[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF OREGON STATE COLLEGE]

Acid-base Exchange Reactions in Liquid Sulfur Dioxide[1]

BY ROWLAND E. JOHNSON,[2] T. H. NORRIS[3] AND J. L. HUSTON

The tracer S^{35} has been used to study the rate of exchange between the solvent liquid sulfur dioxide and three solutes, namely, the "base," tetramethylammonium pyrosulfite, and the two "acids," thionyl chloride and thionyl bromide. The pyrosulfite is found to exchange almost completely within 20 minutes even at ∼−75°. Thionyl bromide exchanges extremely slowly, with a half-time at 25° of about 1.9 years. The maximum exchange rate of thionyl chloride appears to be even lower at this temperature and at best not much greater at 61°. For the case where sulfur dioxide is dissolved in a large excess of thionyl chloride, an even lower maximum rate is observed. These results indicate that while a "base" yields sulfite ions in the solvent sulfur dioxide, "acids" (*i.e.*, thionyl compounds) yield a negligible amount of thionyl ion. The necessity is evident for modification of Jander's conceptions of chemistry in this solvent, particularly those which imply a simple ionic mechanism for neutralization reactions. It is suggested that acid–base phenomena in liquid sulfur dioxide could be better explained in terms of a mobility of oxide ions, analogous to the mobility of hydrogen ions in water.

The "sulfur dioxide system of chemistry," as developed primarily by Jander[4] and co-workers, envisages for the solvent, liquid sulfur dioxide, the self-ionization equilibrium

$$2SO_2 \rightleftarrows SO^{++} + SO_3^{=} \qquad (1)$$

with dissolved thionyl compounds as acids and sulfites as bases, hypothetically ionizing to a small extent according to such equilibria as

$$SOCl_2 \rightleftarrows SO^{++} + 2Cl^- \qquad (2)$$

$$(Me_4N)_2SO_3 \rightleftarrows 2Me_4N^+ + SO_3^{=} \qquad (3)$$

Reactions in this solvent, *e.g.*, neutralizations and double decompositions, are presumed to occur primarily ionically.

Although Jander's concepts have met with a degree of acceptance, his work has been severely critized by Bateman, Hughes and Ingold[5] on both theoretical and experimental grounds. Hence, an isotopic exchange study of the system seemed worth while.

If Equilibria (1), (2) and (3) are of significance a relatively rapid exchange should occur on labeling either solute or solvent with radiosulfur (S^{35}). We have carried out such experiments with sulfur dioxide solutions of the feebly conducting "acids," thionyl chloride and thionyl bromide (the conductance of the latter considerably exceeds that of the former, according to Jander) and with the more strongly conducting and relatively soluble "base," tetramethylammonium pyrosulfite (normal sulfites cannot be isolated from liquid sulfur dioxide).

Experimental

Radioactivity Procedure.—Radiosulfur was obtained from the Atomic Energy Commission. For radioassay all substances were converted to barium sulfate. Details of procedures have been reported elsewhere.[6]

Preparation of Reactants.—**Sulfur dioxide** from a cylinder was freed of any sulfur trioxide and moisture by passage through concentrated sulfuric acid and phosphorus pentoxide in succession. Freezing with liquid air and pumping to a high vacuum ensured the absence of permanent gases.

Thionyl chloride (Eastman Kodak Co. White Label) was purified by fractional distillation from quinoline. It was kept in the dark, sealed, until used.

Labeled sulfur dioxide was prepared according to the method of Johnson and Huston.[7]

Labeled thionyl chloride was prepared, on the vacuum line by reaction of active sulfur dioxide with excess (0.5:5 millimoles) phosphorus pentachloride. After allowing two hours at room temperature for completion of reaction, 120 millimoles of carrier thionyl chloride was condensed in, and then distilled off and the product purified by fractionation *in vacuo*. Comparison of the specific activities of the most and of the least volatile fractions indicated the absence of unreacted sulfur dioxide or other radioactive sulfur-containing compounds. The yield, about 90 millimoles of a pale yellow liquid, was preserved, sealed, in the dark.

