

The Electrochemistry of the Methylhydrazines

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The electrooxidation of methylhydrazine, 1,2-dimethylhydrazine, and 1,1-dimethylhydrazine at a platinum electrode was studied using chronopotentiometry, coulometry, and product analysis. The results show that methylhydrazine is oxidized in an over-all four-electron reaction to nitrogen and methanol. The oxidation of 1,2-dimethylhydrazine proceeds by an initial two-electron oxidation, followed by a chemical reaction leading to formation of formaldehyde and methylhydrazine. The oxidation of 1,1-dimethylhydrazine occurs by a two-electron oxidation to 1,1-dimethyldiazene which undergoes a relatively slow chemical decomposition.

The electrochemistry of the methylhydrazines is of interest for several reasons. Analytical methods carried out by chemical oxidation with halogens or halates²⁻⁴ might also be based on electroanalytical methods. Moreover, the mechanism of the oxidation of the hydrazines is of interest. The results of recent investigations of the electrooxidation of hydrazine^{5,6} have suggested that intermediate reactions occur which are too rapid to study conveniently. A study of the electrooxidation of the methylhydrazines was undertaken to provide evidence for the formation of intermediate species in the reaction and to gain insight into the mechanism for the oxidation of hydrazine itself. Moreover the reactions of the intermediates themselves are of interest. The electrooxidation of methylhydrazine, 1,2-dimethylhydrazine, and 1,1-dimethylhydrazine on a platinum electrode in sulfuric acid solution was investigated using chronopotentiometry and controlled potential coulometry. No similar electrochemical studies have been reported.

Results and Discussion

Chronopotentiometry. The over-all chronopotentiometric behavior of the methylhydrazines is similar to that of hydrazine itself.⁶ For example, if an oxidized platinum electrode is immersed briefly in a 1 mM methylhydrazine solution, 1 M in H₂SO₄, the chronopotentiometric wave characteristic of the reduction of the surface of an oxidized platinum electrode disappears, indicating that methylhydrazine reduces an oxidized platinum surface just as hydrazine does. Moreover the behavior of the methylhydrazines depends strongly upon the pretreatment of the electrode. Typical results are shown in Figures 1 and 2. Oxidation of methylhydrazine at an aged, reduced electrode⁷ does

not occur until potentials at which the electrode is oxidized are attained (curves 1). An aged electrode with appropriate concentrations of any of the methylhydrazines showed oscillations in potential similar to those observed with hydrazine (e.g., Figure 2, curve 1). Oscillations in current were also observed for the controlled potential oxidation of 1,1-dimethylhydrazine under certain conditions (*vide infra*). A detailed explanation of these type of oscillations has not been given, but they have been ascribed to an activating-deactivating process at the electrode surface.^{6,8} Chronopotentiograms taken with an electrode that has been recently oxidized or which has been subject to a.c. activation⁶ show the oxidations to occur at less positive potentials (curves 2). This behavior has been ascribed to activation of the electrode surface caused by formation of a layer of finely divided platinum.^{6,7}

Typical data for these oxidations are shown in Table I. Because of the strong dependence of behavior on

Table I. Chronopotentiometric Data for Oxidation of Methylhydrazines^a

Compound	Current, μ a.	Concn., mM	Transition time, sec.	$i\tau^{1/2}/C$, (μ a.-sec. ^{1/2})/mM	n^b
Hydrazine				230 ^c	(4)
Methylhydrazine	390	12.8	54	225	(4)
	560		27	227	
1,2-Dimethylhydrazine	390	9.6	11.0	135	2.4
			13.0	147	2.6
			15.5	160	2.8
1,1-Dimethylhydrazine	390	13	16	120	2.1
	560		6	106	1.9

^a The supporting electrolyte was 1 M sulfuric acid; the anode was a platinum disk of 0.2 cm.² area. ^b Calculated assuming a four-electron oxidation for hydrazine and methylhydrazine and equal diffusion coefficients for all species. ^c Based on data in ref. 6 at same current density and concentration level, corrected to an electrode with an area of 0.2 cm.².

