[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Peroxy Complexes of Plutonium(IV)[1a]

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Plutonium in the +4 oxidation state in aqueous solution forms complexes with almost every anion. Among the most remarkable of these complexes are the two formed with peroxide, each of which contains two plutonium ions joined by a peroxide bridge. The nature of these complexes together with the experimental work leading to the establishment of their formulas is discussed in this paper.

General Chemistry of Solutions Containing Plutonium and Hydrogen Peroxide.—Cunningham and Werner[1c] were the first to report the appearance of a pink color in solutions of plutonium containing hydrogen peroxide. This evidence of complex formation has since been confirmed by many experimenters.

The interaction of hydrogen peroxide with plutonium in its various oxidation states in aqueous solution is exceedingly complicated. Plutonium(VI) is reduced to plutonium(V) by hydrogen peroxide at a measurable rate in 0.5 *M* hydrochloric acid. The reduction of plutonium(V) by hydrogen peroxide is relatively slow, but in solutions containing *ca.* 10^{-3} *M* plutonium(V), or greater, the plutonium is reduced to lower oxidation states through the simultaneous disproportionation of plutonium(V) to produce plutonium(VI) and plutonium(IV) or plutonium(III), and the reduction of plutonium(VI) by hydrogen peroxide to plutonium(V).

Plutonium(IV) is reduced to plutonium(III) by hydrogen peroxide at a measurable rate in dilute hydrochloric, perchloric and nitric acids. Under certain circumstances the reduction is not complete because of the simultaneously occurring oxidation of plutonium(III) to plutonium(IV) by hydrogen peroxide. When the rates of these two opposing reactions are equal, a steady state is set up in which the net reaction is the catalytic decomposition of hydrogen peroxide. In 0.5 *M* hydrochloric acid the steady state is shifted far toward plutonium(III) so that only a few per cent. of plutonium(IV) is present in the solution. Actually the steady state is not as simple as pictured above because the peroxy complexes of plutonium(IV) act to shift the steady state with changing hydrogen peroxide concentration. In sulfuric acid solutions the steady state is far toward plutonium(IV) because of the stabilizing action of sulfate on plutonium(IV) through complex formation. Thus, dilute hydrogen peroxide oxidizes plutonium(III) in sulfuric acid rapidly and nearly completely to plutonium(IV).[2]

At high concentrations of hydrogen peroxide plutonium(IV) is precipitated. This precipitate has been the subject of extensive investigation[3,4,5,6,7] and is known to contain, in addition to peroxide, anions such as Cl^-, NO_3^-, ClO_4^- and $SO_4^=$, depending on the anions present in solution.

The Peroxy Complexes of Plutonium(IV).—Addition of a small amount of hydrogen peroxide to a light brown solution of plutonium(IV) produces a deep brown color, the color changing within the time of stirring. On adding more hydrogen peroxide the solution turns red, again within the time of mixing. Spectrophotometric observations show the appearance of at least two new species, corresponding to the color changes. The oxidation number of plutonium in these species cannot be +3 since reduction of plutonium(IV) by hydrogen peroxide would have liberated easily observable amounts of oxygen. Experiments on the reduction of plutonium(VI) to plutonium(V), by hydrogen peroxide, demonstrated that neither of these oxidation states was involved in the observed complex formation. Thus it was established that the complexes were of the +4 oxidation state.

The experimental evidence presented below demonstrates that the brown complex, formed at low hydrogen peroxide concentrations, contains two plutonium(IV) ions joined by one peroxide ion; and that the red complex, formed at higher hydrogen peroxide concentrations, is composed of two plutonium(IV) ions and two peroxide ions. The number of hydroxide groups on these complex ions is also discussed.

Experimental Methods

Concentrations of plutonium species were determined spectrophotometrically using a Beckman Model DU spectrophotometer equipped with ten centimeter absorption cells, thermostated within ±0.5°. Because of the rather rapid reduction, by hydrogen peroxide, of plutonium(IV) to plutonium(III), it was necessary to obtain spec-

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[1a] This research was carried out under the auspices of the Manhattan District at the Chemistry Department of the University of California during the period August, 1944, to January, 1946.

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[1c] B. B. Cunningham and L. B. Werner, Manhattan District Report CN-419, B, Part 1, p. 15, January 15, 1943.

[2] J. R. Dam, J. C. Kroner, G. E. Moore, L. Spector and D. E. Koshland, Jr., Manhattan District Report, CLP-374, p. 14, January 9, 1945.

[3] H. H. Hopkins, Jr., Manhattan District Report, CN-1946, p. 21, August 1, 1944.

[4] H. H. Hopkins, Jr., Manhattan District Report, CN-2288, p. 17, November 1, 1944.

[5] J. R. Dam, J. C. Kroner, G. E. Moore, L. Spector and D. E. Koshland, Jr., Manhattan District Report, CLP-376, p. 10, January 13, 1945; Manhattan District Report, CLP-387, p. 16, February 15, 1945.

[6] K. A. Kraus, J. R. Dam, G. E. Moore, L. Spector and J. C. Kroner, Manhattan District Report, CLP-395, p. 5, March 15, 1945.

[7] J. W. Hamaker and C. W. Koch, Manhattan District Report, CN-3018, May 17, 1945.

trophotometric readings on the solution as soon as possible after mixing. To this end the peroxide was added last to the plutonium solution, which had been placed in a beaker; the mixture was quickly stirred and poured through a funnel into the absorption cell. By this technique it was possible to obtain the initial reading within one and one-half minutes after mixing. Rather than extrapolate to zero time, it was found simpler and more accurate to use readings near the start, and to correct for the amount of plutonium(III) formed. The values of the optical density *vs.* time were plotted and smooth curves drawn. In this way values for all wave lengths at the same time could be read from the curves and the additional advantage of an "averaging out" effect on errors in readings was gained.

