## **1051.** *Controlled-potential Electrolysis. Part VII.*[1] *Polarographic Behaviour and Controlled-potential Electrolysis of* 1,1-*Dinitroethane and Dinitromethane.*

By Masaichiro Masui and Hiroteru Sayo.

1,1-Dinitroethane and dinitromethane showed three polarographic waves in very strong acid, two in acid, one in neutral, and two in alkaline solutions. By controlled-potential electrolysis with a mercury pool cathode 1,1-dinitroethane and dinitromethane were reduced mainly to acethydroxamic and formhydroxamic acid oxime by 6-electron reduction, and in alkaline solutions further to acetamidoxime and formamidoxime, respectively, by 8-electron reduction. These results enable the polarograms of both compounds to be interpreted.

The polarography of *gem*-dinitroparaffins seems to have been discussed only by Radin and DeVries[2] and by Stock,[3] and the mechanism of the reduction and the interpretation of the polarograms have not yet become clear. In the preceding Part[1] we reported work on a dinitro-compound which has no hydrogen atom at the carbon carrying the nitro-groups, so that these cannot assume an *aci*-nitro-form. In the present paper, we have studied dinitro-compounds which can assume an *aci*-nitro-form.

### Results

*The Polarography of* 1,1-*Dinitroethane.*—The results of the polarographic study of 1,1-dinitroethane are shown in Figs. 1 and 2 and Table 1. The sum of the heights of the first and the second waves in acid and alkaline solutions is nearly equal to those of the single waves in neutral solutions, except that at pH 4 the second wave is very poorly defined. The relation between the limiting currents and the mercury column heights (Table 2) shows that currents are not diffusion-controlled. The wave form in neutral solution is the best and the limiting current is proportional to the concentration between $4 \times 10^{-5}$ and $4 \times 10^{-4}$ mole $l.^{-1}$. The half-wave potentials of the first wave, in contrast to those of 2,2-dinitropropane, varied markedly with pH of the solution near its p$K_a$, but not much on either side of it. The diffusion-current constant estimated from the wave height in neutral solution is 10·75, being 3·5 times larger than that of the two-electron reduction of 2,2-dinitropropane in alkaline solution. The electron

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[1] Part VI, *J.*, 1961, 4773.
[2] Radin and DeVries, *Analyt. Chem.*, 1952, **24**, 971.
[3] Stock, *J.*, 1957, 4532.

number of the reduction of 1,1-dinitroethane is, therefore, expected to be much larger than two.

*The Polarography of Dinitromethane.*—The results of the polarographic study of dinitromethane are shown in Figs. 3 and 4 and in Table 3. Its behaviour resembles closely that of 1,1-dinitroethane, but the half-wave potentials are slightly more positive and the single wave develops at pH 4—6 instead of pH 6—8. The dependency of the limiting currents on the mercury-column height (Table 4) indicates that the currents are not diffusion-controlled. The sum of the heights of the two waves in acid or alkaline solution is almost the same as that of the single wave at pH 4 and 6.

TABLE 1.

Half-wave potentials and diffusion-current constants of 1,1-dinitroethane.

| pH | | 2·0 * | 4·0 | 6·0 | 8·0 | 10·0 | 12·0 |
|---|---|---|---|---|---|---|---|
| First wave: | $E_{\frac{1}{2}}$(v *vs.* S.C.E.) ... | −0·331 | −0·378 | −0·579 | −0·679 | −0·730 | −0·765 |
| | $i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ .............. | 5·29 | 5·74 | 10·30 | 10·75 | 5·38 | 3·32 |
| Second wave: | $E_{\frac{1}{2}}$(v *vs.* S.C.E.)... | −0·806 | −0·828 | | | −1·390 | −1·490 |
| | $i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ ........... | 3·85 | 1·43 | | | 5·38 | 6·90 |

* A poorly defined third wave exists at −1·151 v.

TABLE 2.

Effect of mercury column height on $i_d$ of 1,1-dinitroethane, $i_dh^{-\frac{1}{2}}$.

| *h* (cm.) | | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|
| pH 2; | first wave | 0·385 | 0·382 | 0·378 | 0·372 |
| | second wave | 0·258 | 0·263 | 0·270 | 0·277 |
| pH 6; | first wave | 0·751 | 0·757 | 0·762 | 0·765 |
| pH 12; | first wave | 0·261 | 0·247 | 0·232 | 0·221 |
| | second wave | 0·490 | 0·509 | 0·516 | 0·526 |

TABLE 3.

