[CONTRIBUTED FROM THE ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

A Spectrophotometric Investigation of the Niobium Pyrogallol Complex[1]

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The water-soluble niobium oxalato complex is capable of reacting with pyrogallol in an alkaline aqueous medium to produce a yellow colored complex. The constitution of this niobium pyrogallol complex present in solution was determined by means of spectrophotometric analysis. Using a combination of the method of continuous variations, a logarithmic analysis and a modification of the molar ratio method, it was possible to show that a definite complex formed wherein the niobium and pyrogallol combined in a one to one ratio. A formation constant has been calculated and the reaction mechanism postulated.

The oxalato and tartrato complexes are the most common examples of the very few water-soluble complexes formed by niobium and tantalum. However, the oxalato complex is further capable of reaction with certain polyhydroxyphenols to form not only water-soluble but also colored complexes, which was demonstrated by Platonov and his colleagues.[2]

Pyrogallol, which forms a yellow-colored complex with niobium in alkaline solutions and with tantalum in acid solutions, has been useful in several analytical schemes[3,4] for the qualitative and the quantitative estimation of these elements when they occur in small amounts in ores.

Because the literature does not give any information concerning the chemical constitution of the yellow-colored complex of niobium with pyrogallol, it was the purpose of this investigation to determine the nature of the complex by spectrophotometric analysis. Using a combination of the method of continuous variations, introduced by Job,[5] a logarithmic analysis similar to that used by Kingery and Hume[6] and a modification of the molar ratio method suggested by Yoe and Jones,[7] it was possible to show that a definite complex was indicated and to calculate a formation constant.

Experimental

Measurements.—Absorption measurements were made with a Beckman model DU spectrophotometer. A pair of matched 1 cm. silica cells, always orientated in the same way, was used for all measurements. A reference blank was used in all cases, and its preparation and composition were identical with the complex solution except that the niobium was missing. The absorption reading for the blank was subtracted from that of the niobium pyrogallol complex to give each value used in the calculations. The measurements were made at room temperature, which ranged from 23 to 26°. A Beckman model G *p*H meter, using a glass electrode, was employed for all *p*H measurements. All pyrosulfate fusions were carried out in Vycor crucibles.

Materials.—The standard pyrogallol solutions were freshly prepared for each spectrophotometric run by weighing out accurately the required quantities of ACS grade chemicals, dissolving them in freshly boiled, distilled water saturated with sodium sulfite and finally diluting to the proper volume with more saturated sodium sulfite solution. The sodium sulfite, however, was not adequate for the stabilization of the pyrogallol solutions when the concentration of the latter exceeded 0.001 molar, consequently they were maintained under a nitrogen atmosphere and exposed to the air only for the few seconds needed to fill a curvette.

The standard niobium oxalato complex solutions were prepared by fusing 0.2658 g. of Nb_2O_5 with 10 g. of $KHSO_4$ to a clear melt, then dissolving the cooled melt in 300 ml. of a saturated $(NH_4)_2C_2O_4$ solution and subsequently diluting to one liter with distilled water. The solution contained 2×10^{-6} mole of the niobium oxalato complex per ml. The Nb_2O_5 was obtained from the Fairmount Co. of Newark, N. J.

Results and Discussion

A number of solutions, made by mixing different volumes of 0.002 molar standard solution of niobium oxalato complex and 0.002 molar standard pyrogallol solution and adjusting the *p*H to 8.5, were prepared and their absorbancies were determined over a range 220 to 600 mμ. These solutions did not show any pronounced absorption peaks; however, a reasonable maximum was noted at 315 mμ. All the mixtures gave similar curves, so it was concluded that only one complex was formed between the niobium and the pyrogallol.

The absorbancy curves determined were almost identical with one reported by Dinnin (*cf.* Fig. 4 of his article)[8] except that his maximum appears to be closer to 325 mμ. When a family of absorption curves spaced at 5 mμ intervals over the wave length range 305–325 mμ were plotted to illustrate the method of continuous variations for the solutions whose concentrations are given in Table I, the observed steepness of the 315 mμ curve on both sides of the maximum suggested this to be the optimum wave length to employ for the other parts of this study; however, the 325 mμ wave length gives almost identical results and would be equally usable.

Because Elson[9] has reported that the niobium oxalato complex gives an absorption peak at 274 mμ and because the oxalate and the hydrogen oxalate ions tend to absorb strongly at wave lengths below 300 mμ, it was concluded that the absorption peak at 315 to 325 mμ was due to the niobium pyrogallol complex.

