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Electrooxidation of Olefins at a Silver Electrode[1]

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The anodic oxidation of ethylene and propylene was carried out at a silver electrode under constant current conditions (galvanostatic) with the olefin and/or oxygen dissolved in the alkaline electrolyte at 23 ± 2°C. At current densities in the range of 10^{-5} to 10^{-9} A/cm^2, the anodic oxidation of silver was accelerated in the presence of dissolved oxygen and retarded in the presence of ethylene. Product analysis demonstrated the formation of ethylene glycol under anodic oxidation conditions in the presence of ethylene and of propylene oxide in the presence of propylene. A mechanism is proposed to elucidate the effects of oxygen and ethylene on the anodic oxidation of silver and ethylene.

INTRODUCTION

Because of its relationship to fuel-cell technology, the electrooxidation of hydrocarbons has received considerable attention in recent years. In most cases these reactions were studied in the presence of noble-metal electrodes and complete oxidation was the goal. In the case of ethylene, the oxidation has been examined on platinum and other noble-metal electrodes in acid and alkaline media (*1*). For some of the alkanes, the buildup of adsorbed species on platinum in an acid solution has been reported (*2*).

In the present study we selected silver as the electrode for anodic oxidation of ethylene in an attempt to explore the feasibility of partial oxidation to ethylene oxide (or ethylene glycol in alkaline solution). Also it was hoped that the information derived from electrochemical studies might shed some light on the mechanism of ethylene oxide formation by heterogeneous gas-phase oxidation of ethylene on silver-based catalysts. The anodic oxidation of silver in alkaline solution (free of dissolved gases) has demonstrated the existence of potential steps on the galvanostatic charging curves (*3–6*). These steps have been associated with the formation of silver oxides of different stoichiometry, which have been identified recently by X-ray diffraction (*7*). Thus the oxidation of a silver electrode under potentiostatic (constant voltage) and galvanostatic (constant current) conditions appears to involve the oxides Ag_2O, AgO, and Ag_2O_3. Also another oxide AgO_x has been postulated (*7*) recently with a silver-to-oxygen ratio between 2:1 and 1:1. In all these measurements special precautions were taken to remove dissolved gases from the electrolyte solution. In the work to be described, polycrystalline silver sheets were anodically oxidized at constant current in an alkaline solution. The electrolyte was exposed to gas mixtures of different compositions containing nitrogen, oxygen, and olefin.

EXPERIMENTAL DETAILS

The three-electrode electrochemical cell shown schematically in Fig. 1 contained a silver anode, a platinum cathode, and a

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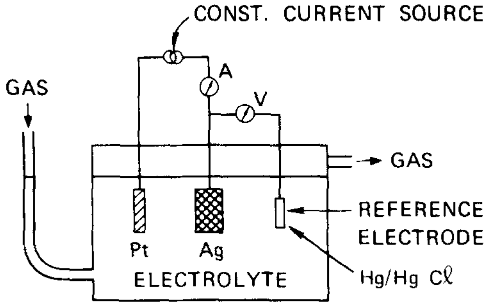

FIG. 1. Schematic diagram of apparatus employed in electrooxidation of ethylene.

saturated calomel electrode employed as a reference cell. A conventional galvanostatic technique was used for the experimental measurements. The potential of the silver electrode, which is related to the thickness of the oxide layer, was monitored by means of a recording voltmeter. The working electrode was cut from a sheet of silver (+99.999%) in the form of a disk (1 cm^2 geometric area). It faced the counter electrode, a platinum wire (+99.99%) located at a distance of 1 cm from the vertically suspended silver surface. The calomel reference electrode was contained in a side arm attached to the electrochemical cell.