The stock solution of plutonium(IV) was prepared by repeated hydroxide precipitation and solution in concentrated hydrochloric acid. The final solution in most cases was *ca.* 8 M in hydrochloric acid. An aliquot was diluted and analyzed spectrophotometrically for plutonium(VI), plutonium(IV) and plutonium(III). The total concentration of plutonium was determined by counting samples in an alpha counter.

Thirty per cent. hydrogen peroxide was the source of peroxide. Conductivity water was used in making up all solutions. Concentrations are expressed in moles per liter of solution at room temperature and the symbol M is used to indicate this quantity.

Spectrum of Brown Complex.—The first step in any spectrophotometric analysis is to obtain the molar extinction coefficients of the species under consideration. In the present case this was difficult because the stoichiometric composition of the complexes was originally unknown, and it is not possible to prepare a solution containing the plutonium entirely in the form of either the brown or the red complex. As the work progressed, it became apparent that in a solution containing *ca.* 4×10^{-3} M plutonium(IV), 0.5 M HCl, and a deficiency of hydrogen peroxide, essentially all of the plutonium is initially in the form of the brown complex and Pu^{+4}.[8] Knowing the amount of peroxide added and the stoichiometry of plutonium and peroxide in the brown complex, which by other work was found to be two plutonium ions to one peroxide, it was possible to calculate the concentration of Pu^{+4} and brown complex in this solution. From the absorption spectrum of this solution at the time of mixing, which was obtained by extrapolation of the measurements back to zero time, the molar extinction coefficients of the pure brown complex were obtained by correcting for the spectral contribution of Pu^{+4}. The absorption spectrum of the brown complex along with that of Pu^{+4} is shown in Fig. 1.

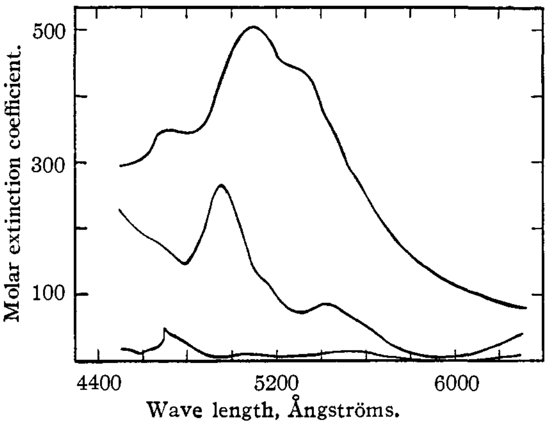

Fig. 1.—Absorption spectra of the brown peroxy complex (center plot), red peroxy complex (top plot), and plutonium(IV) (bottom plot), in 0.5 M HCl at 25°.

Spectrum of the Red Complex.—The determination of the spectrum of this species was less straightforward than that of the brown complex and the method employed is discussed in detail later. The spectrum is shown in Fig. 1. It should be pointed out that comparison on the basis of plutonium atoms would halve the extinction coefficients of the red and brown complexes relative to that of Pu^{+4}, as the complexes each contain two plutonium atoms.

Equilibrium between Pu^{+4} and the Brown Complex.—A series of experiments was run in which the total plutonium concentration did not vary greatly, but in which the hydrogen peroxide concentration was continuously increased. The results are given in Table I (also see Table VIII). Listed are the concentrations of the various plutonium species at the times chosen for analysis. The sixth column gives the free hydrogen peroxide concentration for each experiment, which was calculated by correcting the total hydrogen peroxide for the amount tied up in the brown and red complexes and for the amount of peroxide used in reducing plutonium(IV) to plutonium(III). In the seventh column are tabulated values of the equilibrium quotient defined by the equation where parentheses

$$K_1 = (\text{brown complex})/(Pu^{+4})^2(H_2O_2) \qquad (1)$$

are used to indicate the concentrations of the enclosed species in moles per liter of solution. It is

TABLE I

EQUILIBRIUM BETWEEN BROWN COMPLEX, Pu^{+4}, AND HYDROGEN PEROXIDE; TEMP., 25°; 0.5 M HCl

	Concentrations, moles/liter × 10^4						
		Complexes					
Expt.	Pu^{+4}	Brown	Red	Pu^{+3}	Free H_2O_2	$K_1 \times 10^{-7}$	$\Delta \log I_0/I$
1	0.95	0.85	0.013	0.30	1.31	7.3	+0.001
2	.83	.84	.017	.35	1.65	7.4	+ .001
3	.74	.66	.027	.59	1.89	6.5	− .001
4	.42	.73	.072	.75	6.63	6.4	− .001
5	.35	1.00	.111	.43	7.56	10.7	+ .004
					Weighted av.	7.0	

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[8] The symbol Pu^{+4} is used to designate the species of plutonium (IV) present in these solutions in the absence of hydrogen peroxide. It is believed that in 0.5 M HCl this species is about half Pu^{+4} and half $PuCl^{+3}$.

understood that the values of K_1 apply only to 0.5 M HCl as no attempt has been made here to take into account the dependence of this equilibrium on the hydrogen ion concentration.

