KINETICS OF ANODIC OXIDATION OF THE AZIDE ION

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The evolution of nitrogen at a platinum electrode from an azide solution has been investigated. It has been found that the polarization curves consist of two parts, which, expressed in semilogarithmic coordinates, have slopes of 53 mV (at low current density) and 110 mV (at high current density). For the lower portion of the curves the overpotential is independent of the composition of the solution, while for the higher portion a small, but quite clearly expressed, dependence is found. The electrode capacity, determined from the decay curves, corresponds closely to those of a double layer. The activation energy at an overpotential of 4.67 V is found to be 46 kcal/mole. The accumulated experimental data are best described by a mechanism of retarded barrierless electrochemical desorption of the azide radical, at a degree of surface covering close to unity. For higher potentials the barrierless process ($\alpha = 1$) is converted into the more usual ($\alpha = {}^1/_2$).

The discharge of the azide ion takes place according to the overall equation:

$$N_3^- - e \rightarrow {}^3/_2 N_2.$$

The investigation of this reaction has been carried out by many workers (for a review of the data see [1-3]), but only the publications of Stout [2] and Thomas [3] satisfy contemporary requirements with resepct to fidelity of experimental method.

Using a platinum anode a linear relationship has been found between φ and log i. The value of "b" has been found to equal 57-60 mV [2], while the data gave 43-46 mV in [3]. Similar results have been obtained on other metals investigated, which include palladium, rhodium, iron, nickel, and irridium [1-3].

It was shown in [3] that the potential for the discharge of the ions is not established instantaneously. Before discharge commences a charging up process occurs which is associated with the adsorption on the electrode surface of N_3 radicals. This adsorption is satisfactorily described by a logarithmic isotherm. Thomas suggested that the potential for the stationary discharge of N_3^- ions corresponds to an average filling of the surface with the adsorbed particles. The strong dependence of the degree of filling on the potential leads to a similarly strong dependence of the activation energy of electrochemical desorption on this. This effect is summed up in terms of the usual dependence of rate of desorption on the potential. Although the true value of α has been taken to equal 0.5, the overall dependence of current on potential corresponds, in agreement with experiment, to a value of "b" of 59 mV. Slow combination in the region of average filling can also be used to explain the observed experimental data.*

Another possibility exists, however, for explaining the slope of 59 mV, which was not taken into account in [2, 3]. A slope of this kind could occur in the case of the so-called barrierless electrode processes, which have been observed in particular for the cathodic evolution of hydrogen [4]. The object of the present work was to test the possibility of such an interpretation of the kinetics of the anodic oxidation of the azide ion.

EXPERIMENTAL METHOD

Sodium azide, NaN_3 was purified by precipitation with alcohol from an aqueous solution, and subsequently recrystallized from doubly distilled water. Sodium sulfated and potassium chloride were twice recrystallized from doubly distilled water, and ignited. Solutions were prepared using triply distilled water. The anode consisted of a platinum wire of diameter 0.5 mm or 0.3 mm. The electrode was treated with hot alkali before use in the experiments, followed up by hot aqua regia, and cleaned up with glass powder. After each of these procedures the

*Unlike Thomas, Stout did not arrive at any definite conclusions as to the mechanism of the anodic oxidation of the N_3^- ion.

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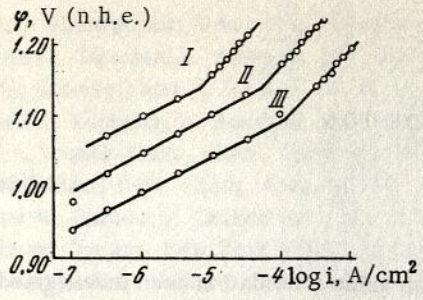

Fig. 1

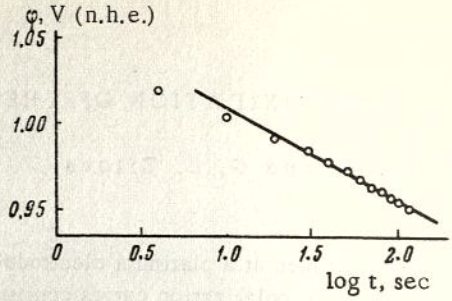

Fig. 2

Fig. 1. Polarization curves in solutions of sodium azide of the following concentrations: I) 10^{-3} N; II) 10^{-2} N; III) 10^{-1} N.

Fig. 2. Curve for decay of potential with time. $i_0 = 10^{-6}$ A/cm^2; 10^{-2} N sodium azide.

electrode was boiled in doubly-distilled water. Before the experiments solutions containing 10^{-1}, 10^{-2}, and 10^{-3} N sodium azide were anodically polarized in a cell separately for pre-electrolysis, using currents of $5 \cdot 10^{-5}$, $5 \cdot 10^{-6}$ and 10^{-6} A respectively, for 24-30 h. More prolonged pre-electrolysis, as tests showed, had no effect on the results of measurement. Oxygen was removed in advance from the cell and the solution by bubbling purified nitrogen through these. During polarization the dilute solutions were stirred by means of nitrogen. All experiments were carried out in an air thermostat at 25 ± 0.2°C. The potential was measured in relation to the saturated calomel electrode. The curves were reproducible in independent experiments on different electrodes with an accuracy of ±5 mV for the lower branch, and ±10 mV for the upper branch of the curves. For a given electrode the reproducibility was as low as ± 2 mV. The data we have obtained lie on the average some 15 mV lower than those of Stout, and some 15 mV higher than those of Thomas.

