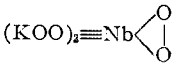
peroxide ions. Structure (9) is indicated


$$(KOO)_2{\equiv}Nb\langle O_2 \rangle \qquad (9)$$

According to reaction 8, three hydrogen peroxide groups are replaced when an alkaline solution of a perniobate is neutralized. It is reasonable to conclude, therefore, that the remaining peroxide ion is the one that is doubly bound to the niobium. This apparent special character of one peroxide–niobium linkage constitutes further support for the contention that a 1:1 peroxy–niobium complex exists in solution.

Summary.—On the basis of the previous discussion, the stoichiometry of the peroxy–niobium system in a large excess of hydrogen peroxide may now be summarized as in Table III.

TABLE III

STOICHIOMETRY OF THE PEROXY–NIOBIUM COMPLEXES

Soln.	Basic	Neut. and dil. H_2SO_4	Intermediate H_2SO_4	Concd. H_2SO_4	Free SO_3
H_2O_2:Nb	4:1 $\rightleftarrows$	1:1 $\rightleftarrows$	2:1 $\rightleftarrows$	3:2 $\rightleftarrows$	None

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Condensation Equilibrium of the Peroxy Complexes of Niobium in Sulfuric Acid[1]

BY N. ADLER AND C. F. HISKEY

RECEIVED AUGUST 3, 1956

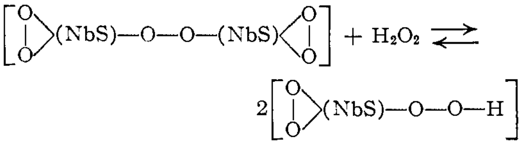
Pentavalent niobium forms two peroxy complexes, with peroxide:niobium ratios of 2:1 and 3:2, respectively, in the presence of an excess of hydrogen peroxide in sulfuric acid between 60–100 wt. % H_2SO_4. The condensation equilibrium between these complexes is now shown to be analogous to the chromate-dichromate equilibrium. The acid dependence of the reaction may be explained as arising from an additional equilibrium between molecular hydrogen peroxide and its conjugate acid, hydroperoxonium ion ($H_3O_2^+$). The distribution of niobium between the two complexes may be quantitatively correlated with acid concentration by use of the Hammett H_0 function.

The equilibrium reactions of niobium and hydrogen peroxide in concentrated sulfuric acid are of considerable interest in relation to a recently proposed[2] method for the simultaneous spectrophotometric analysis of niobium and tantalum in admixture. In this method, the niobium concentration is taken to be directly proportional to the concentration of the 3:2 complex with absorption maximum at 365 mμ. It is apparent that the factors that influence the formation of this complex must be adequately understood to obtain optimum accuracy in the above method of analysis. For this reason, a quantitative investigation has been made of the distribution of niobium between the two peroxy–niobium complexes formed in concentrated sulfuric acid under the analytical conditions of an excess of hydrogen peroxide.

The absorption spectra of the niobium–hydrogen peroxide system in sulfuric acid have been presented and resolved in terms of the three peroxyniobium complexes formed and a medium effect.[3,4] By correcting for the large medium effect, it has been shown that the 3:2 and 2:1 complexes are the only niobium species with other than negligible concentration in the range 59–100% H_2SO_4. The reaction of these complexes will now be considered.

Discussion

The equilibrium reaction between the 3:2 and 2:1 peroxy–niobium complexes is assumed to be given essentially by


$$\left[O_2\rangle(NbS){-}O{-}O{-}(NbS)\langle O_2\right] + H_2O_2 \rightleftarrows 2\left[O_2\rangle(NbS){-}O{-}O{-}H\right] \qquad (1)$$

The symbol S refers to all the coördinated groups with the exception of the peroxides that are necessary to satisfy the pentavalence of niobium and whatever charge state the complexes attain. Implicit in the above formulation is the assumption that condensation affects only the peroxy groups, and that the S groups are therefore the same for each complex.

