a partial decomposition of Schiff base. Possibly a higher activation energy is required to convert compound I to II than that for the Schiff base formation in the absence of metal, since the former requires splitting a nickel–oxygen bond that does not occur in the latter case.

Reaction between Copper(II), Salicylaldehyde and Glycine.—The reactions between glycine and salicylaldehyde with copper(II) ion proved to be not so favorable for quantitative studies as those with nickel. Fig. 8-A, B, C and D are the spectra of copper ion and the copper complexes of salicylaldehyde, glycine and salicylaldehyde–glycine, respectively. The lower three curves of Fig. 9 represent the changes in optical density with time for the addition of salicylaldehyde to copper–glycine. As in the nickel system, there is a transition from the glycine complex spectrum to the Schiff base complex spectrum.

The upper curve of Fig. 9 represents the optical density changes for the addition of copper(II) to salicylaldehyde–glycine. The initial optical density in this case, again as in the nickel system, is not that of the glycine complex but fairly close to the absorption of the Schiff base complex. Again the attainment of equilibrium is much faster when the Schiff base components are mixed initially than when the metal is permitted first to react with one of them. In fact, the initial optical density is equivalent to that obtained after more than 1.5 hr. when salicylaldehyde is added to copper–glycine.

The behavior of copper differs from that of nickel in two respects: (1) copper increases the amount of Schiff base present at equilibrium, and (2) all of the reactions are very much slower than those with nickel, as a comparison of Figs. 2 and 4 with Fig. 9 will demonstrate.

Conclusions

These experiments demonstrate that the nature of the participation of metal ions in Schiff base formation is determined by the order in which the reactants are mixed; equilibrium is achieved most rapidly when the metal ion is added last. It is noteworthy that the thermodynamic stabilization of the product of a reaction by a metal ion can be accompanied by a retardation of the reaction with the metal.

The instantaneous production of the spectrum characteristic of nickel Schiff base complexes upon the addition of nickel to the Schiff base components indicates that the Schiff base is formed in solution without the aid of metal. The addition of either copper or nickel ions to the premixed organic reagents results in the immediate formation of Schiff base complex in concentrations not very different from those at equilibrium; further progress toward equilibrium produces somewhat more Schiff base with copper and less with nickel. The prior formation of a metal complex with glycine results in drastic retardation of Schiff base formation both with nickel and with copper. It is concluded that, even when the metal thermodynamically favors Schiff base formation, as is the case with copper, the metal tends to prevent rapid attainment of equilibrium.

Ikawa and Snell[21] and Christensen and Riggs[19] have found that salicylaldehyde does not participate in transamination and the other vitamin B_6-catalyzed reactions. Salicylaldehyde is therefore not analogous to pyridoxal in the molecular rearrangements that follow Schiff base formation, since these rearrangements require either the pyridoxal nitrogen or another electron-attracting group.[9,19] However, all of the ligands that bind metal in the pyridoxal-amino acid Schiff bases are also present when salicylaldehyde is substituted for pyridoxal. The conclusions drawn from the salicylaldehyde system are therefore also applicable to pyridoxal Schiff base formation. Since this reaction is retarded by metal ions, it would appear that the effect of metal ions on the vitamin B_6-catalyzed reactions occurs after, and not before, Schiff base formation.

Acknowledgments.—The authors wish to thank the Research Corporation for its generous financial support of a portion of this project. They are grateful to Mrs. Mary Ann Stevan and Miss Barbara Randall for technical assistance and to Drs. Jack Dunitz and Bernard Witkop for helpful discussion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK]

The Voltammetric Characteristics and Mechanism of Electroöxidation of Hydrazine

BY STEWART KARP[1] AND LOUIS MEITES

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The oxidation of hydrazine at a mercury or oxide-coated platinum electrode yields nitrogen as the principal product. Under some conditions, however, ammonia also is formed as a result of the dimerization of diimide. A mechanism for the process is suggested: though generally similar to the accepted mechanism for the reaction of hydrazine with a two-electron chemical oxidizing agent, it also serves to explain the effects of such variables as *p*H and chloride-ion concentration on the extent of the dimerization reaction.

Introduction

Many electro-reductions and -oxidations, especially of organic substances, proceed *via* free-radical intermediates whose dimerizations exert marked effects on the products, yields and apparent *n*-values obtained by controlled-potential electrolysis

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[1] This paper is based on a thesis submitted by Stewart Karp to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of M.S. in Chemistry, June, 1960.

and coulometry.[2] This paper presents the results of an inquiry into the utility of coulometry at controlled potential in revealing the detailed mechanism of such a process. Hydrazine was selected for this purpose for two reasons. One was that the mechanism of its chemical oxidation had been thoroughly and carefully investigated by numerous authors,[3–8] whose essentially concordant conclusions left no doubt that a dimerization step is involved in the chemical mechanism and seemed likely to prove valuable in the interpretation of the electrochemical results. The other was that the widespread use of hydrazine as an anodic depolarizer in electrolytic work, as a constituent of supporting electrolytes for polarography,[9] as a constituent of the electrolyte in a gas coulometer,[10] as a reagent in reductometric titrations[11] and for various other electrochemical purposes seemed to make a more detailed knowledge of its electrochemical characteristics desirable.

