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Electrocatalysis of the Electroreduction of Nitric Acid by Metals

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The literature data on the electroreduction of nitric acid to hydroxylamine on various metals is analyzed as regards the electrocatalytic trends. In general moderate values of M–H and M–O bond energies, between the metal M and the anchoring group –H or –O (of $-NO_3$), herald higher electrocatalytic activity; too low M–H interaction energy or too high M–O bond energy is associated with lower activity. Some volcano-type correlations between the M–H or M–O interaction energies and the electrocatalytic activities are observed for the transition metals whereas the *sp* metals do not show such relationships. It is further observed that the ability of the metal to electrocatalyze nitric acid reduction is roughly related to its exchange current density for the hydrogen evolution reaction. These correlations are interpreted on the basis of previous kinetic theory and some mechanistic proposals are put forward.

INTRODUCTION

Khumotov and Stamkulov (*1*) have recently reported on the electroreduction of nitric acid by a large number of metals. The electrode reaction rate data were related to the atomic numbers of the electrodes, within a given period, and some periodicities were noticed. No detailed electrocatalytic analyses of the data, as for the case of the hydrogen evolution reaction (h.e.r.) (*2–6*), oxygen reduction reaction (o.d.r.) (*6, 7*) and oxygen evolution reaction (o.e.r.) (*6, 8*), were, however, presented. The purpose of the present paper is to attempt a detailed interpretation of these data, especially in relation to the M–X interaction energy where X represents the anchoring atom of the adsorbed intermediates likely to be formed during the reduction of nitric acid. Mechanistic ramification of the proposed interpretations would also be pointed out.

THE REDUCTION OF NITRIC ACID

The reduction of nitric acid proceeds in two overall stages—the formation of hydroxylamine and its subsequent conversion to ammonia. Whereas the first overall reaction occurs on all electrodes, the second reduction takes place on some electrodes only, e.g., Zn, Ga, Cd, In, Pt, Au, and Hg (Cu) amalgam. A comparative examination of the reduction of nitric acid on all the metals investigated (33 in number) is thus concerned with the consideration of the electrocatalysis of nitric acid reduction to hydroxylamine. In the acidic medium investigated (*1*), the overall reaction may be represented by one of the following reactions:

$$HNO_3 + 7H_3O^+ + 6e \rightarrow NH_2OH{\cdot}H^+ + 9H_2O, \quad (1)$$

$$NO_3^- + 8H_3O^+ + 6e \rightarrow NH_2OH{\cdot}H^+ + 10H_2O. \quad (2)$$

Each of the above two reactions would, of course, involve a number of elementary steps which are kinetically distinguishable. Considering reaction (1), for example, as the overall reaction, one could formulate a scheme of which the following two elementary steps form an integral part:

$$M + H_3O^+ + e \rightarrow M\text{–}N + H_2O, \quad (3)$$

$$2M + HNO_3 \rightarrow M\text{–}H + M\text{–}NO_3. \quad (4)$$

The steps (3) and (4) simply indicate the discharge of the reactants onto the electrode; it is understood that reaction (4) could, e.g., be written in an alternative form in which the discharge occurs from the NO_3^-. Here M refers to the metal cathode. The important point to note here is that the reducing agent H_3O^+ gets discharged at the electrode giving the adsorbed H, and that the group to be reduced (i.e., NO_3) has also to get adsorbed on the electrode. Subsequent reactions between several M–H and one M–NO_3 (or its reduction products) entities, occurring on the electrode surface, would give rise to the NH_2OH. The NO_3 group, it should be noted, would be adsorbed on the M by forming M–O bonds, and not the M–N bond because the latter are mostly unstable as shown by the *positive* hearts of formation of the nitrides of a large number of metals (*9*, *10*). One is thus going to examine the influence of the magnitude of the M–H and the M–O bonds, and related matters, on the relative rates of nitric acid reduction on various metals.

Khumotov and Stamkulov (*1*) carried out their work under conditions (e.g., rotating disk electrodes and subsequent analysis) which clearly separated the concentration polarization effects from the activation polarization, the latter being, of course, the true measure of the electrocatalytic activity of the metal. Three sets of data were regarded as diagnostic of the relative activity: (i) "half-wave potentials"; (ii) electrode potential at i_c = 50 mA cm^{-2}, where i_c is the cathodic reduction current density, i.e., the reaction rate; (iii) electrode potential at i_c = 90 mA cm^{-2}. These three measures of the electrocatalytic activity follow the same relative trend so that any of them may be taken as the index of activity in the comparative examination of various metals. In the various graphs presented here we have chosen the electrode potential at i_c = 50 mA cm^{-2} as the quantity characteristic of the electrocatalytic behavior of metals.

