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

Catalytic Decomposition of Hypochlorite Solution by Iridium Compounds. II. Kinetic Studies[1]

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A kinetic study has been made of the decomposition of sodium hypochlorite solution, catalyzed by iridium compounds. The influence on reaction rate was determined for several variables, such as hypochlorite concentration, amount of catalyst, rate of stirring, initial *p*H, buffer constituents, added sodium chloride and temperature. The decomposition is a first-order reaction. The reaction rate was approximately doubled by a 10° rise in temperature in the range 20 to 40°. The energy of activation was calculated to be 16.4 kcal. The catalyst appears to be colloidal hydrous iridium dioxide. Catalysis of the disproportionation reaction of hypochlorite to form chlorate was observed, in addition to the reaction which formed oxygen. Mechanisms have been proposed to account for the reactions.

In a previous paper[2] the authors reported the results of a *p*H–time study in the catalytic decomposition of hypochlorite, and offered qualitative explanations for the observed effects. The present paper deals with kinetic studies of the decomposition of hypochlorite solution, catalyzed by iridium compounds.

Experimental

Preparation of the sodium hypochlorite solution and of the sodium hexachloroiridate(IV), and analytical methods for hypochlorite, chlorate, chlorine and oxygen, were given in the previous paper.[2]

Apparatus.—The apparatus for measuring the gaseous products is shown in Fig. 1. The reaction vessel was coated on the outside with black paint, to eliminate photochemical action. An outlet at the bottom of the reaction flask permitted withdrawal of spent solution. Stirring was accomplished through a ball-and-socket ground glass joint which allowed rotation of the shaft while maintaining a sealed system. The stirring shaft was lubricated with silicone grease, and the ball-and-socket joint was lubricated with glycerol. A small piece of glass tubing, mounted on the stirring shaft by means of a tight rubber stopper at a point just below the bottom of the outer stirring shaft, served to prevent any ground glass or lubricants from falling into the reaction flask. Different stirring rates were obtained by a cone drive motor; the stirring rate was checked with a stroboscopic tachometer. The stopcock arrangement in the gas measuring system permitted reading the gas volume at any time while the reaction was in progress, by temporarily isolating the gas buret. The traversing screw carrying the leveling bulb allowed quick, continuous, accurate adjustment to atmospheric pressure as indicated by the manometer.

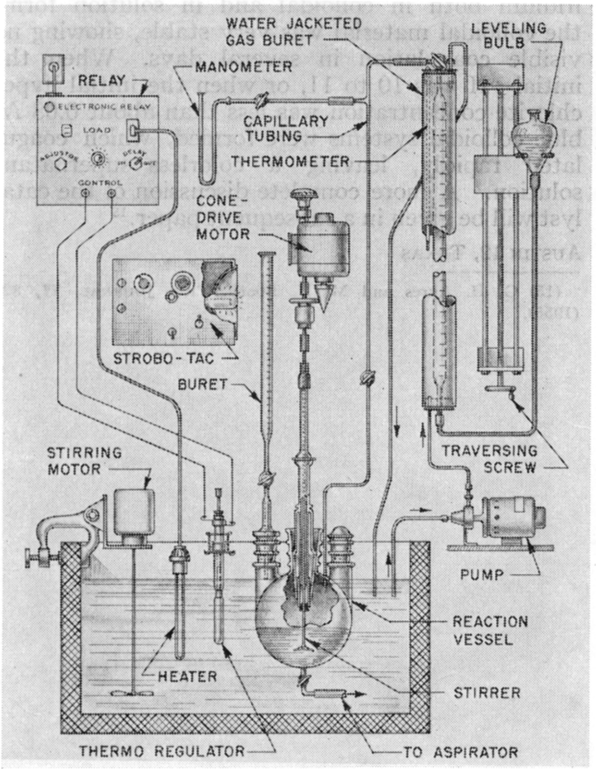

Fig. 1.—Apparatus.

The *p*H measurements were made with a Beckman Model H-2 *p*H meter, using glass electrode and calomel electrode. Examination of the catalyst after use was made with a Bausch and Lomb slit ultramicroscope, with a type E.M.U.-2A R.C.A. electron microscope, and with a Hayes X-ray diffraction unit.

