Reaction of Sodium Perborate with a Chlorinated Cyclic Hindered Amine (TMP–Cl): I. Quantitative Evaluation of Active Oxygen Species in Fabric Bleaching

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ABSTRACT: The reaction of N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP–Cl) with sodium perborate (PB) was investigated with special reference to the generation of singlet oxygen and the possible application to a new oxidative bleaching process. Generation of the singlet oxygen ($^1O_2$), the hydroxyl radical (HO•) and superoxide anion radical ($O_2{\bullet}^-$) in the PB/TMP–Cl mixed solution was confirmed by the trapping reagent method. From the results of another experiment, in which the bleaching abilities of each active oxygen species were confirmed, the main active oxygen species contributing to the bleaching of purpurogallin, the skeleton of black tea pigment, in the PB/TMP–Cl system was concluded to be $^1O_2$.
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KEY WORDS: Activator, active oxygen species, oxidative bleaching agent, steady-state concentration, trapping reagent.

Oxidative bleaching agents, such as sodium perborate (PB) and sodium percarbonate, have been widely used as bleaching components of fabric bleach compositions and heavy-duty detergents for both home and institutional use. However, these hydrogen peroxide adducts provide insufficient bleaching performance, especially in the low-temperature range. Many bleaching activators (1–5) have been proposed to improve this disadvantage. Typical activators are the acetyl compound series, such as tetraacetylethylenediamine (TAED), tetraacetylglycol uril (TAGU) and pentaacetylglucose (PAG), and alkanoyloxybenzenesulfonate (AOBS). In addition to these, many other activating methods, such as the radical decomposition of hydrogen peroxide by heavy metal ions (6,7) and the generation of singlet oxygen by light sensitizing dyes (8), have been reported.

Among these methods, the application of chemically generated singlet oxygen has hardly been investigated yet. As a conventional method for chemical generation of singlet oxygen, the HOO^-/ClO^- system (9) is well known. However, the HOO^-/ClO^- system is considered unacceptable for practical bleaching for home use because sufficient bleaching efficiency cannot be attained by the combination of a conventional source of ClO^-, such as dichloroisocyanurate, with PB. We have reported that N-choro hindered amine compounds, such as N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP–Cl) and N-chloro-*t*-butyl amine, showed high activation efficiency and differed from the usual chlorine-containing compounds (10).

In this report, generation of three active oxygen species, i.e., singlet oxygen ($^1O_2$), hydroxy radicals (HO·) and superoxide anion radicals ($O_2^{\cdot-}$) in the PB/TMP–Cl system was determined by using trapping reagent methods in the first stage. In the second stage, the bleaching ability of each active oxygen species toward purpurogallin (the skeleton of black tea pigment) was investigated by specific generation methods. In the final stage, the principal active oxygen species contributing to the bleaching in the PB/TMP–Cl system is discussed.

EXPERIMENTAL PROCEDURES

Materials. An aqueous solution of reagent-grade hydrogen peroxide (35 wt%) was purchased from Kanto Chemical Co., Ltd. (Tokyo, Japan). PB with an available oxygen content of 15.3% was a commercial product obtained from Mitsubishi Gas Chemical Co., Ltd. (Tokyo, Japan).

TMP–Cl was synthesized according to the method of Rigo *et al.* (11). An aqueous solution of NaClO (0.05M) was added to an aqueous solution (0.05M) of 4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP–H) at about 0°C. The solution was stirred for one hour, followed by extraction with *n*-hexane. Evaporation afforded colorless needles of TMP–Cl (m.p. 86–87°C, λ_{max} = 240–250 nm).

A trapping reagent for hydroxy radicals, *p*-nitrosodimethylaniline (PNDA), was obtained as GR-grade from Tokyo Kasei Industry Co., Ltd. (Tokyo, Japan). Nitrobluetetrazolium (NBT) for trapping of superoxide anion radicals was obtained from Kanto Chemical Co., Ltd. 9,10-Anthracenedipropionic acid (ADPA) for trapping of singlet oxygen was synthesized from anthracene, paraformaldehyde and diethyl malonate according to the method of Miller *et al.* (12). *o*-Tolidine was obtained from Junsei Chemical Co., Ltd. (Tokyo, Japan).

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As reagents for generating active oxygen species, iron (II) sulfate heptahydrate, 22 wt% NaClO aq., potassium superoxide and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) were obtained from Kanto Chemical Co., Ltd., Junsei Chemical Co., Ltd., Soekawa Chemical Co., Ltd. and Aldrich Chemical Co. (Milwaukee, WI), respectively. Purpurogallin, the skeleton of black tea pigment, was obtained from Tokyo Kasei Industry Co., Ltd.

Determination of active oxygen species generated in the bleaching bath. The hydroxy radical (HO·) was detected by the decrease in the absorbance at λ_{max} = 440 nm of PNDA with formation of the PNDA–HO· adduct according to the method reported by Bors *et al.* (13).

The superoxide anion radical ($O_2\cdot^-$) was detected by the increase in the absorbance of blue formazane (λ_{max} = 560 nm), which originated from the NBT–$O_2\cdot^-$ adduct (14).

