The Kinetics and Mechanism of the Oxidation of Amines and Alcohols at Oxide-covered Nickel, Silver, Copper, and Cobalt Electrodes

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A series of alcohols and amines have been oxidised at oxide-covered nickel, silver, copper, and cobalt anodes in aqueous alkaline solutions. The kinetics of these electrode processes have been studied and it is shown that the mechanism of these oxidations involves hydrogen abstraction from the substrate by an oxide species rather than direct electron transfer to the anode. The mechanism put forward is compared with those commonly suggested for the chemical reactions of transition-metal oxides and for heterogeneous catalysis.

UNTIL recently there have been few systematic studies of the partial anodic oxidation of organic compounds at electrodes other than platinum or carbon; early work on passivated iron, nickel, and lead electrodes has been summarised in two reviews.[1,2] The last seven years have seen a number of papers and patents which describe selective oxidation processes at oxide electrodes; these include the oxidation of amines [3,4] and amino-acids [5] at silver oxide anodes, the oxidation of 2,3:4,6-di-*O*-isopropylidenesorbose,[6] ethylene glycol,[7] acridine,[8] alcohols,[9-11] and amines [11] at nickel oxide electrodes and the oxidation of amines and alcohols [12] at a cobalt oxide anode.

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In this paper we compare kinetic and synthetic measurements at oxide-covered nickel, cobalt, copper, and silver electrodes and contrast the reactions with those observed at carbon anodes. These data are used to suggest a detailed mechanism for these reactions which is compared with mechanisms which have been suggested for chemical reactions of transition-metal oxides in aqueous solution and for gas-phase oxidations where the oxides are used as heterogeneous catalysts.

The substrates chosen for this study were aliphatic amines and alcohols since they are simple compounds whose structure is readily varied and are both stable and highly soluble in the rather basic solution required to make the transition metal electrodes passive.

EXPERIMENTAL

The electrochemical experiments were carried out in three-compartment cells with use of a Chemical Electronics valve potentiostat and pulse generator (R.B.1); current–potential curves were recorded on a Bryans series 26000 XY recorder. The reference electrode, against which all potentials in this paper are quoted, was mercury–mercuric oxide in 1M-potassium hydroxide and it was separated from the working electrode by a Luggin capillary and tap. The platinum sheet secondary electrode and the working electrode were separated by an ion-exchange membrane, Permaplex C-20. The working electrodes were constructed from Johnson–Matthey Specpure metals supplied in the form of 5 mm rods. In kinetic experiments the electrodes were in the form of small discs surrounded by Teflon sheaths and mounted so that they could be rotated. Before being used for measurements they were carefully polished and then subjected to a number of potential cycles between 0 and +0·8 V. In preparative electrolyses the working electrode was a rod of the metal with an exposed area of 5 cm^2.

The solutions were prepared from B.D.H. AnalaR potassium hydroxide and triply distilled water and in some experiments AnalaR potassium nitrate was added in order to maintain a constant ionic strength between solutions of varying pH. The deuteriated methanol was supplied by Ryvan Chemical Co Ltd., while the other organic compounds were used as obtained from B.D.H. Ltd. or Koch–Light Ltd.

The pH values of the solutions were determined by acidimetric titration or were measured on a Radiometer pH meter 26. All measurements were made at room temperature except for the determination of activation energies which were carried out with an air thermostat.

Qualitative and quantitative analyses were carried out on a Pye 104 vapour-phase chromatograph with 2 m columns of 10% poly(propylene glycol) on Celite, 10% poly(ethylene glycol) adipate + 1% phosphoric acid on Celite, and 10% potassium hydroxide on Phasepak Q for the ketones, acids, and amines respectively. The analyses were carried out isothermally at suitable temperatures with nitrogen carrier gas. In many cases the product identification was confirmed by use of v.p.c.–mass spectrometry (A.E.I. MS 12 mass spectrometer).

RESULTS

Anodic Behaviour of the Metals in Potassium Hydroxide Solutions.—On anodic polarisation in alkaline media, the surface of each of the metals studied becomes covered with a passive layer of oxide or hydroxide and no steady-state process occurs before oxygen evolution. Changes in the surface layer do, however, take place and these can be studied by non-steady-state techniques. Hence, before discussing the oxidation of organic compounds at transition metal electrodes we must summarise the changes which occur and discuss their kinetics.

