331. *Controlled-potential Electrolysis. Part VIII.*[1] *Polarographic Behaviour and Controlled-potential Electrolysis of* gem-*Polynitroparaffins.*

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The electrochemical reduction of trinitromethane, 1,1,1-trinitroethane, and tetranitromethane at a mercury cathode has been studied by polarography and controlled-potential electrolysis. Using also the results obtained in the previous papers we have found that for *gem*-polynitro-compounds, those which can adopt the *aci*-nitro-form are reduced without C–N bond fission, whereas reduction of those which cannot occur in the *aci*-nitro-form proceeds with C–N bond fission.

IN Part VII [1] the behaviour of dinitromethane and 1,1-dinitroethane on polarography and controlled-potential electrolysis was studied, and it was shown that the waves developed in the polarograms did not represent the reduction stages but were probably caused by the presence of different forms of the compounds and equilibria between them. In the present paper trinitromethane, 1,1,1-trinitroethane, and tetranitromethane have been studied by the same methods and the reduction processes have been clarified. From our results a general rule governing the polarographic reduction of *gem*-polynitroparaffins has been advanced.

Polarography of Trinitromethane.—Half-wave potentials and apparent diffusion current constates, I, of each wave are dependent on the pH of the solution (Fig. 1). Fig. 2 shows some examples of polarograms. The first wave in very acid solution split into two, waves I_a and I_b, but there is only one fairly well-defined wave in weakly acidic solutions. Two waves, the first fairly well defined, the second poorly defined, are observed in alkaline solutions. The last is generally hardly measurable, so that $E_{\frac{1}{2}}$ of the wave is not shown in the Figure except at pH 12. Though the half-wave potential of the first wave is shifted about 53 mv per pH unit between pH 2 and pH 8, it is almost constant above pH 8. At

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[1] Part VII, Masui and Sayo, *J.*, 1961, 5325.

pH 2, I_a is at a more positive potential, but the first wave obtained at higher pH may be a combination of I_a and I_b wave; and so $E_{\frac{1}{2}}$, corresponding to a mean valve of those of I_a and I_b, is shown to fall on a straight line. The height of the first wave decreases in the alkaline region, though that of the second wave increases with increasing pH just like those of dinitromethane and 1,1-dinitroethane.[1] The total wave height is almost constant over the whole pH region studied, and the diffusion-current constant is about twice that of 1,1-dinitroethane. Since n, the number of electrons involved in the reduction of 1,1-dinitroethane, is 6, n for trinitromethane is assumed to be 12. The relation between the limiting currents and the mercury-column heights (Table 1) shows that the wave at pH 6 and the total waves at pH 2 and pH 12 are diffusion controlled whereas the first wave at pH 12 is not. As the wave I_a at pH 2 had no clear plateau where its precise height could be measured, it was not examined.

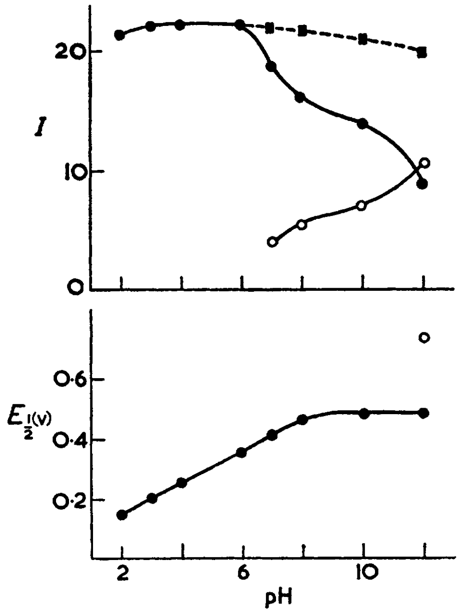

FIG. 1. Variation of apparent diffusion current constant (I) and $E_{\frac{1}{2}}$ of trinitromethane with pH: ●, first wave; ○, second wave; ■ sum of the two waves.

