measured down to −196°, but at 20°K. the magnetization of a hydrogenized sample was found to be about the same as prior to the admission of hydrogen. It was surmised that this effect might be due to a reversal of electron transfer leading to the formation of hydride ions on the nickel surface.

Whatever may be the explanation, the existence of the effect is confirmed by the present work (Fig. 5), in which a small but definite increase of magnetization was found to occur. The attribution of this effect to hydride ion formation receives some support from the results of hydrogen adsorption on a CO-treated U.O.P. sample. Such a sample, containing a relatively small fraction of the nickel in large particles, was found to have less than half the ability (per g. of nickel) to adsorb hydrogen as compared with the original U.O.P. sample. This peculiar effect could be attributed to the larger size of hydride ions and hence to the diminished number which could be accommodated on a surface, as compared with hydrogen atoms. The fact that the 1% of nickel which is ferromagnetic at room temperature, in the CO-treated U.O.P., gives a negative change of magnetization on exposure to hydrogen is, of course, of no significance in this discussion.

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EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Kinetics of the Reaction of Sulfite and Bromate[1-2]

BY FRANK S. WILLIAMSON[3] AND EDWARD L. KING

RECEIVED APRIL 1, 1957

The oxidation of sulfur(IV) by bromate results, very largely, in the formation of sulfate; a deviation of the stoichiometry from that corresponding to sulfate production suggests the formation of a small amount of sulfur(V), presumably dithionate ion. The rate of disappearance of sulfur(IV) has been determined over the *p*H value ranges 3.4–7.4 at 25° and 1.7–4.5 at 0°. The rate data indicate that in the *p*H range studied the reaction proceeds *via* two different transition states with the compositions $[HSO_3 \cdot BrO_3^{=} + nH_2O]^{\ddagger}$ and $[SO_2 \cdot BrO_3^{-} + mH_2O]^{\ddagger}$.

The oxidation of sulfur(IV)[4] by bromate ion in neutral or mildly acidic aqueous solution proceeds at a conveniently measurable rate at 25.0°. Among the facets of this reaction which are of interest is the *p*H dependence of the rate. The reported acid dissociation constant for sulfurous acid are $K_1^0 = 1.72 \times 10^{-2}$ and $K_2^0 = 6.24 \times 10^{-8}$ at 25°.[5] These values, although not valid for a medium with Γ[6] equal to 4.20 (the value for most of the solutions studied in this work), do allow the establishment of the approximate hydrogen ion concentration limits in which each of the sulfur(IV) species are predominant. Thus the equations for the net reactions producing sulfate, the principal product of the oxidation of sulfur(IV), are[7]

$$\text{at } (H^+) > K_1,\ 3H_2SO_3 + BrO_3^- \longrightarrow 3HSO_4^- + Br^- + 3H^+ \quad (1)$$

$$\text{at } K_1 > (H^+) > K_2,\ 3HSO_3^- + BrO_3^- \longrightarrow 3SO_4^{=} + Br^- + 3H^+ \quad (2)$$

$$\text{and at } K_2 > (H^+),\ 3SO_3^{=} + BrO_3^- \longrightarrow 3SO_4^{=} + Br^- \quad (3)$$

Over a significant fraction of the hydrogen ion concentration range studied, hydrogen ion is produced in the reaction; since the rate is hydrogen ion dependent, buffers were used to maintain the hydrogen ion concentration approximately constant during the course of a kinetic run. Because of the high rate of reaction, kinetic studies were not made in the region $(H^+) > K_1$ (eq. 1).

The reaction has been found to be first order in bromate ion, first order in total sulfur(IV) and exhibits a hydrogen ion dependence which indicates that the reaction proceeds *via* two different activated complexes. The rate law is a four parameter equation

$$-\frac{d(S^{IV})}{dt} = (BrO_3^-)(S^{IV}) \left\{ \frac{k_1 + k_2(H^+)}{K_1^{-1}(H^+) + 1 + K_2(H^+)^{-1}} \right\} \quad (4)$$

the parameters K_1 and K_2 being identified as the first and second ionization quotients for sulfurous acid.

