

The effect of pH on the catalytic decomposition of aqueous sodium hypochlorite by cobalt oxide

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When the heavy metal oxide presents in the aqueous sodium hypochlorite, next two reactions occur simultaneously.



Suppose that k_1 is the decomposition rate constant of reaction (1) and k_{II} is that of reaction (2). The many studies of pH effect of k_{II} has been presented, but there have been few studies about a pH effect of k_1 .

In this report, pH effect of reaction (2) without catalyst was studied at 25°C at first. From the experimental result without catalyst, k_{II} in each pH were determined and k_1 of simultaneous reaction with catalyst at low pH k_1 are determined by trial and error.

In these procedure, the following assumption were adopted. That is, k_1 is assumed as next equation.

$$k_1 = k_1 X + k_2 Y \quad (17)$$

In this equation, k_1 and k_2 are the rate constants for the equation (1) and (3)



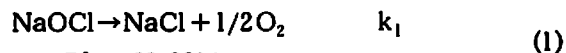
Here, $X = [\text{NaOCl}] / [\text{total available chlorine}]$ and $Y = [\text{HOCl}] / [\text{total available chlorine}]$

k_1 and k_2 were calculated from the experimental data at two pH. Then by using this k_1 and k_2 , k_1 are calculated in all pH ranges. Experimental data agree well with the calculation.

1. Introduction

Aqueous sodium hypochlorite (NaOCl) is widely used as a household bleaching agent and its stability is important for practical use.

Aqueous NaOCl decomposes according to the following parallel equation.



$$\Delta G^\circ = -93.88 \text{ kJ}$$



$$\Delta G^\circ = -153.0 \text{ kJ}$$

The main reaction is a disproportionation (2). But, if heavy metal oxides are present, the reaction (1) proceeds catalytically. The effect of pH on the decomposition reaction (2) has been studied by Lister²⁾ and Nakamori³⁾. As to the reaction (1) there are reports^{4,5)} showing that the oxide of Mn, Ni, Co, and Cu have significant

Received on May 20, 1996

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catalytic effect, though the oxides of Al, Pb, Zn and Pb catalyzed it slightly. Ayres and Booth⁶⁾ reported that the effect of pH on the reaction (1) using the oxide of Ir, but only qualitative results are obtained.

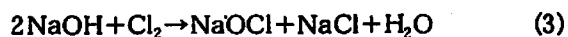
The catalysis of metal oxides generally accelerates the reaction (1), but does not affect the reaction (2). Studies until now have shown that the reaction rate (1) is a first order, and that of reaction (2) is a second order^{2~6)}. Until now the pH effect studies on reaction rate (1) have not been yet performed. In this study, the effect of pH on the reaction rate of (1) was studied in order to obtain quantitative results using cobalt oxide as the catalyst.

2. Experimental

2.1 Preparation of sample

2.1.1 Aqueous sodium hypochlorite

Sodium hypochlorite was prepared by the reaction of cooled 2M sodium hydroxide solution with chlorine gas. The equation is as follows.



Hereafter, NaOCl solution will imply the solution which contains the equimolecular amount of NaCl.

2.1.2 Cobalt oxide

Cobalt(II) nitrate 10 hydrate was dissolved in water. The solution was slowly added to 1,500 cm³ NaOCl solution of 7% available chlorine. After cobalt oxide was precipitated, then 200 cm³ of 1M sodium hydroxide was added and the precipitate was filtered. After being dried in desiccator for 3 days at room temperature, it was pulverized to pass 200 mesh sieve. This sample was dried again for 10 hrs. at 90°C before use. The results of X ray powder diffraction analysis confirmed amorphous.

2.2 Apparatus and operation

Reaction vessel which contained NaOCl solution (250cm³) and cobalt oxide (0.5g) were kept in a thermostat at 25°C. To keep the pH constant, an NaOH solution was continuously added through out the reaction. The sample was agitated at 1,000 r.p.m. and periodically analyzed to determine its NaOCl concentration.

2.3 Method of analysis

2.3.1 Available chlorine

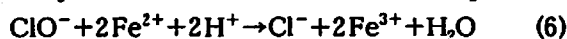
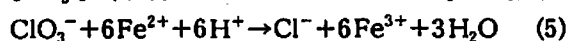
The analytical concentration of available chlorine $C = [\text{NaOCl}] + [\text{HOCl}] + [\text{Cl}_2]$ was determined by iodometry in acetic acid solution.