Procedure.—An appropriate amount of buffer solution was placed in the reaction vessel; the desired amount of catalyst was added from the buret, and the mixture was stirred for 10 minutes to come to the temperature of the bath. Hypochlorite solution was added, by pipet, through the side neck of the flask; the system was closed immediately, and stirring started. The internal pressure was quickly equalized with atmospheric pressure, and timing was started. Reading of the gas buret at this point was recorded. Gas volume readings were taken at one-minute intervals during the first part of the run, and at less frequent intervals as the reaction proceeded, until there was no further change in volume. The final reading of "volume at infinite time," V_∞, was used as a measure of the amount of hypochlorite which had decomposed into oxygen. All gas volumes were reduced to standard conditions.

After reaction was complete, the spent solution was removed through the drain in the flask; the solution and washings were used for subsequent analysis, and for examination of the catalyst.

The initial *p*H of the reaction mixture was determined on a duplicate sample made for that purpose. The *p*H of the spent solution was measured after each run.

For X-ray diffraction examination[3] of the catalyst, the reaction mixture was concentrated, and soluble salts were removed by repeated washing. The concentrated slurry of catalyst material, on a microscope slide, was dried with an infrared lamp; the slide was then mounted in the X-ray unit and the diffraction maxima were recorded.

For making electron diffraction patterns[4] of the spent catalyst, two methods of preparation were used: (1) a drop of the concentrate was evaporated on a nickel screen; (2) a drop of the concentrate was enclosed in a very thin Parlodion film.

Results and Discussion

Determination of Reaction Order.—The integrated form of the rate equation $-dc/dt = kc^n$ may be used to calculate the specific rate constant

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[1] This work was supported jointly by The United States Atomic Energy Commission and The University of Texas, under Contract No. AT-(40-1)-1037.

[2] G. H. Ayres and M. H. Booth, THIS JOURNAL, **77**, 825 (1955).

[3] The services of Dr. S. H. Simonsen are gratefully acknowledged.

[4] The assistance of Mrs. Marvis McCormic is gratefully acknowledged.

from the slope of a plot of $-\log c$ against t. Laidler[5] states that specific rate constants should not be calculated by other methods until the reaction order has been established by the differential method, which gives the most reliable information about reaction order.

In the preliminary experiments of the present study, the catalytic decomposition was carried out in unbuffered solution. A plot of log $(V_\infty - V_t)$ against t was linear for only the first few minutes of reaction, then showed considerable concavity toward the ordinate. This behavior was similar to some of the results obtained by Lewis.[6] At least two causes are known to contribute to the observed effect. First, the *p*H decreased markedly during reaction, from an initial 8.0 to a final 2.2, probably resulting in other reactions which assumed prominence.[2] Second, the ionic strength of the solution increased as decomposition of the weakly ionized hypochlorous acid was converted to highly ionized products; this resulted in a decrease of effective concentration and hence a slower rate.[7]

Subsequent runs were made in borate buffer solutions; the reaction mixture was made 2 *M* in sodium chloride to provide a solution of essentially constant ionic strength. Sodium chloride was chosen for this purpose because it is inherently present in the hypochlorite solution, it is one of the reaction products, and it is reported to have no effect on the course of the reaction. In a series of runs, all conditions were held constant except the initial concentration of hypochlorite, which was varied over a wide range. The value of $(V_\infty - V_t)$ ml. of oxygen evolved was used as a measure of the disappearance of the hypochlorite.

Figure 2 shows the log $(V_\infty - V_t)$ *versus* time plot for five different initial concentrations of hypochlorite; the straight lines are indicative of a first-order reaction. Application of the differential method is shown in Fig. 3, which is typical of the runs at various initial hypochlorite concentrations. The reaction rates, $-dc/dt$, were determined from tangents to the concentration—time curve at several points; the slopes of the tangents, independently and repeatedly drawn by inspection, were reliable to about 1%, which is adequate for the method.[5] Extension of the method by plotting logarithm of initial rates against logarithm of initial concentrations gave a straight line of slope = 1. The period of half-life was independent of initial concentration.

Table I shows the values of the half-life, and also of the specific rate constant determined graphically from the slopes of the curves (Fig. 2), as well as calculated by the method of integration. The latter values represent, for each concentration, averages computed from data taken at one-minute time intervals; by the use of longer time intervals, the calculated values of k showed much smaller variations. There was good agreement, however, between the values of k obtained by the graphical and by the integration method. Although there is a slight variation of rate constant with concentration, the variation has no definite trend. It is evident that the decomposition of hypochlorite solution is a first order reaction.