Experimental

Reagents.—All solutions were prepared using doubly distilled water, the second distillation being carried out in the presence of alkali and permanganate from Pyrex glass apparatus. Reagent grade chemicals were used without further purification with the exception of the sodium perchlorate which was C.P. grade and was recrystallized from water before use. Kinetic runs using completely independent sources of reagents yielded essentially the same value

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[1] Taken in part from the Ph.D. thesis of Frank S. Williamson, University of Wisconsin, 1954; presented before the 126th National Meeting of the American Chemical Society at New York City, N. Y., Sept. 1954.

[2] Supported in part by grants from the Research Committee of the Graduate School, University of Wisconsin, and the U. S. Atomic Energy Commission.

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[4] In this paper, sulfur(IV) refers to the equilibrium mixture of sulfur(IV) species while sulfur dioxide, sulfurous acid, hydrogen sulfite ion and sulfite ion refer to the individual species. These species are in equilibrium with one another. Although the hydration of SO_2 has a measurable rate ($t_{1/2} \cong 10^{-3}$ sec., from work of G. v. Bunau and M. Eigen, *Z. physik. Chem. (Frankfurt)*, **7**, 108 (1956)), it is large compared to the rates under consideration in this work.

[5] H. V. Tartar and H. H. Garretson, THIS JOURNAL, **63**, 808 (1941).

[6] The ional concentration Γ is defined, $\Gamma = \Sigma C_i Z_i^2$, where C_i is the molar concentration of i-th species and Z_i its charge. The ional concentration differs by a factor of *approximately* two from the ionic strength, the difference being only *approximate* because the ionic strength involves the molal concentration scale.

[7] Since K_2 for sulfuric acid is approximately equal to K_1 for sulfurous acid, three equations are sufficient to summarize all of the net reactions.

for the rate of reaction, thus demonstrating that catalysis by trace impurities is very unlikely.

The reaction mixtures were prepared from the appropriate stock solutions. The sulfur(IV) stock solution was freshly prepared for the experiments run each day using reagent grade sodium sulfite and boiled, doubly distilled water; the concentration of each sulfur(IV) solution was determined by analysis.

Details of the Kinetic Runs.—The reaction was initiated by adding either oxygen-free sodium bromate solution or oxygen-free sodium sulfite solution to an oxygen-free solution containing the other reactant and the appropriate buffer. The solutions were rendered free of oxygen by bubbling with oxygen-free nitrogen. Nitrogen which had been saturated with water vapor was also passed through the reaction mixture during each run. The removal of oxygen was important as the rate of disappearance of sulfur(IV) was greater in its presence.

Most of the kinetic runs were carried out in a thermostat maintained at 25.00 ± 0.01°. The few experiments at 0° were carried out in an ice-water thermostat bath.

Analytical Procedures in Kinetic Experiments.—The concentration of sulfur(IV) at a particular time was determined by delivering an aliquot of reaction mixture with a calibrated rapid delivery pipet into an excess of standardized triiodide solution containing a buffering system, acetate (pH $\cong$5) or sodium monohydrogen phosphate–sodium dihydrogen phosphate (pH $\cong$8). The buffer system used in the quenching solution was the same as that which was present in the reaction mixture. The excess triiodide ion was titrated with standardized thiosulfate solution in the acetic acid–sodium acetate buffer solutions and with a standardized arsenic(III) solution in the phosphate buffer solutions in conformity to recommended analytical procedures.[8] Since the quenched reaction mixtures contain bromate ion and iodide ion as well as triiodide ion, it is necessary to rule out the possibility of the reactions involving these species with one another or with the reducing agents used in the titration. It has been found that in 0.5 M acetic acid–sodium acetate buffer the amount of thiosulfate ion required to titrate a given amount of triiodide is not altered by the presence of bromate ion. Thus, the rates of the bromate–thiosulfate and bromate–iodide reactions are negligibly low at the concentration of hydrogen ion existing in this buffer solution. The rate of the bromate–iodide reaction, which is proportional to the square of the hydrogen ion concentration[9] is, therefore, even lower in the phosphate buffer solutions. In addition, bromate does not oxidize arsenic(III) at a significant rate.[10] Therefore, the oxidizing power which disappears from the triiodide solution upon being treated with an aliquot of reaction mixture is due to the reaction with sulfur(IV) in the reaction mixture. The initial composition of the solution *and* the concentration of sulfur(IV) at each particular time allow the evaluation of the concentrations of all species at that time *if the stoichiometry of the reaction is known.*

