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Electron Spin Resonance Studies of Chlorine Dioxide (ClO_2) in Aqueous Solutions

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The ClO_2 radical was obtained from many reaction systems (Ti^{3+}–$NaClO_3$, Ti^{3+}–$NaClO_2$ and H_2SO_4–$NaClO_2$) in aqueous solutions. The formation of the ClO_2 radical was detected by means of the rapid-mixing flow technique coupled with electron spin resonance (ESR) measurements.

Keywords——chlorine dioxide; ClO_2 radical; rapid-mixing flow technique; ESR; Ti^{3+}–$NaClO_3$; Ti^{3+}–$NaClO_2$; H_2SO_4–$NaClO_2$

The stable radical molecule, chlorine dioxide (ClO_2), usually exists as a yellow gas. Since ClO_2 is an excellent bleaching agent or disinfectant, it is widely used industrially.[2] For these purposes, ClO_2 gas is prepared by the exothermic reaction of sodium chlorate in sulfuric acid containing sulfur dioxide (Eq. 1).

$$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4 \quad (1)$$

ClO_2 gas is very soluble in water and aqueous solutions of it are stable in the dark. The ClO_2 radical has been extensively studied by the ESR technique, both in solution[3,4] and in the solid phase in a number of X- or γ-irradiated powders and single crystals.[5,6]

Solution spectra of ClO_2 in a variety of solvents[3,4] have given a measure of the isotropic hyperfine interaction of the chlorine nucleus. In addition, the line width variation with temperature and solvent was studied, and unusually large line widths were explained in terms of modulation of the spin-rotation interaction. The reactivities of ClO_2, however, have not hitherto been investigated either in solution or in the solid state. In order to investigate the reactivities of ClO_2, a stable source of ClO_2 is required. Therefore, we have examined many reaction systems and found that the ClO_2 radical can be obtained either by the use of a redox reaction system such as Ti^{3+}–$NaClO_3$ or Ti^{3+}–$NaClO_2$ or by the acidification of $NaClO_2$ in aqueous solutions by use of the ESR-rapid mixing flow technique.

In this paper, we would like to report these results.

Experimental

Materials——$TiCl_3$ solution (20% w/v), $NaClO_3$ and $NaClO_2$ purchased from Wako Pure Chemical Ind. Ltd. were of reagent grade and were used without further purification. Sulfuric acid, sodium hydroxide and other chemical reagents were of commercial GR grade.

ESR Measurements——ESR measurements were carried out on a JEOL-PE-1X ESR spectrometer (X-band) with 100 kHz field modulation in conjunction with a JEOL mixing chamber. This apparatus enabled us to detect radicals having a lifetime of 5—100 ms at room temperature.[7-10] The hyperfine coupling constants and the g-values were calibrated by comparison with those of an aqueous solution of Fremy's salt ($g = 2.0055$, $a^N = 13.0$ G)[11] kept in a capillary tube attached to the sample tube. Relative concentrations of radicals were measured by comparison of the

peak-to-peak heights of the first derivatives of the appropriate resonances.

Procedure——All solutions were prepared from triply distilled water, and their pH values were adjusted with sulfuric acid or sodium hydroxide.

For the generation of ClO_2 radicals, $TiCl_3$ and $NaClO_3$ or $NaClO_2$ were used. Two solutions were prepared: (a) one contained 0.01 M Ti^{3+} acidified with sulfuric acid and (b) the other contained 0.1 M $NaClO_3$ or 0.1 M $NaClO_2$.

Results and Discussion

Reaction of $NaClO_3$ with Ti^{3+}

It has been reported that the ClO_2 radical is generated during the reaction of Fe^{2+} and $NaClO_3$ according to the following equations:[12]

$$ClO_3^- + H^+ \rightarrow HOClO_2 \quad (2)$$

$$HOClO_2 + Fe^{2+} \rightarrow Fe^{3+} + ClO_2 + OH^- \quad (3)$$

We examined the above reaction system by means of the rapid-mixing flow technique coupled with ESR, but no ESR signal could be observed within the reaction time of 5—100 ms. This result suggests that reaction (3) is slow, because of the weak reducing power of Fe^{2+} (the potential of the Fe^{3+}/Fe^{2+} couple, is 0.77 V).[13] Thus, instead of Fe^{2+} we used Ti^{3+}, a much stronger reducing agent than Fe^{2+} (the potential of the Ti^{4+}/Ti^{3+} couple is 0.1 V).[14]