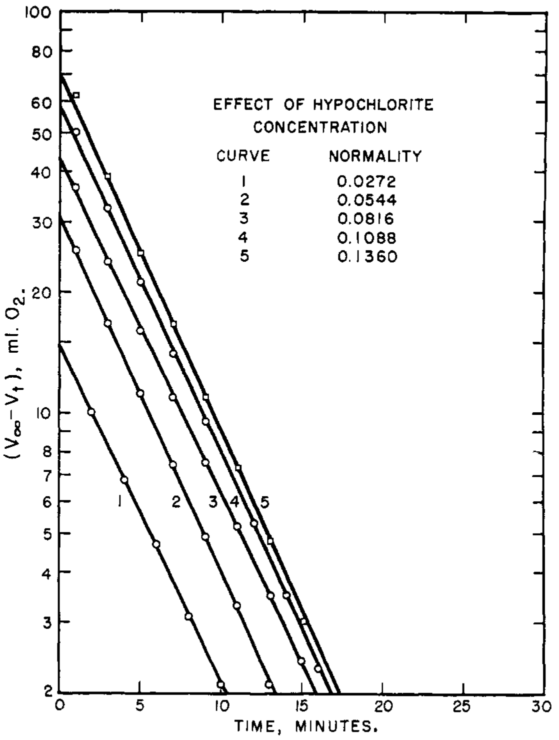

Fig. 2.—Effect of hypochlorite concentration on rate of catalytic decomposition; initial *p*H 8.0, 2.0 mg. of iridium catalyst.

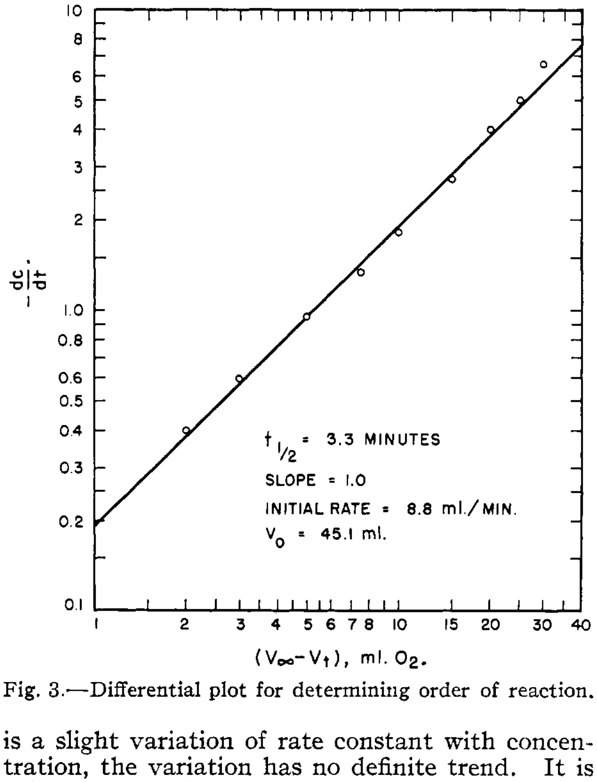

Fig. 3.—Differential plot for determining order of reaction.

Effect of Stirring Rate.—Table II shows the value for the specific rate constant for various stirring rates; at somewhat above 1000 r.p.m. no

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[5] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1950, pp. 13–18.

[6] J. R. Lewis, *J. Phys. Chem.*, **32**, 243, 1808 (1928).

[7] E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 80.

TABLE I

RATE CONSTANT FOR DECOMPOSITION OF SODIUM HYPOCHLORITE SOLUTION

pH 8.0 (borate buffer), 2 M in NaCl, 2.0 mg. iridium catalyst.

NaOCl, N	Half-life, min.	$k \times 10^2$, min.$^{-1}$ (graphical)	$k \times 10^2$, min.$^{-1}$ (integration)
0.0202	3.6	19.3	19.0
.0544	3.4	20.3	20.2
.0816	3.3	19.2	19.7
.1088	3.2	20.2	20.6
.1360	2.9	20.6	20.8

change in reaction rate was detected; all subsequent runs were stirred at 1150 r.p.m.