Studies of the Stoichiometry of the Sulfur(IV)–Bromate Reaction.—Although dithionate ion, $S_2O_6^=$, a species of sulfur(V), is thermodynamically unstable with respect to disproportionation into sulfur (IV) and sulfur(VI), the rate of this reaction is low.[11] The oxidation of sulfur(IV) by many oxidizing agents does not lead exclusively to sulfate but rather to a mixture of sulfate and dithionate; in the case of certain 1-equivalent oxidizing agents reacting with sulfur(IV), dithionate is the predominant product.[12] Thus, the stoichiometry of the oxidation of sulfur(IV) by bromate must be established before data on the concentration of sulfur(IV) as a function of time can be interpreted. Values of the stoichiometric ratio R, $R \equiv$ (moles of sulfur(IV) reacting)/(mole of bromate reacting), were determined in a large number of experiments run at various concentration conditions. These experiments involved the determination of the concentration of bromate or sulfur(IV) in excess in reaction mixtures kept for times sufficient for the reaction to go essentially to completion. In those experiments which contained an excess of sulfur(IV), the same analytical procedure was employed as was used in the kinetic runs. In those experiments containing an excess of bromate, the bromate concentration was determined by the addition of potassium iodide and lowering the pH of the solution. The liberated triiodide ion was determined by titration with standardized thiosulfate solution. In one series of experiments with pH values in the range 1.8–6.9, there was either a twofold excess of sulfur(IV) or a twofold excess of bromate. The average of the observed values of R in eight experiments with excess sulfur(IV) was 3.17 ± 0.05 and in eight experiments with excess bromate was 3.13 ± 0.03. In these experiments, there did not appear to be a significant trend in R with the pH value of the solution. In two other series of experiments, values of R of 3.02 ± 0.03 and 3.26 ± 0.04 were obtained. Thus the studies on the stoichiometry of the reaction do demonstrate that some sulfur(V), presumably dithionate ion, is formed and further, that the amount formed is not completely reproducible. In essentially all of the experiments for which stoichiometric data exist, over 90% of the sulfur(IV) is oxidized to sulfate. Higginson and Marshall[12] have determined the stoichiometry of the reaction of sulfur(IV) with a number of oxidizing agents; they find, for the bromate oxidation, values of R = 3.08 to 3.38 at pH 0.5.

The Kinetics of the Reactions.—A single experiment in which the bromate concentration is large compared to sulfur(IV) serves to fix the order of the reaction with respect to sulfur(IV). In one such experiment with the concentration conditions: $(NaH_2PO_4) = 0.0625\ M$, $(Na_2HPO_4) = 0.500\ M$, $(NaClO_4) = 0.446\ M$, $(Na_2SO_4) = 0.0225\ M$, $(NaBrO_3) = 0.0166\ M$ and $(Na_2SO_3) = 3.57 \times 10^{-3}\ M$ (measured pH value 7.15), the reaction was followed 93% toward completion; all of the experimental points fall on a straight line in a plot of log (S^{IV}) *versus* time. Thus, the reaction is first order in sulfur(IV) under these conditions. A series of five experiments in the same medium with varying bromate ion concentration (1.67×10^{-3} to 1.67×10^{-2} molar), in each of which the sulfur(IV) concentration was low compared to the bromate ion concentration, allowed the evaluation of the order with respect to bromate. The five individual values of the pseudo-first-order rate coefficients divided by the mean bromate ion concentration existing during each run have an average difference of 4% from the average value of this quotient. The reaction is, therefore, first order in bromate ion. The data from all kinetic experiments have been treated under the assumption that in a particular medium the reaction follows the rate law

$$-\frac{d(S^{IV})}{dt} = k(S^{IV})(BrO_3^-) \qquad (5)$$

this equation defining the rate coefficient k. Although the stoichiometry does deviate slightly from R = 3.00, the concentration of bromate ion existing in a reaction mixture was calculated assuming that R = 3.00

$$(BrO_3^-)_0 - (BrO_3^-)_t = \frac{1}{3}\{(S^{IV})_0 - (S^{IV})_t\}$$

In experiments in which the concentrations of the reactants are comparable, a deviation of the second-order plot from linearity results if the reaction is proceeding with an R value differing significantly from 3.00. In most of the experiments, the reaction proceeded 70–80% toward completion before any deviation from second-order behavior was noted. In the evaluation of the second-order rate coefficient, k, only those points on the straight line portion were used.

