

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MICHIGAN]

## Polarographic Behavior of Glyoxal

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RECEIVED OCTOBER 22, 1953

Glyoxal gives one polarographic wave in the pH range of 7.0 to 12.4; an additional wave appears in ammonia buffers. The waves are kinetically controlled which eliminates use of the Ilkovic equation for calculating the number of electrons involved in the electrode process. Coulometric runs indicate that about three electrons are transferred per molecule of glyoxal, which is believed to indicate the average number of electrons involved in the formation of several products. Evidence is presented for the electrode process involving a free radical mechanism. The major process is probably the reduction of glyoxal to glycolic aldehyde followed by reduction of the aldehyde to ethylene glycol, erythritol or both; the waves for the two reduction processes merge into one due to the closeness of the  $E_{1/2}$  values. The earlier wave in ammonia buffer is due to imine reduction. By using carefully standardized conditions, glyoxal can be determined polarographically.

The unique chemical structure of glyoxal indicates that its polarographic behavior should be interesting, while its polarographic determination would be worthwhile because of its widespread utilization. The reactive nature of glyoxal, the simplest dicarbonyl compound, is well known; it forms a fairly stable hydrate and a double acetal, and even at room temperature undergoes an intramolecular Cannizzaro reaction in the presence of sodium hydroxide to form the sodium salt of hydroxyacetic acid.

The polarography of glyoxal has been only superficially investigated. It was reported to give a normal wave at  $-1.50$  v. in ammonium chloride solution; the wave height could not be determined due to continuous polymerization of the glyoxal.<sup>1</sup>  $E_{1/2}$  was found<sup>2</sup> to be  $-1.41$  v. vs. S.C.E. in a biphthalate buffer at pH 3.4 with  $0.1 N$  potassium chloride as the supporting electrolyte; no current values were given. Since no thorough study of glyoxal or interpretation of its reduction has been reported, it was believed worthwhile to investigate its polarographic behavior.

## Experimental

**Chemicals.**—A stock  $10$  mM glyoxal solution was prepared from a 30% solution of C.P. material (Delta Chemical Works), whose concentration was checked by oxidation to formic acid and alkalimetric titration. Nitrogen used for deoxygenating was purified and equilibrated by bubbling through sulfuric acid, an alkaline pyrogallol solution, water and a portion of the test solution. Buffer solutions (Table I) were prepared from C.P. chemicals.

TABLE I  
BUFFER SOLUTIONS

Buffer	pH	Composition
1	2.2	0.5 M KCl with added HCl
2	4.9	0.5 M NaOAc with added HOAc
3	7.0	0.164 M $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , 0.0176 M citric acid monohydrate and 0.073 M KCl
4	8.4, 9.1, 9.6	0.5 M $\text{NH}_4\text{Cl}$ with added $\text{NH}_3$
5	9.1	0.082 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 0.32 M KCl
	9.8	0.082 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , 0.285 M KCl, with added NaOH
6	10.4	0.163 M $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with added NaOH
	11.4	0.145 M $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with added NaOH
	12.4	0.105 M $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with added NaOH

**Apparatus.**—A Leeds and Northrup Type E Electro-Chemograph was used. A Beckman Model G pH Meter was used for pH measurement. All measuring apparatus were calibrated. A thermostated H-cell<sup>3</sup> employing a saturated calomel reference electrode was used. The dropping

mercury electrode, prepared from Corning marine barometer tubing, had  $m$  and  $t$  values of 1.249 mg./sec. and 6.0 sec. at open circuit in distilled water at  $25^\circ$  and 60 cm. mercury head. The coulometric runs were conducted with a modified Lingane<sup>4</sup> apparatus maintained at  $25 \pm 0.1^\circ$ .

**Procedure.**—The test solution, prepared by mixing measured volumes of the standard glyoxal and buffer solutions, had essentially the same pH as the buffer. Five minutes was used for this operation. The test solution was deoxygenated for five minutes and then electrolyzed (ten minutes); the nitrogen atmosphere was maintained throughout the electrolysis. The potentials reported are corrected for  $iR$  drop and are vs. S.C.E. Current values are reported as  $i_1$ , limiting current.

