

Epoxidation of cyclohexene with active oxygen species produced by reducing dioxygen in the presence of Br⁻ ion

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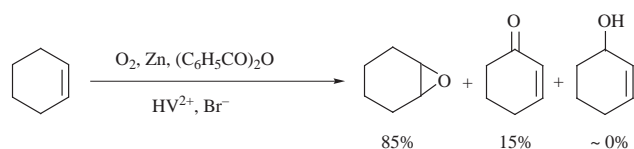
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Oxidation of cyclohexene to cyclohexene oxide, cyclohex-2-en-1-one, and cyclohex-2-en-1-ol proceeded by adding Br⁻ ions to an air-equilibrated acetonitrile suspension containing cyclohexene as a substrate, hexylviologen as an electron mediator, benzoic anhydride as an activating reagent, and insoluble zinc powder as a reductant. With increasing concentration of Br⁻ ions, the epoxidation selectivity increased up to 85% with about 60% Zn-utilizing efficiency. The oxidation mechanism was discussed in relation to the redox properties of the chemical species contained in this catalytic system. The active oxygen species for producing cyclohex-2-en-1-one and cyclohex-2-en-1-ol, and that for producing cyclohexene oxide may be hypobromous radical (BrO[•]) and hypobromous anion (BrO⁻), respectively.

Introduction

Epoxide compounds such as propylene oxide, which is a raw material for urethane rubber, were produced industrially by the oxidation of olefin with peroxide or the chlorohydrin method.¹ Recently, several new catalytic systems for the epoxidation of olefin have been reported, containing molecular dioxygen reductively activated by transition metal complexes which were reduced chemically with a reducing reagent such as BH₄⁻,² zinc powder,^{3,4} H₂/Pt,⁵ aldehyde,⁶ ascorbate,⁷ formate,⁸ or electrochemically on an electrode^{9,10} under mild conditions. A few other catalytic and non-catalytic systems have been reported for the epoxidation of olefin. The former contained the combination of a copper salt and aldehyde¹¹ or a rare earth salt and zinc powder,¹² and the latter contained a reductant such as aldehyde¹³ or a nascent oxygen generated by the electrolysis of water.¹⁴ When a transition metal complex was used as the catalyst, high selectivity towards the epoxide of a cyclic olefin such as cyclohexene had been reported, but when a rare earth salt was used as the catalyst, the epoxidation selectivity of the cyclic olefin was low because the active oxygen species generated in the catalytic system attacked the two allyl positions as well as the double bond. Therefore, the design of the active oxygen species is most important for the selective epoxidation of olefin.

We reported in a preliminary study¹⁵ that highly selective epoxidation of cyclohexene was observed on reductive activation of molecular dioxygen in a new catalytic system containing molecular dioxygen, zinc powder, benzoic anhydride, hexylviologen (HV²⁺), and Br⁻ ions as shown in Scheme 1, where a key species was the Br⁻ ion. In the present paper, the oxidation mechanism is discussed in detail in relation to the



Scheme 1

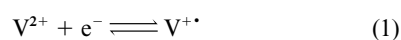
redox properties of chemical species contained in this catalytic system.

Results and discussion

Effect of various viologens on the oxidation of cyclohexene




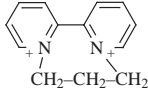
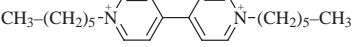
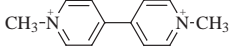
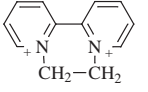
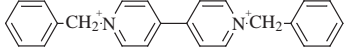
For an air-equilibrated acetonitrile suspension containing 7.3 × 10⁻² M zinc powder, 4.2 × 10⁻² M benzoic anhydride, and 0.47 M cyclohexene, although no oxidation product of cyclohexene was obtained after stirring for 3 h, oxidation products such as cyclohexene oxide (epoxide), cyclohex-2-en-1-one (1-one), and cyclohex-2-en-1-ol (1-ol) were obtained as the oxidation products of cyclohexene after adding both 5 × 10⁻³ M tetrabutylammonium bromide (Bu₄NBr) and 1 × 10⁻⁴ M viologen to the system. Table 1 summarizes the structural formula and the half-wave potential (*E*_{1/2}) of the viologen derivatives used, the amount of the oxidation products (*Q*), and the epoxidation selectivity (*S*) (molar ratio of [epoxide] to [total amount of the oxidation products]). The amount of the oxidation products and the epoxidation selectivity were independent of the kind of viologens, and the epoxidation selectivities were low, 36–39%. When zinc powder as a reductant, dioxygen as an oxygen source, or benzoic anhydride were not used, no oxidation product was obtained. The result suggests that this oxidation was due to the reductive activation of molecular dioxygen, and that benzoic anhydride acted very effectively in the oxidation of cyclohexene.