Singlet oxygen was detected by the decrease in the absorbance at λ_{max} = 400 nm of ADPA due to the formation of ADPA-endoperoxide, according to the method reported by Lindig *et al.* (15).

The detection of perchloro anion (ClO^-) was undertaken with the color development of *o*-tolidine. All these measurements were carried out with a Hitachi (Tokyo, Japan) spectrophotometer model 557. The stable radical species formed in H_2O_2/TMP–Cl system was determined by observing the electron spin resonance (ESR) signal which was composed of three peaks ($g = 2.0063$, $a_N = 17G$), for solutions sealed in a glass capillary with a JEOL JES-FE1X ESR spectrometer (JEOL, Tokyo, Japan).

Generation of active oxygen species and bleaching of purpurogallin. Three active oxygen species were steadily generated, according to the methods shown in Table 1. Their bleaching capacities were evaluated by the degree of discoloration of purpurogallin. Each aqueous generation source solution was introduced to a buffered solution that contained a given amount of purpurogallin at a constant rate through a syringe-type injection apparatus (Model 341; Orion Research Inc., Cambridge, MA), while observing the decrease in the absorbance of purpurogallin (λ_{max} = 440 nm). Although purpurogallin shows a blue color (λ_{max} = 610 nm) immediately after dissolution into alkaline solution, the color changed to yellow (λ_{max} = 440 nm) after stirring for one hour under blowing air. The absorbance of this yellow solution was maintained in the absence of air exposure before the bleaching test.

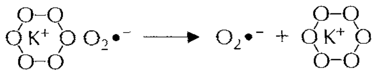
Measurement of oxidation–reduction potential of pigments. After the pigment was completely dissolved in 0.5 M–Na_2CO_3/$NaHCO_3$ buffer (pH = 10.5), N_2 gas was introduced for more than 15 min. The measurement was undertaken with glassy carbon (4 mm ϕ) as the working electrode, platinum wire (0.5 mm ϕ) as the counter electrode, and saturated calomel as the reference electrode, with an applied pulse voltage of 0.05 V, a purse interval of 0.1 s and a sweep rate of 20 mV/s through a differential pulse polarographic apparatus (Voltammetric Analyzer, Model P-1100; Yanagimoto Co., Ltd., Kyoto, Japan).

RESULTS AND DISCUSSION

Active oxygen species generated in H_2O_2 and H_2O_2/TMP–Cl mixed system. Figure 1 shows the pH profile for the decomposition rate of PNDA due to trapping of HO·. The decomposition rate increased with an increase in pH in the case of H_2O_2 alone. For the H_2O_2/TMP–Cl mixed system, the decomposition rate increased steeply in the pH range below 8 but increased slightly at pH = 9.5–10.5. The H_2O_2/TMP–Cl mixed system is assumed to produce only slight amounts of HO· in alkaline medium, where the actual bleaching is undertaken. In the range below pH = 7, a yellow color developed on the addition of *o*-tolidine, which indicates the existence of ClO^-. In the acidic range, HOCl can exist at a certain concentration, because the reactivity of HOCl, originating from TMP–Cl toward H_2O_2 is insufficient. The relatively high decomposition rate of PNDA in the acidic range is assumed to be induced by the abundant supply of HO· due to a cleavage reaction, such HOCl → HO· + Cl·.

Figure 2 shows the pH profile of the decomposition rate of ADPA due to trapping of $^1O_2$. The H_2O_2 system showed a small decomposition rate. On the other hand, the

TABLE 1
Experimental Condition for Generation of Active Oxygen Species

		Solution for generation	
Species	Generating method	In vessel	In syringe
HO·	$H_2O_2 + Fe^{2+} \rightarrow HO\cdot + HO^- + Fe^{3+}$	0.01 M–H_2O_2 0.25M–H_2SO_4	0.1M–$FeSO_4$
$^1O_2$	$H_2O_2 + NaClO \rightarrow {}^1O_2 + H_2O + NaCl$	0.01M–H_2O_2 0.25M–Na_2CO_3/$NaHCO_3$ Buffer (pH = 10.5)	0.1M–NaClO
$O_2\cdot^-$		0.25M–Na_2CO_3/$NaHCO_3$ Buffer (pH = 10.5)	0.1M–KO_2/18 crown 6 in DMSO

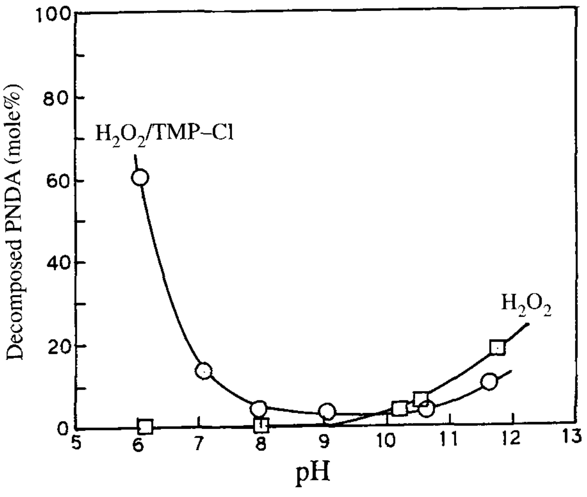


FIG. 1. The pH profile of *p*-nitrosodimethylaniline (PNDA) decomposition in H_2O_2 solution and H_2O_2/N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP–Cl) mixed solution: $[H_2O_2]$ = 0.02 M, $[H_2O_2]$/[TMP–Cl] = 0.02 M/0.02 M, 25°C, 60 min after preparation, 0.5 M phosphate buffer.