the nature electrode surface and perhaps other effects, such as spontaneous catalytic decomposition of the methylhydrazines at the electrode surface such as that found with hydrazine,⁶ the reproducibility of the data was only fair. However, assuming the diffusion coefficients of the hydrazines are about the same, an apparent number of electrons involved in the electrode reaction can be calculated using the Sand equation. Neither methylhydrazine nor 1,2-dimethylhydrazine showed a wave upon reversal of current (Figure 1, curve 3), even for transition times as short as 10 msec. For 1,1-dimethylhydrazine, current reversal produced a

(8) D. T. Sawyer and E. T. Seo, *J. Electroanal. Chem.*, 3, 182 (1962), and references contained therein.

(1) To whom correspondence and request for reprints should be directed.

(2) E. C. Olson, *Anal. Chem.*, 32, 1545 (1960).

(3) W. R. McBride, R. A. Henry, and S. Skolnik, *ibid.*, 25, 1042 (1953).

(4) W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, 79, 572 (1957).

(5) S. Karp and L. Meites, *ibid.*, 84, 906 (1962).

(6) A. J. Bard, *Anal. Chem.*, 35, 1602 (1963).

(7) F. C. Anson and D. M. King, *ibid.*, 34, 362 (1962).

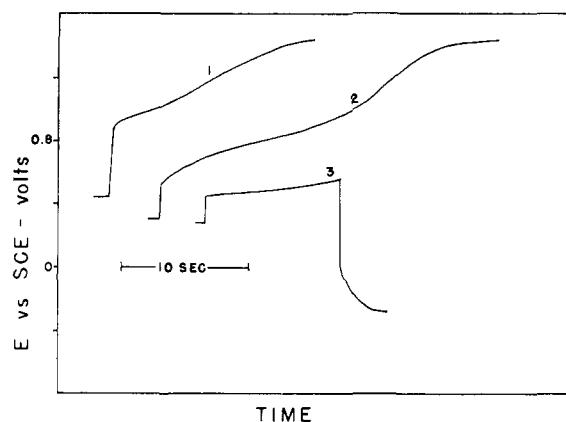


Figure 1. Chronopotentiograms of the oxidation of methylhydrazine at $250 \mu\text{a./cm.}^2$ in 0.7 mM methylhydrazine and 1 M H_2SO_4 : 1, aged, reduced electrode; 2, repeat after 1; 3, with current reversal.

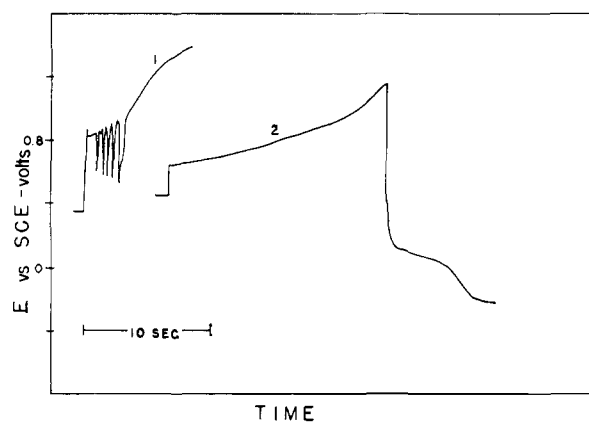


Figure 2. Chronopotentiograms of the oxidation of 1,1-dimethylhydrazine at 1.5 ma./cm.^2 in 13 mM 1,1-dimethylhydrazine and 1 M H_2SO_4 : 1, aged, reduced electrode; 2, a.c.-activated electrode with current reversal.

reverse wave about one-third the size of the forward wave (Figure 2, curve 2) indicating that the product formed on oxidation is reducible and stable during the duration of the experiment.

