# Selectivity of the Chloride-Chlorate Reaction System in Various Reactor Types

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The production of chlorine dioxide and chlorine from chlorate and chloride ions in acidic solution can be described by two parallel reactions (Taube and Dodgen, 1949; Luther and MacDougall, 1908):

$$2H^+ + ClO_3^- + Cl^- \rightarrow ClO_2 + \tfrac{1}{2} Cl_2 + H_2O \qquad (1)$$

and

$$6H^+ + ClO_3^- + 5Cl^- \rightarrow 3Cl_2 + 3H_2O \qquad (2)$$

This reaction system is the basis for several commercial processes which supply $ClO_2$ to pulp and paper plants for the bleaching of pulp (for example, Hirschberg, 1963; Atkinson, 1974; Masschelein, 1979). Various mechanisms have been proposed to explain the behavior of this system in terms of such intermediates as $Cl_2O_2$, $HClO_2$ and HOCl (Taube and Dodgen, 1949; Lenzi and Rapson, 1962; Hong et al., 1967).

In this system, the reactants are in solution whereas the products $ClO_2$ and $Cl_2$ are predominately in the gas phase. $ClO_2$ is produced only in reaction 1. This reaction sets a limit on the product ratio of ½ mol $Cl_2$/mol $ClO_2$. Reaction 2 has the net effect of increasing the product ratio to values greater than ½.

Hong et el. (1967) derived theoretical expressions for the rate of production of $ClO_2$ and $Cl_2$ from a proposed mechanism based upon intermediates $HClO_2$ and HOCl. Their proposed rate expressions are:

$$R_{ClO_2} = 2k_a k_b [H^+]^4 [ClO_3^-]^2 [Cl^-]^2 / D \qquad (3)$$

$$R_{Cl_2} = k_a [H^+]^4 [ClO_3^-][Cl^-]^2 (k_b [ClO_3^-] + 3k_c [Cl^-])/D \qquad (4)$$

where:

$$D = k_a' [Cl_2] + k_b [H^+][ClO_3^-] + k_c [H^+][Cl^-] \qquad (5)$$

These expressions are somewhat cumbersome in that they contain a series of inhibition terms. In experimental studies, simpler forms of Eqs. 3 and 4 can be utilized by operating at conditions where one or more of the terms in the denominator (Eq. 5) are insignificant. An experimental complication arises in fitting kinetic data to these equations because of the non-ideality of ionic system. Hong et al. (1967) found a 12th- to 13th-order dependence on sulfuric acid concentration in $ClO_2$ production; however, they observed a fourth order dependence when acid activity was used instead of acid concentration in Eq. 3.

In industrial situations, often the selectivity of the reaction system is equally important, or more important than, the rate of production of any one product. The ratio of Eq. 4 to Eq. 3 yields a linear expression for the relative rates of production of $Cl_2$ and $ClO_2$ in terms of the reactant ratio, $r = [Cl^-]/[ClO_3^-]$

$$R_{Cl_2}/R_{ClO_2} = \frac{1}{2} + \left(\frac{3}{2}\right)\left(\frac{k_c}{k_b}\right) r \qquad (6)$$

Equation 6 predicts that the selectivity depends only upon the ratio of rate constants and the ratio of reactant concentrations. This equation is amenable to relatively simple laboratory investigation which would lead to measurement of the rate constant ratio.

This paper explores some theoretical aspect of the selectivity behavior of this reaction system in several reactor types.

## Theory

### *Batch reactor*

For a batch reactor, rate of product formation equals the sum of accumulation rates of products in gas and liquid phases and

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the flow rate of product gases leaving the reactors (if the reactor is semibatch). Equation 6 becomes:

$$\frac{\dot{V}_g y_{Cl_2} + V_g dy_{Cl_2}/dt + V_\ell\, d[Cl_2]/dt}{\dot{V}_g y_{ClO_2} + V_g dy_{ClO_2}/dt + V_\ell\, d[ClO_2]/dt} = \frac{1}{2} + \left(\frac{3}{2}\right)\left(\frac{k_c}{k_b}\right) r \qquad (7)$$

Hong et al. (1967) studied the reaction system under conditions at which all products remained in aqueous solution. In their study, $y_i = 0$, and Eq. 7 could be simplified to

$$d(Cl_2]/d[ClO_2] = \frac{1}{2} + \left(\frac{3}{2}\right)\left(\frac{k_c}{k_b}\right) r \qquad (8)$$

They also presented an integrated form of Eq. 8 which showed the left hand side replaced by the product ratio $[Cl_2]/[ClO_2]$. This integrated form would apply to a batch reactor at initial conditions.

