(OH), 1730 (CO), NMR ($CDCl_3$) δ: 0.68 (3H, s), 1.07 (3H, s), 1.19 (6H, s), and 4.98 (1H, d, $J=12$ Hz, 4α-H). *Anal.* Calcd. for $C_{27}H_{45}O_2Br$: C, 67.34; H, 9.42. Found: C, 67.18; H, 9.56.

25-Hydroxycholest-4-en-3-one (4)——To the solution of 3 (1.3 g) in dry dimethylformamide (20 ml), Li_2CO_3 (250 mg) was added and the mixture was refluxed for 1 hr. The reaction mixture was diluted with ethyl acetate, and the whole was washed with H_2O, dried over $MgSO_4$, and evaporated. The residue obtained after evaporation of the solvent was purified by column chromatography using a short column of silica gel. Elution with $CHCl_3$ afforded 950 mg of **4**, mp 147—148° (from MeOH), UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm: 260, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3480 (OH), 1660 (CO), 1610 (C=C), NMR ($CDCl_3$) δ: 0.71 (3H, s), 0.96 (3H, s), 1.20 (6H, s), 5.76 (1H, s, 4-H). *Anal.* Calcd. for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 80.62; H, 11.23.

25-Hydroxycholesterol (6)——To a solution of 4 (102 mg) in dry dimethylsulfoxide (5 ml), freshly prepared NaOEt (1 g) was added, and the mixture was stirred at room temperature for 1 hr under argon atmosphere. The reaction mixture was poured into ice water containing AcOH (1 ml), and the separated oil was extracted with ether. The ether layer was washed with aqueous $NaHCO_3$ solution, and then H_2O, and dried over $MgSO_4$. Evaporation of ether gave the crude 5-en-3-one (**5**) (98 mg).

To the solution of $NaBH_4$ (0.2 g) in MeOH (50 ml), the solution of **5** obtained as above in ether (10 ml) was added dropwise for 10 min under cooling in an ice bath, and the stirring was continued for 30 min. After the excess reagent was decomposed by AcOH, the reaction mixture was evaporated to a small volume and extracted with ether. The ether layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography using silica gel. Elution with $CHCl_3$ gave 65 mg of **6**, mp 175—177° (from acetone), which was identified with the authentic sample[10] by mixed melting point determination.

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Catalytic Effects of Metal Ions on the Anodic Oxidation of Ascorbic Acid at a Platinum Electrode

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The catalytic effects of several metal ions on the anodic oxidation of ascorbic acid (I) at a platinum electrode were studied by a linear sweep voltammetry in 1 M perchloric acid. Contrary to the air-oxidation of I, Bi^{3+} and Pb^{2+} exhibit a marked effect whereas Cu^{2+} shows a minor one.

Keywords——ascorbic acid; anodic oxidation; platinum electrode; electro-oxidation; catalytic effect; Faradaic adsorption; metal ions; voltammetry

The copper (II)-catalyzed oxidation of ascorbic acid (I) by molecular oxygen to form dehydroascorbic acid has been recognized as an example of model systems in studying enzymatic oxidation processes. The catalytic effect of copper (II) was previously investigated by the present authors,[2] comparing with that of other metal ions.

The electrochemical oxidation of I has been studied on mercury[3] and platinum[4] electrodes. In both cases a two-electron oxidation of I takes place to form dehydroascorbic acid. It seems interesting to investigate if the electro-oxidation of I is also enhanced by the presence of certain metal ions.

This paper is concerned with a comparison of the catalytic effects of several metal ions on the oxidation of I at a platinum electrode in connection with adsorption–desorption of

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metal ions on the electrode surface. In the present work, the fact that a marked effect is found for Pb^{2+} and Bi^{3+} instead of Cu^{2+} is particularly interesting.