Controlled Potential Coulometry. Results obtained for controlled potential coulometric oxidation of the methylhydrazines is shown in Table II. Electrolysis studies were performed in a gas-tight cell designed for gas volume measurements and product analysis.⁹ By using this cell, both the total amount of nitrogen evolved and the volume of nitrogen evolved as a function of the coulombs of electricity consumed could be determined. Figure 3 shows a plot of the volume of nitrogen evolved vs. mfaradays for the oxidation of the methylhydrazines. If nitrogen is released in the initial electrode reaction or if all intermediate chemical reactions are rapid, then a linear relationship is expected. This behavior is found for methylhydrazine (curve 1). Curvature in these plots is found with 1,2-dimethylhydrazine (curve 2) and 1,1-dimethylhydrazine (curve 3), which indicates a delay in the release of nitrogen during the electrolysis and suggests that nitrogen is not formed in the initial electrode reaction. In all cases nitrogen evolution stops when the electrolysis is

(9) D. M. King and A. J. Bard, *Anal. Chem.*, **36**, 2351 (1964).

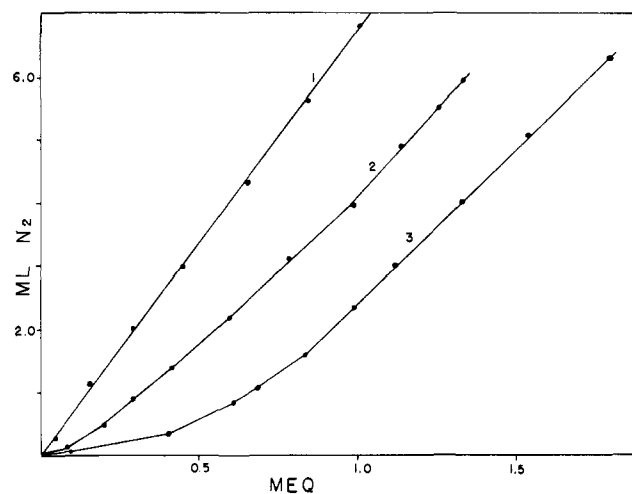


Figure 3. Nitrogen evolved during electrolysis of the methylhydrazines as a function of milliequivalents of substance oxidized (mfaradays of electricity consumed); the solution was 25 ml. of 1 M H_2SO_4 and the control potential was $1.0 \text{ v. vs. s.c.e.}$: 1, methylhydrazine (0.320 mmole); 2, 1,2-dimethylhydrazine (0.239 mmole); 3, 1,1-dimethylhydrazine (0.326 mmole).

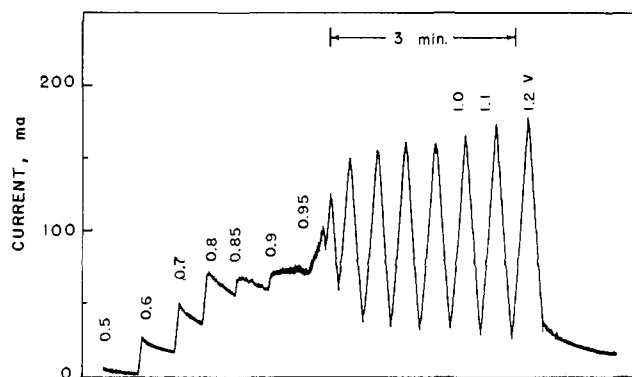


Figure 4. Electrolysis current during controlled potential oxidation of 1,1-dimethylhydrazine at various potentials vs. s.c.e.

stopped, so that nitrogen evolution results from an electrode reaction rather than a homogeneous chemical reaction.

Oscillations in the current were sometimes observed during the coulometric oxidations. Figure 4 shows these current oscillations at different potential settings for the oxidation of 1,1-dimethylhydrazine. The oscillations start at potentials where the electrode is oxidized. Since these results were obtained with an electromechanical potentiostat, the frequency of the oscillations may reflect the balancing time of the servo-device rather than the inherent frequency of the phenomenon. The effect is probably similar to the activation-deactivation process in chronopotentiometry which involves oxidation of the electrode surface and blocking of the electrode reaction, followed by reduction of the oxide film and reactivation of the electrode. At a potential of about 1.2 v. the current stops oscillating and falls to a low value.