No oxidation product was obtained by adding Methylene Blue instead of the viologens, despite the *E*_{1/2} value of Methylene Blue (−0.76 V vs. Fc⁺/Fc) being approximately as same as those of DQ²⁺ and BV²⁺. The characteristic bluish color of the viologen radical monocations (V^{•+}),¹⁶ produced by reducing colorless viologen dications (V²⁺) with a reductant such as zinc powder as indicated by eqn. (1), readily returned to



colorlessness in acetonitrile by an air-oxidation, while the colorless species produced by a one electron reduction of Methylene

Table 1 Structural formula, half-wave potential ($E_{1/2}/V$ vs. Fc^+/Fc) of reduction^a of viologens in acetonitrile at 25 °C, the amount of oxidation products^b ($Q/10^{-3}$ M), and the epoxidation selectivity^c ($S(\%)$)

Viologen	Structural formula	$E_{1/2}$	Q			S
						
PDQ ²⁺		-0.94	3.9	5.4	1.5	36
HV ²⁺		-0.83	4.0	5.0	1.6	38
MV ²⁺		-0.81	4.4	5.6	1.6	38
DQ ²⁺		-0.75	5.0	6.0	1.9	39
BV ²⁺		-0.74	4.6	5.5	1.9	38

^a Concentration of viologen: 5×10^{-4} M, supporting electrolyte: 0.1 M Bu_4NClO_4 , scan rate: 100 mV s^{-1} , working electrode: glassy carbon disk with 0.07 cm^2 area. ^b Concentration of reactants: 1×10^{-4} M viologen, 5×10^{-3} M Bu_4NBr , 7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride, and 0.47 M cyclohexene. Reaction temperature: 30 °C, reaction time: 3 h. ^c (Molar ratio of [epoxide] to [total amount of the oxidation products]) $\times 100$.

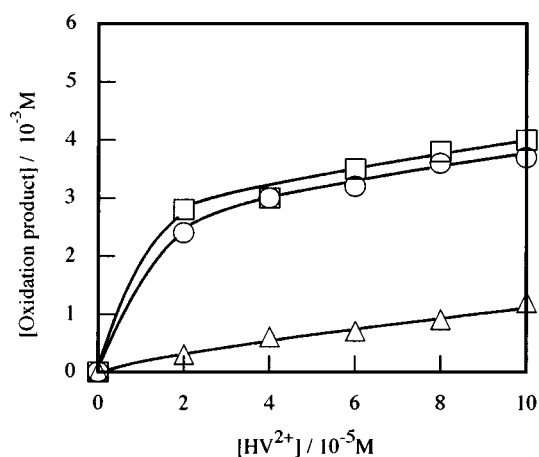
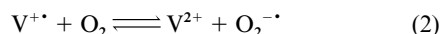


Fig. 1 Dependence of the amount of oxidation products (epoxide (○), 1-one (□), and 1-ol (△)) on the concentration of $HV(ClO_4)_2$ in an air-equilibrated acetonitrile suspension containing 7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride, 5×10^{-3} M Bu_4NBr , and 0.47 M cyclohexene at 30 °C (reaction time: 3 h).

Blue were not easily air-oxidized compared with V^{++} radical ions. Therefore, we assume that the superoxide ion ($O_2^{\cdot-}$) produced by a one electron transfer (eqn. (2)) from V^{++} to molecular dioxygen¹⁷ is responsible for this oxidation reaction.



The dependence of the amount of the oxidation products on the concentration of HV^{2+} , $[HV^{2+}]$, is shown in Fig. 1. The oxidation products were obtained at 2×10^{-5} M HV^{2+} , but the amount of oxidation products increased slightly on adding a higher concentration of HV^{2+} . The turnover number of HV^{2+} (molar ratio of [total amount of the oxidation products] to $[HV^{2+}]$) for 3 h reached about 250 at 2×10^{-5} M HV^{2+} , thus HV^{2+} acted as the electron mediator in this system.

Effect of various salts on the oxidation of cyclohexene

When Bu_4NBr was not added to the catalytic system containing

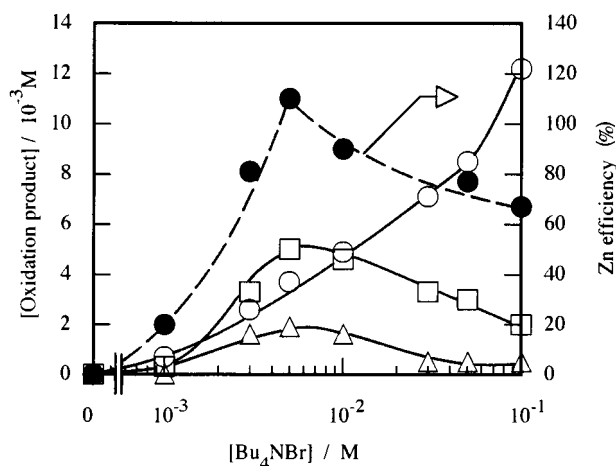


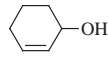


Fig. 2 Dependence of the amount of oxidation products (epoxide (○), 1-one (□), and 1-ol (△)) and the Zn-utilizing efficiency (●) on the concentration of Bu_4NBr in an air-equilibrated acetonitrile suspension containing 1×10^{-4} M $HV(ClO_4)_2$, 7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride, and 0.47 M cyclohexene at 30 °C (reaction time: 3 h).