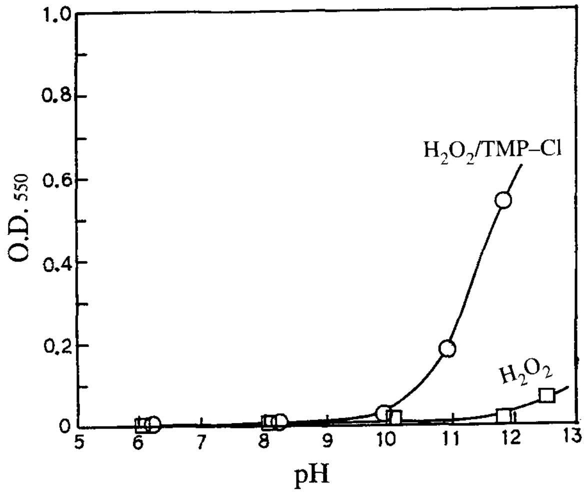
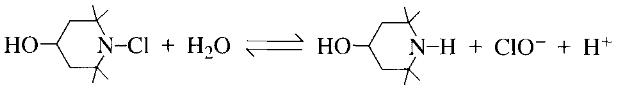


FIG. 2. The pH profile of 9,10-anthracenedipropionic acid (ADPA) decomposition in H_2O_2 solution and H_2O_2/TMP–Cl mixed solution: $[H_2O_2]$ = 0.02 M, $[H_2O_2]$/[TMP–Cl] = 0.02 M/0.02 M, 25°C, 60 min after preparation, 0.5 M phosphate buffer. See Figure 1 for other abbreviation.

H_2O_2/TMP–Cl mixed system clearly showed a larger rate than the H_2O_2 system. Because ADPA is decomposed even by ClO^-, an increase in the decomposition in the pH range below 9 may be ascribed to the presence of ClO^-.

The absence of ClO^- in the alkaline range above pH = 9 was confirmed by the *o*-tolidine method. Therefore, the decomposition of ADPA at a pH higher than pH = 9 is assumed to be ascribed to the $^1O_2$ produced by the following routes:



[1]

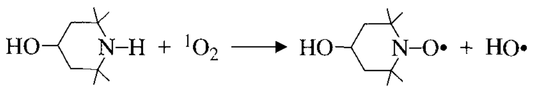
$$H_2O_2 \rightleftarrows HOO^- + H^+ \qquad [2]$$

$$HOO^- + ClO^- \rightarrow {}^1O_2 + HO^- + Cl^- \qquad [3]$$

Figure 3 shows the pH profile for the increase in absorbance of blue formazane, formed by the trapping of $O_2\cdot^-$ by NBT. In the alkaline range, the H_2O_2/TMP–Cl mixed system produced a larger quantity of blue formazane than the H_2O_2 system; consequently, the concentration of $O_2\cdot^-$ in the mixed sytem was higher than in the H_2O_2 system. The generation of $O_2\cdot^-$ in the H_2O_2 system seems to be induced by the following reaction (16):

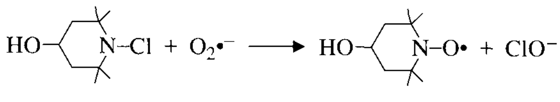
$$HO\cdot + H_2O_2 \rightarrow O_2\cdot^- + H^+ + H_2O \qquad [4]$$

Moan and Wold (17) reported that 2,2,6,6-tetramethyl-4-oxopiperidine traps $^1O_2$ and is converted into a nitroxide radical. TMP–H, formed by the hydrolysis of TMP–Cl, may be converted similarly into a nitroxide radical by the following reaction:



[5]

Figure 4 shows the observation of the ESR signal for the H_2O_2/TMP–Cl solution on standing for a long period. In the alkaline range, an obvious increase in the ESR signal intensity was observed, with can be attributed to the formation of 4-hydroxy-2,2,6,6-tetramethylipiperidine-N-oxyl (TMP–O·). This was considered to be due to the following reaction in addition to Equation 5 because the generation of $O_2\cdot^-$ is enhanced, and its lifetime is long (18) in the alkaline range:



[6]