## Observed Behavior and Discussion

The polarographic data are given in Table II; typical polarograms are shown in Fig. 1. One cathodic wave was obtained in the pH range of 7.0 to 12.4; an additional wave appeared in ammonia buffers. This extra wave was poorly defined and

TABLE II  
EFFECT OF pH, CONCENTRATION, DROP-TIME (HEAD OF MERCURY) AND TEMPERATURE ON POLAROGRAPHIC BEHAVIOR OF GLYOXAL

Buffer no.	pH	Gly-oxal concn. mM	Head, cm.	Pre-wave $-E_{1/2}$ , v.	$i_1$ , $\mu\text{a.}$	Main wave $-E_{1/2}$ , v.	$i_1$ , $\mu\text{a.}$
3	7.0	1.0	50			1.42	0.30
3	7.0	1.0	70			1.41	.30
4	8.4	1.0	60	1.23	0.12	1.41	.42
4	9.1	1.0	50	1.25	.16	1.43	.30
4	9.1	1.0	70	1.28	.17	1.46	.29
4	9.6	1.0	50	1.31	.22	1.48	.24
4	9.6	1.0	80	1.32	.19	1.50	.22
4	9.6	1.0	80 <sup>b</sup>	1.35	.06	1.52	.08
5	9.1	1.0	50			1.53	.28
5	9.9	1.0	50			1.54	.21
5	9.9	1.0	80			1.54	.22
5	9.9	1.0	80 <sup>b</sup>			1.52	.05
6	10.4	1.0	60			1.54	1.16
6	10.4	1.0	80			1.53	1.18
6 <sup>a</sup>	10.4	0.2	60			1.54	0.22
6 <sup>a</sup>	10.4	0.5	60			1.55	0.60
6 <sup>a</sup>	10.4	1.0	60			1.55	1.17
6 <sup>a</sup>	10.4	2.0	60			1.55	2.50
6	11.4	1.0	60			1.59	0.76
6	12.4	1.0	60			1.64	0.49
6	12.4	1.0	80			1.64	0.50
6	12.4	1.0	60 <sup>b</sup>			1.64	0.16

<sup>a</sup> The ionic strength was 0.40 for these runs; it was 0.45 in all other runs. <sup>b</sup> The temperature was  $0^\circ$  in these runs; it was  $25^\circ$  in all other runs.

(1) A. Winkel and G. Proske, *Ber.*, **69**, 1917 (1936).(2) G. Mackinney and O. Temmer, *THIS JOURNAL*, **70**, 3586 (1948).(3) J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).(4) J. J. Lingane, *THIS JOURNAL*, **67**, 1916 (1945).

consequently its polarographic values are only approximate. No reduction wave was detected in buffer 1 due to the prior hydrogen discharge wave. In buffer 2, a wave began at  $-1.3$  v. but the hydrogen discharge wave appeared before its completion.

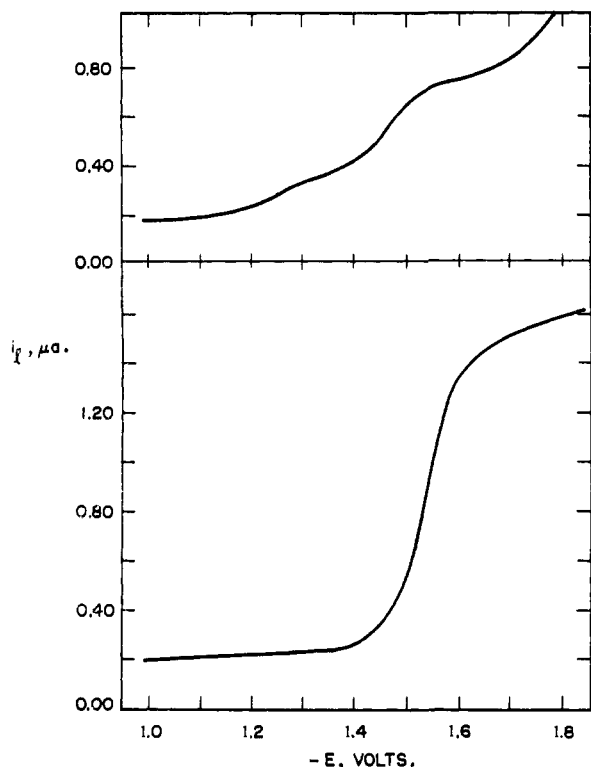


Fig. 1.—Tracings (average current) of polarograms of glyoxal in (top) ammonia buffer at  $pH$  9.6 and (bottom) phosphate buffer at  $pH$  10.4.

