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

Composition of the Peroxy Complexes of Niobium(V) in Sulfuric Acid[1]

BY N. ADLER AND C. F. HISKEY

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The compositions of the three peroxy–niobium complexes formed in sulfuric acid in the presence of an excess of hydrogen peroxide[2] are elucidated. Complex I, favored in concentrated sulfuric acid, is found by continuous variations to be a 2-Nb:3H_2O_2 complex. II, favored in intermediate sulfuric acid, is found, by a new method termed the successive ratio method, to be a 1Nb:2H_2O_2 complex. III, favored in dilute sulfuric acid, is found by continuous variations to be a 1Nb:1H_2O_2 complex.

The near ultraviolet spectra of the niobium–hydrogen peroxide system between 2 and 100% sulfuric acid have been presented in a previous paper.[2] Based on these spectra, it was demonstrated that, in an excess of hydrogen peroxide, niobium(V) may be distributed among at least three peroxy complexes. The distribution among these forms depends on the acid concentration. These complexes were designated as I, II and III. Complex I is that one favored by the highest sulfuric acid concentrations, II is favored by intermediate acid concentrations, while III exists only in dilute sulfuric acid. It is the purpose of this paper to present evidence regarding the composition of these complexes.

The materials, apparatus and procedures were the same as those described previously.[2]

Composition of Complex I.—The ratio of niobium to peroxide in complex **I** was determined by Job's method of continuous variations.[3,4] Representative data obtained over a wide range of wave lengths are given in Fig. 1. The maxima of all the curves occur at a mole ratio of 0.66, corresponding to a complex with three peroxide groups per pair of niobium ions. Inasmuch as continuous variations gives only a ratio, it may only be concluded at this point that I is a polynuclear species with an unknown degree of polymerization.

In order to determine the degree of polymerization or the actual composition of the complex, an attempt was made to formulate an "equilibrium constant" that would be consistent with the data. For this purpose, a number of reactions meeting the requirement of a 3:2 peroxide to niobium ratio were postulated and their constants were calculated. The data presented in Table I for reaction 1 yield a very satisfactory

$$2Nb(V) + 3H_2O_2 \overset{K}{\longleftrightarrow} [Nb_2(H_2O_2)_3] \qquad (1)$$

equilibrium constant (2)

$$K = \frac{[Nb_2(H_2O_2)_3]}{(Nb)^2(H_2O_2)^3} \qquad (2)$$

with an average value equal to 4.96 ± 0.16 × 10^{12}. The constancy of this equilibrium constant may be deduced to be a necessary condition for establishing I as a binuclear complex by considering the effect of the exponents in the equilibrium constant relation for other possible reactions.

TABLE I

FORMATION CONSTANT OF PEROXY–NIOBIUM COMPLEX IN 97.2% SULFURIC ACID

Cor.[a] absorbance at 365 mμ	Initial concn.[b] × 10^3 Nb	Initial concn.[b] × 10^3 H_2O_2	Equilibrium concn. × 10^3 [Complex]	Equilibrium concn. × 10^3 [Nb]	Equilibrium concn. × 10^3 [H_2O_2]	$K \times 10^{-12}$	Dev.
0.274	0.573	1.357	0.157	0.259	0.886	(3.36)	[c]
.307	.688	1.222	.1765	.335	.692	4.75	−0.21
.316	.764	1.147	.181	.402	.604	5.11	+ .15
.312	.802	1.108	.179	.444	.571	4.88	− .08
.308	.879	1.031	.177	.525	.500	5.13	+ .17
.294	.955	0.955	.169	.617	.448	4.92	− .04[d]
.280	1.031	.879	.1605	.710	.398	5.00	+ .04
.251	1.147	.764	.144	.859	.332	5.33	+ .37
.183	1.357	.573	.105	1.147	.258	4.65	− .31

Av. value of formation constant 4.96 ± 0.16

[a] Absorptivity of completely complexed niobium in 97% H_2SO_4 at 365 mμ equals 872 cm.^{2}/g.-atom of niobium. [b] Solvent is 97.2% H_2SO_4; sum of initial concentrations of Nb(V) and H_2O_2 equals 1.910 × 10^{-3} for each solution. [c] Value excluded from mean. [d] These values represent duplicate solutions, and are included twice in the mean value.