Half-wave potentials and diffusion-current constants of dinitromethane.

| pH | | 2·0 | 4·0 | 6·0 | 8·0 | 10·0 | 12·0 |
|---|---|---|---|---|---|---|---|
| First wave: | $E_{\frac{1}{2}}$(v *vs.* S.C.E.) ... | −0·280 | −0·443 | −0·632 | −0·708 | −0·719 | −0·720 |
| | $i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ .............. | 6·54 | 12·46 | 12·53 | 5·61 | 2·64 | 2·53 |
| Second wave: | $E_{\frac{1}{2}}$(v *vs.* S.C.E.)... | −0·665 | | | −1·283 | −1·339 | −1·405 |
| | $i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ ........... | 5·54 | | | 6·54 | 9·14 | 9·35 |

* A poorly defined third wave exists at −1·075 v.

TABLE 4.

Effect of mercury-column height on $i_d$ of dinitromethane, $i_dh^{-\frac{1}{2}}$.

| *h* (cm.) | | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|
| pH 2; | first wave | 0·481 | 0·481 | 0·478 | 0·466 |
| | second wave | 0·386 | 0·382 | 0·381 | 0·379 |
| pH 6; | first wave | 0·949 | 0·945 | 0·941 | 0·931 |
| pH 10; | first wave | 0·204 | 0·195 | 0·191 | 0·191 |
| | second wave | 0·651 | 0·647 | 0·630 | 0·619 |

*Controlled-potential Electrolysis of* 1,1-*Dinitroethane.*—(a) *Electrolysis in alkaline solution.* When 1,1-dinitroethane was electrolysed in 0·1N-aqueous sodium hydroxide with the potential of the mercury cathode at −1·7 v *vs.* S.C.E. (at the plateau of the second wave) the current–time curve exhibited a long tailing curve and a fairly long time was required for complete electrolysis. The amount of electricity required for the reduction corresponded to 8-electron reduction. If reduction began with C–N bond fission as did that of 2,2-dinitropropane, the resulting *aci*-form of the nitroethane and nitrite ion could not be reduced further; nor could these products react with each other in such conditions; so the electricity required should correspond to 2-electron reduction. We conclude that reduction proceeds without C–N bond fission. From the electrolysed solution only 0·1 molar equiv. of nitrite ion was found [4] and nitrate or ammonium ions could not be detected. On addition of concentrated sulphuric acid and distillation, acetic acid,[5] but no aldehyde,[6] was detected. The acetic acid is thought not to be derived

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[4] Snell and Snell, " Colorimetric Methods of Analysis," D. van Nostrand Company, Inc., New York, 3rd edn., Vol. II, 1954, p. 804.

[5] Feigl, " Spot Tests," Elsevier Publ. Co., Amsterdam, 4th edn., Vol. II, p. 247.

[6] Ref. 5, p. 146; and by the 2,4-dinitrophenylhydrazine test.

from the nitroparaffin itself because no polarographic wave developed when the electrolysed solution was acidified as above. The solution was then made alkaline again and distilled; the distillate then contained ammonia. From these results the reduction product was expected to be an acetic acid derivative which could be hydrolysed by acid to acetic acid and ammonia. The ultraviolet absorption spectrum of the solution at first showed an absorption band of 1,1-dinitroethane at 382 mμ whose intensity decreased during the electrolysis while a new peak at 336 mμ appeared and increased in intensity; but this also later decreased and had disappeared at the end of the electrolysis.

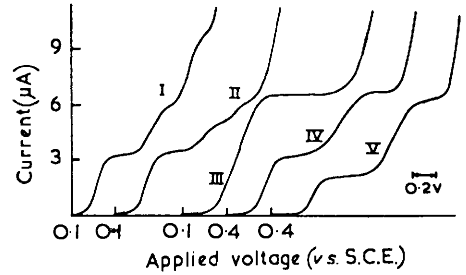


FIG. 1. Polarograms of 1,1-dinitroethane. pH: (I) 2·0; (II) 4·0; (III) 6·0; (IV) 10·0; (V) 12·0.

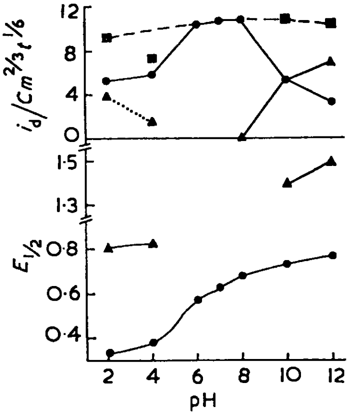


FIG. 2. Relation of $E_{\frac{1}{2}}$ and $i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ to pH for 1,1-dinitroethane.

