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Influence of Br^- Concentration on $(Br)^+$-Mediated Indirect Electrooxidation of Alcohols to the Corresponding Carbonyl Compounds

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Current efficiency for the $(Br)^+$(positive bromine species)-mediated indirect electrooxidation of alcohols to the corresponding carbonyl compounds decreased with increase in Br^- concentration in dichloromethane and aqueous acidic solutions, while no concentration dependence was observed in an aqueous neutral solution. These facts suggested a general and practical guideline for the indirect electrooxidation, i.e. low Br^- concentration is favorable in an electrolytic solution of low nucleophilicity. It was also found that the kind of $(Br)^+$ species formed anodically in the absence of the alcohols in dichloromethane clearly depended on charge(Q) passed as follows: Br_3^- at $Q \leqslant 2/3$F mol^{-1} (1F=96480 C), Br_n^- ($n>3$) at $2/3<Q<1$F mol^{-1}, and Br_2 at $Q=1$F mol^{-1}. Among these species, Br_3^- and Br_2 seemed to be the weakest and strongest oxidizing agents, respectively. Lower efficiency for the indirect electrooxidation in higher Br^- concentration was rationalized as due to more predominant formation of Br_3^- and/or Br_n^- with smaller n values.

It is well-known that indirect electrolysis using redox couples as mediators for electron transfer between electrodes and substrates is one of very useful methods in electroorganic synthesis.[1,2] Among the redox couples, halide(X^-)/positive halogen species-[$(X)^+$] couples have been often used in the indirect electrooxidation of organic compounds.[2]

Recently an interesting phenomenon has been found in the $(X)^+$-mediated indirect electrooxidation: Increase in X^- concentration results in decrease in current efficiency and/or yield.[3-5] In this work, some additional examples of this kind of phenomenon were also found in the $(Br)^+$-mediated oxidation of alcohols to the corresponding carbonyl compounds. This fact seems to indicate that the phenomenon is considerably universal. Since the $X^-/(X)^+$ mediators can be regarded as electrocatalysts, an apparently paradoxical theorem, the smaller amounts of catalyst used, the more smoothly the reaction proceeds, may be induced from the phenomenon.

Although it has been postulated that the $(X)^+$-mediated oxidation involves X^+, X_3^-, X_2, and/or XO^- as the oxidizing agents, their formation and behavior during electrolysis have not been clarified so far. In this work, the formation and behavior of some kinds of $(Br)^+$ species in dichloromethane were investigated by means of electrochemistry and UV-spectroscopy, and also the above strange phenomenon was rationalized as due to low oxidizing power of Br_3^- species which is formed preferentially in high Br^- concentration or at small amounts of charge passed under indirect electrolysis conditions.

Results and Discussion

Influence of Br^- Concentration on $(Br)^+$-Mediated Indirect Electrooxidation of Alcohols. It is known that benzyl alcohol[6] and 2,3-butanediol[7] can be efficiently oxidized to benzaldehyde and acetoin, respectively, by using a $Br^-/(Br)^+$ redox mediatory system. In this work, first the influence of Br^- concentration on current efficiencies for the products was examined in dichloromethane and aqueous solutions. The current efficiencies were determined by analyzing the anodic solutions in which unreacted $(Br)^+$ species were quenched with $NaHSO_3$ just after the electrolyses finished. As shown in Fig. 1, the current efficiencies decreased with increase in Br^- concentration in the oxidation of either benzyl alcohol or 2,3-butanediol at a platinum anode in n-Bu_4NBr–0.2 M (1 M=1 mol dm^{-3}) n-Bu_4NClO_4/dichloromethane containing 3 equiv 2,6-lutidine. Shorter electrolysis time was required in higher Br^- concentration because of larger electrolytic current. However, no dependence of the electrolysis time on the efficiency was observed when a smaller anode, which