The value of K_1 is fairly constant for the first four experiments but deviates appreciably in the fifth. In the last two experiments the concentration of Pu^{+4} is less than in the first three and consequently a given absolute error in the Pu^{+4} analysis produces a greater deviation in the value of K_1. The fact that the Pu^{+4} concentration enters to the second power in the equilibrium quotient makes the value of K_1 very sensitive to small errors in this concentration. In the last column of Table I is presented evidence that the values of K_1 for all of the experiments are within experimental error of the weighted average value of 7.0×10^7. This column gives the change in the experimentally observed value of log I_0/I at 4700 Å., which would be necessary to bring each experiment into agreement with the average value of K_1. The Beckman spectrophotometer is read only to the nearest thousandth of a log I_0/I unit and the reproducibility is somewhat less. It is believed therefore that the deviations listed in column eight all lie within the accuracy of the measurements.

The experimental data of Table I provide satisfactory evidence that the hydrogen peroxide dependence of the equilibrium is that given by equation (1). Other reasonable peroxide dependences were tested and found to be inconsistent with the data. The reader is cautioned that in making such calculations it is necessary to recalculate the extinction coefficients for the brown complex as these depend on the number of peroxides involved in the complex. The necessary data are given in the Appendix. Further, for such calculations the free hydrogen peroxide concentration must be changed in each experiment as determined by the number of peroxides assumed to be present in the brown complex.

The experiments of Table I give a fair check on the assumed dependence of the equilibrium on the Pu^{+4} concentration. Even though the concentration of Pu^{+4} did not vary greatly, the fact that it enters the equation to the second power makes the constant rather sensitive to its value.

An experiment was performed at about one-fifth the concentration of plutonium used in the experiments of Table I to furnish a better check on the inverse second power dependence of the equilibrium quotient on the Pu^{+4} concentration. In Table II the data for this experiment are compared with those of experiment 2 of Table I. The data have been calculated on the basis of two possible formulas for the brown complex: The first assuming the complex to contain one peroxide and two Pu^{+4} ions, the second assuming it to be composed to one peroxide and one Pu^{+4} ion. As mentioned previously it is necessary to recalculate completely the experimental data for each assumption as the extinction coefficients of the brown complex are dependent on the formula assumed. The values for the concentration of the red complex in Table II are very uncertain because of their small magnitude and because their calculation on the basis of various assumed brown complexes is not unambiguous. In any case this does not seriously affect the relative concentrations of the brown complex and Pu^{+4}.

TABLE II

DETERMINATION OF NUMBER OF PLUTONIUM ATOMS IN BROWN COMPLEX, 25°, 0.5 M HCl

		Concentrations, moles/l. × 10^5					
Expt.	Pu^{+4} per complex	Pu^{+4}	Complexes Brown	Complexes Red[a]	Pu^{+3}	Free H_2O_2	K_1 or K_1'
6	2	2.66	0.66	0.07	1.28	18.3	5.1×10^7
2	2	8.3	8.4	.17	3.5	16.5	7.4×10^7
6	1	3.52	0.73	.03	1.33	18.4	1.13×10^3
2	1	16.9	8.5	.1	3.8	16.4	3.1×10^3

[a] Approximate.

In the last column of Table II are given the calculated values of the equilibrium quotients corresponding to the assumed formulas for the brown complex. The values of K_1 in the upper half of Table II correspond to the equilibrium of equation (1). Comparison with the average value of $K_1 = 7.0 \times 10^{+7}$ in Table I makes it appear that the value of $K_1 = 5.1 \times 10^7$ for experiment 6 is not in good agreement; but because of the low plutonium concentration a change of only 0.002 in the experimental value of log I_0/I at 4700 Å. would bring the two values into agreement. Therefore it must be concluded that the value of K_1 of experiment 6 agrees with the values of Table I well within the experimental error.

In the bottom half of Table II it is assumed that the brown complex contains only one Pu^{+4} and one peroxide. The values of K_1' in the last column were calculated for the equation

$$K_1' = (\text{brown complex})/(Pu^{+4})(H_2O_2) \qquad (2)$$

The discrepancy in the values of K_1' lies well outside of the experimental error. It must be concluded that the complex consisting of one Pu^{+4} and one peroxide is not in agreement with the experimental results.

Similar calculations based on the experiments of Table II show that the brown complex cannot consist of one Pu^{+4} and two peroxides nor of one Pu^{+4} and half of a peroxide, the latter formula being highly unlikely in addition. Calculations on experiment 6 of Table II and experiment 4 of Table I show that the brown complex cannot consist of two peroxides and two Pu^{+4}'s. This probably eliminates all other reasonable possibilities for the formula of the brown complex.

Additional evidence as to the nature of the brown complex was furnished by e.m.f. measurements. A 5.0×10^{-3} M solution of plutonium

TABLE III

HYDROGEN ION DEPENDENCE OF THE EQUILIBRIUM BETWEEN Pu^{+4} AND THE BROWN PEROXY COMPLEX; TEMP. 25°

Expt.	Pu^{+4} moles/l. × 10^4	Brown complex, moles/l. × 10^4	Red complex, moles/l. × 10^4	Pu^{+3}, moles/l. × 10^4	Free H_2O_2, moles/l. × 10^4	HCl moles/l.	NaCl, moles/l.	K_1 × 10^{-7}	n
8	0.36	1.47	0.053	0.32	0.59	0.200	0.300	192	3.6
9	1.24	0.188	.005	.69	2.44	1.00	0	0.51	2.9
10	2.00	1.08	.07	.36	4.92	1.00	0	0.55	2.8
11	0.87	0.55	.011	.13	1.90	0.500	0.500	3.9	

in 0.5 M HCl was prepared in which the plutonium was roughly half in the +3 and half in the +4 oxidation state. The potential of this solution was measured against a 0.5 M HCl calomel electrode, using a gold electrode for the plutonium half cell. To this solution was added approximately 0.25 mole of hydrogen peroxide for each mole of plutonium(IV) and the potential redetermined. Under the conditions of the experiment essentially all of the hydrogen peroxide was tied up in the form of the brown complex. For any assumed formula it was possible to calculate the amount of brown complex formed and the resulting decrease in the Pu^{+4} concentration. This in turn permitted the calculation of the change in the potential that theoretically should have occurred on the addition of the hydrogen peroxide. The experimental change in the potential was a decrease of 0.024 volt. If the brown peroxy complex is assumed to contain one peroxide per two plutoniums the calculated change is 0.021 volt, which is within experimental error of the observed potential change. The chief source of uncertainty was in the initial concentration of plutonium(IV) which was not known very accurately. Assuming the brown peroxy complex contains one peroxide per plutonium, the calculated potential change is 0.008 volt which is definitely not in agreement with the observed value. Thus this experiment furnishes additional evidence for the 1:2 ratio of peroxide to plutonium in the brown complex.