1×10^{-4} M HV^{2+} , no oxidation product of cyclohexene was obtained. However, the amount of oxidation products increased linearly until the reaction time of 4 h without an induction period on addition of 5×10^{-3} M Bu_4NBr . The Zn-utilizing efficiency ([total amount of the oxidation products] to [consumed zinc powder]) was 110%.

The dependence of the amount of the oxidation products and the Zn-utilizing efficiency on the concentration of Bu_4NBr , $[Bu_4NBr]$, is shown in Fig. 2. The total amount of the oxidation products and the amount of epoxide product increased with increasing $[Bu_4NBr]$, but the amount of the other products (1-one and 1-ol) and the Zn-utilizing efficiency had maximum values at 5×10^{-3} M Bu_4NBr . At 0.1 M Bu_4NBr , the epoxidation selectivity reached about 85% with about 60% Zn-utilizing efficiency. This improvement of the epoxidation selectivity was apparently correlated with the addition of a large amount of Bu_4NBr . The epoxidation selectivity and the

Table 2 Amount of oxidation products^a ($Q/10^{-3}$ M) and Zn-utilizing efficiency^b ($E(\%)$) obtained by adding a salt containing either Bu_4N^+ ions or halogen ions

Salt	Q			E
				
None	n.d. ^c	n.d.	n.d.	—
Bu_4NBr	4.0	5.0	1.6	110
Bu_4NClO_4	n.d.	n.d.	n.d.	—
$\text{Bu}_4\text{NCF}_3\text{SO}_3$	n.d.	n.d.	n.d.	—
Bu_4NBF_4	n.d.	n.d.	n.d.	—
LiCl	3.4	1.8	0.9	86
LiClO_4	0.6	n.d.	n.d.	9

^a Concentration of reactants: 1×10^{-4} M $\text{HV}(\text{ClO}_4)_2$, 5×10^{-3} M salt, 7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride, and 0.47 M cyclohexene. Reaction temperature: 30 °C, reaction time: 3 h. ^b Molar ratio of [total amount of oxidation products] to [consumed zinc] $\times 100$. ^c Not detected.

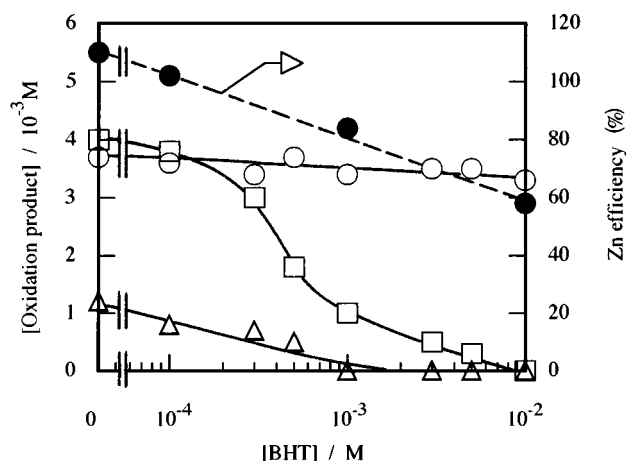


Fig. 3 Effect of the addition of BHT on the amount of oxidation products (epoxide (○), 1-one (□), and 1-ol (△)) and the Zn-utilizing efficiency (●) in an air-equilibrated acetonitrile suspension containing 1×10^{-4} M $\text{HV}(\text{ClO}_4)_2$, 7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride, 5×10^{-3} M Bu_4NBr , and 0.47 M cyclohexene at 30 °C (reaction time: 3 h).

Zn-utilizing efficiency of this catalytic system were comparable to those of the systems using transition metal complexes as the catalyst.^{4,10}

Some salts containing either Bu_4N^+ ions or halogen ions were added to this system instead of Bu_4NBr to clarify whether Bu_4N^+ ions or Br^- ions effectively acted to produce the oxidation products. The amount of the oxidation products and the Zn-utilizing efficiency are summarized in Table 2. When tetrabutylammonium perchlorate (Bu_4NClO_4), tetrabutylammonium trifluoromethanesulfonate ($\text{Bu}_4\text{NCF}_3\text{SO}_3$), or tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) were added, no oxidation product was obtained despite zinc powder being consumed. While, by adding LiCl ,[†] the oxidation products were obtained with 86% Zn-utilizing efficiency. When LiClO_4 was added in a control experiment, some epoxide was obtained as the single oxidation product, but the Zn-utilizing efficiency remained at a very low value of about 9%. These results indicate that halogen ions took part in the oxidation of cyclohexene.

Effect of radical inhibitor on the oxidation of cyclohexene

3,5-Di-*tert*-butyl-*p*-hydroxytoluene (BHT) was added as a radical inhibitor to this catalytic system in order to examine

[†] Since LiBr was insoluble in acetonitrile, LiCl was added to this system instead of LiBr .