● First, ▲ second wave; ■ sum of the two.

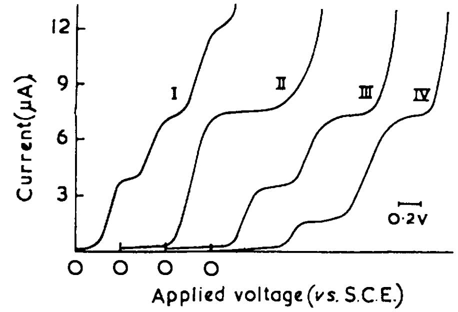


FIG. 3. Polarograms of dinitromethane. pH: (I) 2·0; (II) 6·0; (III) 8·0; (IV) 12·0.

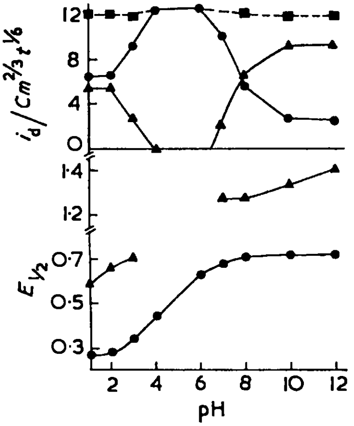
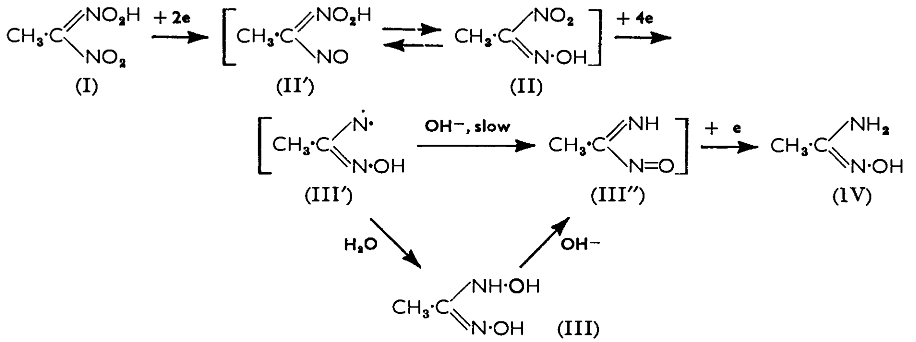


FIG. 4. Relation of $E_{\frac{1}{2}}$ and $i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ to pH for dinitromethane.

● First, ▲ second wave; ■ sum of the two.

Some of the more probable intermediates were prepared and examined. Ethanenitrolic acid (II) which appeared to be the product at the first stage of the reduction showed in 0·1N-NaOH a peak at 323 mμ (ε 8000) and polarographic waves of $E_{\frac{1}{2}} = -0{\cdot}816$ and $-1{\cdot}355$ v (*vs.* S.C.E.), the latter wave being ill-defined. Electrolysis of ethanenitrolic acid under our conditions required electricity corresponding to a 6-electron reduction and there was the same behaviour of the 336 mμ band as for dinitroethane. As a further reduction product acethydroxamic acid oxime (III) was expected; it was synthesised as hydrochloride; it did not show reduction waves or ultraviolet absorption in acid solution but in alkaline solution gave an anodic wave of $E_{\frac{1}{2}} = -0{\cdot}278$ v and two cathodic waves of $E_{\frac{1}{2}} = -0{\cdot}468$ and $-1{\cdot}268$ v (*vs.* S.C.E.) and an absorption band at 336 mμ (ε 17,000). The electrolytic reduction required two electrons per molecule and the absorption peak decreased in intensity during the reduction. There was no indication of the production of ethylazaurolic acid ($\lambda_{\text{max.}}$ 348 mμ) which was expected to be formed from the oxime (III) in alkaline solution. From the electrolysed solution, acetamidoxime (IV) was obtained, which was identical with an authentic sample prepared by Nordmann's method [7] (mixed m. p. and infrared spectrum). Acetamidoxime did not give a reduction wave in acid or alkaline solution, nor was there any ultraviolet absorption around 336 mμ. From these results the most probable reduction scheme may be expressed by scheme (1).



. (1)

First, 1,1-dinitroethane undergoes two-electron reduction, regardless of whether it is in *H-aci*-form or *aci*-ion form, to ethanenitrolic acid (II) or (II′), which is reduced spontaneously by four-electron reduction to (III′) at the electrode, since the reduction potential of the second wave of (II) is more positive than that of (I). (III′) changes into (III″) which undergoes two-electron reduction to acetamidoxime (IV).