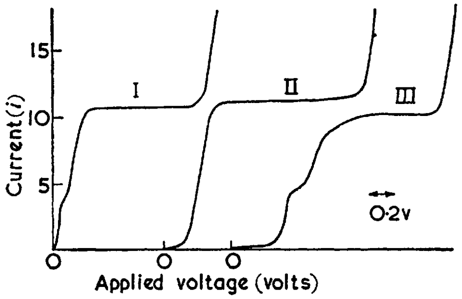

FIG. 2. Polarograms of trinitromethane (5×10^{-4}M-solution). I, pH 2·0; II, pH 6·0; III, pH 12·0.

TABLE 1.

Effect of mercury-column height (h, in cm.) on limiting current (i) of trinitromethane ($3·99 \times 10^{-4}$ mole/l.).

	h	40	50	60	70
pH 2·0	$i_1 + i_2/h^{\frac{1}{2}}$	1·407	1·407	1·394	1·404
pH 6·0	$i_1/h^{\frac{1}{2}}$	1·448	1·448	1·451	1·449
pH 12·0	$i_1/h^{\frac{1}{2}}$	0·553	0·580	0·594	0·598
	$i_1 + i_2/h^{\frac{1}{2}}$	1·296	1·287	1·291	1·321

From this behaviour it is possible that in the case of trinitromethane, as with dinitromethane and 1,1-dinitroethane, there is an equilibrium between two molecular forms in very acid and alkaline solutions.

Polarography of 1,1,1-*Trinitroethane.*—The dependence on pH of the half-wave potentials and of the apparent diffusion-current constants is shown in Fig. 3, and typical polarograms are given in Fig. 4. There are three waves at pH 2, two at pH 4—8, and three again at pH 9—13. The half-wave potential and the height of the first wave are independent of pH, and the diffusion-current constant is nearly the same as that of 2,2-dinitropropane in neutral solution. The reduction of the compound is, therefore, thought to be two-electron reductive fission of one of the C–N bonds to give 1,1-dinitroethane and nitrite. Owing to the reaction between the trinitroethane and mercury in very alkaline solution the wave height tends to decrease in this region, even though the measurement is carried out as soon as possible after the addition of the compound to the basic solution. If the first wave can be attributed to the reduction of trinitroethane to 1,1-dinitroethane, the subsequent waves must be analogous to those of 1,1-dinitroethane, since the nitrite and the dinitroethane produced do not react with each other in the medium. The second and the third wave showed similar behaviour to those of 1,1-dinitroethane in neutral and alkaline solutions. On the other hand, only one wave appeared in acid solution, instead of the two split waves shown by dinitroethane. The third wave, at pH 2, was due to the reduction of nitrite.

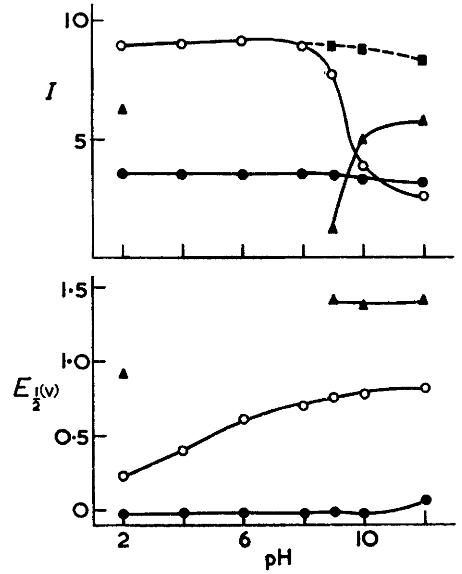

FIG. 3. Variation of apparent diffusion current constant (I) and $E_{\frac{1}{2}}$ of 1,1,1-trinitroethane with pH: ●, first wave; ○, second wave; ▲, third wave; ■, sum of second and third waves in alkali.

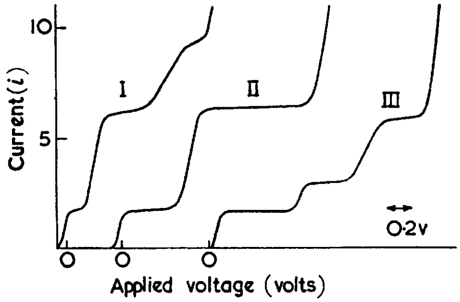

FIG. 4. Polarograms of 1,1,1-trinitroethane (5×10^{-4}M) in 10% ethanol. I, pH 2·0; II, pH 6·0; III, pH 12·0.

