

Reprinted from *ANALYTICAL CHEMISTRY*, Vol. 35, Page 1602, October 1963
 Copyright 1963 by the American Chemical Society and reprinted by permission of the copyright owner

Chronopotentiometric Oxidation of Hydrazine at a Platinum Electrode

ALLEN J. BARD

Department of Chemistry, The University of Texas, Austin 12, Texas

► The effect of electrode pretreatment on the anodic oxidation of hydrazine in sulfuric acid solutions was investigated. The reaction occurred with the smallest activation overpotential at a platinized electrode. An increase of $i\tau^{1/2}/C$ with increasing i and decreasing C , over a concentration range of 0.5 to 25mM hydrazine, was observed, and several possible mechanisms for this variation, involving adsorption of hydrazine, bubble formation, occurrence of an intermediate chemical reaction, and occurrence of catalytic decomposition of hydrazine at the electrode surface, are considered.

THE ELECTROOXIDATION OF HYDRAZINE is interesting both for its possible analytical applications and because hydrazine has been suggested as a possible fuel cell component. Recently Karp and Meites (1) examined the oxidation of hydrazine by voltammetry at mercury and platinum electrodes. They suggested that the oxidation proceeded more rapidly at oxide-coated than at reduced-platinum electrodes.

Anson and King (2), however, have demonstrated that increases in reversibility sometimes ascribed to oxide films may, in fact, be due to platinization of the electrode surface. The present study lends support to this idea, and examines the effect of various electrode pretreatments on the anodic oxidation of hydrazine. A variation of the chronopotentiometric constant, $i\tau^{1/2}/C$, with current density and concentration was also found, and some speculations concerning the source of this variation are considered.

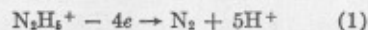
EXPERIMENTAL

The experimental apparatus and procedures have been described (6). The working electrode was a plane shielded platinum disk, oriented horizontally for upward diffusion. The reference electrode was a mercury-mercurous sulfate electrode in contact with a saturated potassium sulfate solution (S.M.S.E.) with a potential of 0.40 volt vs. S.C.E. The reference electrode was positioned so that the tip of its salt bridge was very close to the surface of the platinum working electrode. All potentials given are referred to a S.M.S.E. The chronopotentiometric

cell was thermostated at 25.0° C. The hydrazine solutions were prepared from reagent grade hydrazine sulfate, $N_2H_4 \cdot H_2SO_4$. Although acidic aqueous solutions of hydrazine are stable to air oxidation and autodecomposition (1), test solutions were usually freshly prepared.

RESULTS AND DISCUSSION

Effect of Electrode Pretreatment. The anodic oxidation of hydrazine occurs in acidic solution by the reaction



Equation 1 represents only the overall reaction, and it is not meant to describe the detailed steps in the reaction. The potentials at which this oxidation occurs depend strongly upon the previous history of the platinum anode, and chronopotentiometric waves occurring at potentials separated by as much as 0.5 volt are observed. A chronopotentiogram of the anodic oxidation of hydrazine at an electrode which has been preoxidized by anodization in a 1M H_2SO_4 solution is shown in Figure 1. Also shown in Figure 1 are anodic

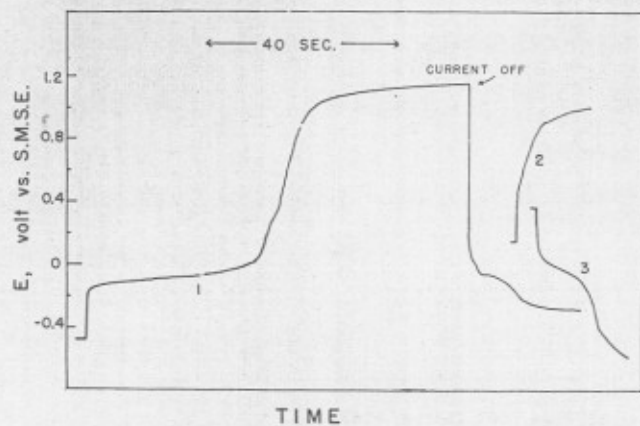


Figure 1. Chronopotentiograms for oxidation of hydrazine and for formation and reduction of PtO