When x ml. of the 0.002 molar niobium oxalato complex solution and $(50 - x)$ ml. of the 0.002 molar pyrogallol solution were mixed and examined spectroscopically at a wave length of 315 mμ, the data given in Table I were obtained. The value of $\bar{D}$, the difference between the absorbancy for the solution containing the niobium pyrogallol com-

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[1] Based upon Kil S. Lee's M.S. thesis research. Presented at the Southeastern Regional Meeting of the American Chemical Society, November 3–5, 1955.

[2] M. S. Platonov, N. F. Krivoshlykov and A. A. Marakaev, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 1815 (1936).

[3] E. C. Hunt and R. A. Wells, *The Analyst*, **79**, 345 (1954).

[4] N. F. Krivoshlykov and M. S. Platonov, *J. Applied Chem.* (*U.S.S.R.*), **10**, 184 (1937).

[5] P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

[6] W. D. Kingery and D. N. Hume, THIS JOURNAL, **71**, 2393 (1949).

[7] J. H. Yoe and L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

[8] J. I. Dinnin, *Anal. Chem.*, **25**, 1803 (1953).

[9] R. E. Elson, THIS JOURNAL, **75**, 4193 (1953).

plex and a blank containing no niobium, was plotted against the ratio of the niobium concentration to the constant total concentration of niobium plus pyrogallol. It was noted that a maximum occurred at a value of 0.5 for the ratio, which corresponds to a niobium–pyrogallol molar ratio of 1:1 in the complex formed in the solution.

Table I

No. ml. 0.002 *M* niobium oxalate soln.	No. ml. 0.002 *M* pyrogallol soln.	Concn. of Nb/total concn.	$\bar{D}$
45	5	0.9	0.75
40	10	.8	1.15
35	15	.7	1.38
30	20	.6	1.51
25	25	.5	1.60
20	30	.4	1.48
15	35	.3	1.38
10	40	.2	1.22

Taking the data in Table I and making the assumption that the concentration of the niobium pyrogallol complex ion was equal to that of the limiting component, it was possible to prepare a plot of this limiting component concentration against $\bar{D}$, the absorbancy, from which two conclusions were apparent. First, the plot showed that absorbancy due to the niobium pyrogallol complex was linear with respect to concentration of the complex when the niobium was the limiting factor, *e.g.*, when the pyrogallol was present in excess. Secondly, when the pyrogallol was present in the limiting amount, the relationship between absorbancy and concentration of the complex showed that the absorbancy rose rapidly with increasing concentration of the complex and approached a straight line relationship as the concentration neared the limiting value of 0.001 mole per liter. These observations indicate that the niobium pyrogallol complex tends to dissociate and that dissociation decreases with increasing pyrogallol concentration, which is to be expected from mass law considerations.

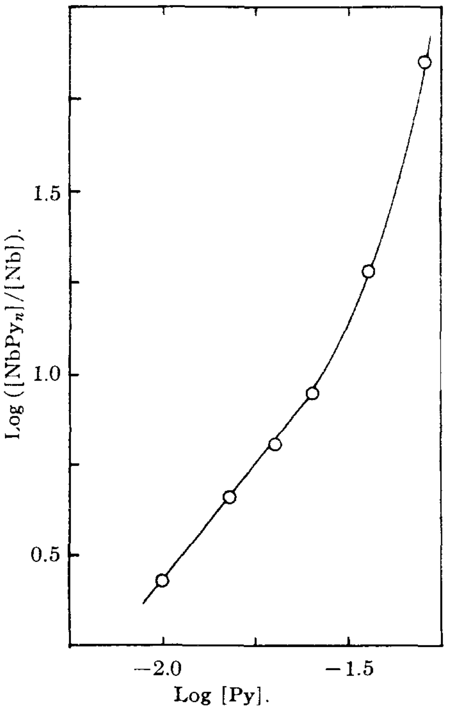

Fig. 1.—Variation of log ([NbPy$_n$]/[Nb]) with log [Py]; 0.0005 *M* niobium oxalato complex solution.