CORRELATION OF ELECTROCATALYTIC ACTIVITY TO VARIOUS QUANTITIES

In Fig. 1, the electrode potentials (at i_c = 50 mA cm^{-2}) for the reduction of nitric acid to hydroxylamine on various metals have been plotted against the hearts of atomization per equivalent, ΔH_{atom}/eq, of the corresponding oxides. The ΔH_{atom}/eq is the *average* value of the M–O bond energy in the bulk metal oxide and is the enthalpy change, per equivalent, corresponding to the reaction:

$$M\text{–}O(S) \rightarrow M(G) + O(G). \qquad (5)$$

Here S and G refer to the solid and gas, respectively. The ΔH_{atom}/eq values have

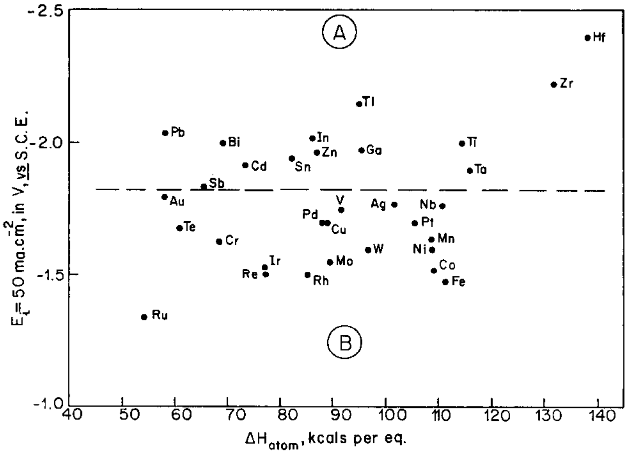

FIG. 1. A plot of the electrode potentials, E_i (SCE), at 50 mA cm^{-2}, for the electroreduction of nitric acid (*1*) against the heats of atomization per equivalent for the oxides (*11*) of the shown metals.

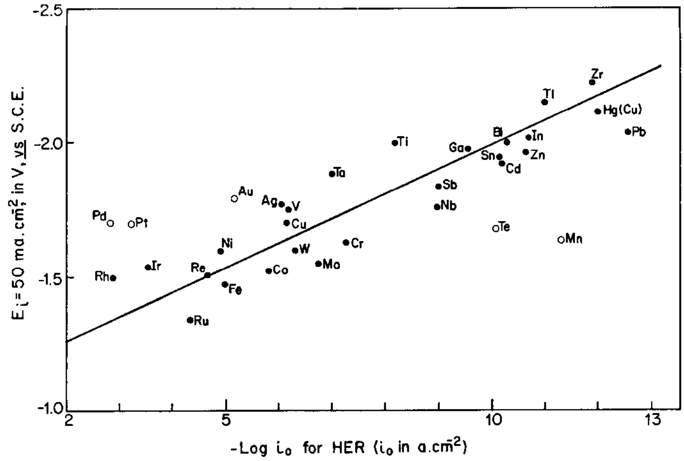

FIG. 2. A plot of E_i (as in Fig. 1) against the $-\log i_0$, where i_0 is the exchange current density for the h.e.r. (*4*, *5*), for the shown metals.

been taken from Sanderson (*11*) and their detailed significance has been discussed previously (*11–13*). Although no clear-cut correlation is observed in Fig. 1, an important general classification is indicated: the poor catalysts, designated as group (A), either have very high ΔH_{atom}/eq values for the oxides (e.g., Ti, Ta, Hf, Zr) or, on the basis of previous work (*2–5*), very low M–H bond energies; the good catalysts, labeled as group (B), on the other hand, have moderately high M–H bond energies (*2–5*) and not-too-high ΔH_{atom}/eq values. This classification must be regarded as merely indicative of a *general* trend rather than a rigorous division of the electrocatalytic activity into two categories; this is because some exceptions such as Te and Mn being situated in class (B) militate against the deductions made from Fig. 1. Also, generally speaking, metals exhibiting low overvoltage for the h.e.r. (*2–5*) also appear to be associated with low overvoltage for the nitric acid reduction. This is indeed directly verified in Fig. 2, in which, higher exchange current densities for the h.e.r. are related to higher activities of the metals towards nitric acid reduction in general, notwithstanding the noticeable departure of Mn, Te, Pd, Pt and Au from the shown trend.

