric acid, instead of 0.127 M . This work was not done in great detail since the nature of the reaction was now known. Only the first approxima-

tion was carried out in the calculations. This was compared to the first approximation calculation at the lower acidity. The results of these measurements and calculations are summarized in Table II.

TABLE II
COMPARISON OF FIRST APPROXIMATIONS TO K_1 AND K_3 IN
0.127 M AND 0.254 M HClO₄

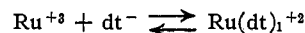
(a) Assuming hydrogen ion dependence		
[HClO ₄], M	$K_1 = \frac{[\text{Ru}(\text{dt})_1^{+2}][\text{H}^+]}{[\text{Ru}^{+3}][\text{Hdt}]}$	$K_3 = \frac{[\text{Ru}(\text{dt})_3][\text{H}^+]^2}{[\text{Ru}(\text{dt})_1^{+2}][\text{Hdt}]^2}$
0.127	1400 ± 400	12000 ± 600
0.254	1300 ± 60	11000 ± 3000
(b) Not assuming hydrogen ion dependence		
[HClO ₄], M	$K_1 = \frac{[\text{Ru}(\text{Hdt})_1^{+2}]}{[\text{Ru}^{+3}][\text{Hdt}]}$	$K_3 = \frac{[\text{Ru}(\text{Hdt})_3^{+2}]}{[\text{Ru}(\text{Hdt})_1^{+2}][\text{Hdt}]^2}$
0.127	11000 ± 3000	740000 ± 32000
0.254	5200 ± 200	180000 ± 40000

From Table II, it is seen that the assumption of hydrogen ion dependence gives agreement in both equilibrium constants at the two acidities, whereas the assumption of no dependence does not. Therefore it must be concluded that dithioöxamide is behaving as an acid, each molecule releasing a proton on formation of the ruthenium complex. This behavior was anticipated since dithioöxamide is known to be a weak monobasic acid.⁹

Although the formation constants for the reactions as they have been written are quite small, the

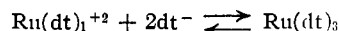
(9) R. P. Yaffe and A. F. Voigt, *THIS JOURNAL*, **74**, 2941 (1952).

ruthenium is held tightly in the complex. This may be illustrated by obtaining the formation constants for the reactions



$$K_1' = \frac{[\text{Ru}(\text{dt})_1^{+2}]}{[\text{Ru}^{+3}][\text{dt}^-]}$$

and



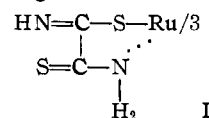
$$K_3' = \frac{[\text{Ru}(\text{dt})_3]}{[\text{Ru}(\text{dt})_1^{+2}][\text{dt}^-]^2}$$

Using the acidity constant of dithioöxamide evaluated at unit ionic strength,⁹ $k_a = (3.78 \pm 0.04) \times 10^{-11}$, K_1' and K_3' were calculated.

$$K_1' = \frac{K_1}{k_a} = \frac{(9.3 \pm 0.3) \times 10^3}{(3.8 \pm 0.1) \times 10^{-11}} = (2.4 \pm 0.1) \times 10^{13}$$

$$K_3' = \frac{K_3}{(k_a)^2} = \frac{(8.3 \pm 0.2) \times 10^3}{[(3.8 \pm 0.1) \times 10^{-11}]^2} = (5.8 \pm 0.2) \times 10^{24}$$

Dithioöxamide has been reported to form five-membered [C-C-N-S-Metal] chelate rings with both platinum and palladium.³⁻⁵ It seems quite likely that the ruthenium-dithioöxamide complexes involve chelate rings of the same type (I).



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(CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY)

The Solubility of Water in Liquid Phosphorus

BY G. L. ROTARIU, E. W. HAYCOCK AND J. H. HILDEBRAND

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Determinations of the solubility of water in liquid phosphorus gave 3.6 ± 0.3 mg./g. at 45° and 3.9 ± 0.5 at 25° . We select 6.7×10^{-3} ml. of H₂O/1 ml. P₄ at 25° for evaluation. Published figures for H₂O in CS₂ and CCl₄ give 1.95 and 1.59 ml. of H₂O/ml. of solvent, respectively. The solubility parameter of water calculated from these data gave 26.2 for H₂O in P₄, 26.1 in CS₂ and 24.7 in CCl₄. A previously published analysis of data for H₂O in paraffins gave values close to 24.5.

In several recent investigations involving white phosphorus¹ we have found it far more convenient to protect it from air by a layer of water than by operating in a vacuum, and we have had satisfying evidence that the properties under investigation were not appreciably affected by dissolved water. We decided, however, that it would be desirable to know the solubility of water in phosphorus, both for its bearing upon past and future experiments, and for its theoretical interest, in view of the extraordinarily high solubility parameter of phosphorus and the dipole moment of water.

The procedure adopted was, briefly, to equilibrate liquid phosphorus with water, freeze it rapidly, presumably entrapping dissolved water in the solid as minute droplets, as in the case of dissolved mercury; wash off all exterior water by repeated application of cold dry methyl alcohol; melt the phosphorus and shake under methyl alcohol to

extract the water, and determine its amount by the Fischer titration method.²

The essential details of the procedure were as follows. The phosphorus used in determinations 1-7 and 16-18 was purified by treatment with dilute acid dichromate, as previously described; that used in determinations 8-15 was distilled *in vacuo*. The methyl alcohol was Eimer and Amend C.P., anhydrous, handled so as to prevent access of water from the air. The Fischer reagent was prepared and standardized carefully by Mr. Tashinian, of our micro-laboratory, to whom we express our grateful appreciation.

Five ml. of purified phosphorus was pipetted under water into a previously tared flask with ground glass cap. This was shaken in a water-bath at a stated temperature. One hour was found amply sufficient for equilibrium. The flask was then quickly chilled to freeze the phosphorus, care being taken to keep it in one compact mass and not entrap droplets of the surrounding water. It was detached from the glass, and the flask cooled in ice-water, to reduce the amount of dissolved phosphorus, which can affect the reagent. The water in the flask was replaced by six washings with 50-ml. portions of precooled methyl alcohol. A seventh 50 ml. was allowed to remain in the flask. The sixth portion was

(1) R. E. Powell, T. S. Gilman, G. J. Rotariu, Eva Schramke and J. H. Hildebrand, *THIS JOURNAL*, **73**, 2525, 2527 (1951).

(2) Cf. J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 19.