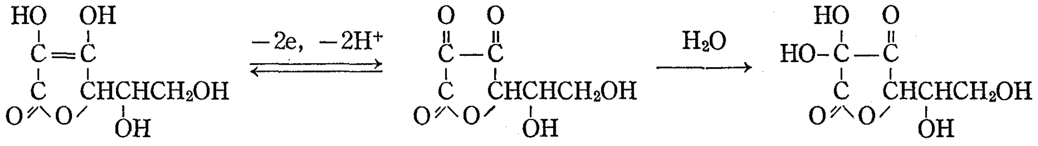
Experimental

The base electrolyte solution of 1 M $HClO_4$ was prepared by dissolving ultrapure grade of 60% perchloric acid in redistilled water. A stock solution of I was prepared by dissolving a known amount of reagent grade *l*-ascorbic acid (Wako Pure Chemical Industries, Ltd.) in the base solution. In preparing the metal solutions the reagent grade metal oxides or sulfates were dissolved in the base solution.

The platinum plate used as a working electrode was 99.99% pure, 0.5 mm thick and 1.0 cm^2 in area. The electrode potential was measured relative to a saturated calomel electrode. Electrolysis was carried out with a linear potential sweep method, the potential being applied from a Hokuto Denko potentiostat (Model PS 1000) in connection with a NF Circuit Design Block function generator (Model FG-104TU) at voltage sweep rate of 100 mV/sec. Before each run to record a potential scan diagram, a sufficient amount of pure nitrogen was bubbled in the electrolytic solution to remove the dissolved oxygen. All the measurements were carried out at 25°.

Results and Discussion

A potential sweep voltammogram (i-E curve) obtained in 1 M perchloric acid containing 5.0×10^{-3} M I is shown in Fig. 1 (curve b), in which an anodic peak at around +0.7 V is clearly seen, but no cathodic peak corresponding to the anodic one is observed. The anodic peak



I

dehydroascorbic acid

Chart 1

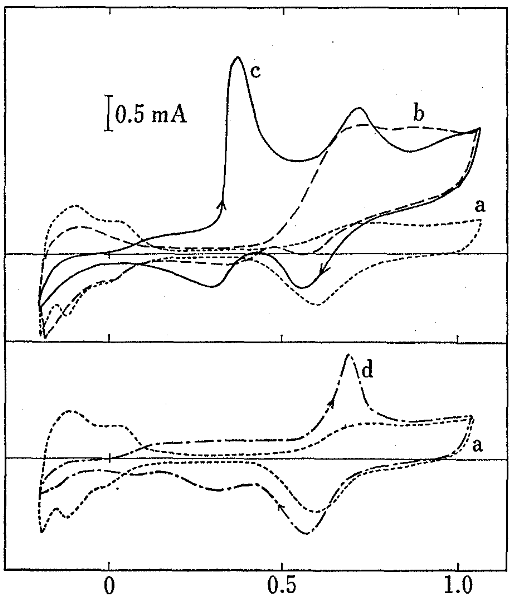


Fig. 1. Effect of Bi^{3+} on Current–Potential (i-E) Curves of I

a: base soln.
b: 5.0×10^{-3}M I.
c: 5.0×10^{-3}M I + 1.4×10^{-4}M Bi^{3+}.
d: 1.4×10^{-4}M Bi^{3+}.