Through the electrolyte (10 cc of 8.7×10^{-3} N NaOH) bathing these electrodes, a gas stream was passed whose composition was controlled by quantitative admixture of various gases monitored by rotameter flowmeters. For the experiments without dissolved oxygen or ethylene, a stream of nitrogen was bubbled through the electrolyte until a constant open-circuit potential (rest potential) was recorded. Similarly for the gas mixtures containing oxygen and/or ethylene, the solution was allowed to come to equilibrium with the gas phase as monitored by a gradual approach to a constant open-circuit potential whose value depended on the gas composition and the degree of oxidation of the silver electrode.

The silver electrode was pretreated by mechanical abrasion of the surface with fine alumina powder (3200 mesh) and thorough rinsing in ethanol and distilled water. In addition, the surface was reduced cathodically by filling the cell with a solution of 1 N H_2SO_4. Subsequently the cell was flushed with distilled water and several aliquots of the alkaline electrolyte employed in the electrochemical studies. All measurements were carried out at ambient temperatures (23 ± 3°C).

RESULTS

At current densities of the order of 10^{-3} A/cm^2 the anodic charging curves for silver in NaOH solution exhibited the characteristics reported by several authors (*4,6,7*). Following a rapid buildup of potential, one observes two pronounced steps associated with the formation of silver oxides of different stoichiometry, Ag_2O and AgO. Finally a potential is reached at which oxygen evolution occurs.

We worked predominantly at current densities of the order of 10^{-7} A/cm^2 in order to examine the electrooxidation kinetics of silver in the presence of O_2 and C_2H_4 dissolved in the electrolyte. Under these conditions the measurements were confined most likely to solid phases with an oxidation state of the silver surface intermediate between silver metal (Ag^0) and Ag_2O (Ag^+). A typical anodic polarization curve shown in Fig. 2 was obtained at relatively low current densities ($<10^{-5}$ A/cm^2) in an oxygen-free electrolyte. We have excluded from this curve the small but steep voltage change associated with the establishment of a space-charge layer when the galvanostatic circuit is closed. An increase in current density over a range of two orders of magnitude of 10 indicates a linear dependence of the initial slope $(dV/dt)_i$ on current. At current densities less than 10^{-9} A/cm^2 the reproducibility of the data became poor.

Of special interest is the variation in the initial slope of the potential vs Faraday curve as a function of the partial pressure of oxygen in contact with the electrolyte.

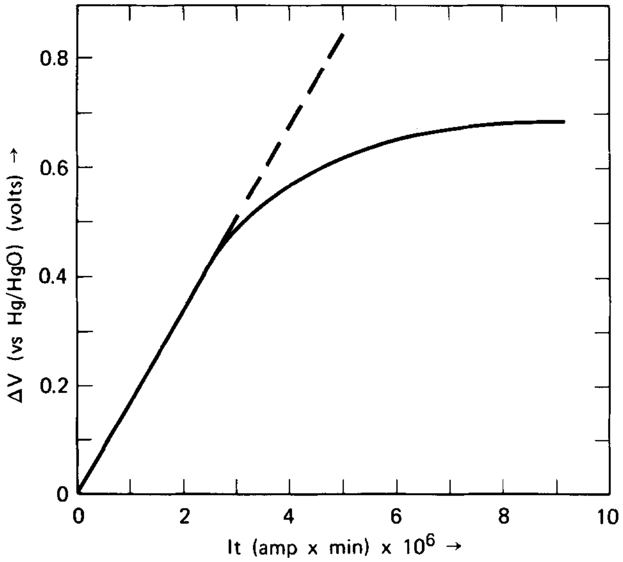

FIG. 2. Anodic polarization curve for silver (current density: 7 × 10^{-8} A/cm^2; temperature: 23°C).

These results are summarized in Fig. 3. The oxidation rate of the silver surface is materially accelerated in the presence of dissolved oxygen as evidenced by the increase in the initial potential change per Farady [$\Delta V_i/\Delta(It)$]. An effect of opposite sign is observed in the presence of ethylene bubbled through the electrolyte. Here a reduction in the anodic oxidation rate of silver occurs, which again is a function of the ethylene partial pressure in contact with the electrolyte (Table 1). In the presence of a gas mixture containing ethylene and oxygen, the potential change per Faraday exhibits an intermediate value between that corresponding to the given mole fraction of ethylene or oxygen alone (Table 1). On the basis of this additive effect, one may conclude that the oxidation process is promoted by oxygen and retarded by ethylene. These results suggested the possible formation of olefin oxidation products.

