bon dioxide and ammonia in dilute aqueous solutions is so far on the dissociation side[18] that enzymatic synthesis of urea in the present experiments accounts for only $10^{-5}\%$ exchange, instead of the 1% actually observed. The mechanism by which N^{15} is incorporated into urea is therefore uncertain and it may only be suggested that it is due to resynthesis of urea from carbamic acid and ammonia, before the former decomposes into ammonia and carbon dioxide.

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[18] G. N. Lewis and G. H. Burrows, THIS JOURNAL, **34**, 1515 (1912).

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

The Oxygen Exchange between Oxy-anions and Water; Bromate and Iodate Ions[1]

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The kinetics of the isotopic exchange reaction between bromate ion and water has been studied. In the region of 0.02 to 0.80 M bromate ion, the reaction follows the rate law ($R = k(H)^{+2}(BrO_3^-)$ where $k = 6.60 \times 10^{-3}$ liter^2 moles^{-2} second^{-1} at 30.00° and ionic strength 0.900. The activation energy is 14,230 cal./mole. The course of the reaction is not affected by light, added Br_2 or increased surface area. The dependence on the water concentration was not measured. The reaction proceeds faster in D_2O with k_D/k_H equal to 1.72. The corresponding exchange between iodate ion and water is complete in the time of separation of one minute. The exchange was studied under a number of different conditions. Different methods of separating the reactants were used. The rate of the bromate–water exchange is compared with that of the reduction of bromate ion by halide ions.

Introduction

This paper is a report of quantitative measurements on the rate of exchange of isotopic oxygen between bromate ion and water. It also describes attempts to measure the kinetics of the iodate–water exchange.

The exchange of isotopic oxygen between bromate ion and water has been studied qualitatively by several workers[3] who have reported the exchange to be slow. The exchange of many oxy-anions and water occurs in acid solutions. Bromic acid is a strong acid and is a good oxidizing agent in acid solutions. Under the conditions of these experiments, bromic acid is stable toward decomposition. The exchange between iodic acid and water has been studied qualitatively[3] and a fast exchange has been reported. Iodic acid is only partially dissociated, is a good oxidizing agent and is more stable toward decomposition than bromic acid. The rates of oxidation by iodic acid are generally more rapid than by bromic acid.

Experimental

Materials.—Oxygen-eighteen tagged potassium bromate and potassium iodate were prepared by the electrolytic oxidation of potassium bromide and potassium iodide in O^{18}-tagged water.[4] All chemicals were reagent grade. The water used as solvent was redistilled from alkaline permanganate.

Procedures.—The bromate water exchange was studied in solutions maintained at constant ionic strength 0.900 with added sodium nitrate. The exchange of oxygen between nitrate ion and the solvent is very slow under the conditions of these experiments.[5] The proper amounts of nitric acid, sodium nitrate and O^{18}-tagged bromate were placed in a volumetric flask and diluted to the mark with water of normal isotope content. The hydrogen ion concentration of each run was determined by the titration of 0.250-ml. samples of the reaction mixture. The reactants were separated by the precipitation of silver bromate. These precipitates were converted to O_2 for isotopic analysis by thermal decomposition.

The iodate exchange was studied by dissolving O^{18}-tagged potassium iodate in solutions of HNO_3 or KOH of the desired *p*H. The iodate fraction was separated by the precipitation of silver iodate in acid solutions or barium iodate in alkaline solutions. These precipitates were decomposed to O_2 for isotopic analysis. In some experiments, samples of water were vacuum distilled from the reaction mixture. The water was allowed to reach isotopic equilibrium with CO_2 and the CO_2 was used for isotopic analysis.[6]

The isotopic analyses were made on an isotope ratio mass spectrometer designed for the measurement of small differences in isotope content.[7] Measurements of 34/32 ratios were made on oxygen. The carbon dioxide samples which were equilibrated with the water from the iodate exchange had relatively small differences in their O^{18} content. These differences were measured by observing the change in the ratio of mass 46 to mass 44 when rapidly shifting back and forth between a standard CO_2 sample and the unknown sample.