EXPERIMENTAL RESULTS AND DISCUSSION

Curves showing the relationship between i and φ were obtained in solutions of 10^{-1}, 10^{-2}, and 10^{-3} N sodium azide (Fig. 1). The lower branches have for various concentrations the average slope of 53 mV, while the upper show the value of 110 mV. It is seen from Fig. 1 that, for the lower branches of the curve, the following relationship is observed: for increase in the concentration of sodium azide by a factor of 10, the current density also increases by a factor of 10. A similar result was obtained earlier by Stout [2]. This relationship is in agreement either with a mechanism of slow barrierliess discharge or desorption, or with the one proposed in [3]. If the low slope of the polarization curves is due to barrierless discharge, then on the φ -log i curves for sufficiently high potentials, a discontinuity should arise, corresponding to transition to normal discharge. It is readily seen from Fig. 1 that this is actually observed experimentally.*

For barrierless discharge the overpotential is independent of the concentration, and the potential therefore varies in the same way as the equilibrium value. For ordinary discharge, η, as is well known [5], depends on the concentration of the ion being discharged, and correspondingly φ should change to a larger extent with change in concentration compared with the barrierless process. On the φ -log i curves this should be expressed by a displacement of the break points to lower current densities with reduction in the concentration of the ion being discharged. We have observed a shift in the break point, but this is smaller than would have been expected from the simplest form of the theory of slow discharge, in which no account is taken of specific adsorption of ions. This fact may be explained if it is assumed that the azide ion undergoes strong specific adsorption, so that its surface concentration changes much more slowly than its volume concentration. This assumption seems to be probable, since many ions undergo strong adsorption on platinum [6].

We also obtained curves in solutions of 10^{-1} and 10^{-2} N sodium azide to which potassium chloride and sodium sulfate had been added. The lower branch of these curves was not displaced by additions of these substances at

*The discontinuity in the polarization curves for large current densities was also observed in [1], but the experiments were carried out under conditions for which an appreciable ohmic potential drop would be expected. Hence, it was not possible to draw any definite conclusion about the shape of the polarization curves for high current densities on the basis of the data obtained in [1].

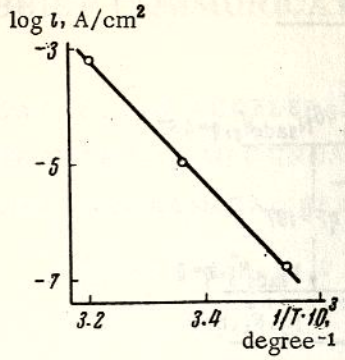

Fig. 3. Temperature dependence of the current at constant overpotential η = 4.67 V in a solution of 10^{-2} N sodium azide.

concentrations even as high as 1 N. The upper portions of the curve was displaced to some extent, but the shift lies within the limits of experimental error. The small shift of the upper branch is presumably also to be explained by specific adsorption of the azide ion. From the charging curves obtained by Thomas [3], it is possible to calculate the capacity of the electrode, which is found to be 1000 $\mu F/cm^2$ of visible surface, which using a coefficient of roughness of 2-3 is of the same order of magnitude as the usual values for electrode capacity in the region of logarithmic adsorption isotherms. If, in the potential region to which the polarization curve applies, equilibrium adsorption of the azide ion from the solution occurred, as Thomas supposed, then the potential decay curves after discontinuing current would be expected to show a large pseudocapacity of the order of 1000 $\mu F/cm^2$. We have obtained curves showing the decay of potential with time. The initial portion of the decay was recorded on an oscillograph, and the later, slower decay, was determined visually using a cathodic voltmeter. The capacity calculated from the slope of the initial portion at t = 0 was found to be 70 ±7 $\mu F/cm^2$. The decay curves for quite large times take the form of straight lines when expressed in coordinates φ -log t (Fig. 2). The slope of these curves is practically coincident with the polarization curve, which suggests that the same mechanism applies to both cases. On the logarithmic portion of the decay curve capacity of 95 ±10 $\mu F/cm^2$ was obtained. Hence the capacity appears to increase somewhat in moving over to the linear portion of the φ -log t curve. The capacity which we have found corresponds with respect to order of magnitude to that of a double layer. On platinum in this region of potentials the double layer capacity obtained from adsorption measurements is equal to 70 $\mu F/cm^2$ [6]. The small deviation in the capacity values obtained from the initial and the logarithmic portions of the decay curves is apparently due to the slowness with which adsorption equilibrium is set up.*

Thus, capacity data clearly contradict any mechanism which would connect the low slope of the polarization curves with any appreciable dependence of the degree of covering the surface by adsorbed azide radicals on the potential. Consequently, the only applicable explanation of the value of "b," which is close to 60 mV, is the assumption that the true value of $\alpha = 1$, that is, that barrierless discharge or barrierless electrochemical desorption occurs.