TABLE II

EFFECT OF STIRRING RATE

NaOCl, 0.079 N, 2 M in NaCl, pH 8.11, 1.0 mg. iridium catalyst.

Stirring rate, r.p.m.	Final vol. of O_2, ml.	$k \times 10^2$, min.$^{-1}$
780	48.6	5.54
900	48.7	6.90
1020	48.7	7.20
1145	49.0	7.44
1270	49.2	7.44

Effect of Amount of Catalyst.—The amount of catalyst was varied over wide limits. Typical data are shown in Table III. Under the conditions used, the rate was approximately proportional to the amount of catalyst up to about 2 mg., above which the rate per unit catalyst decreased. When large amounts of catalyst were used, the reaction was so rapid that it became difficult to follow.

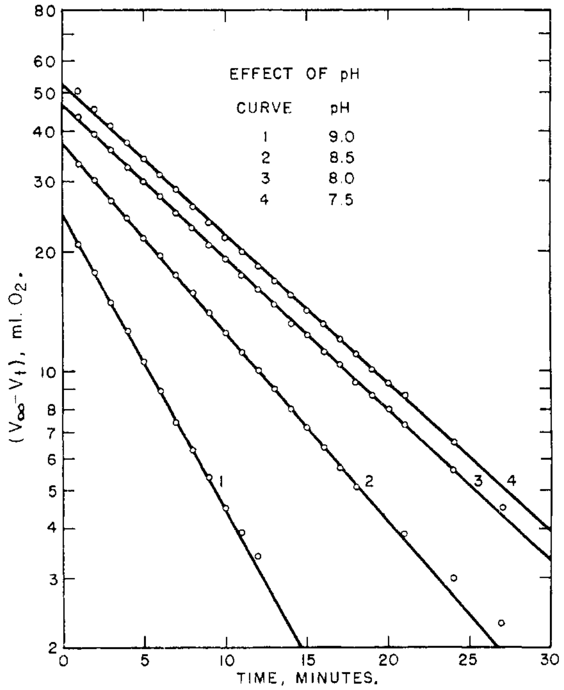

Fig. 4.—Effect of initial pH on rate of catalytic decomposition of hypochlorite; NaOCl = 0.080 N, 1.0 mg. of iridium catalyst.

TABLE III

EFFECT OF AMOUNT OF CATALYST

NaOCl, 0.077 N, 2 M in NaCl, pH 8.0.

Ir catalyst, mg. (= a)	Final vol. of O_2, ml.	$k \times 10^2$, min.$^{-1}$	$(k/a) \times 10^2$, min.$^{-1}$ mg.$^{-1}$
0.6	49.8	4.58	7.64
1.0	47.4	7.97	7.97
1.4	45.8	11.6	8.30
2.0	44.8	17.1	8.55
3.0	45.0	22.7	7.57
4.0	44.7	26.9	6.73
5.0	42.9	30.4	6.08
6.0	42.7	31.1	5.18
7.0	44.7	32.9	4.70

Effect of pH.—The effect of initial pH was studied over the range from pH 11 to 7. Typical results are shown in Fig. 4, and more complete data are given in Table IV. The specific rate constant passed through a maximum at pH 9 and had a minimum at pH 7.5. Calculation from the ionization constant for hypochlorous acid, $K = 3.2 \times 10^{-8}$, shows that at pH 7.5 the ratio $[HOCl]/[OCl^-]$ is unity, whereas at pH 9.0, this ratio is 32. Over this pH interval the rate constant doubled in value. It might appear that the rate of reaction is dependent upon the concentration of hypochlorite ion in solution; this indication may be purely fortuitous, however, for Table I shows that the initial hypochlorite concentration had no effect on the value of the specific rate constant.

TABLE IV

EFFECT OF pH

NaOCl, 0.080 N, 2 M in NaCl, 1.0 mg. iridium catalyst.

pH	Final vol. of O_2, ml.	$k \times 10^2$, min.$^{-1}$	% NaOCl to O_2
11.0	20.1	1.34	28
10.0	13.2	7.21	19
9.0	24.6	17.2	35
8.5	37.8	11.0	53
8.0	48.2	8.80	68
7.5	57.0	8.61	80
7.0	56.9	9.51	80

Variation of Reaction Products with Conditions.—The last column of Table IV shows that the percentage hypochlorite decomposing to oxygen increased as pH decreased, reaching 80% at pH 7.5. Under certain conditions (pH 9 to 11), however, the disproportionation of hypochlorite to chloride and chlorate is the predominant reaction. Latimer[8] states that when hypochlorite is heated with a catalyst, oxygen is evolved, but in the absence of a catalyst, chlorate is formed. The present study showed the disproportionation reaction to be actively catalyzed, as indicated in Table V; all experimental conditions were identical, except for the presence or absence of catalyst; data given are for an initial pH of 8.3.

