Have you any evidence for or against this temporary release of a carboxyl group to give a tetradentate EDTA intermediate?

D. H. BUSCH.—Your suggestion is quite good and is of a nature which had not occurred to us. I do not believe that we have any strong evidence for or against this intermediate; however, the data in basic media will test your mechanism very nicely. A single factor troubles me. I fail to see why the dissociation of a carboxyl group would be rapid, and therefore not rate determining, while the dissociation of a bromide ion is slow and rate determining (data in acid). In fact, I would expect acid acceleration rather than base acceleration if the replacement of a carboxyl group by a water molecule was the first step in the process. I suspect that protonation of the coërdinated carboxyl groups might labilize them. As you recall, we did observe that a slight acid acceleration occurs in the systems studied at $pH \sim 0$; however, the reacting species was also shown to be altered. It might be $[Co(H_2Y)Br]$.

THE AQUEOUS CHEMISTRY OF INORGANIC FREE RADICALS.¹ I. THE MECHANISM OF THE PHOTOLYTIC DECOMPOSITION OF AQUEOUS PERSULFATE ION AND EVIDENCE REGARDING THE SULFATE-HYDROXYL RADICAL INTERCONVERSION EQUILIBRIUM

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The photolytic reaction $S_2O_8^- + H_2O \rightarrow 2HSO_4^- + \frac{1}{2}O_2$ has been studied at $32 \pm 2^\circ$ using 2537 Å. light. At a fixed light intensity the rate is first order in persulfate ion and is essentially independent of the acidity from 0.20 N NaOH to 1.0 N HClO₄, although there is a slight increase in rate with increasing acidity, especially at low persulfate concentration and low ionic strength. Neither hydrogen ion nor sulfate ion alone influences the rate of the process (quantum yield), but the presence of both at moderate concentrations strongly inhibits the photolysis. At high values of $(H^+)(SO_4^-)$ corresponding to saturation inhibition the rate decreases not to zero, but to a value of approximately 20% of that under uninhibited conditions. Both the inhibition studies and tracer experiments using O¹⁸ and S³⁸ suggest that the photolytic decomposition occurs through two parallel reaction paths. One of these, designated as the k_1' path, is inhibited by bisulfate ion (*i.e.*, by $(H^+)(SO_4^-)$), with the inhibition producing an induced S³⁵⁵ exchange between labeled sulfate and unlabeled persulfate. Oxygen produced in the k_1' path has the same O¹⁸ content as the water solvent. The other reaction path, characterized by a rate constant $k_{2'}$, is not inhibited by bisulfate ion, does not induce the S³⁵⁵ exchange, and produces water with an O¹⁸ content which is the average of that of the solvent and the persulfate ion. By way of mechanism it has been suggested that the k_1' path generates sulfate radicals, followed by the rapid reversible equilibrium SO₄⁻ + H₂O = OH + H⁺ + SO₄⁻. At (H⁺)(SO₄⁻) ≥ 0.02 the position of the equilibrium lies far to the left and sulfate radicals recombine to form persulfate ions, and ultimately leave the system as molecular oxygen. The tentative assumption is made that HSO₅⁻ is initially formed in the k_2' path, but that it is destroyed rapidly, forming molecular oxygen by a radical induced chain decomposition.

Introduction

The present paper² deals with the possibility of generating sulfate and hydroxyl radicals by the photolysis of aqueous peroxydisulfate ion, hereafter referred to as persulfate ion. Experiments using S³⁵ and O¹⁸ and kinetic data, all reported below, yield more detailed information about the mechanism of the photolytic decomposition of persulfate ion than has hitherto been available.³⁻⁵ Of particular interest in this study are observations which seem to yield direct information about reaction 1, the hydroxyl-sulfate radical interconversion, a process of major interest both in its own right and in the field of radiation chemistry where aqueous sulfuric acid has most commonly been used as a solvent.

$$SO_4^- + H_2O \longrightarrow OH + H^+ + SO_4^{--}$$
(1)

Of interest also is the implication of the present work that hydroxyl radical is not converted to its conjugate acid H_2O^+ , at least in sulfuric acid solutions, although this species recently has been

This work was supported by the Atomic Energy Commission.
 Later papers in this series will be concerned with the generation

of these radicals by the thermal decomposition of persulfate ion.

(3) L. J. Heidt, J. B. Mann and H. R. Schneider, J. Am. Chem. Soc., 70, 3011 (1948).

(4) L. J. Heidt, J. Chem. Phys., 10, 297 (1942).

(5) R. H. Crist, J. Am. Chem. Soc., 54, 3939 (1932), and earlier papers in this series.

postulated to explain the results of certain radiation experiments.⁶

Experimental

Materials.—The water used in the photolysis experiments and in the recrystallization of chemicals was redistilled from alkaline persulfate solution, with the steam being transported with an oxygen carrier gas through a furnace maintained at $800-900^{\circ}$. All chemicals were of a reagent grade and, except for the J. T. Baker 72% perchloric acid and Baker and Adamson concentrated sulfuric acid, they were recrystallized at least once before use. The water enriched in H₂O¹³ was obtained from the Stuart Oxygen Co. Before use, it was also purified by the procedure outlined above. The O¹⁵ content was determined by mass spectrometry, using the carbon dioxide equilibration procedure. Radioactive S²⁵ was obtained from the Isotope Specialties Co., Inc., in the form of 0.17 N sulfuric acid, with a specific activity of 735 μ c./ml. It was used without further purification. The Rate of Photolysis.—Except in the quantum yield

The Rate of Photolysis.—Except in the quantum yield experiments, the reaction vessels were test-tubes made of No. 791 Vycor glass with a diameter of 3.5 cm. and a well thickness of approximately 2.0 mm. During an experiment the vessels were capped with cork stoppers covered with aluminum foil, with each stopper containing a glass tube and ground joint which could be opened so that aliquots of the solution could be removed with a pipet for analysis. The source of irradiation was a 4-watt low pressure G.E. germicidal lamp (G4T4/1) equipped with a 58G827 ballast. Since 96% of the ultraviolet radiation from this lamp is of wave length 2537 Å., and since persulfate ion does not absorb appr ciably at the longer wave lengths emitted by the lamp, the lamp may be considered as a monochromatic