The  $E_{1/2}$  vs.  $pH$  relation shows that  $E_{1/2}$  becomes more negative by about 0.05 v. per  $pH$  unit over  $pH$  range 7.0 to 12.4; this is near the theoretical value of 0.059 for a reversible  $pH$ -dependent process.  $E_{1/2}$  for both waves in ammonia buffer becomes more negative with  $pH$  at about the same rate. Values of  $\alpha$ , calculated from the slope of the polarographic wave, approximate  $1.0 \pm 0.2$  in most cases.

The  $i_1/C$  vs.  $pH$  relation (Fig. 2) shows that factors other than  $pH$  are affecting the reduction process. It would be expected, as was observed in the case of formaldehyde for one particular buffer species,<sup>5</sup> that the current would be small at low  $pH$  due to hydration of the carbonyl groups and would gradually increase with increasing  $pH$ . However, a decrease was observed. The peak current occurred in phosphate buffer at  $pH$  10.4; the decrease in current in this buffer with increasing  $pH$  may be due to an increasing rate in the intramolecular Cannizzaro reaction which would effectively reduce the concentration of glyoxal. This would also account for the smaller current in borate buffer at  $pH$  9.8 than at  $pH$  9.1 and for the decrease in total current of both waves in ammonia buffer with increasing

(5) K. Vesely and R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 313 (1947).

$pH$ . In addition, the smaller current in borate at  $pH$  9.8 is expected on the basis of greater complexation of glyoxal with borate at the higher  $pH$ ; an increase in imidazole and 2,2'-biimidazole<sup>6</sup> formation would also be a cause of the decreased total current in ammonia buffer with increasing  $pH$ .

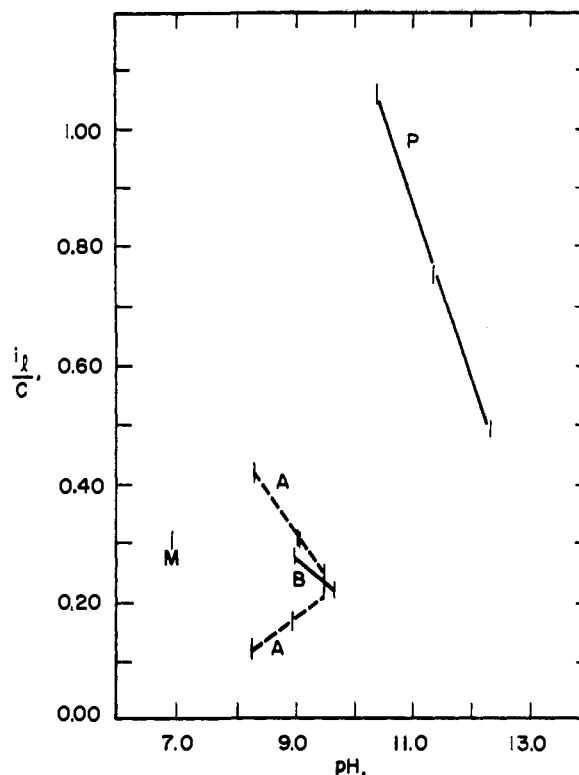
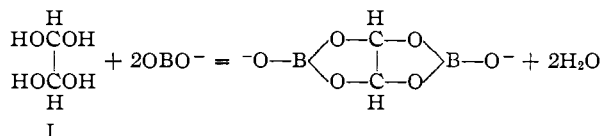


Fig. 2.—Variation of the ratio of  $i_1/C$  of glyoxal with  $pH$ . A indicates ammonia buffers (dashed lines); M McIlvaine buffer; B borate buffers; and P phosphate buffers.

The large difference in glyoxal current between borate buffer at  $pH$  9.8 and phosphate buffer at  $pH$  10.4 is further evidence for borate complexation. In alkaline borate solution the active component is the metaborate ion.<sup>7</sup> Since glyoxal is a polyhydric alcohol in the hydrated form and both carbonyl groups may be hydrated, the following equilibrium is probable



Pasternak<sup>8</sup> gave polarographic and spectrophotometric evidence for a similar borate complex with benzil.