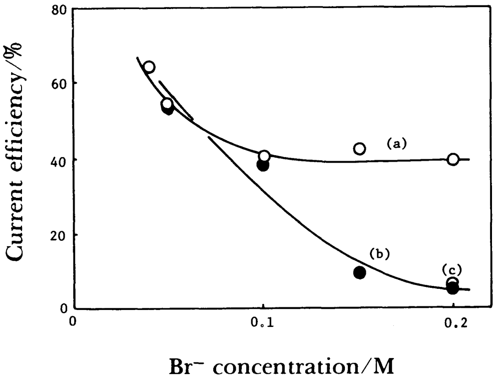

Fig. 1. Influence of Br^- concentration on current efficiency for products in the $(Br)^+$-mediated indirect electrooxidation of alcohols at a platinum anode (5.5 cm^2) in 0.2 M n-Bu_4NClO_4/CH_2Cl_2 containing n-Bu_4NBr and 2,6-lutidine. (a) Oxidation of benzyl alcohol to benzaldehyde at 1.7 F mol^{-1} of charge passed at 1.4 V vs. SCE. (b) Oxidation of 2,3-butanediol to acetoin at 2.0 F mol^{-1} at 1.3 V. (c) Electrolysis similar to (b) using a smaller anode (1.5 cm^2).

required longer electrolysis time, was used (See Fig. 1(c)). This fact indicates that the concentration dependence results directly from concentration effects of Br^- in the anodic solution. A cyclic voltammogram of Br^- gave two oxidation peaks at 0.8 and 1.0 V vs. SCE (See Fig. 3(b)). The oxidation of 2,3-butanediol in a first peak potential region could scarecely proceed even in low Br^- concentration (0.05 M).

A similar concentration dependence was also found in the oxidation of 2,3-butanediol in an acidic aqueous solution (0.2 M H_2SO_4), while no dependence in a neutral solution (0.3 M KH_2PO_4–0.3 M Na_2HPO_4) (See Fig. 2).

The above results may give general guidelines for synthetic use of the $(Br)^+$-mediated indirect electrooxidation: (a) To choose reaction media taking into account their nucleophilicity, (b) to electrolyze at potentials more positive than the second oxidation peak potential of Br^-, and (c) to use auxiliary supporting electrolytes when low Br^- concentration is inevitably required.

An Synthetic Application of the $(Br)^+$-Mediated Indirect Electrooxidation of Benzyl Alcohols with Electron-Withdrawing Groups to the Corresponding Benzaldehydes. Benzaldehydes are very important starting compounds for production of a variety of useful organic chemicals and one of the most common synthetic methods is either chemical or electrochemical oxidation of the corresponding toluenes. However, any practical synthetic method of pentafluorobenzaldehyde, which must be an important compound as a building block for synthesis of useful aromatic fluorine compounds, has not been established, because 2,3,4,5,6-pentafluorotoluene can be prepared only with great difficulty. We have recently reported an efficient conversion method of commercially-available pentafluorobenzoic acid into 2,3,4,5,6-pentafluorobenzyl alcohol.[8] In this work, it was also found that pentafluorobenzyl alcohol could be oxidized by the $(Br)^+$-mediated electrolysis to give pentafluorobenzaldehyde as a sole product without any further oxidation to pentafluorobenzoic acid. These facts suggest a possibility of the conversion of pentafluorobenzoic acid into pentafluorobenzaldehyde via pentafluorobenzyl alcohol.

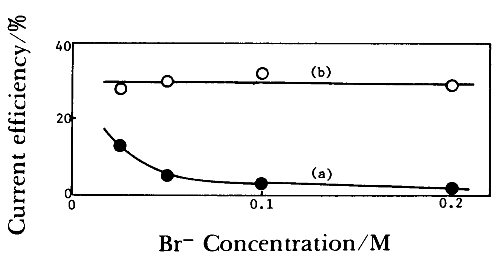

Fig. 2. Influence of Br^- concentration on current efficiency for acetoin in the $(Br)^+$-mediated indirect electrooxidation of 2,3-butanediol at a graphite anode (5.5 cm²) in aqueous solutions. (a) Electrolysis at 1.5 F mol⁻¹ of charge passed at 1.4 V vs. SCE in 0.2 M H_2SO_4. (b) Electrolysis at 2.0 F mol⁻¹ at 1.2 V in 0.3 M KH_2PO_4–0.3 M Na_2HPO_4.