### *CSTR*

For a CSTR operated at steady state, $r_{Cl_2}/r_{ClO_2}$ is proportional to the molar ratio of total $Cl_2$ and $ClO_2$ in the combined gas and liquid effluent streams, or

$$n_{Cl_2}/n_{ClO_2} = \frac{1}{2} + \left(\frac{3}{2}\right)\left(\frac{k_c}{k_b}\right) r \qquad (9)$$

At conditions of constant $k_c/k_b$, all CSTR data, regardless of feed composition, can be represented by a single straight line with a slope of $(3/2)(k_c/k_b)$ and an intercept of $1/2$.

Each of the four variables in Eq. 9 is related to two extent of reaction variables $\epsilon_1$ and $\epsilon_2$. These variables are the fractions of total $ClO_3^-$ which are consumed in reaction 1 and 2, respectively. Equation 9 can be transformed into an equation in $\epsilon_1$ and $\epsilon_2$ as follows. Let

$$n_{Cl_2}/n_{ClO_2} = \left[\left(\frac{1}{2}\right)\epsilon_1 + 3\epsilon_2\right]\Big/\epsilon_1 = \frac{1}{2} + \frac{3\epsilon_2}{\epsilon_1} \qquad (10)$$

and

$$r = [r_0 - \epsilon_1 - 5\epsilon_2]/[1 - \epsilon_1 - \epsilon_2] \qquad (11)$$

Inserting Eqs. 10 and 11 into Eq. 9 yields the expression

$$\epsilon_2/\epsilon_1 = 1/2\,(k_c/k_b)[r_o - \epsilon_1 - 5\epsilon_2]/[1 - \epsilon_1 - \epsilon_2] \qquad (12)$$

Unlike Eq. 9, the inlet reactant ratio, $r_o$, is a parameter in Eq. 12. Rearrangement of Eq. 12 leads to a quadratic equation relating $\epsilon_1$ and $\epsilon_2$. The extents of reaction and total fractional conversion of $ClO_3^-$ are related by the equation:

$$f = \epsilon_1 + \epsilon_2 \qquad (13)$$

Figure 1 shows the relationship, at constant $k_c/k_b$, between $\epsilon_2$ and $f$ as computed by Eqs. 12 and 13. At low values of $r_o$, $\epsilon_2$ passes through a maximum as $f$ increases. At high values of $r_o$, $\epsilon_2$ continually increases with increasing $f$. There is one value of $r_o$, designated $r_o'$, at which $\epsilon_2$ varies linearly with $f$. For $k_c/k_b = 0.1$, Figure 1, this unique value of $r_o'$ is 1.232. A reactor fed with a stream which has a reactant ratio of 1.232, will have an outlet reactant ratio, $r = 1.232$, and a product ratio $n_{Cl_2}/n_{ClO_2} = 0.685$ (by Eq. 9) regardless of $f$. A reactor fed by a stream with $r_o <$ 1.232 will have an outlet reactant ratio $< r_o$; the reverse is true for reactors fed by a stream with $r_o > 1.232$.