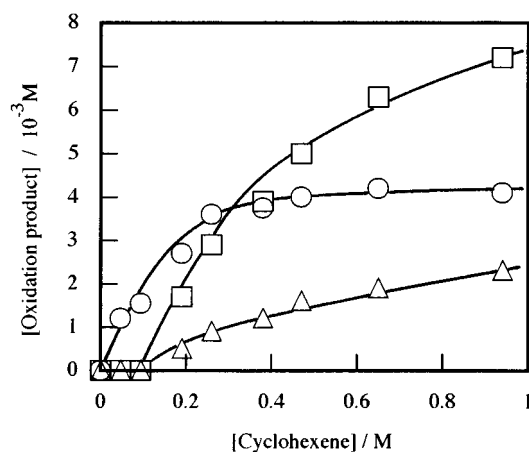


Fig. 4 Dependence of the amount of oxidation products (epoxide (○), 1-one (□), and 1-ol (△)) on the concentration of cyclohexene in an air-equilibrated acetonitrile suspension containing 1×10^{-4} M $\text{HV}(\text{ClO}_4)_2$, 7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride, and 5×10^{-3} M Bu_4NBr at 30 °C (reaction time: 3 h).

whether this oxidation reaction was a radical reaction or not. The dependence of the amount of the oxidation products and the Zn-utilizing efficiency on the concentration of BHT, $[\text{BHT}]$, is shown in Fig. 3. The amount of 1-one, 1-ol, and consumed zinc powder, and the Zn-utilizing efficiency decreased with increasing $[\text{BHT}]$, but the amount of epoxide hardly changed. By adding 1×10^{-2} M BHT, the epoxidation selectivity of 100% was attained with 60% Zn-utilizing efficiency even at the low concentration of 5×10^{-3} M Bu_4NBr . Although the effect of BHT as a radical inhibitor must be discussed carefully, we nonetheless concluded from the results that only active oxygen species which produce 1-one and 1-ol were deactivated by BHT, but other active oxygen species which produce epoxide were not deactivated by BHT. We named the former species “radical active oxygen species”, and the latter species “non-radical active oxygen species”. Thus, 1-one and 1-ol were produced by a reaction between the radical active oxygen species and cyclohexene. On the other hand, epoxide was produced by a reaction between the non-radical active oxygen species and cyclohexene. The non-radical active oxygen species was not produced by the reduction of the radical active oxygen species, because the amount of epoxide did not change on adding BHT.

Fig. 4 shows the dependence of the amount of the oxidation products on the concentration of cyclohexene, $[\text{cyclohexene}]$. In contrast with the epoxide produced by the addition of a small amount of cyclohexene, the 1-one and the 1-ol were produced suddenly above 0.2 M $[\text{cyclohexene}]$, where the amount of the produced epoxide began each saturation. That is, since the non-radical active oxygen species can oxidize cyclohexene much more easily compared to the radical active oxygen species, the latter species began to react with cyclohexene after the former species had reacted preferentially. Fig. 5 shows the dependence of amount of oxidation products on the amount of zinc powder. The amount of the epoxide reached saturation on adding a large amount of zinc powder, but the amount of the 1-one and the 1-ol decreased slightly. The result suggests that the radical active oxygen species were consumed due to the reduction with zinc powder, but the non-radical active oxygen species were hardly consumed by zinc powder.

Influence of $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$, HV^{2+} , and Br^- ions on the redox reaction of $\text{O}_2/\text{O}_2^{\cdot-}$ couple

We have investigated the influence of benzoic anhydride ($(\text{C}_6\text{H}_5\text{CO})_2\text{O}$), HV^{2+} , and Br^- ions on the redox properties of the $\text{O}_2/\text{O}_2^{\cdot-}$ couple using cyclic voltammetry since the redox reaction is one of the elementary reactions in our catalytic system. Further, the active oxygen species in our catalytic

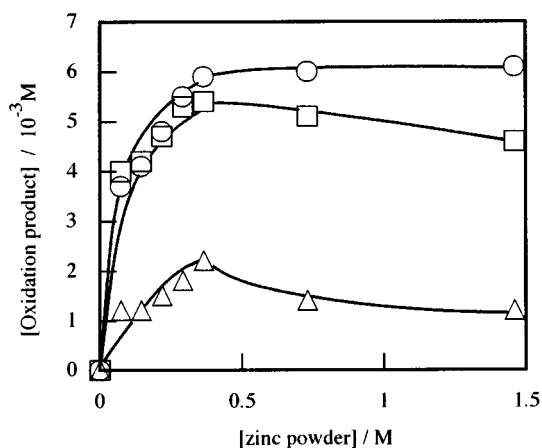


Fig. 5 Dependence of the amount of oxidation products (epoxide (O), 1-one (□), and 1-ol (Δ)) on the concentration of zinc powder in an air-equilibrated acetonitrile suspension containing 1×10^{-4} M $\text{HV}(\text{ClO}_4)_2$, 4.2×10^{-2} M benzoic anhydride, 5×10^{-3} M Bu_4NBr , and 0.47 M cyclohexene at 30 °C (reaction time: 3 h).

