

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

Spectra of the Peroxy Complexes of Niobium in Sulfuric Acid¹

BY N. ADLER AND C. F. HISKEY

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A spectrophotometric investigation of niobium and of niobium plus hydrogen peroxide in aqueous sulfuric acid and in $\text{H}_2\text{SO}_4\text{-SO}_3$ solutions has revealed the existence of three peroxy-niobium complexes. Complex I, with absorption peak at 365 $\text{m}\mu$ in 100% H_2SO_4 , exists in appreciable amounts in 50 to 100% H_2SO_4 . Addition of as little as 2% free sulfur trioxide destroys this complex. Complex II becomes the more important species below 60% H_2SO_4 . Its absorption peak was not accessible although it appeared to be somewhere below 250 $\text{m}\mu$. Below 40% H_2SO_4 the equilibrium shifts to a third complex with a peak at 256 $\text{m}\mu$. A characteristic feature of this system is the pronounced bathochromic shift of the spectra as the sulfuric acid concentration is increased. This medium effect involves only the frequency, and not the intensity, of absorption.

A previous paper² has described a spectrophotometric method for the simultaneous quantitative analysis of mixtures of niobia and tantalum based on the reactions of these elements with hydrogen peroxide in concentrated sulfuric acid. The method is simple and accurate, although serious interference is caused by the presence of several other transition elements. Of those elements likely to be present, however, all readily may be removed prior to analysis³ with the exception of titanium. Recently, methods have been described which permit the quantitative separation of major amounts of titanium from the earth acids by distillation of titanium tetrachloride⁴ or by preferential elution of the earth acid fluorides from cellulose columns.⁵ As a consequence, the peroxide reactions are expected to be of wide utility in earth acid analysis, justifying a more detailed study of these reactions than has been done heretofore. In this first report a preliminary and qualitative investigation of the spectra of niobium pentoxide in sulfuric acid solutions, with and without hydrogen peroxide, is presented.

The absorptiometric behavior of the peroxy-niobium system in H_2SO_4 was first investigated by Klinger and Koch.⁶ Working at 436 $\text{m}\mu$, they found that the system begins to absorb light at 20% H_2SO_4 , and then increases in absorbance until 100% H_2SO_4 is reached. If free SO_3 is added the absorbance reaches a maximum at an acid concentration slightly larger than 100%, and then rapidly decreases. Telep and Boltz⁷ found that in approximately 50% H_2SO_4 the absorption peak is shifted further into the ultraviolet relative to that in concentrated H_2SO_4 and the peak absorbance is decreased.

It appears from this investigation that these spectral changes may be explained in terms of (a) a medium effect, (b) changes in the composition of the peroxy-niobium complexes involved and (c) changes in the equilibrium concentrations of the various complexes.

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Reagents and Apparatus

Niobium(V) Oxide.—The high purity grade sold by the Fansteel Metallurgical Corp., North Chicago, Ill., was used without purification, except for ignition to remove water or other volatile substances. This material analyzes at least 99.7% niobium(V) oxide. The principal impurities are 0.2% tantalum oxide, 0.002% titanium dioxide, 0.001% iron and 0.03% silicon dioxide.

Hydrogen Peroxide.—Merck "Superoxol," an approximately 30% aqueous solution of hydrogen peroxide, was used.

Other Chemicals.—The other reagents were C.P. grade and were used without further purification or treatment.

The absorbance measurements were made with a model D.U. Beckman spectrophotometer equipped with an ultraviolet accessory set. Matched, one centimeter square fused silica cells were used. For some of the measurements of highly absorbing species in the ultraviolet, however, matched silica cell spacers 9 mm. square were inserted in the cells to cut the effective path length to 1 mm. The data obtained by use of the spacers has been converted by calculation, so that all results presented are on the basis of 1 cm. cells.

