Experimental

$KCl^{36}O_3$ was prepared by an electrolytic method described by Walton.[8] The $KCl^{36}O_3$ was purified by double recrystallization from water.

A water solution of 0.056 *N* $KCl^{36}O_3$ and 0.056 *N* $NaClO_4$ was equilibrated. The ClO_3^- was reduced to Cl^- with sulfurous acid ($Na_2S_2O_5$ and H_2SO_4). The excess $SO_3^=$ was oxidized to $SO_4^=$ with H_2O_2 and the excess H_2O_2 was decomposed by heat in the presence of platinum. The Cl^- was collected as AgCl on a micro filter crucible.

The filtrate containing ClO_4^- was reduced to Cl^- by the addition of a sulfuric acid solution of $TiOSO_4$ and passing this solution through a Jones reductor. The reduced solution was allowed to reflux for 30 minutes to ensure complete reduction. The titanous solution was then oxidized with H_2O_2 and the hydrochloric acid was distilled into a $AgNO_3$ solution and the AgCl collected as above.

The results of the experiments are given in Table I.

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[8] H. J. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 169.

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Kinetics of the Chlorite-Glucose Reaction

BY HERBERT F. LAUNER AND YOSHIO TOMIMATSU

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The stoichiometry of the reaction between sodium chlorite and glucose in weakly acidic buffers was investigated recently.[1] In order to draw conclusions regarding the stoichiometry of this reaction it was necessary to evaluate the decomposition of the chlorite in a simultaneous reaction. This was done by assuming the rate of decomposition, in the presence of glucose, to be a function of the geometric mean of the initial and final chlorite concentrations. This decomposition rate function was indirectly tested by comparison of final chlorite titers with calculated values. This involved the assumption that the glucose was completely oxidized (inasmuch as no analytical method for glucose was available over the range studied, 0.6 to 50 micrograms per ml.) in the presence of the sodium dihydrogen phosphate-phosphoric acid buffer used.

It is preferable to test this rate function without the assumption of complete oxidation of glucose. The indicated procedure is to set up the rate law for the disappearance of chlorite in simultaneous decomposition and oxidation reactions. Such treatment would be of general interest for the typical case of analytical reagents that decompose or undergo side reactions during the reaction with the substance being studied or determined. This article describes the derivation of an integrated rate law and the experimental tests thereof.

Experimental

All rate experiments were conducted at 50.00 ± 0.02° in the absence of photochemically active light. The reaction mixtures were buffered with 0.5 *M* sodium dihydrogen phosphate and orthophosphoric acid. For the purpose of varying the *p*H only the acid concentration was changed, in an effort to maintain constant ionic strength. Chlorite was determined iodimetrically, each point corresponding to a separate reaction mixture, analyzed at the time of interest. In the experiments with iron, ferric ammonium sulfate was dissolved in the diluted buffer and filtered through fine sintered glass, in order to avoid heterogeneous catalysis. For details of analysis and of experimental techniques, and for discussion thereof, the reader is referred to the previous paper.[1]

Acidity Functions.—The decomposition of chlorite in the absence of aldose was found by Barnett[2] to follow essentially the second-order rate law

$$-dC/dt = k_D(HClO_2)^2 \qquad (1)$$

Equation 1, in which *C* is the concentration of total chlorite, indicates that the decomposing species is un-ionized chlorous acid.

The quantity $(HClO_2)^2$ is not directly measurable and is expressed in terms of chlorite as h^2C^2, where $h = (H^+)/[K_{HClO_2} + (H^+)]$, and where K_{HClO_2} the dissociation constant of chlorous acid, may be approximated[2] to be 0.011 at 50°, at a salt concentration of 0.5 *M*. However, when the slopes of the four curves[3] of Fig. 1, in which $1/C$ was plotted against time, and which were obtained at various values of *p*H, are related to *h*, it is found that the decomposition is proportional to $h^{1.5}$. Near *p*H 4, it has been found[4] that the rate of formation of chlorine dioxide, one of the products of chlorite decomposition, is proportional to a power definitely less than 2 of the hydrogen ion concentration.

