

The formation and decomposition of sodium hypochlorite anhydrous salt and its pentahydrate

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The crystal of sodium hypochlorite pentahydrate and its anhydrous salt were prepared, and their thermal properties were studied.

In closed system, the decomposition rates of NaOCl and NaOCl · 5H₂O are expressed by zeroth order rate equation $\alpha = kt$. Water of crystallization inhibited decomposition. The decomposition rate of sodium anhydrous hypochlorite was about 12 times larger than that of pentahydrate. The decomposition rate of anhydrous crystals sealed against atmosphere was smaller than that in open state. Carbon dioxide contained in the air accelerated the decomposition largely.

1. Introduction

Aqueous sodium hypochlorite has been recently used as a household bleaching agent. Therefore, it is very important to know its stability. There have been a number of reports¹⁻⁶⁾ on its stability. Meanwhile, efforts have been made to develop a similar bleaching agent in the form of powder. For example, one is a solid solution of NaOCl in sodium phosphate⁷⁻¹⁰⁾, and the others are synthetic organic compounds such as 1, 3-dichloro-5, 5-dimethyl hydantoin and potassium dichloroisocyanurate¹²⁻¹⁴⁾ which generate hypochlorous acid through hydrolysis. These are, however, still not popular because of their high cost.

Sodium hypochlorite crystals were found first in 1898 by Muspratt and Smith^{15,16)} and were studied further by Appleby¹⁷⁾. Its properties have been reported in the literatures^{18,19)}, but have been detailed unknown except that it is unstable. From the view point mentioned the above, the author studied the decomposition rate of the NaOCl crystals.

2. Experimental

2.1 Preparation of sodium hypochlorite pentahydrate

The NaOCl · 5H₂O sample was prepared by the author's method²⁰⁾. The outline of the method is as follows. While maintaining the reaction temperature under 10°C, an aqueous solution of 6M sodium hydroxide was allowed to react with chlorine gas. This reaction produced NaOCl, sodium chloride (hereafter, described as NaCl) and water according to the following equation.



After a short time, NaCl precipitated. Separating of the precipitated NaCl by filtration, the filtrate was subjected to further reaction with chlorine gas.

Confirming that NaOCl present in the solution is higher than about 28wt%, the solution was cooled to -10°C until NaOCl · 5H₂O crystallized out of the solution. NaOCl · 5H₂O was obtained in the form of needle like crystals with a light yellow color.

The sample of NaOCl · 5H₂O thus prepared was kept in a refrigeration chamber for further experimental use.

2.2 Preparation of anhydrous sodium hypochlorite

The anhydrous NaOCl crystals were prepared by dehydration of NaOCl · 5H₂O at 60°C for 3 hours under a reduced pressure of 260 Pa.

2.3 Analysis of NaOCl, NaCl and NaClO₃

Determination of hypochlorite ion was carried out by iodometry in acetic acid.

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Table 1 Composition of anhydrous sodium hypochlorite and its pentahydrate

Sample	NaOCl (wt%)	NaCl (wt%)	NaClO (wt%)	H ₂ O (wt%)	Purity (wt%)
NaOCl·5H ₂ O	42.3	2.57	0	55.1	93.5
NaOCl	85.2	5.80	9.00	0	85.2

Determination of chloride ion coexistent with hypochlorite ion was carried out by the method as follows; after addition of 1cm³ of 30% aqueous solution of hydrogen peroxide to the sample to convert all of the hypochlorite ion to chloride ion, the total chloride ion in the solution was determined by titration with silver nitrate solution. Chloride ion coexistent with hypochlorite ion was calculated as the total chloride ion minus hypochlorite ion.

Determination of chlorate ion²¹⁾ was carried out by the following method; an aqueous solution of ferrous ammonium(II) sulfate was added to sample in excess to reduce chlorate ion and hypochlorite ion to chloride ion. After reduction, the excess ferrous ammonium(II) sulfate was back titrated with potassium permanganate solution.

After the contents of NaCl, NaOCl and NaClO₃ in the crystals of NaOCl were determined, the residual was calculated as the water content.

These analytical results are shown in Table 1, from which it is clearly seen that the crystals of NaOCl contained some impurities both in pentahydrate and anhydride. Available chlorine was 40.2wt% and 75.9wt% in the pentahydrate and anhydride, and the purity was 93.5 and 85.2wt% for the pen-

tahydrate and anhydride.

2.4 Isothermal decomposition

NaOCl·5H₂O and NaOCl anhydride prepared in the form of crystals as mentioned the above were suffered to decompose at 10°C under three different conditions, namely, (1) a reduced pressure of 260 Pa., (2) an atmospheric pressure of air in air tight container and (3) an atmospheric pressure open to the air. Each sample kept in bottles was sampled and analyzed several times.