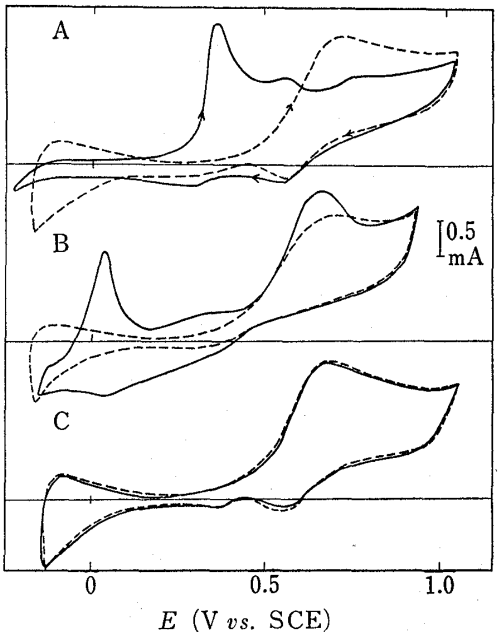


Fig. 2. Effects of Pb^{2+}, Cu^{2+} and Co^{2+} on i-E Curves of 5.0×10^{-3} M I

A: 2.0×10^{-4}M Pb^{2+}, B: 2.5×10^{-3}M Cu^{2+},
C: 2.0×10^{-4}M Co^{2+}.
Dashed line: curves obtained without metal ions.

is attributed to the reaction in Chart 1,[4] where I is oxidized through a two-electron reaction to form dehydroascorbic acid, followed by an irreversible hydration immediately. Adsorption of I on the electrode surface prior to the electron transfer was confirmed by Koryta *et al.*[4]

The presence of Bi^{3+} gives rise to a marked change in the anodic peak of I (Fig. 1, curve c), that is, the peak potential (E_p) shifts to the negative potential side and the peak current (I_p) at E_p increases with increasing concentration of Bi^{3+}. Such a trend is most evident when Bi^{3+} concentration is of the order of 10^{-4} M (E_p goes down to +0.37 V). However, in the presence of Bi^{3+} more than 10^{-3} M, E_p goes back to the positive potential side and I_p decreases. The controlled-potential electrolysis at +0.37 V with the same solution as used in the measurement of the curve c in Fig. 1 led to the decrease of I_p together with the lowering of absorption spectrum of I, and the number of electrons consumed in the oxidation of I was determined as approximately 2. The result clearly indicates that the peak at +0.37 V is also attributed to the anodic oxidation of I. Then it can be considered from this fact that an acceleration of the oxidation by Bi^{3+} brings about the shift in E_p.

Effects of Pb^{2+}, Cu^{2+} and Co^{2+} on the i-E curve of 5.0×10^{-3} M I were also examined. As seen in Fig. 2, Pb^{2+} shows a marked effect similar to that observed with Bi^{3+}. The presence of Cu^{2+} scarcely affects E_p but results in an increase in I_p slightly, so that the catalytic effect of Cu^{2+} is smaller than Bi^{3+} and Pb^{2+}. Co^{2+} gives no significant change in the anodic peak of I. The result is in a contrast to that observed in the air oxidation of I in which Cu^{2+} exhibits a marked activity compared with other metal ions.[2]

No appreciable interaction would be expected between I and metal ions in bulk solution under the present experimental condition. Actually, all the UV spectra of I obtained in 1 M perchloric acid solutions containing each metal ion were essentially identical to the spectrum of I itself. Then it appears likely that metal ions exhibit their catalytic activity not in the solution but at the electrode surface.

Recently, adsorption phenomena involving metal deposition at underpotentials (so-called Faradaic adsorption which proceeds in the potential region more positive than the reversible potential of M^{n+}/M° couple) have been extensively investigated from the electrochemical standpoint.[5] The i-E curve of 1.4×10^{-4} M Bi^{3+} in the base electrolyte without I is shown in Fig. 1 (curve d). The cathodic and anodic peaks are clearly seen at +0.30 and +0.72 V, respectively. The former corresponds to the formation of adsorbed Bi (denoted as Bi_{ad}) and the latter, the dissolution of Bi_{ad}. Both the processes are expressed as,[6]

$$Bi^{3+}(aq) + 3e \rightleftharpoons Bi_{ad}$$

As seen on the anodic branch of curve d, Bi_{ad} remains on the electrode surface until potential sweep reaches around +0.8 V, at which the anodic current falls to the current corresponding to the formation of platinum oxide (*cf.* curve a). Since the oxidation of I initiates at more negative potentials than this potential, I will be oxidized on the electrode surface covered partially by Bi_{ad}. Similar situations are also encountered in the presence of Pb^{2+} and Cu^{2+}. On the other hand, such adsorption does not take place on platinum in the presence of Co^{2+} in the observed potential region. Then it is obvious from all the results stated above that the adsorbed metal (M_{ad}) on platinum plays an important part in the promotion of the anodic oxidation of I.