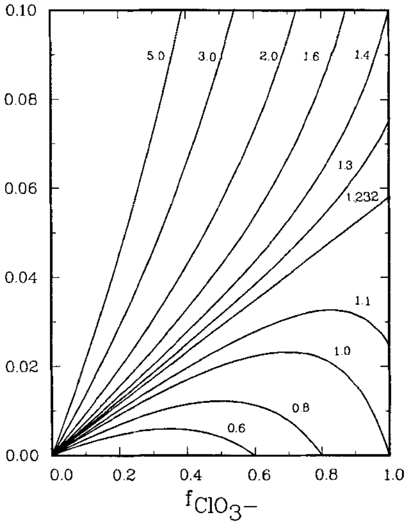

**Figure 1. Relationship between fraction of chlorate consumed by side reaction (Eq. 2) and total fractional conversion of chlorate (for $k_c/k_b = 0.1$ and various inlet reactant ratios).**

For each value of $k_c/k_b$, there is a unique value of $r_o$ (or $r_o'$) which yields a linear relationship between $\epsilon_2$ and $f$. The relationship between $k_c/k_b$ and $r_o'$ can be found by setting the left hand side of Eq. 12 at its limit as $\epsilon_1$ and $\epsilon_2$ approach 0, or

$$\lim_{\substack{\epsilon_1 \to 0 \\ \epsilon_2 \to 0}} (\epsilon_2/\epsilon_1) = \frac{1}{2}\left(\frac{k_c}{k_b}\right) r_o' \qquad (14)$$

and equating $r_o'$ to the effluent reactant ratio, or

$$r = r_o' = [r_o' - \epsilon_1 - 5\epsilon_2]/[1 - \epsilon_1 - \epsilon_2] \qquad (15)$$

Combining Eqs. 14 and 15, and rearranging leads to the quadratic expression:

$$(r_o')^2 + (2k_b/k_c - 5)r_o' - 2k_b/k_c = 0 \qquad (16)$$

The solution to Eq. 15—a relationship between $k_c/k_b$ and $r_o'$—forms an *S* shaped curve on semilogarithmic coordinates, Figure 2. Reactors operating at conditions represented by points lying to the left of the curve in Figure 2, have outlet reactant ratios greater than inlet reactant ratios. The opposite is true for reactors operating at conditions represented by points lying to the right of the curve.

### *PFR*

For a PFR operated at steady state, the relationship between product ratio and reactant ratio is quite different from that of a CSTR. In a PFR, the composition of the reactor effluent represents an accumulation of components produced at different rates along the reactor length. At any axial position, the differential change in product ratio is determined by Eq. 6. To find

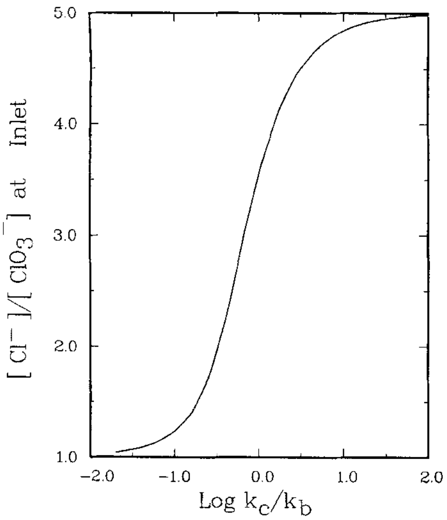

**Figure 2. Parameters $r_o'$ and $k_c/k_b$ at which product ratio and reactant ratio remain constant with chlorate conversion.**

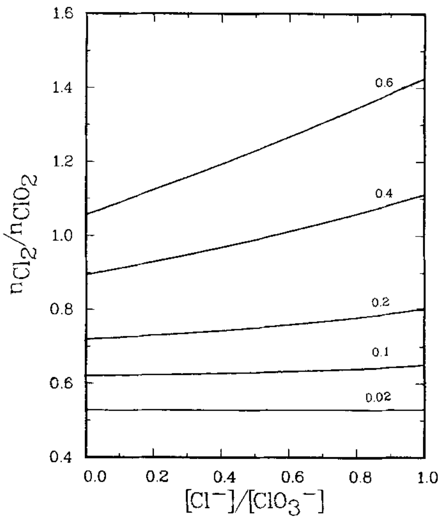

**Figure 3. Influence of $k_c/k_b$ on the relationship between product ratio and reactant ratio in a PFR for $r_o = 1$.**

