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THE AQUEOUS CHEMISTRY OF PEROXYDISULFATE ION. VII. THE FREE RADICAL INDUCED CHAIN HYDROGENATION *,†

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A. INTRODUCTION

Radiation studies carried out in recent years have added materially to our knowledge of the aqueous chemistry of inorganic free radicals [1]. In particular, it has been fairly well established that the hydroxyl radical reacts rapidly with dissolved hydrogen at room temperature.

$$OH + H_2 \rightarrow H_2O + H \qquad (1)$$

In view of the well known inertness of molecular hydrogen, it would seem

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that reaction 1 might be used as a reasonably satisfactory test for hydroxyl radicals, at least under conditions where other reactive free radicals or heterogeneous hydrogenation catalysts might be assumed to be absent. Moreover, if a source of hydroxyl radicals was available, reaction 1 might provide a convenient way of generating hydrogen atoms in aqueous solution.

The work described in this paper involves a study of a number of the features of the aqueous chemistry of hydrogen atoms and hydroxyl radicals, including their interconversion by reaction 1. As a generating source for hydroxyl radicals, we have used the thermal decomposition of aqueous peroxydisulfate ion, hereafter referred to as persulfate ion. The reaction proceeds at a convenient rate for our purposes at 60–75°C. Over the pH range 3–14, where there appears to be only a single important reaction path, the rate is first order in persulfate and essentially independent of the acidity [2]. The net reaction is given by eqn. 2.

$$2S_2O_8^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + 4H^+ + O_2 \tag{2}$$

Tracer studies have shown that the oxygen which is formed comes not from the persulfate ion, but from the water solvent. In addition, the presence of free radical intermediates may be inferred from the ability of the persulfate ion to catalyze free radical polymerization reactions [3]. On the basis of these facts the following mechanism [2] has been proposed:

$$S_2O_8^{2-} \rightarrow 2SO_4^- \text{ rate determining} \tag{3}$$

$$H_2O + SO_4^- \rightarrow OH + HSO_4^- \tag{4}$$

$$2OH \rightarrow H_2O + \tfrac{1}{2}O_2 \tag{5}$$

Equation 5 is evidently only of stoichiometric significance since one or more intermediates must occur between reactants and products.

In the presence of dissolved hydrogen and at temperatures where the thermal decomposition occurs at an appreciable rate, our data demonstrate that the production of oxygen is largely eliminated. Presumably the hydroxyl radical or some other precursor of molecular oxygen is being captured in a process analogous to reaction 1. Under these conditions the principal reaction is the quantitative hydrogenation of persulfate ion.

$$S_2O_8^{2-} + H_2 \rightarrow 2H^+ + 2SO_4^{2-} \tag{6}$$

A variety of evidence to be considered later indicates that the hydrogenation occurs by a chain process, the gross features of which may be represented by eqns. 7–11.

$$\left.\begin{array}{l} S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^- \\ H_2O + SO_4^- \xrightarrow{k_2} SO_4^{2-} + OH + H^+ \end{array}\right\} \begin{array}{l} \text{chain} \\ \text{initiation} \end{array} \qquad \begin{array}{r} (7) \\ (8) \end{array}$$

$$\left.\begin{array}{l} \mathrm{OH} + \mathrm{H_2} \xrightarrow{k_3} \mathrm{H_2O} + \mathrm{H} \\ \mathrm{H} + \mathrm{S_2O_8}^{2-} \xrightarrow{k_4} \mathrm{H^+} + \mathrm{SO_4}^{2-} + \mathrm{SO_4}^{-} \end{array}\right\} \begin{array}{l} \text{chain} \\ \text{carrying} \end{array} \qquad \begin{array}{r} (9) \\ (10) \end{array}$$

$$\mathrm{H} + \mathrm{OH} \xrightarrow{k_5} \mathrm{H_2O} \text{ chain termination} \tag{11}$$

This simplified version of the mechanism neglects, among other things, acid–base reactions of both hydrogen atom and hydroxyl radical, a feature of major interest in this paper. While exact pK values cannot be quoted at the present time, there is strong reason to believe that in weakly acidic solutions the sulfate radical is converted to the hydroxyl radical [4], and that somewhere on the alkaline side of neutrality the oxide radical appears [5]:

$$\mathrm{SO_4}^{-} + \mathrm{H_2O} \rightarrow \mathrm{SO_4}^{2-} + \mathrm{OH} + \mathrm{H^+} \tag{12}$$

$$\mathrm{OH} + \mathrm{OH^-} \rightarrow \mathrm{H_2O} + \mathrm{O^-} \tag{13}$$

At least three pH dependent reactions of atomic hydrogen must also be considered:

$$\mathrm{H} + \mathrm{H^+} \rightarrow \mathrm{H_2}^{+} \tag{14}$$

$$\mathrm{H} + \mathrm{OH^-} \rightarrow \mathrm{H_2} + \mathrm{O^-} \tag{15}$$

$$\mathrm{H} + \mathrm{OH^-} \rightarrow \mathrm{H_2O} + e^- \tag{16}$$

Reaction 14, first proposed by Weiss [6], has received both experimental and theoretical support. It is generally assumed to become important at about pH 1. Calculations indicate that reaction 15 is not implausible, at least in moderately alkaline solution [7]. The position of equilibrium of reaction 16 is usually assumed to be far to the left [8], but data obtained in this laboratory indicate this assumption may be incorrect in the pH region of 12 and above.

To the extent that reactions 7–11 adequately represent the mechanism, the rate of hydrogenation of persulfate should be completely independent of pH. Only reaction 8 is acid dependent, and in the simplified mechanism it is assumed to proceed to completion. Conversely, if the equilibria 12–16 are rapidly established compared to other steps in the mechanism, variation of the acidity would be expected to produce a series of rate plateaux, each plateau representing a region of hydrolytic stability for a pair of radicals derived from the hydrogen atom and hydroxyl radical. Between the plateaux rapid changes in rate would be expected to occur because of the non-quantitative interconversion of radicals and their differing efficiencies in the chain-carrying and terminating steps listed above.

In this paper it will be shown that several rate plateaux do occur in the hydrogenation of persulfate. Although considerable uncertainty exists in the identification of the species involved, a tentative assignment of equilibrium constants will be made for the reactions 12–16.

B. EXPERIMENTAL

(i) Reagents

Initial rate studies demonstrated that the use of commercial distilled water resulted in long induction periods and rate constants which were reproducible to no better than ±100%. In all of the work reported here the water was purified by redistillation from an alkaline persulfate solution, with the steam being transported in an oxygen carrier gas through a Vycor tube maintained at 800–900°. Use of this water eliminated the induction period, and resulted in considerable improvement in reproducibility.