Mechanisms of Reactions. Methylhydrazine is oxidized in an over-all reaction involving four electrons



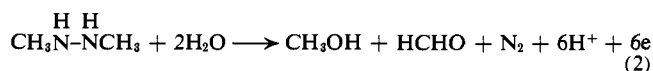
Table II. Controlled Potential Coulometric Results^a

Compound	Amount taken, mmole	n_{app}	Products
Methylhydrazine	0.238	3.86	N ₂ (0.239 mmole), methanol
	0.00694 ^b	3.96 ± 0.02 ^c	
1,2-Dimethylhydrazine	0.510	6.20	N ₂ (0.532 mmole), methanol, formaldehyde
	0.239	5.94	N ₂ (0.240 mmole), methanol, formaldehyde (0.21 mmole)
1,1-Dimethylhydrazine	0.326	4.7 ^d	N ₂ (0.194 mmole), methanol, formaldehyde, dimethylamine
	0.326	5.9 ^e	N ₂ (0.270 mmole), methanol, formaldehyde (0.26 mmole), dimethylamine

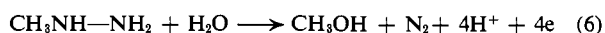
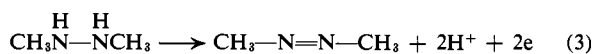
^a The solution was 25 ml. of 1.0 M H₂SO₄; the anode was platinum gauze and the platinum cathode was isolated by a sintered-glass disk and an agar plug; the anode potential was controlled at 1.0 v. vs. s.c.e. ^b Solution volume of 7 ml. in "high speed" cell.¹³ ^c Average of trials at control potentials of +0.6 to +0.9 v. vs. s.c.e. ^d Electrolysis interrupted for about 1 hr. after 0.65 mequiv. of oxidation. ^e Electrolysis carried out continuously.

Since the chronopotentiometric results also indicate a four-electron wave, any intermediate chemical or electrochemical steps involved in this reaction are too rapid to be observed by these techniques.

The coulometric results indicate that the over-all oxidation of 1,2-dimethylhydrazine involves six electrons.



The chronopotentiometric results indicate an n of between 2 and 3, well less than the six-electron change indicated coulometrically. The following mechanism accounts for the behavior of 1,2-dimethylhydrazine.



A similar mechanism was previously suggested by McBride and co-workers³ to account for the 6 equiv. of iodate required for the chemical oxidation of 1,2-dimethylhydrazine. The absence of a reversal wave in the chronopotentiometric studies suggests that reaction 4 is very rapid. Reaction 5 is somewhat slower so that contributions from reaction 6 during chronopotentiometric experiments is small.

The oxidation of 1,1-dimethylhydrazine is more complicated and the over-all mechanism has not been resolved completely. The pronounced curvature in the plot of Figure 3 indicates that nitrogen is not evolved in the initial electrode reaction. Coulometry indicated that the over-all n value varied between 4.7 and 5.9 depending upon whether the electrolysis was interrupted or carried out continuously. The relative transition time from chronopotentiometric experiments indicated an initial two-electron reaction.

That an unstable intermediate undergoing a slow chemical reaction is involved in the reaction was shown clearly by carrying out chronopotentiometric experiments during a coulometric oxidation. During the initial stages of the oxidation a product forms which is not oxidizable but is reducible and produces the reverse chronopotentiometric wave. This reduction wave increases in size during the electrolysis reaching a max-

imum at the point where 2 faradays/mole of hydrazine have been consumed. At this stage nitrogen gas also starts to be evolved in appreciable amounts. In one trial the electrolysis was stopped at this point, and reduction and oxidation chronopotentiograms were recorded as a function of time. The results are shown in Figure 5. Clearly the reducible species is decaying

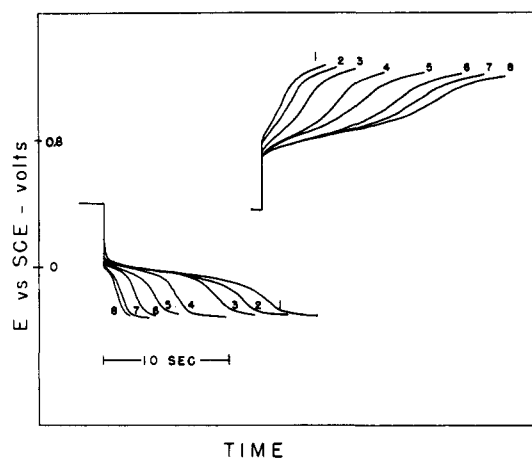
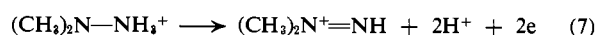