⁽⁶⁾ J. Weiss, Experientia, XII, 280 (1956).

the methods of analysis.

periments, the method of separation was tested and found

light source. In general, two experiments were performed simultaneously, with the two vessels arranged at equivalent to be satisfactory. positions approximately 8.5 cm. from the center of the lamp. Aside from preliminary experiments not reported here, the persulfate concentration was limited to the region 0.0005- $0.0025 \ M$. In the more dilute solutions there was essentially no diminution in the intensity of the light as it passed through the reaction vessel. At the maximum persulfate concentration the error arising from neglect of the internal screening may have been as large as 20%, a figure several screening may have been as large as 20%, a light several times larger than the irreproducibility arising from variations in light intensity, aging of the lamp and analytical errors. Below 0.0005 *M* persulfate, errors larger than 10% would have been encountered because of inadequacies in

In each photolysis experiment 25.0 ml. of solution was used, with four or five 3.0-ml. aliquots being removed at suitable time intervals for analysis. The iodometric method of analysis yielded a separate determination of persulfate ion, HSOs⁻ and hydrogen peroxide.⁷ Measurement of Quantum Yield.—The quantum yield

experiments were carried out using the uranyl oxalate actinometer, with oxalic acid and uranyl oxalate concentrations at 0.005 and 0.001 M, respectively. The procetrations at 0.005 and 0.001 M, respectively. The proce-dure was that described by Noyes and Leighton,⁸ with the exception that the undecomposed oxalate was determined spectrophotometrically.⁹ Six measurements were carried out using 0.0025 M persulfate solutions containing 0.71 Msodium perchlorate and 0.29 M perchloric acid; these are conditions which should yield the same ionic strength as that employed in the experiments presented in Fig. 1. As-suming a quantum yield of 0.65 for the uranyl oxalate actinometer, we obtain a quantum yield of 0.79 \pm 007 for the persulfate photolysis. The accuracy of this value may be less than the reproducibility, because the solutions may be less than the reproducibility, because the solutions were not stirred during the photolysis.

 S^{35} Exchange — The photolysis of solutions containing $H_2S^{35}O_4$ was carried out using the reaction vessels and techniques described above, with the aliquots serving for both iodometric analysis and radio-chemical analysis for S^{35} . After removal from the reaction vessel, each 3.0-ml. aliquot was added to a 15.0-ml centrifuge cone where the sulfate ion was precipitated with excess 1.0 M BaCl₂, removed by centrifugation and discarded. To ensure complete removal of the labeled sulfate ion, a small amount of inactive sulfuric acid then was added, and the sulfate ion was again precipitated and discarded. The concentration of undecomposed persulfate now was determined iodometri-cally in the usual manner with only a fraction of the total solution. The remainder of the solution, now of known persulfate concentration, was added to a second 15.0-ml. centrifuge tube containing excess $BaCl_2$ solution and enough inactive persulfate to reduce the S³⁵ concentration to an activity convenient for handling and counting. The persulfate ion was decomposed completely by heating the sample in a water-bath and the barium sulfate which was produced was washed twice with ethanol and then trans-

produced was wasned twice with ethanol and then trans-ferred as a slurry to an aluminum counting disk. After drying, the surface of the precipitate was "smoothed" by applying pressure with a steel piston of the same size as the indented portion of the counting disk.¹⁰ Each sample contained more than 20 mg. BaSO₄/cm.², a value well above "infinite thickness," and consequently the measured activity was directly proportional to the specific activity of the sample. The S³⁵ analysis was per-formed using a Nuclear Chicago Corn. flow counter and a specific activity of the sample. The S⁵⁰ analysis was per-formed using a Nuclear Chicago Corp. flow counter and a Berkeley Model 100 decimal scaler. In general, the back-ground was approximately 200 counts/min. In a given experiment the activity of the samples varied from back-ground activity, when the samples were removed at short times, to values as large as 3000 counts/min. at later times in the experiment. Before correlate out the concernent in the experiment. Before carrying out the exchange ex-

(10) A. W. Adamson and R. G. Wilkins, ibid., 76, 3379 (1954).

Oxygen Exchange.-In these experiments the Vycor cell was equipped with a ground joint and stopcocks so that the solutions could be evacuated to remove dissolved air before photolysis. The solvent water contained O^{18} at approximately a sevenfold enrichment; there was no appreciable dilution in a given experiment by addition of either the solid reagents or the small amount of concentrated perchloric acid. Condensation of water in the cooler regions near the top of the vessel was prevented by gentle warming of this portion of the apparatus with a nichrome heater. In a given experiment the photolysis was continued until ap-proximately half of the persulfate had been decomposed. The oxygen was then transferred to a gas sampling tube and analyzed with a Nier type mass spectrometer. The re-sidual solution was analyzed for persulfate in the usual manner.

Results

At the fixed light intensity employed in the present work the rate of disappearance of persulfate in any given experiment was represented by a rate constant k defined in terms of equation 2

$$\frac{d(S_2O_8^{--})}{dt} = k(S_2O_8^{--})$$
(2)

Numerical values of k were calculated from the slope of the straight line drawn through the points in a plot of $\ln (\tilde{S}_2 O_8^{--})$ versus time. As the first four entries in Table I indicate, in alkaline solution at fixed ionic strength k proved to be independent of the persulfate concentration, although a slight decrease in rate might have been anticipated at the maximum concentration. At any given ionic strength k was found to increase slowly with increasing acidity, with the over-all increase being somewhat less than a factor of two. This trend is best illustrated by a comparison of experiments 4-7, but it may also be seen in experiments 8, 9 and 11 and in 3, 15 and 16. Experiments 1, 8 and 9 and