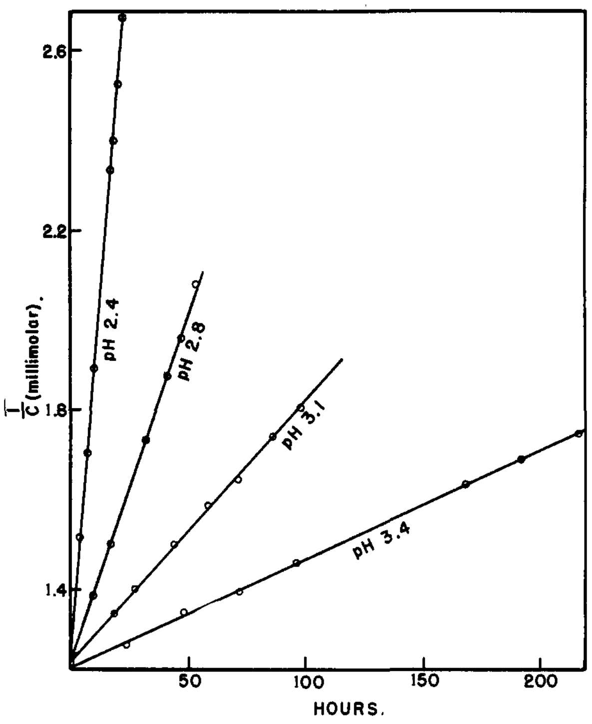

Fig. 1.—Rate of decomposition of sodium chlorite, initially 0.0008 molar, in the absence of glucose.

The straightness of these four curves substantiates the second-order nature of the decomposition with respect to *C*. From similar plots of the rate data of 19 control experiments without glucose the mean value, $k_D = 400 \pm 25$ mole^{-1} liter^{-1} hour^{-1},

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[1] Herbert F. Launer and Yoshio Tomimatsu, *Anal. Chem.* **26**, 382 (1954); presented at the American Chemical Society Meeting, Sept. 6-11, 1953, Chicago, Illinois.

[2] B. Barnett, Ph.D. Dissertation, University of California, Berkeley, Calif., 1935.

[3] Two other experiments at *p*H 2.0 and 1.6 resulted in a still lower exponent for *h* but these were omitted because it was believed that the relatively high concentration of phosphoric acid, 0.39 and 0.72 *M*, exerted specific effects.

[4] F. Stitt, S. Friedlander, H. J. Lewis and F. E. Young, *Anal. Chem.*, to be published.

was obtained. This value appeared to be independent of the concentration of ferric iron when tested at 3, 6 and 12 micrograms Fe^{+++}/ml., in contrast to the catalytic effect of iron impurities observed in acetate buffer.[5] This value applies only in 0.5 *M* sodium dihydrogen phosphate, since it was shown[1,2] that the salt concentration has a large effect upon the rate.

The rate of oxidation of aldoses by chlorite is also known[4–6] to be affected by *p*H, indicating that chlorous acid is the reactive substance[6] in this case as well as in decomposition. In the previous paper[1] a series of curves showed the rate of oxidation of glucose at various values of *p*H. From these curves it can be approximated that the rate of oxidation of glucose is proportional to $h^{0.75}$. This is in good agreement with corresponding results based upon the rate of chlorine dioxide formation,[4] and coincides approximately with the order of the oxidation reaction, which appears[4,5] to be first order with respect to both chlorous acid and glucose. Such fractional exponents indicate that the actual reaction mechanism may be complex, but this is of no concern here.

Derivation of Rate Law.—Based upon the foregoing, the rate of disappearance of chlorite in the presence of glucose is postulated as

$$-\mathrm{d}C/\mathrm{d}t = k_G h^{0.75}\, G \times C + k_D h^{1.5}\, C^2 \qquad (2)$$

in which G and C are the changing concentrations of glucose and chlorite at any time t, h is the acidity function and k_G and k_D are the rate constants of the oxidation and decomposition, respectively.