When solutions of 0.01 M Ti^{3+} at pH 1.5 and 0.1 M $NaClO_3$ at pH 7.0 were mixed in the cavity of the ESR spectrometer, we observed an ESR spectrum consisting of a quartet with a line intensity ratio of 1 : 1 : 1 : 1 and a hyperfine splitting of 18.5 G centered at $g=2.0106$ (Fig. 1). Four lines with equal intensity could arise from hyperfine interaction with ^{35}Cl and ^{37}Cl nuclei, which have $I=3/2$ and very similar magnetic moments (0.82091 and 0.68330 Mc, respectively). Since the ESR parameters of this spectrum are in accord with that of the ClO_2 radical obtained by adding potassium chlorite to sulfuric acid solutions[4] or by γ-irradiation of an H_2SO_4 matrix of $KClO_3$,[5] this spectrum can be assigned to the ClO_2 radical.

The formation of the ClO_2 radical in γ-radiolysis of $NaClO_3$ or $KClO_3$ has been suggested to follow the reaction scheme;

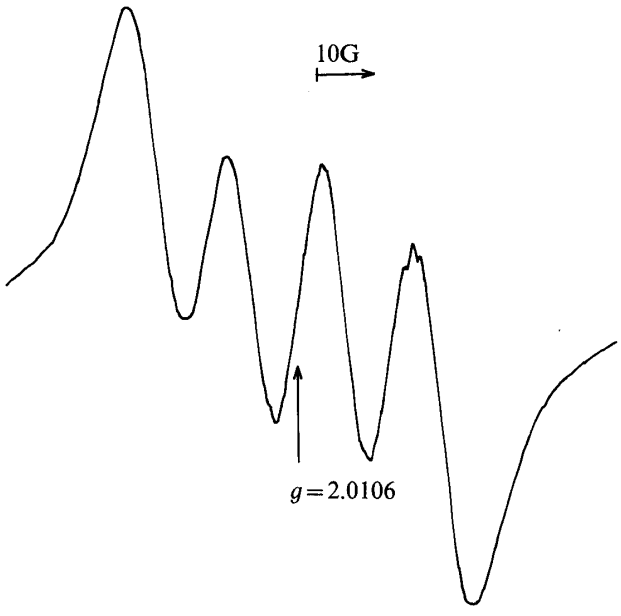

Fig. 1. ESR Spectrum of ClO_2 in Aqueous Solution at Room Temperature

Reaction conditions: $TiCl_3$, 0.01 M; $NaClO_3$, 0.1 M.
Instrument settings: microwave power, 10 mW; modulation amplitude, 0.5 G; time constant, 0.3 s; scan time, 8 min.

$$ClO_3^- \xrightarrow{\gamma\text{-rays}} ClO_3 + e^- \quad (4)$$

$$ClO_3 + ClO_3^- \rightarrow ClO_2 + ClO_4^- \quad (5)$$

However, since in the reaction system of Ti^{3+}–$NaClO_3$, Ti^{3+} is the reducing agent, the above oxidizing mechanism is not applicable to our systems. Thus, we consider that the reaction mechanism of Ti^{3+} and $NaClO_3$ may be the same as in the Fe^{2+}–$NaClO_3$ system (Eqs. 2 and 3) predicted by Chen[12] and follows the next equations,

$$ClO_3^- + H^+ \rightarrow HClO_3 \quad (6)$$

$$O{=}\overset{O}{\overset{\|}{Cl}}{-}OH + Ti^{3+} \rightarrow O{=}\overset{O}{\overset{\|}{Cl}} + OH^- + Ti^{4+} \quad (7)$$

The ClO_2 radical formed in this reaction system is not stable, since its ESR spectrum had almost disappeared at about 100 ms after the start of the reaction. This rapid decay of the ClO_2 radical may be caused by its interaction with Ti^{3+} or Ti^{4+} present in the reaction solution.

Reaction of $NaClO_2$ with Ti^{3+}

Since we observed the formation of the ClO_2 radical in the reaction of Ti^{3+} and $NaClO_3$, we expected that the ClO radical might be formed during the reduction of $NaClO_2$ by Ti^{3+}, and we examined this system by the rapid-mixing flow method.

When a solution of Ti^{3+} (0.01 M) was mixed with a solution of $NaClO_2$ (0.1 M), both solutions being acidified by sulfuric acid at pH 1.5, the same ESR spectrum as shown in Fig. 1 was observed. Contrary to our expectation, the ClO_2 radical was generated in the above systems.