Compound (III) is thought to be converted into (III″) and both exist in alkaline solution, because: (1) though the hydrochloride synthesised is stable in water, it liberates a little nitrite ion when the solution is acidified after once being made alkaline; (2) the strong absorption at 336 mμ should be attributed to the nitroso-group conjugated with a double bond, as the form (III) cannot develop a strong absorption at that wavelength; and (3) the polarogram shows both anodic and cathodic waves, the former thought to be due to a hydroxylamino-group. The form produced by the electrolysis is assumed to be (III′), but it is rather hard to reduce because it contains merely a hydroxylamine and an oxime component but no conjugated system. It seems necessary that (III′) should change into an easily reducible one such as (III″) before it undergoes further reduction; and since this step is rather slower than the preceding ones, the behaviour of the absorption band at 336 mμ during the electrolysis can be explained. Controlled-potential electrolysis at $-1{\cdot}0$ v (*vs.* S.C.E.) (at the plateau of the first wave), though it took a very long time to proceed nearly to completion, decreased the height of the second polarographic wave as well as of the first one, and the behaviour of the absorption band at 336 mμ was identical with that described above except that it did not disappear completely. This implies that in the solution 1,1-dinitroethane, and also ethanenitrolic acid, are in equilibrium between two forms, one of which is easily and the other difficultly reducible, and as the concentration of 1,1-dinitroethane decreases it is supplied from the difficultly reducible form. The reduction scheme is, therefore, not different from the preceding one up to the (III″) stage, but here the lower applied potential causes a slower rate of reduction, and the potential is lower than that of the second wave for (III) in alkaline solution, so that the reduction is not brought quite to completion; the absorption band at 336 mμ, therefore, did not disappear.

(b) *Electrolysis in acid solution.* 1,1-Dinitroethane was electrolysed in the solution of pH 2 at $-0{\cdot}90$ v (*vs.* S.C.E.) (on the plateau of the second wave) and required the electricity corresponding to about a 5·6- instead of an 8-electron reduction. Nitrous acid was detected in the electrolysed solution. When the solution was made alkaline (pH 12·5), it developed the absorption peak at 336 mμ and also showed the polarogram of the acethydroxamic acid oxime (III),

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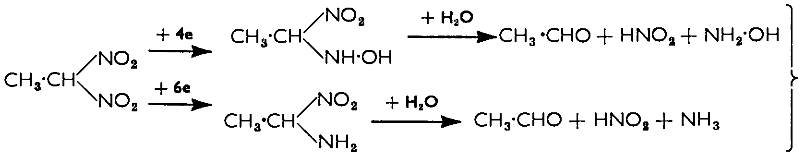
[7] Nordmann, *Ber.*, 1884, **17**, 2747.

though the amount evaluated therefrom was only about 0·6 molar equivalent. As this oxime is not reducible in acid solution, the deficiency in the resulting solution could be caused by the following factors: (1) Ethane-nitrolic or -nitrosolic acid [which is thought to be an intermediate between the nitrolic acid and (III′)] is unstable in acid solution and part of it is decomposed before reduction at the electrode. (2) Part of the dinitroethane is reduced in a different way. Both factors are proved to be operative by the following facts. The electrolysed solution when heated with a small amount of concentrated sulphuric acid and distilled gave 0·1 equivalent of acetaldehyde. Since no acetaldehyde is produced by the processes of eqn. (1), another scheme such as (2) which contains no compound with a C=N bond should be considered, but its contribution is clearly small.



. (2)

Electrolysis at −0·55 v (*vs.* S.C.E.) (on the plateau of the first wave) required a long time for completion and the number of electrons consumed per molecule was 5·3. The polarogram of the solution showed a gradually decreasing height of the second wave as well as of the first wave. The ultraviolet spectrum and the polarogram of the resulting solution in alkaline state were the same as those of the acethydroxamic acid oxime (III) described above. These results resemble closely those of electrolysis at −1·0 v in 0·1N-sodium hydroxide. The amount of the oxime (III) thus found was estimated to be 0·5 equiv. and was less than that obtained at a higher applied voltage. This is explained by the greater probability of decomposition of the intermediates owing to the slower reduction and thus the longer time for interaction with the acid solution. It is therefore concluded that the reductions of 1,1-dinitroethane appearing as the first and the second wave in the polarography, both in the alkaline and acid solution, do not require consecutive reduction steps as is the usual case, but are caused by the existence of the equilibrium between two forms and the rate of its attainment.