Data obtained are plotted in terms of absorbance A defined by the familiar relation

$$A = \log_{10} \frac{I_0}{I} = abc$$

where I_0 is the intensity of light emerging from the solvent, I the intensity of light emerging from the solution, a the absorptivity, b the length of the light path through the absorption cell and c the concentration of the absorber expressed in gram-atoms per liter. Gram-atoms are used in preference to moles in this study to avoid ambiguity. This method of plotting is used consistently in this and the additional two papers of this series. In the systems being studied it was not always apparent whether mono-, di-, or polynuclear species were involved.

A thermospacer attachment surrounded the cell and lamp compartments of the instrument. Water from a large bath maintained at $23 \pm 0.5^\circ$ was forced through this attachment by means of a circulating pump operating at a sufficient rate to maintain a constant temperature in the cell compartment. Cells containing the solutions were allowed to reach thermal equilibrium in the compartment before readings were taken.

General Procedures.—Standard solutions of pentavalent niobium were prepared by dissolving a weighed quantity of niobium(V) oxide in boiling H_2SO_4 , cooling and diluting to mark in a volumetric flask with previously fumed H_2SO_4 . Whenever solutions of niobium in H_2SO_4 were to be diluted, the dilution was accomplished by slowly adding water to the acid solution in an ice-bath. This order of addition was used to keep the acid concentration as high as possible at all times in order to prevent hydrolysis of the niobia.

Stock solutions of approximately 30% H_2O_2 were standardized iodimetrically to at least $\pm 0.2\%$ immediately prior to use. To prepare solutions for measurement, an appropriate quantity of the standardized solution was weighed out and then cooled in an ice-bath. Cooled H_2SO_4 was slowly added at such a rate that the temperature of the resulting solution was always below room temperature. At no time was there evidence of the ozone-like odor that usually accompanies the thermal decomposition of H_2O_2 . The

resulting solution was then transferred quantitatively to a volumetric flask and diluted to mark with the appropriate additional quantities of H_2SO_4 and H_2O , again keeping the solution below room temperature during the additions.

Sulfuric acid solutions, when analyzed, were determined to a precision of at least $\pm 0.2\%$ by titrating a weighed amount of solution with carbonate-free sodium hydroxide. Many solutions were prepared by dilution and not subsequently analyzed. The H_2SO_4 concentrations of these solutions were obtained by calculation, using density values for aqueous H_2SO_4 from the literature. In all cases, % acid refers to the weight % acid. Sulfuric acid solutions containing free sulfur trioxide were prepared by mixing 96% aqueous acid with 20 or 30% fuming acid in various proportions. For the highest concentrations of SO_3 , freshly distilled sulfur trioxide was mixed with appropriate quantities of fumed acid.

A reference solvent was used in all measurements to compensate for the appreciable absorbance of hydrogen peroxide below $340 \text{ m}\mu$. In all cases, measurements were made to the lowest wave lengths attainable with the instrument used. The variable low wave length limit of the spectral curves reflects the absorbance changes in the reference solvent.

Experimental

Absorption Spectra of Niobium in Sulfuric Acid.—The spectra of the sulfate complexes of niobium were determined as a preliminary step to the study of the spectra of the peroxy complexes. A range of concentration from 29 to 100% H_2SO_4 was studied and then extended to 95% free sulfur trioxide. The spectra obtained are presented in Figs. 1 and 2. Those in Fig. 2 have just one-tenth the niobium concentration of those in Fig. 1.

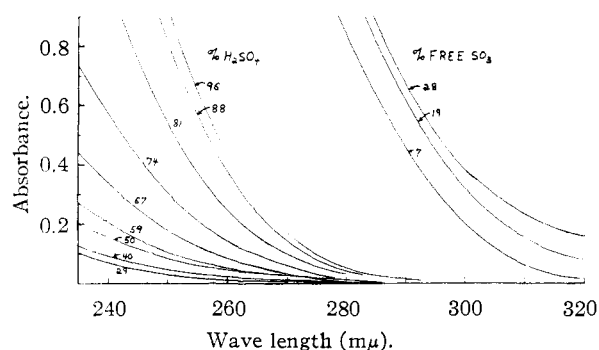


Fig. 1.—Spectra of Nb_2O_5 in H_2SO_4 and free SO_3 solutions; concn. of Nb = 5.67×10^{-4} g. atom/l.