The catalytic effect may be correlated to the surface coverage of M_{ad} (denoted as θ_M). In the case of Bi^{3+} the plots of E_p and I_p against θ_{Bi} are illustrated in Fig. 3 (θ_{Bi} was evaluated from the charge for the anodic dissolution of Bi_{ad}). The maximal enhancement for the oxi-

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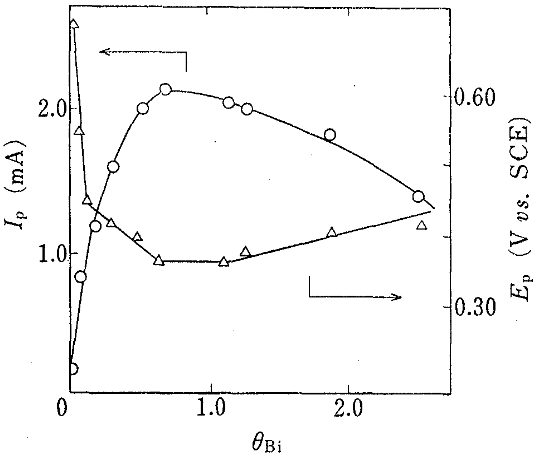

Fig. 3. Dependence of Peak Current (I_p) and Peak Potential (E_p) on Surface Coverage of Bi_{ad} (θ_{Bi})

I_p and E_p were obtained on i-E curves of 5.0×10^{-3}M I in the presence of various concn. of Bi^{3+}.

dation of I is attained at θ=0.5—0.7, that is, the absorbed metals in submonolayer region exhibit the maximal catalytic effect.

The interpretation of such peculiar effects of M_{ad} formed on a platinum electrode can not be made in detail at this time. However, it can be considered that the presence of M_{ad} results in an increase of activated water species (like OH_{ad}) on platinum which behaves as an electron captor for I. This concept would be probable from the analogy to the behavior of adsorbed water in the anodic oxidation processes of some organic compounds on a platinum electrode.[7] Excessive coverage of M_{ad} may lead to lowering of its catalytic activity as a result of the decrease in the active sites on platinum for the adsorption of water and I itself.

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Reaction of α,β-Unsaturated Ketones with Hydrazine Derivatives

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1,3-Diaryl-2-propen-1-one (I) reacted with aroyl- and acyl-hydrazines and ethyl hydrazinecarboxylate (II) in the presence of piperidine to give the corresponding α-[3-(1,3-diaryl-propan-1-one)]-β-acyl or-aroyl-hydrazines and ethyl β-[3-(1,3-diaryl-propan-1-one)]-hydrazine-carboxylate (IV), respectively. The structure and configuration of these compounds are based on chemical analysis and spectroscopic evidence.

Keywords——1,3-diaryl-2-propen-1-one; α-[3-(3-diaryl-propan-1-one)]-β-aroyl or acyl-hydrazines; ethyl β-[3-(1,3-diaryl-propan-1-one)]-hydrazinecarboxylate; synthesis; spectroscopy

The reaction of 1,3-diphenyl-and 3-aryl-1-methyl-2-propen-1-ones with alkyl hydrazinecarboxylate in the presence of acetic acid has been reported to give the corresponding hydrazonecarboxylic esters.[2] The present investigation was intended to study the reaction of 1,3-diaryl-2-propen-1-ones (I) with acyl- and aroyl-hydrazines and ethyl hydrazinecarboxylates in the presence of piperidine as a catalyst and to account for the manipulated methods

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