TABLE I

PHOTOLYSIS	OF	AQUEOUS	PERSULFATE	TON	ат 32 ±	- 2°
1010101010	01	1100000	THEOLEFAIR	TOU	AL 02 -	- <i>4</i>

~ -					
No.	$(S_2O_8^{}), M$	pH	μ^a	Medium	$k \times 10^{5},$ sec. -1
1	0.0025	13.3	0.20	0.2 N NaOH	5.59
2	.0005	13.3	. 20	.2 N NaOH	5.30
3	.0005	13.3	.20	.2 N NaOH	5.30
4	.0010	13.3	. 20	.2 N NaOH	5.60
5	.0010	6.75	. 20		6.42
6	. 0010	3.0^{b}	.20		7.21
7	.0010	0.7	. 20	$.2 N HClO_4$	7,42
8	.0025	13.3	1.0	.2 N NaOH	4.84
9	.0025	13.3	1.0	.2 N NaOH	4.96
10	.0025	5 - 2.5	0.0	Unbuffered	7.10
11	.0025	5-2.5	1.0	Unbuffered	6.15
12	.0025	3.0^{b}	1.0	$0.1 \ M \ Na_2SO_4$	5.63
13	.0025	3.0%	1.0	$.1~M~{ m Na_2SO_4}$	5.66
14	.0025	0.5	1.0	$.29 \text{ HClO}_4$	$5.26 \pm$
					0.19°
15	.0005	0.5	1.0	$.29 \text{ HClO}_4$	7.00
16	. 0005	0	1.0	$1.0 N \text{ HClO}_4$	7.20
17	.0005	3.0^{b}	0.2		8.43

^a The ionic strength, defined as $\mu = 1/2 \Sigma C_i Z_i^2$, was adjusted by addition of sodium perchlorate. ^b These solutions contained phosphate buffers. Based on six experiments carried out under these conditions.

10 and 11 suggest that there is a decrease in k with increasing ionic strength, an effect noted by earlier workers. The remaining experiments in the table

⁽⁷⁾ The iodometric method of analysis will be described in detail in a paper, The Aqueous Chemistry of Inorganic Free Radicals. The Kinetics and Mechanism of the Reaction of Peroxydisulfate Ion and Bromide Ion in Aqueous Solution, to be submitted to the J. Am. Chem. Soc. for publication.

⁽⁸⁾ W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, Chapter 2.

⁽⁹⁾ J. N. Pitts, J. P. Margerum, R. P. Taylor and W. Prim, J. Am. Chem. Soc., 77, 5499 (1955).



Fig. 1.—Bisulfate inhibition at $32 \pm 2^{\circ}$: \bigcirc , (H⁺) = 0.27 \pm 0.02; \times , (H⁺) = 1.25.

serve to show that neither hydrogen ion nor sulfate ion alone influences the rate very appreciably although, as we shall see below, the presence of both ions produces a considerable inhibition. Experiments 11, 12 and 13 show that at pH 3, 0.10 Msodium sulfate produces at most a minor decrease in rate. In experiments 15, 16 and 17 at higher acidity there is no evidence of inhibition by perchloric acid, a result reported by Heidt.⁴

The marked inhibition resulting from the presence of appreciable concentrations of both hydrogen and sulfate ions is illustrated by the data presented in Fig. 1, where we have plotted k versus the product $(H^+)(SO_4^-)$. In the majority of these experiments carried out at $\mu = 0.92 \pm 0.08$ and (H⁺) = 0.27 ± 0.02 only relative values of (H⁺)(SO₄⁻) are known with any accuracy. Since the hydrogen ion concentration was constant, the data really represent only a systematic variation in sulfate ion concentration. A more extensive study of the effect of variation in hydrogen ion concentration is now under way and will be presented in a later publication. The absolute values of the quantity $(H^+)(SO_4^-)$ are rendered uncertain because of the necessity of correcting for the presence of unionized bisulfate ion, a species whose concentration was calculated by assuming rather arbitrarily that the second dissociation quotient of sulfuric acid had a value of 0.15 in the medium under consideration.¹¹ The remaining four experiments presented in Fig. 1 were carried out at $(\hat{H^+}) = 1.25$, and $\mu =$ 2.0. In view of the uncertainty regarding the effect of medium upon the extent of dissociation of bisulfate ion, the second dissociation quotient of

sulfuric acid was regarded as an adjustable parameter in these experiments; the value of 0.21 was chosen so that the points would fall on the smooth curve drawn through the data at $\mu = 0.92$. Although the four experiments confirm qualitatively the existence of bisulfate inhibition at the high acidity, the rate constants may not be of high accuracy since it was necessary to make a correction for the dark reaction using the thermal data presented below. In the extreme case the correction was as large as 40%. The major point of interest in Fig. 1 is that saturation inhibition would appear to reduce the rate not to zero but to a value of appreximately 20% of that observed in the absence of appreciable concentrations of hydrogen and sulfate ions. This behavior obviously suggests that upon photo-excitation the persulfate ion decomposes by either of two parallel paths only one of which is subject to inhibition. For convenience in later discussion we will refer to the inhibition as bisulfate inhibition, although actually it is probably a coincidental feature of the system that inhibition arises at a product of hydrogen and sulfate ion concentrations which corresponds to a quite appreciable bisulfate concentration. Also it will be convenient to refer to the bisulfate inhibition reaction path as the k_1' path, to designate the bisulfate insensitive path as the k_2' path, and to define a rate constant k_0 which refers to the photolysis rate in the absence of bisulfate inhibition as $k_0 = k_1' + k_2'$. The numerical value of k_2' cannot be obtained with any certainty from Fig. 1, since an extrapolation to infinite $(H^+)(SO_4^{--})$ would be required. However, by plotting k vs. $1/(H^+)(SO_4^{--})$, as in Fig. 2, a fairly accurate value of k_{2}' may be obtained from only a short extrapolation to a zero value of the abscissa. The value of k_2' so obtained is indicated by the horizontal line in the lower right-hand corner of Fig. 1. The significance of the theoretical curve in Fig. 1 will be discussed below.

Earlier studies have shown that the thermal decomposition of persulfate also proceeds by two reaction paths. Both of these are kinetically first order in persulfate concentration, one is pH independent and the second, important above a pH of 3, is first order in hydrogen ion. Following the nomen-clature of Kolthoff and Miller,¹² the rates of the two thermal paths may be characterized by the quantities $k_1(S_2O_8^{--})$ and $k_2(H^+)(S_2O_8^{--})$. Under the conditions employed at the higher acidity in the experiments presented in Fig. 1, calculations indicate that the k_2 path would account for more than 99% of the total thermal reaction. By following the thermal reaction for long periods of time it was possible to study the rate of this process under conditions identical with those employed in the photolysis studies. In three experiments at $T = 32.0^{\circ}, \mu = 2.0, (H^+) = 1.25 \text{ and } (H^+) (SO_4^{--})$ equal to $9.4 \times 10^{-2}, 1.95 \times 10^{-2} \text{ and } 6.5 \times 10^{-2}$, it was established that the k_2 thermal path was not inhibited by bisulfate ion. Under these conditions k_2 was found to have the value 5.73 \times 10⁻⁶ liters mole⁻¹ sec.⁻¹.