the relationship between $n_{Cl_2}/n_{ClO_2}$ and $r$ in the reactor effluent, Eq. 6 must be numerically integrated. For convenience of integration, Eq. 6 can be transformed in terms of $\epsilon_1$ and $\epsilon_2$ by substituting

$$R_{Cl_2}/R_{ClO_2} = \frac{\frac{1}{2}\,d\epsilon_1 + 3\,d\epsilon_2}{d\epsilon_1} \tag{17}$$

and Eq. 11 into Eq. 6. The resulting equation is:

$$\frac{d\epsilon_2}{d\epsilon_1} = \left(\frac{k_c}{2k_b}\right) r = \frac{k_c}{2k_b}\,\frac{(r_o - \epsilon_1 - 5\epsilon_2)}{(1 - \epsilon_1 - \epsilon_2)} \tag{18}$$

Figures 3 and 4 show the influence of the parameters $k_c/k_b$ and $r_o$ on the relationship between $n_{Cl_2}/n_{ClO_2}$ and $r$. This relationship differs from that of the CSTR. For the PFR, the curves in Figures 3 and 4 at constant $k_c/k_b$ and $r_o$ are nonlinear, whereas, for the CSTR, the relationship is linear as described by Eq. 9.

Each of the curves in Figure 4 representing a PFR intersects the straight line representing the CSTR at a single point. Each of these points represents the limit of the PFR equation (Eq. 18) as $\epsilon_1$ and $\epsilon_2$ approach 0. At these points, the left hand side of Eq. 18 can be replaced by $\epsilon_2/\epsilon_1$. This substitution is equivalent to replacing the lefthand side of Eq. 6 by $n_{Cl_2}/n_{ClO_2}$.

Another difference between the $n_{Cl_2}/n_{ClO_2}$ vs. $r$ relationship for a PFR and a CSTR is shown by the slopes of the curves in Figure 4. For a CSTR, the slope equals $(3/2)\,k_c/k_b$, whereas for the PFR, the slope at low conversion approaches one half of the slope for the CSTR relationship, or $(3/4)\,k_c/k_b$. The slope for the PFR relationship decreases with increasing conversion.

The reason for the limit of the slope of $n_{Cl_2}/n_{ClO_2}$ vs $r$ for the PRF at low conversion is not obvious; however, the limit can be found by the following procedure. The variable $\epsilon_2$ is expanded about the point $\epsilon_1 = 0$ as follows:

$$\epsilon_2 = \epsilon_2(\epsilon_1 = 0) + \left.\frac{d\epsilon_2}{d\epsilon_1}\right|_{\epsilon_1=0}\epsilon_1 + \left.\frac{d^2\epsilon_2}{d\epsilon_1^2}\right|_{\epsilon_1=0}\frac{\epsilon_1^2}{2} + \mathcal{O}(\epsilon_1^3) \tag{19}$$

Because $\epsilon_2(\epsilon_1 = 0) = 0$, the following two expressions can be derived from Eq. 19,

$$\frac{\epsilon_2}{\epsilon_1} = \left.\frac{d\epsilon_2}{d\epsilon_1}\right|_{\epsilon_1=0} + \left.\frac{d^2\epsilon_2}{d\epsilon_1^2}\right|_{\epsilon_1=0}\frac{\epsilon_1}{2} + \mathcal{O}(\epsilon_1^2) \tag{20}$$

and

$$\frac{d\epsilon_2}{d\epsilon_1} = \left.\frac{d\epsilon_2}{d\epsilon_1}\right|_{\epsilon_1=0} \left.\frac{d^2\epsilon_2}{d\epsilon_1^2}\right|_{\epsilon_1=0}\epsilon_1 + \mathcal{O}(\epsilon_1^2) \tag{21}$$

The differential forms of these equations are:

$$d\left(\frac{\epsilon_2}{\epsilon_1}\right) = \left.\frac{d^2\epsilon_2}{d\epsilon_1^2}\right|_{\epsilon_1=0}\frac{d\epsilon_1}{2} + \mathcal{O}(\epsilon_1^2) \tag{22}$$