1. 5mM hydrazine, 0.1M H₂SO₄ at preoxidized platinum electrode at a current density of 1.172 ma. per sq. cm.
- 2, 3. 1M H₂SO₄, current density of 85 μ a. per sq. cm.

and cathodic scans in 1M H₂SO₄ alone, at a lower current density, showing the formation and reduction of the platinum oxide film. (Throughout the remainder of this paper, this film will be termed PtO only for convenience and should not be taken to mean this particular oxide rather than another or perhaps chemisorbed oxygen.) Therefore, at a preoxidized electrode, oxidation of hydrazine occurs, followed by formation of PtO starting at about 0.4 volt and finally by evolution of oxygen. The ill defined transition corresponding to PtO formation is prolonged by continued diffusion of hydrazine to the electrode. When the current is turned off, the potential rapidly falls to that characteristic of PtO reduction, and a transition is found corresponding to the chemical reduction of PtO by hydrazine diffusing toward the electrode (Figure 1). Apparently, hydrazine rapidly reduces PtO, and a preoxidized electrode when immersed in a solution containing hydrazine is rapidly converted to one with a freshly reduced platinum surface.

That PtO is rapidly reduced by hydrazine is also shown by the following experiment. When a platinum electrode is anodized in a 1M H₂SO₄ solution, removed, washed, replaced, and cathodized, the characteristic PtO reduction wave is found (curve 3, Figure 1). If the electrode is briefly immersed in a hydrazine solution after the anodization, and then washed and replaced, the PtO reduction wave is no longer seen, and upon cathodization, the potential immediately drops to that characteristic of hydrogen ion reduction; the small hydrogen ion reduction prewave found with a platinized electrode by Anson (1) is also observed. Therefore, at a freshly reduced platinum surface [a surface presumably containing a layer of finely divided platinum (2)], called henceforth "an activated surface,"

hydrazine is oxidized at a potential of -0.1 to -0.2 volt vs. S.M.S.E.

At an electrode which has remained immersed in the test solution for long times, or has been treated with aqua regia, the oxidation of hydrazine occurs at a more positive potential, about 0.5 volt, and the chronopotentiograms are sometimes characterized by sharp oscillations in potential (curves 1 and 4, Figure 2). Repeating the oxidation after the electrode has been allowed to evolve oxygen for a brief time and after the solution has been stirred and allowed to come to rest, gives an oxidation scan characteristic of an activated surface (curve 2), although the transition at 0.5 volt is somewhat longer than that found with a preoxidized electrode. If the electrode is removed from this solution, stripped of any finely divided platinum on its surface with aqua regia, and then subjected to a treatment which will be termed "a.c. activation," the most reversible behavior is obtained (curve 3). The a.c. activation consisted of connecting the working electrode and an auxiliary electrode to a source of d.c. biased 60-cycle a.c. (through an autotransformer and step-down transformer) so that the working electrode potential is rapidly cycled between about -0.4 and 0.95 volt vs. S.M.S.E. This treatment results in the repeated formation and reduction of PtO, and forms a lightly platinized, active surface (2). Oxidation of hydrazine at a heavily platinized electrode (formed by cathodic reduction in a H₂PtCl₆ solution at 20 ma. for 200 seconds) occurred at a potential of about -0.4 volt, but the potential-time curve was very drawn out, with several small humps, and no clear transition could be obtained.