2.3.2 Chlorate ion concentration $[\text{ClO}_3^-]$

The sample was added to an excess amount of aqueous ferrous (II) ammonium sulfate to reduce chlorate ion to chloride. After reduction, remained ferrous ion was back titrated with potassium permanganate considering the following equation (5) and (6).

$[\text{ClO}_3^-]$ was calculated as one sixth of total available chlorine minus $2[\text{OCl}^-]$ as Eq. (4) which was based on Eqs. (5) and (6).

$$[\text{ClO}_3^-] = (1/6) \{ \text{total available chlorine} - 2[\text{OCl}^-] \} \quad (4)$$



2.4 Agitation speed

Preliminary experiment shows that no effect of agitation speed on the decomposition was observed above 1,000 r.p.m. So 1,000 r.p.m. was adapted as the agitation speed. It is clear from this result reaction is not diffusion controlled with the agitation speed above 1,000 r.p.m.

3. Results and discussion

3.1.1 Decomposition of aqueous hypochlorite

The noncatalytic decomposition at 25°C was performed at pH 7.0, 8.0, 9.0 and 10.0. The decomposition without catalyst produces chloride and chlorate and none of oxygen gas. This concludes us that the decomposition without catalyst proceeds according to the reaction (2).

Fig. 1 shows the NaOCl concentration vs. time curves for this decomposition reaction. pH effect on the decomposition was recognized and the decomposition reaction at low pH proceeds faster than that at high pH.

Fig. 2, shows $1/C$ vs. time plot for the results of Fig. 1. Every curves are linear showing that this reaction is a second order. The decline of this straight line give the rate constant of the second order decomposition. The obtained rate constants at low pH were larger than that at high pH. These result agreed well with the report of Nakamori et al. which shows this

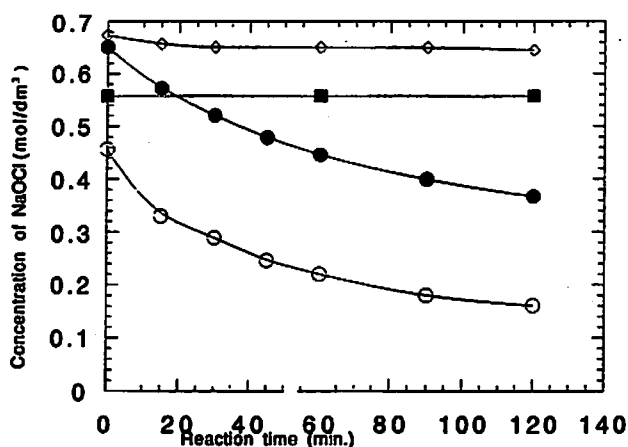


Fig. 1 NaOCl concentration vs time curves for the decomposition of aqueous NaOCl without catalyst at 25°C
○; pH 7, ●; 8, ◇; 9, ■; 10

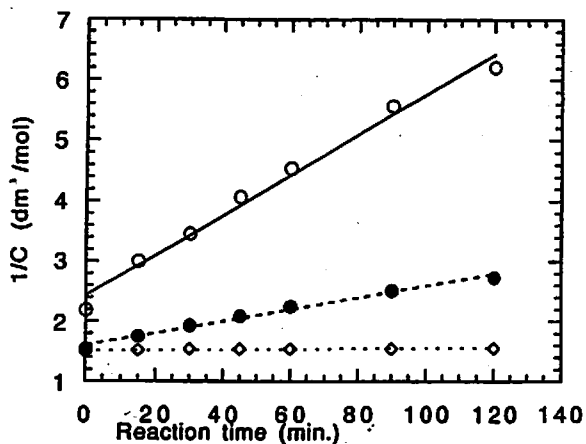


Fig. 2 Second order plots for the decomposition of NaOCl aqueous solution at 25°C
C; Concentration of NaOCl, ○; pH 7, ●; pH 8, ◇; pH 9

disproportionation is a second order³⁾.