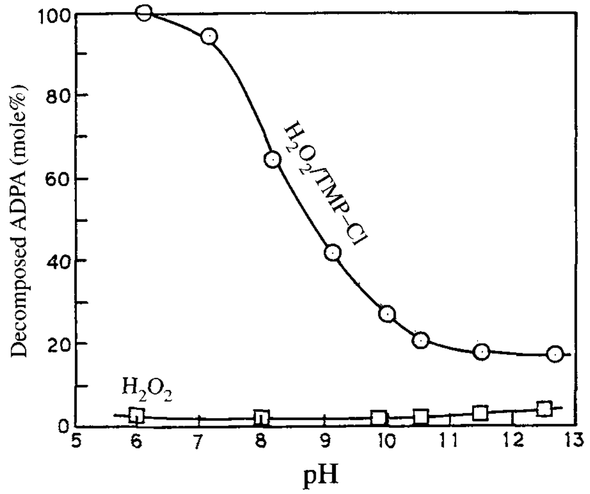


FIG. 3. The pH profile of the production of blue formazane in H_2O_2 solution and H_2O_2/TMP–Cl mixed solution: $[H_2O_2]$ = 0.02 M, $[H_2O_2]$/TMP–Cl] = 0.02 M/0.02 M, 25°C, 60 min after preparation, 0.5 M phosphate buffer. See Figure 1 for other abbreviation; O.D., optical density.

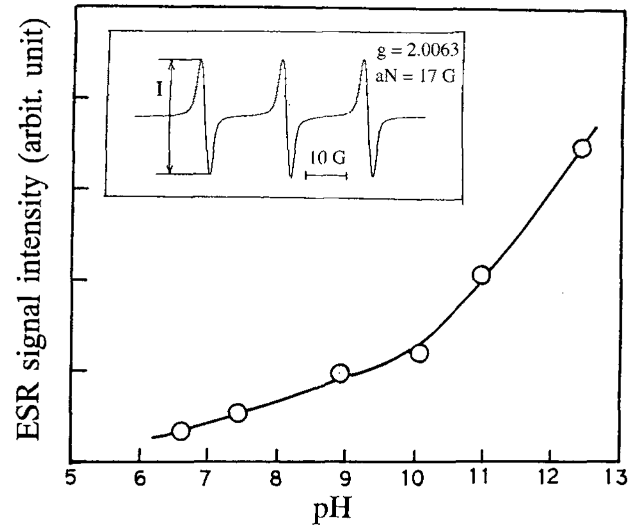


FIG. 4. The pH profile of electron spin resonance (ESR) signal intensity of H_2O_2/TMP–Cl mixed solution: $[H_2O_2]/[\text{TMP–Cl}] = 0.02$ M/0.02 M, 25°C, 8 h after preparation, 0.5M phosphate buffer. Inserted: ex. of ESR chart (pH =10). See Figure 1 for other abbreviation; g, g-value; aN, hypofine coupling constant.

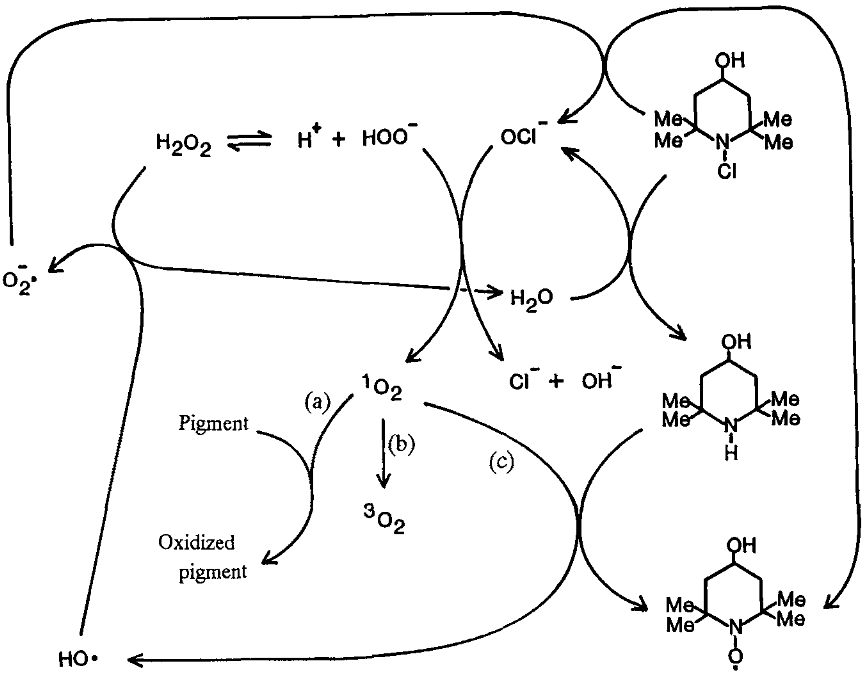
In summing up the experimental results by the trapping reagent method, the active oxygen species generation mechanism in the H_2O_2/TMP–Cl system is proposed as shown in Scheme 1. In other words, $^1O_2$ is generated by Equations 1–3 and disappears through the following three paths: (i) bleaching of the pigment, (ii) self-deactivation into $^3O_2$ and (iii) production of TMP–O· and simultaneous conversion into HO· according to Equation 5. Because HO· causes the generation of $O_2\cdot^-$, as shown in Equation 4, and $O_2\cdot^-$ also regenerates ClO^- through the route shown in Equation 6, $^1O_2$, HO· and $O_2\cdot^-$ are steadily generated, while the consumption of H_2O_2 and TMP–Cl proceeds.