Calculations.—The bromate exchange study requires a measurement of the change in O^{18} content of the bromate fraction as a function of time. The half-time for the exchange was found by plotting the log of one minus the fraction exchanged *versus* time.[8] The rate of the reaction which leads to isotopic exchange was then calculated by[8]

$$R = \frac{3(BrO_3^-) \times (H_2O)}{3(BrO_3^-) + (H_2O)} \times \frac{0.693}{t_{1/2}} \qquad (1)$$

where R is the rate in gram-atom oxygen/liter-second when the quantities in parentheses are the formal concentrations of the exchanging species and $t_{1/2}$ the half-time for exchange in seconds.

If a single reaction path is available for the reaction which leads to isotopic exchange, the rate law at a given temperature may be given by

$$R = k(H^+)^m(BrO_3)^n(H_2O)^p\Gamma \qquad (2)$$

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[1] This work supported by funds supplied by the U. S. Atomic Energy Commission and by the National Science Foundation.

[2] Lion Oil Co., El Dorado, Arkansas.

[3] N. F. Hall and O. R. Alexander, THIS JOURNAL, **62**, 3455 (1940); J. Halperin and H. Taube, *ibid.*, **74**, 375 (1952); T. C. Hoering, Master's Thesis, Washington University, St. Louis, 1951.

[4] K. Elbs, "Electrolytic Preparations," E. Arnold Co., London, 1903.

[5] E. A. Halvei, C. A. Bunton and D. R. Llwewllyn, *J. Chem. Soc.*, 4913 (1952).

[6] M. Cohn and H. C. Urey, THIS JOURNAL, **60**, 679 (1938).

[7] C. R. McKinney, J. M. McCrea, S. Epstein, H. A. Allen and H. C. Urey, *Rev. Sci. Inst.*, **21**, 724 (1950).

[8] A. C. Wahl and N. A. Bonner, "Radioactivity Applied Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951.

where Γ is some function of the activity coefficients of the reactants and the activated complex. The value of m was obtained by continuously varying the hydrogen ion concentration while keeping the bromate ion concentration and the ionic strength constant. In a similar manner, the value of n was determined.

Experimental Results

A. Iodate–Water Exchange.—The iodate–water exchange is complete in a sampling time of one minute at room temperature under all the conditions tried. The conditions were as follows. The *p*H of the solution was varied from 1 to 14 with nitric acid or potassium hydroxide. Buffers were used in the neutral range. Iodate concentrations as low as 0.001 M were tried. The three separation methods, previously described, were used in order to see if separation induced exchange were causing an apparent fast exchange. The same results were obtained by the three methods.

B. Bromate–Water Exchange.—The values for the rate of exchange between bromate ion and water are given in Table I. Each value for the rate was obtained from a separate run consisting of at least five samples of the bromate fraction. Plots of the log of the rate *versus* the log of the hydrogen ion concentration at fixed bromate concentration fell about straight lines of slope two. Plots of the log of the rate *versus* the log of the bromate concentration at fixed hydrogen ion concentration fell about straight lines of slope one. The specific rate constants in Table I were calculated from a third-order rate law.

TABLE I

THE RATE OF OXYGEN EXCHANGE BETWEEN BROMATE ION AND WATER (t = 30.00°, μ = 0.900.)

(H^+), M	(BrO_3^-), M	Rate × 10^4, g. atom/l. sec.	Third-order rate constant × 10^3, $l.^2$/mole^2 sec.
0.600	0.100	2.72	7.55
.600	.080	2.07	7.19
.600	.060	1.53	7.09
.600	.040	0.920	6.45
.400	.100	1.01	6.31
.400	.080	0.815	6.36
.400	.060	.577	6.00
.400	.040	.367	5.72
.200	.100	.262	6.56
.200	.080	.211	6.58
.200	.060	.171	7.13
.200	.040	.106	6.62
1.000	.060	4.08	6.80
0.900	.060	3.36	6.95
.800	.060	2.64	6.91
.700	.060	1.94	6.60
.600	.060	1.53	7.10
.500	.060	0.943	6.30
.400	.060	.577	6.00
.300	.060	.279	5.18
.200	.060	.171	7.13
.100	.060	.0429	7.14
.070	.060	.0224	7.62
.050	.060	.0184	1.22
.040	.060	.00336	3.50
.030	.060	.00324	6.00
.020	.060	.00166	6.94
.010	.060	.000317	5.29

Activation Energy.—The rate of the exchange reaction in 0.800 M hydrogen ion and 0.060 M bromate ion was studied at 20, 25, 30 and 35°. A plot of log rate *versus* $1/T$ gave a straight line with a slope corresponding to an activation energy of 14,230 cal./mole.