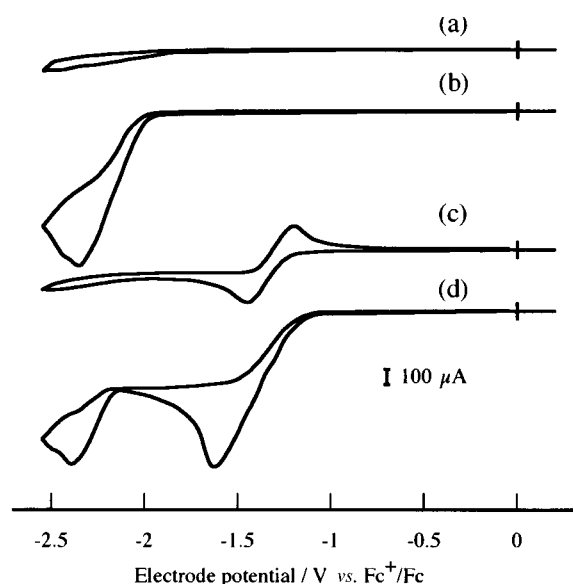
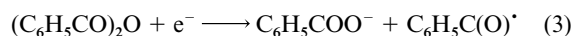


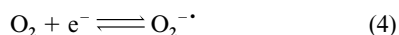
Fig. 6 Cyclic voltammograms of N_2 -purged acetonitrile solutions (a) without and (b) with 5×10^{-2} M $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ and of O_2 -saturated solutions (c) without and (d) with 5×10^{-2} M $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$. The solutions were at 25 °C and contained 0.1 M Bu_4NClO_4 as a supporting electrolyte. Scan rate: 100 mV s^{-1} . Working electrode: glassy carbon disk with 0.07 cm^2 area.

system was identified from the previously reported reaction mechanism in the literature.^{18,19}

Fig. 6 shows the cyclic voltammograms of N_2 -purged and O_2 -saturated acetonitrile solutions with and without $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$. A large cathodic current flowed around -2.3 V in the cyclic voltammogram of the N_2 -purged solution containing $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ (Fig. 6(b)) because $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ was directly reduced by electrolysis as indicated by eqn. (3).



An $\text{O}_2/\text{O}_2^{\bullet -}$ redox wave appeared around -1.4 V in the cyclic voltammogram of the O_2 -saturated blank solution (Fig. 6(c)), being indicated by eqn. (4). By adding $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ to this



system (Fig. 6(d)), the cathodic peak current (i_{pc}) around -1.4 V increased remarkably and no anodic peak caused by $\text{O}_2^{\bullet -}$ was observed. These results suggest that the electrochemically

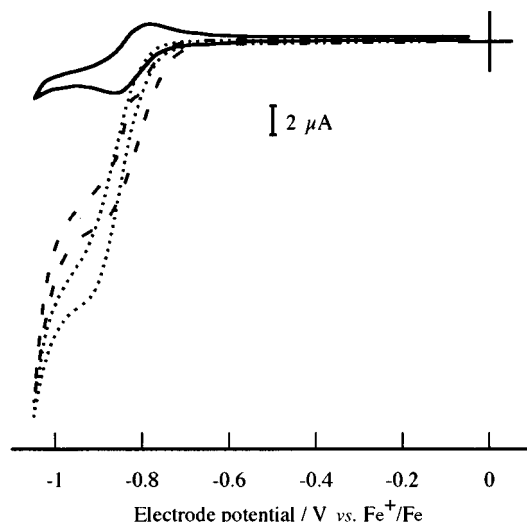
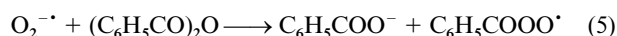


Fig. 7 Cyclic voltammograms of $(5 \times 10^{-2} \text{ M } (\text{C}_6\text{H}_5\text{CO})_2\text{O} + 5 \times 10^{-4} \text{ M } \text{HV}(\text{ClO}_4)_2)$ in N_2 -purged acetonitrile solution containing 0.1 M Bu_4NClO_4 as a supporting electrolyte (solid line), in O_2 -saturated solution containing 0.1 M Bu_4NClO_4 (broken line), and in O_2 -saturated solution containing 0.1 M Bu_4NBr (dotted line) instead of 0.1 M Bu_4NClO_4 . Scan rate: 20 mV s^{-1} . Working electrode: glassy carbon disk with 0.07 cm^2 area.

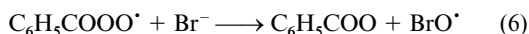
generated $\text{O}_2^{\bullet -}$ attacked benzoic anhydride to form a radical species such as benzoylperoxyl radical ($\text{C}_6\text{H}_5\text{COOO}^\bullet$) as indicated by eqn. (5) and the species formed were further reduced around -1.4 V.



The directly reductive electrolysis of $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ was observed around -2.3 V under O_2 -saturated conditions as well as under N_2 -purged conditions (Fig. 6(b),(d)).