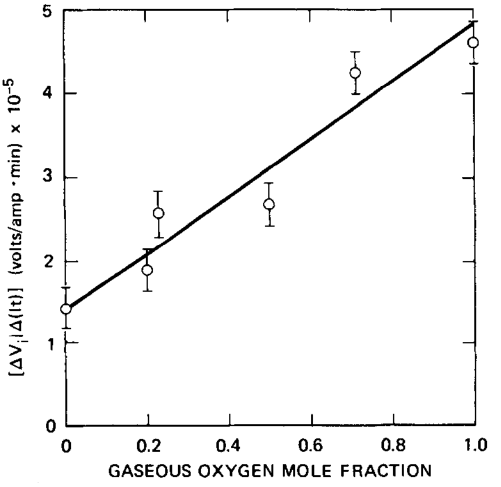

FIG. 3. Rate of change of potential ΔV with time at various partial pressures of oxygen. (ΔV vs saturated Hg/HgCl; current density varied from 10^{-9} to 10^{-7} A/cm^2; temperature 23°C).

Although carbon dioxide, one of the products of complete oxidation, could not

TABLE 1

INITIAL RATE OF ANODIC POTENTIAL CHANGE AS A FUNCTION OF OXYGEN AND ETHYLENE[a]

O_2	C_2H_4	N_2	$\Delta V_i/\Delta(It)$ (V/A min) 10^{-5}
0	0	1.0	1.4
0	0.13	0.87	0.60
0	0.17	0.83	0.46
0.17	0	0.83	1.9
0.17	0.17	0.66	0.92

[a] Experiments at constant current density of 8.7 × 10^{-7} A/cm^2.

be detected in the alkaline electrolyte solution because of the conversion to carbonate ion, the existence of partial oxidation products, such as epoxy compounds, was considered. For chemical analysis of the olefin oxidation products, aliquots of the liquid electrolyte were withdrawn and injected into a gas chromatographic apparatus provided with a flame ionization detector (Hewlett-Packard Model No. 5750). The column material was composed of Porapak Q (Water Associates, Inc.). Good separation of water, ethylene glycol, propylene glycol, and their respective epoxy compounds was achieved by operating the column at 453°K with helium as the carrier gas.

At anodic current densities in the range 10^{-6} to 10^{-7} A/cm^2 and an electrolyte temperature of 296°K the formation of ethylene glycol was detectable. In accordance with the reaction:

$$C_2H_4 + 2\ OH^- \rightarrow C_2H_4(OH)_2 + 2e,$$

one computes for a typical experiment of 3.24×10^{-6} A sec a maximum Faraday efficiency for the dihydroxy-compound of 6×10^{-7} moles. Semiquantitative analysis by gas chromatography of the solution indicated a yield of about 10^{-7} moles. In view of the lack of accuracy of the analytical procedure it is not established what fraction of the ethylene was converted to the glycol and what fraction underwent complete oxidation. However, we did observe that under the same conditions the introduction of a mixture of ethylene and oxygen into the solution led to complete oxidation of the olefin. As a matter of fact, the ethylene glycol, formed earlier in the experiment in the absence of added oxygen, gradually disappeared from solution, indicative of further oxidation in the presence of dissolved oxygen.

The introduction of propylene into the electrolyte resulted in the formation of propylene oxide (rather than propylene glycol) during anodic oxidation on a silver electrode. Material yields were comparable to those found during ethylene oxidation.