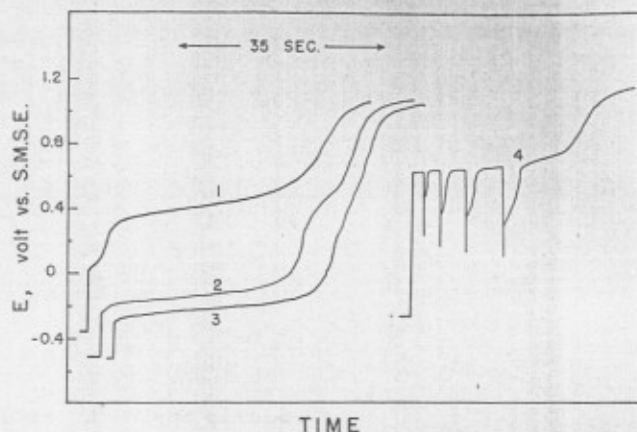


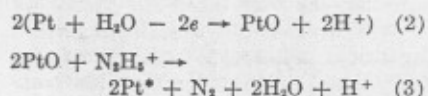
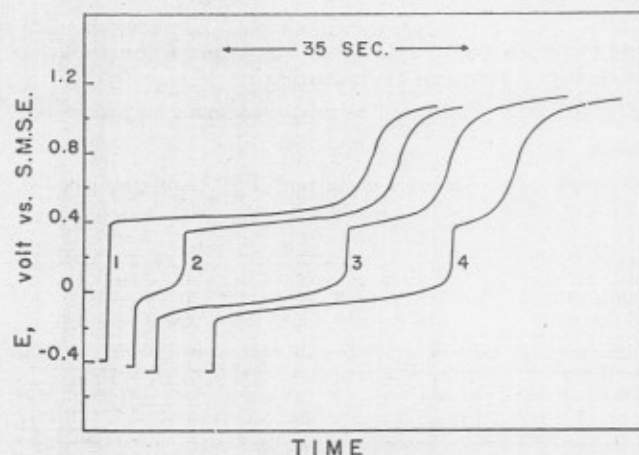
Figure 2. Chronopotentiograms for oxidation of hydrazine at activated and deactivated electrodes

Solution contained 5mM hydrazine and 0.1M H₂SO₄; current density was 1.17 ma. per sq. cm.

1. After several hours immersion in test solution
2. Repeat after 1
3. After a.c. activation
4. After treatment with aqua regia

Precathodization of the platinum electrode—with or without finely divided platinum on its surface, either potentiostatically in 1M H₂SO₄ or at a constant current in the test solution—at potentials where hydrogen ion reduction occurs, leads to behavior characteristic of a deactivated surface (such as that found after long immersions in the test solution or aqua regia treatment) (curve 1 in Figure 3). Repeated trials (curves 2, 3, and 4), after oxidation of the electrode has occurred, indicate partial activation of the surface.

Mechanism of Pretreatment Effects. The following mechanism for the electrode reaction is consistent with the above results. The platinum electrode may be in either an activated or deactivated state, depending upon its previous treatment. The activated state has a surface of freshly prepared, finely divided platinum, which may be produced by reduction of PtO, platinization, or a.c. activation, and upon which the direct oxidation of hydrazine, Equation 1, occurs at -0.1 to -0.2 volt. The deactivated state is characterized by an electrode which has been allowed to remain in contact with the hydrazine solution for long periods of time, which has been treated with aqua regia, or which has been used to evolve hydrogen. Presumably in this case the finely divided platinum on the surface of the electrode is either missing or is poisoned by adsorption of impurities at the active sites or by recrystallization of the surface. The oxidation of hydrazine on a deactivated surface occurs at the same potential as that for PtO formation, and since hydrazine rapidly reduces PtO, the reaction may occur as follows.



The reduction of PtO by hydrazine (reaction 3) may occur either directly or by an electrochemical reaction such as that postulated by Breiter (8) for the reaction of PtO and hydrogen. In the course of these reactions, activated platinum (represented as Pt*) is formed, and active sites are produced at the electrode. On repeated scans—e.g., curves 2, 3, and 4 in Figure 3—hydrazine will be oxidized first at the active sites; when these are used up, for example by adsorption of products on the sites or coverage of the sites with gaseous nitrogen, the potential shifts sharply to that characteristic of the deactivated surface. Alternately, the shift in potential may be caused by the complete occurrence of concentration polarization at the active sites. The overall transition time is about the same, except for the small contribution from PtO formation, at activated and deactivated electrodes.

The oscillations in potential sometimes seen at a deactivated electrode have also been found during the oxidation of hydrogen (8, 14) and methanol and formaldehyde (9). An explanation similar to that given by Sawyer and Seo (14) can be proposed, namely, that oxidation occurs at the deactivated surface, and in the course of reactions 2 and 3 forms active sites. The potential then drops to that for oxidation of hydrazine at an activated surface, but when the few active sites are covered with nitrogen or adsorbed intermediates, the potential again rises to that characteristic of oxidation at a deactivated electrode, forming more active sites, etc. This explanation conforms better to experimental observations than the one which ascribes the oscillations to gas evolution at the electrode. The oscillations when viewed on an oscilloscope are each shaped like an individual chronopotentiogram, and their sequence is usually quite regular and involves

longer and longer times within each oscillation until the transition occurs. The regularity of the oscillations and the absence of oscillations in many other electrode reactions in which a gas is evolved argues against the gas evolution mechanism. On the other hand, if the activation-deactivation mechanism is correct, it is difficult to explain why oscillations are not always obtained at a deactivated electrode, and why an intermediate steady potential is not obtained. Similar oscillations are also found during the electrooxidation of some substituted hydrazines and will be the subject of further investigation.