The above described experiment was continued by adding additional portions of hydrogen peroxide and measuring the potential after each addition. In the region where there was approximately one-half peroxide per plutonium(IV), the measured potentials deviated somewhat from the values calculated from the average K_1 and K_2 of Tables I and IV. (It was necessary to use K_2 of Table IV to correct for the amount of red complex present.) However, the calculated values were very sensitive in this region to errors in the initial concentration of plutonium(IV), because they depended on the small difference between the peroxide concentration and twice the plutonium(IV) concentration. It is believed that the deviations were all within experimental error.

At higher peroxide concentrations the results were no longer highly sensitive to errors in the initial concentrations and the measurement of the potential provided a good check on the value of K_1. The experimental results agreed well with the calculated potentials. Thus when 1.7 moles of hydrogen peroxide had been added per mole of plutonium(IV), the observed potential was 0.580 volt while the calculated potential was 0.579 volt. Under these conditions the calculated concentrations were: 6.9×10^{-5} M Pu^{+4}, 7.7×10^{-4} M brown complex, 2.27×10^{-3} M H_2O_2, 2.42×10^{-4} M red complex. In all of the calculations it was necessary to make a small but appreciable correction for the reduction of plutonium(IV) to plutonium(III), by hydrogen peroxide, which was continuously occurring during the experiment.

In the use of spectrophotometric measurements for the determination of complex ions there is always the possibility that some species is being overlooked because its absorption spectrum does not differ sufficiently from that of some other species to make it readily detectable. It is therefore advisable to check equilibrium constants, etc., measured spectrophotometrically by some thermodynamic method. The above potential measurements constitute such a check and the excellent agreement of the results of the two methods provides a very gratifying confirmation of the proposed formula of the brown complex and of the equilibrum constant for its formation.

Hydroxide Groups in the Brown Complex.—By a study of the hydrogen ion dependence of the equilibrium between Pu^{+4}, the brown complex and hydrogen peroxide, it is possible to determine the number of hydroxide groups present in the brown complex. Two sets of experiments were performed and the results are given in Table III.

In the first set the value of the equilibrium quotient, K_1, of experiment 8 of Table III was compared with the average value of K_1 from Table I. These two values are for solutions of the same ionic strength but with 0.2 M HCl in experiment 8 rather than 0.5 M HCl. The ionic strength was maintained constant in an attempt to avoid activity coefficient changes. The value of n of Table III is the power to which the hydrogen ion concentration must appear in the expression for the equilibrium constant. Since two hydrogen ions are liberated by the peroxide with the formation of the brown complex, the value of $n = 3.6$ indicates that there are 1.6 hydroxide groups also present in the complex. (The assumption has been made that plutonium (IV) is unhydrolyzed in these solutions; if there is actually some hydrolysis the number of hydroxide groups on the brown complex would be greater.)

The experimental uncertainty in the above determination is quite large owing to the fact that the concentration of Pu^{+4} in experiment 8 was very small and because approximately 75% of the hydrogen peroxide was used up in forming the peroxy complexes. The last fact means that small errors in the concentrations of the peroxy complexes introduce rather large errors in the free hydrogen peroxide concentration. Considering all of these factors it is not impossible that the value of n determined from experiment 8 could be as low as 3.0 or as high as 4.0.

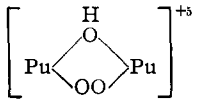
In an attempt to decrease the uncertainty in the above results a second set of experiments was carried out at higher acidity—experiments 9, 10 and 11 of Table III. The ionic strength was maintained at 1.00 M and the hydrogen ion concentration was varied by a factor of 2. From these experiments values of n of 2.9 and 2.8 were obtained, which in turn gave 0.9 and 0.8 hydroxide groups in each brown complex ion. The experimental error should be less than in the first set but could easily be ±0.3 unit in n. In this set of experiments there was an additional uncertainty introduced by the fact that the extinction coefficients for all species at 1.0 M Cl^- were assumed to be the same as for 0.5 M Cl^- which assumption may have given rise to appreciable error.

It should be pointed out that the results of the two sets of experiments should not necessarily be the same as they apply to different acidities. Thus if appreciable amounts of two species were present, one of which contained one hydroxide group and the other two hydroxide groups, the value of n would appear to be greater at low acidity. This variation in n would be small, however, compared to the change shown in Table III.

In conclusion it may be stated that there is approximately one hydroxide group associated with each brown complex ion in 0.5 M HCl. Assuming exactly one hydroxide group the formula for the brown complex becomes

$$[Pu—OO—Pu—OH]^{+5}$$

or



There is no direct way of deciding from the experimental data which of these formulas is correct. It is found that the double bridge model can be constructed using approximately the same angles for the Pu–OO–Pu group that have been proposed for HOOH.[9]

Equilibrium between Brown Complex, Red Complex and Hydrogen Peroxide.—As the concentration of hydrogen peroxide is increased in a plutonium(IV) solution the color of the brown peroxy complex finally is replaced by a red color, indicating the formation of a new species. Qualitatively this red peroxy complex must contain more peroxides per plutonium than does the brown complex in order that it be more stable at higher hydrogen peroxide concentrations. The composition of the red complex was determined in experiments described below.