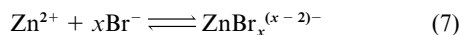
To clarify the role of HV^{2+} and Br^- ions in our catalytic system, cyclic voltammetry of the $((\text{C}_6\text{H}_5\text{CO})_2\text{O} + \text{HV}^{2+} + \text{Br}^-)$ system under N_2 -purged and O_2 -saturated conditions was carried out at electrode potentials of -0.05 to -1.05 V, at which potentials the $\text{O}_2/\text{O}_2^{\bullet -}$ redox reaction does not occur directly. In the cyclic voltammograms of the solution containing only HV^{2+} (the $E_{1/2}$ of HV^{2+} was -0.83 V), the cathodic current increased slightly under O_2 -saturated conditions in comparison with under N_2 -purged conditions. This implies that the reductively generated $\text{HV}^{+ \bullet}$ ions were oxidized by O_2 , where $\text{O}_2^{\bullet -}$ may be produced by this process. The cyclic voltammogram of the solution containing only $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ under O_2 -saturated conditions was approximately the same as that under N_2 -purged conditions. Though the cyclic voltammogram of the $((\text{C}_6\text{H}_5\text{CO})_2\text{O} + \text{HV}^{2+})$ system under N_2 -purged conditions (solid line in Fig. 7) was approximately the same as that of only HV^{2+} , the cyclic voltammogram of the former system under O_2 -saturated conditions (broken line in Fig. 7) differed considerably. The cathodic current increased remarkably under O_2 -saturated conditions compared to under N_2 -purged conditions, and no anodic peak of $\text{HV}^{+ \bullet}$ was observed. This indicates that the reductively generated $\text{HV}^{+ \bullet}$ ions did not react directly with $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ but did react with dioxygen molecules, and the $\text{O}_2^{\bullet -}$ produced may react with $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ to form $\text{C}_6\text{H}_5\text{COOO}^\bullet$ radicals. Thus, their radicals were reduced further around -1.0 V. That is, HV^{2+} acted as the effective electron-transfer mediator for the reductive activation of molecular dioxygen in our catalytic system. In the cyclic voltammogram of the $((\text{C}_6\text{H}_5\text{CO})_2\text{O} + \text{HV}^{2+} + \text{Br}^-)$ system under O_2 -saturated conditions containing 0.1 M Bu_4NBr instead of 0.1 M Bu_4NClO_4 as a supporting electrolyte (dotted line in Fig. 7), the i_{pc} around -0.9 V reached about 1.5 times in comparison with that of the $((\text{C}_6\text{H}_5\text{CO})_2\text{O} + \text{HV}^{2+})$ system containing 0.1

M Bu₄NClO₄ (broken line in Fig. 7). We infer that radical active oxygen species such as the hypobromous radical (BrO[•]) were rapidly produced by a reaction between C₆H₅COOO[•] and a large amount of Br⁻ ions, being given by eqn. (6), and they were further reduced around -0.9 V.

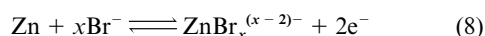


Thus, radical active oxygen species which produce 1-one and 1-ol may be BrO[•] radicals, and the BrO[•] radicals may be deactivated by BHT though we could not propose any experimental evidence for this.

Since the complex formation reaction (7) occurs between zinc



ions and Br⁻ ions according to the literature,²⁰ the oxidative dissolution of zinc as indicated by eqn. (8) may be promoted,

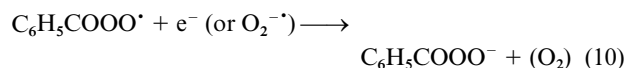


and eventually the Nernst equation for the oxidation potential (*E*) is given by eqn. (9), where *E*[°](Zn/Zn²⁺), *Kx*, *R*, *F* and *T* are

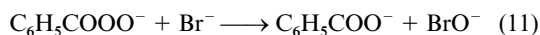
$$E = E^\circ(\text{Zn}/\text{Zn}^{2+}) - RT(\ln Kx)/2F + (RT \ln([\text{ZnBr}_x^{(x-2)-}]/[\text{Br}^-]^x))/2F \quad (9)$$

the standard redox potential of Zn/Zn²⁺ couple, the complex formation constant of eqn. (7), the gas constant, the Faraday constant, and the absolute temperature, respectively. It is predicted from the Nernst eqn. (9) that the standard redox potential of the ZnBr_{*x*}^{(*x*-2)-}/Zn couple shifts to a more negative potential for *RT*(ln*Kx*)/2*F* than the *E*[°](Zn²⁺/Zn). Further, according to the literature,²⁰ the *x* value increases from one to three with increasing concentration of Br⁻ ions, [Br⁻], in DMSO, and the *Kx* value increases with increasing [Br⁻] since it is given by *K*₁ = β₁, *K*₂ = β₁ × β₂, or *K*₃ = β₁ × β₂ × β₃, where β₁, β₂, and β₃ represent the equilibrium constants for the consecutive reactions of *x* = 1, 2, and 3, respectively, and they are more than unity. Therefore, the *E* shifts to a more negative potential with increasing [Br⁻], indicating an increase of the reducing power of Zn. This prediction is supported by the experimental evidence that the reduction (1) from colorless HV²⁺ to bluish HV^{•+} was accelerated by adding a large amount of Br⁻ ions in an N₂-purged acetonitrile suspension containing zinc powder.