Thionyl bromide (inactive) was prepared by metathesis in sulfur dioxide solution, as suggested by Jander

$$SOCl_2 + 2KBr \longrightarrow SOBr_2 + 2KCl \qquad (4)$$

Potassium chloride is less soluble than the bromide. A threefold excess of finely divided potassium bromide was shaken with thionyl chloride in sulfur dioxide (130 and 590 mmoles), in a sealed vessel at room temperature for four hours, during which the liquid turned the bright orange of thionyl bromide. After connection of the vessel to the vacuum system and evaporation of the more volatile fractions, the product was distilled off at ∼40°: yield ∼60 mmoles; density 2.65 at 25° (expected 2.672[8]). *Anal.* Calcd. for $SOBr_2$: S, 15.4; Br, 76.9. Found: S, 13.9; Br, 78.2. A qualitative test showed only a very small amount of chloride present. Portions of this material, further concentrated by evaporation before use in a particular experiment, gave a vapor pressure of ∼7 mm. at room temperature (expected ∼8 mm.[8]). The preparation was preserved, sealed, at Dry Ice temperature.

Tetramethylammonium Pyrosulfite.—The 10% hydroxide solution was evaporated *in vacuo* to a dry hydrate, which was then dissolved at ∼−75° in liquid sulfur dioxide. After clarification by filtration through sintered glass, the solution was evaporated to complete dryness and the residue pumped to a good vacuum. Twice repeated, this procedure finally yielded a good white product. A second preparation was also made, using a slightly modified procedure. Both preparations were analyzed for total sulfur gravimetrically and for S^{IV} iodometrically. *Anal.* Calcd. for $(Me_4N)_2S_2O_5$: S, 21.9. Found: Prepn. I: S, 20.6; S^{IV}/total S, 90.4; Prepn. II: S, 19.9; S^{IV}/total S, 91.0.

Some oxidation to sulfate evidently resulted from momentary exposures of the preparations to air, but it did not seem essential to eliminate this by improvement of procedure. Assuming the preparations mixtures of $(Me_4N)_2S_2O_5$ and $(Me_4N)_2SO_4$, one calculates corrected $S^{IV}/(Me_4N)_2S_2O_5$ percentages: Prepn. I: 21.9; Prepn. II: 21.1.

Run Procedure.—All experiments were performed in high vacuum apparatus. Runs with thionyl chloride and thionyl bromide were carried out in sealed-off bomb tubes. In the presence of these compounds it was necessary to minimize the use of stopcock grease and ensure the absence of mercury (from manometers, for instance).

Tetramethylammonium Pyrosulfite and Sulfur Dioxide.—Three exchange experiments were performed. About one

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[2] Taken from the thesis of Rowland E. Johnson, submitted in partial fulfillment of the requirements for the Ph.D. degree, at Oregon State College, September, 1950.

[3] For inquiries address T. H. Norris.

[4] G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, pp. 209–307.

[5] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 243 (1944).

[6] T. H. Norris, THIS JOURNAL, **72**, 1220 (1950).

[7] R. E. Johnson and J. L. Huston, *ibid.*, **72**, 1841 (1950).

[8] H. A. Mayes and J. R. Partington, *J. Chem. Soc.*, 2594 (1926).

milliliter of labeled sulfur dioxide was rapidly condensed (at ∼−75°) onto the solid (160 mg. in the first case, 80 mg. in the second and third), and solution effected as quickly as possible. The first experiment stood 2.5 hours at −21°; the solvent was then evaporated off completely. A portion of the solvent and the dry solid residue were each converted to barium sulfate for comparison of their specific activities. The second and third experiments were similar except that the solutions were not allowed to warm above ∼ −75°, and all operations were expedited so that the total solute–solvent contact time was only 20 minutes. Preparation II was used in the first two cases, Preparation I in the third. The per cent. exchange, 100 F, is obtained from the expression: $F = x/y$ where x and y represent the specific activities of the solute and solvent, respectively.

Thionyl Bromide and Sulfur Dioxide.—These experiments were carried out in sealed tubes of about 5-ml. capacity, constructed from 10/30 standard taper male ground joints. Tubing of small diameter was sealed to the small end of the joint, drawn out, sealed off and bent to one side in such a manner as to form a break-off tip. This reaction tube was then filled, on the vacuum line, from the other end and sealed off. At the termination of a run, the male joint was inserted into a female joint provided with an indentation in its shank. Rotation of one joint within the other broke the tip against the indentation, thus opening the reaction tube to the vacuum system.