To explore some of these matters further, one may plot the experimental $\Delta H_{\text{ads.H}}$ values, the heats of adsorption of atomic hydrogen (which are also the measure of the M–H interaction energies), against the potentials (at i = 50 mA cm^{-2}) for the nitric acid reduction for the metals for which the data (*1*, *14*) are available (Fig. 3). A volcano-type correlation is obtained. To extend this correlation to many more metals for which the experimental $\Delta H_{\text{ads.H}}$ values are not available, one may attempt to calculate these values by means of the Stevenson equation (*15*) and construct Fig. 4. Generally, for the transition and the near-transition (e.g., Ag, Cu, Au) metals, a volcano-type curve is again obtained whereas for the *sp* metals (shown in the box, plus mercury) no correlation is indicated. It should be emphasized that

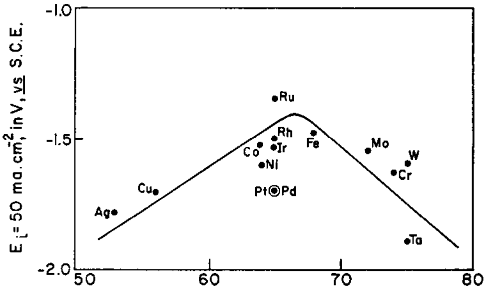

FIG. 3. A plot of E_i (as in Fig. 1) against the experimental $\Delta H_{\text{ads.H}}$ values (*14*).

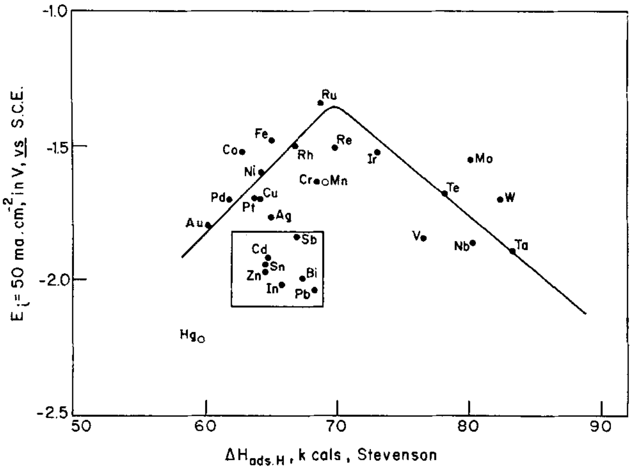

FIG. 4. A plot of E_i (as in Fig. 1) against the calculated (*5*, *15*) $\Delta H_{ads.H}$ values.

the correlation in Fig. 4 has only a rough validity, because of the well-known limitations (*16*) of the Stevenson equation in estimating the M–H interaction energies of metals that adsorb H_2 poorly. Similar comments also apply, of course, to the Pauling or the Eley equation (*2*, *3*, *7*, *8*).

In electrode reactions (6) as well as in heterogeneous catalysts (*13*, *17*) by oxides, it has been suggested that the appropriate M–O is not the enthalpy change in reaction (5) but instead the enthalpy change involved in the transformation:

$$\text{M-O(S)} \rightarrow \text{M(S)} + \text{O(G)}. \qquad (6)$$

In Eq. (6) the metal stays as the *solid* after the bond rupture, as indeed is the case in all catalytic reactions including the electrocatalytic, in contrast to Eq. (5) in which the metal assumes the gaseous form. The enthalpy change, per equivalent, in reaction (6) is given by:

$$(\Delta H_e)_6 = -(\Delta H_f)_e + \tfrac{1}{4}\Delta H_{\text{diss.}} \qquad (7)$$

where $(\Delta H_f)_e$ is the heat of formation (standard state) per equivalent of the oxide and $\Delta H_{\text{diss.}}$ is the bond dissociation energy of the oxygen molecule to give two O atoms. In other words the M–O bond energies as corresponding to the bond rupture (or formation) in Eq. (6), for various metals are essentially $-(\Delta H_f)_e$ values since $\frac{1}{4}$ $\Delta H_{\text{diss.}}$ is constant for all metals. Since the $-NO_3$ group is adsorbed on M through M–O bonds, it is of interest to examine the plot of $-(\Delta H_f)_e$ of oxides vs the electrode potentials for nitric acid reaction at a given current (Fig. 5). It is observed that, in general, the sp metals (shown in the box) show no correlation whereas a volcano plot is obtained for the rest of the metals, although some metals like Ru and Te show noticeable exceptions. It is thus clear that there are some interesting trends not only between the M–H interaction energy and the electroactivity (Figs. 3 and 4) but also between the latter and an appropriate index of the M–O interaction energy (Fig. 5).