The polarographic and voltammetric behavior of hydrazine has been studied only rather briefly, and its behavior toward controlled-potential electrolysis has not been studied at all. Vivarelli[12] investigated the polarography of hydrazine in alkaline solutions and concluded correctly that nitrogen was the final product of its oxidation. Goon[13] found that neither the half-wave potential nor the ratio of limiting current to concentration was quite independent of the hydrazine concentration when a rotating platinum electrode was employed in an acidic solution. Neither of these authors, however, studied the mechanism of the reaction. Page and Lingane[10] found that the volume of the nitrogen–hydrogen mixture obtained from the constant-current electrolysis of a hydrazine sulfate solution was several tenths of a per cent. smaller than the expected value. All of these observations are in general accord with those reported below.

Experimental

Polarograms were obtained with a locally constructed and carefully calibrated recording polarograph. A conventional dropping electrode assembly was employed; the dropping electrode itself was a length of Corning marine barometer tubing. Rotating platinum electrodes were of the conventional type and were rotated at 600 r.p.m. by a synchronous motor. Modified H-cells[14] were used; their saturated calomel electrodes were frequently checked and replaced whenever necessary. All potentials are referred to the s.c.e.

Except in some work with platinum electrodes in fairly acidic solutions, where dissolved air had been found to have no effect on the results obtained, all solutions were deaerated with prepurified nitrogen which had been scrubbed with chromous chloride and then with water at the temperature of the thermostat. All polarographic and voltametric measurements were made at 25.00 ± 0.02°; controlled-potential electrolyses were made at 25 ± 1°.

The potentiostat and current integrator have been described previously.[15] A double-diaphragm cell[15] was used in most of the coulometric experiments. Where replicate experiments conducted in the presence and absence of air had shown deaeration to be unnecessary, a beaker was sometimes employed instead in work with platinum electrodes in acidic media. In this case magnetic stirring was used, and the auxiliary cathode was isolated inside a glass tube having a sintered-glass disc at its lower end and filled with the pure supporting electrolyte to a level well above that of the solution in the beaker. Beckman fiber-type electrodes usually were employed as reference electrodes in the coulometric work. In some experiments described below, however, mercury–mercurous sulfate–saturated potassium sulfate electrodes were used instead.

Stock solutions (about 0.1 F) of hydrazine dihydrochloride and hydrazine sulfate were prepared from the reagent-grade salts; hydrazine perchlorate solutions were prepared by mixing dilute solutions of hydrazine and perchloric acid. These solutions were frequently standardized against potassium iodate by the method of Jamieson.[16] Though the concentration of 0.1 F hydrazine dihydrochloride decreased about 0.2% per month, 0.1 F hydrazine perchlorate retained the same titer within experimental error for at least 7 months.

Mercury was purified by the procedure of Meites and Moros.[17] All other chemicals were ordinary reagent grade.

A Beckman Model G pH meter, calibrated against standard reference buffers, was used for all pH measurements. Hydroxyl-ion activities in $\mathbf{C}F$ sodium hydroxide solutions ($\mathbf{C} > 0.1$) were estimated, following Haight,[18] from the values of $f_{\pm}$ obtained by Akerlöf and Kegeles.[19] For convenience of comparison with data obtained in less strongly alkaline solutions, these estimates are expressed below in the form of nominal pH values calculated from the equation $p\text{H} = 14 + \log f_{\pm}\mathbf{C}$.

Weights and volumetric apparatus were calibrated by conventional procedures.

Results and Discussion

Polarography in Alkaline Solutions.—In agreement with Vivarelli,[12] we find 4 F sodiun hydroxide to be the supporting electrolyte best suited to the practical polarographic determination of hydrazine. At higher sodium hydroxide concentrations, the diffusion current constant decreases markedly because of the increasing viscosity; in less strongly alkaline solutions the half-wave potential shifts toward more positive values, the plateau becomes shorter and less accurately parallel to the residual current curve, and the wave height becomes less amenable to precise measurement.

The diffusion current was found to be strictly proportional to the concentration of hydrazine above 0.1 mM in 4 F sodium hydroxide. Slightly low values of i_d/C were obtained with 0.04 mM hydrazine, perhaps because of oxidation by a trace of air introduced along with the aliquot of stock hydrazine solution. In the mechanism described below it is important that there is no indication of any decrease of i_d/C in this medium on increasing the hydrazine concentration up to even 9 mM.

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(4) (a) W. C. E. Higginson, D. Sutton and P. Wright, *J. Chem. Soc.*, 1380 (1953); (b) W. C. E. Higginson and D. Sutton, *ibid.*, 1402 (1953); (c) W. C. E. Higginson and P. Wright, *ibid.*, 1551 (1955).

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(15) L. Meites, *ibid.*, **27**, 1116 (1955).

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(17) L. Meites and S. A. Moros, *Anal. Chem.*, **31**, 23 (1959).

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(19) G. Akerlöf and G. Kegeles, *ibid.*, **62**, 620 (1940).