The number of plutonium(IV) ions involved in each red complex ion was first investigated. Two experiments were run in which the total plutonium concentration was four times greater in one than in the other, while all other conditions remained nearly the same. The hydrogen peroxide concentration was chosen such that there were easily measurable amounts of both the brown complex and the red complex. Experimentally it was found that the ratio of the concentration of red complex to brown complex remained the same in spite of the four-fold change in plutonium concentration. The data are given in Table IV experiments 14 and 15. The lack of dependence of the equilibrium on the total plutonium concentration proves unequivocally that the number of plutonium(IV) ions present in each complex is the same. Therefore each red complex ion must contain two plutonium ions.

The determination of the number of peroxide groups in each red complex ion was carried out by a study of the effect of the hydrogen peroxide concentration on the equilibrium between the red and brown complexes. Because of the precipitation of the green plutonium(IV) peroxide at high hydrogen peroxide concentrations, it was not possible to obtain pure solutions of the red peroxy complex and thus measure the extinction coefficients of the red complex directly. However, the results of two experiments at differing hydrogen peroxide concentrations could be used to solve simultaneously for the extinction coefficients of the red complex and the value of the equilibrium quotient for the formation of the red complex from the brown complex. Different answers would be obtained depending on the number of peroxides assumed to be taking part in this equilibrium. Actually the data from a series of experiments were plotted and the best curve with the two arbitrary parameters corresponding to the equilibrium quotient and a factor for calculating the extinction coefficients of the red complex was fitted to the experimental points.

The following method was used. The molar extinction coefficients from one of the experiments at high hydrogen peroxide concentration were arbitrarily assumed to be those for a species we shall call C_1. These extinction coefficients, which actually correspond to those of a mixture of the red and brown complexes, were then used to calculate concentrations of the brown complex and the C_1 complex for all of the remaining experiments. The concentration of brown complex in this case

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[9] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934).

TABLE IV

EQUILIBRIUM BETWEEN THE BROWN PEROXY COMPLEX AND THE RED PEROXY COMPLEX, TEMP. 25°, 0.50 *M* HCl

Expt.	Pu^{+4} [a] moles/l. × 10^4	Brown complex, moles/l. × 10^4	Red complex, moles/l. × 10^4	Pu^{+3} moles/l. × 10^4	Free H_2O_2, moles/l. × 10^4	K_2	Δ log I_0/I
4	0.42	0.73	0.071	0.75	6.63	147	−0.001
5	.35	1.00	0.111	0.43	7.56	147	− .001
12	(− .74)	7.5	1.36	3.9	11.3	160	− .012
13	.08	0.75	0.257	0.57	24.1	142	.002
14	.08	0.816	0.328	0.49	27.0	149	− .003
15	.244	3.48	1.44	1.24	29.2	142	.002
16	.002	0.362	0.391	0.33	76.4	142	.001
17	(− .068)	.310	.428	1.16	83.3	166	− .007
18	(− .044)	.488	.692	0.63	92.0	154	− .005
19	(− .070)	.169	.602	1.67	257.8	138	.001
20	(− .035)	.256	.930	0.70	279.5	130	.004
21	(− .036)	.231	.108	0.283	315.5	148	− .001
22		.090	.71	*ca.* 0.85	953	83	.007

[a] The negative values for the +4 concentration indicate that a slightly erroneous value has been used for the extinction coefficient of one of the peroxy complexes at 4700 Å. They further demonstrate that the calculated concentration of Pu^{+4} is very inaccurate in these experiments at high hydrogen peroxide concentration.

is not the true concentration as part of its concentration is included in that of the C_1 complex. We shall designate this apparent concentration of brown complex by C_2. Then

$$\text{(red complex)} = x(C_1)$$
$$\text{(brown complex)} = (C_2) + (1 - x)(C_1)$$

where x represents the fraction of C_1 that is actually red complex. Assuming one hydrogen peroxide to be involved in the equilibrum we may write

$$K_2 = \text{(red complex)}/\text{(brown complex)}(H_2O_2)$$

To obtain a form which, for convenience in plotting, gives straight lines in the limit, we write

$$\frac{C_1 + C_2}{C_1} = x\,\frac{\text{(brown complex)} + \text{(red complex)}}{\text{(red complex)}}$$
$$= x\left[\frac{1}{K_2(H_2O_2)} + 1\right]$$
$$\log\frac{(C_1 + C_2)(H_2O_2)}{C_1} = \log x\left[\frac{1}{K_2} + (H_2O_2)\right] \quad (3)$$

Then log $(C_1 + C_2)$ $(H_2O_2)/C_1$ was plotted as ordinate against log (H_2O_2) as abcissa. At very low hydrogen peroxide concentrations the ordinate should approach a constant value equal to log x/K_2, according to equation (3). At very high hydrogen peroxide concentrations the ordinate should be come proportional to log $x(H_2O_2)$ and again approach a straight line. The ordinate of this straight line at log (H_2O_2) = 0 should be equal to x.