Table VI shows the way in which the products varied with pH, with hypochlorite concentration, and with amount of catalyst. Each line in the table is the average of from 2 to 5 runs under the conditions given; in cases where wide variation in con-

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(8) W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solution," 2nd ed., Prentice-Hall, New York, N. Y., 1952, p. 57.

TABLE V

EFFECT OF CATALYST ON RELATIVE YIELD OF PRODUCTS

	NaOCl remaining after 90 min., %	NaOCl to chlorate, %	NaOCl to oxygen, %
With Ir catalyst	0	46	54
Without catalyst	75	4	21
Without catalyst[a]	89	Negligible	11

[a] Between runs, reaction vessel was cleaned with hot alkali to remove any adsorbed catalyst from previous runs.

ditions produced no significant change in relative amounts of products, only the range of variation is given. In borate buffered solution 2 *M* in sodium chloride, the amount of catalyst and the concentration of hypochlorite were without influence on the kind and amount of products formed; the initial *p*H of the reaction mixture was the major factor affecting the relative yield of products. Increasing amounts of oxygen and decreasing amounts of chlorate were produced with increasing initial *p*H from 7.0 to 10.0.

TABLE VI

VARIATION OF PRODUCTS WITH CONDITIONS

Buffer 1, phosphate; buffer 2, borate, in 2 *M* NaCl except where indicated by (a).

Buffer type	*p*H	NaOCl, *N*	Catalyst, mg.	NaOCl to oxygen, %	NaOCl to chlorate, %
1	7.0	0.1510	2.0	64	36
1	7.0	.1480	2.0	57	43
1	8.0	.0723	2 0	62	38
1	8.1	.1810	2.0	61	39
2	7.0	.0558	2.0	80	20
2(a)	7.0	.0558	2.0	82	18
2	7.5	.0545	2.0	74	26
2(a)	7.5	.0545	2.0	80	20
2	8.0	.0545	2.0	62	38
2(a)	8.0	.0545	2.0	72	28
2	8.5	.0545	2.0	45	55
2	9.0–11.0	.0558	2.0	33–38	67–62
2	8.0	0.0278–0.1360	2.0	63–67	
2	8.0	0.0774	1.0–7.0	62–69	

Effect of Temperature. Energy of Activation.—Figure 5 shows the rate curves for the reaction at temperatures from 20 to 40°. The specific rate constant for each temperature was calculated by multiplying the slope of the curve by 2.303. Representative data are summarized in Table VII.

TABLE VII

EFFECT OF TEMPERATURE

NaOCl, 0.077 *N*, *p*H 8.0, 1.0 mg. iridium catalyst.

Temp., °C.	Final vol. of O_2, ml.	$k \times 10^2$, min.$^{-1}$	$1/T \times 10^3$
20	50.6	2.35	3.41
25	50.6	3.82	3.35
30	47.3	6.60	3.30
35	49.8	8.06	3.25
40	46.2	14.1	3.23

The temperature coefficient of the reaction rate, for a 10° temperature change, was as follows: $k_{30}/k_{20} = 2.8$; $k_{35}/k_{25} = 2.1$; $k_{40}/k_{30} = 2.1$. Temperature control was least accurate at 20°, which may account for the higher coefficient in the 20 to 30° range. The coefficient of 2.1 was in agreement with the empirical generalization that the rate of a chemical reaction is doubled by a 10° temperature increase. It appears likely, therefore, that the rate-controlling step is chemical in nature, *e.g.*, the formation of an activated catalyst–hypochlorite complex on the catalyst surface; rate of diffusion of reactant to the surface of the catalyst and/or rate of diffusion of products away from the catalyst are probably not rate-controlling steps.