Nickel. When nickel is placed in contact with 1M-potassium hydroxide its surface becomes spontaneously covered with nickel(II) hydroxide.[13] A linear potential sweep in an anodic direction at 0·3 V s^{-1} shows a peak 150 mV before oxygen evolution.[11] This is due to the process (1) and the charge under this peak indicates that the

$$\mathrm{Ni(OH)_2} \longrightarrow \mathrm{NiO(OH)} + \mathrm{H^+} + e \qquad (1)$$

surface is covered by only a few monolayers (0·5—4·0) of the nickel(III) species. Linear sweeps using various concentrations of hydroxide ion shows that $(\mathrm{d}E/\mathrm{dpH})_i = 60$ mV showing that the reaction is of the first order with respect to hydroxide ion while for each pH, the peak potential is independent of sweep rate and the peak current is proportional to the potential sweep rate. Hence the formation of the thin layer of the higher oxide follows a Langmuir isotherm, the establishment of the equilibrium being rapid compared with the sweep rate and this is also shown by a plot of coverage against the function of potential appropriate to the Langmuir isotherm[14] (Figure 1). In contrast, for thick layers of nickel hydroxide, diffusion of the electroactive species in the film becomes rate-determining.[15,16]

Cobalt. The surface of cobalt readily becomes covered with cobalt(II) hydroxide and this change is well characterised.[17] Although a further transition to a cobalt(III) oxide does occur before oxygen evolution,[18] it is markedly retarded and a linear potential sweep experiment shows a rather drawn-out wave for this process in contrast to the well formed peak obtained for the corresponding transition on nickel. Further a significant self-discharge reaction occurs[12] and hence the exact nature and thickness of the cobalt(III) oxide is uncertain.

Silver. A linear potential sweep experiment on a silver anode shows two distinct peaks for the transitions silver to argentous oxide and argentous oxide to argentic oxide.[19] Both these reactions have been well characterised.[20-22] A linear sweep study of the latter process shows that the charge under this peak is dependent on the pH and sweep rate; in 1M-potassium hydroxide and at a sweep rate of 0·1 V s^{-1} the charge is 11—14 mC cm^{-2} confirming that we are dealing with a multilayer of argentic oxide.

Although the interpretation of the conversion of argentous

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into argentic oxide is complicated by the fact that the process is controlled by nucleation and crystal growth of the higher oxide,[22] it is of interest that the peak potentials observed in the linear sweeps vary according to $(dE_p/dpH) = 60$ mV, indicating that the process is of the first order with respect to hydroxide ion in this potential range. This agrees with earlier observations; at higher potentials the reaction becomes of zeroth order with respect to hydroxide ion.[22]

Argentic oxide is correctly formulated as a silver(I)–silver(III) mixed oxide as shown by its diamagnetism [23] and by neutron diffraction.[24]

Copper. The changes copper to copper(I) and copper(I) to copper(II) which occur on anodic polarisation of the metal have been widely studied.[25-27] A linear potential sweep experiment carried on beyond these processes and into the oxygen evolution current shows signs of a further change in the surface which occurs concurrently with oxygen evolution. Miller has used ring disc electrodes to confirm that indeed a copper(III) species is being formed [28] and cyclic voltammetry shows the reverse copper(III) to copper(II) transition. The inflection in the *i–E* curve at 0·65 V which corresponds to the copper(II)–copper(III) change is too close to the oxygen evolution current for detailed study. It is apparent from the charge under the peaks, however, that the electrode will be covered by a multilayer of the copper(III) species.

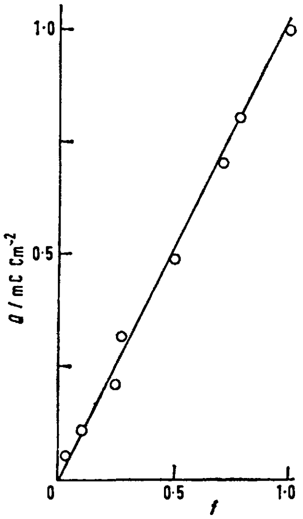

FIGURE 1 Plot of charge per cm^2 against the function $f = [\exp(F\Delta E/RT)]/[1 + \exp(F\Delta E/RT)]$ for a nickel anode in aqueous 1M-potassium hydroxide; $\Delta E = E - E_p$ where E_p is the peak potential. This plot gives a value of 1·00 mC cm^{-2} for saturation coverage

For the metals nickel, cobalt, and silver, the mechanism for the formation of their highest surface oxide can and have been written as in Scheme 1 and it is probable that the copper(II)–copper(III) transition conforms to this pattern.

Oxidation of Amines and Alcohols at the Oxide-covered Electrodes.—Voltammograms and polarisation curves were obtained for the oxidation of a wide range of aliphatic alcohols and amines at nickel, cobalt, silver, and copper in aqueous 1M-potassium hydroxide. For each of the compounds listed in Table 1, the voltammograms showed a steady-state current at potentials where, in the absence of an organic compound, only a non-steady-state current had been observed for the surface transitions $Ni^{II} \rightarrow Ni^{III}$, $Co^{II} \rightarrow Co^{III}$, $Ag^{I} \rightarrow Ag^{II}$ and $Cu^{II} \rightarrow Cu^{III}$. The oxidation waves were well formed although the limiting currents on the plateaux of these waves were much smaller than those expected for a diffusion-controlled process; further experiments with rotating disc electrodes showed that the currents were independent of the rotation speed of the electrodes and hence kinetically controlled. The voltammograms for the oxidation of amines at a silver anode also showed a process occurring at potentials where the surface of the electrode is covered with argentous oxide. This process has been shown [3] to be the corrosion reaction (2). No corrosion of the silver occurs in the absence of an amine or once argentic oxide covers the electrode surface.