The data for the series of experiments are given in Table IV (see also Table VIII) and have been plotted in Fig. 2. In the last column of Table IV is given the change in log I_0/I at 5300 Å. (one of the points used for analysis) necessary to make each equilibrium quotient equal to 145. These changes in some of the experiments seem rather large but apparently are to be attributed to experimental error as nearly duplicate experiments in some cases show the largest changes. Experiment 12, which requires the largest change of log I_0/I to bring it into agreement, was one of the first performed and the deviation is probably attributable to the larger experimental inaccuracy at that time. It should be pointed out that the right side of Fig. 2 is much less sensitive to a given per cent. error in K_2 than the left side. This is shown by experiment 22 which has much too low a value of K_2 but falls fairly close to the curve. This experiment should perhaps not be included as precipitation of the plutonium(IV) peroxide was observed twenty minutes after mixing; however, no precipitation or Tyndall effect could be detected at the time taken for analysis.

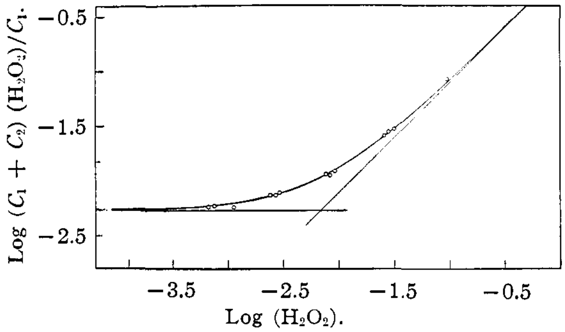


Fig. 2.—Equilibrium between brown peroxy complex, red peroxy complex and hydrogen peroxide in 0.5 *M* HCl at 25°.

It was found that the data could be fitted only by assuming a first power hydrogen peroxide dependence for the equilibrium. The solid curve in Fig. 2 corresponds to the best fit for this case; the values of x and K_2 are 0.786 and 145, respectively. From the first power hydrogen peroxide dependence of the equilibrium it must be concluded that the red complex contains one additional peroxide group over that in the brown complex and therefore each ion contains two peroxides and two plutonium(IV) ions.

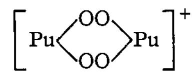
TABLE V

HYDROGEN ION DEPENDENCE OF EQUILIBRIUM BETWEEN BROWN AND RED COMPLEXES, TEMP. 25°

Expt.	Pu^{+4} mole/l. × 10^4	Brown complex mole/l. × 10^4	Red complex mole/l. × 10^4	Pu^{+3} mole/l. × 10^4	Free H_2O_2 moles/l. × 10^4	HCl, mole/l.	NaCl mole/l.	K_2	n
23	0.005	0.58	0.48	0.08	23.7	0.20	0.30	349	0.96
24	(− .03)	.445	.378	.06	23.6	.20	.30	360	.99

Hydroxide Groups in the Red Complex.—The hydrogen ion dependence of the equilibrium quotient relating the brown and red complexes was used to determine the number of hydroxide groups in the red complex. The experimental results are given in Table V. The values of K_2 obtained in these two experiments at 0.20 M H^+ and an ionic strength of 0.5 were compared with the average value of $K_2 = 145$ of Table IV in order to calculate the hydrogen dependence, n, of K_2. The experimental uncertainty here was much less than in the corresponding experiments on the brown complex as very appreciable amounts of both the brown and red complex were present and the free hydrogen peroxide concentration was known accurately. It is seen that the value of n is very close to unity.

The determination of the number of hydroxide groups on the red complex depends on the similar determination for the brown complex which has been previously discussed. The uncertainty in the latter value must therefore apply here also, and it is only possible to say that the red complex contains roughly zero hydroxide groups if the second peroxide has lost both hydrogen ions or one hydroxide group if the second peroxide is present as OOH^-. We may then write two possible structural formulas



$$[HO\text{–}Pu\text{–}OO\text{–}Pu\text{–}OOH]^{+4}$$

It does not seem possible to distinguish at present between these two alternative structures. By means of models it was shown that the double bridge arrangement is sterically possible, even assuming about the same bond angles for the Pu–OO–Pu group as those proposed for hydrogen peroxide.[9]

Discussion

In the interpretation of the foregoing results it has been tacitly assumed that the peroxy complexes of plutonium(IV) do not contain chloride ion. The basis for this assumption is the following. Chloride ion complexes plutonium (IV) only weakly in the absence of hydrogen peroxide. The value of the equilibrium quotient expressed in terms of concentrations, for the reaction

$$Pu^{+4} + Cl^- = PuCl^{+3} \qquad (4)$$

is about 2 in 1 M HCl at 25°.[10] When negatively charged peroxide ions are bound to the Pu^{+4}'s it is believed that the tendency of a chloride ion to attach itself to a Pu^{+4} would be significantly diminished.

Additional evidence against chloride complexing is obtained from experiment 11 of Table III. In this experiment the chloride concentration was raised to 1 M by the addition of sodium chloride to give a solution 0.5 M in HCl and 0.5 M in sodium chloride. Because of the change of ionic strength and consequent variation of activity coefficients, it is difficult to compare this experiment with those employing only 0.5 M HCl, but it appears, if anything, that the brown peroxy complex becomes less stable as the chloride concentration is increased. This change is in the opposite direction from that to be expected if the brown peroxy complex contains chloride ion.