The Influence of the Concentration of the Buffer Constituents upon the Rate.—The hydrogen ion concentration was maintained approximately constant during the course of each kinetic experiment by the use of two different buffer systems, acetic acid–sodium acetate or sodium dihydrogen phosphate–disodium hydrogen phosphate. In order to maintain the medium as constant as possible, *both* the *ional concentration* and the *salt normality* were held constant. All solutions studied at 25° had compositions consistent with the relationships: $[(NaClO_4) + (NaAc) + (NaH_2PO_4)] = 0.525$ molar, and $[(Na_2SO_4) + (Na_2HPO_4)] = 0.525$ molar; the concentrations of bromate and sulfur(IV) did not contribute significantly to the total ional concentration.

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(8) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, pp. 619–621.

(9) R. H. Clark, *J. Phys. Chem.*, **10**, 679 (1906).

(10) F. C. Bowman, *ibid.*, **11**, 292 (1907).

(11) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 328–329, 358.

(12) W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957); these authors suggest the term 1-equivalent oxidizing agent be used instead of the term 1-electron oxidizing agent if no implications regarding the mechanism of the reaction are intended.

Kinetic experiments at varying concentrations of buffer were performed in order to learn whether the buffer constituents were exerting any specific influence upon the rate of reaction; two series of such experiments were performed, one using each buffer system. The acetic acid–sodium acetate series (eight experiments) was carried out at (HAc)/(Ac$^-$) = 1.00; the concentration of acetic acid varied by a factor of ten (0.05–0.50 *M*). The phosphate series (six experiments) was carried out at ($H_2PO_4^-$)/($HPO_4^=$) = 1.00; the concentration of each phosphate species varied by a factor of four (0.125–0.500 *M*). In the experiments of both series, the reaction was followed to between 65 and 90% of completion. In each series, the average difference between the individual values of k and the average value of k for that series was less than 3%. Thus, this reaction is not subject to catalysis by the constituents of either buffering system. This conclusion is of some interest in view of the observation that the hypochlorite–hydrogen peroxide reaction is subject to catalysis by the constituents of an acetate buffer.[13,14] (In two of the experiments in the phosphate series, sodium perchlorate was replaced by sodium bromide at 0.27 molar with no influence upon the rate.)

The Acidity Scale.—In the hydrogen ion concentration range studied, there is a change in the predominant species of sulfur(IV) which exists in solution, sulfite ion being predominant at the lower acidities and hydrogen sulfite ion being predominant at higher acidity. The apparent value of the second dissociation quotient for sulfurous acid in the medium used in the kinetic studies will be considered to be a parameter, the value of which will be chosen to obtain the best possible correlation of the experimental data. Thus it is not necessary to know the absolute value of the hydrogen ion concentration; only the relative concentration of hydrogen ion existing in each solution is required. With each particular buffer, values of the relative concentration of hydrogen ion can be calculated from the value of the pH measured with a Beckman model G pH meter or from the known ratio of the concentrations of the buffer constituents. If the former approach is used, the assumption is made that the conversion factor α $\{\alpha = (p\text{H}/\log(\text{H}^+)^{-1})\}$ is a constant in media with constant values of the ional concentration and electrolyte normality. If the latter approach is used, the assumption is made that the activity coefficient factor relating the acid dissociation equilibrium quotient to the corresponding thermodynamic equilibrium constant is a constant in the media under consideration. The correlation with the measured pH values seems preferable since, to some extent at least, it takes into account any variation in the activity coefficient factor.