**Polarographic Determination of Glyoxal.**—The straight line relationship between current and concentration in phosphate buffer at  $pH$  10.4 (Table II) indicates that glyoxal could be determined

(6) H. Debus, *Ann.*, **107**, 199 (1858); G. Wyss, *Ber.*, **9**, 1543 (1876); *ibid.*, **10**, 1366 (1877).

(7) J. H. Hibben, *Am. J. Sci.*, **35A**, 113 (1938); Y. Tsuzuki, *Bull. Chem. Soc. Japan*, **16**, 23 (1941); *ibid.*, **13**, 337 (1938); Y. Tsuzuki and Y. Kemura, *ibid.*, **15**, 27 (1940).

(8) R. Pasternak, *Helv. Chim. Acta*, **30**, 1984 (1947).

polarographically. The largest current was obtained in this medium, which, however, has the disadvantage that a slight change in pH affects the current considerably; a change in pH from 10.4 to 10.6 (Fig. 2) would cause a 6% decrease in current. Therefore, any analytical method developed using this buffer would have to control pH closely. In addition, the time between preparing and running the test solution would have to be standardized since the glyoxal wave decreased upon standing with a specific reaction rate constant of about  $2 \times 10^{-3} \text{ min.}^{-1}$ ; this is equivalent to a 4% loss for the 20 minutes required to prepare and run a sample. A correction could be applied or a standard could be run under similar conditions.

**Nature of the Reduction Process.**—The variations of current with drop-time, *i.e.*, head of mercury, and temperature (Table III) indicate that kinetic processes control both waves. The rate-determining step of the major wave is probably the dehydration of glyoxal hydrate to the unhydrated glyoxal, which is then reduced. The presence of only one wave except in ammonia buffers indicates that glyoxal is reduced to: (a) glycolic aldehyde or some other compound which is then reduced at approximately the same potential so that only one wave is observed; (b) a non-reducible compound; or (c) a compound which is reduced at a more negative potential than that of the background wave.

TABLE III

VARIATION OF CURRENT OF GLYOXAL WITH DROP-TIME AND TEMPERATURE

Buffer no.	pH	Ratio of $i$ at two heads of mercury <sup>a</sup>		Temp. coefficients <sup>b</sup>	
		1st wave	2nd wave	1st wave	2nd wave
3	7.0		1.00		
4	9.1	1.06	0.97		
4	9.6	0.86	0.92	9.5%	9.4%
5	9.9		1.05		9.6%
6	10.4		1.02		
6	12.4		1.02		9.5%

<sup>a</sup> Theoretical value for a purely kinetic-controlled process is 1.00, for a diffusion-controlled process 1.16 to 1.27 depending on the heads; and for an adsorption-controlled process, 1.34 to 1.62. <sup>b</sup> Temperature coefficients were calculated from the compound interest formula:  $(T_2)i_2 = (T_1)i_1 [1 + \text{Temp. coeff.}]^{(T_2 - T_1)}$ .

The closeness of the  $E_{1/2}$  values (Table IV) of glyoxal and glycolic aldehyde (obtained by hydrolysis of chloroacetaldehyde in solutions of high pH<sup>9</sup>), the coulometric data and the analysis of coulometrically reduced solutions as subsequently described indicate the probability of alternative (a) involving glycolic aldehyde. The  $E_{1/2}$  values of glycolic aldehyde (Table IV) agree closely with those reported by Bieber and Trumpler.<sup>10</sup>

Successive reduction of glyoxal to glycolic aldehyde to ethylene glycol would consume a total of four electrons. Since the Ilkovic equation cannot be applied to kinetic-controlled processes, the number of electrons transferred could not be calculated from the polarographic waves.

Coulometric electrolyses were made in the attempt to establish the nature of the electrode proc-

(9) P. Federlin, *Compt. rend.*, **232**, 60 (1951); P. J. Elving and C. E. Bennett, work in preparation for publication.

(10) R. Bieber and G. Trumpler, *Helv. Chim. Acta*, **31**, 5 (1948).

TABLE IV

COMPARISON OF  $E_{1/2}$  FOR GLYOXAL AND GLYCOLIC ALDEHYDE (HYDROXYACETALDEHYDE)

Buffer no.	pH	$-E_{1/2}$ , v., vs.	
		glyoxal	glycolic aldehyde
5	9.9	1.54	1.55
6	10.4	1.55	1.59
6	12.4	1.64	1.65

ess. Runs in McIlvaine buffer indicate that about three electrons are consumed in the reduction process.