$$OH^- \rightleftharpoons OH_{ADS} + e$$

$$\text{Lower oxide} + OH_{ADS} \xrightarrow[\text{step}]{\text{Rate-determining}} \text{higher oxide}$$

SCHEME 1

$$2Ag + 2OH^- + nRNH_2 \xrightarrow{-2e} H_2O + Ag_2O(RNH_2)_n \quad (2)$$

TABLE 1

Rate constants, k, for the oxidation of organic substrates at the metal oxide electrodes calculated from equation (4) by use of steady-state current–concentration plots at the potentials indicated below

	Rate constant, k/cm s^{-1}			
Substrate	Nickel (0·6 V)	Silver (0·85 V)	Copper (0·7 V)	Cobalt (0·6 V)
Methylamine	$1·1 \times 10^{-4}$	$1·9 \times 10^{-4}$	$2·8 \times 10^{-4}$	$1·8 \times 10^{-5}$
Ethylamine	$7·0 \times 10^{-5}$	$1·4 \times 10^{-4}$	$1·4 \times 10^{-4}$	$9·0 \times 10^{-6}$
n-Propylamine	$4·2 \times 10^{-5}$	$8·2 \times 10^{-5}$	$1·1 \times 10^{-4}$	$5·5 \times 10^{-6}$
n-Butylamine	$3·7 \times 10^{-5}$	$6·3 \times 10^{-5}$	$1·0 \times 10^{-4}$	$4·5 \times 10^{-6}$
s-Propylamine	$1·3 \times 10^{-5}$	$2·6 \times 10^{-5}$	$8·0 \times 10^{-5}$	$<10^{-6}$
s-Butylamine	$8·0 \times 10^{-6}$	$1·2 \times 10^{-5}$	$7·3 \times 10^{-5}$	$<10^{-6}$
t-Butylamine	$<10^{-7}$	$<10^{-7}$	$1·0 \times 10^{-6}$	$<10^{-6}$
Diethylamine	$2·4 \times 10^{-6}$	$3·6 \times 10^{-6}$	$5·6 \times 10^{-5}$	$<10^{-6}$
Pyrrolidine	$6·0 \times 10^{-5}$	$6·8 \times 10^{-5}$	$2·15 \times 10^{-4}$	$<10^{-6}$
Methanol	$7·0 \times 10^{-6}$	$4·5 \times 10^{-6}$	$6·2 \times 10^{-5}$	$<10^{-6}$
Ethanol	$8·5 \times 10^{-6}$	$2·5 \times 10^{-6}$	$4·0 \times 10^{-5}$	$<10^{-6}$
n-Propanol	$5·2 \times 10^{-6}$	$2·0 \times 10^{-6}$	$2·4 \times 10^{-5}$	$<10^{-6}$
Propan-2-ol	$4·0 \times 10^{-6}$	$<10^{-6}$	$1·1 \times 10^{-5}$	$<10^{-6}$
Mandelic acid	$7·0 \times 10^{-5}$	$7·0 \times 10^{-5}$	$3·8 \times 10^{-4}$	$4·5 \times 10^{-5}$

Steady-state polarisation curves were run at each metal for various concentrations of the organic substrates and at various solution pH; typical curves, those for n-butylamine at a copper anode, are shown in Figure 2 (similar curves at nickel anodes have been published [11]). The concentration-dependences of these polarisation curves indicate that at copper and nickel anodes, the electrode reaction is of the first order in the Tafel region and of zeroth order in the limiting current region with respect to the hydroxide-ion concentration but of first order with respect to the concentration of the organic substrate over the whole potential

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range (provided its concentration is less than 0·2M); the Tafel slope is (60 mV)$^{-1}$. The corrosion of silver at less anodic potentials and the low current densities combined with the self-discharge reaction at cobalt, prevent accurate kinetic data being obtained at these metals in the Tafel region. In the limiting current region, however, the currents are again of the first order with respect to the concentration of the organic compound and zeroth order with respect to hydroxide ion. Current–concentration plots, measured at a potential in the limiting-current region, for a series of organic compounds at each of the metals are shown in Figure 3. At concentrations above about 0·2M, these plots show deviations from linearity.