In the experiments under consideration at (H^+)

(12) I. M. Kolthoff and I. K. Miller, ibid., 73, 3055 (1951).

⁽¹¹⁾ In designing these experiments it was our intention to work at variable sulfate ion concentrations, but with fixed values of $(H^+) = 0.286$ and $\mu = 1.0$. At the time it was assumed that the second dissociation constant of sulfuric acid had the value 0.38, on the basis of data presented in a paper by M. Kerker, J. Am. Chem. Soc., **79**, 3664 (1957). While this value may be a good choice for pure sulfuric acid, the system considered by Kerker, the calculations and data later presented by C. F. Base, Jr., *ibid.*, **79**, 5611 (1957), suggested that the value of 0.15 ± 0.05 might represent a better choice for a medium containing large concentration of sodium ion.

= 1.25, the rate constants for both the thermal and photolytic reactions were based upon the rate of disappearance of persulfate ion. However, it should be noted that quite different reaction products were produced in the two series of experiments. In the photolysis reactions only oxygen and sulfate ion were formed, whereas in the thermal reaction HSO_5 was the predominant product. Despite this apparent difference, further experiments showed that HSO_5^- might also have been an initial, but unstable product in one or both of the paths of the photolysis reaction. This possibility was revealed by studying the photolysis of a solution which initially contained $(S_2O_8^-) = 0.0014$, $(HSO_5^-) = 0.0009$ and $(H^+) = 1.25$. In this solution the persulfate ion was photolyzed at about the expected rate, but the HSO₅- disappeared very much more rapidly, and soon reached a concentration which was undetectably small. Calculation indicated that the quantum yield for the disappearance of HSO_5^- would greatly exceed unity, even if based upon the absorption of light by both the persulfate and HSO₅- ion. Evidently under these photolytic conditions HSO₅- is consumed by a quite efficient chain decomposition reaction.¹³

Previous studies have shown that there is no exchange of persulfate and S³⁵ labeled sulfate under a variety of experimental conditions, including temperatures high enough to lead to decomposition of the persulfate ion.¹⁴⁻¹⁷ In the experiments summarized in Table II it was found that under photolytic conditions the S³⁵ exchange could readily be observed, but that the rate of exchange became appreciable only when the photolysis was inhibited by bisulfate ion. On the basis of the mechanism and equations developed in the Discussion section, it may be concluded that the rate of sulfur exchange should be characterized by a rate constant k_s defined in terms of equation 3.

$$-\ln(1 - F_{\rm B}) = k_{\rm S}t + \frac{k_{\rm S}}{k}\ln\left(\frac{a+b}{a} - \frac{b}{a}e^{-kt}\right) \quad (3)$$

In equation 3 the various undefined symbols have the following significance: a = the total gram atoms of sulfur initially present as sulfate and bisulfate ion; b = total gram atoms of sulfur initially present as persulfate ion; $F_{\rm B} = (S_{\rm B} - S_{\rm B0})/(S - S_{\rm B0})$, where $S_{\rm B0}$ and $S_{\rm B}$ are the specific activity of the persulfate ion at time zero and t, respectively, and S = the specific activity which would be calculated for the persulfate ion, assuming complete isotopic equilibrium in the system.

Tracer experiments also were carried out using unlabeled persulfate ion in O^{18} enriched water. In each experiment the persulfate was photolyzed until at least half had been decomposed and the

(13) Experiments have also shown that at $T = 50^{\circ}$ and (H⁺) = 0.10, HSO₆⁻ also disappears rapidly in the thermal system, although it would be relatively inert at a higher acidity. The significance of these observations will be discussed in a later paper.

(14) P. C. Riesebos and A. H. W. Aten, Jr., J. Am. Chem. Soc., 74, 2440 (1952).

(15) H. Elkeles and C. Brosset, Svensk, Kem Tidskr., 65, 26 (1953).
(16) R. L. Eager and K. J. McCallum, Can. J. Chem., 32, 692 (1954).

(17) None of the studies in the literature were carried out in the pH range 2-3, where exchange may be observed, as indicated in the later sections of this paper.



oxygen which had accumulated was then subjected to mass spectrometer analysis. In all, three such experiments were completed, and the results are listed in column four of Table III as N_{obsd} , the observed atom fraction of O¹⁸ in the molecular oxygen.

TABLE II

Photolytic Induced Exchange of Sulfate and Persulfate Ion

All experiments were at $T = 32 \pm 2^{\circ}$, $\mu = 1.0$ and (S₂O₅⁻) = 0.0025

No.	(H ⁺)(SO4 ⁻)	Medium	$k_{\rm S} \times 10^{5}$, sec. ⁻¹	$\begin{array}{c} k \times \\ 10^5, \\ \mathrm{sec.}^{-1} \end{array}$	$(kg + k) \times 10^{5}, sec. ^{-1}$
549	0.026	$0.29 N HClO_4$	3.93	1.08	5.01
548	.0045	$.29 N HClO_4$	3.35	2.00	5.35
550	< .0002ª	$.29 N HClO_4$	0.1	5.25	5.4
569	. 0000	.20 N NaOH	$<1.7 \times$	4.94	4.94
			10-8		

^a An average value for an experiment where (H⁺)(SO₄⁻) varied over the range 1.3 \times 10⁻⁵ to 2.5 \times 10⁻⁴; the corresponding value of k_s was not determined with high accuracy.