Reagent-grade potassium persulfate, potassium dihydrogen phosphate, sodium perchlorate, potassium chloride, barium hydroxide, and aluminum sulfate were all crystallized several times from purified water before use. Sulfuric acid was fractionally distilled in a Vycor still. Baker and Adamson 85% phosphoric acid and 70% perchloric acid were used without purification, since distillation of either solution results in decomposition. Phosphate buffers were prepared from potassium dihydrogen phosphate and either sodium hydroxide or phosphoric acid. Linde Air Products water-pumped hydrogen was passed through a Baker and Co. Deoxo unit with a stated capacity of reducing the oxygen content to less than 1 ppm. Apart from the alkali discussed below, all other chemicals were of reagent grade and were used without further purification.

Three different methods were employed to prepare aqueous alkali free from carbonate and perhaps other trace impurities: (a) Solutions were obtained by diluting centrifuged, saturated solutions of reagent-grade sodium hydroxide which had been treated with an amount of barium hydroxide sufficient to precipitate the quantity of carbonate stated to be present as indicated by the bottle label; (b) purified water was allowed to react with sodium amalgam formed in the electrolysis of reagent grade sodium hydroxide at a mercury cathode; and (c) metallic sodium purified by distillation was added to purified water. In the latter method the techniques used in distillation and storage were those described by Strong [9], except that the heating was performed with a flame. During the distillation considerable discoloration of the pyrex glass was observed, indicating reaction of the glass with the hot metal vapor.

The results of the various purification methods are presented in Table 1.

TABLE 1

Variation in rate constant with the source of alkali [a]

Source of NaOH	$k \times 10^{-5}$ [b] (s^{-1})
Reagent-grade alkali	
B and A, K106 [c], K244, K343	24 ± 1
B and A, 13	18 ± 1
B and A, K106 [c], J309	17 ± 1
B and A, H322J, K061	15 ± 1
B and A, J309	62 ± 1 [g]
Purified alkali	
B and A, K343 [d]	37 ± 1
B and A, K061 [d]	27 ± 1
($Na + H_2O$) [e]	30 ± 1
($Na + H_2O$) [f]	45 ± 2
(Na amalgam + H_2O)	78 ± 1 [g]

[a] All experiments were carried out at 60°C in 0.80M sodium hydroxide with the hydrogen pressure 0.8 atm., and at an initial persulfate concentration of 0.024M. [b] In experiments such as these run in parallel on the same day the reproducibility is considerably greater than the ± 15% quoted above. [c] Different bottles of the same lot number. [d] The same alkali listed above after treatment with barium hydroxide to precipitate the carbonate impurity. [e] Prepared from singly distilled sodium. [f] Prepared from doubly distilled sodium. [g] At 75°C.

The rate of hydrogenation is expressed as the pseudo first order rate constant, k, defined by eqn. 17:

$$\ln\left([S_2O_8^{2-}]_0/[S_2O_8^{2-}]_t\right) = kt \qquad (17)$$

The increase in rate upon removal of carbonate ion strongly suggests that it played a major role in the inhibition. This conclusion was confirmed by the inhibition studies discussed below. However, even after the removal of the carbonate, the value of the rate constant depended upon the source of the alkali, indicating the presence of other inhibitors.

The principal trace metal impurities present in the alkali were determined by comparative spectrographic analysis *. The analysis revealed that Baker and Adamson reagent grade NaOH, lots K343 and K061, contained iron, silver, and lead in the concentration range of 1–20 ppm with the metals being somewhat more concentrated in the latter sample. These heavy metal impurities could not be detected in alkali prepared from doubly distilled sodium, but the analysis revealed the presence of strontium, barium,

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* We are indebted to Dr. T. Gillmore of the Pathology Department of the Los Angeles County Hospital for these analyses.

aluminum, boron and silicon, with the latter three elements presumably originating from the reaction of sodium and glass during the distillation procedure.

(ii) Kinetic studies

In some studies, particularly the earlier ones, the rate of the reaction was followed by measuring the absorption of hydrogen at constant pressure, using the apparatus and magnetically stirred reaction cells previously described [10].

Preliminary degassing was performed by evacuation of the stirred solutions for periods of 20–40 min before hydrogen was admitted to the system. New reaction vessels, even after cleaning with 5% hydrofluoric acid, gave erratic results with the rates gradually increasing by a factor of two during the initial experiments. Usually this "conditioning" of the cell required six to eight hydrogenation experiments, customarily performed in 0.30M alkali; presumably impurities were being desorbed from the glass during this interval. When in use, the cells were periodically checked for contamination by repeating a hydrogenation under a standard set of conditions. At infrequent intervals "poisoning" occurred, as evidenced by a considerable decrease in rate and non-linear plots of $\log[S_2O_8^{2-}]$ vs. time. It would then be necessary to repeat the conditioning cycle. Between runs the cells were rinsed several times with purified water only; treatment with hydrofluoric acid, cleaning solution, or other oxidants resulted in contamination of the cell. After conditioning rate constants could usually be reproduced to within ±2% when the experiments were either run in parallel or within a period of a few days. For a time interval of the order of a few months, the irreproducibility was ±10%. But when considering all of the data accumulated over a period of 2 years, the irreproducibility must be assumed to be as large as ±25%, even when the experiments under consideration were carried out using a common source of chemicals.

Most of the experiments were carried out in cells designed to permit hydrogen to flow continuously through the solution. In these cells, one of which is illustrated in Fig. 1, the solution was maintained within ±0.05°C of a given temperature by pumping oil through the outside chamber, H. The solutions in the reaction chamber were found to be within 0.1°C of the desired temperature 8 min after the oil entered the outer jacket. Hydrogen, flowing at a rate of approximately 3 ml s^{-1}, first passed through the pre-saturator, B, containing alkali, and then into a persulfate solution, contained in E, of the same ionic strength. At 75°C it was found necessary to wrap the outlet tube, F, with a heating tap to prevent extensive condensation of water vapor. Blank runs indicated that the spray chamber, C, prevented appreciable transfer of alkali into E. When first placed in use the cells were conditioned and cleaned in the manner described above. At the beginning of an experiment, degassing was achieved by bubbling hydrogen through the solutions for 15 min at room temperature. No significant change in reaction rate was observed when the rate of flow of hydrogen was varied by a factor of two, and the numerical values of the rate constants were in agreement with those obtained in the stirring cells.

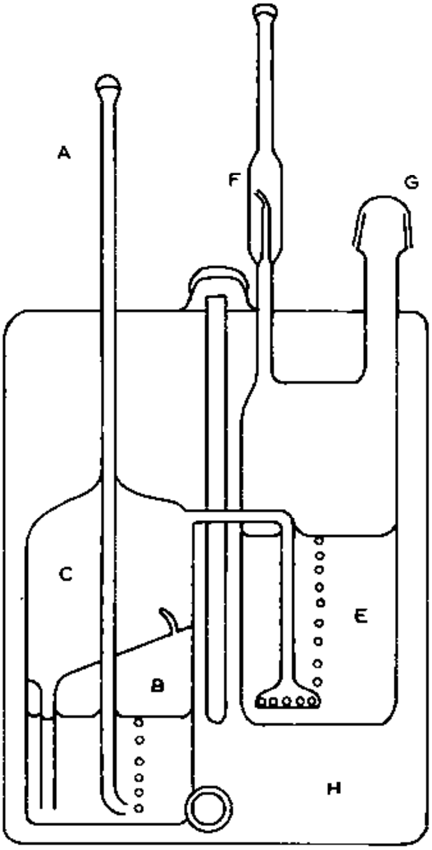

Fig. 1. Flow hydrogenation cell.