The poorly defined third wave in the solution of pH 2 is due to the reduction of nitrite ion produced by decomposition of the components, because on electrolysis at −1·15 v no nitrite ion was detected though the ultraviolet spectrum and the polarogram showed the presence of 0·55 equivalent of the oxime (III) in the solution as above.

(c) *Electrolysis in neutral solution.* As the polarogram in neutral solution was a simple single wave, the reduction mechanism was also thought to be simple, but the controlled-potential electrolysis did not give a simple result. The electron number for the reduction was 5·5, so the reduction does not proceed further than the oxime (III). Examination of the electrolysed solution as above showed that the amount of this oxime was only about 0·1 molar equivalent and that of nitrite about 0·23 equivalent. In the distillate from the acidified solution a very small amount of acetaldehyde and a large amount of acetic acid (0·76 equivalent) were found. The amount of acetic acid formed suggests that reduction takes the same course as in alkaline and acid solution. The deficiency in the oxime (III) is interpreted by its decomposition and/or by non-electrolytic reactions of (III), (III′), or (III″) which occur in the neutral condition producing substances having no absorption band near 336 mμ and giving no polarographic wave. The fact that during the electrolysis the intensity of the 336 mμ band passed a maximum supports this interpretation, but the nature of the substance produced is not known.

*Controlled-potential Electrolysis of Dinitromethane.*—(a) *Electrolysis in alkaline solution.* Electrolysis in 0·1N-sodium hydroxide at −1·7 v (*vs.* S.C.E.) consumed electricity corresponding to an ~8-electron reduction, 0·1 molar equivalent of nitrite being formed. The absorption band of dinitromethane at 365 mμ decreased in intensity during the electrolysis; a band at 334 mμ appeared and increased but disappeared by the end of the electrolysis. These observations are closely similar to those for 1,1-dinitroethane and a precisely similar reduction scheme is proposed.

Formhydroxamic acid oxime $HO\cdot NH\cdot CH{:}N\cdot OH$, when synthesised, showed an absorption band at 334 mμ in alkaline solution as expected and formamidoxime $NH_2\cdot CH{:}N\cdot OH$, which was also prepared, did not. From the electrolysed solution crystalline formamidoxime was isolated.

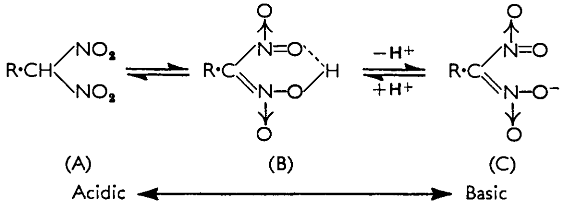
(b) *Electrolysis in acid solution.* Electrolysis at −0·76 v in a solution of pH 2 required the electricity corresponding to a 6·0-electron reduction. Nitrous acid was detected in the final solution. The absorption band at 334 mμ did not develop when the electrolysed solution was made alkaline to pH 12·5. As formhydroxamic acid oxime is very unstable in acid, it would be expected to decompose rapidly in this reaction. Detection of formaldehyde [8] in the electrolysed solution suggests that a small part of the dinitromethane was reduced according to a scheme analogous to scheme (2).

The electrolyses at the potentials on the plateau of the first and the third wave gave 5·5 and 11, respectively, as the electron numbers; there was no absorption band at 334 mμ in either case and no nitrous acid was formed in the latter. These results are explained as for dinitroethane, with the additional instability just mentioned.

(c) *Electrolysis in a solution of* pH 6. The results were almost the same as for 1,1-dinitroethane.

## DISCUSSION

*Interpretation of the Polarograms.*—Since the polarographic waves of 1,1-dinitroethane and dinitromethane do not represent the steps of the reduction as described above, the polarograms obtained are best explained [9] by assuming the equilibrium expressed by scheme (3) and a fairly rapid attainment of equilibrium.