TABLE III

The Photolysis of Persulfate in O¹⁸-enriched Water In all experiments $(S_2O_8^-)_0^a = 0.0025, \mu'='0.92 \pm 0.08, \mu'='0.08, \mu'='0.08,$

$H^{+} = 0.29$ and $T = 32 \pm 2^{\circ}$				
No.	(H ⁺)(SO ₄ -)	$k \times 10^{5}$, sec. $^{-1}$	Nb (obsd.)	N (caled.)
524	0.026	1.10	0.0196	0.0199
523	.0045	2.18	.0234	.0252
522	< .0002	5.00	.0293	.0283
^a Initial	concentration.	^b Atom	fraction of	O^{18} in the O_2 .

Discussion

In view of the satisfactory reproducibility and a quantum yield of less than unity, it will be assumed that in the photolysis persulfate ion is not consumed by a chain decomposition although, as we shall suggest below, chain processes may destroy a possible reaction intermediate, the HSO_5^- ion. Any reasonable interpretation of the present data would seem to require that the photolysis proceed by two parallel reaction paths. Other alternatives proposed by earlier workers are no longer tenable, since they would fail to account for the results of the S³⁵ and O¹⁸ experiments. The mechanism to be presented below provides an explanation for not only our own data but the other data in the literature as well, with the possible

exception of Heidt's observation that perchloric acid inhibited the photolysis.⁴ Even here the results may well be in agreement with our own, since the supposed perchloric acid inhibition was not present in the initial stages of the experiment and was probably caused by the reaction product sulfuric acid formed in his more concentrated persulfate solutions.

The mechanism to be proposed for the more important k_1' photolysis path involves the generation of sulfate and hydroxyl radicals and, in general, is entirely analogous to that suggested for the k_1 path of the thermal decomposition,¹² except for the mode of activating the persulfate ion. As a justification for this procedure, there is a wide variety of experimental evidence, but only a fraction of this is available in the present paper and in the chemical literature.¹⁸ Consequently, several of the more pertinent unpublished observations will be presented in summary at this point. Perhaps most important is the observation that under appropriate conditions the k_1 thermal path induces the sulfur exchange of sulfate and persulfate ion, just as the k_1' path does.¹⁹ Of almost equal significance is the fact that both the k_1 and k_1' reactions induce the homogeneous hydrogenation of persulfate ion, a chain reaction which is almost certainly initiated by a radical attacking the hydrogen molecule. Lastly, we note that the O¹⁸ tracer experiments indicate that both reactions generate molecular oxygen which originates not in the persulfate ion, but in the water solvent.

A detailed although somewhat oversimplified mechanism for the k_1' path may be presented in terms of the equations

$$S_2O_8^{--} \xrightarrow{k_1'} 2SO_4^{--}$$
 rate determining (4)
 k_3

$$H_2O + SO_4 - \xrightarrow{n_3}_{k_4}OH + H^+ + SO_4^{--}$$
 (5)

$$2\mathrm{SO}_4^- \xrightarrow{k_5} \mathrm{S}_2\mathrm{O}_8^{--} \tag{6}$$

$$2OH \xrightarrow{\mathcal{K}_6} H_2O_2 \tag{7}$$

$$\begin{array}{cccc} H_2 O_2 &\longrightarrow & H_2 O_2 + \frac{1}{2} O_2 & (3) \\ H_2 O_2 + S_2 O_8^{--} &\longrightarrow & 2H^+ + 2SO_4^{--} + O_2 & (9) \end{array}$$

Of major importance is the assumption that the interconversion of sulfate and hydroxyl radical by reaction 5 closely approaches equilibrium, despite the very short half-lives of the radical species involved. Reaction 5 would then provide for sulfur exchange between sulfate radicals and labeled sulfate ion and for the production of labeled persulfate under conditions where reaction 6 was favored. Reactions 5 and 6 also account for the apparent inhibition of the photolysis of bisulfate ion, since at high values of $(H^+)(SO_4^{--})$ the position of the equilibrium in reaction 5 will be far to the left, sulfate radicals will predominate, and persulfate

will be regenerated by reaction 6. Conversely, low $(H^+)(SO_4^-)$ would lead to the formation of hydroxyl radicals and to the production of hydrogen peroxide by reaction 7, except in alkaline solution, a restriction which will be discussed below.

Equations 8 and 9 do not carry mechanistic significance; they serve only to indicate that hydrogen peroxide may disappear from the system by at least two paths, only one of which involves the concurrent consumption of persulfate ion. Both of these reactions are rapid enough so that the steadystate concentration of hydrogen peroxide would be undetectably small. They proceed by rather complicated chain mechanisms which we have studied in some detail in the thermal system. It will be necessary to present certain conclusions arising from these studies if the more subtle features of the photolysis are to be appreciated, despite the fact that this brevity and absence of experimental data may make the conclusions seem rather arbitrary. The point of interest is whether hydroxyl radicals may not interact to form oxygen atoms, an exothermic process first proposed by J. Weiss 20

$$2OH \longrightarrow H_2O + O \tag{10}$$
$$2O \longrightarrow O_2$$

It is our conclusion that something approaching reaction 10 must occur in alkaline solution, although the actual mechanism may involve catalysis by impurities or in other ways be more complicated than equation 10 would suggest. Under these conditions, i.e., at 0.2 N alkali, the rate of disappearance of persulfate would be a true measure of the photolysis rate, with the rate increasing slightly with decreasing ionic strength, a salt effect to be expected for a reaction of the present sort. Conversely, in acid solution formation of peroxide by reaction 7 is relatively efficient, at least at low ionic strength, perhaps because of the relatively low impurity level. As the data in Table I indicate, under these conditions there is a considerable increase in the apparent rate of photolysis because of the secondary consumption of persulfate by peroxide in reaction 9.²¹ This secondary decomposition is never particularly efficient, since it never reaches a value of more than 50% that calculated, assuming reactions 7 and 9 to be quantitative. At an ionic strength of unity, the conditions employed in the S³⁵ and bisulfate inhibition, it is small enough so that it may be ignored in the calculations outlined below. Lastly, we note that the over-all inhibition in rate of photolysis by inert electrolyte observed by earlier workers³⁻⁵ was caused in part by an effect on the primary process and in part by a decrease in the extent of the secondary decomposition, reaction 9.

⁽¹⁸⁾ Unpublished experiments carried out in this Laboratory include kinetic studies of the reaction of persulfate with molecular hydrogen, with hydrogen peroxide, and with bromide ion.