In a given experiment 25 ml of solution was added to the reaction chamber, E, with 3 ml aliquots being removed at suitable time intervals for iodometric analysis. The time intervals were long in comparison with the time required to bring the solutions to temperature. The analysis was performed by adding the 3 ml aliquot to a glass-stoppered flask containing 5 ml of solution which was 3.0M in potassium iodide and 0.0075M in ferrous sulfate. Oxygen was removed from the ferrous iodide solution immediately before and after addition of the aliquot by flushing with nitrogen. After waiting 20 min, a time which proved to be sufficient for quantitative reduction of the persulfate, the iodine was titrated with 0.02N thiosulfate using a semi-micro buret. Blank tests established that the analysis was accurate to ±2% and ±6% at 0.01M and 0.002M persulfate, respectively.

Within the limit of reproducibility of ±15% identical rates were obtained using either quartz or pyrex reaction cells. Addition of pyrex helices sufficient to increase the surface area by a factor of five produced no significant change in rate. However, somewhat lower rates were observed in a Teflon cell or in glass cells containing untreated Teflon powder. After various kinetic studies it was concluded that powdered Teflon could be cleaned by treatment with fuming perchloric acid followed by hot alkaline persulfate solution, but that massive Teflon objects contain an inhibitor which can be removed only with great difficulty, if at all.

C. RESULTS

(i) The thermal decomposition of persulfate

This reaction was reinvestigated in considerable detail after it became clear that our observations suggested slightly more complicated behavior than the data in the literature would imply. In early work at persulfate concentrations of 0.012–0.096M the rate was found to be readily reproducible and independent of pH over the range 3–14. Our rate constant of $4.3(\pm 0.2) \times 10^{-5}\ s^{-1}$ appeared to be in good agreement with the value of $4.7 \times 10^{-5}\ s^{-1}$ obtained by interpolation of the data of Kolthoff and Miller in 0.10M alkali [2]. However, at these persulfate concentrations there was no enhancement of rate in buffer solutions, an effect which Kolthoff and Miller observed at the lower temperature of 50°. Later work, part of which is presented in Table 2, was carried out at the lower persulfate concentration of 0.0025M. These experiments yielded somewhat larger rate constants, especially in weakly acidic phosphoric acid buffers, where values as large as $6.5 \times 10^{-5}\ s^{-1}$ were obtained. As the last four entries in Table 2 indicate, the enhanced rate does not arise from a general acid catalysis of the thermal decomposition, since the rate seems to remain constant or even to decrease slightly with increasing buffer concentration. The absence of general acid catalysis was also confirmed by experiments in unbuffered solutions which initially contained 0.001M alkali. Under these conditions the acidity of the solution increased as the reaction proceeded but, by removing aliquots for analysis, it was possible to follow rate and pH simultaneously, except near the neutral point where the pH changed very rapidly. In these experiments

TABLE 2

First order rate constant for the thermal decomposition of persulfate [a]

Buffer	pH [b]	$k \times 10^5 (s^{-1})$
0.1M NaOH	13 [c]	4.5
0.025M H_3BO_3 + 0.025M NaH_2BO_3	0.02 ± 0.04	4.9
5.0×10^{-3}M KH_2PO_4 + 4.5×10^{-2}M $NaKHPO_4$	7.57 ± 0.07	5.1
0.025M KH_2PO_4 + 0.025M $NaKHPO_4$	6.67 ± 0.05	5.4
0.045M KH_2PO_4 + 0.005M $NaKHPO_4$	5.53 ± 0.17	6.2
0.005M H_3PO_4 + 0.05M KH_2PO_4	2.95 ± 0.06	6.5
0.09M KH_2PO_4 + 0.01M $NaKHPO_4$	5.4 ± 0.05	5.5 [d]
0.18M KH_2PO_4 + 0.02M $NaKHPO_4$	5.5 ± 0.05	5.4
0.27M KH_2PO_4 + 0.03M $NaKHPO_4$	5.5 ± 0.05	5.1
0.36M KH_2PO_4 + 0.04M $NaKHPO_4$	5.5 ± 0.05	4.9

[a] At 75°C with $[S_2O_8^{2-}]_0 = 2.5 \times 10^{-3}$M; ionic strength 0.2M maintained with $NaClO_4$. [b] The pH measurements were carried out at room temperature. [c] Calculated from the alkali concentration. [d] Ionic strength 0.49M.

the rate was found to increase abruptly in weakly acidic solution. The exact position of the break was too near the neutral point to be determined accurately, but it seemed to be consistent with that observed in the buffers studied. In the pH region of 2.8–3.7, where a rate constant could be calculated, the value of $7.7\,(\pm 0.2) \times 10^{-5}\ s^{-1}$ was obtained. Finally, it might be noted that when bromide ion, a known scavenger for hydroxyl radical [11], was added to the solution in small amounts the rate of disappearance of persulfate was decreased by approximately a factor of two over the maximum value cited above *. Our conclusion, based on these bromide inhibition studies, is that the rate of reaction 3 is independent of the pH, but that the rate constant for this process is somewhat smaller than that observed for the uninhibited thermal decomposition of persulfate. Presumably the intermediates in reaction 5 contribute to the total disappearance of persulfate.

In solutions more acidic than pH 3 the decomposition of persulfate also

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* Between pH 2.8 and 0.5M alkali the rate law for the reaction of persulfate and bromide may be formulated as $-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][Br^-]$. At 75°C, k_1, believed to be a true measure of the rate of reaction 1, has the value $3.8 \times 10^{-5}\ s^{-1}$. The value of k_2 is strongly dependent upon ionic strength and somewhat dependent upon the exact medium, but an average value of $2.0 \times 10^{-4}\ M^{-1}\ s^{-1}$ may be cited for an ionic strength of 1.0. The reaction mechanism seems to consist of two parallel non-chain paths, as evidenced by the fact that the observed rate law is essentially independent of the products which are formed. In acid solution only bromine is formed, but above pH 9 molecular oxygen becomes an increasingly important product. Calculations indicate that the oxidation of bromide ion by hydroxyl (or oxide) radical is probably endothermic under these latter conditions.

proceeds by an acid-catalyzed path leading to the formation in strong acid of peroxymonosulfuric acid and eventually hydrogen peroxide [2]. In work not reported here the presence of the acid-catalyzed decomposition path was confirmed, but so far no effort has been made to study either the kinetics or reaction products in any detail. In strongly alkaline solution, a region not investigated by Kolthoff and Miller, there appears to be a further path for the decomposition of persulfate. As Table 3 indicates, this reaction becomes significant at about 2.0M alkali, with the rate increasing continuously up to 6.0M alkali, the maximum concentration which was studied. In any given experiment the rate was first order in persulfate, except in 6.0M alkali where initial rate constants are reported. The order with respect to hydroxide ion has not been established since the data at 3.0M alkali indicate a strong dependence of rate upon ionic strength. Finally, it should be noted that all of these experiments were carried out with a single source of alkali, and the possible catalytic effect of trace impurities in these concentrated solutions has not been investigated.