For the experiments carried out in acetic acid–sodium acetate buffers, the two approaches prove to be equivalent since the measured pH values of twenty eight solutions used in kinetic runs yield an approximately constant value of pK'_{HAc} where $pK'_{\text{HAc}} = p\text{H} + \log\{(\text{HAc})/(\text{Ac}^-)\}$, with (HAc)/(Ac$^-$) varying over the range 10 to 1/10. The average value of pK'_{HAc} was 4.48 with an average difference between the individual values and the average value of 0.02_3. It is of interest to note that this value is in the range of values of pK_{HAc} for Γ = 4.2 for solutions containing various single salts, barium chloride, lithium chloride, sodium chloride and potassium chloride.[15]

In the phosphate buffer solutions in which ($H_2PO_4^-$)/($HPO_4^=$) = 1 to 10, the concentration of dihydrogen phosphate ion was held constant while the concentrations of monohydrogen phosphate ion and sulfate ion varied; for ($H_2PO_4^-$)/($HPO_4^=$) = 0.1 to 1, the concentration of monohydrogen phosphate ion was held constant while the concentrations of dihydrogen phosphate ion and perchlorate ion varied. These medium changes must influence the activity coefficient factor and/or the value of α (defined in an earlier paragraph) since the value of $\Delta p\text{H}/\Delta(\log(H_2PO_4^-)/(HPO_4^=))$ is -0.80 for $\{(H_2PO_4^-)/(HPO_4^=)\} < 1$ while it is equal to -1.0_6 for $\{(H_2PO_4^-)/(HPO_4^=)\} > 1$.

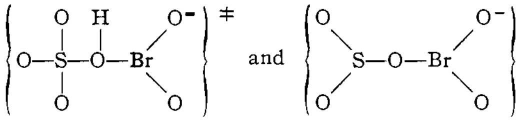
The pH meter was standardized with pH 4.00 and pH 7.00 Beckman buffers; these are phthalate and phosphate buffers, respectively, prepared according to NBS specifications.

The Dependence of Reaction Rate upon Electrolyte Concentration.—Although medium effects have not been a point of major concern, kinetic experiments have been perfomed at values of Γ = 1.05, 2.62 and 4.20 at both pH 4.01 ± 0.02 and 5.56 ± 0.03. At pH $\cong$ 4.0, the second-order rate coefficient *decreased* by 29% with an increase of Γ from 1.05 to 4.20 and at pH $\cong$ 5.6, the second-order rate coefficient *increased* by 23% with the same increase of Γ. Although no justification exists for a theoretical quantitative correlation of these trends in rate with Γ at such high values of Γ, it does seem reasonable to conclude that the sign of ΔZ^2 for the conversion of the reactants into the activated complex is different at these two pH values.

Kinetic Runs at 0°.—The rate of reaction in solutions which are more acidic than pH 3.4, the low pH limit of the experiments already reported, is of some interest. It is in this low pH region that the predominant form of sulfur(IV) becomes H_2SO_3. The rate of reaction is inconveniently high at such pH values if the measurements are made at 25°. In an effort to determine the rate in this pH region some experiments were run at 0°. These experiments were run in media with $\Gamma \cong 1.05$, the electrolyte being exclusively of the 1-1 type. Three of the experiments were run in HAc–NaAc buffer solutions and three were run in H_3PO_4–NaH_2PO_4 buffer solutions. The second-order rate coefficients calculated from the 0° data were correlated with the calculated hydrogen ion concentration of the solutions using known or estimated values of the acid dissociation quotients for acetic acid and phosphoric acid (K_1).[16]