It may be fruitful to speculate further on the nature of the active sites. The familiar concept in heterogeneous catalysis, that of active sites at edges and corners of crystals, and at grain boundaries, cracks, dislocations, and other imperfections in crystals, was first suggested by Taylor (10). Preferential adsorption of products, intermediates, or other substances is known to block these active sites. To test the effect of this type of poisoning of the surface, the experiments yielding the results shown in Figure 4 were undertaken. The electrode was given the a.c. activation treatment, and the activated electrode oxidation wave of hydrazine (curve 1) was obtained. The electrode was removed from the cell, immersed for about 15 seconds in a dilute acidified potassium iodide solution, washed well with water, and returned to the cell. The resulting chronopotentiogram (curve 2) was now characteristic of a deactivated surface. The electrode could be returned to its activated state by an a.c. activation treatment. When the electrode was treated with several other substances known to poison a platinum catalyst for other heterogeneous reactions, such as hydrogen sulfide and arsenic(III), only slight changes in the behavior of an activated electrode were observed. Iodide ion may preferentially adsorb and block the active sites, or it may alter the nature of the surface by, for example, promoting

Figure 3. Effect of precathodization on chronopotentiograms for oxidation of hydrazine

Solution contained 5mM hydrazine and 0.1M H_2SO_4 ; current density was 1.17 ma. per sq. cm.

1. After potentiostatic cathodization of electrode in 1M H_2SO_4 at -0.8 volt for about 2 minutes
- 2, 3, 4. Consecutive trials following 1

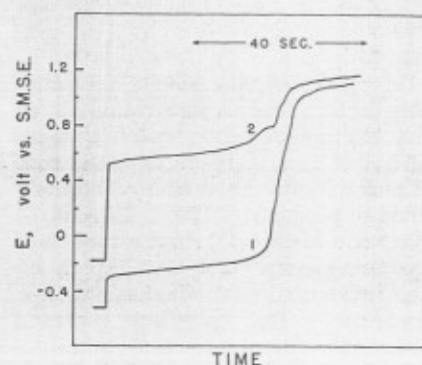


Figure 4. Effect of iodide ion on chronopotentiogram for oxidation of hydrazine

Solution contained 5mM hydrazine and 0.1M H_2SO_4 ; the current density was 1.18 ma. per sq. cm.

1. After a.c. activation
2. After the electrode was immersed for about 15 seconds in an acidified potassium iodide solution, washed, and returned to the test solution

Table I. Variation of $i\tau^{1/2}/C$ with τ for Various Concentrations of Hydrazine

Solution was 1.44M H_2SO_4 . Platinum electrode had projected area of 1.0 sq. cm.

C, mM	i, ma. per sq. cm.	τ , sec.	$i\tau^{1/2}/C$, ma.-sec ^{1/2} /mM
			sq. cm.
25	2.131	127.0	0.96
	2.963	67.0	0.97
	4.732	28.32	1.01
	6.490	16.68	1.06
	7.540	12.94	1.08
10	0.9002	149.7	1.10
	1.174	90.4	1.12
	2.244	27.7	1.18
	3.537	12.44	1.25
5	0.5175	134.9	1.20
	0.8663	50.2	1.23
	1.175	27.8	1.24
	1.488	17.91	1.26
	1.808	12.4	1.27
2.11	0.2266	141.7	1.28
	0.2826	92.8	1.29
	0.4235	41.9	1.30
	0.7167	15.26	1.33
0.98	0.1252	106.4	1.32
	0.1615	65.8	1.34
	0.2104	39.2	1.34
	0.3581	14.76	1.40
0.50	0.05505	125.9	1.24
	0.09382	40.6	1.20
	0.1620	16.51	1.32

the crystallization of the freshly deposited platinum into a more ordered, less active configuration. Deactivation of the electrode by treatment with aqua regia probably involves removal of the finely divided platinum from the surface. Long standing in the test solution might involve adsorption of impurities and products of the electrode reaction. Deactivation of the electrode upon cathodization may arise from the destruction of active sites by hydrogen (11, 14).