Since the electrocatalysis of the nitric

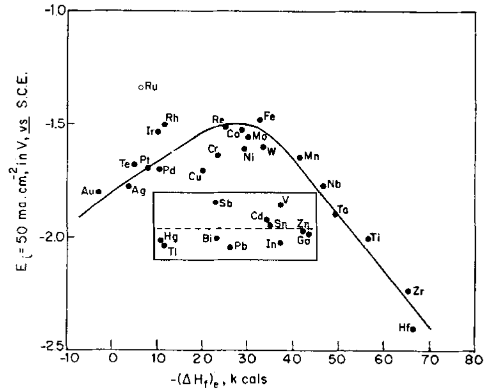

FIG. 5. A plot of E_i (as in Fig. 1) against the heats of formation per equivalent $(\Delta H_f)_e$ values (*9*, *11*).

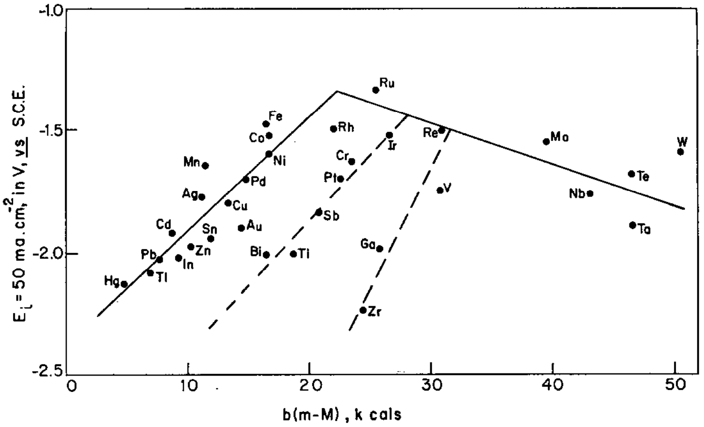

FIG. 6. A plot of E_i (as in Fig. 1) against the metal–metal bond energy, b(M–M), values (5).

acid reduction appears to be intimately related to that of the h.e.r. (Figs. 2–4), it is of interest to examine the possible correlation between the former and the M–M bond energy, b(M–M), following similar previous correlations (*3*, *4*) for the h.e.r. No clear-cut correlation is obtained although some rough volcanic trends are obvious (Fig. 6). The left arm of the volcano shows three branches, the main one and the two auxiliary ones, whereas the right arm does not show such multiplicity. The significance of b(M–M) is roughly similar to the significance of the M–X interaction energies since the former constitutes an important constituent of the latter (*2–5*, *15*).

DISCUSSION

The main thrust of the preceding correlations is that some volcanic trends are observed between the electroactivity and the M–X interaction energy [or a quantity related thereto, e.g., b(M–M)] where X represents the anchoring group in the adsorbed intermediate, and is either H or O in the present case. Such volcano-type relationships have been theoretically predicted by Parsons (*18*) and Gerischer (*19*) for the case of the h.e.r. and are presumably applicable to all electrode reactions proceeding by formation of adsorbed intermediates. For example, for the h.e.r., these authors (*18*, *19*) derive the following expression:

$$i_0 = k_v a^{(1-\alpha)} \left(1 + P^{1/2} \exp\left(-\frac{\Delta G_A}{2RT}\right)\right)^{-1} \cdot \left(P^{1/2} \exp\left(-\frac{\Delta G_A}{2RT}\right)\right)^{\alpha} \cdot \exp\left(\frac{-\alpha \Delta G_{\bar{V}}^{\ddagger} - (1-\alpha)\Delta G_V^{\ddagger}}{RT}\right) \quad (8)$$

Here i_0 is the exchange current density; k_v and α are the electrochemical rate constant and the transfer coefficient, respectively; a is the activity of (H_3O^+) in the Helmholtz d.l.; ΔG_A is the equilibrium free energy of adsorption; $\Delta G_{\bar{V}}^{\ddagger}$ and $\Delta G_V^{\ddagger}$ are, respectively, the electrochemical free energies of activation for the forward and the backward reactions at equilibrium. In this expression, Langmuir conditions of adsorption have been assumed although an essentially similar expression may also be derived under the Temkin conditions of electrode coverage (*18*).