(ii) Stoichiometry of the hydrogenation reaction

Various techniques were used to establish the stoichiometry of the hydrogenation reaction. In experiments carried out in the stirring cell at 75°C, 0.10M alkali, and a partial pressure of hydrogen of 0.62 atm., it was found that each mole of persulfate consumed 0.99 ± 0.01 moles of hydrogen and 1.99 ± 0.02 moles of hydroxide ion, in good agreement with eqn. 6. Using essentially the same apparatus, mass spectrometer analysis was made of samples of hydrogen removed directly from the cell at various times during a hydrogenation. In the pH regions of 3–7 and 11–13.5, the amount of oxygen formed was immeasurably small; at most not more than 0.1% of the

TABLE 3

First order rate constants for the thermal decomposition of persulfate in strong alkali [a]

[NaOH] (M)	$k \times 10^5$ (s^{-1})
0.10	4.3
1.0	4.3
2.0	8.3
3.0	15.5
3.0	43 [b]
4.0	38
5.0	70
6.0	125

[a] At 75°C with $[S_2O_8^{2-}]_0 = 0.024M$. [b] With $[NaClO_4] = 1.0M$ added.

TABLE 4

First order rate constants for the hydrogenation of persulfate at 75°C and at 0.62 atm. hydrogen [a]

$[S_2O_8^{2-}]$ [b] (M)	pH			0.5M NaOH (J309)
	2.8±0.2 [c]	6.7±0.2 [c]	11.1±0.2 [c]	
0.048	67	12.6	6.7	88
0.024	62	12.7	7.3	93
0.012	57	12.9	8.2	73
0.006	53	13.4	6.1	92

[a] All values tabulated as $k \times 10^5$ s^{-1}. [b] Initial concentration. [c] Phosphate buffers.

persulfate which reacted yielded oxygen as a product. However, in the pH region 7–11 oxygen was definitely produced in amounts corresponding to 1–25% of the total persulfate consumed. In experiments involving the iodometric method of analysis, the presence of more than trace amounts of hydrogen peroxide or peroxymonosulfuric acid would have been revealed. Neither of these substances has ever been detected in a hydrogenation experiment.

(iii) Kinetics of the hydrogenation reaction

All of the rate constants given in this paper are defined in terms of eqn. 17. They are functions not only of the temperature, but of the pH and hydrogen pressure as well. In any given experiment the plot of $\log[S_2O_8^{2-}]$ vs. time was linear, with minor positive or negative deviations occurring only late in the second half-life of the reaction *.

(a) Persulfate dependence

The data in Table 4 cover an 8-fold variation in persulfate concentration in four different pH regions. The consistency of the rate constants to within the normal error of reproducibility definitely establishes the first order dependence of rate upon persulfate concentration in the four important pH regions under consideration.

(b) Hydrogen dependence

The order with respect to hydrogen was first investigated at 60°C in 1.0M

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* The source of these deviations has not been elucidated. It is perhaps significant that they were most pronounced when a cell was known to be "contaminated", or when conditioning of a cell was in progress.

sodium hydroxide (K343), using the stirring cell so that pressures above 1 atm. might be obtained. These data are shown in Fig. 2, where the triangles represent rate constants plotted against the pressure and the squares the same constants plotted against the square root of the pressure. While the square root plot is linear, it is felt that this arises from a compensation of two or more terms in the rate law, since the negative rate constants obtained by extrapolation of the data to low hydrogen pressures has no physical significance. The first order plot appears to be linear below 1 atm. and extrapolates as it should to the rate of thermal decomposition, a value indistinguishable from zero in the graph.

In later work at 75°C using the flow system, the hydrogen pressure was varied from 0.15 to 0.65 atm. by dilution with helium. At pH 3 and in 0.8M alkali the results closely resemble those plotted in Fig. 2. Again the plot of rate constant against either pressure or square root of pressure was linear,

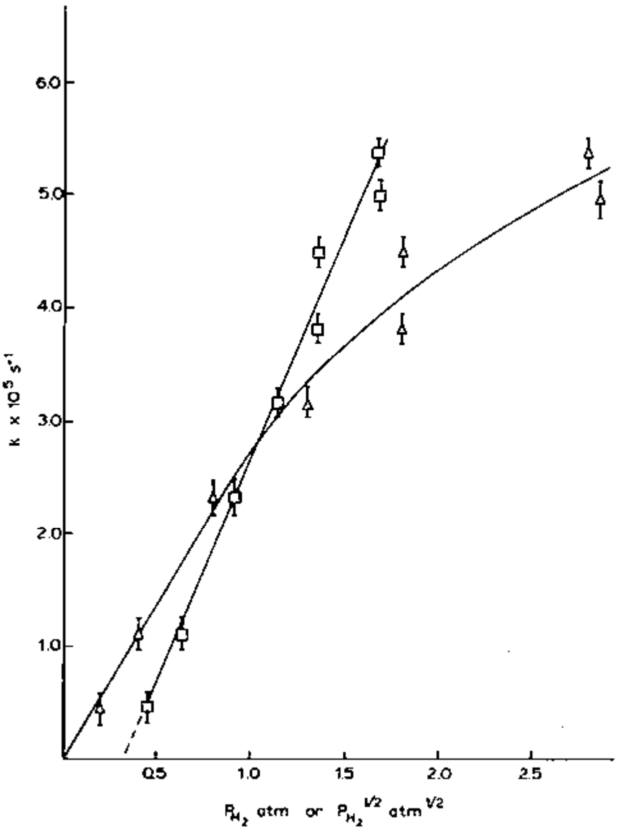

Fig. 2. Observed first order rate constant for disappearance of persulfate vs. hydrogen pressure (△) or square root of hydrogen pressure (□).

with a negative ordinate intercept being obtained in the square root plot. The data have not been presented here, since the pressure range is less than that covered in Fig. 2 and the reproducibility was approximately the same. Experiments at pH 7.7 and 0.05M alkali were rather inconclusive, since the rate of hydrogenation is rather low under these conditions, but the results were at least not incompatible with a linear dependence of rate upon hydrogen pressure.