With a capillary for which m = 3.01 mg./sec. and t = 3.31 sec. at −0.20 v. *vs.* s.c.e., $I\ (= i_d/Cm^{2/3}t^{1/6})$ was found to be −6.95 ± 0.08 in 4 F sodium hydroxide. Vivarelli[12] reported −5.4 ± 0.1. No reasonable explanation for the discrepancy is apparent.

The diffusion current constant of hydrazine decreases from −9.2 ± 0.1 in 0.1 F to −4.2 ± 0.05 in 10 F sodium hydroxide. This decrease is less rapid than the concomitant increase of viscosity; using values of Z, the specific viscosity, taken or extrapolated from data in the International Critical Tables, the value of $IZ^{1/2}$ was found to increase steadily from −9.3 in 0.1 F to −13.6 in 10 F sodium hydroxide. Evidently the solvation number of hydrazine decreases markedly with increasing sodium hydroxide concentration.

According to the Ilkovic equation, the value of I in 1 F sodium hydroxide corresponds to $607nD_{N_2H_4}^{1/2} = -8.9$. The diffusion coefficient of hydrazine is unknown, but extrapolating that of ammonia, as given in the International Critical Tables, to 25° and applying Jander's equation[20] to the result (2.36 × 10^{-5} cm.²/sec.) gives $D_{N_2H_4}$ = 1.39 × 10^{-5} cm.²/sec. in a dilute aqueous solution at 25°. This in turn gives n = −3.94, so that the over-all half-reaction must be $N_2H_4 + 4\ OH^- \rightarrow N_2 + 4\ H_2O + 4\ e$. This is supported by Vivarelli's demonstration[12] that the diffusion current constant of hydrazine is almost exactly twice that of hydroxylamine, for which n = −2, and is further confirmed by the results of controlled-potential coulometric experiments, which give n = −4 unambiguously.

The diffusion current constant of hydrazine in 4 F sodium hydroxide is not wholly independent of capillary characteristics. Typical data, obtained with a capillary for which mt was 9.9 mg., showed that I decreased uniformly from −7.05 at t = 2.5 sec. to −6.52 at t = 6.1 sec. This is in the opposite direction from the effect predicted by the Strehlow–von Stackelberg equation,[21] but is similar to the behavior, for which no explanation has been advanced, that was observed by Loveridge[22] for hydroquinone and by Meites and Meites[23] for bismuth.

A plot of $E_{d.e.}$ *vs.* $\log i/(i_d - i)$ for the wave obtained in 4 F sodium hydroxide is linear; its slope is +58 mv. when average currents are employed in the log term. This indication of the irreversibility of the over-all half-reaction is confirmed by a comparison of the observed half-wave potential (−0.334 ± 0.004 v. *vs.* s.c.e.) in 4 F sodium hydroxide with that calculated (−1.38 v. *vs.* s.c.e.) from Latimer's value[24] for the standard potential of the nitrogen–hydrazine couple with $[N_2H_4] = 2 \times 10^{-4}\ M$ and p_{N_2} = 1 atm. It may be mentioned that, in further violation of the thermodynamic expectations, varying the hydrazine concentration from 0.02 to 9 mM in 4 F sodium hydroxide had no detectable effect on the half-wave potential.

According to Kern,[25] the slope of a log plot constructed with average currents is given by $\Delta E_{d.e.}/\Delta[\log i/(i_d - i)] = -59.1/\alpha n_a$ mv. at 25°. This gives αn_a = −0.98 in 4 F sodium hydroxide. Other values of αn_a, as well as of $k_{f,h}{}^0$, obtained by the procedure described by Delahay[26] and founded on the calculations of Koutecky,[27] are given in Table I. The value of αn_a is independent of pH. Since it is higher than any value ever recorded for any process whose rate-determining step was definitely known to involve just one electron, it appears to correspond to n_a = −2 (so that α = 0.45 ± 0.02).

If the equation for the rate-determining step is

$$N_2H_4 + p\ OH^- \xrightarrow{k} \text{products} + 2\ e$$

where k is the true standard heterogeneous rate constant, then the variation of $k_{f,h}{}^0$ with hydroxyl-ion concentration will be given by

$$k_{f,h}{}^0 = k[OH^-]^p$$

or

$$\log k_{f,h}{}^0 = C + p(pH) \qquad (1)$$

where $C = \log k - 14\ \mathbf{p}$. The values in the last column of Table I were calculated with C = −15.86 and $\mathbf{p}$ = 1; their agreement with the experimental values shows conclusively that one hydroxyl ion is involved in the rate-determining step.