In conclusion, the results presented here confirm Anson's observations (1, 2) that electrode reactions tend to be more reversible on a platinum electrode containing a freshly prepared layer of finely divided platinum. The conclusion of Karp and Meites (12), that oxidation of hydrazine occurs much more rapidly on an oxide-coated electrode, has not been confirmed. The half-wave potential obtained by these authors for an oxide-coated rotating platinum electrode is several tenths of a volt more positive than that obtained for the activated electrode in these studies. The current increase during the controlled potential oxidation of hydrazine at a pre-reduced electrode [Figure 2 in (12)] may simply involve the activation of the electrode surface by a mechanism corresponding to Equations 2 and 3, rather than an increase in reaction rate due to oxide film formation.

Variation of $i\tau^{1/2}/C$. In all further experiments, before a series of trials, the electrode was treated with aqua regia to remove any old finely divided platinum from its surface, and then it was given an a.c. activation treatment for 90 seconds to form an activated electrode with a reproducible surface area. This type of pretreatment is also useful for several other applications of a platinum electrode in chronopotentiometry. Chronopotentiograms were carried to oxygen evolution in every trial, so that the electrode was maintained in an activated state throughout a series of experiments. Data for the oxidation of 0.5 to 25mM hydrazine in a 1.44M H_2SO_4 solution at various current densities are given in Table I. Each entry represents the average of at least two trials at the same current. Note that the chronopotentiometric constant, $i\tau^{1/2}/C$, increases with increasing current density, and decreases with increasing concentration of hydrazine. Several alternate mechanisms can be suggested to account for this variation of $i\tau^{1/2}/C$. These are discussed below.

Adsorption Mechanism. When only charging of the double-layer, oxide-film formation, and adsorption of the electroactive species complicate the diffusion controlled electrode reaction, $i\tau^{1/2}/C$ will increase with increasing i . A previously proposed

Table II. Slopes and Intercepts of $i\tau^{1/2}/C$ vs. $\tau^{-1/2}$ Plots and Apparent Extent of Adsorption of Hydrazine

Experimental conditions as in Table I. Values of Γ calculated assuming only adsorption contributes to B .

C, mM	Intercept ^a	Slope $\times C$ (or B), mcoulombs/sq. cm.	$\Gamma \times 10^8$ moles/sq. cm.
25	0.89 \pm 0.01 ^b	0.68 \pm 0.06	4.4 \pm 0.4
10	1.041 \pm 0.002	0.73 \pm 0.01	1.89 \pm 0.02
5	1.174 \pm 0.004	0.35 \pm 0.02	0.46 \pm 0.02
2.11	1.259 \pm 0.004	0.26 \pm 0.02	0.14 \pm 0.01
0.98	1.268 \pm 0.008	0.51 \pm 0.04	0.13 \pm 0.01
0.50	1.16 \pm 0.08	0.6 \pm 0.5	0.07 \pm 0.06

^a Theoretically constant for only the cases of adsorption, double layer charging, or oxide film formation effecting the diffusion controlled reaction, and equal to $nFD^{1/2}\tau^{1/2}/2$.

^b Variations represent the standard deviations.

model for correcting for these effects yielded the following equation (5).

$$\frac{i\tau^{1/2}}{C} = \frac{nFD^{1/2}\tau^{1/2}}{2} + \frac{B}{C\tau^{1/2}} \quad (4)$$