In addition, a nitro-substituted benzyl alcohol, which is hardly oxidized due to the electron-withdrawing effect of nitro group, could be oxidized in a similar manner.

Electrolytic results obtained are summarized in Table 1.

Cyclic Voltammetric Behavior of Br^- and $(Br)^+$ Species. Anodic behavior of Br^- in organic solvents may be generally characterized by two oxidation waves which indicate the occurrence of the following reactions from wave height ratio:[9,10]

$$3Br^- \longrightarrow Br_3^- + 2e \text{ at the 1st wave} \tag{1}$$

$$Br_3^- \longrightarrow \frac{3}{2}Br_2 + e \text{ at the 2nd wave} \tag{2}$$

Figures 3(b) and (c) show cyclic voltammograms of Br^- measured at a platinum electrode in dichloromethane. The above reactions seem to be responsible for two oxidation peaks (P_{a2} and P_{a1}) observed. In the curve(c) which was returned at 1.4 V, a small cathodic peak (P_{c1}) was observed. This may be responsible for the reduction of Br_2 to Br_3^-. When benzyl alcohol was added (See the curve (e)), any change of the two peaks (P_{a2} and P_{a1}) was not observed. In addition, the oxidation peak of benzyl alcohol, which appeared in a potential range more positive than 1.8 V, did not significantly decrease. These facts suggest that the oxidation of the alcohol by $(Br)^+$ species formed at P_{a2} is not fast.

Br_3^- may be formed by the reaction of Br^- with Br_2 generated at an anode.[10]

$$Br_2 + Br^- \rightleftarrows Br_3^- \tag{3}$$

Table 1. The $(Br)^+$-Mediated Indirect Electrooxidation of Benzyl Alcohols to the Corresponding Benzaldehydes

Benzyl alcohol	Anode potential[a)]	Conversion	Yield[b)] of benzaldehyde	Current efficiency
	V vs. SCE	%	%	%
Benzyl alcohol	1.4	89	83	46
p-Nitrobenzyl alcohol	2.0	79	65	31
Pentafluorobenzyl alcohol	2.0	57	67	22

a) 3.3 F mol⁻¹ of charge were passed at potentials less positive than those for oxidation of the starting benzyl alcohols themselves in the presence of Br^- (0.05 M). b) Based on benzyl alcohols consumed.

It is well-known that Br_3^- is much less active than Br_2 as a oxidizing agent.[11-13] Therefore, lower current efficiency for the $(Br)^+$-mediated indirect electrooxidation in higher Br^- concentration (See Fig. 1) can be rationalized as due to more smooth formation of Br_3^-. In the neutral aqueous solution which has a higher nucleophilicity than the acidic aqueous and dichloromethane solutions, no dependence of Br^- concentration was observed as shown in Fig. 2(b). This may be rationalized as due to the formation of another active $(Br)^+$ species as shown below:[11]

$$Br_2 + H_2O \longrightarrow HBrO + HBr \tag{4}$$

At the next stage of investigation, cyclic voltammetric behavior of Br_2 was examined in dichloromethane. As shown in Figs. 4(a)—(c), Br_2 showed many reduction and oxidation peaks, among which P_{c1}, P_{c2}, P_{a2}, and P_{a1} seemed to be responsible for the following reactions:

$$Br_2 + \frac{2}{3}e \underset{P_{a1}}{\overset{P_{c1}}{\rightleftarrows}} \frac{2}{3}Br_3^- \tag{5}$$

$$\frac{2}{3}Br_3^- + \frac{4}{3}e \underset{P_{a2}}{\overset{P_{c2}}{\rightleftarrows}} 2Br^- \tag{6}$$

However, any reactions responsible for the other peaks (P_{c3}, P_{a4}, and P_{a3}) could not be reasonably thought out.