TABLE I

ELECTROCHEMICAL KINETIC PARAMETERS FOR THE OXIDATION OF HYDRAZINE AT DROPPING MERCURY ELECTRODES

$[N_2H_4]$ = 0.2 mM: m = *ca.* 3 mg./sec.; t = *ca.* 3.3 sec. The values in the last column were calculated from the equation $\log k_{f,h}{}^0 = -15.86 + p$H

Supporting electrolyte	pH	$E_{1/2}$, v. *vs.* s.c.e.	αn_a	Log $k_{f,h}{}^0$ Obsd.	Log $k_{f,h}{}^0$ Calcd.
10F NaOH	15.5[a]	−0.410	−0.90	−0.337	−0.36
4 F NaOH	14.6[a]	− .337	− .95	−1.24	−1.26
0.1 F NaOH	12.9	− .221	− .85	−3.01	−2.96
0.1 F NaOH + 0.1 F H_3BO_3	10.2	− .051	− .86	−5.64	−5.66
		Mean:	$-0.89 \pm 0.03_5$		

[a] The procedure employed for the estimation of this quantity is outlined in the "Experimental" section above.

An equivalent method of estimating $\mathbf{p}$ consists of plotting $E_{1/2}$ *vs.* pH and obtaining the slope of the resulting straight line. Since[28]

$$E_{1/2} = \frac{0.0591}{\alpha n_a} \log \frac{1.349\ k_{f,h}{}^0\ t^{1/2}}{D_{N_2H_4}{}^{1/2}} \qquad (2)$$

equations 1 and 2 give

$$\Delta E_{1/2}/\Delta(pH) = 0.0591p/\alpha n_a$$

or, since αn_a = −0.89

$$\Delta E_{1/2}/\Delta(pH) = -0.0655p \qquad (3)$$

The experimental data over the range of pH values from 7 to 15.5 are best fitted by the equation

$$E_{1/2} = +0.60 - 0.064\ pH \qquad (4)$$

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[20] G. Jander and H. Spandau, *Z. physik. Chem.*, **A185**, 325 (1939).

[21] H. Strehlow and M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

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[23] L. Meites and T. Meites, *J. Am. Chem. Soc.*, **72**, 3686 (1950).

[24] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 99.

[25] D. M. H. Kern, *J. Am. Chem. Soc.*, **76**, 4234 (1954).

[26] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 78–81.

[27] J. Koutecky, *Chem. Listy*, **47**, 323 (1953).

[28] L. Meites and Y. Israel, *J. Am. Chem. Soc.*, **83**, 4903 (1961).

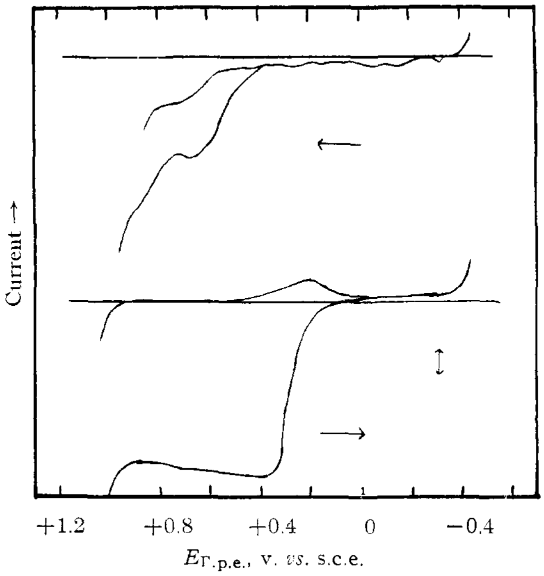

Fig. 1.—Residual current curves and current–potential curves for hydrazine, obtained with (upper curves) precathodized and (lower curves) preanodized rotating platinum electrodes. Horizontal arrows indicate directions of polarization; the height of the vertical arrow corresponds to 25 μamp.

with only minor deviations at the highest pH values (where the liquid-junction potential is significant) and at the lowest (where the wave is no longer well-defined). Clearly $p = 1$.

Hence the rate-determining step in the oxidation of hydrazine at a dropping mercury electrode may be written

$$\mathrm{N_2H_4 + OH^- \longrightarrow N_2H_3^+ + H_2O + 2\,e} \quad (5)$$

The kinetically equivalent scheme $\mathrm{N_2H_4 = H^+ + N_2H_3^-}$; $\mathrm{N_2H_3^- \rightarrow N_2H_3^+ + 2\,e}$ appears less probable because hydrazine is not known to display any appreciable acidic properties. The nature of the subsequent steps is discussed in a later paragraph. Here it will be noted only that, although $\mathrm{N_2H_3^+}$ itself has not previously been written as an intermediate in the oxidation of hydrazine, its conjugate base, $\mathrm{N_2H_2}$ (diimide), first was postulated by Kirk and Browne.[3]

Voltammetry at Rotating Platinum Electrodes.—Tracings of typical voltammograms obtained with solutions of hydrazine in 0.5 F sulfuric acid are shown in Fig. 1. The upper curves in this Figure were obtained by precathodizing the electrode for about a minute at −0.2 v., then recording in the direction of increasingly positive potentials. The lower curves were obtained by polarization toward increasingly negative potentials after preanodization at +1.2 v. The residual current curves show the characteristic patterns due to platinum oxide formation and dissolution that were described by Kolthoff and Tanaka[29] and further studied by Anson and Lingane[30] and Lee, Adams and Bricker.[31] In general, as is the case in Fig. 1, much better defined waves and much more reproducible wave parameters were obtained by polarizing a preanodized electrode toward more negative potentials.