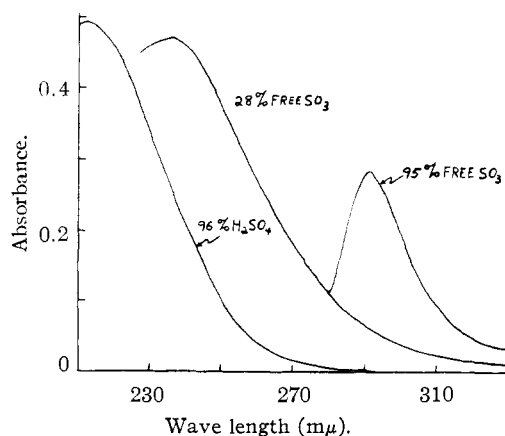


Fig. 2.—Spectra of Nb_2O_5 in H_2SO_4 and free SO_3 solutions; concn. of Nb = 5.67×10^{-5} g. atom/l.

An examination of these data reveals a number of points of interest to this study. It may be noted that there is a continuous bathochromic shift of the spectra with increasing acidity extending to solutions containing free sulfur trioxide. The shift appears to be fairly uniform in aqueous H_2SO_4 and

in H_2SO_4 containing free SO_3 , except for the possibility of an abrupt shift at the transition from aqueous to anhydrous H_2SO_4 . However, since the curves are not congruent with respect to absorbance, if wave length position is temporarily ignored, the shift must be more than a simple lateral displacement of the spectra. For strict validity, this comparison should be made on a frequency abscissa, but the same conclusion would prevail. The aqueous acid spectra suggest that, in addition to the lateral shift, there is a simultaneous progressive increase in concentration of the species whose spectral peak is first seen at 96% H_2SO_4 . The rough congruity, other than for wave length position, of the curves marked 88, 96 and 7 further suggests that the concentration of this species reaches a maximum at about 88%. The peak occurs at about $213 \text{ m}\mu$ with gram-atom absorptivity of about 8700 in 96% H_2SO_4 .

It will be seen subsequently that the absorption of the sulfate-niobium complexes is always less than that of the peroxy-niobium complexes over the entire range of acidity studied, if comparison of the two systems is made at the same acidity.

Absorption Spectra of the Peroxy Complexes.

Spectra of the peroxide system were obtained over the same H_2SO_4 and SO_3 range examined previously with niobium alone. In these studies the H_2O_2 concentration was approximately 200 times that of the niobium. The data obtained are presented in Figs. 3, 4 and 5. They are assembled in such a way that each figure covers a significant region of the concentration range studied. Thus, Fig. 3 shows the spectra obtained when a 2% variation in free SO_3 was made in 100% H_2SO_4 . Figures 4 and 5 represent the spectra observed when the H_2SO_4 concentration was varied from 59–100% and from 16–56%, respectively. Each of these figures will now be considered in greater detail.

In Fig. 3, the limiting curves labeled 1 and 9 represent, respectively, the spectra of the system in 100% H_2SO_4 to which two and zero % free SO_3 has been added. The intermediate curves, 2 through 8, are spectra of solutions containing successively decreasing but otherwise unspecified concentrations of SO_3 .

The problem of obtaining data in this solvent range is complicated by the great sensitivity of the