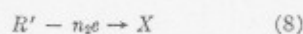
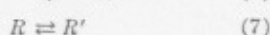
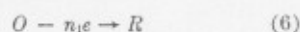
where B , the correction factor, is a function of double-layer capacity, of the amount of electricity involved in formation of PtO , and of the amount of electroactive substance adsorbed. When $i\tau^{1/2}/C$ is plotted against $\tau^{-1/2}$, a series of straight lines is obtained. The slopes and intercepts of these lines, and the standard deviations of each, computed by a linear least squares treatment of the data using a computer program designed for determining the extent of adsorption (15), are given in Table II. For the oxidation of hydrazine under these conditions, especially at higher concentrations of hydrazine, contributions to B from charging of the double layer and from electrode oxidation will be negligible. Assuming that adsorption of hydrazine is the only complicating factor, and using the model previously proposed (15), values of Γ , the amount of adsorption of hydrazine in moles per sq. cm., can be calculated (Table II). Two factors argue against these computed values of Γ actually representing the amount of hydrazine adsorbed. First, according to the model employed, the intercepts of the lines should be constant and equal to $1/2nFD^{1/2}\tau^{1/2}$. In this case, the intercepts decrease with increasing hydrazine concentration. Using the value for the diffusion coefficient found in 1M NaOH (12), 1.35×10^{-5} sq. cm. per second, and correcting for the difference in viscosity between 1M NaOH and 1.44M H_2SO_4 , we calculate a D of 1.47×10^{-5} sq. cm. per second for hydrazine in our supporting electrolyte (assuming the additional protonation of the molecule does not decrease D appreciably), and a theoretical $1/2nFD^{1/2}\tau^{1/2}$ of 1.31 ma.-second^{1/2} per sq. cm.-mM. This value is larger than all of the values found here, and corresponds almost exactly to an extrapolation of the observed intercepts to a zero concentration of hydrazine (ex-

cluding the less accurate value for 0.5mM hydrazine). A second argument against an adsorption mechanism is the very large extent of adsorption computed. Construction of various modes of orientation of the molecule on the electrode surface indicates that a monolayer of adsorbed hydrazine should involve less than 0.5×10^{-8} mole per sq. cm. of hydrazine. Therefore the calculated values of Γ , for concentrations of hydrazine greater than 5mM, represent adsorption of multilayers, with the Γ at 25mM, hydrazine representing at least 8 layers of hydrazine. Although this extent of adsorption is possible—e.g., by hydrogen bonding of additional layers of hydrazine molecules—it seems unlikely.

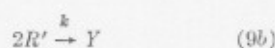
Bubble Mechanism. Since nitrogen gas is produced during the electrode reaction, bubbles of gas accumulating during the electrolysis possibly block portions of the electrode. The effect of this type of blockage, effectively and continually increasing the current density during the electrolysis, was calculated using a simple model of bubble formation and assuming maximum possible coverage per bubble—i.e., that the effective blocking area of each bubble is its cross-sectional area—for various numbers of bubbles. The effect indeed produces an increasing $i\tau^{1/2}/C$ with increasing i , but the overall effect becomes smaller at higher concentrations of the electroactive substance, and should be negligible for 25mM hydrazine solutions at short transition times. Details of this work will be presented elsewhere, but we conclude that this effect is not a major contribution to the variation of $i\tau^{1/2}/C$ in this case.

Competing Intermediate Chemical Reaction. The variation may be caused by a competing chemical reaction involved in the overall electrode reaction. Most types of complicating chemical reactions, such as slow preceding reactions producing the electroactive species, or catalytic reactions regenerating the electroactive species, lead to a decrease of $i\tau^{1/2}/C$

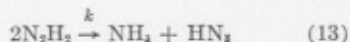
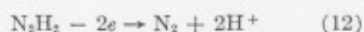
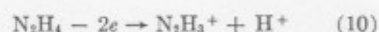
with increasing i . However, consider a reaction scheme such as



or



where O is the original electroactive species, R is the product of the primary electrode reaction, and X and Y are not electroactive. Although this scheme has not been treated mathematically for chronopotentiometry, the overall behavior should qualitatively involve increases of $i\tau^{1/2}/C$ with increasing i . At very short times the effect of the competing chemical reaction, 9, becomes negligible, and $i\tau^{1/2}/C$ will essentially equal $1/2(n_1 + n_2)FD^{1/2}\pi^{1/2}$. At very long times, reaction 9 becomes important, effectively consuming all of R' in the limit, and $i\tau^{1/2}/C$ becomes equal to $1/2n_1FD^{1/2}\pi^{1/2}$. Therefore, in an intermediate time range, depending upon the magnitude of k , $i\tau^{1/2}/C$ will increase with increasing i . If the competing reaction is a second order reaction, such as 9b, the effect will become larger at higher concentrations of O leading to a decrease in $i\tau^{1/2}/C$ with increasing C . The proposed mechanism of the anodic oxidation of hydrazine in acidic solutions (12) [written in a somewhat condensed form (7)] is similar to (but more complicated than) the scheme presented above.