⁽¹⁹⁾ Experiments by Dr. Maak-Sang Tsao indicate that the exchange occurs only at pH of 2-3, as expected. In more alkaline solution the sulfate radical is converted to the hydroxyl radical, in more acidic solutions the acid-catalyzed thermal path predominates and produces reaction intermediates which act as efficient radical scavengers.

⁽²⁰⁾ Weiss' point of view is perhaps most clearly presented in the article by J. Weiss, Trans. Faraday Soc., 36, 856 (1940).

⁽²¹⁾ In the thermal system where entirely analogous processes occur, it has been possible to detect the magnitude of the persulfate peroxide reaction by the diminution in rate of disappearance of persulfate caused by the addition of bromide ions. Bromide ion acts as a scavenger for hydroxyl radical, thus preventing the formation of hydrogen peroxide and its subsequent reaction with persulfate. A summary of this work may be found in the abstracts of the papers presented at the American Chemical Society meeting in San Francisco on April 13-18, 1958.

Before the exchange and inhibition experiments may be considered quantitatively, it is necessary to postulate a tentative mechanism for the k_2 photolysis path. As a guide we note that, by definition, the process is not inhibited by bisulfate ion. Also, apparently the process does not induce the sulfur exchange of sulfate and persulfate ion. Finally, and perhaps most important in influencing our choice of mechanism, there is the unusual feature that the molecular oxygen generated by this path appears to have an O¹⁸ content which is the average of that of the persulfate ion and the water solvent. This latter conclusion has strong experimental support. If the alternative assumption were made that the oxygen atoms in the molecular oxygen produced by the k_2' path all originated in the persulfate ion, then k_2' would have only onehalf the value of 9×10^{-6} sec.⁻¹ obtained from the ordinate intercept of Fig. 2. While there is some scatter of the points in Fig. 2, it is very difficult to believe that the true intercept has a value half that which has been chosen, especially since any theory which we have developed would not predict an abrupt change in slope at low abscissa values.

The O¹⁸ data may be understood readily in terms of the formation of an unstable intermediate, the HSO_6^- ion, which has solvent labelling only on the terminal peroxide atom, and which ultimately produces molecular oxygen containing both peroxide atoms, just as hydrogen peroxide does.²² The following mechanism is compatible with this concept. It is presented in detail, despite its tentative nature, primarily to permit a more ready visualization of the route followed by the oxygen atoms. To this end structural formulas and in some instances equations for half reactions have also been adopted.

$$S_{2}O_{8}^{-} + H_{2}O^{18} \xrightarrow{k_{2}'} [O \xrightarrow{S} O \xrightarrow{O} O^{18}]^{-} + H^{+} + SO_{4}^{-} (11)$$

$$O \xrightarrow{I} O \xrightarrow{I} O^{-} O^{18}]^{-} + SO_{4}^{-} (or OH) \xrightarrow{I} O^{-} O^{18} \xrightarrow{I} O^{-} O^{-} O^{-} O^{18} \xrightarrow{I} O^{-} O^{-} O^{18} \xrightarrow{I} O^{-} O^{-} O^{-} O^{18} \xrightarrow{I} O^{-} O^$$

$$e^{-} + H^{+} + [O - S - O - O^{18}]^{-} \longrightarrow H_2O^{18} + SO_4^{-}$$
 (14)

Despite the apparent complexity of reactions 12, 13 and 14, it may be noted that they constitute a chain mechanism entirely analogous to that usually postulated for the decomposition of H_2O_2 , with HSO_5^- , HSO_5 and SO_4^- replacing H_2O_2 , HO_2 , and OH, respectively.

(22) J. P. Hunt and H. Taube, J. Am. Chem. Soc., 74, 5999 (1952).

It is now possible to attempt to calculate the rate under the conditions of bisulfate inhibition covered by the data presented in Fig. 1. Before proceeding, it should be recognized that a priori there is every reason to believe that HSO_5^- may be formed by combination of hydroxyl and sulfate radicals, a process not included in the simplified mechanism presented above

$$OH + SO_4 \xrightarrow{k_7} HSO_5 \xrightarrow{} (15)$$

Reaction 15 would presumably reach its maximum importance at intermediate bisulfate concentrations where hydroxyl and sulfate radicals would be present at roughly equal concentrations. The $HSO_5^$ arising from this source would presumably disappear rapidly in the chain process discussed above, along with that produced by the k_2' path. When reaction 15 is considered along with equation 4–8, it is possible to derive equation 16, making only the usual steady-state approximations and assuming equilibrium in reaction 5.

$$k = k_{1}' + k_{2}' - \frac{k_{1}'}{1 + \frac{k_{6}K^{2}}{k_{6}(\mathrm{H}^{+})^{2}(\mathrm{SO}_{4}^{-})^{2}} + \frac{2k_{7}K}{k_{6}(\mathrm{H}^{+})(\mathrm{SO}_{4}^{-})}}$$
(16)

Here, K is the equilibrium quotient for reaction 5, and the other constants have previously been defined as symbols over the appropriate equations. Neglect of reaction 15 would have resulted in a simplification of the last term of equation 16, the quantity which represents the decrease in rate caused by bisulfate inhibition. The simplification referred to would have been the disappearance of the quantity $2k_7K/k_5(H^+)(SO_4^-)$, a result arising from the assumption that k_7 equals zero. In this simplified form the best fit which may be made of the points in Fig. 1 is apparently somewhat outside of the limit of error of the experiment; the inhibition is not as pronounced as that required by an inverse term $(\dot{H}^+)^2(SO_4^-)^2$. However, if the reasonable assumption is made that $k_7 = 2k_6 =$ $2k_5$, with the factor of two arising from the greater statistical probability for collision of unlike particles, the theoretical line calculated from equation 16 without simplification approaches within the limit of error of the experimental points.