. . . . . (3)

In very alkaline solution the compound takes a form (C) which shows a strong absorption band at 382 mμ (R = Me), and in very acid solutions under the polarographic conditions almost all of the compound exists as (A) since this band is diminished in intensity and instead the weak absorption of the nitro-form appears at 273 mμ. The negative charge on the nitro-group of (C) causes the reduction potential to be more cathodic, as for carboxylic acids,[10] and the second wave in alkaline solution is assigned to form (C). Because the inductive effect of one nitro-group on the other in form (A), as in general, does not make the reduction potential as positive as the resonance effect in form (B) does, form (B) should be regarded as the more easily reducible form. The second wave in acid solutions, therefore, is regarded as the reduction wave of (A), and the first wave which develops an S-shaped curve extending over all pH regions in its $E_{\frac{1}{2}}$–pH plots (Figs. 2 and 4) is attributed to the reduction of form (B). The above results and the fact that interconversion between the forms is fast, explain the behaviour of wave height in respect of pH (Figs. 2 and 4) and the formation, on electrolysis, of much acetic acid at all pH's and a little aldehyde in acid and none in alkaline solution. Reviewing the examples [11] we have found S-shaped $E_{\frac{1}{2}}$–pH curves to occur when the reduction contains a kinetic current process derived from the equilibrium between an easily (*e.g.*, undissociated) and a difficultly reducible (*e.g.*, dissociated) form, the slope of the curve being steepest in the pH region around pH = p$K_a$. In the present study the $E_{\frac{1}{2}}$–pH relation of the first wave has the same characters. The p$K_a$ values of 1,1-dinitroethane and dinitromethane, determined potentiometrically, are 5·27 and 3·74, respectively. The steepest slopes in Figs. 2 and 4 are at about the same pH regions and their values are about the same.

From these observations, the behaviour of the first wave and the split-wave phenomenon observed in alkaline region can be attributed to the equilibrium between the *H-aci*-nitro-form and the ionized *aci*-nitro-form. As form (C) represents the second wave in

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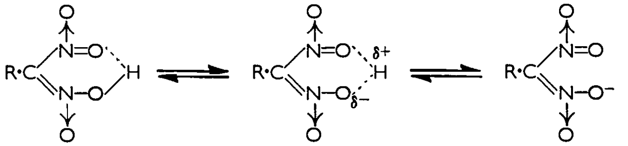
[8] Ref. 5, p. 240.

[9] Cf. Turnbull and Maron, *J. Amer. Chem. Soc.*, 1943, **65**, 212.

[10] Kolthoff and Lingane, " Polarography," Interscience Publ. Inc., New York, 1952, pp. 269, 729.

[11] (*a*) Elving, Rosenthal, and Kramer, *J. Amer. Chem. Soc.*, 1951, **73**, 1717; Elving, *ibid.*, 1957, **79**, 1546; (*b*) Elving and Rosenthal, *Analyt. Chem.*, 1954, **26**, 1454; (*c*) Gergely and Iredale, *J.*, 1951, 3502.

alkaline region, the continuous increase of $E_{\frac{1}{2}}$ of the first wave in the pH region around pH = p$K_a$ requires an intermediate such as (B′) between (B) and (C) [scheme (4)].



. . . . . (4)

The first wave in acid solutions is attributed to (B) and that in alkaline solutions to (B′), and the charge expressed as $\delta^-$ in (B′) increasing with pH makes (B′) more difficultly reducible than (B). In other words, form (C) recombines with a proton to produce (B) or (B′). The magnitude of $\delta^-$ depends on the pH of the solution. As attainment of equilibrium is fairly fast, the amount of (B) consumed is supplied from (A) or/and (C), and this contributes to the height of the first wave, which is much greater than expected from its p$K_a$ value or from its absorption band; it decreases the height of the second wave, and in a certain pH region only one wave is observed. The rates of recombination of the *aci*-nitro-anion with a proton for dinitroethane and dinitromethane are calculated to be about $8 \times 10^7$ and $3 \times 10^5$ l. mole$^{-1}$ sec.$^{-1}$, respectively, by the method used for carboxylic acids.[11b,12]

The total wave heights in acid and alkaline solution and the height of a single wave near neutral region are almost constant except that the height at pH 4 for dinitroethane is highly affected by its ill-defined form. If the diffusion constant $D$ of 1,1-dinitroethane, calculated by the relation[13] $D\sqrt{M} = D'\sqrt{M'}$, where $M$ is the molecular weight and $D'$ and $M'$ refer to 2,2-dinitropropane, is correct, $n$ values estimated for dinitroethane by means of the Ilkovic equation for the total height are 6·7 and 7·0 at pH 6 and 12, respectively. If the 2-electron reduction from (III) to (IV) observed on controlled-potential electrolysis in alkaline solution occurs fully at the dropping-mercury electrode, the $n$ value should be substantially larger than in acid or neutral solution. The almost constant wave height with pH shown in Fig. 2 and 4 implies that the 2-electron reduction does not take place at the dropping-mercury electrode in the basic region to the extent of being easily recognized; and if it could occur the lower diffusion constant of highly charged species[11b] would compensate for the increments due to the reduction. In any case, the $n$ value for the total wave height should be closer to 6, even though a value of *ca.* 7 is derived from the Ilkovic equation.