The existence of the additional reaction, 14, and the proposed electroactivity of $N_2H_3^+$ itself (12) make the exact theoretical treatment of this scheme difficult. While this type of reaction mechanism would give the $i\tau^{1/2}/C$ behavior found here, it is unlikely that this is the sole contribution to the variation. Although conditions existing at the electrode are somewhat different in chronopotentiometry and controlled potential coulometry, results obtained with the latter technique (12) indicated that the effect of reaction 13 should be negligible in a 1.44M H_2SO_4 solution, a fact which originally suggested the choice of this medium for the chronopotentiometric experiments. A more detailed study of the mechanism of the anodic oxidation of hydrazine is currently being undertaken.

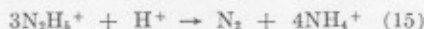
Table III. Calculated and Experimental Values of $i\tau^{1/2}/C$ Assuming the Catalytic Decomposition Mechanism

Experimental conditions as in Table I. Calculations performed by assuming
 $i_0 = nFk C_{N_2H_4}^2$
 $K = nFD^{1/2}\pi^{1/2}/2 = 1.31$ ma.-sec.^{1/2}/sq. cm.-mM
 $k = 2.5 \times 10^{-11}$ mole/sq. cm.-sec.

C, mM	i_0 , ma. per sq. cm.	i , ma. per sq. cm.	$i\tau^{1/2}/C$, ma.-sec. ^{1/2} /sq. cm.-mM		Experimental	
			Calcd. assuming $t_1 = 60$ sec.	$t_1 = 120$ sec.		
25	0.625	2.131	0.97	0.92	0.96	
		2.963	1.02	0.97	0.97	
		4.732	1.07	1.01	1.01	
		6.490	1.09	1.02	1.06	
		7.540	1.10	1.02	1.08	
10	0.100	0.9002	1.16	1.14	1.10	
		1.174	1.18	1.16	1.12	
		2.244	1.22	1.19	1.18	
		3.537	1.23	1.20	1.25	
5	0.025	0.5175	1.24	1.23	1.20	
		0.8663	1.26	1.24	1.23	
		1.175	1.26	1.25	1.24	
		1.488	1.27	1.25	1.26	
		1.808	1.27	1.25	1.27	
2.11	0.00445	0.2266	1.28	1.28	1.28	
		0.2826	1.28	1.28	1.29	
		0.4235	1.29	1.28	1.30	
		0.7167	1.29	1.29	1.33	

For concentrations of 0.98 and 0.5mM hydrazine, corresponding to i_0 's of 0.00096 and 0.00025 ma. per sq. cm., respectively, the theoretical $i\tau^{1/2}/C$ calculates as 1.30 for all values of i .

Catalytic Decomposition of Hydrazine. Finally the variation in $i\tau^{1/2}/C$ may be caused by the catalytic decomposition of hydrazine. Although acidic aqueous solutions of hydrazine are stable, hydrazine sulfate is readily decomposed on contact with active platinum (4) in accordance with the equation (in acidic solutions).



Hydrazine is not decomposed on smooth or deactivated platinum. Since the activated platinum electrode contains a layer of finely divided platinum on its surface, reaction 15 must occur before, and simultaneously with, the electrode reaction. The effect of this heterogeneous chemical reaction is to decrease the concentration of hydrazine in the vicinity of the electrode before electrolysis, during the waiting period of 1 to 2 minutes after stirring, when the solution is allowed to come to rest. As a simple model of this effect, we can consider the heterogeneous chemical reaction to be equivalent to a small constant current density, i_0 , flowing continually at the electrode surface. After the solution has been stirred before a trial, i_0 flows until time t_1 , when the actual electrolysis current, i , is switched on. The fictitious current density, i_0 , is assumed to be related to the rate constant of reaction 15 and the concentration of hydrazine at the electrode surface, $C_{N_2H_4}(x=0)$.