3. 1. 2 Catalytic decomposition of aqueous hypochlorite

Experiments of the isothermal decomposition of NaOCl aqueous solution at pH 12 with cobalt oxide were carried out at 25°C under agitation speed for 1,000 r.p.m. When the catalyst was added, oxygen gas evolved. Analytical result show that NaOCl concentration decreases monotonously with time and that NaClO₃ concentration remains unchanged. Fig. 3 shows a representative concentration vs. time curves for catalytic decomposition at high pH. The results that the decomposition with catalyst proceed

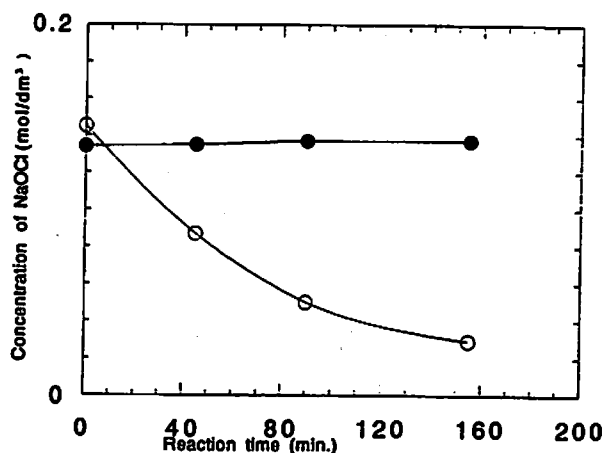


Fig. 3 Catalytic decomposition of NaOCl solution at pH 12
The volume of NaOCl solution; 500cm³, amount of cobalt oxide; 2.0g, temperature; 25°C, revolution rate; 1000 r.p.m
●; NaClO₃, ○; NaOCl

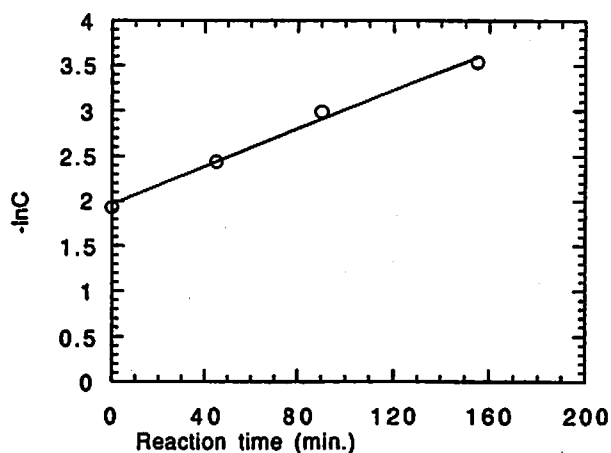


Fig. 4 First order plots for the catalytic decomposition of NaOCl solution
The volume of NaOCl solution; 500cm³, amount of cobalt oxide; 2.0g, temperature; 25°C, revolution rate; 1000 r.p.m

with evolution of oxygen gas and constant chlorate concentration conclude us that only the reaction (1) occurred, but that none of the reaction (2) did occur. Fig. 4 shows the results of concentration lnC vs. time plot for the data of Fig. 3. It is linear showing that the reaction is first order.

3. 1. 3 The effect of pH on the decomposition of aqueous hypochlorite with catalyst

Fig. 5 shows concentration vs. time curves for the decomposition of aqueous hypochlorite with catalyst at 25°C and at various pH. As the

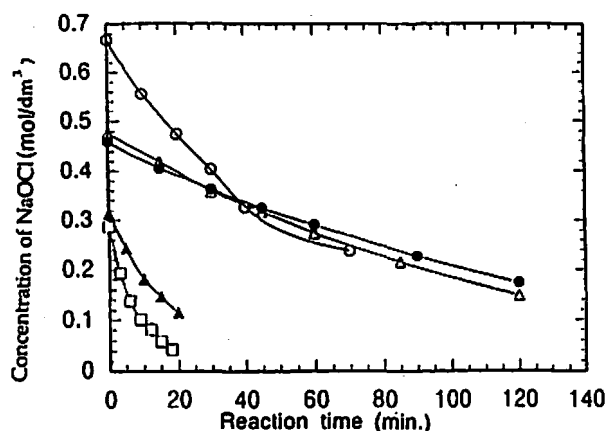


Fig. 5 The effect of pH on the catalytic decomposition of aqueous NaOCl at 25°C
Volume of NaOCl; 250cm³, amount of catalyst; 0.5g
●; pH 11, △; 10, ○; 9, ▲; 8, □; 7

pH is lower, decomposition rates are larger. At pH=7.0, 8.0 and 9.0, the decomposition proceeds with evolving oxygen gas and forming chlorate. This concludes us that the reaction (1) and (2) occurred in parallel at low pH. At pH 10 and 11 none of chlorate formation was recognized. So, this shows that a disproportionation can not occur at high pH.