Although the equilibrium between the complexes is obviously acid dependent, (1) does not directly show this dependence. The acid dependence may be explained as being due to an additional equilibrium between molecular hydrogen peroxide and its conjugate acid, the hydroperoxonium ion, $H_3O_2^+$. Evans and Uri[5] have calculated from thermochemical measurements that the value of the equilibrium constant for (2) is approximately of the order of 10^3, thus indicating that $H_3O_2^+$ behaves as a strong acid in water and is therefore completely dissociated. As a consequence, it may be expected that the properties of the hydroperoxonium ion will only be manifest in solvents of sufficient acidity to repress its dissociation, such as the strong mineral acids.

$$H_3O_2^+ + H_2O \rightleftarrows H_2O_2 + H_3O^+ \qquad (2)$$

The equilibrium between the hydroperoxonium ion and molecular hydrogen peroxide is of the type of a charged acid going to a neutral base. The

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[1] Abstracted from the Ph.D. Dissertation of Norman Adler, Polytechnic Institute of Brooklyn, 1954. Presented in part at the 126th Meeting, American Chemical Society, New York, 1954.

[2] F. C. Palilla, N. Adler and C. F. Hiskey, *Anal. Chem.*, **25**, 926 (1953).

[3] N. Adler and C. F. Hiskey, THIS JOURNAL, **79**, 1827 (1957).

[4] N. Adler and C. F. Hiskey, *ibid.*, **79**, 1831 (1957).

[5] M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949).

Hammett[6] acidity function H_0 may therefore be used to relate the distribution of H_2O_2 between these two species to the concentration of aqueous H_2SO_4. The relation is

$$H_0 = pK_a - \log \frac{(H_3O_2^+)}{(H_2O_2)} \qquad (3)$$

The quantitative relation governing (1) may now be derived. The equilibrium constant K and the ratio R are defined as

$$K = \frac{A^2{}_{2:1}}{A_{3:2}A_{H_2O_2}} = \frac{R}{(H_2O_2)} \times \frac{f^2{}_{2:1}}{f_{3:2}f_{H_2O_2}} \qquad (4)$$

$$R = \frac{(2:1)^2}{(3:2)} = \frac{[C_{Nb} - 2(3:2)]^2}{(3:2)} \qquad (5)$$

The symbols 3:2 and 2:1 as subscripts or normal scripts refer to the respective complex species, A and f to activity and activity coefficients, respectively, parentheses to equilibrium molar concentrations, and C_{Nb} to the total niobium concentration. By assuming eq. 6 as a boundary condition, the ratio R also may be given the second definition

$$C_{Nb} = 2(3:2) + (2:1) \qquad (6)$$

in (5). This assumption, namely, that all the niobium introduced into solution exists in the form of one or the other of the two complexes considered, is demonstrably valid[2-4] when the concentration ratio of peroxide to niobium exceeds approximately 100. The experimental work described in this article is restricted to this condition, and subsequent discussion is based on the applicability of eq. 6.

If (3) is now combined with (4) and (5), (7) is obtained

$$H_0 = \log R - \log(H_3O_2^+) - \log K - \log K_a + \log \frac{f^2{}_{2:1}}{f_{3:2}f_{H_2O_2}} \qquad (7)$$

This equation describes the distribution of niobium between the two peroxy complexes as a function of acid and H_2O_2 concentration in the presence of an excess of the latter. The following sections describe the results of tests of the validity of this equation.

Evaluation of Experimental Quantities.—The H_0 values used are from Hammett[6] and have been corrected by the algebraic addition of −0.29 unit.[7] The R term has been evaluated from spectra similar to and including those in Fig. 4 of a previous paper[4] in the following manner. In approximately 100% H_2SO_4 and a sufficient excess of H_2O_2, virtually all the niobium is present as the 3:2 complex with molar absorbtivity of 1744 at 365 mμ. The wave length of the absorption peak of this complex does not remain at 365 mμ at lower acidities, however, due to the medium effect. To correct for the medium effect, use is made of a previous observation[3] that the medium effect causes only a lateral displacement of the absorption peak but does not otherwise affect the absorption intensity at the peak. As a result, $(3:2) = A_{peak}/1744$, where A_{peak} is the experimentally determined absorbance at the absorption maximum at any acidity. The A_{peak} values in 59% H_2SO_4 have been corrected for the overlap of the absorption band of the 2:1 complex. The other term is given by $(2:1) = C_{Nb} - 2(3:2)$, where C_{Nb} is the total niobium in solution.