Results and Discussion

In all, eighty-four kinetic experiments were carried out at 25.0° to elucidate the dependence of the second-order rate coefficient (defined in equation 5) upon the acidity of the solution. The value of k was approximately proportional to (H$^+$) for pH > 6.4 and pH < 4.4 but showed a less pronounced dependence at intermediate pH values. Since a different species is the predominant form of sulfur(IV) in the two different pH regions where k is proportional to (H$^+$), the reaction must proceed *via* two different activated complexes. These activated complexes have the compositions $[HSO_3 \cdot BrO_3^= + nH_2O]^\ddagger$ and $[SO_2 \cdot BrO_3^- + mH_2O]$,‡ the number of water molecules in an activated complex not being determined by the kinetic data. Taube[17] has suggested these geometrical arrangements for the two activated complexes. One



identifies k_1 of equation 4 as the rate constant for the forming of the first of these activated complexes from HSO_3^- and BrO_3^- and k_2 as the rate constant for the forming of the second of these activated complexes from HSO_3^-, H$^+$ and BrO_3^-. Since the reaction is first order in sulfur(IV) and zero order in sulfur(VI), it is the first step in the six-equivalent reduction of bromate which is rate-determining. The bromine-containing intermediate which is produced in the break-up of these transition states as well as the bromine-containing intermediates formed in subsequent steps react relatively rapidly. Neither the nature of these

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[13] R. E. Connick, THIS JOURNAL, **69**, 1514 (1947).

[14] J. O. Edwards, *J. Phys. Chem.*, **56**, 280 (1952).

[15] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 524.

[16] The values of $K_1{}^0$ for acetic acid and phosphoric acid at 0° were taken as 1.66 × 10^{-5} and 8.97 × 10^{-3}, respectively (ref. 15, p. 580). The calculated values at Γ = 1.0, made by assuming the activity coefficient factor to be the same as $\gamma^2_\pm$ for HCl, $(0.776)^2$ (ref. 15, p. 547), are 2.8 × 10^{-5} and 1.5 × 10^{-2}, respectively. The value of the first ionization quotient for sulfurous acid at 0° and Γ = 1.0 is estimated to be 3.1 × 10^{-2}.

[17] H. Taube, *Record Chem. Prog.*, **17**, 32 (1956).

steps nor the details of the side reaction which is responsible for the observed values of R being over 3.00 are elucidated by these kinetic data.

The observed mild dependence of the empirical second-order rate coefficient upon Γ is consistent with the complete rate law; at $p\text{H} \cong 5.6$, the empirical second-order rate coefficient is approximately equal to k_1 which corresponds to ΔZ^2_{act} of $+2$, while at $p\text{H} \cong 4$, the empirical second-order rate coefficient is approximately equal to k_2 which corresponds to ΔZ^2_{act} of -2. (The use of this latter value is subject to some uncertainty since the salt effect upon the buffer equilibrium must be taken into account; if one writes for the formation of the transition state the reaction $\text{HSO}_3^- + \text{HAc} + \text{BrO}_3^- = \{\text{H}_2\text{SO}_3{\cdot}\text{BrO}_3^-\}^\ddagger + \text{Ac}^-$, the value of ΔZ^2_{act} is zero.)

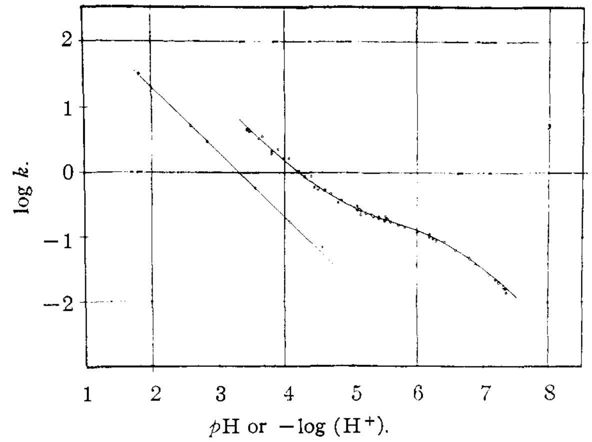

Fig. 1.—Log k (defined by equation 5) *versus* pH (measured) (for 25° data, upper line) or $-\log(\text{H}^+)_{\text{calculated}}$ (for 0° data, lower line). The solid lines are calculated using the parameters given in the text.

