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INFLUENCE OF HYDROGEN COVERAGE ON THE HYDROGENATION MECHANISM OF ACRYLONITRILE

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The electrolytic hydrodimerization of acrylonitrile has been the subject of several recent investigations (1 - 4). The side reactions usually produce either the saturated nitrile or amine. The dimerization is expected to involve an electron transfer process while the side reactions probably involve direct addition of hydrogen atoms to the molecule. It is generally stated that acrylonitrile is hydrogenated catalytically on the surface of metals of relatively low hydrogen overvoltage such as platinum, palladium and nickel, but is hydrogenated electrochemically on the surface of metals of high hydrogen overvoltage such as mercury.

Recently (5) a technique was described for distinguishing between reduction by an electron transfer mechanism and reduction by hydrogen addition on metals with relatively low hydrogen overvoltages. This technique consisted of relating the potential of the hydrogen electrode to the fraction of the surface covered with hydrogen. It was shown that if the compound is reduced by catalytic addition of atomic hydrogen the potential of the electrode is given by the following expression at 25°C,

$$E = E^{o} - .059 \log \frac{\theta}{1-\theta}, \qquad \text{(I)}$$

where θ is the fraction of the surface covered with hydrogen. On the other hand, if the compound is reduced by an electron transfer process and the rate of reaction of the compound is governed by diffusion, then the rate of diffusion of the compound will equal the rate of removal of the hydrogen as obtained from electrochemical kinetics.

$$k_2(\text{compd}) = k_{-1}\ \theta \exp \frac{(1-\alpha)\ F\eta}{RT} - k_1\ (H_3O^+)\ (1-\theta) \exp \frac{-\alpha F\eta}{RT}$$

where η is the overvoltage ($E - E^o$) and α is the transfer coefficient (½). Rearranging this equation at 25.0°C and constant H_3O^+ concentration, one obtains the expression,

$$E = E'^{o} - \frac{.059}{\alpha} \log \theta + \frac{.059}{\alpha} \log \frac{K_2 + \sqrt{K_2^2 + 4K_1\theta(1-\theta)}}{2}\ , \qquad \text{(II)}$$

where K_1 and K_2 contain the rate constants and the concentration of the compound. Since the last term is approximately constant, the equation becomes

$$E = E^o - 0.12 \log \theta. \qquad \text{(III)}$$

Thus one can differentiate between mechanisms of reduction by investigating the relationship between θ and E to determine whether Equation I or III is obeyed. This procedure was used to determine the mechanism of reduction of acrylonitrile on platinized platinum.

EXPERIMENTAL TECHNIQUE

The procedure consisted of a study of the relationship between the potential of the hydrogen electrode and the fraction of the surface covered with hydrogen in the presence of acrylonitrile. The electrolytic cell consisted of an "H" cell containing a platinized platinum electrode and a large nonpolarizable platinum gauze separated by a sintered glass disk. The solutions were bubbled with helium, and hydrogen was generated on the electrode at a specific potential until the current reached zero. The current was cut off; the potential between the electrode and a reference hydrogen electrode was measured; and then, a polarogram was obtained for the oxidation of the hydrogen adsorbed on the electrode. Fig. 1 shows the polarogram obtained for the oxidation of hydrogen at a platinized platinum electrode in 2N sulfuric acid, the conditions of this experiment. It can be seen, from the two peaks, as is well known (6), that there are two major forms of hydrogen adsorbed on platinum. The graphical method used to separate the two peaks and obtain areas is shown in the figure.

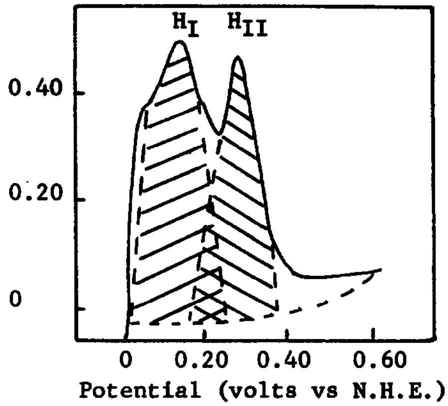

Fig. 1
A Typical Current Voltage Curve for the Oxidation of Hydrogen at the Platinized Platinum Electrode in Two Normal Sulfuric Acid

The area under each peak is equal to the number of coulombs necessary to oxidize that form of hydrogen. The fraction of each region of the platinum covered by that particular form of hydrogen, θ_I and θ_{II}, was calculated by taking the measured amount of hydrogen, H_I and H_{II}, and dividing by the amounts adsorbed at equilibrium at one atmosphere pressure with no additive present, $(H_I)_o$ and $(H_{II})_o$, respectively. After determining the equilibrium potential and amount of adsorbed hydrogen in the two normal sulfuric acid solution, the solution was made 0.6×10^{-3} molar in acrylonitrile and the amount of adsorbed hydrogen was determined at several potentials.

RESULTS AND DISCUSSION OF RESULTS

Fig. 2 shows the data obtained for the reduction of acrylonitrile on

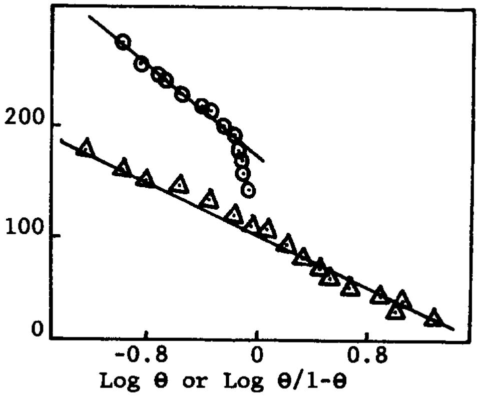

Fig. 2
Potentials Plotted Against Log θ or Log θ/(1-θ) in the Presence of Acrylonitrile

○ - Log θ for H_{II}
△ - Log θ/1-θ

platinized platinum in sulfuric acid solutions. It can be seen that when the surface is highly covered with hydrogen (at equilibrium and slightly anodic potentials), H_I and H_{II} are both present on the surface of the electrode. The slope of a log $\theta/1-\theta$ vs potential plot for the removal of the first form of hydrogen, (H_I), by acrylonitrile is a straight line with a slope of -0.062 indicating that the compound is reduced primarily by hydrogen addition, probably to produce either the saturated nitrile or the amine. However, as the amount of hydrogen on the electrode decreases and one reaches a potential region in which only a fraction of the surface is covered with hydrogen (only H_{II} is present) the plot of log θ vs potential is a straight line at low coverages with a slope of -0.12. The curvature at high coverages is expected from Equation II. This indicates that in this potential region the acrylonitrile is reduced by an electron transfer mechanism probably to produce the dimer.

This change in mechanism is logical where the possibility for two such reactions exists. At very high coverages catalytic hydrogenations should proceed readily, since the concentration of the hydrogen is high. At low coverages the electron transfer process, which is independent of the amount of adsorbed hydrogen, but is dependent on the availability of bare surface and the overvoltage, should proceed readily.

ACKNOWLEDGMENT

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