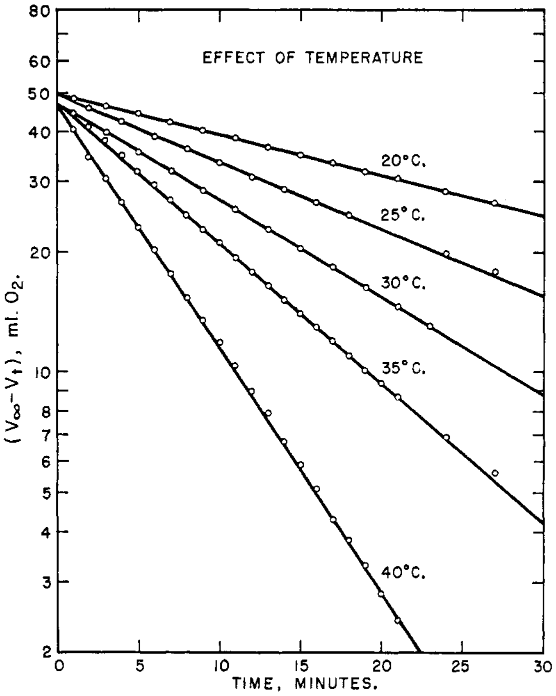

Fig. 5.—Effect of temperature on rate of catalytic decomposition of hypochlorite; initial *p*H 8.0, NaOCl = 0.077 *N*, 1.0 mg. of iridium catalyst.

A plot of logarithm of the rate constants against the reciprocal of absolute temperatures gave a straight line the slope of which was used in the Arrhenius equation, $d \ln k/dT = E/RT^2$, to calculate the energy of activation, *E*. The value of 16.4 kcal. was in good agreement with the value of 16.6 kcal. reported by Howell.[9]

Effect of Buffer Constituent and of Added Sodium Chloride.—When phosphate buffer was used to control the initial *p*H, the specific rate constant decreased considerably with increasing hypochlorite concentration, as shown in Table VIII.

TABLE VIII

EFFECT OF HYPOCHLORITE CONCENTRATION IN PHOSPHATE BUFFER SOLUTION

*p*H 8.2, 2.0 mg. iridium catalyst.

NaOCl, *N*	Final vol. of O_2, ml.	$k \times 10^2$ min.$^{-1}$
0.028	15.6	27.7
.0566	33.4	15.2
.072	41.4	13.4
.142	80.1	11.1
.180	100.5	11.1

Further studies were made with phosphate and with borate buffers, with and without added

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(9) O. R. Howell, *Proc. Royal Soc.* (*London*), **104A**, 134 (1923).

sodium chloride. Typical data are shown in Table IX. Reaction was faster in the phosphate buffer than in the borate buffer; addition of sodium chloride affected the reaction rate in both buffers, but to a greater extent in borate solution than in phosphate. In the absence of added sodium chloride, the reaction in borate buffer no longer strictly followed the first-order rate law, but approached the zero-order rate law.

TABLE IX

EFFECT OF BUFFER CONSTITUENT AND OF ADDED SODIUM CHLORIDE

NaOCl, 0.0566 *N*, 2.0 mg. iridium catalyst.

Buffer soln.	*p*H	Final vol. of O_2, ml.	$k \times 10^2$ min.$^{-1}$
Phosphate	8.2	33.4	15.2
Phosphate, 2 *M* NaCl	8.2	30.9	28.7
Borate, 2 *M* NaCl	8.2	29.2	18.1
Phosphate	8.0	33.4	15.4
Borate	8.0	36.0	[a]
Borate, 2 *M* NaCl	8.0	32.6	20.3

[a] Did not conform to first-order rate law.

In the two different buffer solutions, the amount of oxygen formed was essentially the same, indicating that the reaction probably followed the same mechanism. Because the *p*H was the same in both buffers, the ratio of hypochlorite ion to undissociated hypochlorous acid would be the same. The difference in rates may be associated with the catalyst itself, especially in the amount of active catalyst surface available. In the phosphate buffered solutions, a light yellow colloidal system was observed, whereas a greenish-yellow system was produced in the borate buffered solutions. The differences in color might be due to differences in particle size and hence in specific surface; this feature of the problem was not further explored.

Differences in rate due to use of the different buffers might be associated with differences in the ionic strength of the solutions; for a *p*H of 8.0, phosphate was used at a much higher molar concentration than the borate.