Bleaching ability of each active oxygen species. To elucidate which species among the three oxygen species, i.e., $^1O_2$, HO· and $O_2\cdot^-$, contributes principally to the bleaching of pigment, the bleaching rate of purpurogallin was examined with each generated species according to the method in Table 1. Figure 5 shows the molecular structures of purpurogallin and theaflavine. Theaflavin is reported to be a main component of black tea pigment (19). Figure 6 shows the polarograms of aqueous solutions of black tea extract and purpurogallin. Although the chemical structures of both pigments differed, similar oxidation curves were obtained. From the similar oxidizing behavior, purpurogallin seems an appropriate model of black tea pigment. Figure 7 shows the bleaching behavior of purpurogallin by constant generation of $^1O_2$, HO· and $O_2\cdot^-$. The highest rate was obtained by the addition of HO·, which was seven times that of $^1O_2$. In contrast, $O_2\cdot^-$ did not show recognizable bleaching ability.

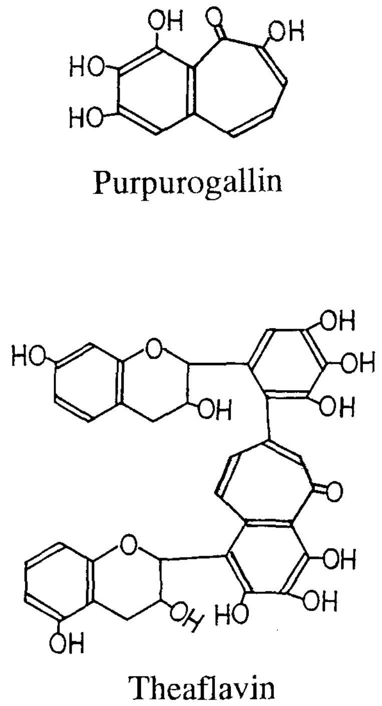
Steady-state concentration of active oxygen species in PB/TMP–Cl system. To determine the degree of the contributions of HO· and $^1O_2$ toward bleaching, their steady-state concentrations in a practical PB/TMP–Cl mixed system were estimated by the decomposition rates of each trapping reagent. The rates of decomposition of the trapping reagents, V_t, can be expressed by the following equations:

$$V_{t\,(\mathrm{PNDA})} = k_{t\,(\mathrm{PNDA})}[\mathrm{PNDA}][\mathrm{HO}\cdot] \qquad [7]$$

$$V_{t\,(\mathrm{ADPA})} = k_{t\,(\mathrm{ADPA})}[\mathrm{ADPA}][^1\mathrm{O}_2] \qquad [8]$$



SCHEME 1


Purpurogallin

Theaflavin

FIG. 5. Molecular structures of purpurogallin and theaflavin.

where $V_{t\,(\mathrm{PNDA})}$, $V_{t\,(\mathrm{ADPA})}$ are the decomposition rates of PNDA, ADPA, respectively, $k_{t\,(\mathrm{PNDA})}$, $k_{t\,(\mathrm{ADPA})}$ are second-order rate constants of the respective species and [PNDA], [ADPA], [HO·] and [$^1O_2$] are the concentrations of each component. Assuming that HO· and $^1O_2$ are continuously generated from the reaction of PB and TMP–Cl and their concentrations are steady-state, Equations 7 and 8 may be simplified to:

$$V_{t\,(\mathrm{PNDA})} = k_{t\,(\mathrm{PNDA})}[\mathrm{PNDA}][\mathrm{HO}\bullet] = k'_{t\,(\mathrm{PNDA})}[\mathrm{PNDA}] \qquad [9]$$

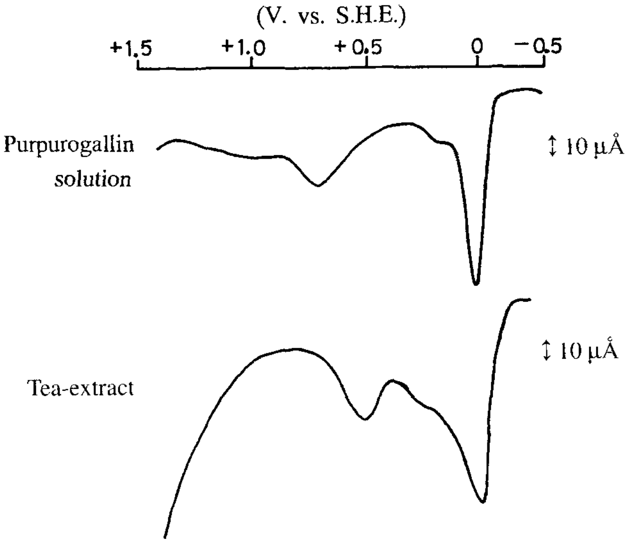


FIG. 6. Polarograms of purpurogallin solution and tea-extract solution. V., volt; S.H.E., saturated hydrogen electrode.