Accurate coulometric values could not be determined in the normal way in phosphate, borate or ammonia buffers due to decomposition of glyoxal as indicated by a decrease in its polarographic wave with time. However, the number of electrons consumed in phosphate buffer was determined in two different runs by a modified procedure to be 2.96 and 3.14. The modified procedure involves (a) determination of the rate constant of the chemical decomposition; (b) determination of the rate constant of the over-all chemical and electrochemical decomposition; (c) calculation of the rate constant of the electrochemical decomposition; (d) calculation of the amount of glyoxal actually reduced; and (e) calculation of the number of electrons consumed using the concentration obtained from (d). The rate constants were determined by following the decrease in glyoxal concentration polarographically. The calculation of the glyoxal concentration actually reduced was adapted from a procedure for simultaneous reactions described by Glasstone.<sup>11</sup>

**Mechanism for the Reduction.**—Several workers<sup>12</sup> have postulated and given evidence for a free radical mechanism in the electrolytic reduction of carbonyl compounds. On the basis of such a mechanism, the following sequence of reactions would be expected for glyoxal.

Of the predicted products, tartraldehyde (III and IV) would liberate only formic acid if oxidized with periodic acid, ethylene glycol (VI) only formaldehyde, while erythritol (V) would give both formaldehyde and formic acid. Since only a free radical mechanism seems feasible to explain the formation of such compounds as III, IV or V, the formation of formic acid on treating products of the glyoxal reduction with periodic acid would be strong evidence for a free radical mechanism.

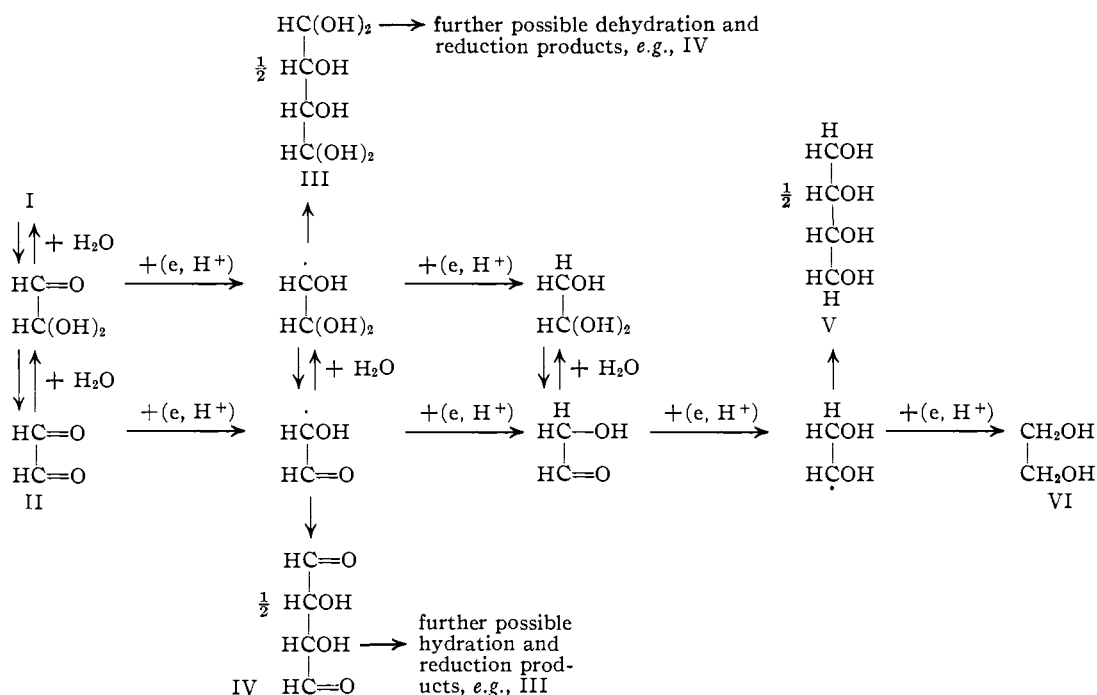
Glyoxal was reduced in 0.5 M lithium chloride-lithium hydroxide solution of pH 11.0 at  $-1.9 \text{ v. vs. S.C.E.}$  The electrolyzed solution was then treated with periodic acid, and the reaction products were isolated and identified. Specific evidence was obtained for the presence of both formic acid<sup>13</sup> and formaldehyde.<sup>14</sup> Since glyoxal itself reacts with periodic acid to give formic acid, the residual glyoxal in the electrolyzed solution was measured polar-

(11) S. Glasstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co. Inc., New York, N. Y., 1946, p. 1086.