(c) pH dependence

The study of the variation of rate with pH was a major objective of this work. In one extensive series of experiments carried out in the flow system at 75°C, the persulfate concentration was maintained at 0.24M and the hydrogen pressure at 0.62 atm., the residual 0.38 atm. being water vapor. These are conditions where the rate is definitely first order in persulfate and first order in hydrogen, at least to the extent indicated by the data given above. Rate constants obtained in these experiments are plotted against the pH in Fig. 3. The points at higher alkalinity have also been plotted in Fig. 4, with the concentration scale as the abscissa so that the region near 1.0M base may be more closely examined.

In alkaline solution most of the experiments were carried out using commercial alkali, since it was not practical to prepare large amounts of

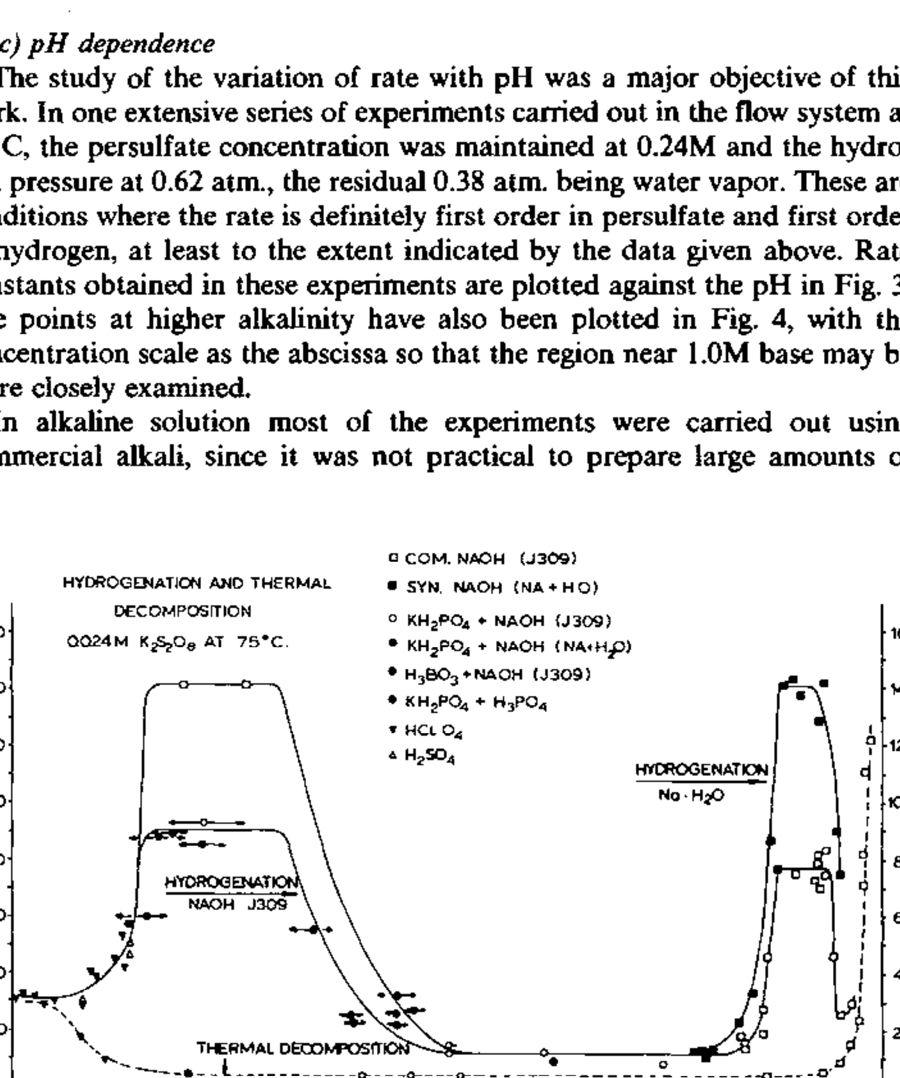

Fig. 3. Thermal decomposition (- - - - - -) and hydrogenation (————) of persulfate at 75°C with $[S_2O_8^{2-}]_0 = 0.024M$. Observed first order rate constants vs. pH.

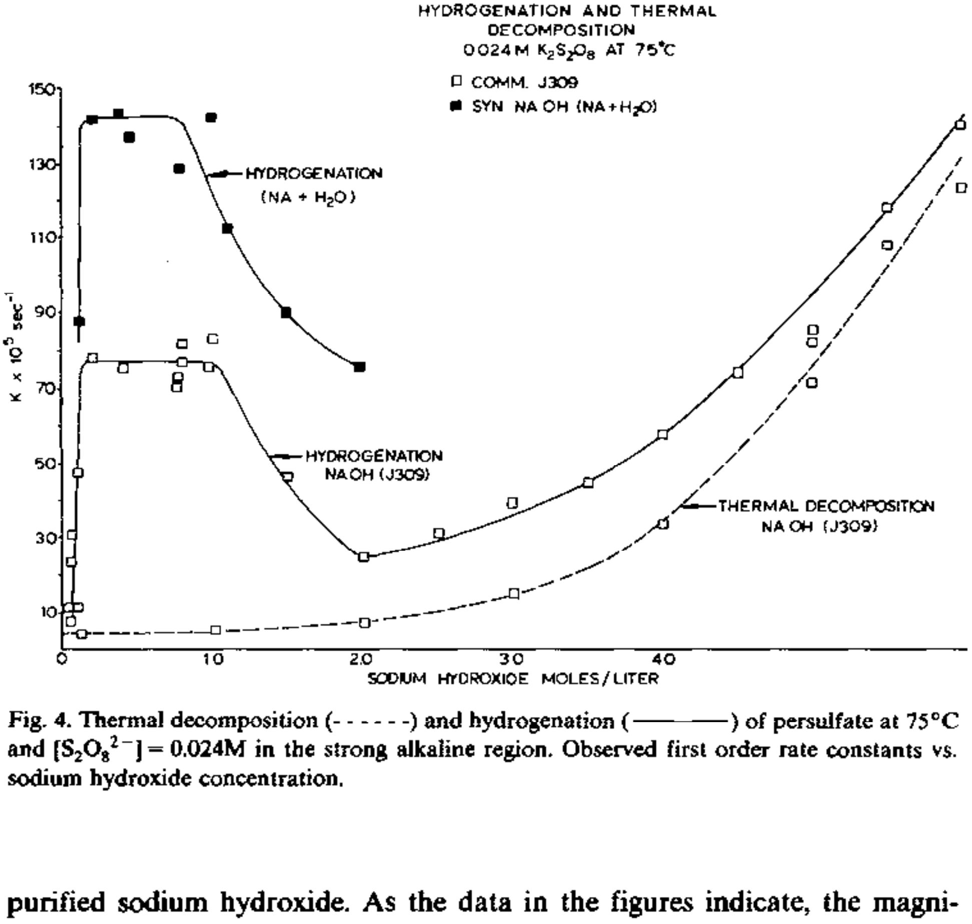

Fig. 4. Thermal decomposition (- - - - - -) and hydrogenation (————) of persulfate at 75°C and $[S_2O_8^{2-}] = 0.024M$ in the strong alkaline region. Observed first order rate constants vs. sodium hydroxide concentration.