Composition of Complex II.—In a previous investigation[2] of the niobium–hydrogen peroxide system in sulfuric acid, conditions were not found where II is the only complex in solution. Fortunately, an acid concentration readily may be selected where the interference is limited to only

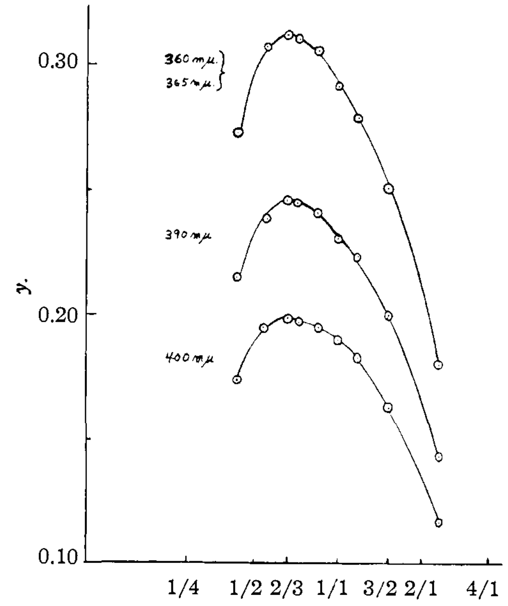

Fig. 1.—Continuous variations study of the peroxy-niobium complex in 97.2% H_2SO_4. Stock solutions of Nb and H_2O_2 were 1.910 × 10^{-3} *M*.

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

[3] P. Job, *Ann. Chim.*, **9**, 113 (1928).

[4] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

one other complex whose composition is known. A general method has been devised that allows the composition of the unknown complex to be determined under such conditions.

Successive Ratio Method.—The formation reactions of two complexes formed from the same components may be written in the general case as

$$a\mathrm{MX}_y + g\mathrm{L}^- \overset{K_1}{\rightleftarrows} [\mathrm{M(X}_{y-g})]_a\mathrm{L}_g + g\mathrm{X}^- \quad (3)$$

$$b\mathrm{MX}_y + h\mathrm{L}^- \overset{K_2}{\rightleftarrows} [\mathrm{M(X}_{y-h})]_b\mathrm{L}_h + h\mathrm{X}^- \quad (4)$$

where M refers to the central group nucleus or metal ion, X refers to whatever anions are associated with the central group in the particular solvent used, K_i represents the equilibrium constants of the two reactions, respectively, L refers to the ligand or complexing anion, and the other symbols are small integers.

In the usual situation, the anions constituting the X groups are those resulting from the autoprotolysis of the solvent or dissociation of the buffer, and will be present, or can be adjusted to be present, at such concentration in the medium that the additional quantity liberated in the equilibria will have only a negligible effect on their total concentration. Under the assumption that this occurs, the X^- concentration may be considered constant and incorporated into the equilibrium constants. However, since these species are invariably acid dependent, the acidity must be kept constant for these modified equilibrium constants, or formation constants, to have meaning.

The K_i's may now be defined as

$$K_1 = \frac{(\mathrm{M}_a\mathrm{L}_g)}{(\mathrm{M})^a(\mathrm{L}^-)^g};\quad K_2 = \frac{(\mathrm{M}_b\mathrm{L}_h)}{(\mathrm{M})^b(\mathrm{L}^-)^h} \quad (5)$$

where the parentheses refer to equilibrium concentrations. In general, a and b are integers, and may be related by the expression $a = Zb$. Raising K_2 to the Z power and taking the ratio of the formation constants, eq. (6) is obtained

$$(\mathrm{L}^-)_\alpha{}^{Zh-g} = \frac{(\mathrm{M}_a\mathrm{L}_g)_\alpha}{(\mathrm{M}_b\mathrm{L}_h)_\alpha{}^Z} \times \frac{K_2{}^Z}{K_1} \quad (6)$$

where the subscript α has been added to represent one particular solution. If this solution is now compared to another solution, β, containing a different equilibrium ligand concentration but otherwise similar, eq. 7 is obtained

$$\left[\frac{(\mathrm{L}^-)_\alpha}{(\mathrm{L}^-)_\beta}\right]^{Zh-g} = \left[\frac{(\mathrm{M}_a\mathrm{L}_g)_\alpha}{(\mathrm{M}_a\mathrm{L}_g)_\beta}\right]\left[\frac{(\mathrm{M}_b\mathrm{L}_h)_\beta}{(\mathrm{M}_b\mathrm{L}_h)_\alpha}\right]^Z \quad (7)$$