Taking cognizance of the uncertainty in the relationship between (H^+) and the measured pH value, a quantity h, defined $\log h = -p\text{H}$, will be used in the rate equation; equation 4 becomes

$$-\frac{\text{d}(\text{S}^{\text{IV}})}{\text{d}t} = (\text{BrO}_3^-)(\text{S}^{\text{IV}}) \left\{\frac{k'_1 + k'_2h}{h/K'_1 + 1 + K'_2/h}\right\} \quad (4')$$

where $k'_1 = k_1$, $k'_2 = k_2(\text{H}^+)/h$, $K'_1 = K_1h/(\text{H}^+)$ and $K'_2 = K_2h/(\text{H}^+)$. At the lowest acidity studied at 25°, $h/K_1 < 1$; therefore values of only the three parameters k'_1, k'_2 and K'_2 are obtained from the data at 25.0°. The values calculated by the method of averages are $k'_1 = 0.173$ 1 mole^{-1} sec.$^{-1}$, $k'_2 = 1.29 \times 10^4$ 1^2 mole^{-2} sec.$^{-1}$ and $K'_2 = 4.45 \times 10^{-7}$. Figure 1 shows both the experimental points and the curve calculated using these parameters; the average difference between the experimental values of k (defined by equation 5) and the values calculated using the parameters of equation 4′ is 6.0%.

The values of k obtained at 0° are also presented in Fig. 1. Except for the point at the lowest acidity studied, the values of the second-order rate coefficient are consistent with the equation $k/(\text{H}^+) = 2.0_3 \times 10^3$ 1. mole^{-1} sec.$^{-1}$; this is the value of k_2 at 0°. At the lowest hydrogen ion concentration studied, $(\text{H}^+) \cong 2.8 \times 10^{-5}$, the k_1 term is, presumably, contributing significantly to the rate, accounting for this point falling above the line. At the highest hydrogen ion concentration studied, $(\text{H}^+) \cong 1.5 \times 10^{-2}$, approximately one-third of sulfur(IV) is present as SO_2 plus H_2SO_3, and one would expect a change in the slope of the log k *versus* log (H^+) plot. Such is not observed. This could be due to the fortuitous equality $[(\text{SO}_2) + (\text{H}_2\text{SO}_3)]/(\text{HSO}_3^-) = (\text{SO}_2{\cdot}\text{BrO}_3{\cdot}\text{H})^\ddagger/(\text{SO}_2{\cdot}\text{BrO}_3^-)^\ddagger$, or more likely to the fact that there are simply insufficient data in the region $(\text{H}^+) \geqslant K_1$ to lead to any definite statement regarding the activated complex $\{\text{SO}_2{\cdot}\text{BrO}_3{\cdot}\text{H} + p\text{H}_2\text{O}\}^\ddagger$.

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MADISON, WISCONSIN

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

The Reaction of Sodium Hydride with Methyl Borate in Solvents. Convenient New Procedures for the Synthesis of Sodium Borohydride[1,2]

BY HERBERT C. BROWN, EDWARD J. MEAD[3] AND PAUL A. TIERNEY[4]

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The product obtained by the reaction of methyl borate with sodium hydride in the absence of a solvent has been established to be essentially sodium trimethoxyborohydride. This product is soluble in diglyme. The dissolution is followed by a rapid disproportionation into soluble sodium borohydride and insoluble sodium tetramethoxyborohydride. Sodium trimethoxyborohydride also undergoes rapid disproportionation in tetrahydrofuran. In this solvent sodium borohydride is insoluble and sodium tetramethoxyborohydride is highly soluble. However, in this solvent the sodium borohydride formed as a result of the disproportionation fails to precipitate completely as a result of its solubility in sodium tetramethoxyborohydride–tetrahydrofuran solutions. The passage of diborane through a solution of sodium tetramethoxyborohydride in tetrahydrofuran results in the quantitative conversion of the salt into sodium borohydride.

Sodium trimethoxyborohydride originally was prepared through the reaction of sodium hydride with methyl borate in excess methyl borate under reflux.[5] The sodium hydride available at that time

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(1) Addition Compounds of the Alkali Metal Hydrides. VIII.

(2) Based upon theses submitted by E. J. Mead and P. A. Tierney in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Research assistant on a grant from the National Science Foundation, 1953–1954.

(4) Standard Oil Research Foundation Fellow, 1955–1956. Parke, Davis and Company Fellow, 1956–1957.

(5) H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, THIS JOURNAL, **75**, 192 (1953).