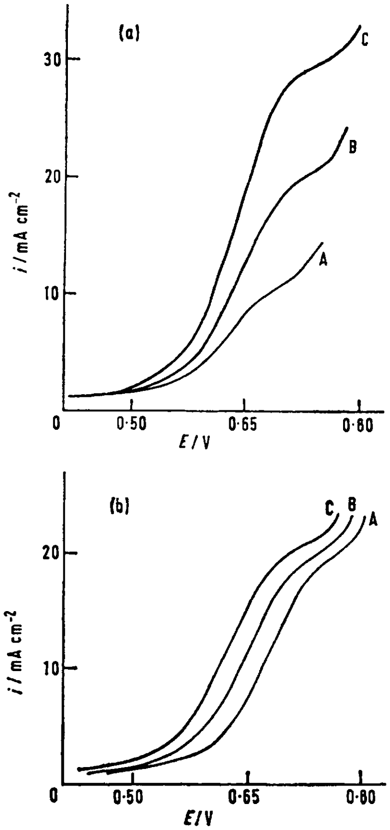


FIGURE 2 i–E curves for n-butylamine in potassium hydroxide at a copper anode: (a) Solutions in 1M-KOH; A, 0·05M-n-butylamine; B, 0·09M-n-butylamine; C, 0·17M-n-butylamine; (b) Solutions 0·09M in butylamine and at constant ionic strength; A, 0·19M-OH$^-$; B, 0·60M-OH$^-$; C, 2·00M-OH$^-$

Cyclic voltammograms were also run on these systems. In the absence of an organic substrate, peaks or waves are obtained on the sweep towards more anodic potentials for the surface transitions $\mathrm{Ni^{II} \rightarrow Ni^{III}}$, $\mathrm{Co^{II} \rightarrow Co^{III}}$, $\mathrm{Ag^{I} \rightarrow Ag^{II}}$, and $\mathrm{Cu^{II} \rightarrow Cu^{III}}$ and on the sweep towards cathodic potentials the reverse processes are observed. On addition of an alcohol or amine, waves at a much higher current density are obtained on the positive-going sweep while at normal sweep rates (0·1—1·0 V s^{-1}) the cathodic peak on the negative-going part of the ramp is removed completely; at higher sweep rates (30 V s^{-1}) the cathodic peak is again observed.

These observations are in accord with the mechanism of Scheme 2. It has been shown [11] that if the rate-determining step is assumed to involve a molecule of the organic compound which is not adsorbed on the anode surface, then this

$$\mathrm{OH^- + lower\ oxide \underset{k_E'}{\overset{k_E}{\rightleftharpoons}} higher\ oxide + H_2O + e}$$

$$\text{Higher oxide + organic substrate} \xrightarrow[\text{rate-determining step}]{k_C} \text{lower oxide + intermediate}$$

$$\text{Intermediate} \xrightarrow{\text{fast}} \text{product} + (n-1)\ \mathrm{e}$$

SCHEME 2

mechanism leads to a current in the Tafel region given by equation (3) where A is the electrode area, β the roughness

$$i = nFA\beta \frac{k_C k_E}{k_E'} C_{\mathrm{org}}\, C_{\mathrm{OH^-}} \exp \frac{F\phi}{RT} \qquad (3)$$

factor, and ϕ the electrode potential; and a limiting current given by equation (4). It can be seen that equations (3)

$$i = nFA\beta k_C C_{\mathrm{org}} = nFAkC_{\mathrm{org}} \qquad (4)$$

and (4) reproduce the concentration-dependences of the polarisation curves and the Tafel slopes. Further equation (4) can be used to determine the ' rate constant,' k, provided n, the total number of electrons transferred in the electrode reaction, can be found. In Table 1, the ' rate constants ' for a selection of alcohols and amines at each of the metals are listed. Tertiary amines and alcohols do not oxidise.

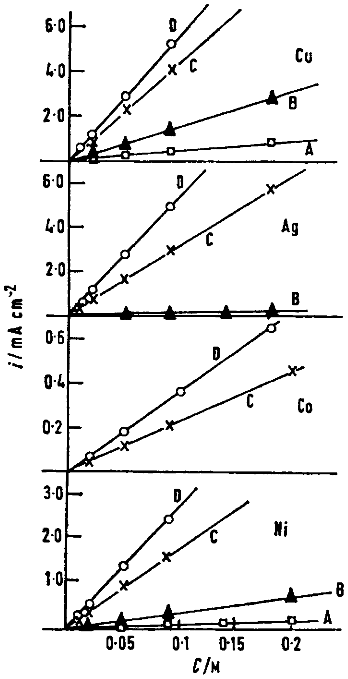


FIGURE 3 Current–concentration plots at nickel, cobalt, silver, and copper anodes in 1M-potassium hydroxide; A, propan-2-ol; B, ethanol; C, n-propylamine; D, ethylamine