purified sodium hydroxide. As the data in the figures indicate, the magnitude of the rate constant is decidedly dependent on the source of the alkali, but the general shape of the curve is independent of this variable. Within the limit of reproducibility the rate is constant from 0.10 to 1.0M base, a region where the chain length reaches a value of at least 30. Below pH 13 the rate drops abruptly, leveling off to a chain length of approximately three for the region from 12 down to 8. The anomalously low point just above pH 11 corresponds to data also given in Table 4. The discrepancy here seems to be well outside the limit of error, and may indicate that these phosphate buffers are subject to radical attack. In view of this uncertainty it is important to note that the low plateau in rate does not arise simply from buffer inhibition. This was established in experiments of the sort mentioned above where rate and pH were followed simultaneously in unbuffered solutions initially containing 0.005M alkali. In these experiments the rate of hydrogenation proceeded at the expected rate until somewhat past the neutral point, then rapidly increased, leveling off at a chain length comparable to that found in synthetic 1.0M alkali. By using phosphate buffer solutions the shape of the acid plateau was somewhat more sharply defined, but in the rather inaccessible region between pH 4 and 6 there is considerable uncertainty in the exact shape of the curve. As the two curves in Fig. 3 indicate, the rate constants obtained in buffered solutions were almost a factor of two smaller than those obtained in unbuffered solutions. Present evidence suggests that the discrepancy here arises from impurities in the commercial phosphoric acid, a reagent that has not been successfully purified. Above pH 2 the rate again diminishes, with the point of decrease corresponding to conditions where the acid-catalyzed decomposition of persulfate is becoming appreciable.

Another similar series of experiments not presented in this paper was carried out at 60°, with the results being entirely analogous to those presented in Figs. 3 and 4. The reproducibility was obviously too poor to determine precise kinetic parameters, but a formal calculation yields an activation energy of 22–25 kcal/mole over the pH range 3–14.

(iv) Inhibition studies

The exploratory studies reported in Table 5 were carried out in the flow system using commercial sodium hydroxide (J309). The rate constant listed

TABLE 5

Rate constants obtained in inhibition studies at 60°C in 0.80M alkali [a]

Inhibitor [b]		Conc. (M)					
		10^{-5}	10^{-4}	10^{-3}	10^{-2}	5×10^{-2}	10^{-1}
Fe^{3+}	17	5.3	4.7	4.3			
Ag^{+}	17		2.5				
Cu^{2+}	17	5.8	2.5				
BrO_3^{-}	17	17	16	11	3.7		
Br^{-} [c]	17		15	19	17	6.7 [d]	
Pb^{2+}	17		17	11			
Ac^{-}	17					1.5	1.5
CrO_4^{2-}	17					2.6	2.3
CO_3^{2-}	17		16	14	6.7		
$H_2BO_3^{-}$	17		17	17	14	11	
Al^{3+}	17		18	18	17	14	
Sn^{2+}	17		16	17			

[a] All solutions were prepared using Baker and Adamson's reagent-grade alkali, lot number J309. Rate constants were measured at 0.80 atm. hydrogen pressure and are tabulated as $k\times10^5$ s^{-1}. [b] Metal ions added as sulfate salts: Anions added as sodium salts. Added Na_2SO_4 at this pH has an effect no different from that of $NaClO_4$. [c] Bromide ion is an active inhibitor in more acidic solutions. [d] Under these conditions, oxidation of Br^- to BrO_3^- becomes significant.

in the second column of the table refers to solutions containing "uncontaminated" commercial alkali. For simplicity in presentation, the concentration values listed at the top of each column were calculated on the assumption that all of the inhibitor remained in solution, although precipitation of heavy metal hydroxides presumably occurred. The ions are arranged approximately in order of decreasing efficiency, with the most active inhibitors placed at the top. The results indicate that the iron, silver, copper, and carbonate impurities present in 0.1–1.0M commercial alkali would have produced a considerable inhibition in the rate of hydrogenation. Boron and aluminum, two of the principal impurities present in our synthetic alkali, may be completely inert, since the inhibition which was found only at high concentration may result from impurities. Although the heavy metal ions exist in the alkaline solutions, at least in part, in the solid or colloidal state, the mechanism of the inhibition appears to be a chemical one, in the sense that the mere presence of a solid surface does not lead to inhibition. No significant variation in rate was caused by a 10-fold increase in surface to volume ratio of pyrex glass, nor by addition of large amounts of freshly precipitated barium sulfate, magnesium hydroxide, or aluminum hydroxide.

Studies were also made of the effect of impurities introduced by reaction of hot metallic sodium and glass. A sample of distilled sodium was heated in an evacuated pyrex tube at about 350°C until considerable destruction of the walls of the tube had occurred. Use of sodium hydroxide synthesized from this metal yielded rate constants within 15% of the expected value. Alkali prepared from distilled metal was also contaminated by heating a 2.5M solution in a pyrex vessel at 75°C until a copious precipitate of sodium silicate had formed. After centrifugation and dilution to 0.80M, the expected rate constants were again obtained.

In later work at 75°C the inhibition studies were extended to alkaline and weakly acidic solutions. In general, these exploratory studies will not be presented in detail, since the results were entirely in harmony with the data presented in Table 5. Again, copper, silver, and iron were found to be active inhibitors at pH 7.7 and 3.0. Studies with oxygen were carried out over the entire pH range. In all experiments, irrespective of pH, the use of hydrogen containing 1% oxygen produced approximately a 25% decrease in rate, but the general shape of the pH curve remained unchanged. The presence of additional oxygen up to 10%, the maximum concentration studied, did not depress the rate further. As the discussion below will indicate, these experiments are of major importance in the interpretation of our overall results.

D. DISCUSSION

After considering the inhibition studies, there can be little doubt that the hydrogenation of persulfate is a chain reaction. We will consider the pH range 3–14, since only a single thermal decomposition path is of importance. It would seem that the hydrogenation must be initiated by reaction 6, or at least by some closely related pH-independent process. As one alternative to reaction 6, it might be concluded on the basis of evidence reported by Fronaeus and Ästerman [12], that the process is actually the reduction of a persulfate ion by a water molecule, with the subsequent formation of one hydroxyl and one sulfate radical. This formulation would in no way change our overall mechanism since, anticipating the discussion below, it will be concluded that the sulfate-hydroxyl radical interconversion is rapid compared to the chain-carrying steps in the system. To a first approximation, the rate constant for reaction 7 may be assumed to be equal to that observed for the uninhibited thermal decomposition of persulfate. Although our bromide inhibition studies provide evidence for a somewhat smaller value for k_1, the uncertainty here does not seriously influence any of the conclusions to be drawn in this paper.