In order to examine the effect of carbon dioxide on the decomposition, anhydrous hypochlorite was exposed to three different atmospheres, namely (1) decarbonated air which was produced by bubbling the air to NaOH solution, (2) oxygen which was supplied by oxygen vessel and (3) carbon dioxide which was supplied from carbon dioxide tank. These gases were filled up to the samples for three minutes in the bottle. Isothermal decomposition of the sample corked tightly were carried out at 25°C for 24 hrs and analyzed for hypochlorite.

3. Results and Discussion

3.1. Reaction formula for the decomposition.

Table 2 shows the analytical results for the NaOCl crystals before and after standing in the air for 70 minutes at 60°C. From Table 2, it is clear that the total chlorine remained constant during the reaction. This means that chlorine was not liberated from the reaction system at all.

Sodium hypochlorite solution decomposes according to the following parallel equations³⁾.



Table 2 Analytical results for the composition of before and after the isothermal decomposition of NaOCl crystal.

Analytical term (mol/g NaOCl)	Reactants mol×10 ⁴ /g NaOCl	Products mol×10 ⁴ /g NaOCl	Difference mol×10 ⁴ /g NaOCl
NaOCl	97.40	12.50	84.90
NaCl	8.03	67.00	58.97
NaClO ₃	0	27.30	27.30
Total chlorine	105.43	106.80	1.37
Available chlorine wt%	69.05	8.86	60.19
Weight (g) of sample	0.40	0.39	0.01

Sample : NaOCl anhydride prepared by dehydration of NaOCl·5H₂O at 60°C for 70min. (purity of NaOCl=72.5wt%)

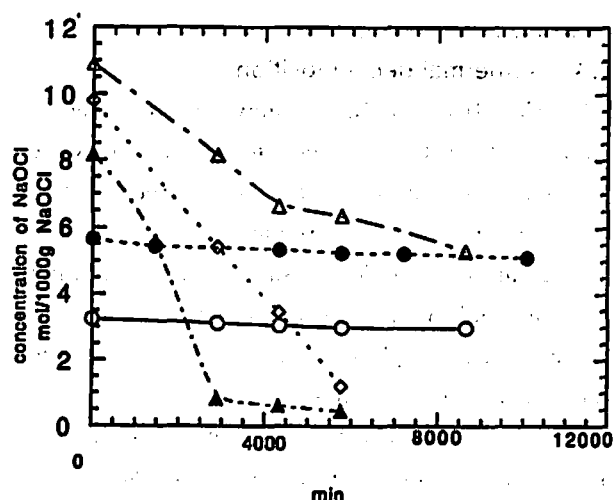


Fig.1 The decomposition of anhydrous hypochlorite and its pentahydrate at 10°C

- ; Solution in air using closed reaction vessel
- ; NaOCl · 5H₂O in air using closed reaction vessel
- ◇ ; Anhydrous salt in air using closed reaction vessel
- △ ; NaOCl under reduced pressure of 260Pa
- ▲ ; Anhydrous salt in air using open reaction vessel

and



The quantity of hypochlorite consumed according to Eq.2 can be calculated from Table 2 as follows.

$$[\text{OCl}^-] = [\text{Cl}^-] - 2[\text{ClO}_3^-] = (58.97 - 2 \times 27.3) \times 10^{-4} \\ = 4.37 \times 10^{-4} \text{ mol} / 0.400 \text{ g sample} \quad (4)$$

The percentage of hypochlorite consumed according to Eq. (2) is, therefore, as follows:

$$100 \times 4.37 / 84.90 = 5.15\%$$

From this result, it is clearly concluded that the decomposition of crystal occurred mainly according to disproportionation reaction of Eq.3 just like the decomposition in aqueous solution in the literature³⁾.

3.2 Reaction kinetics of the decomposition

Fig.1 shows the results of the decomposition behavior of hypochlorite crystals at 10°C in air. As approximately linear relation exists between the fractional decomposition and the reaction time in Fig. 1, so zeroth reaction order can be supposed.

Generally, a solid-state reaction is highly complicated, depending on experimental conditions of the sample such as its history, particle size, number of

Table 3 Reaction order and rate constant for the isothermal decomposition of NaOCl · 5H₂O and NaOCl at 10°C

Experiment No	Reaction order	Rate constant × 10 ⁴ min
No.1	0	0.08
No.2	0	1.52
No.3	0	0.90
No.4	0	3.21

No.1 ; NaOCl · 5H₂O in sealed container

No.2 ; NaOCl in sealed container

No.3 ; NaOCl under vacuum (260Pa.)

No.4 ; NaOCl in open container

lattice defects, strain in the surface structure, quantity used and so on. As a result, various equations have been proposed to explain it. In this experiment, however, the following empirical equation²³⁾ of zeroth order (5) can explain the results of isothermal decomposition:

$$\alpha = kt \quad (5)$$

where α is the fraction of decomposition, and k is the rate constant of zeroth order.