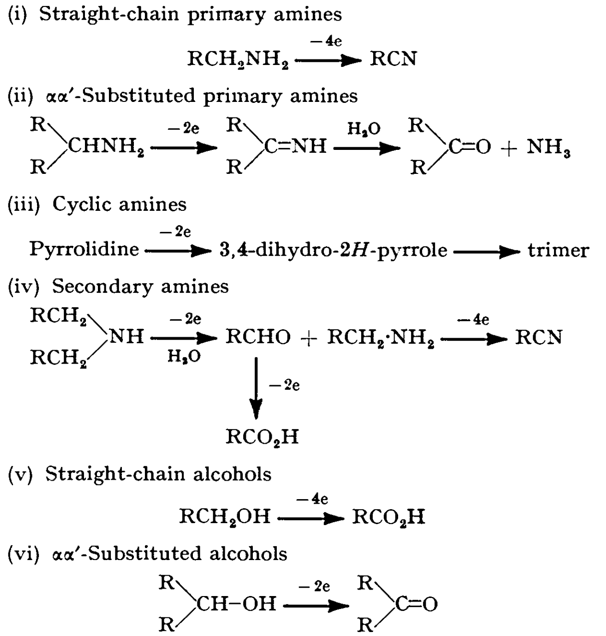
Controlled-potential electrolyses were carried out at a potential on the limiting current plateau for certain of the compounds in order to determine n and the products; the results obtained are summarised in Table 2. The choice of substrates and anodes was largely controlled by the need to have tolerably high cell currents. It is clear that the

TABLE 2

Products from the oxidation of a selection of alcohols and amines at oxide covered nickel, silver, and copper anodes

Substrates	Products	Current yields (%) Nickel (0·55 V)	Silver (0·75 V)	Copper (0·7 V)
n-Propylamine	Ethyl cyanide	84	83	85
	Propionaldehyde	11	2	2
n-Butylamine	Propyl cyanide	85	85	
	Butyraldehyde	6	2	
Isopropylamine	Acetone	80	70	85
Diethylamine	Acetonitrile	46	27	30
	Acetaldehyde	3	3	5
	Acetic acid	36	29	40
Pyrrolidine	Trimer of 3,4-dihydro-2*H*-pyrrole	>50%		
Ethanol	Acetic acid	98		96
Propanol	Propionic acid	95		
Propan-2-ol	Acetone	90		93

products obtained are formed by the routes shown in Scheme 3.



SCHEME 3

Further Results at a Nickel Anode.—Oxidation of p-*aminophenol and ferrocyanide.* Both *p*-aminophenol and ferrocyanide ion are readily oxidised at nickel in 1M-potassium hydroxide and the reactions occur in the potential region where the electrode surface is covered by nickel(II) hydroxide; *p*-aminophenol gives a wave at approximately +0·3 V and ferrocyanide a wave with a half-wave potential at +0·21 V. For both compounds, the current is of the first order with respect to the concentration of the electroactive species [10^{-3}—10^{-1}M] and of zeroth order with respect to hydroxide ion [10^{-2}—1·0M] over the whole oxidation wave and the currents in the limiting-current region are diffusion-controlled since a rotating disc experiment showed these currents to be proportional to the square-root of the rotation speed of the electrode.

A polarisation curve for *p*-aminophenol showed a Tafel slope of (120 mV)$^{-1}$ indicating that in this potential region the current is determined by the kinetics of the electron-transfer process. Conversely a similar experiment with ferrocyanide gave a 'Tafel slope' of (60 mV)$^{-1}$ and hence this oxidation is reversible, *i.e.*, the electron transfer is fast compared with diffusion even in the 'Tafel region' and hence the *i–E* curve is described by the Nernst equation.

These oxidations show conclusively that electron transfer through the thin layer of nickel(II) hydroxide can be rapid.

Deuterium isotope effect. Current–concentration plots obtained at a nickel anode in 1M-potassium hydroxide and at a potential on the limiting current plateau for methanol and fully deuteriated methanol were used to obtain rate constants for the electrode processes; methanol gave a rate constant of $7{\cdot}0 \times 10^{-6}$ cm s^{-1} while the deuteriated compound had a rate constant of $1{\cdot}0 \times 10^{-6}$ cm s^{-1}. Since the fully deuteriated methanol will rapidly exchange its alcoholic hydrogen under the experimental conditions, it is equivalent to CD_3OH. Thus $k_{CH_3OH}/k_{CD_3OH} = 7{\cdot}0$ clearly showing that there is a primary isotope effect for the hydrogen on the carbon atom α to the functional group. Regrettably, no further aliphatic alcohol or amine specifically and solely deuteriated at the α-position could be obtained.