Equation (8) predicts a volcano-type correlation between Log i_0 (or any other measure of the electroactivity) and ΔG_A, the ideal representation of the M–H interaction energy. This prediction is roughly verified by the correlations presented here although the situation is much more complex probably because of the presence of both M–H and M–O bonds. Several other features of the preceding correlations may be summarized as follows.

1. In the electrocatalytic reactions, too low or too high values of the M–X interaction energies lead to low activity as for the (A) group in Fig. 1; a moderate value

of the M–X interaction energy for all the reaction intermediates is conductive to high reaction rates [Fig. 1, group (B)].

2. In a typical electroreduction, the catalytic activity of the metal towards the h.e.r. may perhaps also be taken as an index of its activity towards the reduction under discussion (Fig. 2).

3. It appears that the rates of electroreduction on *sp* metals are relatively unaffected by the magnitudes of the M–X interaction energies (Figs. 4 and 5); on the transition and near-transition metals, however, plots between electroactivity and the M–X interaction energies (or quantities related thereto) show some rough volcanic trends (Figs. 3–6).

It is interesting to note that the volcanic plots in Figs. 4 and 5 indicate that, in general, the same metals tend to lie on the left or the right arm of the volcano in both figures, i.e., irrespectively of the fact whether one considers the M–H or M–O interaction energy. For example, Au, Ag, Pt, Pd, Cu, Rh, Re, and Cr lie on the left arm, i.e., higher activity with higher M–H or M–O interaction energy; this shows that an initial discharge step (involving formation of an M–H or M–O bond) is perhaps the rate-determining step on these metals. The opposite would appear to be true for Ta, Nb, W, Mo and Ti which lie on the right arm of the volcano, i.e., decreasing rate with the increasing M–X interaction energy. This would follow from the Horiuti–Polanyi (*20*) treatment of the hydrogen evolution reaction. It is fair to add, however, that these mechanistic conclusions are rather tentative since several metals in Figs. 3, 4, and 5 tend to lie on either arm of the volcano. Rough correlations of this type (Figs. 1–6) do not pinpoint the mechanism for every individual metal, although they do constitute a starting point for establishing trends in a given series of metals (*21*).

It is perhaps relevant to comment here on the complexity of the electroreduction of nitric acid and therefore on the somewhat approximate nature of the viewpoint presented here in which reduction is assumed to occur all the way up to NH_2OH and NH_3. Although the experimental evidence (*1*) supports this assumption, the possibility of other parallel or parasitic reactions must be mentioned, however. Depending on the electrode potential, the reduction may only yield NO which then may be oxidized by the oxygen in the air to NO_2. This would be particularly likely on the *sp* metals on which steady-state concentration of adsorbed hydrogen is usually low. It appears, however, that the results quoted here are for highly cathodic potentials so that the more extensive reduction of hydroxylamine and ammonia is the likely process. That reduction does indeed lead up to hydroxylamine on all metals was established by Khumotov and Stamkulov (*1*) in the following way: they examined the effect of addition of NO_2^- and NH_2OH, separately, on the main reduction wave and found that the NO_2^- had no effect whereas NH_2OH addition increased the wave height. Also, a *negative* pH effect was observed so that reactions such as (1), (2) and (3) here are strongly indicated. Despite the foregoing, it is clear that formation of NO (and then NO_2) as a side product cannot be excluded. The formation of NO would also take place, on several of the baser metals, by means of their spontaneous reaction with $HNO_3 \cdot aq$, as in the open-circuit corrosion situation. At the high cathodic potentials at which the data quoted here were obtained (*1*), this reaction would occur only as a parasitic side reaction whose rate, at least in most of the cases, never becomes quite as high as that of the electrochemical reaction driven by the externally applied potential. The foregoing complications in the reaction of nitric acid reduction are perhaps not serious enough to change substantially the general catalytic trends presented in the Figs. 1–6 here, although it is realized that the position of some individual points in these graphs might undergo modification when detailed mechanistic studies on all metals become available.

CONCLUSIONS

An analysis of the data on the electroreduction of nitric acid on various metals shows the volcanic relationship of the electroactivity to the M–H and M–O interaction energies on transition metals; on the *sp* metals such correlations do not exist.

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