Since no evidence was found for the existence of a complex higher than the 1:1 ratio, the extinction coefficient of this complex could be determined by measurements in solutions where the pyrogallol concentration is much greater than the niobium. The absorbancies of a series of solutions 0.0005 molar with respect to niobium and containing increasing pyrogallol concentrations were determined. From these data a plot was made wherein it was observed that the absorbancy curve rose rapidly as the concentration of the pyrogallol increased, then changed to a more gradual slope, and finally leveled off to approach an asymptotic value of 1.4, which corresponds to the absorbancy of a 0.0005 *m* niobium pyrogallol complex solution. By use of this extrapolated value for the absorbancy, the extinction coefficient was calculated to be 2800 liter mole^{-1} cm.$^{-1}$. This provided the necessary value for determining the amount of niobium pyrogallol complex in all solutions.

If the symbols [Nb], [Py] and [NbPy$_n$] are allowed to represent the equilibrium concentrations in solution of the niobium oxalato complex, the pyrogallol and the niobium pyrogallol complex, respectively, and if the formation of the niobium pyrogallol complex is represented by the equation $\text{Nb} + n\text{Py} = \text{NbPy}_n$, then K, the formation constant is given by $K = [\text{NbPy}_n]/[\text{Nb}]\,[\text{Py}]^n$. The logarithmic form is $\log([\text{NbPy}_n]/[\text{Nb}]) = n \log [\text{Py}] + \log K$. (It is true that the oxalate ion must also be involved in this reaction, but with the high concentration of the oxalate ion used, its concentration is considered constant.) It is noted that a plot of log ([NbPy$_n$]/[Nb]) against log [Py] should give a straight line with slope of n and an intercept equal to the formation constant. This treatment was applied to the data found in these determinations and the results are shown in Fig. 1. This curve is a straight line only at the lower concentrations with a slope of 1.25 where K is 8.7×10^2.

The value of n determined here is slightly larger than that found by the method of continuous variations; however, it is believed that the disagreement is not too large since Bent and French[10] have shown that this treatment is strictly applicable only to solutions wherein the complex is highly dissociated.

Using a modification of the molar ratio method, solutions were prepared in which the niobium concentration was maintained constant while the concentration of the pyrogallol was increased and the absorbancy measured. Such data should give a plot where the absorbancy would rise from the origin as a straight line and break sharply to constant absorbancy at the molar ratio of the two components in the complex. Plotting the measured absorbancy against the ratio of the concentration of pyrogallol to that of niobium gave such a plot, how-

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(10) H. E. Bent and C. L. French, This Journal, **63**, 568 (1941).

ever, the curve produced did not break sharply, although extensions of the straight portions of the curve showed a break at the molar ratio of 1:1 for the niobium and pyrogallol. The absence of a sharp break here was further evidence that the niobium pyrogallol complex was partially dissociated.

The above observations, which seem to show that one pyrogallol molecule complexes with one niobium, do not give the nature of the complex formed. It is uncertain whether the pyrogallol simply adds itself to the niobium oxytrioxalato ion already present or whether it displaces one oxalate ion. If the addition compound is formed, the coördination number of niobium would be eight, which is possible according to Sidgwick.[11] Work in progress in this Laboratory, it is hoped, will give more information regarding the relative dissociation constants of the pyrogallol and oxalato complexes of niobium.

[11] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. I, Oxford University Press, London, 1950, pp. 840–841.

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Vibrational Spectra and Structure of Disiloxane and Disiloxane-d_6[1]

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Disiloxane and disiloxane-d_6 have been prepared by the hydrolysis of chlorosilane and chlorosilane-d_3. Infrared and Raman spectra have been obtained of the gaseous and liquid samples, respectively, down to about 250 cm.$^{-1}$. In the infrared, the fundamentals have been located at 2169, 1107, 957 cm.$^{-1}$ (parallel) and 2183, 957, 764 cm.$^{-1}$ (perpendicular) in $H_3SiOSiH_3$, and at 1575, 1094, 713 cm.$^{-1}$ (parallel) and 1575, 720, 593 cm.$^{-1}$ (perpendicular) in $D_3SiOSiD_3$. In the Raman effect fundamentals are located at 2174, 1009, 606 cm.$^{-1}$ (sharp) and 2174, 947, 716 cm.$^{-1}$ (diffuse) in $H_3SiOSiH_3$, and at 1575, 771, (555) cm.$^{-1}$ (sharp) and 1546, 699, 532 cm.$^{-1}$ (diffuse) in $D_3SiOSiD_3$. One perpendicular infrared-active fundamental, believed to lie well below 250 cm.$^{-1}$, was not observed. High-resolution spectra were obtained but insufficient rotational structure was found to permit interpretation. Vibrational analysis indicates that the point-group symmetry of the molecule is D_{3d}, that is, the Si–O–Si bond angle equals or approaches 180°. The results are equally compatible with a structure in which the silyl groups undergo free internal rotation about a linear Si–O–Si axis.