Table 3 shows the rate constant obtained from Fig.1. It can be seen from Table 3 that the rate constant of NaOCl decomposition became larger with a decrease in the content of water of crystallization mentioned above. From Fig.1, the value of the decomposition rate of NaOCl anhydride was calculated at 10°C under three different atmospheric conditions; namely, under a reduced pressure of 260Pa, atmospheric pressure in an air-tight container and atmospheric pressure open to the air. The rate constants were found to be a ratio of 0.90 : 1.52 : 3.21 in the order of the conditions mentioned the above, which indicates that the effect of air was great.

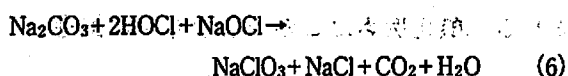
Table 4 shows the results of NaOCl decomposition under various conditions. The results shown in Table 4 indicate that the effect of carbon dioxide is the greatest. The effect of carbon dioxide can probably be explained by a mechanism according to the following equation (5) and (6)



Table 4 The effect of CO₂ gas on the decomposition of NaOCl

Atmosphere	Air without carbon dioxide	Oxygen	Carbon dioxide
Amount of NaOCl before (wt%) reaction	71.98	71.98	71.98
Amount of NaOCl after (wt%) reaction	71.34	59.50	0
Fraction of decomposition	0.009	0.174	1.000

Temperature ; 25°C, reaction time ; 25hrs



The mechanism involves the catalytic action of carbon dioxide. It has been reported that, in the form of an aqueous solution, HOCl showed a larger decomposition rate than NaOCl²⁾. The idea that this is also the case in the form of crystals has led to the mechanism above mentioned.

Conclusions.

In the thermal decomposition of NaOCl crystal, the total chlorine remained constant during the reaction and a very small loss was observed. The latter concludes that the NaOCl crystal cause a disproportionation reaction represented by Eq.3.

The crystals of anhydrous NaOCl and NaOCl·5H₂O decompose according to the zeroth order reaction rate. But the decomposition rate of anhydrous salt is about 12 times larger than that of pentahydrate. It was also found out that the decomposition is inhibited by the presence of water of crystallization and greatly accelerated by carbon dioxide in the air.

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References

- 1) M. W. Lister, Can. J. Chem., 30, 879 (1952)
- 2) I. Nakamori, H. Takama, M. Miura, 15th meeting of Chem. Soc. Japan (1962) p373
- 3) J. M. Mellor, "Supplement to the Comprehensive Treatise on Inorganic and Theoretical Chemistry

- Vol 2, Supp. 1 "Halogens", Longmans (1965) p549
- 4) M. W. Lister, Can. J. Chem., 34, 479 (1959)
- 5) G. H. Ayres, H. Booth, J. Am. Chem. Soc., 77, 825 (1955)
- 6) A. Hamano, The report of Sasebo College of Technology, 6, 139 (1970)
- 7) Kirk-Othmer, "Encyclopedia of Chemical Technology, 13", Interscience Encyclopedia (1949) p684
- 8) M. Hayamizu, Graduation thesis, Department of Industrial Chemistry of Kyushu Institute of Technology (1962)
- 9) R. N. Bell, Ind. Eng. Chem., 41, 2901 (1949)
- 10) U.S.P at, 2, 524, 324, U.S.P at, 2, 536, 456
- 11) For example, U.S.Pat, 2, 789, 078
- 12) Yabe Hayasi, Oils and Fats, 2, 98 (1964)
- 13) Nissan Chemical Catalog, 12th month, 10 day (1963)
- 14) Monsanto Technical Bulletin, 1-177
- 15) M. Musprat, E. M. Smith, J. Soc. Chem. Ind., 17, 1096 (1893)
- 16) M. Musprat, E. M. Smith, J. Soc. Chem. Ind., 18, 210 (1893)
- 17) M. P. Appleby, J. Chem. Soc., 115, 1106 (1919)
- 18) Kirk-Othmer, "Encyclopedia of Chemical Technology", Vol. 3, Interscience Encyclopedia (1945) p682
- 19) M. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 2, Longmans (1965) p67
- 20) Jap. Chem. Soc., "New Chemical Experimental Chair", Vol. 8, Maruzen, Tokyo (1978) p468
- 21) R. Nakamura, "Chlorine and its bleaching agents", Gihodo (1954) p206
- 22) K. Kubo, E. Suito, Y. Nakagawa, S. Hayakawa, "Powder theoretical and application", Maruzen (1968) p35-387
- 23) A. Hamano, The report of Sasebo College of Technology, 6, 144 (1969)

次亜塩素酸ナトリウム無水和物と5水和物の合成と熱分解

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次亜塩素酸ナトリウム無水和物結晶と5水和物結晶を合成し、その熱分解反応を検討した。

無水和物の熱分解においては全塩素量は反応の前後で変化しなかった。閉じ系ではこの無水和物結晶の分解速度式は $\alpha = kt$ で示される零次反応で表わせることがわかった。しかし、無水和物結晶は5水和物結晶の10倍の速度で分解した。密栓した無水和物結晶は解放系の結晶より分解速度は遅かった。空気中に含まれる二酸化炭素はこの分解を非常に促進した。

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