We assign BrO[•] to the radical active oxygen species for the production of 1-one and 1-ol, but the non-radical active oxygen species which produces epoxide is not produced by the reduction of the radical active oxygen species, because the amount of the produced epoxide did not decrease on adding BHT. *E*[°](Zn²⁺/Zn) in acetonitrile is about -1.5 V vs. Fc⁺/Fc.²¹ Since the reducing power of Zn increases on adding a large amount of Br⁻ ions, radical species such as the C₆H₅COOO[•] radical may be reduced to non-radical species such as benzoylperoxide ions (C₆H₅COOO⁻) by zinc powder or a large amount of O₂^{-•}¹⁸ produced by the mediation reaction of HV²⁺ ions, being indicated by eqn. (10). Consequently the non-radical active oxygen

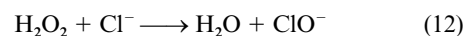


species such as hypobromous anion (BrO⁻) is produced by a reaction between C₆H₅COOO⁻ ions and a large amount of Br⁻ ions as indicated by eqn. (11). We infer that a C₆H₅COOO[•]



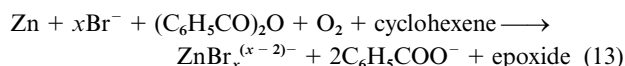
radical was preferentially reduced to C₆H₅COOO⁻ ion by zinc powder or O₂^{-•} before deactivation by BHT though we could not propose any experimental evidence for this.

Thus, the non-radical active oxygen species which produce epoxide may be BrO⁻ ions. Such production of BrO[•] radicals and BrO⁻ ions is analogous to the following experimental observation from reference 22; ClO⁻ ion, which is a powerful oxidizing agent, is produced from the enzymatically catalyzed reaction between H₂O₂ and Cl⁻ ion by myeloperoxidase in a neutrophil, being indicated by eqn. (12).

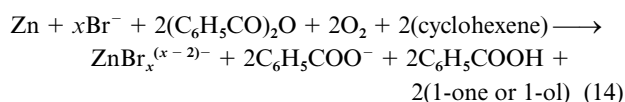


Conclusions

In the oxidation of cyclohexene by the reductive activation of dioxygen molecules, the O₂^{-•} ions were efficiently produced because HV²⁺ acted as an effective electron mediator from zinc powder to O₂ molecules. Though the reducing power of Zn was increased somewhat by adding a small amount of Br⁻ ions, C₆H₅COOO[•] radicals were produced through eqns. (1), (2), and (5) because of the relatively weak reducing power of Zn. Then, BrO[•] radicals were produced by a reaction between C₆H₅COOO[•] radicals and Br⁻ ions at the lower [Br⁻] as indicated by eqn. (6), oxidizing cyclohexene to 1-one and 1-ol. On the other hand, since the reducing power of Zn increased further on adding a large amount of Br⁻ ions, the C₆H₅COOO[•] radicals immediately after their production were reduced to C₆H₅COOO⁻ anions as indicated by eqn. (10). Then, BrO⁻ anions were produced by a reaction between C₆H₅COOO⁻ and Br⁻ ions at the higher [Br⁻] as indicated by eqn. (11), oxidizing cyclohexene to epoxide. The reactivity between cyclohexene and BrO⁻ ions may be much larger than that between cyclohexene and BrO[•] radicals, thus the epoxide was produced in preference to the 1-one and 1-ol at the higher [Br⁻], see Fig. 2. The catalytic mechanism proposed in this study is summarized in Scheme 2. The electron-transfer number of the overall reaction (13) producing cyclohexene oxide is two, and that of the overall



reaction (14) producing cyclohex-2-en-1-one and cyclohex-2-en-1-ol is one.