Maintaining for the moment the simplification afforded by ignoring the acid–base dependent reactions 12–16, let us consider the mechanism of chain termination, a process which plays a major role in determining the rate law. Here, although the order with respect to hydrogen is somewhat uncertain, it would seem that the data favor a first order dependence on both persulfate concentration and hydrogen pressure, at least at hydrogen pressures below 1.0 atm. Equation 11, based upon the reaction of hydrogen atoms and hydroxyl radicals, would predict a first order dependence on persulfate concentration, but only a half order dependence on hydrogen pressure. A single termination step involving symmetrical combination of either hydrogen atoms or hydroxyl radicals is even more certainly excluded, as neither of these processes would predict a first order dependence on persulfate concentration *. In addition to these discrepancies, it must be noted that none of these reactions provides a path for termination by impurities, a feature which can scarcely be neglected when commercial alkali is used, either as such or as a component of buffers. In this connection it is of interest to consider the relative concentrations of the various species present in the

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* In a discussion held at the Gordon Research Conference Professor R.M. Noyes pointed out that when more than one radical is present in a system, several termination reactions are usually of approximately equal importance. It is by no means certain that this generalization is applicable to symmetrical combination of such species as aqueous electrons, oxide, and sulfate radicals. However, it is possible that the correct form of the rate law might be deduced by assuming the simultaneous occurrence of more than one termination reaction, but the resulting mechanism would still be unsatisfactory, in that it would ignore the effect of impurities upon reaction rate.

solution. Hydrogen atoms[*] and presumably hydroxyl radicals exist at steady state concentrations of approximately 10^{-9}M, heavy metal impurities are present at 10^{-6}–10^{-7}M, and carbonate ion (impurity), sulfate ion, and hydrogen are 0.001M and above. Collision frequencies will evidently favor reaction of the radicals with hydrogen, persulfate, or impurities over their direct recombination.

A satisfactory rate law can be derived on the assumption that at low hydrogen pressures impurity termination is the predominant process. The equation can most simply be obtained by assuming that a soluble impurity acts as a radical scavenger, picking up either hydrogen atoms or hydroxyl radicals. Although the nature of products formed in the radical impurity reaction need not be specified, the inhibition studies certainly suggest that these reactions involve a cyclic oxidation and reduction of the impurity.

$$X_R + OH \overset{k_a}{\rightarrow} X_O + OH^- \tag{18}$$

$$X_O + H \overset{k'_a}{\rightarrow} X_R + H^+ \tag{19}$$

X_O and X_R represent the oxidized and reduced forms of an impurity assumed to be present in the solution at a total concentration $[X]_t$. Adopting the usual steady state methods, and making only the justifiable approximation that $k_1[S_2O_8{}^{2-}]$ may be neglected in comparison to $k_4[S_2O_8{}^{2-}][H]$[†], it is possible to derive the following rate law, with the rate constants defined by the equations given above:

$$\frac{-d[S_2O_8{}^{2-}]}{dt} = \frac{k_1k_3}{k_a}\,\frac{[S_2O_8{}^{2-}][H_2]}{[X]_t} + \frac{k_1k_4}{k'_a}\,\frac{[S_2O_8{}^{2-}]^2}{[X]_t} + k_1[S_2O_8{}^{2-}] \tag{20}$$

Equation 20 would seem to be acceptable, at least at low hydrogen pressures, if it may be concluded on the basis of experiment that the last two terms to the right of the equality sign may be neglected. From the standpoint of theory, it is clear that the contribution of the last term is insignificant[**].

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[*] The hydrogen atom concentration may be calculated from the results obtained by following the rate of parahydrogen conversion during a hydrogenation experiment. It is assumed in the calculation that the exchange occurs through reaction 22, and that the rate constant may be obtained by extrapolating gas phase data to the appropriate temperature.

[**] In the region where the chain length is long, $-d[S_2O_8{}^{2-}]/dt$ is essentially equal to $k_4[S_2O_8{}^{2-}][H]$; both quantities are very large compared to $k_1[S_2O_8{}^{2-}]$, the rate of thermal decomposition in the absence of hydrogen. For the second term to the right of the equality sign in eqn. 20 to be negligible compared to the first, it is evidently necessary that $k_3[H_2]/k_2 \gg k_4[S_2O_8^{2-}]/k'_a$. In the region of long chain length it can be shown that this latter ratio very closely approximates to the quantity $[X_R]/[X_O]$.

The ratio of the first term to the second may be shown to be equal to $[X_R]/[X_O]$. While the value of the latter ratio may be large, thus justifying the overall approximation, neither theory nor experiment yields any direct information on this point. Finally, it might be noted that while direct combination of the radicals has been neglected, any contribution to chain termination by such paths would cause the rate to be lower than that predicted. This may well be the cause of the deviation from the first order dependence of rate upon hydrogen pressure at pressures above 1 atm., since the total radical concentration would tend to increase under these conditions.

In deriving eqn. 20 it has been assumed that only hydrogen and hydroxyl radicals are involved in the chain-carrying and termination reactions. However, entirely analogous rate laws may be obtained by assuming mechanisms in which the hydrogen atom is replaced by either H_2^+ or the electron, or with the oxide or sulfate radical replacing the hydroxyl radical. The equations for these rate laws would differ from eqn. 20, only in that the rate constants k_2–k_5 would then refer to the reactions of the particular pair of radicals assumed in the mechanism. It is evident then that the theory is compatible with the interpretation that there is a change in radical intermediates in going from one rate plateau to another, without there being a corresponding change in the general form of the rate law. However, it should be emphasized before proceeding to a discussion of the radical interconversion reactions that the validity of the interpretation which will be presented is not critically affected by uncertainties regarding the manner of chain termination, or by lack of exact agreement between the predicted and the observed rate law. In fact, given almost any reasonable mechanism, it is evident simply from qualitative considerations that acid–base reactions are occurring in the pH regions where rapid changes in rate are observed, especially when the regions under consideration occur at opposite ends of a long rate plateau such as that which extends from pH 8 to 12.

In attempting to identify the radicals involved in the interconversion reactions, it is of interest to consider first the inhibition data obtained using hydrogen–oxygen mixtures. As we have noted above, oxygen inhibition sets in at a low oxygen concentration but, unlike the other inhibitors, oxygen in excess of 1% is without further effect, the total decrease in rate being only of the order of 25% over the entire pH region. To explain this phenomenon of inhibition saturation, it is necessary to assume that when excess oxygen is present the hydrogen atom (or its counterpart) is quantitatively converted to another rather efficient chain-carrying species. This new species is presumably HO_2 or in the region above pH 3 more likely O_2^-. With O_2^- replacing the hydrogen atom at all points in the mechanism, any changes in rate associated with hydrogen atom equilibria should disappear, except, if by coincidence, an acid–base equilibria of each species should occur in the same region of pH. This latter possibility cannot be definitely excluded [13], especially in the rather inaccessible pH region 4–7, but the evidence would seem to favor there being no change in the general shape of the rate vs. pH curve in the oxygen inhibition experiments. Accepting this conclusion, it may be proposed, tentatively, that two hydroxyl radical equilibria have been detected. In the absence of other more plausible alternatives these may be identified as reactions 12 and 13, with reaction 12 converting the sulfate radical to the hydroxyl radical between pH 5 and 7, and neutralization of the hydroxyl radical setting in above pH 12 * [14].