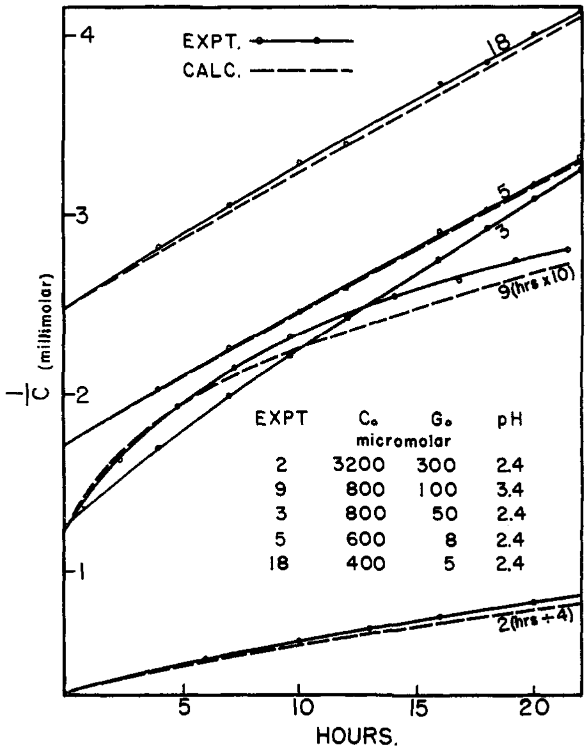

Fig. 2.—Rate of disappearance of sodium chlorite in the presence of glucose.

From the stoichiometry[1] of the oxidation reaction, G at any time t may be expressed in terms of measurable quantities

$$G = G_0 - 1/3 \times (C_0 - C - k_D h^{1.5} t C_0 C) \qquad (3)$$

G_0 and C_0 are initial glucose and chlorite concentrations and $k_D h^{1.5} t\, C_0 C$ is the amount of decomposition undergone by the reagent in time t, which is based upon the assumption[1] that the mean chlorite concentration during the interval t is equal to the geometric mean of the initial and final chlorite concentrations, regardless of simultaneous glucose oxidation.

G may be eliminated by combining equations 2 and 3 and rearranging terms to give

$$-\mathrm{d}C/\mathrm{d}t = 1/3 \times k_G h^{0.75}[(1 + k_D h^{1.5} t C_0 + 3k_D h^{0.75}/k_G)C^2 - (C_0 - 3G_0)C] \qquad (4)$$

Equation 4 may be integrated between the limits C_0, 0 and C, t and the variables separated by substitution in Bernoulli's formula to give

$$\frac{1}{C} = \frac{1}{C_0 - 3G_0}(1 + k_D h^{1.5} t C_0 - B) + e^{-1/3 \times k_G h^{0.75} t (C_0 + 3G_0)}\left(\frac{1}{C_0} - \frac{1 - B}{C_0 - 3G_0}\right) \qquad (5)$$

where $B = (3k_D h^{0.75}/k_G) \times (3G_0/C_0 - 3G_0)$, and e is the natural log base.

Equation 5 is in a form best suited for plotting, since it may be noted that when $G_0 = 0$, *i.e.*, in the absence of glucose, equation 5 becomes

$$\frac{1}{C} = \frac{1}{C_0}(1 + k_D h^{1.5} t C_0) \qquad (6)$$

Equation 6 is the integrated form of equation 1 when the decomposition rate is properly expressed as $k_D h^{1.5}\, C^2$, and is the equation for the straight lines of Fig. 1.

Rate Results and Discussion

Equation 5 permits the calculation of chlorite concentrations for comparison with experimental values determined at any time t, as a test of underlying theory. Values for k_D were calculated from the control experiments without glucose which always accompanied the runs with glucose. By trial and error it was found that $k_G = 2400$ gave the best results throughout.

Values for $1/C$ at corresponding t's were calculated from equation 5 by substituting the rate constants, initial concentrations and h values (at *p*H 2.4, $h = 0.300$ and at *p*H 3.4, $h = 0.036$) therein. These values were plotted in Fig. 2, along with curves from typical experiments,[7] of which the chemical data are inscribed in the figure.

In experiments 18, 5 and 3 the deviations between calculated and experimental curves are negligible, especially in 3 in which the curves are coincident. In experiments 2 and 9 the deviations are appreciable but small, amounting to less than 5% differences. The disagreement could be expected to increase with the ratio G_0/C_0, inasmuch as large

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(5) H. F. Launer, W. K. Wilson and J. H. Flynn, *J. Research Natl. Bur. Standards*, **51**, 237 (1953).

(6) A. Jeanes and H. S. Isbell, *ibid.*, **27**, 125 (1941).

(7) Four of these experiments were mentioned[1] previously in other connections and their original numbers have been retained.

relative changes in chlorite concentration through glucose oxidation imposes a severe strain upon the assumption that the mean chlorite concentration is equal to the geometric mean.

In equation 5, $k_D h^{1.5} t C_0$ is by far the most important factor, for at the mid-point of the experiments the exponential factor contributed less than 2%, and B, usually 10%, of the total. Thus, for higher values of G_0/C_0, $k_D h^{1.5} t\ C_0$ appears somewhat low, which implies that the geometric mean, $(C_0 C)^{1/2}$, gives slightly low values. This in turn would explain the slightly high values for glucose previously reported.[1]

The agreement, however, of calculated with experimental chlorite values appears adequate to substantiate the assumption involved in the derivation, particularly in view of the wide ranges of time and of concentrations of reactants.