## EXPERIMENTAL

*Materials.*—1,1-Dinitroethane potassium salt, prepared by reaction[14] between bromonitroethane and methanolic potassium hydroxide, had m. p. 151° (decomp.) (from water). Dinitromethane potassium salt,[15] prepared from dibromodinitromethane, arsenious acid, and potassium hydroxide, had m. p. 205° (decomp.) (from water). Ethanenitrolic acid,[16] prepared from nitroethane and nitrous acid, had m. p. 86° (decomp.) (from ether–light petroleum). Acethydroxamic acid oxime hydrochloride,[17] obtained from acethydroxamoyl chloride and hydroxylamine, had m. p. 154° (decomp.) (from ethanol–ether). Potassium ethanenitrosolate,[18] prepared by adding methanolic potassium hydroxide to acethydroxamic acid oxime hydrochloride, had m. p. 207° (decomp.) (from dilute aqueous ethanol). Acetamidoxime hydrochloride,[7]

[12] Delahay, " New Instrumental Methods in Electrochemistry," Interscience Publ. Inc., New York, 1958.
[13] Riehl and Wirths, *Z. phys. Chem.*, 1944, *B*, **194**, 97.
[14] Wieland and Sakellarios, *Ber.*, 1919, **52**, 904.
[15] Macbeth and Orr, *J.*, 1932, 539.
[16] Meyer and Constam, *Annalen*, 1882, **214**, 329.
[17] Wieland, *Annalen*, 1907, **353**, 86.
[18] Wieland, *Annalen*, 1907, **353**, 93.

prepared from acetonitrile and hydroxylamine hydrochloride, had m. p. 140° (from ethanol–ether). Ethylazaurolic acid,[16] prepared by reduction of ethanenitrolic acid with sodium amalgam, had m. p. 142° (decomp.) (from ethanol). Formamidoxime [19] obtained from potassium cyanide and hydroxylamine hydrochloride, had m. p. 115° (decomp.) (from ethyl acetate). Formhydroxamic acid oxime [20] was prepared by adding hydroxylamine hydrochloride to formamidoxime; as it was not obtained crystalline, the reaction solution separated from the ammonium chloride formed was used. Methanenitrosolic acid,[20] prepared by adding methanolic potassium hydroxide to the solution of formhydroxamic acid oxime, had m. p. 194° (decomp.) (from dilute aqueous ethanol).

All the compounds (except formhydroxamic acid oxime) gave correct analysis.

*Apparatus.*—The apparatus for polarography and controlled-potential electrolysis, and the buffer solutions for the polarographic studies were the same as those used in the previous studies.[1] Dropping-mercury electrode having $m^{2/3}t^{1/6}$ = 1·395 was used. Polarographic measurements were carried out at 25° ± 0·1°.

A Toadempa Model HM-5 pH meter with glass S.C.E. was used for p$K_a$ determinations which were carried out on solutions more dilute than $4 \times 10^{-3}$ mole l.$^{-1}$.

A Beckman DU type spectrophotometer and Hitachi automatic recording spectrophotometer EPS-2 were used for ultraviolet spectroscopy, but only the former for the quantitative determinations.

Infrared spectra were obtained by using a Hitachi EPI-2 double-beam prism spectrophotometer.

*Controlled-potential Electrolysis of* 1,1-*Dinitroethane.*—(*a*) 1,1-Dinitroethane potassium salt (63·3 mg.) was electrolysed as usual in 0·1N-sodium hydroxide (200 ml.) at −1·7 v. The current was at first 600 mA and decreased to 5 mA in about 1·5 hr. During the electrolysis the ultraviolet spectrum of the solution was measured from time to time by pipetting 0·5 ml. of the solution and diluting it 20-fold. The electricity required was estimated from the current–time curve, the amount (304 coulombs) corresponding to 7·89 electrons per molecule. In this 0·5 ml. 0·12 equivalent of nitrous acid was determined.[4] Similarly electrolysed solutions of four runs were combined and acidified to pH 4 by dilute hydrochloric acid, then evaporated under reduced pressure at ~40°, and the residue was extracted with dry ethanol. The extract was evaporated again and the residue again extracted with dry ethanol. The precipitates produced on adding dry ether to the solution recrystallised from ethanol–ether. The m. p., 140° (decomp.), of the resulting product was not depressed on admixture with acetamidoxime prepared by Nordmann's method.[7] The samples gave identical infrared spectra ($\nu_{max.}$ 3322s, 3215s, 1684s, 1629m, 1059m cm.$^{-1}$).