It is well known that in an acidic solution of $NaClO_2$, the ClO_2 radical is formed by the following reactions,[15]

$$NaClO_2 + H^+ \rightarrow HClO_2 + Na^+ \quad (8)$$

$$5HClO_2 \rightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O \quad (9)$$

Therefore, we compared the rate of formation of ClO_2 in the Ti^{3+}–$NaClO_2$ system with that in the H_2SO_4–$NaClO_2$ system. Figure 2 shows the rate of formation of ClO_2 in both systems. It can be seen from Fig. 2(a) and 2(b) that there is a difference in the rate of the formation of

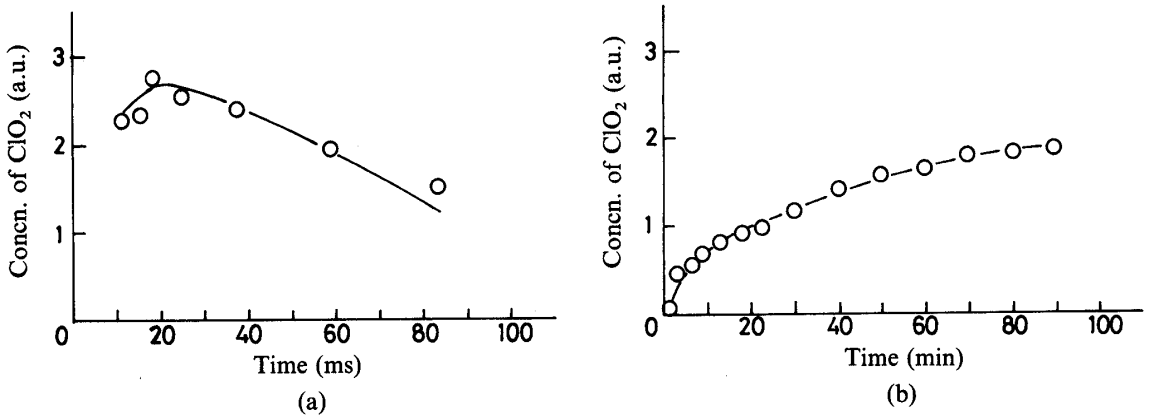

Fig. 2. Concentration of ClO_2 as a Function of Time

(a) Ti^{3+}–$NaClO_2$ system.
Reaction conditions: $TiCl_3$, 0.01 M; $NaClO_2$, 0.1 M.

(b) H_2SO_4–$NaClO_2$ system.
Reaction conditions: 0.1 M $NaClO_2$ solution acidified with sulfuric acid to pH 1.5.

the ClO_2 in these systems. Thus, the formation of the ClO_2 radical from the Ti^{3+}–$NaClO_2$ system is not caused by reactions (8) and (9), but is due to the direct reaction of Ti^{3+} with $NaClO_2$ according to the next equations,

$$ClO_2^- + H^+ \rightarrow HClO_2 \quad (10)$$

$$O=Cl-OH + Ti^{3+} \rightarrow ClO + OH^- + Ti^{4+} \quad (11)$$

$$ClO + HClO_2 \rightarrow HClO + ClO_2 \quad (12)$$

The ClO radical formed by reaction (11) should not be detected by the ESR-rapid mixing flow technique, because of its very short lifetime.[16] This radical could not be detected even by the spin trapping method.[17]

The kinetic behavior of the ClO_2 radical is different in the two systems, as shown in Fig. 2. The disappearance of the ClO_2 radical in Ti^{3+}–$NaClO_2$ is faster than in the H_2SO_4–$NaClO_2$ system, where the concentration of the ClO_2 radical gradually increases with time (Fig. 2(b)). The ClO_2 radical in the latter system could be observed even after 2 d of standing at room temperature in the dark. These results suggest that the reaction rate between H_2SO_4 and $NaClO_2$ is small.

Although the ClO_2 radical is an odd-electron molecule, it has no marked tendency to dimerize, perhaps because the electron is more effectively localized than in other odd-electron molecules such as NO_2.[18] Thus, the rapid disappearance of ClO_2 in the Ti^{3+}–$NaClO_2$ system is not attributed to dimerization (Eq. 13).

$$ClO_2 + ClO_2 \rightarrow Cl_2O_4 \quad (13)$$

Since Ti^{3+} or Ti^{4+} ion is present in the Ti^{3+}–$NaClO_2$ system, the ClO_2 radical formed may be rapidly removed by reaction with these ions.

References and Notes

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