Validity of Derived Equation.—Data for two series of solutions are listed in Table I and are plotted in Fig. 1. The solid lines are drawn with the slope of unity. This is justified by the experimental points below 80% H_2SO_4. Above this acidity, less than 3% of the total niobium is present as the 2:1 complex. The error in determining R accordingly becomes appreciable, as the concentration of the 2:1 complex is obtained as a small difference between large values and then appears as a square term. The deviations of the two points above 80% H_2SO_4 from their respective curves are within the large experimental error for this region. Points below 59% H_2SO_4 are not included, as the concentration of another complex (1:1)[3] becomes appreciable in this region.

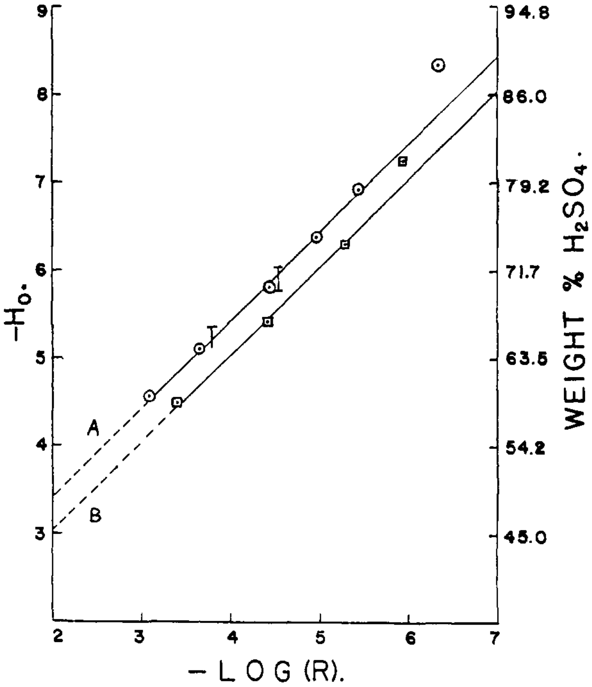

Figure 1.—Acid dependence of the equilibrium between the 3:2 and 2:1 peroxy-niobium complexes. Curve A: $C_{Nb} = 5.00 \times 10^{-4}$ g. at./l., $C_{H_2O_2} = 0.23$ M, T for 59.6% H_2SO_4 + 1.16 M $HClO_4$, I for 59.6% H_2SO_4 + 2.32 M $HClO_4$. Curve B: $C_{Nb} = 5.67 \times 10^{-4}$ g. at./l., $C_{H_2O_2} = 0.089$ M.

The unit slope of both curves is consistent with (7) only if the $H_3O_2^+$ concentration and the activity coefficient ratio terms are individually constant or constant as a sum over this range of acidity. The former explanation is favored. Considering the terms individually, eq. 3 requires a minimum pK_a of about −2.5 for the dissociation of the hydroperoxonium ion in order that this ion be the principal species above 59% H_2SO_4. A pK_a value in this range appears reasonable.[5] More negative pK_a values would be expected to be manifest as a downward curvature of the lines of Fig. 1 with decreasing acidity. Since a constant concentration

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[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. IX.

[7] J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).

of hydrogen peroxide was added in each series, a pK_a value of -2.5 would result in a constant log $(H_3O_2^+)$ term. As for the activity coefficient term, it is not expected that the individual coefficients will be constant in the applicable acidity range. However, it is possible for the activity coefficient term as a whole to be essentially constant due to the cancellation of the variations of the individual coefficients by virtue of appearing in a ratio.[8] While the charge types of the complex species are unknown, the nature of the reaction as formulated requires that the 3:2 complex have twice the charge of the 2:1 complex. In view of this relation, the most favorable case for a constant activity coefficient term in (7) occurs for neutral complex species, as in this case a symmetrical ratio would be obtained.

TABLE I

EQUILIBRIUM DATA FOR 3:2 AND 2:1 PEROXY-NIOBIUM COMPLEXES

All solutions in series A (top group) contain a total concn. of niobium, C_{Nb}, of 5.00×10^{-4} g. at./l., and a total concn. of H_2O_2 of 0.23 *M*. All solutions in series B contain $C_{Nb} = 5.67 \times 10^{-4}$ g. at./l., $C_{H_2O_2} = 0.089$ *M*.