For the electrolysis at −1·0 v (*vs.* S.C.E.) in 0·1N-sodium hydroxide the compound (63·5 mg.) was dissolved in 200 ml. of solution. The current was at first 140 mA and decreased to 5 mA in about 4 hr. The electricity required was 250 coulombs, corresponding to 6·45 electrons per molecule.

(*b*) The compound (63·3 mg.) was electrolysed at −0·9 v (*vs.* S.C.E.) in 0·1M-phosphoric acid–sodium hydroxide buffer solution (200 ml.) of pH 2 containing 0·1M-potassium chloride. The current, 250 mA at the beginning of the run, decreased to 2 mA after 1 hr. Electricity required was 216 coulombs, corresponding to 5·6 electrons per molecule. The electrolysed solution exhibited a reduction wave of $E_{\frac{1}{2}}$ = −0·45 v (*vs.* S.C.E.) when made alkaline with 20% aqueous sodium hydroxide to about pH 12·5. The alkaline solution was diluted 20-fold and examined for the absorption band at 336 mμ.

Electrolysis at −0·55 v was performed on 63·2 mg. of the compound, which consumed 202 coulombs for 1·5 hr., corresponding to 5·24 electrons per molecule.

(*c*) The compound (63·3 mg.) was electrolysed for 50 min. at −1·0 v in 0·1M-phosphate buffer solution (200 ml.) of pH 6 containing 0·1M-potassium chloride. The electricity consumed was 211 coulombs, corresponding to 5·47 electrons per molecule. A portion of the electrolysed solution was made alkaline as above to about pH 12·5 and its ultraviolet spectrum and polarogram were investigated.

*Determination of Acetic Acid.*—A solution was electrolysed as above, sulphamic acid (200 mg.) and a sufficiency of concentrated sulphuric acid were added, and the whole was distilled. The distillate was titrated with 0·1N-sodium hydroxide (phenolphthalein), then with 0·1N-silver

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[19] Nef, *Annalen*, 1894, **280**, 320.

[20] Wieland and Hess, *Ber.*, 1909, **42**, 4178.

nitrate potentiometrically after addition of 2 drops of concentrated nitric acid. The difference of the two titration gave the amount of the acetic acid.

*Controlled-potential Electrolysis of Dinitromethane.*—(*a*) The compound (72·1 mg.) was electrolysed in 0·1N-sodium hydroxide (200 ml.) at −1·7 v (*vs.* S.C.E.). The current was 560 mA at the beginning and 2 mA after 80 min. From time to time the absorption spectrum of portions of the solution was measured after 50-fold dilution. The electrolysed solutions from five runs were combined, brought to pH about 7·2 with 10% hydrochloric acid, and evaporated at ~35°. The residue was extracted with anhydrous ethanol and the extract evaporated to dryness, and this residue extracted with ethyl acetate. Evaporation and recrystallization from ethyl acetate gave formamidoxime, m. p. 114° (decomp.) Found: C, 19·7; H, 6·6; N, 46·6. Calc. for $CH_4N_2O$: C, 20·0; H, 6·7; N, 46·65%), $\nu_{max.}$ 3401s, 3205s, 1675s, 1613m, 1316m, 958m, and 885m cm.$^{-1}$ (coincident with maxima of formamidoxime prepared by Nef's method).

For the electrolysis at −1·0 v of 31·6 mg., 138 coulombs, corresponding to 6·53 electrons per molecule, were required for 3 hr.

(*b*) The compound (28·8 mg.) was electrolysed in 200 ml. of the buffer solution of pH 2 used in (*b*) above, at −0·76 v (*vs.* S.C.E.). The current was 130 mA at the beginning and less than 2 mA after 1 hr. The electricity consumed was 116 coulomb, corresponding to 6·01 electrons per molecule. 20% sodium hydroxide solution was also used to bring the solution to pH 12·5.

For the electrolysis at −0·55 v 29·8 mg. of dinitromethane were used. 117 coulombs, corresponding to 5·86 electrons per molecule, were required for 1·5 hr.

(*c*) The compound (28·8 mg.) was electrolysed at pH 6; 116 coulombs, corresponding to 6·01 electrons per molecule, were consumed. Other operations were as described above.

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