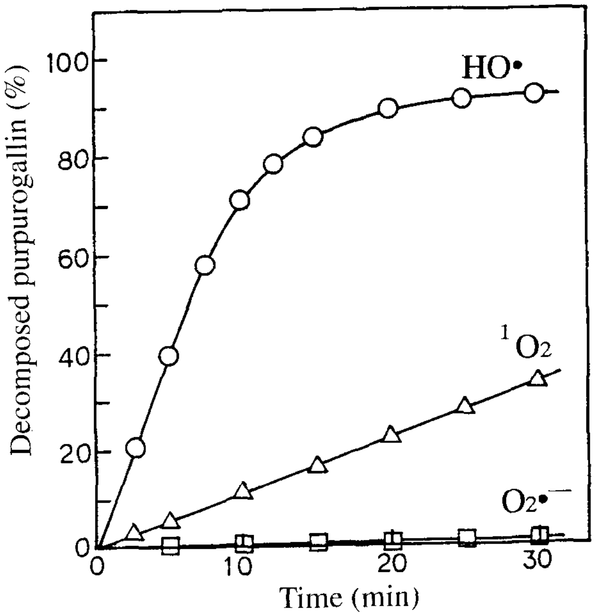


FIG. 7. Bleaching rates of purpurogallin by each active oxygen species. Feed rate of each generation source = 6.7 × 10^{-7} M • s^{-1}, 25°C [purpurogallin] = 1 × 10^{-4} M.

$$V_{t\,(\mathrm{ADPA})} = k_{t\,(\mathrm{ADPA})}[\mathrm{ADPA}][^1\mathrm{O}_2] = k'_{t\,(\mathrm{ADPA})}[\mathrm{ADPA}] \qquad [10]$$

Because Equations 9 and 10 are pseudo-first-order equations, k' can be obtained from the slope of the log [trapping reagent] vs. time plot as shown in Figure 8. Because $k_{t\,(\mathrm{PNDA})}$ and $k_{t\,(\mathrm{ADPA})}$ are known to be 1.25 × 10^{10} M^{-1} · s^{-1} and 1.74 × 10^7 M^{-1} · s^{-1} (20, 21), [HO·] and [$^1O_2$] could be calculated from Equation 9 or 10. The results are listed in Table 2. [HO·] in the PB/TMP–Cl mixed solution decreased to *ca.* half, and [$^1O_2$] increased by approximately thirteen times that of the PB system.

Figure 9 shows the bleaching rates of purpurogallin in the same systems as those for Figure 8. If one considers that both species in the steady state with the concentrations, as shown in Table 2, contribute to the bleaching, the rates of decomposition of purpurogallin, $V_{p\,(\mathrm{PB})}$ and $V_{p\,(\mathrm{PB/TMP})}$, are obtained similarly to the reaction of the tapping reagent.

$$V_{p\,(\mathrm{PB})} = \{k_{p\,(\mathrm{HO}\cdot)}[\mathrm{HO}\cdot]_{(\mathrm{PB})} + k_{p\,(^1\mathrm{O}_2)}[^1\mathrm{O}_2]_{(\mathrm{PB})}\}[\mathrm{purpuro.}]$$

$$= k''_{(\mathrm{PB})}[\mathrm{purpuro.}] \qquad [11]$$

$$V_{p\,(\mathrm{PB/TMP})} = \{k_{p(\mathrm{HO}\cdot)}[\mathrm{HO}\cdot]_{(\mathrm{PB/TMP})} + k_{p\,(^1\mathrm{O}_2)}[^1\mathrm{O}_2]_{(\mathrm{PB/TMP})}\}[\mathrm{purpuro.}]$$

$$= k''_{(\mathrm{PB/TMP})}[\mathrm{purpuro.}] \qquad [12]$$

where $k''_{(\mathrm{PB})}$ and $k''_{(\mathrm{PB/TMP})}$ are pseudo-first-order rate constants of the decomposition of purpurogallin in the PB and PB/TMP–Cl systems. From the plot of log [purpuro.] vs. time in Figure 9, $k''_{(\mathrm{PB})}$ was calculated to be 8.28 × $10^{-5}$$s^{-1}$, and $k''_{(\mathrm{PB/TMP})}$ was calculated to be 21.4 × $10^{-5}$$s^{-1}$. Introducing these k'' values and results from Table 2 into Equations 11 and