From the experimental results, and assuming one hydroxide ion in the brown complex, we can write the following equations and equilibrium quotients

$$2Pu^{+4} + H_2O_2 + H_2O = Pu(OO)(OH)Pu^{+5} + 3H^+$$

$$K_b = \frac{(Pu(OO)(OH)Pu^{+5})(H^+)^3}{(Pu^{+4})^2(H_2O_2)} = 8.8 \times 10^6 \qquad (5)$$

$$2Pu^{+4} + 2H_2O_2 = Pu(OO)_2Pu^{+4} + 4H^+$$

$$K_r = \frac{(Pu(OO)_2Pu^{+4})(H^+)^4}{(Pu^{+4})^2(H_2O_2)^2} = 6.3 \times 10^8 \qquad (6)$$

Parentheses indicate concentrations in moles per liter of solution. In equations (5) and (6), as elsewhere in this paper, the term (Pu^{+4}) represents the sum of the concentrations of the +4 plutonium ion, Pu^{+4}, and its chloride complex, $PuCl^{+3}$. The extent of chloride complexing is not known for an ionic strength of 0.5 but probably about half of the plutonium(IV) is in the complexed form. It should be emphasized that the values of these equilibrium quotients apply only to 0.5 M hydrochloric acid solution. Activity coefficient changes would alter the values for other solutions.

The most striking fact about the peroxy complexes of plutonium(IV) is the great stability of the species containing two plutonium atoms relative to those containing but one plutonium atom. No evidence was obtained of complexes containing only one plutonium atom even though most of the experiments were carried out at very low plutonium concentrations, which would favor the formation of this type of complex. It is of interest to consider the reason for the great stability of the complexes containing two plutonium atoms relative to those containing one. The most obvious difference in the two types of complex is the possibility in the former of forming

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(10) W. H. Reas, unpublished work.

a double bridge between the plutoniums, *i.e.*, a ring structure. As has already been pointed out, such structures appear to be sterically possible for both the brown and the red complex.

Peroxy complex formation is also shown by other +4 ions, *i.e.*, Ti(IV), Zr(IV), Hf(IV) and probably Th(IV). These complexes have not been investigated with sufficient thoroughness to establish their formulas. It seems likely that some or all of them will be found to consist of two +4 ions connected by peroxide ion(s), similar to the peroxy complexes of plutonium (IV).

Appendix

Calculations of Concentrations of Plutonium Species from Spectrophotometric Data.—The results of the foregoing work depend almost entirely on spectrophotometric analyses and it therefore seems appropriate to present in some detail the methods used and values of the extinction coefficients obtained.

In Table VI are given the molar extinction coefficients for the various plutonium species at the wave lengths selected for analysis.

TABLE VI

MOLAR EXTINCTION COEFFICIENTS OF PLUTONIUM SPECIES AT WAVE LENGTHS USED FOR ANALYSIS

Wave length, Å.	Molar extinction coefficients Pu^{+3}	Pu^{+4}	Brown complex	Red complex
4700	2.47	49.7	172.6	350
4955	0.22	5.6	266	425
5300	2.19	6.0	74.0	441
6000	34.6	0.91	8.72	115.7

These data were used to calculate the amounts of Pu^{+3}, Pu^{+4}, brown complex and red complex present in solutions containing hydrogen peroxide and plutonium in the +3 and +4 oxidation states. The 4700 Å. point was used to calculate the amount of Pu^{+4}; the 4955 Å. point, the brown complex; the 5300 Å. point, the red complex; and the 6000 Å. point was used to calculate the amount of Pu^{+3}. The general procedure was as follows: The amounts of Pu^{+3} and Pu^{+4} were estimated and the observed molar extinction coefficients at 4955 and 5300 Å. were corrected for these species. These values were then used in two simultaneous equations involving the brown and red complex molar extinction coefficients at 4955 and 5300 Å. and fractions of red and brown complex present. The equations were solved for the fractions of the two species. Next the observed molar extinction coefficients at 4955 and 4700 Å. were corrected for the presence of the red complex and Pu^{+3}, and the brown complex and the Pu^{+4} were solved for simultaneously. Finally the observed molar extinction coefficient at 6000 Å. was corrected for the amounts of Pu^{+4}, brown complex and red complex and the amount of Pu^{+3} was calculated. If the initial assumption of the amounts of Pu^{+3} and Pu^{+4} differed significantly from those calculated, the calculation was repeated using the more nearly correct values for the amounts of Pu^{+3} and Pu^{+4}.

The extinction coefficients of the brown complex were determined in the following manner. To a solution containing 3.59×10^{-3} *M* Pu^{+4}, 0.55×10^{-4} *M* Pu^{+3} and 0.5 *M* HCl was added a small volume of hydrogen peroxide to give a concentration of 1.38×10^{-3} *M*. From other work it was known that essentially all of the peroxide is used in forming the brown complex under these conditions. Thus, on mixing, the solution contained 1.38×10^{-3} *M* brown complex, 0.83×10^{-3} *M* Pu^{+4}, 0.55×10^{-4} *M* Pu^{+3} and 0.5 *M* HCl. The spectrum was measured as a function of time and the extinction coefficients extrapolated back to zero time. These values, which are given in Table VII, were corrected for the absorption of Pu^{+3} and Pu^{+4} to give the molar extinction coefficients for the brown complex. The values obtained may be in error in an absolute sense by as much as 7% but the relative accuracy certainly is greater.

The method of determining the molar extinction coefficients of the red complex has already been treated. Here again the relative accuracy of the extinction coefficients is appreciably greater than the absolute accuracy.