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[8] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

COMMUNICATIONS TO THE EDITOR

THE EXCHANGE OF HYDROGEN BETWEEN AMMONIUM SALTS AND ALCOHOLS

Sir:

The exchange reactions of hydrogen bonded to nitrogen, like those of hydrogen bonded to oxygen, have generally been considered to be immeasurably fast. Brodskii and Sulima[1] attributed the rapid exchange to the presence of free electron pairs, and predicted that hydrogen exchange of ammonium ions, in analogy to tetrahedral carbon, would be slow. To test this hypothesis, they measured the rate of exchange of a number of ammonium salts in aqueous solutions of the corresponding acids. The reactions were studied, using deuterium as a tracer, by analyzing the salt precipitated at intervals by the addition of acetone. The slowest exchange observed, that between ammonium nitrate and 54% aqueous nitric acid, had a half-time between one and ten minutes at 0°. Because of the importance of this result to the theory of acid–base reactions, we have repeated this experiment using tritium as a tracer and have observed a half-time of about three minutes.

In order to find a reaction with a half-time which would permit more accurate kinetic measurements, we have investigated the exchange of hydrogen between alcohols and substituted ammonium salts. Butyl alcohol labeled with tritium was added to a solution of the salt in chloroform. At intervals the salt was precipitated from aliquots of the solution by addition of hexane, and the extent of exchange was determined by comparing the tritium content of the precipitate with the value found after equilibrium had been attained. With both salt and alcohol at concentrations of 0.1 M, the half-time of exchange at 0° was found to be about ten hours for diethylammonium chloride and two minutes for trimethylammonium chloride. That the large difference in the rates of exchange is not simply related to the acidity constants of the salts was shown by the observation that the half-time for the exchange reaction of a 0.2 M solution of guanidinium nitrate in ethyl alcohol was less than one minute at 0°. These and similar exchange reactions are being further investigated in order to establish the factors influencing the rates of exchange.

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RECEIVED APRIL 7, 1954

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[1] A. I. Brodskii and L. V. Sulima, *Doklady Akad. Nauk S.S.S.R.*, **74**, 513 (1950).

THE APPARENT CONDUCTIVITY OF HEXAPHENYLETHANE IN SULFUR DIOXIDE SOLUTION

Sir:

The conductivity which has been observed with solutions of hexaphenylethane in liquid sulfur dioxide[1] has, in conjunction with observations of color[2] and spectroscopic data,[3] been subject to several chemical interpretations[3b,4] which differ in detail but which all assume an ionization mechanism involving only hexaphenylethane and sulfur dioxide. This conductivity is now found to be an artifact of at least two processes, namely, reaction with dissolved oxygen and a photochemical transformation.

Experiments employing crystalline samples of ethane of purity established by quantitative oxygenation[5] and a refinement of the conductivity technique of Lichtin and Glazer[6] which avoids all contact of the solute with oxygen prior to dissolution reveal a lack of reproducibility like that apparent in older work.[1] Although irradiation with a Burton ultraviolet lamp produces slow but large increases in conductivity, variable exposure to light cannot be the sole source of the discrepancies since consistent data do not result from experi-

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[1] (a) P. Walden, *Z. physik. Chem.*, **43**, 443 (1903); (b) M. Gomberg and L. H. Cone, *Ber.*, **37**, 2033 (1904).

[2] M. Gomberg and F. W. Sullivan, THIS JOURNAL, **44**, 1829 (1922).

[3] (a) K. H. Meyer and H. Wieland, *Ber.*, **44**, 2557 (1911); (b) L. C. Anderson, THIS JOURNAL, **57**, 1673 (1935).

[4] (a) M. Gomberg, *Chem. Rev.*, **1**, 102 (1924); (b) P. Walden "Chemie der Freien Radikale," S. Hirzel, Leipzig, 1924, p. 154; (c) W. A. Waters, "Chemistry of Free Radicals," Oxford Press, London, 1948, p. 35; (d) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 712.

[5] N. N. Lichtin and G. R. Thomas, THIS JOURNAL, **76**, 2594 (1954).

[6] N. N. Lichtin and H. Glazer, *ibid.*, **73**, 5537 (1951).