H_2SO_4, wt. %	(3:2) × 10^4	(2:1) × 10^4	*R*	$-H_0$
91.5	2.45	0.10	4.10×10^{-7}	8.65
78.6	2.35	.30	3.84×10^{-6}	6.92
74.4	2.25	.50	1.11×10^{-5}	6.38
70.3	2.07	.87	3.66×10^{-5}	5.82
64.3	1.56	1.88	2.26×10^{-4}	5.10
59.6	1.05	2.91	8.11×10^{-4}	4.56
81	2.75	0.18	1.18×10^{-6}	7.26
74	2.65	.37	5.17×10^{-6}	6.30
67	2.36	.95	3.82×10^{-5}	5.41
59	1.59	2.49	3.90×10^{-4}	4.50

Effect of Absolute Concentrations.—Equation 5 requires that a change in the total concentration of niobium in the system be manifested as a change in the distribution of niobium between the peroxy complexes, but only to the extent consistent with the requirement that the ratio *R* remain constant. On the other hand, eq. 7 states that a change in the hydrogen peroxide concentration, at constant total niobium concentration and constant acidity, will also alter the distribution of niobium between the complexes, but that this redistribution will now result in a change in the value of *R*. Both parameters may be simultaneously tested by comparing series A to series B.

Equation 7 requires that the ratio $R/(H_3O_2^+)$ be constant at a selected acidity in the applicable acidity range for solutions of variable niobium and hydrogen peroxide concentrations, assuming that the activity coefficient term remains constant and that (6) applies. The former assumption is quite reasonable at any one acidity in view of the relatively low concentrations of the species in the activity coefficient term in relation to the high concentration of ionic species[7,9] contributed by the highly polar solvent. With the additional assumptions that the pK_a of $H_3O_2^+$ is larger than about -2.5 and that the activity coefficient term does not vary appreciably with acidity, the relationship may be tested over the entire applicable acidity range by means of the alternative statement given by (8). Here the intercept of curve A of Fig. 1 is designated I_A, and that of curve B as I_B.

$$\Delta I = I_B - I_A = \log \left[\frac{(H_3O_2^+)_A}{(H_3O_2^+)_B}\right] \qquad (8)$$

ΔI may be evaluated at any one value of *R*, and has the value 0.40. The total free H_2O_2 concentration in the solutions is obtained by subtracting the amount of H_2O_2 consumed by the complexes from the total concentration added. By now assuming that all the free H_2O_2 is present as the protonated form, the right-hand side of (8) is calculated to be 0.41. The agreement of these values, not only in algebraic sign but in magnitude, is taken as support for (7).

Generalized Acidity Dependence.—Implicit in the formulation of (1) and the derivation of (7) is the assumption that, providing sufficient bisulfate ion or sulfuric acid is present to ensure that only the 3:2 and 2:1 complexes are formed, the equilibrium between these complexes is due solely to an acidity effect. If this assumption is valid, the replacement of part of the H_2SO_4 in solutions containing more than 59% H_2SO_4 by an equivalent amount of another strong acid, such as perchloric acid, should be without appreciable effect on the equilibrium position of the reaction. The results of a test of the behavior of the system under these conditions are listed in Table II and are plotted as vertical dashes in Fig. 1.

TABLE II

EFFECT OF PERCHLORIC ACID

H_2SO_4, wt. %	$HClO_4$, *M*	*R*	$-H_0$[a]	$-H_0$[b]
59.6	1.16	1.86×10^{-4}	5.12	5.37
59.6	2.32	2.88×10^{-5}	5.76	6.03

[a] Assumes $HClO_4$ makes same contribution to H_0 as H_2SO_4 on mole for mole basis. [b] Method of calculation explained in text.

The $HClO_4$ was added to solutions containing an amount of H_2SO_4 that, had these solutions been diluted to volume only with water, would have given a H_2SO_4 concentration of 59.6%. In all other respects the solutions were similar to those of series A of Table I. Since the exact H_0 values for the resulting solutions are not known, dashes are used in Fig. 1 to represent the differences between the limiting values of H_0 calculated with the aid of different assumptions. The lower limit of the dashes represents H_0 values for the system $HClO_4$–H_2SO_4–H_2O calculated on the basis that $HClO_4$ makes the same contribution to H_0 on a mole for mole basis as does H_2SO_4 in the region of acidity starting at 59.6% H_2SO_4.[6] The upper limits represent H_0 values that would be obtained by adding the amounts of $HClO_4$ indicated to solutions of aqueous $HClO_4$ of such concentration as to have a H_0 value corresponding to H_0 for 59.6% H_2SO_4. This method takes into account that the H_0 contribution of $HClO_4$ is actually somewhat greater than that of H_2SO_4 on a molar basis in this region

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(8) N. C. Deno and R. W. Taft, Jr., THIS JOURNAL, **76**, 244 (1954).

