Kinetics of the Reaction Between Hypochlorous Acid and Chlorine Dioxide

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RECENT INVESTIGATIONS by Dodgen and Taube (1949*a*) of the reaction between hpyochlorous acid and chlorine dioxide indicate that the phenomenon of an exchange of the chlorine atoms of the reactants occurs during the reaction. This reaction can be represented as follows:

(1) $$2ClO_2 + HOCl + H_2O \rightarrow 3H^+ + 2ClO_3^- + Cl^-$$

The exchange was demonstrated by preparing hypochlorous acid containing radioactive chlorine and allowing it to react with chlorine dioxide. After the reaction had proceeded to an appreciable extent, the remaining chlorine dioxide was observed to contain radioactive chlorine. Similarly, when the chlorine dioxide was initially radioactive, its specific activity decreased after the reaction had proceeded to an appreciable extent. Since it was also observed that chlorine dioxide did not exchange with Cl^-, ClO_3^- or with HOCl under conditions where the above reaction had not occurred appreciably, it was concluded that the exchange of chlorine atoms must occur during the course of the above reaction. It is hoped that when the mechanism of the reaction is derived, a logical explanation of the atom interchange will also be apparent.

At present, this study has been conducted along two lines of investigation in an effort to insure concrete checks and substantiation of the data. One of these has involved the use of a reaction vessel, maintained at constant temperature, from which samples can be removed at any desired time and titrated. The resulting calculations can then show the extent to which the reaction has progressed during the time interval since the last titration. The second method has involved the use of the Beckman Spectrophotometer. This instrument measures the optical density of the solution which can then be related to the concentration of the reactant still remaining in the reaction cell. Inasmuch as the hypochlorous acid is uncolored, or relatively so, at the concentrations employed, the measurement of the light intensity reveals the concentration of chlorine dioxide still unreacted. Chlorine dioxide is deeply colored and because of its ability to absorb light can be readily detected by the Beckman Spectrophotometer. Hence, if all variables, except the chlorine dioxide, are maintained constant, the concentration of chlorine dioxide can be accurately measured to very low limits with the aid of this instrument.

By combining the data obtained by these two methods, the following reaction rate equation was derived:

$$(2) \qquad \frac{-d(ClO_2)}{dt} = k\,f\,\{(H^+)\}\,(ClO_2)\,(HOCl)\,.$$

Now, if as was done in the experiments, the hydrogen ion concentration is kept constant by the use of an appropriate buffer system, such as the KH_2PO_4-K_2HPO_4 system, then the product, $kf\{(H^+)\}$ can be represented by a single constant K_1. Thus, we may now substitute this constant K_1 in equation (2) to obtain:

$$(3) \qquad \frac{-d(ClO_2)}{dt} = K_1(ClO_2)\,(HOCl)\,.$$

If a plot is now made in the usual manner of the integrated form of this equation, then a straight-line graph should result. However, when the experimental data are substituted in the integrated equation, a curved line is found.

On the other hand, if other possibilities as $(HOCl)^0$ and $(HOCl)^2$ are substituted in the reaction rate equation (3), then the plots obtained with the integrated forms yield curves which differ far more drastically from a straight line than the first attempted curve. Accordingly, the best plot, in agreement with the experimental data, is obtained when the concentrations of both the chlorine dioxide and the hypochlorous acid are of the first order. Nonetheless, this is apparently only a partial explanation of what occurs, for the resulting curve only approximates a straight line.

If we examine some of Bray's (1906) work on the disproportionation of chlorine dioxide, a possible explanation of the bent curve becomes evident. Bray found that the disproportionation of chlorine dioxide proceeded in the following manner:

$$2ClO_2 + H_2O \rightarrow ClO_2^- + ClO_3^- + 2H^+ \,. \qquad (4)$$

He found that this reaction was slow but that the presence of chloride ion would catalyze the reaction. Further, the reaction rate equation which he derived for this disproportionation was:

$$\frac{-d(ClO_2)}{dt} = k(ClO_2)^2\,(OH^-) \,. \qquad (5)$$

Consequently, from the slowness of this reaction, it had been initially assumed that the disproportionation reaction would produce no appreciable effect upon the reaction under investigation. However, to account for the results obtained on the kinetics of reaction (1), an investigation of the disproportionation reaction was undertaken. This showed that the chloride ion concentrations produced in reaction (1) and which ranged from 0.00M to 0.04M had no noticeable effect upon the hydrolysis of the chlorine dioxide. On the other hand, it was apparent that the disproportionation was appreciable in the system under investigation and that a correction to the reaction rate equation (3) must be made.

Consequently, k and (OH^-) of equation (5) were combined to yield a new constant, namely, K_2. Then, the result of this disproportionation rate equation, $K_2(ClO_2)^2$ was added to equation (3) to give:

$$\frac{-d(ClO_2)}{dt} = K_1(HOCl)\,(ClO_2) + K_2(ClO_2)^2 \,. \qquad (6)$$

It should be noticed now that both K_1 and K_2 represent a product of k and some function of the hydrogen or hydroxyl ion concentrations for each specific reaction. Hence, if a plot is made of the integrated form of this new equation in the same manner as was done previously, a straight-line relationship results. Therefore, the indication is that both reactions are occurring simultaneously and that both must be considered if the representative picture of the over-all reaction is desired.

Furthermore, it should be noted that the data obtained up to the present confirm the stoichiometry indictaed by equation (1). The reason for this result is apparent if we consider the disproportionation reaction together with the reaction of chlorite ion with hypochlorous acid. Taube and Dodgen's

(1949*b*) qualitative study of the latter reaction has shown it to be an extremely fast reaction which proceeds as follows:

(7) in acid solution: $Cl_2 + 2ClO_2^- \rightarrow 2ClO_2 + 2Cl^-$,

(8) in neutral solution: $HOCl + ClO_2^- \rightarrow H^+ + ClO_3^- + Cl^-$.

Since the present work has been limited to the neutral region, the reaction represented by equation (8) could be expected to occur. However, chlorite ion is necessary for the reaction. Therefore, if we examine equation (4), we see that chlorite ion is indeed produced in the hydrolysis of chlorine dioxide. Consequently, as soon as the chlorite ion is produced, it is consumed by the reaction indicated by equation (8) and since equation (8) represents a rapid reaction, the hydrolysis reaction is the rate controlling step. In addition, if equations (4) and (8) are added, the resulting sum represents reaction (1), the one under investigation. The following addition will verify this and show why the stoichiometry has been confirmed:

(4) $2ClO_2 + H_2O \rightarrow ClO_2^- + ClO_3^- + 2H^+$ (slow),

(8) $HOCl + ClO_2^- \rightarrow H^+ + ClO_3^- + Cl^-$ (fast),

(1) $HOCl + H_2O + 2ClO_2 \rightarrow 3H^+ + 2ClO_3^- + Cl^-$.

In conclusion, it should be noted that much work yet remains before the mechanism of this reaction can be ascertained. One important study remaining is the determination of the hydrogen ion dependency. At the moment, the experimental data seem to indicate this to be the reciprocal of the hydrogen ion concentration. However, further work is necessary to confirm this assumption. Similarly, the effects of temperature on the reaction rate must be investigated. To this end, a special thermostated cell compartment similar to that developed by Bell and Stryker (1947) has been built for the Beckman Spectrophotometer to enable control and variation of temperature about the reaction cells.

In like manner, further work with radioactive chlorine along the lines investigated by Dodgen and Taube (1949*b*) is planned. At the conclusion of this, it is hoped that a plausible explanation or mechanism of the interchange of chlorine atoms will be forthcoming.

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