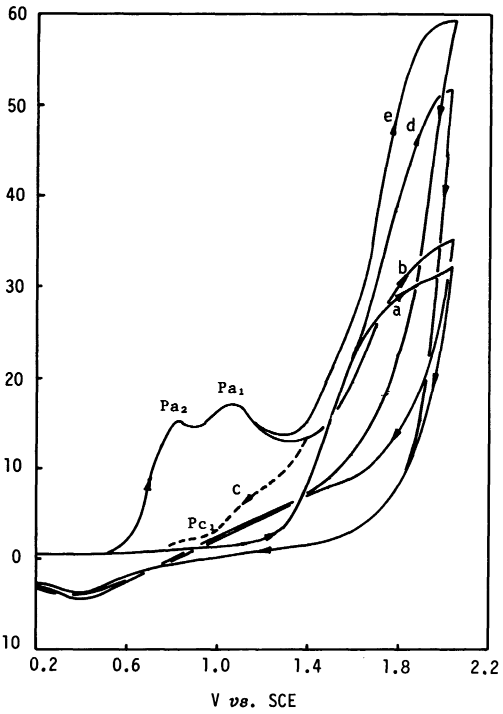

Fig. 3. Cyclic voltammograms of Br^- at a platinum electrode (1.3 mm^2) in the presence of benzyl alcohol. (a) Background solution, 0.1 M n-Bu_4NClO_4/CH_2Cl_2. (b) 5 mM n-Bu_4NBr. (c) 5 mM n-Bu_4NBr (returned at 1.4 V vs. SCE). (d) 10 mM benzyl alcohol. (e) 5 mM n-Bu_4NBr-10 mM benzyl alcohol. Scan rate: 0.1 V s^{-1}.

As shown in Fig. 4(d), the addition of 1 equiv Br^- resulted in a decrease of P_{c1} and increases of P_{a2} and P_{a1}. However, P_{c2} disappeared unexpectedly, while a new peak (P_{c4}) appeared in a negative potential range around −1.8 V but a reaction responsible for this peak also could not be thought out.

UV-Spectroscopic Study of $(Br)^+$ Species Formed Chemically and Electrochemically. Considerable ambiguity has been ramained in the above analysis of the cyclic voltammetric behavior of Br^- and Br_2. Therefore, next it was attempted to identify $(Br)^+$ species by UV-spectroscopy.

Figures 5(a) and (b) show the spectra of Br_2(λ_{max} 230 nm) and Br^-(λ_{max} 231 nm), respectively. A mixture of 2 mM Br_2 and 0.03 mM Br^- gave the spectrum(c) consisting of an absorption peak for Br_2 with an almost equal height to that in the spectrum(a) and a new peak at λ_{max} 271 nm. The height of this new peak increased in proportion to Br^- concentration (See spectra(c)—(e)), while the Br_2 peak decreased gradually (spectra(c), (d)) and disappeared in the concentration equivalent to Br_2(spectrum(e)). As shown in the spectrum(f), the presence of excess Br^- resulted in no change in height of the new peak and in appearance of the Br^- peak as a shoulder. Formation constants of Br_3^- on the basis of Eq. 3 are as extremely large as 10^7—10^9 in aprotic solvents.[14] Gabes and Stufkens[15] reported the λ_{max} and ε_{max} of Br_3^-

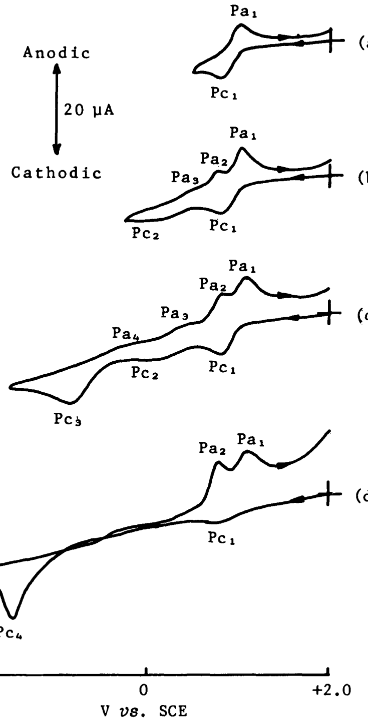

Fig. 4. Cyclic voltammograms of Br_2 at a platinum electrode (1.3 mm^2) in 0.1 M n-Bu_4NClO_4/CH_2Cl_2. (a)—(c) 2 mM Br_2. (d) 2 mM Br_2+2 mM n-Bu_4NBr. Scan rate: 0.1 v s^{-1}.