3. 2 Estimation of rate constant

3. 2. 1 Analysis of reaction rate equation

As stated previously, the reactions (1) and (2) proceed in parallel at low pH. Therefore, the decomposition was analyzed by the next equation. When time is t and total concentration is C , the rate equation is as follows.

$$-dC/dt = k_1 C + k_{II} C^2 \quad (7)$$

where k_1 is a first order rate constant for a catalytic decomposition and a function of temperature, pH and the amount of catalyst. k_{II} is a second order rate constant and a function of temperature and pH.

Integrating Eq. (7), Eq. (8) was obtained as a rate equation in integrated form.

$$k_1 t = \{\ln(k_1 + k_{II} C) / C\} + \text{const} \quad (8)$$

When $t=0$, Eq. (9) was obtained. If $C=a$ (initial available chlorine) was substituted into Eq. (8), then

$$k_1 t = \ln \{a(k_1 + k_{II} C) / C(k_1 + k_{II} a)\} \quad (9)$$

Using this equation, k_1 at pH 7, 8 and 9 were determined as follows. At first, k_{II} at pH 7~9 were determined at each pH from the data of Fig. 2. Using this k_{II} , then k_1 at pH 7~9 were determined by substituting an initial concentration a , total available chlorine concentration C and the data of Table 1 into Eq. (9), by trial and error. The obtained k_1 were tabulated in Table 2.

As stated before, a disproportionation is very slow or can not occur at above pH 10. So, k_1 at above pH 10 can be directly determined by a decline of the $\ln C \sim$ time curves for the data of Fig. 3 and 6. k_1 thus obtained were also tabulated in Table 2. From these results it was found out that k_1 became greater as pH in the solution lower.

3. 2. 2 Estimation of decomposition rate constant k_1 at various pH

In aqueous solution chlorine exists as OCl^- .

Table 1 First order rate constant k_1 for the NaOCl decomposition using Eq. (9) at each pH at 25°C

pH=7							
t(min)	3	6	9	12	15	18	average
$k_1 \times 10$	1.2	1.0	0.9	1.0	1.5	0.95	1.05
pH=8							
t(min)	5	10	15	20			
$k_1 \times 10$	0.48	0.57	0.50	0.49			0.51
pH=9							
t(min)	10	20	30	40	70		
$k_1 \times 10^2$	1.82	1.71	1.67	1.78	1.45	1.69	

Volume of solution; 250cm³, catalyst; 0.5g

Table 2 First order rate constants k_1 for the catalytic decomposition of NaOCl at 25°C

pH	7	8	9	10	11	12
$k_1 \times 10^2$ $\text{min}^{-1} \text{g-cat}^{-1} \text{dm}^3$	5.25	2.55	0.85	0.48	0.39	0.30

Volume of solution; 250cm³, Amount of catalyst; 0.5g

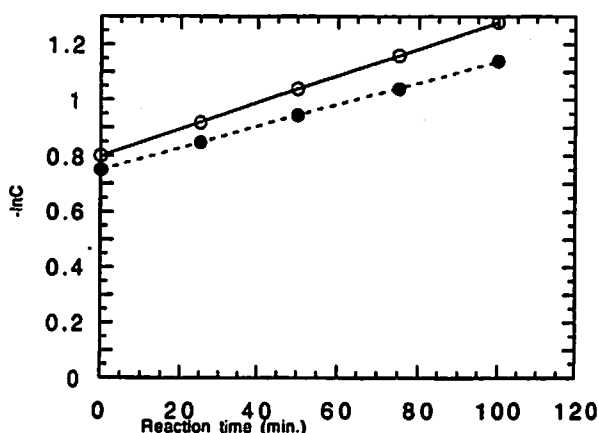


Fig. 6 First order plot for the catalytic decomposition of aqueous NaOCl solution of pH 10 and 11 at 25°C
○; pH 10, ●; pH 11

