Decomposition of Free Chlorine with Tertiary Ammonium

Hajime KATANO,*† Kohei UEMATSU,* Hirosuke TATSUMI,** and Toshihide TSUKATANI***

*Department of Bioscience, Fukui Prefectural University, Eiheiji, Fukui 910-1195, Japan

**International Young Researchers Empowerment Center, Shinshu University, Matsumoto, Nagano 390-8621, Japan

***Research and Development Division, Nicca Chemical, Co. Ltd., Bunkyo, Fukui 910-8670, Japan

The reaction of free chlorine with tertiary ammonium or amine compounds in aqueous solution was studied by the amperometry at a rotating Pt-disk electrode. The amperometric method can be applied to follow the concentration of free chlorine (c_{Cl}) even in the presence of chloramine species. By addition of mono- and dibutylammonium to the solution containing free chlorine, the step-like decrease in c_{Cl} was observed, indicating the rapid formation of the stable chloramine species. By addition of tributylammonium, the c_{Cl} was decreased exponentially to nearly zero even if the free chlorine was present initially in excess. The $c_{\text{Cl}}-t$ curves can be explained by tributylammonium-species-catalyzed decomposition of free chlorine to chloride ion. The catalytic decomposition was observed also with the tertiary-ammonium-based anion-exchange resins. Furthermore, the anion-exchange resins exhibited the decomposition of not only free chlorine but also chloramines in water.

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Introduction

Chlorine has been used for purification of water, in disinfectants, and in bleach. Regardless of the type of chlorine added, it exists in water as free chlorine, which is defined as dissolved gas Cl_2 , hypochlorous acid HOCl , and/or hypochlorite anion OCl^- . The three forms of free chlorine exist together in the equilibria:¹⁻³

and

At the normal pH of tap water (pH 5.8 – 8.6), the predominant species are HOCl and OCl^- . The free chlorine reacts with ammonia or organic amines, which can be found in natural or polluted waters, to produce chloramines (also known as combined chlorines).¹⁻³ For example, HOCl reacts with NH_3 to produce mono-, di-, and trichloramine species:

and

The concentration of free chlorine (c_{Cl}) can be determined by

the amperometry with a rotating Pt-disk electrode.⁴ The amperometric current is proportional to c_{Cl} without interference from chloramines, so that the electrochemical method can be applied to follow the c_{Cl} in the reaction mixture of free chlorine and ammonium or amine compounds more advantageously than the conventional spectrophotometric determination with chromogenic reagents.^{5,6} In this study, the reactions of free chlorine with different ammonium compounds in aqueous solution were investigated.

By addition of mono- and dibutylammonium (BuNH_3^+ and Bu_2NH_2^+) species to a test solution containing free chlorine, a step-like decrease in c_{Cl} was observed. The decrease in c_{Cl} can be attributed to the formation of chloramine species. On the other hand, by addition of tributylammonium (Bu_3NH^+) species, c_{Cl} was decreased exponentially to nearly zero even if the free chlorine was present initially in excess. The $c_{\text{Cl}}-t$ curves can be explained by Bu_3NH^+ -species-catalyzed decomposition of free chlorine to Cl^- ion. Other tertiary ammonium or amine species also showed the catalytic effect.

In wastewater treatment, free chlorine has usually been neutralized by the reduction with thiosulfate and sulfite compounds.⁷ Also, activated carbon can reduce free chlorine to Cl^- ion.^{8,9} The catalytic decomposition by tertiary ammonium or amine species seems available to the neutralization of free chlorine advantageously. Thus the study has been extended to the reaction of free chlorine with tertiary-ammonium-based anion-exchange resins as heterogeneous catalyst. Interestingly, the polymer resins have exhibited the decomposition not only of free chlorine but also of chloramines.

Experimental

The amperometric and voltammetric experiments were

† To whom correspondence should be addressed.
E-mail: hajime@fpu.ac.jp

Fig. 1 Current vs. potential curves of the 0.05 M $\text{KH}_2\text{PO}_4\text{-K}_2\text{H}_2\text{PO}_4$ buffer (pH 6.9, 25°C) in the (a) absence and (b) presence of 0.5 mM free chlorine with the rotating Pt-disk electrode at $N = 1000$ rpm.

performed using a three-electrode system. A platinum disk electrode (BAS 002067) was used as the working electrode. The working electrode was rotated by a rotator (BAS RDE-2). A platinum coil and an Ag | AgCl (0.1 M KCl) electrode were used as the counter electrode and the reference electrode, respectively. The body of the reference electrode was made from a glass tube (BAS 002243), to which a liquid conjunction tip of Vycor porous glass was attached. A special piece of glassware (BAS 010038) was used for the cell vial. The current vs. applied potential (I - E) curves and the current vs. time curves, that is, the $c_{\text{Cl}}\text{-}t$ curves, were recorded with a laboratory-made electrochemical analyzer.