An important feature of eq. 7 lies in that it requires only the ratios of the equilibrium concentrations of the species involved rather than their absolute concentrations. For this reason, these terms may be replaced by the ratios of any physical property that is proportional to the concentration of each individual complex (*i.e.*, light absorption). For strong complexes, the ligand term may be similarly evaluated. Alternatively, when weak complexes are involved, the excess of ligand in both solutions may be sufficiently large to allow the equilibrium ligand concentration to be replaced by the total ligand concentration with negligible error.

Equation 7 may be solved explicitly for h and Z, but the resulting equations may involve small differences between large quantities, and hence may not be suitable for calculation. An alternative method is to assume reasonable values for Z and make a trial and error search for an integral value of h. Since most complexes are mononuclear, Z will usually equal unity. The particular system investigated will often suggest appropriate values for Z.

The successive ratio method has been applied to the niobium–hydrogen peroxide system in 60% sulfuric acid. A series of solutions were prepared containing identical niobium and acid concentrations, but with successively increasing hydrogen peroxide concentrations. The absorption spectra were obtained using a corresponding acid reagent blank, and corrections applied for the absorbance of the hydrogen peroxide. The corrected spectra are shown in Fig. 2. Absorption at 335 mμ is representative of complex I, whereas that at 290 mμ and below is representative of II.

Several preliminary deductions may be made. The curves show that as the hydrogen peroxide concentration is increased, the concentration of the 3:2 complex first increases rapidly, but then reaches a maximum and begins to decrease. II, however, continuously increases, rapidly at first and then more slowly. Although the extent of polynuclear condensation of this complex is not known, this behavior must mean that the peroxide to niobium ratio in II is larger than 1.5. The existence of an isosbestic point for curves 3–5 at 299 mμ is evidence not only that very little uncomplexed niobium is present in solution when the competition between the complexes becomes appreciable, but that only two complexes are present under these conditions.

$\mathrm{M}_a\mathrm{L}_g$ in (7) was selected arbitrarily as the complex whose composition is known (I), or as $\mathrm{M_2L_3}$. The composition of the other complex was then found by evaluating the unknown exponent, h, for various assumed values of Z. The concentration ratios of the complexes were replaced by the ratios of absorbance at a given wave length for the two solutions that were compared. This may be done directly at wave lengths above 350 mμ for I, but corrections are required for the absorption contribution of I at the wave lengths were II absorbs appreciably. Only the three solutions corresponding to curves 3–5 in Fig. 2 were used. For these solutions, the free hydrogen peroxide concentration was taken to be directly proportional to the total hydrogen peroxide added initially. The results of the assumption of various values of Z are shown in Table II. Integral values for h are only obtained for $Z = 2$. Complex II, therefore, is a mononuclear complex containing two peroxide groups.

Table II

Composition of Peroxy–Niobium Complex II

	Curve no. from Fig. 2	$\left(\frac{[\mathrm{Nb_2(H_2O_2)_3}]_\beta}{[\mathrm{Nb_2(H_2O_2)_3}]_\alpha}\right)$	$\left(\frac{[\mathrm{Nb}_b\mathrm{(H_2O_2)}_h]_\alpha}{[\mathrm{Nb}_b\mathrm{(H_2O_2)}_h]_\beta}\right)^Z$	$\frac{(\mathrm{H_2O_2})_\alpha}{(\mathrm{H_2O_2})_\beta}$	h	
					if Z = 2	if Z = 1
α	5	$(1.55 \pm 0.04)^a$	$(1.68 \pm 0.10)^b$	5.0	1.9$_6$	3.6
β	4					
α	4	$(1.16 \pm .00)^a$	$(1.25 \pm .03)^b$	2.0	1.9$_3$	3.4
β	3					

[a] Ratios of absorbance averaged over wave lengths 350, 360, 370 and 380 mμ. [b] Ratios of absorbance averaged over wave lengths 280, 285, 290 and 295 mμ.