Introduction

Although considerable attention has been directed toward spectroscopic and other structural investigations of silicon compounds, it is rather surprising that disiloxane, the parent of silicones, has never been the object of such studies.[3] Spectra of substituted disiloxanes have been reported[4] and electron diffraction,[5] dipole moment,[6] and nuclear magnetic resonance[7] studies have appeared with some structural interpretation. No precise measurements of the Si–O–Si bond angle have been made on these compounds, but the fact has been established that the angles are much greater—probably between 130 and 160°—than those found when first period elements replace silicon. Furthermore, the wide angle is not general for the second period since, for example, the angle in Cl_2O is only $110.8 \pm 1°$.[8] The present investigation confirms the unexpectedly wide Si–O–Si bond angle in unsubstituted disiloxane.

Experimental

Preparation of Disiloxane and Disiloxane-d_6.—Although many attempts were made to reduce hexachlorodisiloxane to disiloxane using lithium aluminum hydride and other similar reducing agents, in no case could a reaction be found yielding the product sought. The Si–O–Si linkage was always cleaved giving SiH_4 as the only volatile product.[9] Disiloxane was prepared by the method of Stock[10] in which monochlorosilane is hydrolyzed. Silicon tetrachloride[11] was reduced to silane, SiH_4, with lithium aluminum hydride by the method described by Finholt, Bond, Wilzbach and Schlesinger.[12]

The silane was converted to monochlorosilane by heating for about 30 hours at 100° with hydrogen chloride in the presence of aluminum chloride. The monochlorosilane was separated from unreacted silane and hydrogen chloride by fractionation of these more volatile compounds through a trap immersed in allyl chloride slush. It was separated from dichlorosilane by repeated fractionation through a trap immersed in carbon disulfide slush. The monochlorosilane was hydrolyzed with twice the theoretical amount of water at 30°; the resulting disiloxane was then washed with about fifty times as much water at 0°. A total of 0.78 g. of disiloxane was prepared in this manner.

Disiloxane-d_6 was produced by similar reactions with some modifications. Silicon tetrachloride was reduced with lithium aluminum deuteride purchased from Metal Hydrides, Inc. The silane-d_4 formed was then chlorinated with deuterium chloride prepared by hydrolysis of benzoyl chloride with deuterium oxide. However, because long heating

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[1] Based on the Ph.D. thesis of Dean W. Robinson, submitted to the Graduate Department of Chemistry, Massachusetts Institute of Technology, May, 1955.

[2] Du Pont Instructor in Chemistry, 1954–1955.

[3] After the present work was completed, the authors learned of the investigation of Emeléus, MacDiarmid and Maddock (*J. Inorg. Nucl. Chem.*, **1**, 194 (1955)). Their structural conclusion that disiloxane is an asymmetric top based on infrared studies only is somewhat at variance with those drawn in this paper. We believe that the additional evidence of the infrared spectrum of disiloxane-d_6 and of the Raman spectra of both compounds enables firmer conclusions to be drawn.

[4] C. C. Certo, J. L. Lauer and H. C. Beachell, *J. Chem. Phys.*, **22**, 1 (1954); H. Murato and M. Kumada, *ibid.*, **21**, 945 (1953); L. Savidon, *Bull. soc. chim. France*, 411 (1953); I. Simon and H. O. Mahon, *J. Chem. Phys.*, **20**, 905 (1952); N. Wright and M. J. Hunter, THIS JOURNAL, **69**, 803 (1947).

[5] K. Yamasaki, A. Kotera, M. Yokoi and Y. Ueda, *J. Chem. Phys.*, **18**, 1414 (1950).

[6] R. S. Holland and C. P. Smyth, THIS JOURNAL, **77**, 268 (1955).

[7] E. G. Rochow and H. G. LeClair, *J. Inorg. Nucl. Chem.*, **1**, 92 (1955).

[8] J. D. Dunitz and K. Hedberg, THIS JOURNAL, **72**, 3108 (1950).

[9] W. C. Schumb and D. W. Robinson, *ibid.*, **77**, 5294 (1955).

[10] A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).

[11] Obtained from the City Chemical Company, Brooklyn, New York. The lithium aluminum hydride was kindly donated by Dr. M. D. Banus of Metal Hydrides, Inc., Beverly, Massachusetts.

[12] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).