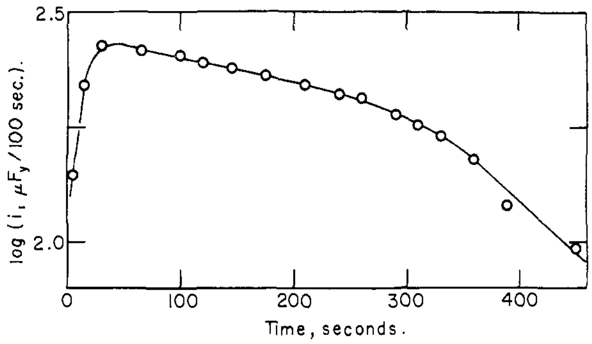

Fig. 2.—Initial portion of the chronoamperogram obtained for the oxidation of 10 mM hydrazine in 1 F hydrochloric acid at an initially oxide-free platinum gauze electrode.

Over the range of pH values from 0 (1 F hydrochloric or sulfuric acid) to 13 (0.1 F sodium hydroxide), and in buffers containing tartrate, acetate, ammonia or borate, the half-wave potential of hydrazine at a rotating platinum electrode is given by the equation

$$E_{1/2} = +0.53 - 0.062\,p\mathrm{H} \quad (6)$$

It is believed, however, that the similarity between equations 4 and 6 is largely coincidental. The most striking characteristic of a voltammogram for the oxidation of hydrazine on a preanodized platinum electrode at any pH is the fact that the rising portion of the hydrazine wave always occurs in exactly the same range of potentials as the cathodic oxide dissolution pattern. This is illustrated by the lower curves of Fig. 1. It shows that the presence of an oxide film on the surface of the electrode plays a vital role in the oxidation process—or, more explicitly, that the oxidation of hydrazine proceeds much more rapidly on an oxide-coated than on a bare platinum surface.

This idea is supported by two additional observations. One is that no wave is obtained for the oxidation of hydrazine in concentrated hydrochloric acid, in which a platinum oxide film cannot form.[30] The other is that the shape of the chronoamperogram obtained during the controlled-potential oxidation of hydrazine at a large platinum gauze working anode depends on the prior history of the electrode. When the electrode is preanodized and hydrazine then is added without interrupting the electrolysis circuit, so that the oxide film remains on the electrode surface, the electrolysis current decreases with time in the normal exponential fashion. However, if the electrolysis circuit is opened while the hydrazine is being added, the oxide film previously formed is chemically reduced by the hydrazine, and for the resulting bare platinum electrode the current *increases* at the start of the electrolysis. This is shown in Fig. 2. Evidently the oxidation of hydrazine is very slow on the bare platinum surface that is initially exposed to the solution. However, as the electrolysis proceeds the oxide film becomes thicker and the rate of hydrazine oxidation in-

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(29) I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, **26**, 632 (1954).

(30) F. C. Anson and J. J. Lingane, *J. Am. Chem. Soc.*, **79**, 4901 (1957).

(31) J. K. Lee, R. N. Adams, and C. E. Bricker, *Anal. Chim. Acta*, **17**, 321 (1957).

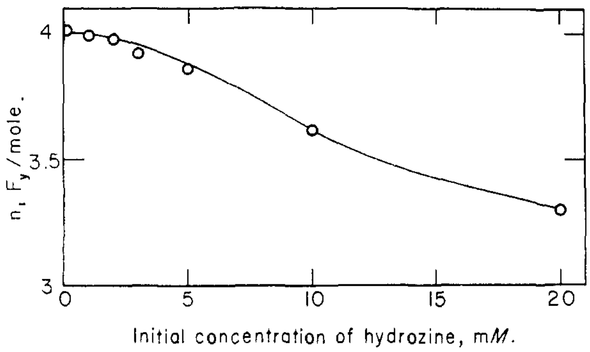

Fig. 3.—Effect of initial concentration of hydrazine on its coulometric *n*-value. The data were obtained in 1 *F* hydrochloric acid solutions, using platinum gauze working electrodes at $E_{\mathrm{w.e.}} = +0.90$ v. *vs.* s.c.e.

creases. Finally, when the oxide film has attained a constant thickness, the current begins to decrease in the customary exponential manner that reflects control by mass transfer alone. This variation of oxidation rate with the thickness of the oxide film is no doubt responsible for the distorted voltammograms obtained with precathodized electrodes and illustrated by the upper curves in Fig. 1.

Similar differences between the rates of various half-reactions on bare and on oxide-coated platinum electrodes have been reported previously by Davis[32] and by Lingane.[33]

The manner in which the limiting current of hydrazine varies with its concentration is importantly affected by *p*H, and this can be directly correlated with the manner in which the controlled-potential coulometric *n*-value depends upon hydrazine concentration at different *p*H values.