Addition of sodium chloride accelerated the reaction in both buffer solutions. Skrabal and Berger[10] reported that the (uncatalyzed) decomposition of hypochlorite was accelerated by chloride ion, and that there was a considerable "salt effect." Chirnoaga[11] reported no effect from variation in the amount of sodium chloride; Howell[9] observed that sodium chloride accelerated the reaction; he attributed the effect to the sodium ions, and stated that chloride ion had no effect.

Colloidal Nature of the Catalyst.—As the *p*H of the reaction mixture was varied, marked color changes were observed; the stability of the colloidal catalyst was also dependent upon *p*H. At high *p*H values (10 to 11) the colloidal system was blue and relatively unstable; the particles coagulated rapidly when stirring was stopped, leaving a colorless supernatant solution. At *p*H about 9, the system was light yellow in color, and greenish-yellow at *p*H of about 7; in this *p*H range, the colloid was very stable, showing no visible coagulation in several days. The color changes may be associated with changes in particle size,[12] and hence in specific surface.

In the Gilchrist and Wichers[13] scheme of separation of the platinum elements, iridium is precipitated as its blue hydrous dioxide at a *p*H of 6 to 7; the precipitate is easily peptized. It seems likely, therefore, that the catalyst in the present study is colloidal hydrous iridium dioxide, stabilized by hydroxyl ion; electrophoresis tests showed the particles to be negatively charged. The observed differences in reaction rate with change in *p*H of the solution are probably due to change in particle size and in surface.

Attempts were made to identify the composition of the catalyst. The spent reaction mixture was evaporated; after removal of soluble salts, the iridium residue was examined by X-ray diffraction methods, and compared with a known iridium hydrous dioxide formed by hydrolytic precipitation. Although the patterns were quite indistinct, due probably to very small particle size, they did have some similarity. Electron diffraction patterns were not reproducible. From electron photomicrographs, the average particle size was estimated to be about 0.25 micron.

Proposed Reaction Mechanism.—The reaction mechanism proposed by Howell[9] for the decomposition of hypochlorite into oxygen and chloride, catalyzed by cobalt peroxide, was based on the ease with which cobalt may change its oxidation state. In the present study, a proposed mechanism cannot be as specific as the one proposed by Howell, because of the uncertainty of composition of the iridium catalyst. The kinetic scheme proposed by Herzfeld[14] and extended by Laidler and Socquet[15] for catalysis involving only one substrate, is used as the basis for the proposed mechanism.

If C^- represents the active catalyst of unknown composition, X^- the intermediate activated complex, and k_1 and k_{-1} the rate constants for the forward and the reverse reaction, respectively, the reaction may be represented as occurring in two steps

$$OCl^- + C^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X^- + Cl^- \qquad (1)$$

$$X^- \xrightarrow{k_2} C^- + O \qquad (2)$$

k_2 is the rate constant for the irreversible decomposition of the complex to form an oxygen atom. Another plausible mechanism would involve adsorption of the hypochlorite ion on the catalyst surface, in an activated form, with subsequent decomposition of the hypochlorite into an oxygen atom and a chloride ion. The only difference between these two mechanisms is the time at which the oxygen-chlorine bond is broken.

If the hypochlorite ion approaches the negatively charged catalyst surface with the oxygen oriented toward the catalyst, the hypochlorite ion would become polarized in such a way as to shift

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(10) A. Skrabal and A. Berger, *Monatsh.*, **70**, 168 (1937).

(11) E. Chirnoaga, *J. Chem. Soc.*, 1693 (1926^2).

(12) S. Glasstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., New York, N. Y., 1946, p. 1238.

(13) R. Gilchrist and E. Wichers, THIS JOURNAL, **57**, 2565 (1935).

(14) K. F. Herzfeld, *Z. physik. Chem.*, **98**, 151 (1921).

(15) K. J. Laidler and I. M. Socquet, *J. Phys. Colloid Chem.*, **54**, 519 (1950).

electrons toward the positively charged chlorine and away from the negatively charged catalyst particle; subsequent transfer of two electrons from the oxygen to the chlorine would result in the rupture of the oxygen–chlorine bond. In the activated complex the oxygen atom would probably share electrons with the catalyst surface; this unstable complex may then decompose as shown by equation 2, or combine with chloride ion to form the reactants again. The oxygen atom liberated in reaction (2) reacts very rapidly either with another oxygen atom to form molecular oxygen, or it may react with hypochlorite ion to form other products, for example, chlorate.