With only these kinetic studies as a source of information, little further progress can be made in the actual identification of the radicals. However, tracer studies yield other valuable information. A brief summary of these results will be presented here only to clarify certain of the problems under discussion. Studies using labeled oxygen gas were suggested by the observation that in several systems presumed to contain hydroxyl radicals a radical-catalyzed exchange of oxygen and water was observed [14,15]. In view of the fact that the exchange proved to be much more rapid in alkaline solution, it was proposed that the hydroxyl radical itself was relatively inert, but that its conjugate base O^- was able to exchange rapidly with oxygen, the chain reaction presumably occurring through the formation of the symmetrical species $O_3{}^-$, with the subsequent exchange of the labeled O^{*-} and water [15].

$$O_2^* + O^- \rightarrow O_2 + O^{*-} \tag{21}$$

$$O^{*-} + OH^- \rightarrow O^*H^- + O^-$$

In our system oxygen tracing was carried out over the pH range 3–11.5 and at 0.3M base by stirring persulfate solution in an atmosphere of labeled oxygen and periodically removing oxygen for mass spectrometer analysis. At 75°C only a very slow exchange was observed at pH 3–11.5, but in the region corresponding to the high plateau in hydrogenation rate at 0.30M base, the oxygen was found to exchange rapidly with the aqueous solution. This correlation between the rate of hydrogenation and the rate of exchange implies the existence of a common intermediate in the two reactions. Since hydrogen atoms or their counterparts can scarcely be present in the oxygen exchange systems, it would appear that the studies confirm the presence of a hydroxyl radical equilibrium in the pH range 11.5–13.5. Assuming the validity of the mechanism proposed by Hart and co-workers, the equilibrium in question may again be identified as that represented by eqn. 13.

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* In addition to other uncertainties, it should be noted that the equilibrium constants under consideration do not necessarily correspond exactly to the pH values midway between the rate plateaux.

Before considering our tracer studies with hydrogen, it should be noted that Gordon and Hart have shown that when acidic or neutral solutions containing D_2 are irradiated with γ-rays, HD is formed, presumably through reaction 22 [16]:

$$D_2 + H \rightarrow HD + D \tag{22}$$

Under the conditions mentioned the yield of HD did not indicate the presence of a chain reaction, and all deuterium atoms were assumed to disappear by symmetrical recombination. Of interest in our work is their observation that the rate of exchange decreased rapidly in alkaline solution, and became immeasurably small above pH 11. Recognizing that the decreased rate of exchange implied a lower steady state concentration of hydrogen atoms, these authors assumed that oxide radical was much more efficient than hydroxyl radical in competing with D_2 for hydrogen atoms. In short, in alkaline solution combination of oxide radicals and hydrogen atoms took place before reaction 22 could occur.

In our experiments it was difficult to follow rate of exchange and hydrogenation simultaneously, so the exchange data were usually compared with those obtained from hydrogenation experiments carried out under exactly comparable conditions. Since hydrogenation data using D_2 were not generally available, most of our work involved the use of parahydrogen as a tracer, thus eliminating complications arising from isotope effects. However, a number of exchange studies were carried out with D_2, HD, and mixtures of D_2 and H_2, with the results validating the assumption that parahydrogen conversion implied hydrogen atom exchange. Exchange was found to be rapid at pH 3, a result which confirms the presence of hydrogen atoms under these conditions, since the magnitude of the exchange was incompatible with any other paramagnetic or heterogeneous catalyst for parahydrogen conversion. In 0.10 M alkali the exchange was found to be immeasurably slow, in agreement with the radiation studies. However, the combination of *rapid hydrogenation* and *slow conversion* cannot be understood in terms of the mechanism advanced by Gordon and Hart, since the rate of exchange and hydrogenation should both parallel the hydrogen atom concentration *. Evidently, at least in our system, when the hydrogen atoms disappear in the basic solution, they do so in a reaction in which they are replaced by a reducing agent capable of carrying the hydrogenation chain. Before drawing further conclusions about the nature of the new reducing species, it is important to note that if oxygen was present in the solution at appreciable

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* In the region of long chain length the rate law for the hydrogenation may be written as $d[S_2O_8^{2-}]dt = k_4[S_2O_8^{2-}][H]$.

concentrations, its reaction with hydrogen atom would both inhibit the exchange reaction and produce O_2^-, a chain-carrying species. However, the evidence indicates that while traces of oxygen may be present, the actual concentration is not sufficient to produce the observed inhibition *. Alternative processes, which represent reasonable paths for the disappearance of hydrogen atom, are given by eqns. 14–16. Of these, eqn. 14 may be eliminated, since there is considerable evidence that H_2^+ is not a stable species, although something approaching this unit may exist as part of the activated complex formed in acid-catalyzed reductions of the hydrogen atom **. Equation 15 must also be rejected, since this would require that H_2 be the first product in D_2 exchange, which was never observed. Of the equilibria under consideration there remains only reaction 16, a process in which the solvated electron is formed by "neutralization" of the hydrogen atom. In the absence of other more plausible alternatives it is our tentative conclusion that reaction 16 provides the most satisfactory explanation for the exchange data summarized above and that the pK_a of the hydrogen atom is of the order of 12 †.

A summary of our tentative conclusions regarding the identity of the dominant forms of the chain carriers is as follows:

pH:	2–5	8–12	13–14
oxidizing chain carrier:	SO_4^-	OH	O^-
reducing chain carrier:	H	H	e^-

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*As we have indicated, at pH 2.3–3.1 and 13.5 the amount of oxygen produced during a hydrogenation is immeasurably small with the upper limit being 0.01% of the hydrogen present. At least ten times this amount is required to produce serious inhibition of the exchange reaction. By contrast, in the pH region 7.5–12.0, the oxygen developed during hydrogenation is sufficient to decrease greatly the rate of hydrogen exchange. It should be noted that this variation in oxygen production with pH is not inexplicable, since the radical species which is a precursor of oxygen in the pH region 7.5–12 is presumably not present at either higher or lower acidity.

**In addition to unpublished work carried out in this laboratory, radiation studies show rather conclusively that aqueous deuterium atoms do not exchange with the protons in unlabelled water, even under conditions where H_2^+ has been assumed to be a "stable" species. Existence of H_2^+ would imply the existence of HD^+, a species whose reversible formation would catalyze the exchange of deuterium atom and water.

†Editor's note: it was not until the mid 1960s that the pK_a value of ~10 for H became available from pulse radiolysis studies.

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