The reactants, about 5.5 mmoles of labeled sulfur dioxide and 0.50 millimole of thionyl bromide in each case, were dosed out, the sulfur dioxide as gas, the thionyl bromide as liquid, and then condensed into the reaction tube. All runs were made in a 25.0° thermostat and kept dark to guard against the possibility of photodecomposition of the thionyl bromide.

At the end of a run the bulk of the sulfur dioxide was evaporated off in a reproducible manner in the vacuum system. The small but reproducible amount of active sulfur dioxide thereby left in the relatively non-volatile thionyl bromide led to moderately reproducible small zero time blanks: three "blank" runs gave 4.7, 5.2 and 3.3% apparent exchange. The two fractions, after absorption in sodium hydroxide, were converted to barium sulfate for counting. The per cent. exchange, 100F, is obtained from the expression: $F = x/(xa + yb)$ where x and y represent the observed specific activities of thionyl bromide and sulfur dioxide and a and b represent their mole fractions in the reaction mixture as determined by analysis.

An upper time limit was set to the practical length of these runs by the fact that the thionyl bromide showed signs of decomposition. After about two weeks a deepening of the color of the reaction mixture was evident.

Thionyl Chloride and Sulfur Dioxide.—In all but two runs involving excess of this compound, the thionyl chloride was labeled and the sulfur dioxide initially inactive; thionyl chloride mole fractions ranged from ∼ 0.005 to ∼ 0.09. At mole fraction ∼ 0.09 the techniques resembled those for thionyl bromide except for dosage of the chloride as vapor and differences in analytical procedure necessitated by the greater volatility of this compound. Small vapor samples (∼ 10%) of the solvent were reproducibly evaporated off and converted to barium sulfate for radioassay. The presence of small amounts of thionyl chloride in these samples was expected to lead to small, reproducible zero time blanks. Apparent per cent. exchange is obtained from the expression: $F = y/ax$ where y is the *total* activity in all the sulfur dioxide, calculated from the specific activity of the vapor sample; x is the sum total activity in the two reactants together; and a is the mole fraction of sulfur dioxide. Experiments were performed at 25.0° and 61 ± 1°.

Preliminary experiments appeared to indicate a reproducible zero time blank of ∼ 9%. The erratic results obtained in the actual exchange experiments are therefore most puzzling.

Experiments were also performed to check the tendency of thionyl chloride to decompose under the experimental conditions. Such an occurrence, producing active sulfur dioxide in the reaction solution, would simulate exchange. No significant effect was observed after 2415 hours at 25° or 1034 hours at 61°.

A modified procedure was used at lower thionyl chloride mole fractions. The reaction vessel was a larger container, provided with a number of ground joint break-off tips of the type described, arranged like limbs on a tree. Three "trees" received, respectively, 0.54, 0.54 and 2.2 millimoles of labeled thionyl chloride, followed by ∼ 100 millimoles of sulfur dioxide in each case. Vapor samples, each constituting ∼ 0.5% of the total sulfur dioxide, were drawn off successively, as the run proceeded, by use of one break-off tip at a time. After sampling, the "limb" would be sealed off below the ground joint. Finally, the liquid residue was analyzed and counted and the per cent. exchange figures calculated as before.

Two pieces of data for excess thionyl chloride, mole fractions 0.83 and 0.96, were obtained in an early, futile attempt to prepare labeled thionyl chloride by exchange with a small amount of highly active sulfur dioxide. Analysis was made by distilling off almost all the reaction mixture until only a few drops, presumably almost pure thionyl chloride, remained. Comparison of its specific activity with that of the bulk of the solution served to set an upper limit to the per cent. exchange: the actual exchange might be considerably less.

Results

Tetramethylammonium Pyrosulfite and Sulfur Dioxide.—The apparent exchange observed in each of the three experiments was: (1) 92% after 150 minutes at −21°; (2) 87% and (3) 72%, each after 20 minutes at ∼−75°. Assuming that exchange occurs only with S^{IV} in these preparations,[9] and correcting these figures for this factor, we obtained for exchange involving only S^{IV}: (1) 101%; (2) 96%; (3) 80%. Evidently exchange is substantially complete under the experimental conditions. We hope, by modification of our procedure to shorten the run time sufficiently to determine whether, as the third result suggests, a measurable rate is to be found.