(9) T. F. Young and S. R. Grinstead, *Ann. N. Y. Acad. Sci.*, **51**, 765 (1949).

of acidity.[10] It is reasonable to expect that the true H_0 values lie somewhere in between these limits, which would bring the experimental points into fair agreement with curve A. It would appear, then, that in the presence of a constant excess of H_2O_2 and H_2SO_4, the position of equilibrium is governed solely by acidity.

The behavior of the peroxy–niobium system is best exemplified by comparison to the chromate–dichromate system. The similarity of (9) to (1) is readily apparent. An additional point of interest may be noted in that a bathochromic shift

$$Cr_2O_7^- + H_2O \rightleftarrows 2HCrO_4^- \qquad (9)$$

of the spectra occurs for both systems on condensation.

Acknowledgment.—The authors wish to thank Professor J. Steigman for many fruitful discussions and for his encouragement during the course of this work and Dean R. E. Kirk for his support in the final stages of manuscript preparation.

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[10] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[CONTRIBUTION NO. 497 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

Dismutation of the Mercurous Dimer in Dilute Solutions

BY HERBERT C. MOSER AND ADOLF F. VOIGT

RECEIVED DECEMBER 10, 1956

The dismutation of the mercurous dimer into mercuric ions and dissolved free mercury has been studied in highly dilute mercurous nitrate solutions. Radioactive tracer techniques have been used to permit measurements in the 10^{-7} M range. Use is made of the extraction of free mercury into non-polar organic solvents to measure the extent of dismutation. The equilibrium constant for the dismutation reaction was found to be 5.5×10^{-9}. The solubility of mercury metal in aqueous solutions was found to be $(3.0 \pm 0.1) \times 10^{-7}$ M at 25°.

Introduction

It has been shown in a number of ways that mercurous ions exist in solution in the form of dimers.[1–3] The instability of these dimeric ions with respect to the formation of liquid mercury and mercuric ions is also well established. Values of 0.0060 to 0.0120 have been reported for the equilibrium constant at 25° of the reaction[2,4–7]

$$Hg_2^{++} = Hg(1) + Hg^{++}$$

Higginson[8] added a new consideration about the instability of the mercurous ion by suggesting that, at concentrations below 10^{-6} M in mercurous perchlorate, there is a significant degree of dissociation of the dimer into individual mercurous ions. He estimated a dissociation constant within the limits 10^{-8} to 10^{-6}. No other experimental value appears to have been reported although values of 10^{-30} and 10^{-18} have been inferred from other observations and calculations.[8–10]

This paper presents results of a study of the dismutation reaction

$$Hg_2^{++} = Hg^{++} + Hg(aq)$$

using radioactive tracer techniques to permit the measurement of concentrations in the 10^{-7} M range. Use is made of the fact that while metallic mercury is soluble to a very limited extent in water, it is considerably more soluble in non-polar organic solvents.[11–13] Thus free mercury can be extracted into solvents such as *n*-hexane and cyclohexane from highly dilute solutions of mercurous nitrate in dilute nitric acid. This extraction is related to the dismutation equation in such a way that the equilibrium constant for this reaction can be calculated.

The Distribution Ratio.—Providing that the oxidized forms of mercury do not extract into the organic phase, a distribution ratio, E, and a distribution constant, E^0, can be defined as

$$E = [Hg]_{tot.aq}/[Hg]_o$$

and

$$E^0 = [Hg]_{aq}/[Hg]_o$$

In these expressions $[Hg]_{tot,aq}$ is the total molar concentration of mercury in the aqueous phase, and $[Hg]_{aq}$ and $[Hg]_o$ are the concentrations of dissolved free mercury in the aqueous and organic phases. In the condition of both dismutation and dissociation occurring in a dilute solution of mercurous ions

$$[Hg]_{tot.aq} = [Hg]_{aq} + [Hg^{++}] + [Hg^+] + 2[Hg_2^{++}]$$

If a sample of pure mercurous nitrate in the absence of any mercuric nitrate or free mercury were diluted to a certain volume and extracted with an equal volume of an organic solvent, then

$$[Hg^{++}] = [Hg]_{aq} + [Hg]_o$$
$$= (1 + E^o)[Hg]_o$$

The distribution ratio, E, can now be expressed in

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