The Rate of Exchange in D_2O Solvent.—The rate of the exchange in 0.0510 M hydrogen ion and 0.0500 M bromate ion was studied in ordinary water and in D_2O of greater than 98% deuterium concentration. The reaction proceeded faster in D_2O with a half-time of 19.7 hr. compared to 33.6 hr. in ordinary water. This represents a ratio of rate constants in the two solvents of

$$k_D/k_H = 1.72 \qquad (3)$$

Attempts to Measure the Water Dependence.—Attempts to measure the dependence of the rate of the exchange on the water concentration were unsuccessful. The only common solvent used to vary the water concentration that resisted the oxidation of bromic acid was dioxane. The effect on the exchange rate by small amounts of added dioxane was very large. As the water was necessarily in large excess, and since the effect on the activity coefficients by the changing dielectric constant is large, these experiments were inconclusive.

Catalysis.—Experiments were performed to check for catalysis by glass surfaces, light and by added bromine. No effect on the rate of exchange was noticed.

Discussion

The exchange of oxygen between bromate ion and water at constant water concentration follows a third-order rate law

$$R = k(H^+)^2(BrO_3^-) \qquad (4)$$

where k has the value $6.60 \pm 0.50 \times 10^{-3}$ liter^2-mole^{-2}-second^{-1} at 30.00° and ionic strength 0.900.

The rate of reduction of bromate ion by halide ions in the presence of arsenous acid has been studied by Skrabal and Schreiner.[9] These reductions followed a fourth-order rate law

$$R = (H^+)^2(BrO_3^-)\{96.6(I^-) + 5.00(Br^-) + 0.00150(Cl^-)\} \qquad (6)$$

where k is in liter^3-mole^{-3}-second^{-1} at 25°. Sclar and Reisch[10] give 3.6 and Bray and Davis[11] give 1.6 as the specific rate constant for the bromate–bromide reaction. If we assume a first-order water dependence for the isotopic exchange reaction, the fourth-order specific rate constant at 25° becomes 7.98×10^{-5}.

Edwards[12] has postulated the exchange of water with bromate ions may occur by the equilibria

$$H^+ + BrO_3^- = HBrO_3 \quad \text{fast} \qquad (7)$$

$$H^+ + HBrO_3 = H_2BrO_3^+ \quad \text{fast} \qquad (8)$$

which may be followed by either a unimolecular

$$H_2BrO_3^+ \longrightarrow BrO_2^+ + H_2O \quad \text{slow} \qquad (9)$$

dissociation or by a bimolecular nucleophilic displacement

$$H_2O^* + H_2BrO_3^+ \longrightarrow H_2O + H_2BrO_3^{+*} \text{ slow} \qquad (10)$$

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[9] A. Skrabal and H. Schreiner, *Monatsh.*, **65**, 213 (1934).

[10] M. Sclar and L. C. Reisch, THIS JOURNAL, **58**, 667 (1936).

[11] W. Bray and P. R. Davis, *ibid.*, **52**, 1435 (1930).

[12] J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952).

The deuterium isotope effect on the rate of the exchange supports the idea that reactions (7) and (8) precede the rate-determining step. Deuterium oxide is less basic than protium oxide[13] hence reactions (7) and (8) should lie farther to the right in D_2O. The relative rates of reduction of bromate ion by halide ions in D_2O and H_2O has been studied.[14] The ratio of k_D/k_H is 3.5 for chloride ion, 2.5 for bromide ion and 2.4 for iodide ion.

A bimolecular nucleophilic displacement was assumed for the bromate–water exchange and for the bromate–halide reactions. An attempt was made to correlate the specific rate constants by the relationship proposed by Edwards[15]

$$\log k/k_0 = \alpha E_n + \beta H \qquad (11)$$

The specific rate constants for halide and water substitution are given k and by k_0, E_n and H are nucleophilicity and basicity constants for the donor and α and β are constants of the substrate. Edwards[15] has given values for E_n and H for halide ions and water. When the bromate rate data are fitted into equation 11, a qualitative agreement was obtained between the observed and calculated specific rate constants when the values $\alpha = 0.36$ and $\beta = -0.63$ were used.