The concentration of NaOCl in a sodium hypochlorite solution (Nacalai Tesque) was determined by spectrophotometry with diethyl-*p*-phenylenediamine (DPD).^{5,6} Then, the NaOCl solution was diluted to 50 mM. The 50 mM NaOCl solution was prepared freshly every day, and was used as the free chlorine standard solution. Solutions containing 10 mM mono-, di-, and tributylamine and 10 mM HCl were prepared, and were used as the 10 mM BuNH_3^+ , Bu_2NH_2^+ , and Bu_3NH^+ standard solutions, respectively. Similarly, the standard solutions of triethanolammonium ($(\text{HOC}_2\text{H}_4)_3\text{NH}^+$), diethanolmethylammonium ($\text{Me}(\text{HOC}_2\text{H}_4)_2\text{NH}^+$), trimethylammonium (Me_3NH^+), triethylammonium (Et_3NH^+), and tripropylammonium (Pr_3NH^+) solutions were prepared with triethanolamine, methyldiethanolamine, trimethylamine, triethylamine, and tripropylamine, respectively. Anion-exchange resins Amberlite IRA96SB and IRA67 (Organo Corp.), and Diaion WA30 (Mitsubishi Chemical Corp.) which have dimethylamino group as functional group were used as heterogeneous catalysts. The resins were pretreated with basic solution, and were used as the free base form. The test solution was buffered at pH 6.9 with 0.05 M $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$, and was kept at $25 \pm 1^\circ\text{C}$ unless otherwise stated.

Results and Discussion

Amperometry of free chlorine

Curve a in Fig. 1 shows the I - E curve of the 0.05 M $\text{KH}_2\text{PO}_4\text{-K}_2\text{H}_2\text{PO}_4$ (pH 6.9, 25°C) with the rotating Pt-disk electrode at the rotation rate (N) of 1000 rpm. The I - E curve was recorded by the linear potential sweep technique at the rate of 0.01 V s^{-1} . Curve b shows the I - E curve obtained by addition of 0.5 mM free chlorine to the test solution. A well-defined cathodic wave, that is, an S-shaped I - E curve with a limiting

Fig. 2 Time dependence of c_{Cl} for the solution (pH 6.9, 25°C) of $c_{\text{Cl,init}} = 0.5 \text{ mM}$ without (dashed line) and with (solid line) addition of 0.10 mM (a) BuNH_3^+ , (b) Bu_2NH_2^+ , and (c) Bu_3NH^+ at the point indicated by the arrow.

current, is exhibited. The limiting current at $E = 0.2 \text{ V}$ was proportional to c_{Cl} and $N^{1/2}$, indicating that the limiting current was controlled by the diffusion of free chlorine species in the aqueous solution.

The limiting current was almost independent of pH in the range from 4.5 to 7.5. The half-wave potential was shifted to positive potentials with decreasing pH. The voltammetric current can be attributed to the reduction of free chlorine at the Pt electrode as given by¹⁰⁻¹²

with the protonation equilibrium of Eq. (2).

By addition of 1 mM NH_4Cl to the test solution containing 0.5 mM free chlorine, the cathodic wave of Fig. 1b disappeared within the potential range. The reaction of free chlorine with ammonia or ammonium ion is not simple, and the products vary with conditions such as pH and ratio of free chlorine to ammonium ion.¹⁻³ However, it has been reported that NH_2Cl is formed predominantly when the ammonium ion is present in excess of free chlorine at near neutral pH.³ The back reaction in Eq. (3) has been reported to be considerable slow (the rate constant has been reported to be $3 \times 10^{-5} \text{ s}^{-1}$).² Therefore the experimental result indicates that the chloramine itself is electrochemically inactive and does not give kinetic current due to regenerating HOCl. Thus the amperometric method can be applied to follow the concentration of free chlorine c_{Cl} even in the presence of chloramine species. In the following, $c_{\text{Cl}}\text{-}t$ curves can be obtained by recording the amperometric current at $E = 0.2 \text{ V}$.