As a further test of the mechanism we may now consider the quantitative features of the S³⁵ exchange. Although the desired relationship may be derived algebraically, it is possible to see intuitively that the rate of the sulfur exchange should exactly equal the decrease in rate caused by bisulfate inhibition, since both phenomena are produced by the occurrence of reaction 6. In the nomenclature employed above the desired relationship may be written as $k_s = k_0 - k$ and tested, as in the last column of Table II, by the constancy of $k_s + k$. The derivation of the equation defining k_s may be made readily by following the methods of Luehr, Challenger and Masters, and integrating equation 4 of their paper for the special case corresponding to our mechanism.²³

(23) C. P. Luchr, G. E. Challenger and B. J. Masters, *ibid.*, **78**, 1314 (1956). In the notation of these authors our mechanism corresponds to the special case where $R_1(t) = 0$, v(t) = constant, $R_2 = 2k_0 - k(S_2O_5^{-})$, and $R_3 = 2k(S_2O_5^{-})$.

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Lastly, a calculation may be made of the O¹⁸ content of the molecular oxygen produced under various conditions. Again assuming the simplified mechanism which ignores reaction 15, in any given experiment the fraction of the oxygen coming from the k_1' path will be $(k - k_2')/k$, and the fraction from the k_2' path k_2'/k . With the atom fraction of O¹⁸ in the solvent and persulfate equal to 0.0307 and 0.0041, respectively, the calculated atom fraction of O¹⁸ in the molecular oxygen is given by equation 17

$$N_{\text{(calod)}} = \frac{0.0307(k - k_2')}{k} + \frac{0.0174k_2'}{k} \quad (17)$$

The agreement with experiment at high and low $(H^+)(SO_4^-)$ is within the limit of error, but at an intermediate value of $(H^+)(SO_4^-)$, $N_{(calcd)}$ again deviates appreciably from experiment in the direction to be anticipated because of participation of reaction 15.

At this point some consideration should be given to the choice of formula for the sulfate radical and the possible inclusion of the H₂O⁺ ion in the proposed reaction mechanism. The formula SO_4^- has been adopted since HSO₄ would almost certainly be a stronger acid than HSO₄⁻, although perhaps not as strong as HClO₄. Assuming this formula it is then informative to note that the ratio $(H_2O^+)/(SO_4^-)$ is *p*H independent.

$$\mathrm{SO}_4^- + \mathrm{H}_2\mathrm{O} \xrightarrow{\longrightarrow} \mathrm{SO}_4^- + \mathrm{H}_2\mathrm{O}^+ \tag{18}$$

In solutions containing relatively large concentrations of both hydrogen and sulfate ion our mechanism provides an adequate explanation for the S^{35} exchange and the bisulfate inhibition only if the H_2O^+ ion is unimportant compared to the sulfate radical. Under these conditions the ratio $(H_2O^+)/$ (SO_4^{-}) is presumably smaller than unity, although it is possible that the H_2O^+ ion remains undetected, in part because it is kinetically inert compared to other radicals in the system. In weakly acidic solutions but still at high sulfate ion concentration, where our observations suggest that the sulfate radical is unimportant, the H₂O+ ion must be correspondingly even less important, since the ratio of the concentrations of the two species must be constant at any given sulfate concentration. In summary, it may be concluded that in our system the H₂O⁺ ion is not an important species, being unstable with respect to either the sulfate or hydroxyl radical. Unfortunately, our data do not permit any conclusion to be drawn regarding the possible presence of H_2O^+ in an acidic system not containing sulfate ion.

The present results may be of some importance in the field of radiation chemistry. In $0.8 N H_2SO_4$, the aqueous medium most commonly employed, it is generally assumed that along with other products, the radiation produces the "hydroxyl radical," although it has long been recognized that "the formula might better be written $H_2SO_5^-$ or HSO_4 , and it is called OH throughout this paper merely to avoid confusion."²⁴ Although the recognition of this complexity may be quite wide-spread, many workers have studied the competition of several species for the "hydroxyl radical" and on the basis

(24) A. O. Allen, Radiation Research, 1, 85 (1954).

of their experiments have tabulated relative values of rate constants. Although the hydroxyl-sulfate radical equilibrium may be established in our system where the only competing process is bimolecular reactions of radicals, it is not evident that equilibrium would be established in the presence of high concentrations of radical scavengers. The possibility therefore exists that the relative rate constants for the different scavengers are in themselves composite quantities, representing the relative reaction rates of the scavenger with more than one radical.²⁵

Very recently it has been reported that both persulfate ion and HSO_5^- are formed in the Co⁶⁰ bombardment of 2.5 M sulfuric acid and in lesser but still detectable amounts in 0.4 M acid.²⁶ If our interpretation of the photolysis data is correct persulfate ion should be produced whenever $(H^+)(SO_4^-)$ exceeds a value of about 0.02. The failure to detect persulfate ion after irradiation of such dilute solutions suggests it may be destroyed immediately after formation by other irradiation products. Plans have been made to test this postulate by carrying out S³⁵ experiments of the sort described above in irradiated systems.

Acknowledgment.—The tracer experiments were made possible through the use of Professor Arthur W. Adamson's counting equipment and a mass spectrometer designed and constructed under the direction of Professor Sidney W. Benson. Mr. Concetto R. Giuliano designed and built the photolysis apparatus and carried out some valuable preliminary photolysis experiments. We are also indebted to Professor Adamson for his advice regarding the handling of the S³⁵ and to Professor Henry Taube for several very helpful suggestions regarding the interpretation of the O¹⁸ experiments.

DISCUSSION

H. TAUBE.-Does your work furnish evidence for the extent to which the association of H⁺ and OH takes place?

W. K. WILMARTH.—This point was not discussed in detail in the oral presentation, but it is covered in the complete paper.

H. TAUBE.—Is it at all certain that the reaction producing the intermediate which reduces $S_2O_8^-$ is sensitive to ionic strength? Presumably an impurity in the NaClO₄ could cause the decrease in rate of formation of the intermediate.

W. K. WILMARTH.—Rather extensive kinetic experiments have been carried out in an effort to learn the mechanistic details of a seemingly simple reaction, the self-destruction of hydroxyl radicals. Despite the rather large amount of data now available, no completely satisfactory mechanism can yet be written. However, it is clear that the fate of hydroxyl radicals depends to a considerable extent upon the presence of trace impurities, as you suggest. By contrast, sulfate radicals appear to be well behaved species, in so far as their interaction with impurities is concerned.