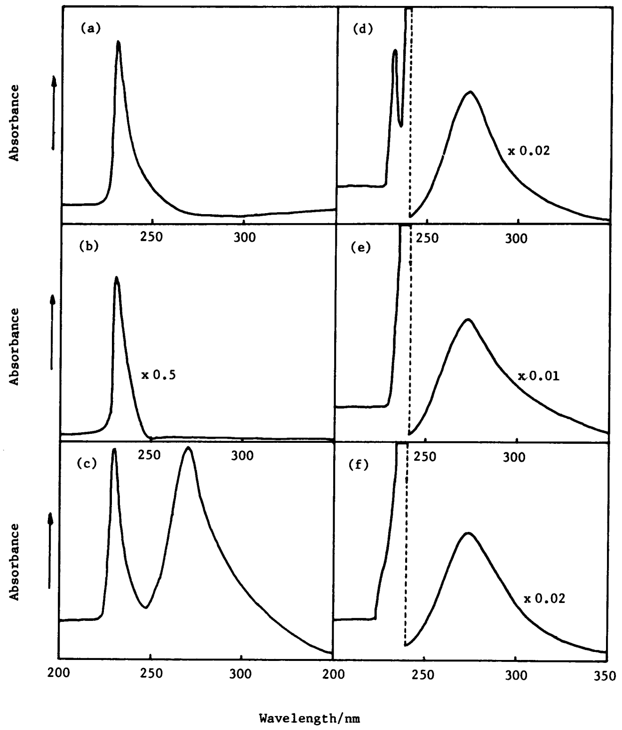

Fig. 5. UV-Spectra of bromine species prepared by mixing Br_2 and n-Bu_4NBr in CH_2Cl_2.
(a) 2 mM Br_2. (b) 2 mM n-Bu_4NBr. (c) 2 mM Br_2+0.03 mM n-Bu_4NBr. (d) 1 mM Br_2+2 mM n-Bu_4NBr. (e) 2 mM Br_2+2 mM n-Bu_4NBr. (f) 2 mM Br_2+1 mM n-Bu_4NBr.