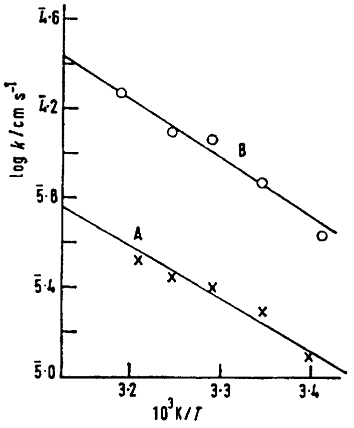


FIGURE 4 Plots of log *k* against 1/*T* for substrates at a nickel anode in aqueous 1M-potassium hydroxide; A, ethanol; B, n-butylamine

Temperature effects. Concentration–current plots at a potential on the limiting current plateau were used to determine the rate constants for the oxidation of propylamine and ethyl alcohol at a nickel anode in 1M-potassium hydroxide at a series of temperatures between 20 °C and 40 °C. These data were used to construct the plots of log *k* against 1/*T* shown in Figure 4. The activation energies determined from the slopes of these graphs were 13·5 ± 1·0 kcal mol^{-1} for propylamine and 11·2 ± 1·0 kcal mol^{-1} for ethanol; the *A* factors were $5{\cdot}2 \times 10^5$ and $2{\cdot}5 \times 10^3$ cm s^{-1} respectively.

DISCUSSION

Mechanism of the Oxidations at Oxide Electrodes.—There is clearly a marked similarity between the mechanisms for the anodic oxidation of amines and alcohols at the four oxide-covered metals. Further it is immediately apparent that this mechanism is not simple electron transfer; such behaviour is found by use of a carbon anode for the oxidation of aliphatic amines in aqueous hydroxide,[29] and, in contrast to the results at the transition-metal oxide electrodes, the oxidation potentials for the substrates at a carbon anode vary with the structure of the amine. In fact, tertiary amines oxidise at less anodic potentials than secondary amines, as would be expected from comparisons with gas-phase ionisation potentials,[30,31] and primary amines do not oxidise at all before bulk oxygen evolution.

A postulate that all the oxidations occur at the potentials where the oxide transitions take place because the lower oxides are non-conducting and act as a barrier to electron transfer is also untenable in view of the observations that tertiary amines do not oxidise and that *p*-aminophenol and ferrocyanide ion are both oxidised rapidly on the nickel(II) hydroxide surface. Hence the facts that (i) at each of the metals, the oxidation of aliphatic amines and alcohols occur at the same potential, the potentials at which the surface transitions $\mathrm{Ni^{II}} \longrightarrow \mathrm{Ni^{III}}$, $\mathrm{Co^{II}} \longrightarrow \mathrm{Co^{III}}$, $\mathrm{Cu^{II}} \longrightarrow \mathrm{Cu^{III}}$, and $\mathrm{Ag^{I}} \longrightarrow \mathrm{Ag^{II}}$ take place; (ii) the current for the oxidations become independent of potential at very low values of the current; (iii) the limiting rate is independent of the rotation speed of a disc electrode; (iv) the electrode process has a high activation energy; and (v) the cathodic peak for the surface transitions $\mathrm{Ni^{III}} \longrightarrow \mathrm{Ni^{II}}$, $\mathrm{Ag^{II}} \longrightarrow \mathrm{Ag^{I}}$, and $\mathrm{Cu^{III}} \longrightarrow \mathrm{Cu^{II}}$ are absent on cyclic voltammograms run in the presence of substrate at low sweep rates but are present when the potential scan rate is increased, all strongly indicate that the electrode reactions take place by a mechanism involving a rate-determining chemical reaction between the higher oxide and the organic substrate. This is confirmed by the ability of the theory based on this mechanism to reproduce the observed *i*–*E* curves and their concentration-dependences. Thus the kinetic data reported in this paper are, in fact, for the chemical reaction between the higher oxides and the alcohols and amines.

Equation (4), which was used to obtain the rate constants, was derived by assuming that the chemical reaction involved a solution-free molecule of the organic substrate. This is not necessarily correct and, indeed, there are several indications that adsorption of the substrate is required before the chemical reaction can occur. First, the concentration-limiting current plots deviate from linearity at high concentrations of the substrate; this is the behaviour expected if at low concentrations of the substrate, their coverage of the electrode surface is low and in the region where Henry's law is obeyed while at higher concentrations a more complex isotherm is required. Secondly, there are the kinetic data themselves; at each of the electrodes, the rate constants decrease with increasing size of the substrate molecule and also steric factors close to the hetero-atoms, the atoms likely to be involved in the bond with the surface, appear to be important (*e.g.*, branching at the α carbon atom decreases the rate; also compare diethylamine and pyrrolidine). Any reaction mechanism where hydroxyl radicals and molecules of the substrate compete for the same sites on the surface would lead to *i*–*E* curves with large and pronounced current maxima (at high overpotentials, the coverage by the hydroxyl radical, $\theta_{\mathrm{OH}\cdot}$, tends to unity and in consequence the coverage by the organic compound, θ_{org}, must fall sharply. Hence the rate of the process, $k_{\mathrm{C}}\theta_{\mathrm{OH}}\theta_{\mathrm{org}}$ will also decrease). Since these maxima are not observed, a reaction model in which the organic molecule adsorbs on the surface of the lower oxide and reacts with a neighbouring adsorbed hydroxyl radical or molecule of higher oxide must be ruled out. Consequently, if adsorption occurs, it must be on the surface of the higher oxide; to account for this adsorption equilibrium

$$\mathrm{Organic_{SOL}} \underset{k_{\mathrm{A}}'}{\overset{k_{\mathrm{A}}}{\rightleftharpoons}} \mathrm{Organic_{ADS}} \qquad (5)$$