The fast exchange between iodate ion and water in alkaline solution indicates that the mechanism for this exchange may be different for this ion than for bromate. This assumes that the rapid exchange observed is not due to separation induced exchange. This seems likely since different methods of separation were used.

Several mechanisms have been proposed that could account for such a rapid exchange. The basic dissociation of HIO_3 has been postulated[16] to account for some oxidations by iodate ion

$$H + IO_3^- = HIO_3 = IO_2^+ + OH^- \qquad (12)$$

Taube[3] has considered an increase in the coördination number of iodine as a reasonable possibility

$$H_2O + HIO_3 = H_3IO_4 \qquad (13)$$

The corresponding hydration reaction with periodate ion is known to come to equilibrium rapidly.[17]

The relationship[18] between the rate of exchange and the difference in electronegativity between the oxygen and the central atom of the oxy-anion is in agreement with the results of these experiments. Preliminary experiments in this Laboratory[19] show that the chlorate–water exchange is very slow and follows a different rate law than the bromate–water exchange.

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[13] The subject of deuterium isotope effects has been reviewed by K. Wiberg, *Chem. Revs.*, **55**, 721 (1955).

[14] E. Abel and F. Fabian, *Monatsh.*, **71**, 153 (1937).

[15] J. O. Edwards, This Journal, **76**, 1540 (1954).

[16] E. Abel, *Helv. Chim. Acta*, **33**, 785 (1950); K. J. Morgan, *Quart. Revs.*, **8**, 123 (1954).

[17] C. E. Crouthamel, A. M. Hayes and D. S. Martin, This Journal, **73**, 82 (1951).

[18] M. Haissinsky and R. Daudel, *Bull. chim. soc. France*, 557 (1947).

[19] F. Ishimori and T. Hoering, unpublished work.

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[Contribution from the Department of Chemistry, University of Rochester]

Photochemical Studies. L. The Ketene–Oxygen System at Higher Temperatures[1]

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Carbon monoxide, carbon dioxide, ethylene, formaldehyde and formic acid have been identified as products in the photochemical ketene–oxygen reaction. At room temperature the yields of all of these products are essentially independent both of intensity and of oxygen concentration except at very low oxygen concentrations. At 160° all quantum yields except that of ethylene are linearly dependent on the inverse of the square root of the light intensity. This fact and the values attained by the number of molecules of oxygen disappearing per quantum absorbed indicate strongly that a chain reaction occurs at 160°. In spite of these facts the quantum yield of ethylene formation is virtually independent of intensity and varies only slowly with change in oxygen concentration. The significance of ethylene formation in the reaction mechanism is open to some doubt, but it is very nearly certain that methylene radicals react rapidly with oxygen. The chain carriers must be radicals which do not form ethylene, and they are almost certainly mono- and not di-radicals. A reasonable mechanism for the chain reaction can be given, but definite proof of it is not now available. Methylene radicals seem to react with oxygen as though they were true radicals.

Introduction

A study of the photochemical ketene–oxygen reaction has recently been presented.[3] At room temperature and at 107° the rates of formation of products were essentially independent of oxygen concentration. A difference in behavior between 2700 and 3700 Å. was noticed both when oxygen was absent and when it was present. A plot of the reciprocal of the carbon monoxide yield against concentration in the absence of oxygen gave straight lines at the temperatures studied at 3700 Å., thus indicating the possibility that active molecules subject to collisional deactivation were present in the system. In the presence of oxygen at 3700 Å. the ratios of products were different from what they were at 2700 Å., thus affording contributory evidence that the active species at the two wave lengths are different.

It proved impossible to state definitely whether methylene radicals react so rapidly with oxygen that the reaction with ketene may be neglected or whether they react so rapidly with ketene that oxygen reactions are secondary. The present study was undertaken to provide additional evi-

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[1] This work was supported in part by contract with the Office of Naval Research, United States Navy. This material may be reproduced or used in any way by the United States Government.

[2] National Science Foundation Predoctoral Fellow, 1953–1954, Eastman Kodak Company Fellow, 1954–1955.

[3] A. N. Strachan and W. A. Noyes, Jr., This Journal, **76**, 3258 (1954).