Reactions of free chlorine with mono-, di-, and tributylammonium ions

The dashed line in Fig. 2 shows the $c_{\text{Cl}}\text{-}t$ curve of the 0.5 mM NaOCl, 0.05 M $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$ buffer (pH 6.9, 25°C), that is, the $c_{\text{Cl}}\text{-}t$ curve of $c_{\text{Cl,init}} = 0.5 \text{ mM}$ ($c_{\text{Cl,init}}$ being the initial concentration of free chlorine) without addition of the ammonium salts. The c_{Cl} decreased slightly with time. This may be due to a spontaneous decomposition or to volatilization of free chlorine.¹³

Curve a in Fig. 2 shows the $c_{\text{Cl}}\text{-}t$ curve of the test solution by addition of 0.10 mM BuNH_3^+ at the point indicated by the arrow (in the following, the time is taken as $t = 0$). By addition of BuNH_3^+ , c_{Cl} decreased rapidly, and then decreased as slight as the dashed line in the figure. The step-like decrease in c_{Cl} may be ascribed to the formation of chlorinated monobutylammonium

Fig. 3 Experimental c_{Cl} - t curves for the addition of (a) 0.020, (b) 0.050, (c) 0.10, (d) 0.20, and (e) 0.40 mM Bu_3NH^+ in the test solution (pH 6.9, 25°C) of $c_{Cl,init} = 0.2$ mM and the c_{Cl} -values calculated by Eq. (9) with $k_{app} = 0.005$ (●), 0.013 (■), 0.035 (▲), 0.077 (▼), and 0.126 (◆) s^{-1} .

species. The decrease in c_{Cl} was *ca.* 0.28 mM at $t = 240$ s, suggesting that a butyltrichloramine species. The step-like decrease in c_{Cl} was observed also by the addition of $Bu_2NH_2^+$ as shown by curve b in Fig. 2. The decrease in c_{Cl} was 0.14 mM, suggesting the formation of dibutylchloramine and dibutylchloramine species. We also recorded the c_{Cl} - t curve by addition of 0.10 mM tetrabutylammonium chloride to the test solution of $c_{Cl,init} = 0.5$ mM. The c_{Cl} - t curve was almost the same as the dashed line in Fig. 2, indicating that the quaternary ammonium ion do not react with chlorine.

Reaction of free chlorine with tributylammonium ion

Curve c in Fig. 2 shows the c_{Cl} - t curve obtained by addition of 0.10 mM Bu_3NH^+ to the test solution of $c_{Cl,init} = 0.5$ mM. The c_{Cl} appears to decrease exponentially. The decrease in c_{Cl} exceeds the initial concentration of Bu_3NH^+ ($c_{Bu_3N,init}$), and the c_{Cl} reached nearly zero when $t > 500$ s. Using DPD method with KI,¹⁴ a chloramine species was detected in the reaction mixture when $t = 60 - 240$ s, but it was no longer detected when $t > 500$ s. We assume that Bu_3NH^+ species reacts with free chlorine, *e.g.* HOCl, to form a tributylchloramine species Bu_3NCl^+ as intermediate by

and the Bu_3NCl^+ decomposes to produce Bu_3NH^+ species and chloride anion Cl^- by

If the decomposition of Eq. (8) is so fast that the concentration of free Bu_3NH^+ can be assumed to be equated to $c_{Bu_3N,init}$ during the reaction proceeds, the rate-determining step Eq. (7) can be approximated to the first-order with respect to free chlorine. Under such assumptions, the c_{Cl} - t curve is given by

$$c_{Cl} = c_{Cl,init} \exp[-k_{app}t], \quad (9)$$

where k_{app} is the apparent first-order rate constant. However, Eq. (9) could not be fitted to the experimental c_{Cl} - t curve of Fig. 2c in the range of $0 < c_{Cl}/c_{Cl,init} < 1$, indicating that the decomposition of Eq. (8) is not so fast.

