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Chem. Pharm. Bull.
32(4)1587—1589(1984)

Electron Spin Resonance Studies on the Reactive Character of Chlorine Dioxide (ClO_2) Radical in Aqueous Solution

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(Received August 23, 1983)

The reactivities of the ClO_2 radical towards some organic substrates were investigated in aqueous solution by use of a rapid-mixing flow technique coupled with electron spin resonance spectroscopy. The ClO_2 radical could oxidize some aromatic amines to the corresponding cation radicals, whereas it could neither abstract hydrogen from saturated compounds such as methanol and ethanol nor add to unsaturated compounds having a double or triple bond.

Keywords——chlorine dioxide; ClO_2 radical; rapid-mixing flow technique; ESR; aromatic amine; cation radical; Wurster's salt

By the use of a rapid-mixing flow technique coupled with electron spin resonance (ESR) spectroscopy, we have recently found that the chlorine dioxide (ClO_2) radical can be generated either by redox reaction systems such as Ti^{3+}–$NaClO_3$ or Ti^{3+}–$NaClO_2$, or by the acidification of $NaClO_2$ in aqueous solution.[2] There are several reports concerning the reactive character of this radical.[3] However, there is only one report describing the detection of the intermediates during the reaction of the ClO_2 radical with organic substrates by ESR spectroscopy; in that case, the cation radical from triethylenediamine was observed.[3d] Therefore, we examined its reactivities towards many kinds of organic substrates by use of ESR spectroscopy, in order to determine the nature of the ClO_2 radical in aqueous solution. In this paper, we report the results.

Experimental

Materials and Methods——The 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 life-time of 5—100 ms.[4-8] The hyperfine coupling constants and g-factors were calibrated by comparison with an aqueous solution of Fremy's salt ($g=2.0055$, $a^N=13.0$ G)[9] kept in a capillary tube attached to the sample. For the generation of the ClO_2 radical, commercial samples of $NaClO_2$ and sulfuric acid were used. Two solutions were prepared to investigate the reactions of the ClO_2 radical with organic substrates: (a) contained 0.1 M $NaClO_2$ acidified with sulfuric acid (pH 1.5)[10] and (b) 0.1—0.3 M organic substrates in acidic aqueous solution (pH 1.5).

All organic substrates used were of reagent grade and were used without further purification.

Results and Discussion

When the ClO_2 solution and the aqueous solutions containing saturated compounds such as methanol and ehtanol or unsaturated compounds having $C=C$, $C=S$, $C=N$ or $C\equiv C$ bonds were mixed in the cavity of the ESR spectrometer, only the signal due to the ClO_2 radical (1 : 1 : 1 : 1 quartet line, $a^{Cl}=18.5$ G and $g=2.0106$)[2] was observed and no new signal was detected. These results suggest that the ClO_2 radical can neither abstract the hydrogen

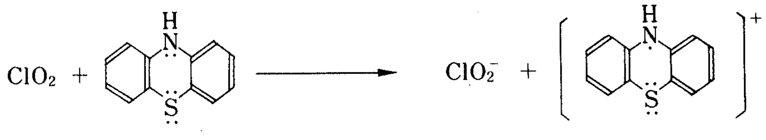


Chart 1

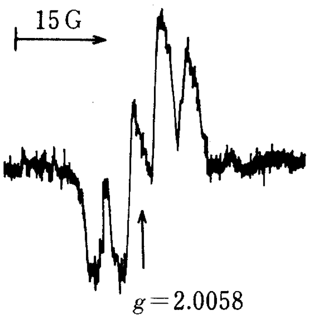
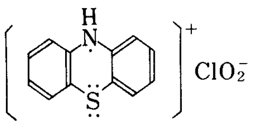


Fig. 1. ESR Spectrum Observed during the Reaction of the ClO_2 Radical with Phenothiazine in Aqueous Solution at Room Temperature



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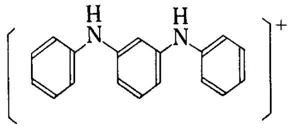