For example, the limiting current of hydrazine is directly proportional to its concentration in 0.1 *F* sodium hydrogen tartrate–0.1 *F* tartaric acid (*p*H 3.0). Using preanodized electrodes polarized toward increasingly negative potentials, the mean deviation (± 3.1%) of i_l/C is of the same order as that which is considered customary in work with rotating platinum electrodes, and there is no indication of a trend in the values. Similarly, coulometry at controlled potential gives *n*-values in fair agreement with the expected −4.00 even at quite high initial concentrations of hydrazine.[34]

Distinctly different behavior is observed at lower *p*H values. Table II shows the relationship between limiting current and hydrazine concentration in 1 *F* hydrochloric acid. To permit the study of fairly concentrated solutions, the sensitivity of the electrode was decreased by amputating the protruding portion of the platinum wire and grinding the stub with fine emery cloth until it was flush with the surrounding glass. The large decrease of i_l/C at the higher concentrations of hydrazine is closely paralleled by the coulometric data shown in Fig. 3. At the highest concentrations of hydrazine the limiting currents fluctuated rather widely, because the rapid formation and disengagement of nitrogen bubbles on the electrode surface caused the effective area of the electrode to vary from one instant to the next and also caused some turbulence in the surrounding layer of solution. Although the values of i_l/C therefore become less and less precise as the concentration of hydrazine increases, the general trends of the values of i_l/C and of *n* are strikingly similar.

TABLE II

LIMITING CURRENT OF HYDRAZINE IN 1 *F* HYDROCHLORIC ACID

The electrode shape is described in the text. To avoid loss of hydrazine by chemical oxidation by chlorine formed on more extensive preanodization, the voltammograms were simply recorded from +1.2 v. toward more negative potentials. Values accompanied by mean deviations are the means of individual data obtained with replicate solutions on different days.

$C_{\mathrm{N_2H_4}}$, m*M*	i_l, microamp.	i_l/C
0.100	− 4.08	−40.9
0.505	− 20.65 ± 0.05	−40.85 ± 0.1
0.998	− 39.8	−39.9
5.05	−163 ± 2	−32.3 ± 0.4
9.98	−310 ± 16	−31.0 ± 1.6
20.0	−526	−26.3

The decrease of *n* with increasing hydrazine concentration was accompanied by the formation of increasing amounts of ammonium ion. Several solutions were analyzed for ammonium ion after they had been quantitatively electroöxidized. This was done by adding excess alkali, distilling the ammonia into excess boric acid solution and back-titrating with standard acid. Within a reasonable estimate of the experimental errors involved in dealing with such small amounts of ammonia, the results agreed well with those predicted by the equation

$$N_{\mathrm{NH_4^+}} = \frac{1}{3}(4\,N_{\mathrm{N_2H_4}}{}^0 - Q) \qquad (7)$$

where $N_{\mathrm{NH_4^+}}$ is the number of millimoles of ammonium ion expected, $N_{\mathrm{N_2H_4}}{}^0$ is the number of millimoles of hydrazine present at the start of the electrolysis, and Q is the number of millifaradays consumed. Equation 7 follows directly from stoichiometric considerations if ammonium ion and nitrogen are assumed to be the only products of the electrolysis. The familiar ferric chloride test showed that hydrazoic acid was not present at a detectable concentration at the completion of an electrolysis.

These effects of hydrazine concentration are the expected results of a second-order chemical side reaction that competes with the principal electrochemical process and that involves the dimerization of some intermediate to yield a substance (ammonium ion) which cannot be converted to the desired product under the conditions employed.[2]

Further information regarding the nature of this competing reaction was obtained by experiments employing sulfuric acid solutions and mercury–mercurous sulfate–saturated potassium sulfate

(32) D. G. Davis, *Talanta*, **3**, 335 (1960).

(33) J. J. Lingane, *Anal. Chim. Acta.*

(34) The mean of the *n*-values obtained with 6–10 m*M* hydrazine was actually −4.04. This is believed to reflect the occurrence of some oxidation of tartrate, initiated by an attack on the tartrate by some intermediate in the oxidation of hydrazine. As this seemed irrelevant to the principal purpose of this work, it was not investigated further. Similar experiments in 0.1 *F* sodium acetate–0.1 *F* acetic acid (*p*H 4.6) gave *n*-values near −4.8 with 6–10 m*M* hydrazine.

reference electrodes (to prevent contamination by chloride) isolated from the working solutions by potassium sulfate bridges (to prevent contamination by mercury(I) or (II)). The results are shown in Table III. In agreement with Fig. 3, these data show that nearly theoretical results are obtained in very dilute hydrazine solutions and that the extent of the side reaction increases as the initial concentration of hydrazine increases. In addition, they show that the extent of this side reaction is markedly affected by acidity: in 1.5 *F* sulfuric acid there is no evidence for its occurrence at all, while in 0.05 *F* sulfuric acid the error increases to −18% with 10 m*M* hydrazine.

TABLE III

COULOMETRIC *n*-VALUES FOR THE OXIDATION OF HYDRAZINE IN SULFURIC ACID MEDIA

$E_{w.e.} = +0.93$ v. *vs.* s.c.e.; see text for other experimental details.