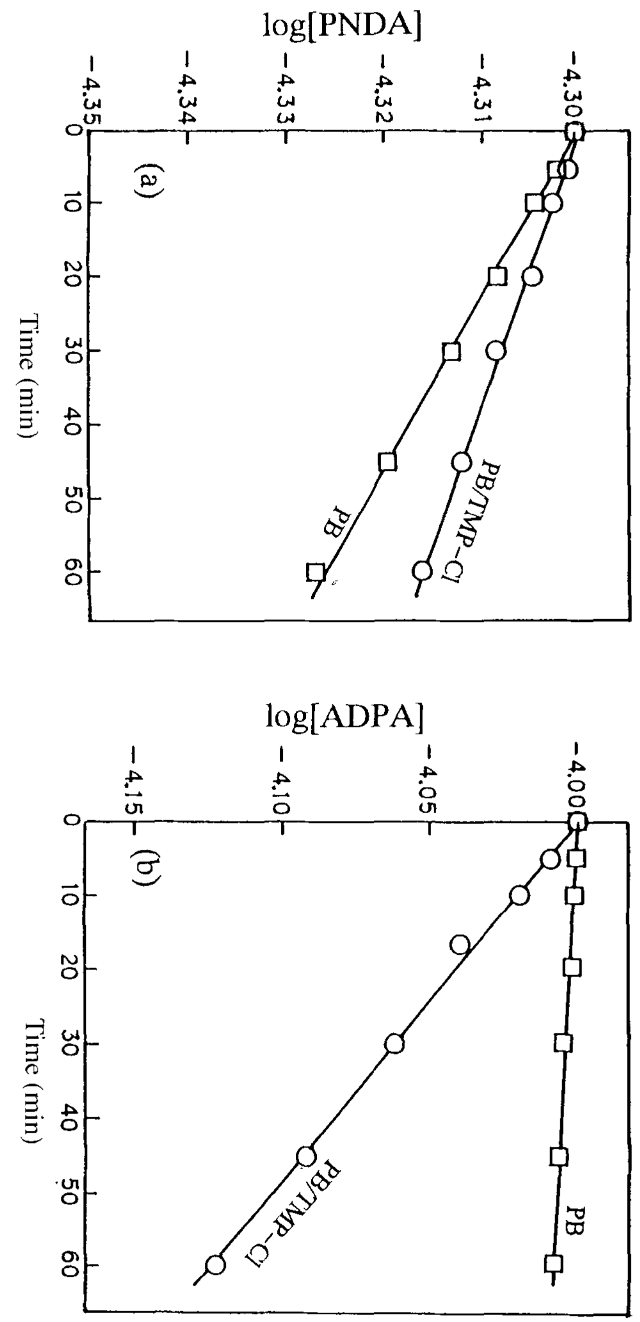


FIG. 8. The (a) log[PNDA] vs. time plot and (b) log[ADPA] vs. time plot for PB solution and PB/TMP-Cl mixed solution: [PB] = 0.02M, [PB]/[TMP-Cl] = 0.02M/0.02M, [PNDA] = 5 × 10^{-5} M, 25°C. 0.5 M phosphate buffer (pH = 10.5). See Figures 1 and 2 for abbreviations.

12, the following relationships were obtained:

$$1.36\times10^{-15}k_{p(\mathrm{HO\cdot})} + 3.45\times10^{-13}k_{p(^1\mathrm{O_2})} = 8.28\times10^{-5} \quad [13]$$

$$7.76\times10^{-16}k_{p(\mathrm{HO\cdot})} + 4.45\times10^{-12}k_{p(^1\mathrm{O_2})} = 2.14\times10^{-4} \quad [14]$$

From Equations 13 and 14, $k_{p(\mathrm{HO\cdot})}$ and $k_{p(^1\mathrm{O_2})}$ were obtained as $5.10\times10^{10}\mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$ and $3.92\times10^{7}\mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$, respectively. In other words, HO· has a higher bleaching rate for purpurogallin than $^1O_2$ by a factor of 1.3 × 10^3. Considering the difference between the steady-state concentrations of HO· and $^1O_2$ in the two systems, shown in Table 2, the contributions of the two active oxygen species are comparable for the bleaching of purpurogallin, where the primary contributing active species in the PB system is HO·, but it is $^1O_2$ in the PB/TMP-Cl mixed system. Koberstein *et al.* (22,23) reported that the primary contributing active species in the PB system is the HOO^- ion. If HOO^- ions are the primary species, the higher the pH, the better bleaching efficiency should be observed, because at the higher pH the HOO^- ions are more concentrated in the PB system, according to Equation 2. However, the maximum has been observed in the actual pH profile of bleaching efficiency as reported by Dannacher and Schlenker (24). Therefore, HOO^- ions cannot be regarded as the primary species contributing to the bleaching in the PB system. Although Dannacher and Schlenker (24) realized this inconsistency, they concluded in error that $O_2\cdot^-$ is the primary species in the H_2O_2 system from the result that the maximal pH of the bleaching efficiency agreed with that of the $O_2\cdot^-$

TABLE 2
The Steady-State Concentrations of Active Oxygen Species in Bleaching System[a]

	Concentration of active oxygen species	
Bleaching system	[HO·] (× 10^{-16} M)	[$^1O_2$] (× 10^{-13} M)
PB	13.6	3.45
PB/TMP-Cl	7.76	45.5

[a] PB, sodium perborate; PB/TMP-Cl, PB/N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine.