TABLE VII

EXPERIMENTALLY MEASURED MOLAR EXTINCTION COEFFICIENTS

Expt.	ΣPu moles/l. $\times 10^4$	ΣH_2O_2 moles/l. $\times 10^4$	Extinction coefficients, Å. 4700	4955	5300	6000
1	3.14	2.34	63.3	75.3	23.8	6.4
2	2.79	2.69	68.9	84.0	26.9	7.9
3	2.59	2.90	62.3	74.0	25.6	11.5
4	2.86	7.87	60.3	78.8	31.1	14.3
5	2.97	9.00	77.5	106.1	42.2	12.3
6	0.548	1.98	49.6	40.1	17.3	10.9
7	50	6.83	E. m. f. experiment, first addition of H_2O_2			
8	3.76	2.32	76.9	110.0	35.0	7.7
9	2.29	2.98	41.8	25.1	10.1	12.4
10	4.67	6.37	63.8	66.9	22.5	5.8
11	2.10	2.55	67.9	74.8	24.0	5.2
12	23.1	23.5	77.2	114.5	51.6	15.0
13	2.81	25.7	80.0	110.0	60.5	19.9
14	2.99	28.7	87.0	119.0	68.5	20.7
15	12.22	36.2	90.3	127.0	73.2	19.5
16	1.911	77.7	105.0	137.0	104.0	32.0
17	2.50	85.0	81.2	105.6	85.2	36.8
18	2.94	94.2	110.6	144.0	115.8	35.8
19	3.05	260.0	78.7	98.5	91.6	42.0
20	2.95	282.0	131	164.5	152	45.2
21	2.98	318.0	139.8	176.1	165.0	45.6
22	2.47	955	...	132.2	129.5	...
23	2.38	25.4	112.4	149.8	106.1	26.3
24	1.81	25.5	114.6	154.0	109.7	27.2
[a]	36.4	13.8	76.6	102.0	29.4	4.03

[a] Experiment to determine extinction coefficients of brown complex.

In each experiment the composition of the solution was calculated from the extinction coefficients five to ten minutes after the start of the experiment. The results of the calculations, *i. e.*, the concentrations of the various species, have been given in the body of this paper. In Table VII are given the original data presented in the form of stoichiometric molar extinction coefficient of plutonium which is defined here as the observed log I_0/I divided by the product of the cell length in centimeters and the stoichiometric molar concentration of plutonium. (Here one mole of the red or brown dimer is to be calculated as two moles of plutonium.) The calculated percentages of the four species in general added up to nearly 100% of the α counting analysis with deviations in only a few cases of more than 5% from this value. This degree of agreement is of the expected order of magnitude. In the calculations the spectrophotometric values were used while the total plutonium concentrations given in Table VII are based on the α analysis.

Summary

Two peroxy complexes of plutonium(IV) have been identified in aqueous solution. The equilibria of these ions with hydrogen peroxide and Pu^{+4} were measured spectrophotometrically as a function of the $\mathrm{H_2O_2}$, plutonium and H^+ concentrations and formulas of the ions were deduced from these data.

The first complex, which is brown in color, contains two plutonium ions, one peroxide ion and probably one hydroxide group. The second complex, which is red, is made up of two plutonium ions and two peroxide ions. Alternatively the red complex may be a hydrate of this species consisting of two plutonium ions, one peroxide ion, one perhydroxide ion and an hydroxide ion.

The equilibrium quotients of the reactions in 0.5 M HCl were measured

$$2\mathrm{Pu}^{+4} + \mathrm{H_2O_2} + \mathrm{H_2O} = \mathrm{Pu(OO)(OH)Pu}^{+5} + 3\mathrm{H}^+$$

$$K_\mathrm{b} = \frac{(\mathrm{Pu(OO)(OH)Pu}^{+5})(\mathrm{H}^+)^3}{(\mathrm{Pu}^{+4})^2(\mathrm{H_2O_2})} = 8.8 \times 10^6$$

$$2\mathrm{Pu}^{+4} + 2\mathrm{H_2O_2} = \mathrm{Pu(OO)_2Pu}^{+4} + 4\mathrm{H}^+$$

$$K_\mathrm{r} = \frac{(\mathrm{Pu(OO)_2Pu}^{+4})(\mathrm{H}^+)^4}{(\mathrm{Pu}^{+4})^2(\mathrm{H_2O_2})^2} = 6.3 \times 10^6$$

Possible structural formulas for the complexes are presented. Attention is called to the remarkable fact that both complexes contain two plutonium ions and that no evidence was obtained for peroxy complexes involving only one plutonium ion.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

Activation of the Fluorescence of Chlorophyll Solutions*

BY ROBERT LIVINGSTON, W. F. WATSON AND JAMIE McARDLE

The fluorescence of chlorophyll in living plants has been studied in recent years in the hope of obtaining evidence regarding the process of photosynthesis. However, there has been a difference of opinion as to how these measurements should be interpreted. One group of investigators maintains[1] that photosynthesis and fluorescence are complementary processes. Others believe[2] that the relation between the two processes is an indirect one, the fluorescence intensity being controlled by the concentrations of certain photosynthetic intermediates and inhibitors. Studies *in vitro*[3] of dye-sensitized systems show in general that photochemical reactions and fluorescence are not complementary. However, there is little direct information available about the factors which determine the fluoresence intensity of chlorophyll solutions. The present experiments are part of a study designed to throw light on this problem.

It has been commonly accepted, on the basis of very scanty evidence, that the fluorescence of dissolved chlorophyll is substantially independent of the nature of the solvent. In contradiction to this view it was discovered recently[4] that chlorophyll dissolved in pure, dry hydrocarbons is practically non-fluorescent. Furthermore, the addition of a trace of water, alcohol or amine to such a solution raises the fluorescent yield to the "normal maximum" value of approximately 10%,[5] which is observed in pure alcohols and related solvents. Quantitative measurements of the intensity of fluorescence, at several temperatures and in a number of mixed solvents of known composition, indicate that the activation of the fluorescence is the result of the formation of an addition compound between a molecule of chlorophyll and one of the activator (*i. e.*, polar solvent).

Experimental Methods and Materials

The Fluorimeter.—The intensity of that part of the fluorescent light which is transmitted by a Wratten filter No. 88 was measured with a Photovolt Corporation (Model 512) photocell and amplifier. The photocell was placed

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