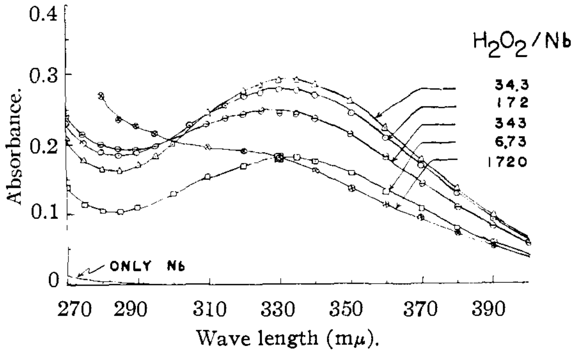

Fig. 2.—Variation of the H_2O_2/Nb ratio at constant niobium concentration in 60% H_2SO_4: Curve 1, H_2O_2/Nb = 6.73; 2, 34.3; 3, 172; 4, 343; 5, 1720. Nb concn. = 5.67 × 10^{-4} g. atom/l.

Composition of Complex III.—The composition of III was investigated by the continuous variations method. The first study was performed in 22.9% sulfuric acid, using stock solutions of the components of 1.15 × 10^{-2} g.-atoms/l. concentration. It was found that the stock solution of niobium had anomalously high absorbance when compared to a solution prepared separately of a 20-fold lower niobium concentration but of the same acidity. In fact, the absorbance was larger than that of the complex in the spectral region used. As a result, the continuous variations curves for the wave lengths between 315–340 mμ, the region investigated, possessed minimum rather than maximum points. These points occurred at a mole fraction of 0.5, but the curves were not symmetrical about these points, deviations occurring when an excess of niobium was present in the solutions. It was noticed subsequently that the stock niobium solutions were unstable, visible hydrolysis occurring within one month. Presumably, then, the high apparent absorbance of the niobium was due to scattering by colloidally dispersed particles of niobia.

This system has been investigated[5] previously by the same method, but in 30% sulfuric acid, only at 436 mμ, and at a higher concentration, 0.1 g.-atom/l. of niobium. A 1:2 peroxy–niobium complex was reported, but no mention was made of colloidal phenomena. In view of this uncertainty, another study was made. The stock solutions contained 3 × 10^{-2} g./atoms/l. of the components in 41.7% sulfuric acid. As in the earlier study, the absorptivity of the niobium stock solution was high compared to a more dilute niobium solution. However, interference from this behavior could be partially circumvented by restricting measurements to above 360 mμ, where the niobium did not absorb. While the stock solution was found to be unstable over a period of a month, duplicate solutions prepared at the time of the experiment gave the same results within experimental error. Typical results for the region between 360–436 mμ are shown in Fig. 3. All maxima occurred almost exactly at a mole fraction of 0.5, again indicating a 1:1 complex.