$$i_0 = nFk C_{N_2H_4}(x=0) \quad (16a)$$

or

$$i_0 = nFk C_{N_2H_4}^2(x=0) \quad (16b)$$

The simplifying assumption of a constant i_0 implies that reaction 15 is slow, so that the concentration of hydrazine at the electrode surface is not significantly depleted before the electrolysis, and it neglects the variation of i_0 during the electrolysis, as $C_{N_2H_4}(x=0)$ goes to zero. A model with a varying i_0 could readily be treated by the method proposed below, but would yield a more complicated final expression. The quantitative results of the proposed model are obtained using the treatment of chronopotentiometry with step functional changes in current (13, 16), and they lead to the equation

$$\frac{\pi^{1/2}nFD^{1/2}C}{2} = i_0(t_1 + \tau)^{1/2} + i\tau^{1/2} \quad (17)$$

where τ is the observed transition time, measured from t_1 . Writing $\pi^{1/2}nFD^{1/2}/2 = K$, and assuming that $i_0 < i$ and that $i_0 t_1^{1/2} < KC$, the solution of reaction 17 is

$$\tau^{1/2} = \frac{iKC - i_0[(i^2 - i_0^2)t_1 + K^2C^2]^{1/2}}{(i^2 - i_0^2)} \quad (18)$$

Values of $\tau^{1/2}$ and $i\tau^{1/2}/C$ were calculated, using Equation 18, assuming $K = 1.31$ ma.-sec.^{1/2}/mM-sq. cm. and various values for t_1 and i_0 , for each experimental i and C . The best fit to the experimental data for a t_1 of 60 to 120 seconds (the usual waiting period between stirring the solution after a trial) was obtained for a second order dependence of i_0 on C (Equation 16b) and a k of about 2.5×10^{-11} mole per sq. cm.-sec. The agreement between

calculated and experimental values of $i\tau^{1/2}/C$ in Table III is quite good, considering the approximate nature of the theoretical model and the actual experimental variability in t_1 . Moreover k depends upon the condition of the electrode surface, and decreases to zero as the electrode becomes deactivated. Note that the effective currents involved in the catalytic decomposition would not alter the total bulk concentration of hydrazine appreciably. For example, even in the worst case, where i_0 is 0.6 ma. in 25mM hydrazine, the bulk concentration would only decrease about 0.2% per hour. The formation of various intermediates and products during the catalytic decomposition, and the accumulation of these on the electrode surface may account for the loss of activity of the electrode upon standing in the hydrazine solution.

Clearly the relatively small amount of data and the present unavailability of other supporting experiments do not allow a satisfactory choice to be made

from among the possible mechanisms proposed. Probably all of the perturbing effects, adsorption, bubble formation, a secondary intermediate chemical reaction, and catalytic decomposition, occur to some extent. Because the relative contribution of these effects is not currently understood, no attempt was made in this study to interpret the experimental potential-time curves.

ACKNOWLEDGMENT

Discussions with Harvey Herman were most helpful. Some preliminary experiments were performed by Anthony Petropoulos. The support of the Robert A. Welch Foundation and The University of Texas Research Institute is gratefully acknowledged.

LITERATURE CITED

- (1) Anson, F. C., *ANAL. CHEM.* **33**, 934 (1961).
- (2) Anson, F. C., King, D. M., *Ibid.*, **34**, 362 (1962).

- (3) Armstrong, G., Butler, J. A. V., *Discussions Faraday Soc.* **1**, 122 (1947).
- (4) Audrieth, L. F., Ogg, B. A., "The Chemistry of Hydrazine," pp. 145-8, Wiley, New York, 1951.
- (5) Bard, A. J., *ANAL. CHEM.* **35**, 340 (1963).
- (6) *Ibid.*, **33**, 11 (1961).
- (7) Bard, A. J., Mayell, J. S., *J. Phys. Chem.* **66**, 2173 (1962).
- (8) Breiter, M. W., *J. Electrochem. Soc.* **109**, 425 (1962).
- (9) Buck, R. P., Griffith, L. R., *Ibid.*, p. 1005.
- (10) Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., p. 1148, Van Nostrand, New York, 1946.
- (11) Hammett, L. P., Lorch, A. E., *J. Am. Chem. Soc.* **55**, 70 (1933).
- (12) Karp, S., Meites, L., *Ibid.*, **84**, 906 (1962).
- (13) Murray, R. W., Reilley, C. N., *J. Electroanal. Chem.* **3**, 182 (1962).
- (14) Sawyer, D. T., Seo, E. T., *Ibid.*, **5**, 23 (1963).
- (15) Tatwawadi, S. V., Bard, A. J. Southwest Regional Meeting, ACS, Dallas, Texas, December 1962.
- (16) Testa, A. C., Reinmuth, W. H., *ANAL. CHEM.* **33**, 1324 (1961).

RECEIVED for review May 24, 1963.
Accepted July 26, 1963.