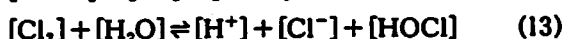
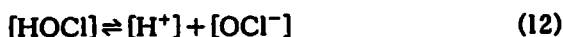
HOCl and Cl₂ in aqueous solution according to its pH. OCl⁻ decomposes to chloride ion and oxygen according to Eq (1') and hypochlorous acid decompose to hydrogen chloride and oxygen according Eq. (11)



On the other hand, chlorine in aqueous solution escapes to the outer in the form of gas. k_1 and k_2 are rate constants for the reaction (1') and (11) k_3 is a escaping rate constant of chlorine. So, first order rate constant k_1 can be written by the following Eq. (10).

$$k_1 C = k_1 [\text{OCl}^-] + k_2 [\text{HOCl}] + k_3 [\text{Cl}_2] \quad (10)$$

There exists the following equilibrium among [HOCl], [OCl⁻], [Cl⁻], [H⁺] and [Cl₂],



Equilibrium constant K_1 of Eq. (12) is $= 3.2 \times 10^{-8}$ (7) and $K_2 = 4.66 \times 10^{-4}$ (8).

Here, [OCl⁻] + [HOCl] + [Cl₂] means total available chlorine C. Moreover, we define $X = [\text{OCl}^-]/C$, $Y = [\text{HOCl}]/C$ and $Z = [\text{Cl}_2]/C$

Then, we get Eq. (14) as X

$$\begin{aligned} X &= [\text{OCl}^-]/C = [\text{OCl}^-]/([\text{OCl}^-] + [\text{HOCl}] + [\text{Cl}_2]) \\ &= (K_1 [\text{HOCl}]/[\text{H}^+]) / \{K_1 [\text{HOCl}]/[\text{H}^+] \\ &\quad + [\text{HOCl}] + [\text{HOCl}] [\text{H}^+] [\text{Cl}^-]/K_2\} \\ &= K_1 K_2 / \{K_1 K_2 + [\text{H}^+] K_2 + [\text{H}^+]^2 [\text{Cl}^-]\} \quad (14) \end{aligned}$$

Similarly, we get Eq (15) and (16) as Y and Z

$$Y = K_2 [\text{H}^+] / \{K_1 K_2 + [\text{H}^+] K_2 + [\text{H}^+]^2 [\text{Cl}^-]\} \quad (15)$$

$$Z = [\text{H}^+]^2 [\text{Cl}^-] / \{K_1 K_2 + [\text{H}^+] K_2 + [\text{H}^+]^2 [\text{Cl}^-]\} \quad (16)$$

Using X, Y and Z, Eq. 10 can be described as Eq. (10').

$$k_1 = k_1 X + k_2 Y + k_3 Z \quad (10')$$

Z may be neglected because [H⁺]² is smaller than [H⁺] and chlorine concentration is very small in this experimental pH region. As the result of this simplification, Eq (17) was obtained instead of Eq. (10)

$$k_1 = k_1 X + k_2 Y \quad (17)$$

Substituting (14) (15) into (17), k_1 was represented by Eq. (18).

$$k_1 = \{k_1 K_1 K_2 + k_2 K_2 [\text{H}^+]\} / \{K_1 K_2 + [\text{H}^+] K_2 + [\text{H}^+]^2 [\text{Cl}^-]\} \quad (18)$$

Here, [H⁺]² << [H⁺]. Therefore, k_1 can be described by the following simplified equation 19.

$$k_1 = \{k_1 K_1 K_2 + k_2 K_2 [\text{H}^+]\} / \{K_1 K_2 + [\text{H}^+] K_2\} \quad (19)$$

First order reaction rate constant k_1 is expressed by k_1 , k_2 , [H⁺], K_1 and K_2 .

Using the k_1 at pH 7 and 11 from table 2 and the values of X and Y which were calculated from Eq. (14) and (15), Eq. (17) was represented as the following equation.