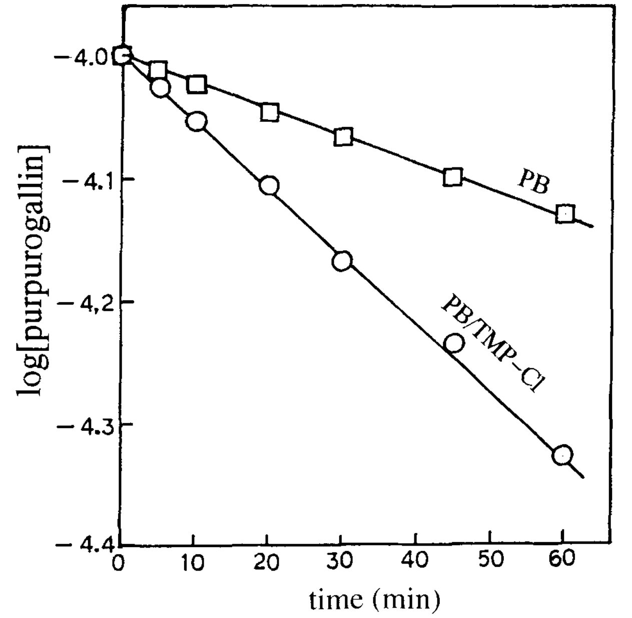


FIG. 9. The log[purpurogallin] vs. time plot for sodium perborate (PB) solution and PB/TMP-Cl mixed solution: [PB] = 0.02M, [PB]/[TMP-Cl] = 0.02M/0.02M, [purpurogallin] = 1 × 10^{-4} M, 25°C. 0.5 M phosphate buffer (pH = 10.5). See Figure 1 for other abbreviation.

concentration. Because we confirmed that $O_2\cdot^-$ has hardly any bleaching ability, HO· was concluded to be the primary species contributing to the bleaching efficiency in the PB system. On the other hand, the activation mechanism of TMP–Cl for the bleaching of pigment can be illustrated as in Scheme 1, which specifically includes the increase in steady-state concentration of $^1O_2$ in solution.

So, we can conclude that: (i) The order of the bleaching rate of each active oxygen was HO· > $^1O_2 \gg O_2\cdot^-$. $O_2\cdot^-$ did not bleach purpurogallin significantly. (ii) The major active oxygen species detected were HO· and $O_2\cdot^-$ in the H_2O_2 system, but $^1O_2$ and $O_2\cdot^-$ in the H_2O_2/TMP–Cl mixed system. (iii) The activation mechanism of TMP–Cl in the PB/TMP–Cl mixed system is mainly due to the specific increase in the steady-state concentration of $^1O_2$.

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REFERENCES

1. Reicht, J.S., S.A. McKnight and A.A. Elston, U.S. Patent 2,362,401 (1945).
2. Boldingh, J., L. Heslinga, E. Schmicil and R. Syrovataka, U.S. Patent 3,686,127 (1972).
3. Fine, L.W., V.S. Grayson and M. Grayson, *Soap & Cosm. Chem. Spec. 50*:42 (1974).
4. Marry, L.T., *J. Am. Oil Chem. Soc. 45*:493 (1968).
5. Grime, J.K., *Tenside 29*:23 (1992).
6. Konecny, J.O., and R.E. Meeker, U.S. Patent 3,156,654 (1964).
7. Das, B., and K.G. van Senden, U.S. Patent 3,398,096 (1968).
8. Saccob, N.Y., *Jpn. Tokkyo Kokai Koho 54*:135806 (1979).
9. Kashu, M., and A.V. Khan, *NY Acad. Sci. 171*:5 (1970).
10. Akabane, Y., T. Tamura and M. Fujiwara, U.S. Patent 4,820,437 (1989).
11. Rigo, A., E. Argese, R. Stevanto, E.F. Orsega and P. Viglino, *Inorg. Chim. Acta. 24*:L71 (1977).
12. Miller, M.W., R.W. Amidow and P.O. Tawney, *J. Am. Chem. Soc. 77*:2845 (1955).
13. Bors, W., C. Michel and M. Saran, *Eur. J. Biochem. 95*:621 (1979).
14. Beauchap, C., and I. Fridorich, *Anal. Chem. 44*:276 (1971).
15. Lindig, B.A., M.A.J. Rodgers and A.P. Schaap, *J. Am. Chem. Soc. 102*:5590 (1980).
16. Asada, K., *Seikagaku 48*:226 (1976).
17. Moan, J., and E. Wold, *Nature 279*:450 (1979).
18. Markland, S., *J. Biol. Chem. 251*:7504 (1976).
19. Takino, Y., A. Fretti, V. Flanagan, M. Gianturco and M. Vogel, *Tetrahed. Lett. 45*:4019 (1965).
20. Baxendale, J.H., and A.A. Khan, *Int. J. Radiat. Phys. Chem. 1*:11 (1969).
21. Nakamura, N., and S. Teoi, *Kasankashishitsu Zikken-ho,* edited by T. Kaneda, and N. Ueta, I-Shi-Yaku Schppan, 1983, pp. 119–131.
22. Koberstein, E., H.G. Bachmann, H. Gebauer, G. Kohler, E. Lakatos and G. Nonnenmacher, *Z. Anorg. Allgem. Chemie. 374*:125 (1970).
23. Koberstein, E., and H. Kurzke, *Tenside 24*:210 (1987).
24. Dannacher, J., and W. Schlenker, *Textilveredlung 25*:205 (1990).

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