For unimolecular reactions, it is generally assumed that the rate of change of concentration of the activated complex is zero. If reaction (2) is very rapid, the concentration of activated complex is very small, and the steady state equation for the activated complex is

$$d[X^-]/dt = k_1[OCl^-][C^-] - k_{-1}[X^-][Cl^-] - k_2[X^-] = 0$$

Solving for the concentration of activated complex

$$[X^-] = \frac{k_1[OCl^-][C^-]}{k_{-1}[Cl^-] + k_2}$$

The chloride ion concentration of the solution is essentially constant, hence

$$k_{-1}[Cl^-] = k'_{-1}$$

and

$$[X^-] = \frac{k_1[C^-][OCl^-]}{k'_{-1} + k_2}$$

The rate of reaction is given by

$$-\frac{d[OCl^-]}{dt} = k_2[X^-] = \frac{k_1k_2[C^-][OCl^-]}{k'_{-1} + k_2}$$

But $[C^-]$, the amount of catalyst in the system, is essentially constant, therefore

$$\frac{k_1k_2[C^-]}{k_{-1} + k_2} = k', \text{ and } -\frac{d[OCl^-]}{dt} = k'[OCl^-]$$

which is the usual expression for first-order reaction rate.

In Table VIII it was shown that for phosphate buffered solution, the specific rate constant decreased with increasing hypochlorite concentration. This increased concentration of hypochlorite is accompanied by a proportional increase in chloride concentration, because these substances are formed in equi-molecular amounts in the preparation of the hypochlorite solution. The rate constant, k', used in the above expression, should be inversely proportional to the chloride ion concentration. If the rate controlling step were the formation of the activated complex, a plot of the reciprocal of the rate constant against the chloride ion concentration should be a straight line. Except for the highest concentration (Table VIII), this appeared to be approximately the case.

It was stated above that the oxygen atom liberated by reaction (2) might react with hypochlorite to form other products. Experimentally, it was known that beside oxygen and chloride ion, the principal product was chlorate ion. The formation of chlorate from hypochlorite is generally considered to give rise to second or third-order kinetics. The authors propose that in the system used in this study, the formation of chlorate can originate by first-order kinetics, by the mechanism of reactions (1) and (2) previously given, and

$$O + OCl^- \longrightarrow ClO_2^- \qquad (3)$$

The chlorite thus formed may react in either of two ways to form chlorate

$$ClO_2^- + O \longrightarrow ClO_3^- \qquad (4)$$

$$\text{or } ClO_2^- + OCl^- \longrightarrow ClO_3^- + Cl^- \qquad (5)$$

This mechanism would account for the observed catalysis of the disproportionation reaction, and would lead to first-order kinetics, since the over-all rate of disappearance of hypochlorite would be limited by the rate of formation of the activated complex which subsequently decomposed to form oxygen atoms.

AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Kinetics of the Racemization of α-Phenethyl Chloride in Phenols

BY HAROLD HART AND WILLIAM L. SPLIETHOFF

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The rates of racemization of α-phenethyl chloride in benzene or xylene solutions containing phenol, *o*- and *p*-cresol, 2,6-xylenol and mesitol were measured at 50°. The rates of the concurrent nuclear alkylation of the first four of these phenols were also determined using *dl*-chloride. The kinetic equation which fits the racemization data requires three simultaneous racemization paths; racemization brought about by the original phenol, by its alkylation product and by the hydrogen chloride evolved during the alkylation. The activation energy and entropy for the racemization and alkylation in phenol (30 to 50°) were determined. The mechanisms are discussed.

Studies on the racemization of α-phenethyl chloride have been important in developing the theory of displacement and elimination reactions. α-Phenethyl chloride racemizes at a measurable rate in polar solvents such as liquid sulfur dioxide[1] and formic acid,[2] more rapidly in the latter. The rate in sulfur dioxide was unaffected by excess chloride ion, indicating an ionization mechanism. Hughes, Ingold and Scott suggested[3] a reversible equilibrium with styrene and hydrogen chloride as a possible racemization path. The racemization with metallic halides in non-polar solvents has been studied recently[4] because of the interest in these halides as

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[1] E. Bergmann and M. Polanyi, *Naturwiss.*, **21**, 378 (1933).

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