Figure 5. Chronopotentiograms of intermediate formed during controlled potential oxidation of 1,1-dimethylhydrazine. The solution initially contained 0.326 mmole of 1,1-dimethylhydrazine in 25 ml. of 1 M H₂SO₄ and was electrolyzed with the passage of 0.65 mfaraday of electricity. The current density was 1 ma./cm.² for chronopotentiograms 1-8 taken successively between 0 and 39 min. after interruption of controlled potential electrolysis.

with time by a chemical reaction and forming a new oxidizable species. The relative transition times suggest that these reactions also involve a two-electron oxidation. Figure 6 shows a plot of the log of the square root of the transition time, τ , vs. time; the linearity shows that the intermediate is undergoing a first-order reaction with a half-life of about 25 min.

The first step in the reaction is probably the formation of a diazene (eq. 7). McBride and Kruse⁴ described



and isolated the perchlorate salt of 1,1-dimethyldiazene by the oxidation of 1,1-dimethylhydrazine with halogens or halates. In neutral or alkaline solutions

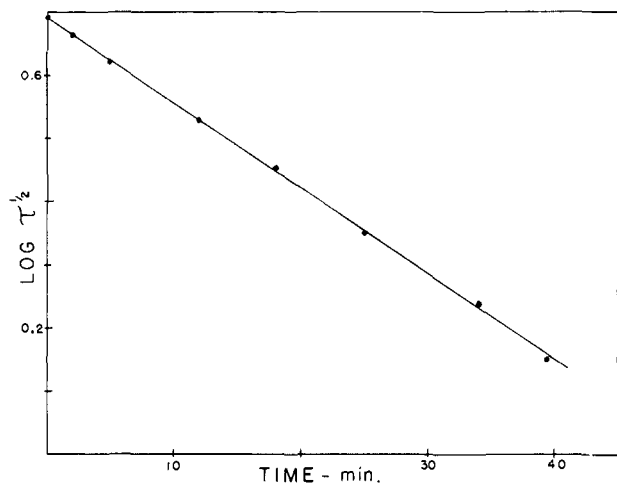
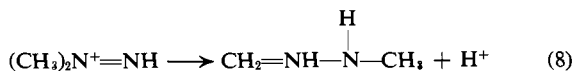


Figure 6. Variation of transition time for the intermediate formed during oxidation of 1,1-dimethylhydrazine (data from Figure 5).

they found that the species coupled to form a tetrazene but in acidic solutions the 1,1-dimethyldiazonium ion did not couple, but underwent a slow decomposition. The experimental evidence indicates that more than one reaction path exists from this stage. The chronopotentiometric data suggest that the electrooxidizable species formed during the chemical reaction undergoes a two-electron reaction. However, the coulometric data indicate that subsequent reactions must involve at least four more electrons. The electrolysis times required for 1,1-dimethylhydrazine were quite long (more than 1 hr.). Additional amounts of electricity required in the coulometry experiments may be the result of the oxidation of a species generated slowly and kept at a low concentration through a reversible reaction. Thus this species might escape notice during the chronopotentiometry experiments, but contribute to the over-all electrolysis. The products of the electrolysis include nitrogen, methanol, formaldehyde, dimethylamine (identified upon making the solution alkaline), and a yellow soluble unidentified species. This yellow species was formed in larger amounts during the electrolysis with interruption and appeared only after electrolysis was resumed. Note that essentially equal quantities of nitrogen and formaldehyde were formed, but that the total quantities were less than that which would result from the complete conversion of 1,1-dimethylhydrazine to these substances.