The relation between i and the mercury-column heights (Table 2) shows that the first

TABLE 2.

Effect of mercury-column height (h, in cm.) on limiting current (i) of 1,1,1-trinitroethane ($5{\cdot}02 \times 10^{-4}$ mole/l.).*

	h	40	50	60	70
pH 2·0	$i_1/h^{\frac{1}{2}}$	0·308	0·307	0·303	0·301
	$i_2/h^{\frac{1}{2}}$	0·790	0·778	0·775	0·759
	$i_3/h^{\frac{1}{2}}$	0·632	0·594	0·562	0·544
pH 10·0	$i_1/h^{\frac{1}{2}}$	0·269	0·269	0·269	0·268
	$i_2/h^{\frac{1}{2}}$	0·340	0·322	0·314	0·306
	$i_3/h^{\frac{1}{2}}$	0·467	0·467	0·456	0·452
pH 6·0	$i_1/h^{\frac{1}{2}}$	0·277	0·276	0·284	0·299
	$i_2/h^{\frac{1}{2}}$	0·806	0·806	0·794	0·783

* 10% ethanol was added.

wave is diffusion controlled but that the second and the third, at pH 2 and pH 10, are not simple diffusion-controlled waves. The smaller diffusion-current constant (~9) for the second wave up to pH 8 and for the sum of the second and the third wave between pH 8 and pH 12 of the trinitroethane compared to that of 1,1-dinitroethane (~10) may be due to the smaller diffusion constant of the larger trinitroethane molecule.

Polarography of Tetranitromethane.—Only brief polarographic data for this compound have been reported by Cruse and Haul.[2] As it reacts easily with mercury in every pH region, an H-type cell had to be used, but reaction with the mercury of the dropping-mercury electrode could not be avoided. Also, it reacted by itself in very alkaline solution without contact with mercury, the solution became yellow, and the polarographic waves were so much obscured that it was almost impossible to measure its half-wave potentials and wave heights except for the first wave (Table 3).

TABLE 3.

Half-wave potentials and diffusion-current constants of the first wave of tetranitromethane in buffer solutions containing 10% of ethanol.

pH	2·0	4·0	6·0	8·0	10·0	12·0
E (volts)	+0·062	+0·063	+0·062	+0·064	+0·041	−0·155
$i_d/Cm^{2/3}t^{1/6}$	1·98	1·98	1·98	1·98	2·19	1·98

The half-wave potential of the first wave is independent of pH between pH 2 and pH 10, and the diffusion-current constant is slightly smaller than that of 1,1,1-trinitroethane. Therefore the wave may be due to reductive fission of one of the C–N bonds to trinitromethane and nitrite as with 1,1,1-trinitroethane. Therefore, the waves of the mixture of trinitromethane and nitrite should appear after the first wave, but owing to the disturbing action of these undesirable reactions the polarogram was more complicated.

Controlled-potential Electrolysis of Trinitromethane.—(a) *Electrolysis in buffer solution of* pH 6. The electrolysis at the cathode potential of −1·0 v, below 3° to avoid decomposition of the components, consumed 11·3 electrons/molecule. The resulting solution gave a faint Griess reaction for nitrous acid, and a dark green colour with Fehling's solution. Tests for formaldehyde [3] and formic acid [4] were negative, both with this solution and also after hydrolysing it with mineral acid. The ultraviolet spectrum of the solution during the electrolysis showed an absorption maximum of the *aci*-nitro-form of trinitromethane at 352 mμ, which diminished in the course of the electrolysis and disappeared at the end. When the electrolysed solution was adjusted to pH 12, it became yellow and showed an absorption peak at 385 mμ and also a reduction wave of $E_{\frac{1}{2}} = -0{\cdot}386$ v. For the reduction, a scheme like (1) must be abandoned, because the following phenomena, which should occur with the reduction of dinitromethane, have not been observed: (i) as nitrite is neither active in the reaction with dinitromethane nor reducible under those conditions, only the reduction of dinitromethane, which consumes electricity corresponding to $n = 6$, should follow; that is, the total value of n should be <8;[1] (ii) hydrolysis of the resulting solution by acid should yield formic acid, and the solution should have $\lambda_{\text{max.}}$ 334 mμ at pH 12;[1] (iii) the amount of nitrite in the electrolysed solution should be about equivalent to the original compound. Therefore we think that the reduction may proceed without