(5) the kinetic equations must be modified to (6) in the

$$i = nFA\beta\,\frac{k_{\mathrm{C}}k_{\mathrm{E}}k_{\mathrm{A}}}{k_{\mathrm{E}}'k_{\mathrm{A}}'}\,C_{\mathrm{org}}\,C_{\mathrm{OH^-}}\exp\frac{F\phi}{RT} \qquad (6)$$

Tafel region and (7) at high potentials [*cf.* equations

$$i = nFA\,\frac{\beta k_{\mathrm{C}}k_{\mathrm{A}}}{k_{\mathrm{A}}'}\,C_{\mathrm{org}} = nFAC_{\mathrm{org}} \qquad (7)$$

(3) and (4)]. Hence the measured rate constants contain the rate constants for any adsorption and desorption steps as well as the rate constant for the actual chemical process.

The nature of the chemical step between the higher metal oxides and the organic substrates must be considered. It is unlikely that the reaction involves a solution-free transition-metal ion since there is a complete absence of corrosion of the anode. Further, although the equilibrium constant for the adsorption of the amines is an unknown factor, the observations that tertiary amines do not oxidise at a measurable rate while secondary amines oxidise much more slowly than primary amines, make a mechanism with a rate-determining electron-transfer reaction unlikely. The data obtained at the oxide electrodes therefore suggest that the initial and rate-determining step is hydrogen abstraction from the substrate; this is confirmed by the difference in the rate constants for $\mathrm{CH_3OH}$ and $\mathrm{CD_3OH}$ at a nickel electrode which clearly shows a primary isotope effect for the hydrogen on the carbon atom. Such radical mechanisms have previously been discussed for the chemical reaction between transition-metal oxides and organic substrates (for a review see ref. 32); for example, both deuterium-labelling and e.s.r. spectroscopy have been used to prove that the reactions of nickel peroxide proceed *via* hydrogen abstraction.[33]

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It is tempting to suggest that the important chemical step in the electrode reaction involves hydroxyl radicals adsorbed on the surface of the oxide rather than the higher oxide itself. It appears, however, that this is unlikely since at each of the metals the reaction of hydroxyl radical with the lower oxide (Scheme 1) is much faster than with the organic substrate. Further a reaction with the adsorbed hydroxyl radical would almost certainly involve a mechanism where hydroxyl radicals and substrate were competing for the same sites on the surface and, as discussed above, this is ruled out by the shape of the *i–E* curves and their concentration dependences.

Hence all the data obtained at the transition-metal oxide electrodes is compatible with the mechanism of Scheme 4.

$$\text{OH}^- + \text{lower oxide} \xrightleftharpoons{\text{fast}} \text{higher oxide} + \text{H}_2\text{O} + \text{e}$$

$$(\text{Organic substrate})_{\text{SOL}} \xrightleftharpoons{\text{on higher oxide}} (\text{organic substrate})_{\text{ADS}}$$

$$\text{Higher oxide} + (\text{organic substrate})_{\text{ADS}} \xrightarrow[\text{hydrogen extraction}]{\text{rate determining}} \text{lower oxide} + \text{radical intermediate}$$

$$\text{Radical intermediate} - (n-1)\text{e} \longrightarrow \text{product}$$

or

$$\text{Radical intermediate} + (n-1)\text{higher oxide} \longrightarrow (n-1)\text{lower oxide} + \text{product}$$

SCHEME 4

Comparison of Rate Data.—In interpreting the kinetic data in Table 1, we must remember that the measured rate constants are mixed constants containing three factors: (*a*) the roughness factor of the electrode surface, β, (*b*) the equilibrium constant for the adsorption of the organic molecule, $K_A = k_A/k_A'$, and (*c*) the rate constant for the hydrogen-abstraction reaction. Although the surface area of the electrode, βA, is of critical importance in determining the current, the thickness of the oxide is not, provided that transport of the charge carrier through the layer is fast compared with the rate of the chemical process and hence the surface concentration of the higher oxide is unimpaired; this is apparently the case with silver and perhaps copper. β Is, of course, a constant for each of the metals and, hence, only (*b*) and (*c*) need be considered when comparing the different substrates at one of the metals.