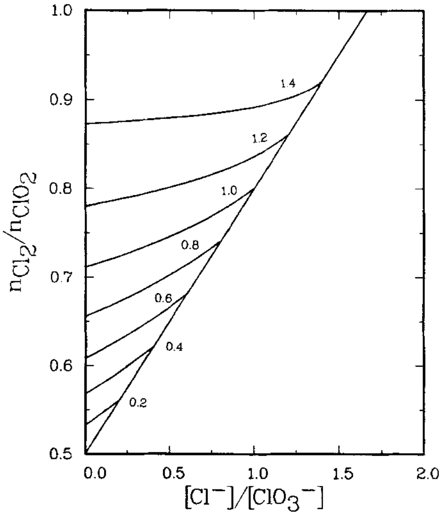

**Figure 4. Influence of inlet reactant ratio on the relationship between product ratio and reactant ratio for $k_c/k_b = 0.2$ in a CSTR (diagonal straight line) and PFR (curved lines).**

and

$$d\left(\frac{d\epsilon_2}{d\epsilon_1}\right) = \left.\frac{d^2\epsilon_2}{d\epsilon_1^2}\right|_{\epsilon_1=0} d\epsilon_1 + \mathcal{O}(\epsilon_1^2) \tag{23}$$

Equation 10 relates $n_{Cl_2}/n_{ClO_2}$ and $\epsilon_2/\epsilon_1$ based on the stoichiometry of the reaction system Eqs. 1 and 2. The differential form of Eq. 10 is:

$$d\left(\frac{n_{Cl_2}}{n_{ClO_2}}\right) = 3d\left(\frac{\epsilon_2}{\epsilon_1}\right) \tag{24}$$

Equation 18 relates $r$ and $d\epsilon_2/d\epsilon_1$ for a PRF. The differential form of Eq. 18, after rearranging, is

$$dr = \left(\frac{2k_b}{k_c}\right) d\left(\frac{d\epsilon_2}{d\epsilon_1}\right) \tag{25}$$

The ratio of Eq. 24 to 25 is the derivative,

$$\frac{d\left(\frac{n_{Cl_2}}{n_{ClO_2}}\right)}{dr} = \left(\frac{3}{2}\right)\left(\frac{k_c}{k_b}\right)\frac{d(\epsilon_2/\epsilon_1)}{d(d\epsilon_2/d\epsilon_1)} \tag{26}$$

which represents the slope of a plot of $n_{Cl_2}/n_{ClO_2}$ vs. $r$ for a PFR, as in Figure 4. The limit of the slope as $\epsilon_1 \to 0$ is found by combining Eqs. 22, 23 and 26 and neglecting higher order terms. The resulting expression is:

$$\left.\frac{d(n_{Cl_2}/n_{ClO_2})}{dr}\right|_{\epsilon_1\to 0} = \left(\frac{3}{4}\right)\frac{k_c}{k_b} \tag{27}$$

For each value of $k_c/k_b$, there is one value of $r_o$ (designated $r_o'$) for which both the product ratio and reactant ratio remain constant regardless of fractional conversion. This value can be found by setting the left hand side of Eq. 18 at its inlet value, or

$$\frac{d\epsilon_2}{d\epsilon_1} = \left(\frac{d\epsilon_2}{d\epsilon_1}\right)_{\text{inlet}} = \frac{k_c}{2k_b} r_o' \tag{28}$$

and equating $r_o$ to the effluent reactant ratio as in Eq. 15. Combining Eqs. 15 and 28, and rearranging leads to the quadratic equation (Eq. 16) which was previously derived for the CSTR. This result shows that Figure 2—the relationship between $k_c/k_b$ and $r_o'$—applies to both the CSTR and PFR.

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## Notation

$[i]$ = liquid-phase molar concentration of species $i$
$k_a, k_b \ldots$ = rate parameters
$\mathcal{O}$ = order
$R_i$ = molar rate of production of species $i$
$t$ = time
$\dot{V}_g$ = total volumetric gas flow rate
$V_g$ = total gas volume in batch reactor
$V_1$ = total liquid volume in batch reactor
$y_i$ = gas-phase molar concentrations of species $i$

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