$[H_2SO_4]$,	*n*-Value obtained at an initial hydrazine concentration of		
F	0.1 m*M*	1.0 m*M*	10 m*M*
0.05	−4.016 ± 0.012	−3.80 ± 0.07	−3.27
0.5	−3.996 ± .015	−3.992 ± .012	−3.944 ± 0.012
1.5	−3.984 ± .016	−3.992 ± .004	−3.984

Chloride ion exerts an important effect on the results obtained, as is shown by the following data. In 0.5 *F* sulfuric acid the *n*-value obtained with 10 m*M* hydrazine was −3.944 ± 0.012, as given in Table III. In the presence of the trace of chloride derived from a saturated calomel electrode dipping into the working solution, this decreased to − 3.90 ± 0.04, and replacing the sulfuric acid with 1 *F* hydrochloric acid decreased the value still further to −3.62 ± 0.11.

The Mechanism of the Electroöxidation of Hydrazine.—Those who have studied the mechanism of the chemical oxidation of hydrazine[3-8] are generally agreed that the course of the reaction depends on the number of electrons that can be transferred to a single ion or molecule of the oxidizing agent. When, as is the case with a mercury or platinum electrode, the latter can accept two electrons simultaneously, one of the important steps is considered to be the dimerization of diimide to tetrazene

$$2N_2H_2 \longrightarrow N_4H_4 \qquad (8)$$

followed by the decomposition of the latter into ammonia and hydrazoic acid (or ammonium and azide ions)

$$N_4H_4 \longrightarrow NH_4^+ + N_3^- \qquad (9)$$

In the electrochemical mechanism proposed here, reaction 8 is identified as the second-order reaction that is responsible for the variations of i_l/C and *n* with hydrazine concentration at platinum electrodes in acidic media.

The first step in the oxidation of hydrazine at a dropping mercury electrode was shown above to be

$$N_2H_4 + OH^- \longrightarrow N_2H_3^+ + H_2O + 2\ e \qquad (5)$$

There is no basis for assuming that a wholly different initial step is involved in the oxidation of hydrazine at an oxide-coated platinum electrode; on the contrary, it suffices to suppose that the same rate-determining step occurs, though much more rapidly at an oxide-coated than at a bare platinum surface. The concordance between equations 4 and 6 lends support to, but does not prove the correctness of, this hypothesis. On this basis, the following mechanism can be shown to account for all of the experimental observations

$$N_2H_3^+ = N_2H_2 + H^+ \qquad (10)$$

$$N_2H_3^+ \longrightarrow N_2 + 3\ H^+ + 2\ e \qquad (11)$$

$$N_2H_2 \longrightarrow N_2 + 2\ H^+ + 2\ e \qquad (12)$$

$$2\ N_2H_2 \longrightarrow N_4H_4 \qquad (8)$$

$$N_4H_4 \longrightarrow NH_4^+ + N_3^- \qquad (9)$$

$$N_3^- \longrightarrow \frac{3}{2}\ N_2 + e \qquad (13)$$

$$N_2H_2 = N_2H^- + H^+ \qquad (14)$$

$$N_2H^- \longrightarrow N_2 + H^+ + 2\ e \qquad (15)$$

$$N_2H_3^+ + Cl^- = N_2H_3Cl \qquad (16)$$

$$2\ N_2H_3Cl \longrightarrow N_4H_4 + 2\ H^+ + 2\ Cl^- \qquad (17)$$

In a strongly alkaline solution the equilibria of reactions 10 and 14 may be assumed to lie all the way to the right, so that the N_2H^+ initially formed is nearly completely converted to N_2H^-. The dimerization of this anion would presumably involve a rather large electrostatic repulsion and hence a substantial activation energy: accordingly, since the concentration of diimide itself is maintained at a low value by the operation of the equilibrium of reaction 14, little dimerization will occur. This mechanism, consisting of reactions 5, 10, 14 and 15, accounts for the constancy of i_d/C and of *n* at mercury electrodes in alkaline solutions and at platinum electrodes in solutions of *p*H 3 or above.

In a very strongly acidic solution (*e.g.*, 1.5 *F* sulfuric acid), it similarly may be presumed that reaction 10 occurs to only a very small extent. The positive changes of the predominating N_2H^+ ions again would tend to prevent dimerization, and the rate of reaction 8 again would be small. Thus the reaction would proceed almost exclusively by the path described by equations 5 and 11. (It may be emphasized that equations 11, 12 and 15 are purely stoichiometric and express only the final fates of the species involved.)

In solutions of intermediate acidity (*e.g.*, 0.05–0.5 *F* sulfuric acid), this reasoning leads to the expectation that higher concentrations of diimide will be present than at either higher or lower acidities under otherwise identical conditions. Since an increase of the diimide concentration causes the rate of reaction 8 to increase more rapidly than that of reaction 12, this would lead to the formation of ammonium ion by the path described by equations 5, 10, 8 and 9. Incidentally, the occurrence of reaction 13 at platinum electrodes is well known, and it accounts for the absence of hydrazoic acid at the end of an electrolysis. If this were the sole reaction path, the over-all half-reaction could be expressed by the equation $2\ N_2H_4 \rightarrow NH_4^+ + {}^3/_2\ N_2 + 4\ H^+ + 5\ e$, so that the apparent *n*-value would be −2.5. The lowest value obtained during the present work was −3.27 (with 10 m*M* hydrazine in 0.05 *F* sulfuric acid), indicating that under the conditions of this experiment about half of the $N_2H_3^+$ formed underwent oxidation by reaction 11, reactions 10 and 12 or reactions 10, 14 and 15.