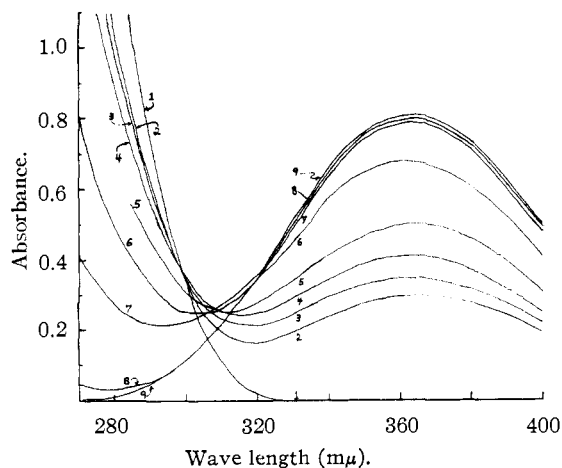


Fig. 3.—Spectra of the H_2O_2 - Nb_2O_5 system in 100 to 102% H_2SO_4 ; concn. of Nb = 9.5×10^{-4} g. atom/l., concn. of H_2O_2 = 0.18 M. Curve 1, 2% free SO_3 . This curve is identical with one containing no H_2O_2 . Curves 9-2 represent a progressively increasing amount of free SO_3 in 100% H_2SO_4 . Actual concentrations unspecified but curve 2 is less than 2% SO_3 .

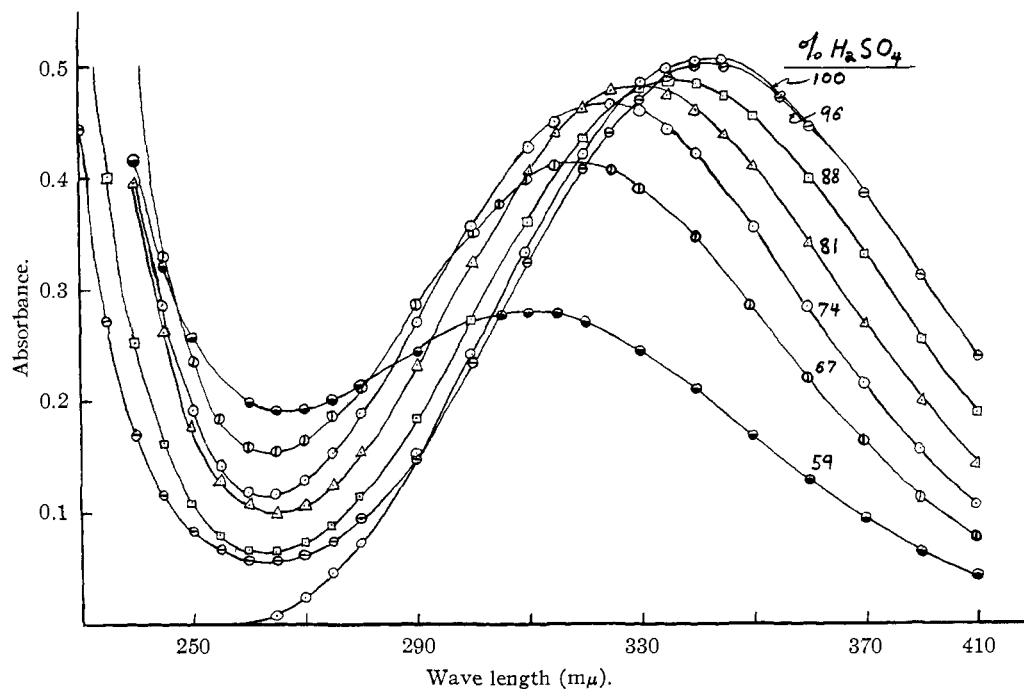


Fig. 4.—Spectra of the $\text{H}_2\text{O}_2\text{-Nb}_2\text{O}_5$ system in 59–100% H_2SO_4 ; % H_2SO_4 indicated by numbers on curves; concn. of Nb = 5.67×10^{-4} g. atom/l.; $\text{H}_2\text{O}_2 = 0.089$ M.

spectra to moisture pickup. The problem was partially overcome by sealing the solution in the cuvette. For this purpose the cuvette cover was moistened with the solution by inversion. The liquid seal so formed prevented any moisture diffusion into the body of the solution during the period of the measurement. This was checked by repeating measurements in selected parts of the spectrum. The data in curves 2 to 9 were obtained by starting with a 2% sulfur trioxide solution and exposing it to the atmosphere until enough moisture had been absorbed to cause the absorption band to appear. The cuvette was then sealed and the measurements taken. When complete, the cuvette cover was removed, the solution was again exposed for a few minutes, and the cell was then resealed. After shaking the cuvette to ensure uniformity in the sample a second spectral curve was measured. This process was repeated six times until enough moisture had been absorbed to bring the composition to about 100% H_2SO_4 .