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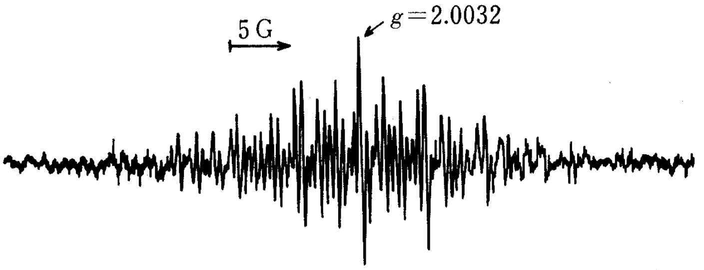

Fig. 2. ESR Spectrum Observed during the Reaction of the ClO_2 Radical with *p*-Phenylenediamine in Aqueous Solution

from saturated compounds such as methanol and ethanol nor add to $C=C$, $C=S$, $C=N$ or $C\equiv C$ bonds.

When an aqueous acetone solution containing phenothiazine was mixed with the ClO_2 solution, the signal due to the ClO_2 radical disappeared, with the appearance of another signal as shown in Fig. 1. This spectrum gave $a^{N}=a^{H}_{NH}=7.3\,G$ and $g=2.0058$. These values are essentially identical with those reported for the phenothiazine cation radical.[11,12] This cation radical is formed by one-electron abstraction from phenothiazine, as shown in Chart 1. Since this cation radical is stable for more than 30 min at room temperature, it is thought that it does not exist in the free state, but in the ion pair known as Wurster' salt (**1**) in aqueous solution.

When aqueous solutions of ClO_2 and *p*-phenylenediamine (*p*-PD) were mixed, the ESR spectrum of the ClO_2 radical disappeared and a new ESR spectrum was observed as shown in Fig. 2. This spectrum gave $a^{N}(2)=5.08\,G$, $a^{H}_{NH}(4)=5.82\,G$, $a^{H}_{ring}(4)=2.15\,G$ and $g=2.0032$. These values are almost identical with those accepted for the *p*-PD cation radical.[13]

A similar ESR spectrum was obtained from the reaction of the ClO_2 radical with diphenyl *p*-phenylenediamine. The 1:6:15:20:15:6:1 septet pattern ($a^{N}(2)=a^{H}_{NH}(2)=5.98\,G$ and $g=2.0033$) can be explained by the coincidental equality of a^{N} and a^{H}, and so this radical species is assigned as the diphenyl *p*-PD cation radical (**2**). In this case, hyperfine splitting from ring protons was not observed, because of dipolar broadening caused by dissolved oxygen.

In the reactions of the ClO_2 radical with *o*-, *m*- and *p*-aminophenol, diphenylamine and *p*-toluidine, only a broad singlet line ($\Delta H_{msl} = ca.\ 50\,G$) was observed in place of the signal due to the ClO_2 radical. This signal broadening may be explained as follows: the radicals generated from the reaction with ClO_2 react rapidly with the dissolved oxygen, and the hyperfine splittings disappear because of dipolar broadening.

In the reaction of metanilic acid with the ClO_2 radical, the ESR spectrum due to ClO_2 disappeared, but no new signal was observed. This result indicates that the life-time of the radical formed may be too short for detection. When a solution of *p*-aminobenzoic acid or amidole was mixed with a solution of ClO_2, only the ESR spectrum of the ClO_2 radical was observed. Therefore, it is considered that these compounds do not react with the ClO_2 radical.

From the results described above, it is concluded that the ClO_2 radical has oxidizing ability towards several aromatic amines, but its oxidizing ability is not sufficiently strong to abstract hydrogen from saturated compounds such as methanol and ethanol or to add to unsaturated compounds with $C=C$, $C=S$, $C=N$ or $C\equiv C$ bonds.

References and Notes

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10) Solution (a) is useful, because in this solution the decay of the ClO_2 radical is very slow and no metal ions are present.[2]

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