$$\mathrm{HO_2N{:}C(NO_2)_2 \xrightarrow{+\,2e} HO_2N{:}CH{\cdot}NO_2 + NO_2^-} \qquad \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \quad (1)$$

initial bond fission like scheme (1), requiring 12 electrons per molecule, and most probably yields dihydroxyguanidine as a final product. The authentic sample prepared by Wieland's method [5] showed in basic medium the same absorption at $\lambda_{\text{max.}}$ 385 mμ ($\varepsilon = 10{,}060$) and

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[2] Cruse and Haul, *Z. Elektrochem.*, 1949, **53**, 115.

[3] Feigl, " Spot Tests," Elsevier Publishing Co., Amsterdam, 4th edn., Vol. II, p. 240

[4] *Ibid.*, p. 245.

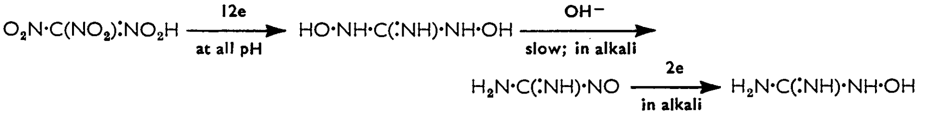
[5] Wieland, *Ber.*, 1905, **38**, 1449.

the ill-defined polarographic waves at $E_{\frac{1}{2}} = -0{\cdot}382$ and $I = 2{\cdot}99$, though it showed neither absorption band nor reduction wave in neutral and acidic media; these facts were in good agreement with results for the electrolysed solution. The small difference between the experimental and theoretical value (12) of n may be ascribed to the instability of dihydroxyguanidine and probably of the intermediate compounds, because (*a*) when a neutral solution of dihydroxyguanidine was kept at 25° for one day its absorption band decreased to less than one tenth of the original amount; (*b*) electrolysis at 20—25° consumed electricity corresponding to only $n = 9$, and the resulting solution showed less than one half of the original absorption. The amount of dihydroxyguanidine found in the final solution when it was ice-cold was estimated as 0·87 equivalent by both the spectrographic and the polarographic method.

(b) *Electrolysis in the buffer solution of* pH 2. The required electricity corresponded to 9·9 electrons/molecule at a cathode potential of —0·7 v at <3°. The electrolysed solution gave a faint positive test for nitrite by the Griess method, a green colour with Fehling's solution, and negative tests for formaldehyde and formic acid. The solution at pH 12 had $\lambda_{\text{max.}}$ 385 mμ, and the reduction wave of $E_{\frac{1}{2}} = -0{\cdot}393$ v, both representing dihydroxyguanidine, but the amounts estimated by both methods were 0·48 and 0·47 equivalent, respectively. Since, as we observed, the decomposition of dihydroxyguanidine is fast in acid solution, and the intermediates similar, the smaller amount of the compound and the lower value of n are easily understood. As wave I_a is very close to I_b the controlled-potential electrolysis at the plateau potential of wave I_a was not examined.