However, the experimental c_{Cl} - t curves obeyed the pseudo

Fig. 4 Plot of k_{app} vs. $c_{Bu_3N,init}$ for the test solution (pH 6.9, 25°C) of $c_{Cl,init} = 0.2$ mM.

first-order kinetics at certain conditions described below. Figure 3 shows the c_{Cl} - t curves obtained by addition of Bu_3NH^+ at different concentrations to the test solution of $c_{Cl,init} = 0.2$ mM. In the figure, the ordinate is normalized by $c_{Cl,init}$. When $c_{Bu_3N,init} = 0.10, 0.20$, and 0.40 mM and $c_{Cl,init} = 0.2$ mM, Eq. (9) can be fitted to the c_{Cl} - t curve in the range of $0.1 < c_{Cl}/c_{Cl,init} < 1$ to obtain $k_{app} = 0.035, 0.077$, and 0.126 s^{-1} , respectively. When $c_{Bu_3N,init} = 0.020$ and 0.050 mM and $c_{Cl,init} = 0.2$ mM, Eq. (9) can be fitted to the c_{Cl} - t curve in the range of $0.8 < c_{Cl}/c_{Cl,init} < 1$ and $0.6 < c_{Cl}/c_{Cl,init} < 1$ to obtain $k_{app} = 0.005$ and 0.013 s^{-1} , respectively. The calculated $c_{Cl}/c_{Cl,init}$ -values by Eq. (9) with the k_{app} -values are plotted also in Fig. 3. The k_{app} -values are plotted against $c_{Bu_3N,init}$ in Fig. 4. The regression line is given by

$$k_{app}/s^{-1} = (0.32 \pm 0.1)(c_{Bu_3N,init}/mM) + (0.001 \pm 0.02), \quad (10)$$

indicating that k_{app} is proportional to $c_{Bu_3N,init}$. Also, the c_{Cl} - t curves recorded when $c_{Bu_3N,init} = 0.20$ mM and $c_{Cl,init} = 0.050$ and 0.10 mM to obtain $k_{app} = 0.08 \pm 0.02$ and 0.075 ± 0.02 s^{-1} , respectively. The values are in agreement with $k_{app} = 0.077$ s^{-1} when $c_{Bu_3N,init} = 0.20$ mM and $c_{Cl,init} = 0.2$ mM.

As shown in Fig. 5, k_{app} was increased with pH, suggesting that the reaction of Eq. (7) consists of the acid dissociation equilibrium of Bu_3NH^+ :

and the reaction of Bu_3N with HOCl:

The time-dependence of the concentration of Bu_3NH^+ and Cl^- in the reaction mixture has not been measured successfully. However, by combination of Eqs. (7) and (8), the whole reaction is given as

Thus Eq. (8) as well as Eq. (11) may be verified by the decrease of pH of the reaction mixture in the absence of buffer components. In the experiment, heterogeneous catalyst, *e.g.* tertiary-ammonium-based anion-exchange resin, can be applied advantageously because the ammonium and amine species, that is, the buffer components are not solved in the test solution.

Fig. 5 Plot of $\log[k_{\text{app}}]$ vs. pH for the test solution (25°C) of $c_{\text{Bu}_3\text{N},\text{init}} = 0.10$ mM and $c_{\text{Cl},\text{init}} = 0.2$ mM.

A 250-mg of IRA96SB (free base form) and a 50-ml of 50 mM NaOCl solution (pH ~11) were added in a sealed vessel. The mixture was stirred overnight so that the conversion of NaOCl to NaCl took place completely. Then the mixture was filtered off. The pH of the reaction mixture was lowered to 7–9.

Other tertiary ammonium/amine

The $c_{\text{Cl}}-t$ curves were recorded by addition of 0.10 mM $(\text{HOC}_2\text{H}_4)_3\text{NH}^+$, $\text{Me}(\text{HOC}_2\text{H}_4)_2\text{NH}^+$, Me_3NH^+ , Et_3NH^+ , and Pr_3NH^+ to the test solution (pH 6.9, 25°C) of $c_{\text{Cl},\text{init}} = 0.2$ mM. The c_{Cl} was decreased exponentially in a similar manner to that obtained by addition of Bu_3NH^+ , suggesting that other tertiary ammonium or amine catalyze the decomposition of free chlorine. The k_{app} -value increased in order of $(\text{HOC}_2\text{H}_4)_3\text{NH}^+ < \text{Me}(\text{HOC}_2\text{H}_4)_2\text{NH}^+ < \text{Bu}_3\text{NH}^+ < \text{Me}_3\text{NH}^+$, which corresponds to the order of the acid dissociation constant $\text{p}K_{\text{a}}$ of the ammonium species in aqueous solution: $(\text{HOC}_2\text{H}_4)_3\text{NH}^+ < \text{Me}(\text{HOC}_2\text{H}_4)_2\text{NH}^+ < \text{Me}_3\text{NH}^+ \approx \text{Bu}_3\text{NH}^+$,¹⁵ suggesting that the tertiary amine of higher basicity has the more effective catalytic activity.