(12) D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937); C. L. Wilson and K. B. Wilson, *Trans. Electrochem. Soc.*, **80**, 151 (1941); S. Swann, Jr., P. E. Ambrose, R. C. Dale, R. C. Rowe, H. M. Ward, H. D. Kerfman and S. Axelrod, *ibid.*, **85**, 231 (1944); G. R. Hennig and G. E. Kimball, *J. Chem. Phys.*, **12**, 415 (1944); R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

(13) N. Allen, H. Y. Charbonnier and R. M. Coleman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 384 (1940).

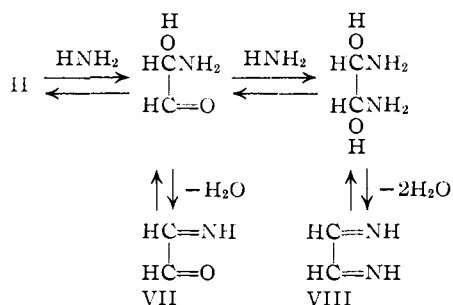
(14) S. L. Tompsett and D. C. Smith, *Analyst*, **78**, 209 (1953).



ographically; a concentration of ten times this amount was necessary to obtain an identical formic acid test.

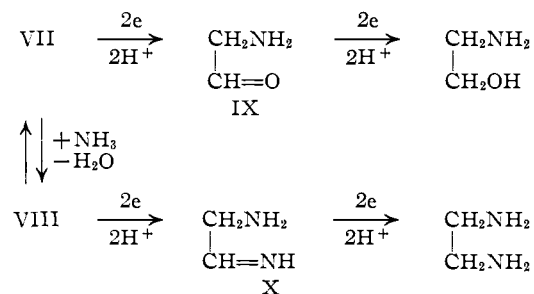
Based on the preceding scheme of possible electrode reactions, if glyoxal were selectively reduced (a) to tartraldehyde (III or IV), one electron would be consumed; (b) to erythritol (V), three electrons; and (c) to ethylene glycol (VI), four electrons. However, it is probable that the value of approximately three electrons in McIlvaine and phosphate buffers does not indicate that glyoxal is being reduced entirely to erythritol, but rather that all possible products are formed in such proportion that the average number of electrons used is three.

From its  $E_{1/2}$  and behavior, the additional glyoxal wave in ammonia buffer is due to the reduction of the imino group resulting from the reaction of ammonia with a carbonyl group.<sup>15</sup> The reaction of ammonia with glyoxal to form iminoglyoxal or 1,2-diiminoglyoxal would be



(15) M. Brezina, Congress of Practical Polarography, Bratislava, February, 1953; cited in *Anal. Chem.*, **24**, 916 (1952); C. M. Callahan, M.S. Thesis, The Pennsylvania State College, 1952; R. E. Van Atta, Ph.D. Thesis, The Pennsylvania State College, 1952; P. Zuman, *Nature*, **165**, 485 (1950); *Sbornik Mezinarod. Polarog. Sjesdu Praze, 1st Congr.*, 1951, Pt. I, Proc., 711-717.

The electrode processes accounting for the reduction of imine groups could then be



The latter equations do not show the hydration of the carbonyl group or possible free radical products since these were discussed previously. The reduction of VII or VIII leads to products (IX and X) which may be reduced further to produce waves either (a) near enough to the first imine wave or the glyoxal wave to merge with them or (b) at a potential which would be included in the background discharge wave.

The kinetic nature of the first wave is then due to an equilibrium between ammonia and glyoxal while the kinetic nature of the second wave is due to hydration-dehydration of the glyoxal carbonyl groups. The increase of the first wave with increasing pH and ammonia concentration while the second wave decreases is explained by an equilibrium shift from II to VII or VIII; both waves disappear upon standing, probably as a result of the formation of imidazole and 2,2'-biimidazole.<sup>6</sup>

**Acknowledgment.**—The authors wish to thank the Atomic Energy Commission which helped support the research described.

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