The absorption band with peak at 365 m μ is attributed to a peroxy-niobium complex, subsequently denoted by I. The approximate isosbestic point at 310 m μ indicates that only one peroxy complex is involved. The lack of a more clearly defined point is attributed not only to experimental error but to the possibility of a large medium effect shift of the niobium spectra in this region.

A small excess of free SO_3 evidently is sufficient to cause I to dissociate into a sulfate-niobium complex and the various sulfuric acid and sulfur trioxide solvates of hydrogen peroxide.⁸ In 2% SO_3 , the spectrum of the system containing H_2O_2 is identical with that obtained when the H_2O_2 is replaced by an equivalent quantity of water. Stud-

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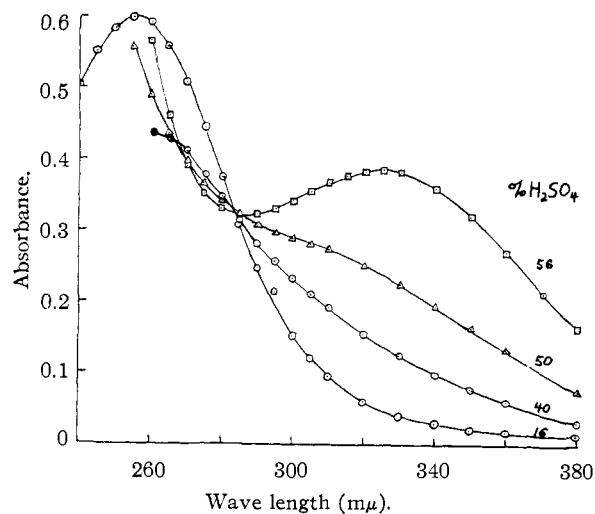


Fig. 5.—Spectra of the $\text{H}_2\text{O}_2\text{-Nb}_2\text{O}_5$ system in 16 to 56% H_2SO_4 ; concn. of H_2SO_4 indicated on curves; concn. Nb = 1.00×10^{-3} g. atom/l., $\text{H}_2\text{O}_2 = 0.11$ M.

ies were also made at higher SO_3 concentrations without revealing any spectra that could be ascribed to peroxy complexes. It may be concluded, therefore, that H_2O_2 does not react with niobium above 2% SO_3 .

In Fig. 4, the spectra show three phenomena as the acid concentration is varied between 59–100% H_2SO_4 . First, it is evident that as the acid concentration is decreased, the concentration of I decreases. Second, a simultaneous increase in absorption, not due to uncomplexed niobium, occurs at wave lengths below 290 m μ . Third, a lateral shift of the absorption band of I occurs due to a medium effect. In the conventional direction, it is a

bathochromic shift with increasing acid concentration.

The medium effect must be considered first in order to appreciate the significance of the other phenomena. Similar bathochromic shifts have been observed previously for widely different systems, both inorganic^{2,9} and organic.¹⁰⁻¹³ For solutes with single absorption bands, the effect appears to be only a change in the transition moment (frequency) of absorption with no change in the transition probability (intensity) of absorption. This is partially supported by the data in Table I,

TABLE I
MEDIUM EFFECT ON HALF PEAK INTENSITY BAND WIDTH OF COMPLEX I

H ₂ SO ₄ , wt. %	100	96	91.5	88	81	78.6	74.6	74
Band width, $\mu \times 10^{-14}$, sec. ⁻¹	1.99	1.94	1.96	1.99	2.02	2.00	2.03	2.05

where it is seen that the half-band width remains constant ($2.00 \pm 0.03 \times 10^{14}$ sec.⁻¹) within the experimental error for I for a shift of 21 $m\mu$ (4.8 kcal./mole). The continuous nature of the shift is demonstrated in Fig. 6 where it is seen that a