In summary, it can be said that the production of peroxide is a reasonably efficient process if the ionic strength is low and the acidity great enough to dissolve heavy metal hydroxides. However, at pH 6 our kinetic studies should have revealed the formation of hydrogen peroxide; it does not seem to form under these conditions or in more alkaline solutions. At present, our only explanation is based on the assumption that heavy metal ions are particularly efficient

(26) M. Daniels, J. Lyon and J. Weiss, J. Chem. Soc., 4388 (1957).

⁽²⁵⁾ In a communication to the Editor, J. Am. Chem. Soc., 78, 1768 (1956), J. T. Sworski has discussed the possible competition of hydroxyl and sulfate radicals for cerous ion and formic acid. For later work see J. T. Sworski, Radiation Research, 6, 645 (1957).

catalysts for some process resembling reaction 10 when they are present as very low molecular weight colloids. I

would be happy to find an alternative to this admittedly not very appealing mechanism.

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THE AQUEOUS CHEMISTRY OF INORGANIC FREE RADICALS.¹ II. THE PEROXYDISULFATE INDUCED EXCHANGE OF OXYGEN ATOMS BE-TWEEN WATER AND MOLECULAR OXYGEN AND EVIDENCE REGARDING THE ACIDITY CONSTANT OF THE HYDROXYL RADICAL

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The radical catalyzed exchange of O^{13} between water and molecular oxygen has been studied at 60° , using the thermal decomposition of persulfate ion as a means of generating the radicals. In each exchange experiment the persulfate concentration may be assumed to be constant, since the thermal decomposition was very much slower than the exchange reaction and could be ignored. The exchange process was found to proceed by a chain mechanism, with a chain length of unity being defined as exchange of two oxygen atoms for each persulfate ion which decomposed. In solutions ranging from pH 3 to 11 the chain length was approximately constant, with the value of 4.3 ± 1.5 obtained at an oxygen pressure of 0.5 atm. As the alkalinity was increased above pH 11 at the same oxygen pressure the chain length first increased rapidly, then levelled off to a value of 450 above 0.2 N alkali. In this region of maximum rate, the only condition investigated, the chain length was found to increase linearly with increasing persulfate concentration. In the proposed mechanism it has been assumed that the decomposition product. In solutions more alkaline than pH 11, neutralization of hydroxyl radical occurs with increasing participation of the highly active catalyst O^- in the exchange reaction. The constancy in chain length in strongly alkaline region suggests that essentially complete neutralization of the hydroxyl radical has been achieved, but the interpretation here is complicated somewhat by the possible action of trace impurities in the alkali as radical scavengers.

Introduction

In recent years several studies have shown that there is a catalyzed exchange of oxygen atoms between water and molecular oxygen in systems which may reasonably be assumed to contain the hydroxyl radical or a species derived from it.²⁻⁵ On the basis of their observation that the exchange

$$H_2O + O_2^{18} \longrightarrow H_2O^{18} + O_2 \qquad (1)$$

seemed to occur at an appreciable rate only in alkaline solution, Hart, Gordon and Hutchison first made the interesting suggestion that the catalysis involves not the hydroxyl radical itself, but instead its conjugate base, the O⁻ion,² with the exchange proceeding through the reversible formation of the symmetrical species $O_3^{-.4}$

$$OH + OH^{-} \xrightarrow{} O^{-} + H_2O \qquad (2)$$
$$O_2^{18} + O^{-} \longrightarrow O_2 + O^{18-}$$

The present study of the radical catalyzed exchange of water and molecular oxygen was designed to yield more detailed information about the acidity constant of the hydroxyl radical. The thermal decomposition of persulfate ion was used as a means of generating the radicals, since the general features of the thermal decomposition mechanism seem to be well understood.^{6,7} Further, its use had the added advantage that it permitted a comparison of the exchange data with our other unpublished free radical studies using this same reagent.⁸ By way of summary it can be said that although it has not been possible to obtain a quantitative measure of the acidity constant of the hydroxyl radical, it has been established fairly definitely that neutralization occurs in the region above pH 12. The acidity of the hydroxyl radical thus appears to be analogous to that of its dimer, hydrogen peroxide.

Experimental

The purification of the water and chemicals has been described elsewhere.⁹ In all experiments involving alkali the sodium hydroxide was used without purification, but it was taken from the same bottle of Baker and Adamson reagent grade material, lot number J309. Because of the difficulty in obtaining reproducibility in a chain reaction of the present sort, some description should be given of the special precautions which must be employed. It is essential that only repurified water be used, both as a solvent and in recrystallizing solids. All unpurified reagents should be taken from the same reagent bottle; in a study of the hydrogenation of persulfate it was found that appreciable differences in rate were observed when the sodium hydroxide was taken from different bottles, despite the fact that the labels listed the same lot number. In another experiment in the O¹⁸ exchange studies, 0.3 N sodium hydroxide was prepared by partial neutralization of 1.0 N alkali using concentrated perchloric acid; the rate obtained in this experiment was only 45% of the expected value, presumably because of inhibition caused by impurities introduced in part in the alkali and in part in the perchloric acid. Finally, and most important of all, before reproducible data can be obtained it is necessary to condition the reaction vessel by carrying out a number of consecutive runs. In the present study during the conditioning period involving approximately a dozen experiments, the rate constant increased

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 E. J. Hart, S. Gordon and D. A. Hutchison, J. Am. Chem. Soc., 74, 5548 (1952).

⁽³⁾ E. J. Hart, S. Gordon and D. A. Hutchison, *ibid.*, 75, 6165 (1953).

⁽⁴⁾ O. L. Forschheimer and H. Taube, ibid., 76, 2099 (1954).

⁽⁵⁾ H. Taube, Ann. Rev. Nuclear Sci., 6, 294 (1956).

⁽⁶⁾ I. M. Kolthoff and I. K. Miller, J. Am. Chem. Soc., 73, 3055 (1951).

⁽⁷⁾ Unpublished work carried out in this Laboratory.

⁽⁸⁾ A summary of this work may be found in the Abstracts of Papers for the 131st meeting of the American Chemical Society, held in Miami, Florida, in April, 1957.

⁽⁹⁾ Maak-Sang Tsao and W. K. Wilmarth, This JOURNAL, 63, 346 (1959).