A comparison of the different substrates at the four oxide electrodes shows that at each of the metals the following trends are apparent: (*a*) primary amines are always oxidised more rapidly than the corresponding alcohol; (*b*) for a series of amines RNH_2, R_2NH, and R_3N $k_{RNH_2} > k_{R_2NH} > k_{R_3N}$; (*c*) the cyclic amine, pyrrolidine, always oxidises much more rapidly than the corresponding acylic amine diethylamine; (*d*) branching of the hydrocarbon skeleton at the carbon α to the heteroatom decreases the rate; and (*e*) the rate of oxidation decreases with the number of carbon atoms in the alcohol or amine.

It is noteworthy that trends (*a*) and (*b*) are also observed in gas-phase hydrogen-abstraction reactions (data from ref. 34). In contrast to (*a*), however, gas-phase hydrogen abstractions increase in rate with increasing carbon chain length; this suggests that adsorption on the surface is important in the electrode reaction and (*c*) and (*d*) support this theory.

A comparison of the rates at the different metal oxides shows that for amines the rate constants decrease along the series $k_{Cu} > k_{Ag} > k_{Ni} > k_{Co}$ whilst for alcohols the order changes to $k_{Cu} > k_{Ni} > k_{Ag} > k_{Co}$. This difference in order might be due to the well known strong affinity of silver(I) for amines causing the coverage by amine on the silver oxide to be unusually high.

A few experiments were carried out at iron and gold electrodes under the same solution conditions and it was clear that amines were oxidised by a similar mechanism but at a lower rate than at a cobalt anode. Hence the rate data show a close correlation to the position of the metal in the Periodic Table; the rate of the anodic oxidations increases across the first row of the transition-metal series $k_{Fe} < k_{Co} < k_{Ni} < k_{Cu}$ and decreases down group IB $k_{Cu} > k_{Ag} > k_{Au}$. Attempts to correlate the kinetic data with electronic properties, *e.g.*, *d*-electron availability, are impossible owing to an absence of reliable structural information concerning the higher oxides, whilst inspection of other properties which are possibly related to steps in the mechanism, *e.g.*, oxidation potential for the higher oxide–lower oxide couple, and stability constants for metal amine complexes, always produce the conclusion that the differences between the rate constants at the metal oxide electrodes are surprisingly small. This may be due to the properties considered affecting β, k_A, and k_C in opposite senses so that the overall changes in the measured rate constants are minimised.

Comparison of the Electrode Reactions with Related Chemical Reactions and Heterogeneous Catalysis.—Silver(II), nickel(III), cobalt(III), and copper(III) oxides are all known chemical compounds although only the former two oxides have been used to any extent as oxidising agents in organic chemistry. Nickel peroxide is normally prepared *in situ* by treatment of alkaline solutions of nickel(II) salts with hypochlorite and it has been used in several studies for the oxidation of amines[35-37] and alcohols.[33,38-40] Silver(II) oxide is a fairly common oxidant in organic chemistry and its use for oxidation of amines and alcohols has been reported.[41] The products from these chemical reactions are identical

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with those found by electrolysis in this work. No kinetics have been reported, however, and no detailed mechanism has been suggested for these reactions but heterogeneous reactions with transition-metal oxides are often considered to occur *via* adsorption of the organic compound on the surface of the oxide followed by a chemical reaction, commonly hydrogen abstraction.[32] Hence there appears to be much common ground between electrode reactions at transition-metal oxides and the chemical reactions of the higher oxides.

Some similarity between these electrode reactions at metal oxide anodes and the mode of operation of transition-metal oxides as heterogeneous catalysts for the gas-phase or solution reactions between oxygen and organic compounds is also to be found. Cobalt(II), nickel(II), copper(II), and silver(I) oxides do not appear to have been used for the catalytic oxidation of amines or alcohols but they have been applied to catalysis of gas-phase reactions of oxygen with hydrocarbons [42] and ammonia, sulphur dioxide, and carbon monoxide [43] and to the aqueous oxidation of hydrocarbons.[44] The mechanism of these reactions are commonly discussed in terms of the adsorption of oxygen to give ' excess of lattice oxygen and excess of surface oxygen ' [45] and of adsorption of organic and inorganic substrates. Moreover attempts have been made to correlate electronic, physical, and chemical properties of the oxides with the coverage of their surface by adsorbants and hence catalytic activity.[46,47] Adsorption of oxygen as described in these mechanisms appears to be equivalent to conversion of at least the surface of the oxide into a higher oxide by the reaction (8). The catalytic reactions

$$\text{Lower oxide} + O_2 \longrightarrow \text{Higher oxide} \qquad (8)$$

are carried out at high temperatures and pressures, partly to drive this reaction at an appreciable rate. Further the reaction of the substrate with the higher oxide has been suggested to lead to radicals by hydrogen abstraction. Hence the electrode reactions and the oxide-catalysed reaction between oxygen and substrates seem to have great similarity. Indeed the electrode reactions may be considered as heterogeneously catalysed reactions where the use of electric power instead of oxygen allows the conversion of the oxide into the active species under much milder conditions.

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