Thionyl Bromide and Sulfur Dioxide.—Six runs, at a thionyl bromide mole fraction of ∼0.090 and a temperature of 25°, were made for periods of time up to 816 hours. They appear to indicate a true exchange, although the rate is extremely slow. At 816 hours 3.5% exchange, corrected for zero time blank, was observed. For each per cent. exchange we have calculated an apparent half-time, according to the expected first order rate law, and obtained an average value of 1.9 years, with an experimental standard deviation of ∼±0.4 year. The fair constancy in the values obtained appears to indicate conformity with the first order law and hence to imply that the observed percentages, though small, do represent a true exchange. It is worth mentioning that decomposition of the thionyl bromide would not simulate exchange since the sulfur dioxide was labeled in these runs.

Thionyl Chloride and Sulfur Dioxide.—Our first few experiments appeared to indicate some exchange. These results encouraged us to accumulate considerable data in the hope of learning something of the kinetics of the "exchange." Runs of considerable duration were carried out and showed various apparent per cent. exchanges. Unfortunately, however, it became evident that the net picture at any of the mole fractions was not that of a progressing exchange, and we can only conclude that our experimental technique yielded highly erratic results. Contamination of the sulfur

[9] Exchange rates between +4 and +6 sulfur are negligible except at elevated temperatures in all cases which have been investigated.[6,10,11,12]

[10] H. H. Voge, THIS JOURNAL, **61**, 1032 (1939).

[11] J. L. Huston, Ph.D. Thesis, University of California, Berkeley, 1946.

[12] J. L. Huston, THIS JOURNAL, **73**, 3049 (1951).

dioxide vapor sample, from which the exchange was calculated, with excessive amounts of active thionyl chloride or its decomposition products[13] would have yielded unduly high apparent exchanges, and hence all errors are expected to be on the high side. Thus, since it seems clear that those long time figures which show relatively small per cent. exchanges (apparent) set an upper limit, we have used them to calculate a minimum half-time at each mole fraction.

Sets of runs were made, at 25°, with thionyl chloride mole fractions of 0.0049, 0.0062, 0.017 and ~0.088 and, at 61°, of ~0.091, with about five or six observations in each set. Minimum half-times have been calculated from the following observed long-time apparent exchange figures for each of the sets, respectively: 1652 hours, 17%; 1003 hours, 16%; 1335 hours, 8%; 3012 hours, 16%; and 767 hours, 8%. The minimum half-times (in years) so obtained are, respectively: 0.7, 0.5, 1.3, 1.4 and 0.7.

As indicated in the experimental section, two figures were obtained for excess thionyl chloride, mole fractions 0.83 and 0.96, both at room temperature. After 840 and 334 hours, respectively, these both indicated <1% apparent exchange, corresponding to minimum half-times of 6.6 and 2.6 years, respectively.

Although the data are very disappointing, we can reach the one conclusion which is important to our discussion, namely, that the exchange at all mole fractions (including excess thionyl chloride) is exceedingly slow, if it occurs at all. The fact that raising the temperature to 60° hardly modified the apparent rate suggests that the true half-times at 25° may be much greater than those recorded. Comparison with the data of the previous section indicates that the maximum rate here is close to the thionyl bromide rate. Very likely we can say that the thionyl bromide exchange is faster for comparable conditions.

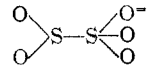
Thionyl Chloride, Sulfur Dioxide and Potassium Bromide.—Some interesting results were obtained in four experiments which were carried out in exactly the same manner as the thionyl chloride exchanges at mole fraction ~0.090, except that in each case a threefold excess, according to Equation (4), of potassium bromide was added; this was in the hope of forming labeled thionyl bromide *in situ* and thus studying its exchange with the solvent. The results were highly erratic, a large amount of activity appearing in the sulfur dioxide fraction at zero time in every case. Apparent exchanges, seemingly greater than one hundred per cent. in two cases, were indicated. This seems to be a specific effect of the potassium bromide and not a true thionyl bromide exchange, as is evident from the sulfur dioxide–thionyl bromide results already described. We plan to investigate this interesting reaction further.