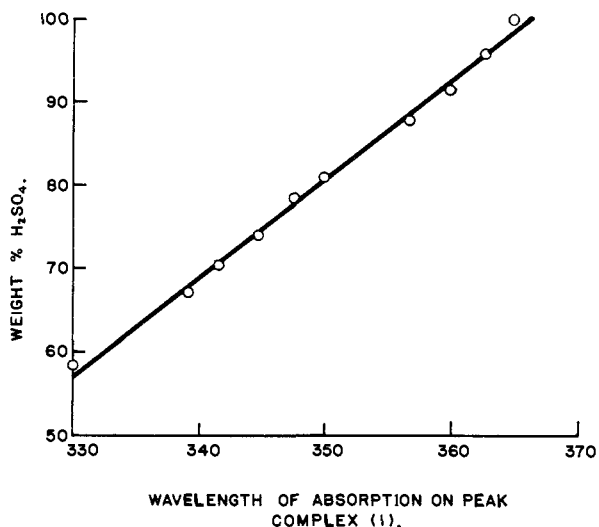


Fig. 6.—Medium effect shift of absorption maximum.

plot of acid concentration against the wave length of the absorption peak of I is approximately linear. (A frequency abscissa does not materially alter this result.) The linear nature of the shift coupled with the lack of any apparent relationship to any specific solvent moieties suggest that the effect is due to the gradual variation of the forces exerted

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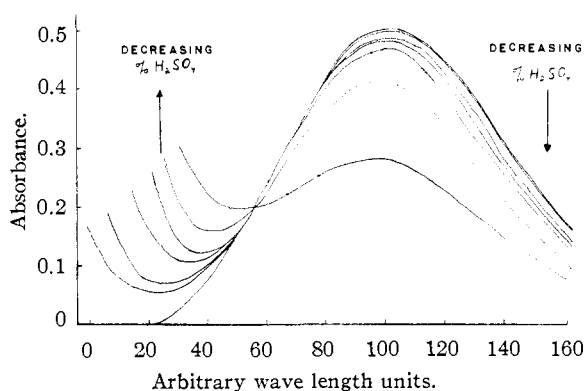


Fig. 7.—Normalized spectra of Fig. 4.

on the absorbing solute by the changing solvent structure.

The approximate linearity of the Fig. 6 plot readily permits normalization of the Fig. 6 spectra. This was accomplished by arbitrarily selecting the 100% H₂SO₄ curve as the reference curve and then displacing each other curve toward it by an amount equal to the displacement shown in Fig. 6. The result of this procedure is shown in Fig. 7. The resulting family of curves now possess a well-defined isobestic point, clearly demonstrating an equilibrium reaction between I and another peroxy-complex, II, and the absence of any additional niobium species.

If the data of Fig. 5 are now considered, evidence for a third peroxy species is obtained. In this figure it is seen that I in 56% H₂SO₄ has its absorption peak at about 330 $m\mu$. It is in equilibrium with II whose absorption peak is not accessible. As the H₂SO₄ concentration is reduced I decreases in concentration while II does not rise proportionately. Finally when the acid concentration is 16% or less, it becomes possible to observe a peak at 256 $m\mu$. The absorptivity at this wave length is 600. Spectra also were taken at 8.7 and 2.0% acid. They were essentially identical with that at 16% with no evidence of any lateral shift.

The data here strongly suggest that the peak at 256 $m\mu$ represents a third peroxy complex, III. If one traces out the curve for 50% acid, it will be seen that this curve is appreciably lower than that for 56% not only in the 300 to 380 $m\mu$ region, but also in the 260–270 $m\mu$ region. Thus it seems that both I and II have diminished in concentration, although I has decreased relatively more than II. It is also evident that the peak for II is substantially below 250 $m\mu$. When the sulfuric acid is reduced to 40%, I diminishes even further, while in the 260 $m\mu$ region the first indications of a new peak become evident. In general then it appears that as I decreases, it at first is replaced by II which at lower concentrations gives way to III.

BROOKLYN, N. Y.