The $\text{p}K_{\text{a}}$ values of the conjugate acid of mono- and dimethylchloramines $(\text{CH}_3)_2\text{NCl}$ and $(\text{C}_2\text{H}_5)_2\text{NCl}$ are reported to be $\text{p}K_{\text{a}} = 0.46$ and 1.0, respectively.¹⁵ The much lower $\text{p}K_{\text{a}}$ -values suggest that the cationic form of the chloramines is not stable in aqueous media. Since the chloramine of tertiary amine exists only in the cationic form, $\text{Cl}(+\text{I})$ in the cationic chloramine may be converted to Cl^- according to Eq. (8).

Tertiary-ammonium-based anion-exchange resin

Figure 6 shows the $c_{\text{Cl}}-t$ curves for the addition of 50 mg of IRA96SB in 10 ml of 0.2 mM NaOCl, 0.05 M $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$ buffer (pH 6.9, 25°C). The Pt disk electrode was rotated at $N = 2000$ rpm to stir the resin beads. In the range of the amount of IRA96SB from 10 to 100 mg, the $c_{\text{Cl}}-t$ curves can be fitted to Eq. (9) in the range of $0.1 < c_{\text{Cl}} < 1$. The obtained k_{app} -values were proportional to the amount of IRA96SB. Similar results were obtained with other tertiary-ammonium-based anion-exchange resins such as Amberlite IRA67 and Diaion WA30, which have dimethylamino group, and Amberlite IRC748, which has iminodiacetate group. For a comparison, the $c_{\text{Cl}}-t$ curves for the addition of 50 mg Amberlite IRA400J, which is a quaternary-ammonium-based anion-exchange resin, was recorded. As shown by curve b in Fig. 6, the decrease in c_{Cl} was not so fast.

The total exchange capacity of IRA96SB has been reported to

Fig. 6 Time dependence of c_{Cl} for the addition of 50 mg (a) IRA96SB and (b) IRA400J in 10 ml of the test solution (pH 6.9, 25°C) of $c_{\text{Cl},\text{init}} = 0.2$ mM.

be 1.25 equivole l^{-1} by the supplier. If the density is assumed to be 1 g cm^{-3} , 50 mg of IR96SB contains *ca.* 60 μmol of Me_2N -group. The 100 μl of 50 mM NaOCl (5 μmol) was added 25 times at a 1200-s interval to 10 ml of 0.5 M $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$ (pH 6.9, 25°C) in which 50 mg of IRA96SB was stirred, and the $c_{\text{Cl}}-t$ curves were recorded each time. The k_{app} -value tended to decrease slightly each time, indicating again that the decomposition of Eq. (8) is not so fast. However, even after the reaction with 125 μmol chlorine in total, the 50 mg of IR96SB resin exhibited the catalytic effect.

Thus polymer resins comprising tertiary amine can be applied as a heterogeneous catalyst for decomposition of free chlorine of Eq. (11). A 80-ml portion of IRA96SB resin beads was packed in a glass tube of 30 mm diameter to prepare a column reactor. The sample solution (pH 6.9, 25°C) containing 4 mg l^{-1} (as Cl) free chlorine was run through the column reactor at a flow rate of 160 ml min^{-1} . The free chlorine was not detected in the running water by DPD method, indicating that the column reactor can decompose the free chlorine completely within 30 s.

Reaction of monochloramine with tertiary-ammonium-based anion-exchange resin

A 1 mM NH_4NO_3 was added to the 4 mg l^{-1} free chlorine solution (pH 6.9, 25°C) to prepare the 4 mg l^{-1} ammonium chloramine solution. The concentration of the chloramines was determined by the DPD method with KI.¹⁴ The solution was run through the column at a flow rate of 160 ml min^{-1} . Interestingly, the concentration of the chloramines in the running water was lowered to 0.4 mg l^{-1} . Chloramines produce free chlorine according to the back reaction of Eqs. (3)–(5), that is, hydrolysis. However, since the hydrolysis reactions are very slow,^{2,16} the decrease in the concentration of the chloramines cannot be explained by the hydrolysis preceding the catalytic reaction of Eq. (11). Probably the chloramines gave $\text{Cl}(+\text{I})$ directly to the Me_2N -group according to

Thus, the electrochemical method can be applied advantageously to the study of the reactants for free chlorine. The experimental results showed that tertiary ammonium or amines catalyze the decomposition of free chlorine to chloride ion.

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