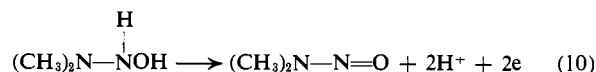
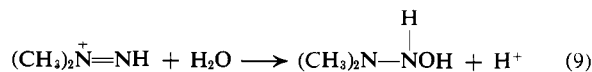
There are several mechanisms which can account for these observations. Rearrangements of 1,1-disubstituted diazenes to the corresponding hydrazones¹⁰ is well known. The following is suggested (a discussion of details in the mechanisms of this transformation are given by Lemal and co-workers).



This hydrazone could then hydrolyze (reaction 5) leading to methylhydrazine and a subsequent four-electron oxidation. This path would lead to an over-all six-electron reaction and lead to the formation of nitrogen, methanol, and formaldehyde.

(10) See, e.g., D. M. Lemal, F. Menger, and E. Coats, *J. Am. Chem. Soc.*, **86**, 2395 (1964), and numerous references contained therein.

Another sequence of reactions (eq. 9 and 10) could involve hydrolysis of the diazene followed by electro-oxidation to N-nitrosodimethylamine. This sequence



would involve an over-all four-electron reaction leading to a yellow product. An unequivocal identification of the yellow species produced in the electrolysis as N-nitrosodimethylamine was not accomplished, however. The N-nitrosodimethylamine may slowly hydrolyze in the acidic solution to dimethylamine and nitrous acid; the small final background current, which is higher than the original residual current, may result from oxidation of nitrous acid.

A third possible reaction involves coupling to the tetrazene.



However, McBride and Bens¹¹ have shown that coupling of the dialkyldiazonium ion in acidic solution is only important at concentrations of this species greater than 0.2 M. Furthermore a coupling reaction would be second order in diazenium ion, whereas a first-order decomposition was found during the electrolysis. We conclude that reaction 11 is probably not important in this case.

Conclusion

The electrooxidation of the dimethylhydrazines has been shown to proceed by an initial two-electron oxidation involving cleavage of the nitrogen-hydrogen bonds. Although the intermediate reactions of methylhydrazine are too rapid to observe, a similar mechanism may be involved. These results are in agreement with results for the electrooxidation of hydrazine in which an initial two-electron oxidation was proposed on the basis of analysis of current-potential curves.⁵ Further work on the electrochemistry of other substituted hydrazines is in progress.

Experimental

Stock solutions were prepared by weight from methylhydrazine sulfate and 1,1-dimethylhydrazine obtained from Eastman Kodak Co., and from *sym*-dimethylhydrazine dihydrochloride obtained from Aldrich Chemical Co. and were used as received. All test solutions were 1 M in sulfuric acid.

The chronopotentiometric apparatus was conventional and was previously described.¹² The working electrode was a horizontal platinum disk with a projected area of 0.2 cm.²

Controlled potential coulometric experiments were carried out using both a Wenking potentiostat and a "high-speed" coulometric cell¹³ and an electromechanical potentiostat¹⁴ and a cell designed for measurement of gas volumes.⁹ Measurements were made at room temperature (23 ± 2°).

(11) W. R. McBride and E. M. Bens, *ibid.*, **81**, 5546 (1959).

(12) A. J. Bard, *Anal. Chem.*, **33**, 11 (1961).

(13) A. J. Bard, *ibid.*, **35**, 1121 (1963).

(14) R. W. Lamphere, *ibid.*, **23**, 258 (1951).

Gases were analyzed by mass spectrometry. Solutions were analyzed qualitatively by distillation of the sample solution either with or without neutralization of the sulfuric acid, and examination of the distillate using vapor phase chromatography. Formaldehyde was

determined by precipitation with 5,5-dimethyl-1,3-cyclohexanedione.

Acknowledgment. The support of the Robert A. Welch Foundation and the National Science Foundation (Grant No. GP-1921) is gratefully acknowledged.