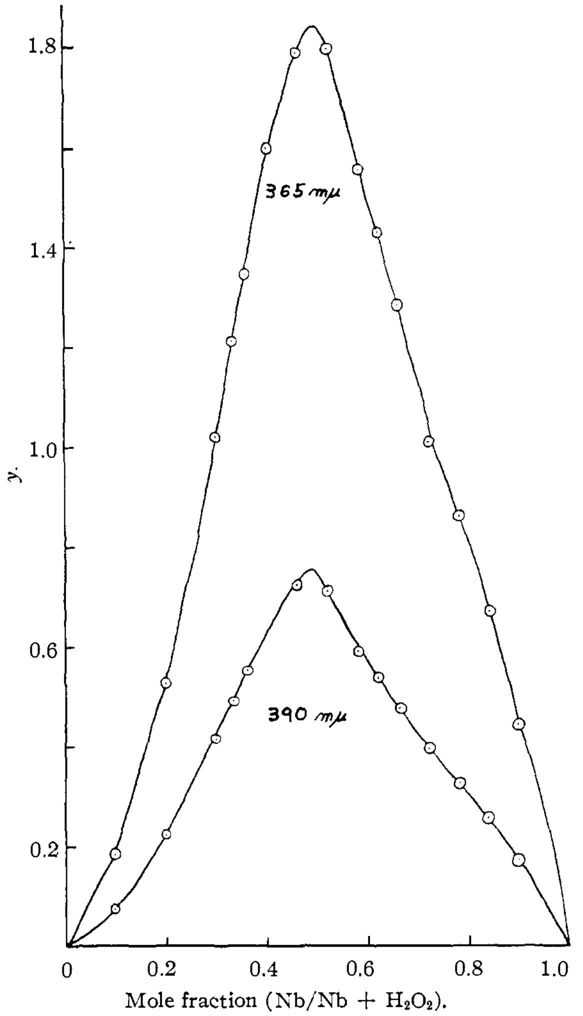

Fig. 3.—Continuous variations study of the peroxy–niobium complex in 41.7% H_2SO_4. Stock solutions of Nb and H_2O_2 were 3.00 × 10^{-2} *M*.

Additional evidence for a 1:1 complex may be obtained by considering the solid peroxy–niobium compounds known to exist. Numerous workers have reported[6–8] that niobium forms an insoluble, yellow 1:1 peroxy compound, perniobic acid, in neutral solution. Sieverts and Müller[8] have found that by titrating a concentrated solution of potassium perniobate with an amount of sulfuric acid equivalent to the potassium in the salt, precipitation of the peracid will occur in accordance with the reaction

$$2K_3NbO_8 + 3H_2SO_4 + 4H_2O \rightleftharpoons 2HNbO_4 + 3K_2SO_4 + 6H_2O_2 \quad (8)$$

The free peroxide in the filtrate agreed on titration with the amount to be expected on the basis of this equation.

The stoichiometry of the perniobates requires that one peroxide ion be bound to the niobium ion in a different manner than the remaining three

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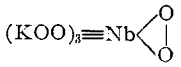
[5] Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

[6] C. Balke and E. F. Smith, THIS JOURNAL, **27**, 1140 (1905); **30**, 1666 (1908).

[7] P. Melikov and M. Pissarjewsky, *Z. anorg. Chem.*, **20**, 344 (1899).

[8] Von A. Sieverts and E. L. Müller, *ibid.*, **173**, 297 (1928).

peroxide ions. Structure (9) is indicated


$$(\mathrm{KOO})_3\equiv\mathrm{Nb}<\!\begin{array}{c}\mathrm{O}\\|\\\mathrm{O}\end{array} \qquad (9)$$

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 ⇄	1:1 ⇄	2:1 ⇄	3:2 ⇄	None

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

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

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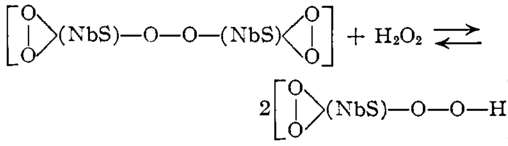
Pentavalent niobium forms two peroxy complexes, with peroxide:niobium ratios of 2:1 and 3:2, respectively, in the presence of an excess of hydrogen peroxide in sulfuric acid between 60–100 wt. % H_2SO_4. The condensation equilibrium between these complexes is now shown to be analogous to the chromate-dichromate 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 peroxy-niobium 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


$$\left[\begin{array}{c}\mathrm{O}\\|\\\mathrm{O}\end{array}\!>(\mathrm{NbS})\text{—O—O—}(\mathrm{NbS})<\!\begin{array}{c}\mathrm{O}\\|\\\mathrm{O}\end{array}\right] + H_2O_2 \rightleftarrows 2\left[\begin{array}{c}\mathrm{O}\\|\\\mathrm{O}\end{array}\!>(\mathrm{NbS})\text{—O—O—H}\right] \qquad (1)$$

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).