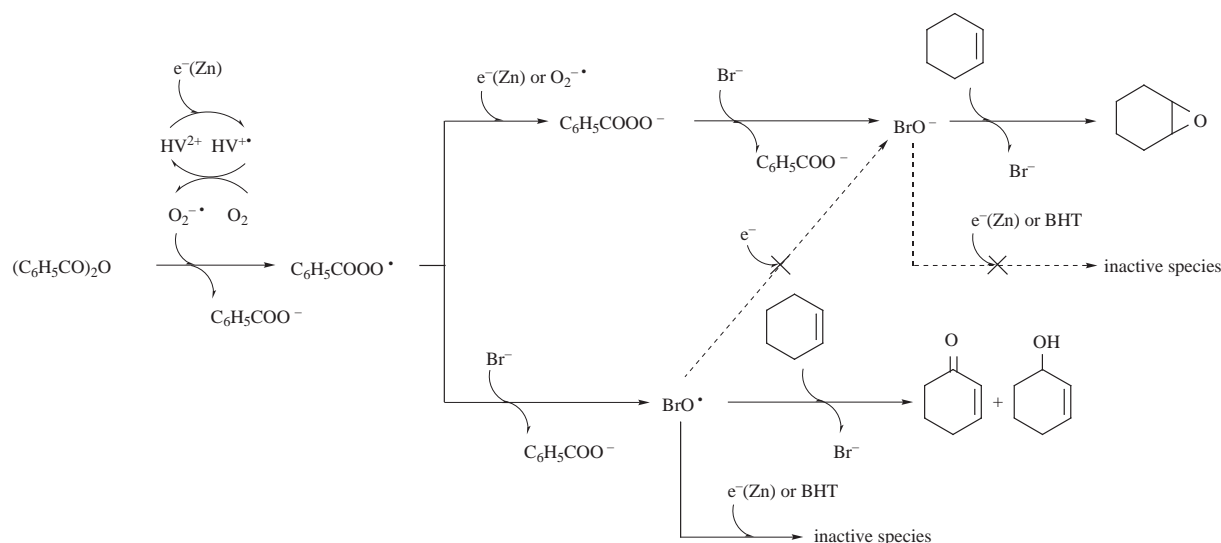


Therefore, as shown in Fig. 2, the utilizing efficiency of zinc powder which can release two molar electrons per one molar Zn was 110%, at the lower concentration of 5 × 10⁻³ M Bu₄NBr where a one electron transfer reaction (14) preferentially occurred, and it was 60%, at the higher concentration of 0.1 M Bu₄NBr where a two electron transfer reaction (13) preferentially occurred.

Experimental

Materials

Acetonitrile and cyclohexene were distilled after dehydration by calcium hydride and molecular sieves (3 Å), respectively, and they were stored over molecular sieves (3 Å) in brown bottles. Benzoic anhydride ((C₆H₅CO)₂O) was recrystallized from ethanol-water (1:4 by volume) after removal of the contained acid by washing with aqueous sodium hydrogencarbonate. Synthesis and purification of the viologen dibromide, methylviologen dibromide (MVBr₂), hexylviologen dibromide (HVBr₂), benzylviologen dibromide (BVBr₂), 6,7-dihydrodipyrido[1,2-*a*:2,1-*c'*]pyrazinediium dibromide (DQBr₂), and 7,8-dihydro-6*H*-dipyrido[1,2-*a*:2,1-*c'*][1,4]diazepinediium dibromide (PDQBr₂) were described in a previous paper.¹⁰ Viologen



Scheme 2

perchlorate and tetrabutylammonium perchlorate (Bu_4NClO_4) were obtained as precipitates by mixing the aqueous solution of the corresponding bromide with concentrated perchloric acid, and they were recrystallized from ethanol and ethyl acetate–hexane (1:4 by volume), respectively. $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$, viologen perchlorate, and Bu_4NClO_4 were used after drying *in vacuo* at room temperature. Tetrabutylammonium bromide (Bu_4NBr), tetrabutylammonium trifluoromethanesulfonate ($\text{Bu}_4\text{NCF}_3\text{SO}_3$), and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) were recrystallized from benzene–hexane (1:4 by volume), dichloroethane–diethyl ether (1:4 by volume), and ethyl acetate–pentane (1:4 by volume), respectively, and they were dried *in vacuo* at 80°C . Lithium chloride (LiCl) and lithium perchlorate (LiClO_4) were used without further purification but after drying *in vacuo* at 80°C and at room temperature, respectively.

Oxidation of cyclohexene

The oxidation of cyclohexene was carried out as follows. An air-equilibrated acetonitrile suspension of 10.5 cm^3 containing zinc powder (50 mg , $7.3 \times 10^{-2}\text{ M}$ ($\text{M} = \text{mol dm}^{-3}$)), viologen perchlorate (0.57 mg in the case of $\text{HV}(\text{ClO}_4)_2$, $1 \times 10^{-4}\text{ M}$), benzoic anhydride (100 mg , $4.2 \times 10^{-2}\text{ M}$), cyclohexene (0.5 cm^3 , 0.47 M), and differing amounts of Bu_4NBr was stirred at a constant rate with a magnetic stirrer at 30°C for 3 h. The quantitative analysis and the identification of the oxidation products were performed by a Yanaco G-2800 GC with a silicon DC 550 column. To estimate the Zn-utilizing efficiency, the amount of consumed zinc powder was determined by EDTA titration.¹⁰

Cyclic voltammetry

Cyclic voltammetry was performed using a glassy carbon disk (3 mm diameter) as the working electrode, a Pt coil as the counter electrode, and $\text{Ag}/0.1\text{ M AgNO}_3$ in acetonitrile solution as the reference electrode at 25°C . Potential control was carried out using a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator. Cyclic voltammograms were recorded on a Rikadenki RW-21 X-Y recorder. Half-wave potentials ($E_{1/2}$) were estimated as the average of cathodic and anodic peak potentials. The electrode potential and the half-wave potential were described on the basis of the half-wave potential of ferrocene/ferrocenium ion couple (Fc^+/Fc).

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