The choice between these two possible mechanisms has been made on the basis of data on the activation energy of the reaction. The fact is that for barrierless processes the activation energy is equal to the heat of the elementary act, so that on the basis of this value we may find the energetic characteristics of the intermediate reaction products. Comparison of these with the probable values of the corresponding quantities give some indication as to which of the possible schemes is more reasonable.

To calculate the activation energy we obtained polarization curves at 10°, 25°, and 40°C. To find the real value of the activation energy it is necessary to know the value of the quantity $\partial \ln i/\partial(1/T)$ for constant value of the overpotential. For the determination of this quantity it is necessary to calculate $\partial E/\partial T$ for the azide-nitrogen electrode.

The temperature coefficient for the electrode $N_3^-/AgN_3/Ag$ was obtained from [7]. Data on the entropy of formation of silver azide were obtained from [8]. For 40° and 10°C the temperature coefficients for the azide-nitrogen electrode were found to be $2.80 \cdot 10^{-3}$ and $2.87 \cdot 10^{-3}$ V/deg.†

The dependence of log i on 1/T for a constant overpotential of 4.67 V is shown in Fig. 3. From the slope of this straight line a value of the activation energy for the given overpotential was found to be 46 kcal/mole.

We assume that the slow stage is the barrierless discharge of the azide ion and proceed to consider the energy scheme of the process (Fig. 4). The overpotential for which the activation energy is calculated corresponds to an energy of 107 kcal/mole. The energy of formation of the free N_3 radical is 116 kcal/mole [8, 10]. From this scheme it would appear that the energy of adsorption of the N_3-radical is a negative quantity, which is improbable.

*In this connection it is interesting to observe that similar deviations in nature, but even more clearly expressed, between the adsorption data and capacity measurements of a platinum electrode have been found using alternating current [6].

†In calculating the temperature coefficient from the less accurate values for the entropy of formation of the azide ion [9], an approximate value was obtained.

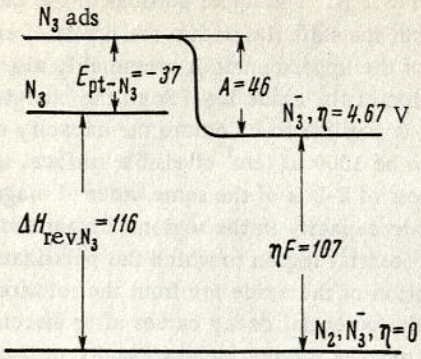

Fig. 4. Energy scheme for the mechanism of barrierless discharge.

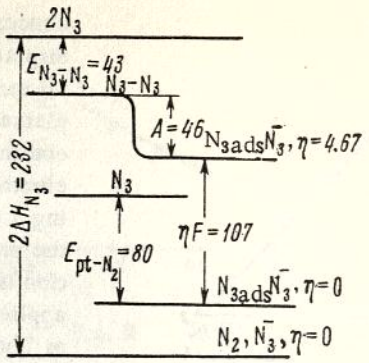

Fig. 5. Energy scheme for the mechanism of barrierless electrochemical desorption.

In addition, assuming a slow discharge mechanism, it is impossible to explain the fact that for the attainment of the potential of any appreciable discharge of the N_3^- ions, it would be necessary for a quite large quantity of electricity to be passed [3].

The experimental data are well explained on the assumption that the slow stage is a barrierless electrochemical desorption, in which case the important factor arises that Θ_{N_3} is close to unity. If this is so, it would be practically independent of the potential, and therefore we should not observe pseudo-capacity on the decay curves. We suggest that as a result of the elementary electrochemical desorption act, the first product formed is the hypothetical molecule N_3-N_3, which is subsequently decomposed with the formation of N_2. Assuming this mechanism of barrierless electrochemical desorption with the formation of N_3-N_3 we obtain the energy scheme sketched in Fig. 5. The energy of the N_3-N_3 has been calculated in [3] as ca. 43 kcal/mole, which may be regarded as a reasonable value, since it represents something like the average of the ordinarily accepted values of the N—N bond (20-70 kcal[10]. It follows from this scheme that the energy of the Pt—N_3 bond is 80 kcal/mole, which is entirely reasonable. If the electrochemical desorption scheme proposed in [3] is accepted, from a consideration of the energy diagram we obtain an energy of adsorption of N_3 equal to 269 kcal/mole, which is less likely. In addition, it is difficult to imagine that the elementary act of the reaction results in the formation simultaneously of free nitrogen molecules. Hence, if we suppose that N_3^- is discharged by a barrierless electrochemical desorption mechanism, it is possible to explain practically all the experimental facts. Of the two possible variants of the electrochemical desorption mechanism, the more probable one is the formation of an unstable intermediate product N_6, which subsequently decomposes rapidly into three nitrogen molecules.

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