Characteristics of Anodic Currents at Dropping Amalgam Electrodes

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Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota. Received October 9, 1964

Anodic polarograms at dropping amalgam electrodes exhibit two apparently different types of anomalies on the negative and positive sides of the electrocapillary maximum (e.c.m.), respectively. In 0.1 M supporting electrolyte solutions, current-potential curves of amalgams which are oxidized on the negative side of e.c.m. exhibit a maximum, the current decreasing abruptly at a potential near e.c.m. As the potential is made further positive, current gradually increases again instead of giving a diffusion current plateau. Streaming was found to occur on both sides of e.c.m., in the downward direction on the negative side and in the upward direction on the positive side. At amalgam electrodes which give an anodic wave on the positive side of e.c.m., no maximum appears, but the limiting current is considerably greater than the true diffusion current and increases gradually as the potential is shifted toward more positive values. Streaming occurs in the upward direction at these electrodes. Experimental evidence is presented, showing that despite the considerable difference in appearance both types of anomalies (termed negative maximum and positive exaltation) can essentially be accounted for in terms of the factors which are considered responsible for the occurrence of the so-called maxima of the first kind. The contribution of the "Spüleffekt" also cannot be ignored for the positive exaltation. In the presence of a sufficient amount of a suitable maximum suppressor, neither the positive exaltation nor the negative maximum appears and the polarogram becomes normal in appearance. However, analysis of current-time curves reveals that the "Spüleffekt" prevails even in the presence of maximum suppressors, and current becomes diffusion-controlled only when the rate of amalgam flow m is smaller than about 0.5 mg. sec.⁻¹. Under these conditions current-time curves closely follow the original Ilkovic equation rather than the von Stackelberg-Toome equation.

Cathodic maxima at the dropping mercury electrode have been studied extensively by several groups of investigators and thorough, critical discussions of their characteristics have appeared in recent years.^{1,2} On

(1) M. von Stackelberg and R. Doppelfeld, "Advances in Polarography," Vol. 1, I. S. Longmuir, Ed., Pergamon Press, New York, N. Y., 1960, pp. 68-104.

(2) V. G. Levich, "Physicochemical Hydrodynamics," translated by

the other hand, only fragmentary descriptions are found in the literature of characteristics of anodic maxima at dropping amalgam electrodes. Furman and Cooper³ reported that sharp anodic maxima occur at dropping cadmium and zinc amalgam electrodes in dilute solutions of potassium chloride, while no maxima occur at some amalgams in certain media. Heyrovsky⁴ observed a vigorous streaming which occurs in the downward direction at potentials of the maximum current at cadmium and zinc amalgam electrodes. He also states that no maximum nor streaming occurs at dropping amalgam electrodes of bismuth, copper, lead, and tin. We confirmed the occurrence of sharp maxima and streaming at cadmium and zinc amalgam electrodes, but contrary to Heyrovsky's statement, we found that at the dropping copper amalgam electrode weak upward streaming takes place and that the limiting current decreases considerably upon addition of surface-active substances.⁵ Recently Schupp, Youness, and Watters⁶ studied the dependence of anodic limiting currents at a dropping copper amalgam electrode on the capillary characteristics in the absence of surface-active substances and found that the limiting current constant decreases with decreasing value of $m^{2/3}t^{1/6}$. They attribute this to stirring within the amalgam drop caused by the flow of amalgam into the amalgam drop (Spüleffekt).^{7,8}

It was the purpose of the present investigation to study systematically effects of various factors on acute maxima observed with dropping amalgam electrodes which yield waves at the negative side of the electrocapillary maximum (e.c.m.) and on exaltation of limiting currents at the positive side of the e.c.m. Experiments are described to throw light on the cause of the two apparently different types of anomalies.

A study was also made of the characteristics of current-time curves during the lifetime of a single amalgam

Scripta Technica, Inc., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

(3) N. H. Furman and W. C. Cooper, *J. Am. Chem. Soc.*, **72**, 5667 (1950).

(4) J. Heyrovsky, *Z. physik. Chem.* (Leipzig), **7** (1958).

(5) I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, **83**, 47 (1961).

(6) O. E. Schupp, III, T. Youness, and J. I. Watters, *ibid.*, **84**, 505 (1962).

(7) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

(8) M. von Stackelberg and V. Toome, *ibid.*, **58**, 226 (1954).