DISCUSSION

The experimental results show that the partial oxidation of olefins is promoted under anodic conditions on silver and gold surfaces as manifested by the formation of ethylene oxide (or glycol) and propylene oxide from ethylene and propylene. Although incomplete, the data suggest, in the case of silver, that the maximum rate of ethylene oxide formation occurs on a fresh or partially oxidized silver surface. Once the electrode has been oxidized to Ag_2O or AgO, the rate of ethylene oxide production is diminished. An attempt was made to carry out the oxidation process at low current densities in order to favor the oxidation of the olefin over that of the silver electrode. Such experiments indicated that the limiting step in olefin oxidation may be the adsorption of the olefin molecules. Since the solubility of these organic molecules in the electrolyte is relatively low, the degree of surface coverage with olefins is small. By operating in a high-pressure system, one may overcome such a limitation and enhance the yield of epoxy compound.

Of interest is the effect of dissolved oxygen on anodic oxidation of the silver electrode and on olefin oxidation. Since the rate of oxide-layer growth on the silver electrode is increased in the presence of oxygen a reaction mechanism is suggested involving the formation of an O_3^- species as a consequence of the following steps:

$$OH^- \rightarrow OH^{\cdot} + e, \qquad (1)$$

$$OH^{\cdot} + OH^- \rightarrow O^- + H_2O, \qquad (2)$$

$$O^- + O_2 \rightleftarrows O_3^- \qquad (3)$$

As a result the conventional step of anodic oxidation of the metal electrode M by

$$M + 2\ OH^-_{(s)} \rightarrow M\text{-}O_{(s)} + H_2O + 2e \quad (4)$$

or

$$M + O^-_{(s)} \rightarrow M\text{–}O_{(s)} + e \qquad (5)$$

would be replaced by the more rapid reaction

$$M + O^-_{3(s)} \rightarrow M\text{–}O_{(s)} + O_2 + e. \qquad (6)$$

The O_2 produced in step (6) undergoes surface reaction (3) so that no net O_2 evolution occurs.

The inhibition in anodic oxidation rate due to ethylene may be associated with a surface coverage of the metal by the olefin or, its interaction with one of the species involved in the metal-oxidation process. In the former case the oxidation rate of the metal surface would decrease because the olefin reduces the number of surface sites available for the oxygen-containing species. Such a process could be interpreted as a "surface-poisoning" effect. However since C_2H_4 does not adsorb on a silver surface it is more likely that competition for the oxygen-containing species by the metal on one hand and the olefin on the other lead to the reduction in oxidation rate and conversion of the ethylene to another product. Our experimental study demonstrates that a silver electrode has the property of promoting partial oxidation of olefins.

Thus, in the electrooxidation of ethylene on silver, we may be dealing with a reaction sequence such as the following:

$$C_2H_4 + O^-_{(s)} \rightarrow C_2H_4O + e$$

or

$$C_2H_4 + 2\ OH^-_{(s)} \rightarrow C_2H_4(OH)_2 + 2e.$$

The different oxygen species involved could also account for the variation in product distribution during the electrooxidation of ethylene. While the $O^-_{(s)}$ species would favor the formation of the epoxy compound, the $O^-_{3(s)}$ species [Eq. (3)] leads to complete oxidation of the olefin molecule.

To explain the difference in the degree of electrooxidation of ethylene exhibited by various metals, Blake *et al.* *(9)* suggested that the anodic oxidation of C_2H_4 on a palladium electrode in sulfuric acid solution involves the formation of a Pd–organic complex in solution and not the heterogeneous oxidation of a chemisorbed species. Similar conclusions were drawn by Goodrich and King *(10)* in a more recent study on the Pd/C_2H_4 system. Ethylene–Pd complexes in solution, such as Pd $(C_2H_4)^{2+}$, have been proposed as intermediates in the homogeneous oxidation of ethylene to acetaldehyde and in the dimerization of ethylene to butene. Also the chemistry and stability of silver(I) ion/olefin complexes was examined *(11)*. However, our experimental work did not indicate their presence.

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