Discussion

The exchange of the "base," tetramethylammonium pyrosulfite with the solvent is extremely rapid, even close to Dry Ice temperatures. The fact that this compound is a pyrosulfite rather than a sulfite immediately suggests as a possible exchange mechanism the equilibrium

$$S_2O_5^{=} \rightleftarrows SO_3^{=} + SO_2 \qquad (5)$$

However, it has been shown[14] that pyrosulfite ion has the structure



and consequently, since the two sulfurs are nonequivalent, Equilibrium (5) would be expected to lead directly to exchange with only one of the sulfurs; *i.e.*, to yield a maximum apparent exchange of 50%. The most reasonable interpretation of the observed complete exchange appears to be to assume: (a) that sulfite ion is formed in the solution *via* Equilibrium (5); and (b) that this sulfite ion itself exchanges rapidly with the solvent. This exchange could, of course, occur *via* operation of Equilibrium (1). However Huston's[12] results appear to indicate a very small concentration of sulfite ion derived from self-ionization of sulfur dioxide. Consequently, an alternative mechanism seems more inviting, namely, a direct interaction between solvent and sulfite, wherein the solvent acts as an acid and receives an oxide ion from the sulfite base

$$SO_3^{=} + S^*O_2 \rightleftarrows SO_2 + S^*O_3^{=}$$

This mechanism would simply short-cut the intermediate ionization step (Equation (1)) and presents a situation analogous to that of hydronium ion in water where it seems altogether reasonable that proton exchange with the solvent occurs *via* direct interaction of the ion and a water molecule, without intermediate self-ionization of the water

$$H_3O^+ + H_2O^* \rightleftarrows H_2O + H_3O^{*+}$$

Thus we arrive at a picture of acid–base chemistry in the solvent sulfur dioxide as involving mobile oxide ions analogous to the mobile hydrogen ions of aqueous solutions. In support of this view we have Huston's[12] results combined with those of Nakata.[15] Nakata, using O^{18} as tracer observed a rapid exchange between sulfur dioxide and sulfur trioxide in the liquid phase, whereas Huston, using S^{35}, found the exchange rate to be triflingly slow. According to our picture the sulfur dioxide here acts as a base toward the strong acid sulfur trioxide, yielding to it an oxide ion in some such equilibrium as

$$SO_2 + SO_3 \rightleftarrows SO^{++} + SO_4^{=}$$

This, of course, would lead to oxygen but not sulfur exchange. Again the mobility of oxide ion is demonstrated.

What now of the observed non-exchange of the thionyl compounds? The conclusion seems clear that there can be but little ionization according to Equilibrium (2) and hence but little SO^{++} formed in solution from these compounds. It seems certain, in view of the foregoing discussion, that any thionyl ion so formed would exchange rapidly with

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(13) The reaction tubes, after removal of the reaction mixture, were examined for residual activity, such as an active sulfur deposit. None was ever observed.

(14) W. H. Zachariasen, *Phys. Rev.*, **40**, 923 (1932).

(15) S. Nakata, *J. Chem. Soc. Japan*, **64**, 635 (1943).

the solvent: if not *via* Equilibrium (1), then by pulling an oxide ion off a solvent molecule.

We may conclude that Jander's concepts, at least as far as thionyl compounds are concerned, are in need of modification. As has been pointed out,[5] for instance, an ionization equilibrium for thionyl chloride intrinsically more likely than Equation (2) would be

$$SOCl_2 \rightleftarrows SOCl^+ + Cl^- \qquad (6)$$

In general it seems clear that Jander places too great emphasis on strictly ionic mechanisms for his reactions in sulfur dioxide. It seems likely that the concept of mobile oxide ions might be more fruitful for the understanding of chemical reactions in this solvent.

Having rejected the concept of the direct production of thionyl ions from thionyl compounds, we are left with an open question as to the mechanisms by which they react. We are at present planning chloride ion exchange experiments to investigate the possibility of Equilibrium (6). An O^{18} tracer study of the thionyl chloride–sulfur dioxide exchange would be of considerable interest as a test of the possible operation of such an equilibrium as

$$SO_2 + SOCl_2 \rightleftarrows SO^{++} + SO_2Cl_2^{=} \qquad (7)$$

We are also projecting, as mentioned above, a tracer study of the potassium bromide–thionyl chloride reaction (in sulfur dioxide) which may be of considerable interest in this connection. If, as appears to be the case in this reaction, considerable activity finds its way from the thionyl chloride into the solvent, this might come about through the operation of Equilibrium (7) followed by the reaction

$$S^*O_2Cl_2^{=} \rightleftarrows S^*O_2 + 2Cl^-$$

The thionyl bromide would then be formed by combination of bromide ions with the thionyl ions produced in Equilibrium (7).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium[1]