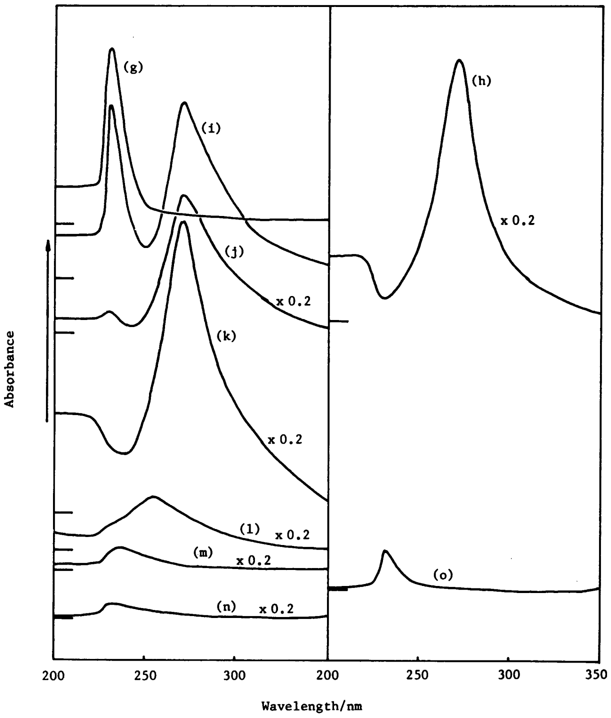

Fig. 6. Changes in UV-spectra of 50 mM n-Bu_4NBr/CH_2Cl_2 with increase in charge passed at a platinum anode (5.5 cm^2). The spectra were measured after diluted fifty times. (g) 50 mM n-Bu_4NBr. (h) 0.70 F mol^{-1} at 1.0 V vs. SCE. (i) 0.06 F mol^{-1} at 1.7 V. (j) 0.28 F mol^{-1} at 1.7 V. (k) 0.67 F mol^{-1} at 1.7 V. (l) 1.00 F mol^{-1} at 1.7 V. (m) 1.10 F mol^{-1} at 1.7 V. (n) 1.13 F mol^{-1} at 1.7 V. (o) 1.10 F mol^{-1} at 2.0 V.

in dichloromethane to be 272 nm and 46600, respectively. Based on these facts observed in this work and reported in the literatures, the new peak was assigned to Br_3^- and its ε_{max} was estimated to be ca. 47000. It is hereby confirmed that Br_3^- is formed almost quantitatively through the reaction shown in Eq. 3 and any $(Br)^+$ species can not be formed in dichloromethane even if excess Br_2 were used.

Figure 6 shows spectra of anodic solutions (50 mM n-Bu_4NBr/CH_2Cl_2) which were electrolyzed by passing various amounts of charge at various potentials using a platinum anode in a divided cell. The spectrum(g) was measured before the electrolysis. When the solution was electrolyzed coulometrically at 1.0 V, the electrolytic current diminished to a residual current level at 0.70 F mol^{-1} (1 F=96480C) of charge passed. Spectrum(h) of the solution after the electrolysis showed a Br_3^- peak, of which height corresponded to 15 mM of Br_3^- concentration, and no Br^- peak. This fact indicates the almost complete occurrence of the reaction shown in Eq, 1, if the reaction mechanism is left out of consideration, since the theoretical Br_3^- concentration is calculated to be 17 mM.

Larger amounts of charge could be passed at more positive potentials. Figures 6(i)—(n) are spectra of the solutions electrolyzed at 1.7 V. When 0.06—0.67 F mol^{-1} were passed, the concentrations of Br_3^- and Br^- were estimated from their peak heights (spectra(i)—(k)) as follows: 1.9 mM Br_3^- (theoretical, 1.5 mM) and 49 mM Br^-(theoretical, 46 mM) at 0.06 F mol^{-1}; 8 mM Br_3^-(theoretical, 7 mM) and 31 mM Br^-(theoretical, 29 mM) at 0.28 F mol^{-1}; 17 mM Br_3^-(theoretical, 17 mM) and 0 mM Br^-(theoretical, 0 mM) at 0.67 F mol^{-1}. These aqreements of found values of the concentrations with the theoretical ones indicate the predominant occurrence of the reaction shown in Eq. 1. However, a strange phenomenon was observed at charge more than 0.67 F mol^{-1} which is the theoretical amount based on Eq. 1.

As shown in Fig. 6(l) and (m), a new peak appeared, while the Br_3^- peak disappeared. Moreover, the λ_{max} and height of this new peak shifted to shorter wavelengths and decreased, respectively, though the Br_3^- and Br_2 peak heights should decrease and increase, respectively, with increase in charge passed if the Eq. 2 reaction occurred following Eq. 1.[9,10] A small Br_2 peak could be observed only as a shoulder in the spectrum(l). When a slightly larger amount of charge than 1 F mol^{-1}, which is the theoretical amount based on the combination of Eqs. 1 and 2, was passed, the electrolytic current diminished to the residual current level and the new peak apparently overlapped the Br_2 peak. However, Br_2 concentration calculated from the overlapped peak was as much higher as 60 mM than the theoretical value (25 mM). This fact means the peak contains a contribution of another component which has a larger ε_{max} than that of Br_2. The electrolysis at a more positive potential such as 2.0 V resulted in the formation of Br_2(found, 23 mM; theoretical, 25 mM) (See spectrum(o)).