Table 3 k_1 calculated from eq. (18) at 25°C

pH	$k_1(\text{min}^{-1} \text{g-cat}^{-1} \text{dm}^3)$	Log k_1
0	3.19×10^{-5}	-4.50
1	3.18×10^{-4}	-3.50
2	3.06×10^{-3}	-2.51
3	2.18×10^{-2}	-1.66
4	5.64×10^{-2}	-1.25
5	6.69×10^{-2}	-1.18
6	6.69×10^{-2}	-1.18
7	5.30×10^{-2}	-1.28
8	1.93×10^{-2}	-1.72
9	5.80×10^{-3}	-2.24
10	4.08×10^{-3}	-2.39
11	3.89×10^{-3}	-2.41
12	3.89×10^{-3}	-2.41
13	3.89×10^{-3}	-2.41
14	3.89×10^{-3}	-2.41

$$0.53 \times 10^{-1} = 2.42 \times 10^{-1} k_1 + 7.57 \times 10^{-1} k_2$$

At pH=7 (17)'

$$3.89 \times 10^{-3} = 1.00 k_1 + 3.12 \times 10^{-4} k_2$$

At pH=11 (17)''

Solving the above simultaneous equation, k_1 and k_2 were calculated as $k_1 = 3.89 \times 10^{-3} \text{ min}^{-1} \text{ g-cat}^{-1} \text{ dm}^3$ and k_2 as $6.8 \times 10^{-2} \text{ min}^{-1} \text{ g-cat}^{-1} \text{ dm}^3$

Using these k_1 and k_2 , k_1 was calculated from equation (18) at each pH and results, are shown in Table 3 and Fig. 7. At pH under 7, chlorine gas escaped from the system. Therefore, in this pH range, k_1 could not be calculated with good accuracy.

4. Conclusion

At various pH, a second order rate constant k_{II} for the disproportionation reaction (2) were determined by the results of Fig. 2. k_1 were also determined by experimental data of Table 1 and Fig. 3 and 6.

Assuming Eq. (17) as k_1 , k_1 and k_2 were solved.

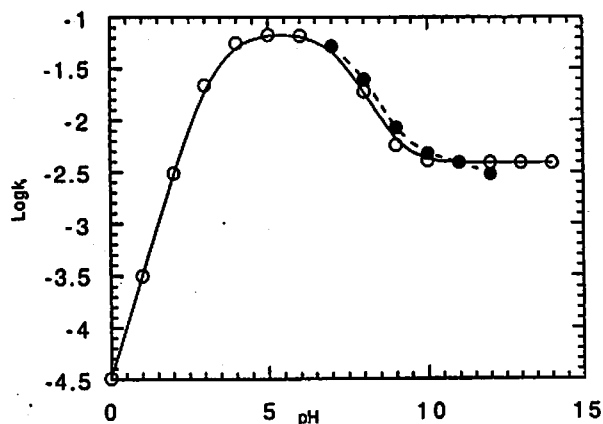


Fig. 7 Experimental and calculated values of k_1 for various pH at 25°C
○; Calculated, ●; Experimental

At pH 7 and 11, the obtained values of k_1 and k_2 were solved. At pH 7 and 11 the obtained values of k_1 and k_2 were $3.89 \times 10^{-3} \text{ min}^{-1} \text{ g-cat}^{-1} \text{ dm}^3$ and $k_2 = 6.80 \times 10^{-2} \text{ min}^{-1} \text{ g-cat}^{-1} \text{ dm}^3$, respectively.

Substituting this k_1 , k_2 , X and Y into Eq. (17), k_1 were calculated at all pH (Fig. 7). At all pH range, k_1 from experiments agree well with that from calculation.

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コバルト酸化物による次亜塩素酸ナトリウム水溶液の 接触分解速度におよぼすpHの影響

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次亜塩素酸ナトリウム水溶液は重金属酸化物触媒が混入すると、次の二つの反応が同時に起こる。



(2)の反応は2次反応速度式にしたがって起こり、その速度定数 k_{11} のpH依存性については多くの研究がある。一方、(1)式は1次反応速度式にしたがって起こるが、その速度定数 k_1 のpH依存性についての研究はまだ無い。

本研究はコバルト触媒を添加した場合の(1)および(2)式におよぼすpHの影響について検討し、以下の結論を得た。

触媒無添加および添加系の各pHにおけるNaOClの分解実験より、pHの低下とともに k_1 は大きくなる。いま k_1 を OCl^- の分解の1次反応式(1)の速度定数 k_2 をHOCl分解の1次分解反応(11)式の速度定数とする。



OCl^- およびHOClの全有効塩素に対する割合をX, Yとすると k_1 は(17)式で示される。

$$k_1 = k_1 X + k_2 Y \quad (17)$$

k_1 および k_2 を実験データ(pH 7および11)から求めた。ついで、この k_1 および k_2 を(17)式に代入して全pH域での k_1 を計算した。計算値と実験値はよく一致した。

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