BY I. M. KOLTHOFF AND I. K. MILLER[2]

Evidence is given that potassium persulfate decomposes thermally in aqueous solutions by two reactions, (a) a symmetrical rupture of the O–O bond to form two sulfate free-radicals which disappear by reaction with water to liberate oxygen, and (b) an acid-catalyzed reaction involving the unsymmetrical rupture of the O–O bond of the $HS_2O_8^-$ ion to form sulfur tetroxide and bisulfate. In dilute acid solutions sulfur tetroxide decomposes rapidly to form oxygen and sulfuric acid while in solutions 2 to 5 *M* in perchloric or sulfuric acid sulfur tetroxide hydrolyzes rapidly to Caro's acid (H_2SO_5). The kinetics of the thermal decomposition of the persulfate ion are described by the equation $-dS_2O_8^{=}/dt = k_1[S_2O_8^{=}] + k_2[H^+][S_2O_8^{=}]$. The values of k_1 and k_2, respectively, are 6.0×10^{-5} min.$^{-1}$ and 3.5×10^{-3} (min.$^{-1}$)(m./l.)$^{-1}$ at an ionic strength of 0.4 at 50°. The activation energy for the uncatalyzed reaction is 33.5 kcal. and for the acid-catalyzed reaction 26.0 kcal. The rate of the uncatalyzed reaction is independent of ionic strength but the rate of the acid-catalyzed reaction decreases with increasing ionic strength. The oxygen liberated by the uncatalyzed reaction comes from the water while the oxygen liberated by the acid-catalyzed reaction comes from the persulfate ion.

Since the discovery of persulfuric acid ($H_2S_2O_8$) in 1878 by Berthelot,[3] numerous papers have appeared concerning the properties and reactions of persulfuric acid and persulfates. Elbs and Schönherr[4] found that persulfuric acid is unstable in aqueous solutions, decomposing in dilute sulfuric acid solutions with liberation of oxygen while in more concentrated sulfuric acid solutions hydrogen peroxide rather than oxygen is formed. The formation of monopersulfuric acid (H_2SO_5) by strongly acid persulfate solutions was observed by Caro[5a] while later work by Palme[5b] showed that this acid is an intermediate in the decomposition of persulfuric acid in strongly acid solutions to form hydrogen peroxide.

Thus the decomposition of persulfate in aqueous solutions involves the reactions

$$S_2O_8^{=} + H_2O \longrightarrow 2HSO_4^- + {}^1/_2O_2 \qquad (1)$$
$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4 \qquad (2)$$
$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4 \qquad (3)$$

In alkaline, neutral and dilute acid solutions persulfate decomposes according to reaction (1) while in strongly acid solutions reactions (2) and (3) occur.

Studies of the kinetics of the decomposition of the potassium and sodium salts of persulfuric acid in alkaline, neutral and dilute acid solutions were first made by Levi and Migliorini[6] and later by Green and Masson[7] and by Kailan and co-workers.[8] There is general agreement among these workers that persulfate decomposition in aqueous solutions is first order and that the reaction is catalyzed by hydrogen ion. Since the data in the literature are not adequate to make possible a quantitative treatment of the influence of hydrogen ion on the rate of persulfate decomposition in aqueous solutions, the kinetics of the reaction have been reinvestigated in more detail.

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[1] This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the synthetic rubber program of the United States Government.

[2] From a thesis submitted by I. K. Miller to the Graduate School of the University of Minnesota, 1950.

[3] M. Berthelot, *Ann. chim. phys.*, **14**, 345 (1878).

[4] K. Elbs and O. Schönherr, *Z. Elektrochem.*, **1**, 468 (1895).

[5] (a) H. Caro, *Z. angew. Chem.*, 845 (1898); (b) H. Palme, *Z. anorg. Chem.*, **112**, 97 (1920).

[6] M. G. Levi and E. Migliorini, *Gazz. chim. ital.*, **36**, **II**, 599 (1906).

[7] L. Green and O. Masson, *J. Chem. Soc.*, **97**, 2083 (1910).

[8] A. Kailan and L. Olbrich, *Wien. Akad. Ber.*, **IIb 135**, 423 (1926).