It was also confirmed by iodometry using $Na_2S_2O_3$ that the anodic solutions always had oxidizing capacities equivalent to amounts of charge passed at all the potentials used.

From the results obtained above, it is likely that the peaks observed in the spectra(l)—(n) are assigned to polybromides(Br_n^-, $n>3$) of which the possible preparation as the corresponding quaternary ammonium salts (n=5, 7, 8, 9, 11, and 33) by the direct reaction of bromide salts with liquid or gaseous Br_2 has been reported,[16–18] though only an uncertain evidence for the formation of Br_5^- in solutions has been reported.[19] It is noticeable that a possibility for the formation of Br_n^- ($n>3$) by the anodic oxidation of Br^- in solutions was suggested in this work.

Conclusion

(a) The formation of Br_3^- depends not on potential(E) as indicated by Eqs. 1 and 2 but on charge(Q) passed as shown below.

$$Q \leqslant \frac{2}{3}\text{F mol}^{-1};\ E,\ \text{independent:}$$

$$2Br^- \xrightarrow{-2e} [Br_2] \xrightarrow{Br^-} Br_3^- \qquad (7)$$

(b) The formation of Br_n^- ($n>3$) occurs by a cascade type of reactions shown below. The reactions depend on both E and Q, in other words n is a function of E and Q.

$$\frac{2}{3} < Q < 1\ \text{F mol}^{-1};\ 1 < E < 2\ \text{V vs. SCE:}$$

$$Br_3^- \longrightarrow \frac{3}{4}Br_4^- + \frac{1}{4}e$$

$$Br_4^- \longrightarrow \frac{4}{5}Br_5^- + \frac{1}{5}e$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$Br_{n-1}^- \longrightarrow \frac{n-1}{n}Br_n^- + \frac{1}{n}e \qquad (8)$$

Remarkably sensitive changes observed in the spectra of Br_n^- with increase in Q can be reasonably rationalized as due to the occurrence of this type of reactions.

(c) The formation of Br_2 as a final product occurs when 1 F mol^{-1} is completely passed at potentials more positive than 2 V. $\lim_{n\to\infty} Br_n^-$ actually corresponds to Br_2.

(d) The order of oxidizing powers of $(Br)^+$ species is speculated as below.

$$Br_3^- < Br_4^- < \cdots\cdots < Br_n^- < \cdots\cdots < Br_2$$

(e) Low current efficiency for the $(Br)^+$-mediated indirect electrooxidation in high Br^- concentration is explained on the basis of the above items(a)—(d). Therefore, it is recommended for efficient $(Br)^+$-mediated indirect electrooxidation to use low Br^- concentration and positive potential as possible: It is undesirable to make bromide salts serve a double purpose for the mediator and supporting electrolyte, since their concentration must be so high that electroconductivity of the electrolytic solutions is high enough. It is also recommended to use large amounts of other salts, which can play a role as the supporting electrolytes, in addition to small amounts of bromides, in order to perform the electrolysis at a satisfactorily low cell voltage.

Experimental

Materials. All the chemicals were commercially supplied and were used, if necessary, after purification by common methods. Platinum electrodes, which were used as the working electrodes, were polished with alumina powder and washed with acetone before used. Graphite electrodes were also polished with an emery paper (No. 1200), washed with water, polished again with the emery paper, and then washed with acetone. Platinum counter electrodes were used after treatment with diluted nitric acid.

Controlled-Potential Electrolysis. All the macro electrolyses of the alcohols were carried out using 40 cm^3 of anodic solutions in a divided cell at room temperature. The electrolyses of Br^- were also carried out in a similar manner.

Product Analysis. Anodic solutions were subjected to gas chromatography (on PEG 20 M column at 120—160 °C) for analysis of products of electrolyses of the alcohols after quenched with aqueous $NaHSO_3$.

Cyclic Voltammetry. All the measurements were carried out at room temperature in an ordinary procedure.

UV-Spectroscopic Measurement. All the spectra were measured in a 1 cm cell, if necessary after dilution of the sample solutions, using a spectrometer (Hitachi Degital Spectrophotometer Model 624).

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