The above mechanism thus serves to explain the effects of pH on i_l/C and on n. Since an increase of the initial hydrazine concentration leads to a proportional increase of the diimide concentration at every instant during an electrolysis, and since, as above, this causes the rate of the dimerization to increase more rapidly than the rate of the further oxidation, it obviously also serves to explain the effects of the initial concentration of hydrazine. It thus provides a simple and consistent description of the phenomena observed over a wide range of experimental conditions.

It remains to be said only that the effect of chloride ion in decreasing the n-values obtained in strongly acidic solutions must reflect a decrease of the activation energy required for the dimerization of N_2H^+ brought about by the presence of chloride. Reactions 16 and 17 serve to account for this effect.

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Exchange of Methyl Groups in Organometallic Compounds[1]

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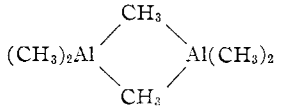
Rapid, intermolecular exchange of methyl groups in solutions of trimethylaluminum and dimethylcadmium and in solutions of dimethylzinc and dimethylcadmium has been demonstrated by nuclear magnetic resonance. For trimethylaluminum and dimethylcadmium dissolved in benzene, an upper limit of the average lifetime of a methyl group before exchange was estimated. For solutions of dimethylzinc and dimethylcadmium in five solvents, the average pre-exchange lifetimes, reaction orders and rate constants were determined. For the dimethylzinc–dimethylmercury and the dimethylcadmium–dimethylmercury system, lower limits of the pre-exchange lifetimes were calculated.

Introduction

The bridge structure of trimethyl aluminum probably exists in benzene solutions[2] and in the



gas phase[3] and is definitely present in the solid state as shown by X-ray techniques.[4] To investigate the existence of the bridge structure in the liquid phase, the proton magnetic resonance spectrum was obtained. Only one sharp peak in the spectrum was observed and is consistent with the bridge structure only if the methyl groups change environments often. Recently,[5] two peaks were found at low temperatures in cyclopentane solution and were attributed to two magnetically different types of protons. The nuclear magnetic resonance (n.m.r.) spectrum of trimethylaluminum at room temperature can be accounted for by either an intermolecular or an intramolecular exchange process. Also, exchange of methyl groups has been demonstrated for systems containing methylaluminum chlorides.[6] This paper discusses the investigation of intermolecular exchange in several systems of organometallic compounds. This investigation of relatively simple organometallic compounds also was prompted by observations of the n.m.r. spectra of Grignard reagents and of organolithium compounds.

Experimental

Preparation of Compounds and Solutions.—Dimethylmercury was prepared by the method of Gilman and Brown.[7]

Trimethylaluminum was prepared by refluxing dimethylmercury with three times the stoichiometric quantity of aluminum in a nitrogen atmosphere. About one-third of the aluminum was foil and the remainder thin turnings. The product was removed by vacuum distillation from the reaction flask to a mercury-sealed storage container. The melting point was 14.5–15.0° (reported[2] m.p. 15°).

Dimethylzinc was obtained from the reaction of dimethylmercury and 20 mesh granular zinc. The reactants were maintained at the reflux temperature of dimethylmercury by distilling from time to time the accumulated product, b.p. 45–46°, through a 25 cm. Vigreux column. By this procedure 35 g. of dimethylmercury was converted into dimethylzinc in 48 hr.

Dimethylcadmium was prepared by the reaction of cadmium dichloride and methylmagnesium iodide[8] and purified by high-vacuum techniques. The product melted at 3.5–5.0° (reported[8] 4.5°). The n.m.r. spectrum of this product, and of each of the above products, consisted of only one peak and indicated the absence of any other hydrogen-containing compound.

Approximately 0.5 molar methylmagnesium iodide in diethyl ether was prepared from methyl iodide and magnesium turnings.

Approximately 0.5 molar methyllithium in diethyl ether was obtained from the reaction of methyl iodide and lithium shot.

The solvents were dried (benzene and cyclohexane over sodium, nitrobenzene over phosphoric anhydride, ether over sodium and pyridine over potassium hydroxide and then over phosphoric anhydride) and fractionally distilled. Also, benzene was fractionally crystallized twice.

The 5 mm. o.d. Pyrex sample tubes for n.m.r. spectra were filled with a long, 1.5-mm. o.d. capillary tube containing the reference and with a pure organometallic compound or solution to a height of 11 cm. The volumes of the metal alkyls were measured at 25° in a calibrated capillary tube. For concentrations greater than 1 M, the metal alkyl was transferred directly to the sample tube by high vacuum techniques. For concentrations less than 1 M, the metal alkyl was vacuum distilled into a 30-ml. flask containing 25 ml. of solvent and then an aliquot of the stirred solution transferred to the n.m.r. tube. The maximum concentra-

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