(c) *Electrolysis in the buffer solution of* pH 12. With a cathode potential of —1·7 v at <3° the cathodic reduction consumed electricity corresponding to 13·4 electrons/molecule. During the electrolysis the absorption band ($\lambda_{\text{max.}}$ 385 mμ) appeared and increased, but diminished again until it disappeared at the end of the run. Only a slight amount of nitrite was detected, and formaldehyde or formic acid was not found in the solution. When dihydroxyguanidine was reduced by the same method, it consumed electricity corresponding to 2·1 electrons/molecule, and the characteristic absorption band ($\lambda_{\text{max.}}$ 385 mμ) diminished with time and disappeared at the end of the run. Therefore the reduction process at pH 12 should be analogous to the above two cases (a) and (b), as far as dihydroxyguanidine, but an easily reduced substance, probably $H_2N{\cdot}C(NO){:}NH$, which is the entity exhibiting the absorption, may be produced from dihydroxyguanidine by a rather slow reaction [as shown by the appearance of the absorption band] and it may be further reduced in this medium by a two-electron reduction probably to hydroxyguanidine. The electrolysed solution was then treated with benzoyl chloride, as the hydroxyguanidine itself was very unstable, and stable dibenzoyloxyguanidine was isolated as expected. It was identical (mixed m. p. and infrared spectrum) with an authentic sample prepared by Adams's method.[6]

From these results the reduction process can be expressed by scheme (2).



$$O_2N{\cdot}C(NO_2){:}NO_2H \xrightarrow[\text{at all pH}]{12e} HO{\cdot}NH{\cdot}C({:}NH){\cdot}NH{\cdot}OH \xrightarrow[\text{slow; in alkali}]{OH^-} H_2N{\cdot}C({:}NH){\cdot}NO \xrightarrow[\text{in alkali}]{2e} H_2N{\cdot}C({:}NH){\cdot}NH{\cdot}OH \quad (2)$$

Though the overall reduction at pH 12 requires 14 electrons the final two-electron reduction does not appear to take place at the dropping-mercury electrode as the total wave height in this region is rather small. But this may be explained by considering the slow step in scheme (2); that is, the rate of the conversion is too slow for the compound to be reduced at the dropping-mercury electrode before it diffuses from the electrode surface to the bulk of the solution, but by the controlled-potential electrolysis all reducible compounds contained in the solution are reduced.[1]

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[6] Adams, *J. Org. Chem.*, 1953, **18**, 934.

The Controlled-potential Electrolysis of 1,1,1-*Trinitroethane.*—(a) *Electrolysis in the buffer solution of* pH 12. When the electrolysis was carried out with the cathode potential at which the limiting current of the first wave was reached, the absorption band of 1,1-dinitroethane, $\lambda_{\text{max.}}$ 382 mμ, and a positive reaction for nitrite were observed. The amounts of both compounds were estimated from the light absorption and it was found that the reduction was almost stoicheiometric, with $n = 2$. The first wave was absent from the polarogram of the resulting solution which showed similar waves to those of 1,1-dinitroethane. Further, dinitroethane was isolated from the solution as a potassium salt and identified by the infrared spectrum. From these results it was confirmed that the first wave of the trinitroethane was due to fission of one of the C–N bonds (scheme 3).

$$CH_3{\cdot}C(NO_2)_3 \xrightarrow{2e} CH_3{\cdot}C(NO_2){:}NO_2^- + NO_2^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

As the nitrite ion does not react with 1,1-dinitroethane in the solution, the second and the third wave of 1,1,1-trinitroethane should correspond to the first and second waves of dinitroethane. The variation of the absorption at $\lambda_{\text{max.}}$ 336 mμ,[1] when the electrolysis was carried out at a cathode potential on the plateau of the third wave, was qualitatively analogous to that of 1,1-dinitroethane. The electrolysis at a plateau potential of the second wave caused the third wave as well as the second to decrease almost to zero, although it took a fairly long time. The behaviour of the absorption spectrum was also analogous to that of 1,1-dinitroethane. From the solution electrolysed at a potential on the third-wave plateau acetamidoxime was isolated as its benzoyl derivative, as the solution could not be acidified to prevent reaction between acetamidoxime and nitrite. These results confirm the course of the reaction.

(b) *Electrolysis in the buffer solution of* pH 6. From the solution electrolysed at a potential on the first-wave plateau 1,1-dinitroethane and nitrite were detected as in (a). The absorption band ($\lambda_{\text{max.}}$ 336 mμ) at pH 12 obtained from the solution electrolysed at a potential on the second-wave plateau corresponded to only one tenth of the acethydroxamic acid oxime expected, and this is identical with the case described for 1,1-dinitroethane in the preceding paper.[1]

(c) *Electrolysis in the buffer solution of* pH 2. Production of 1,1-dinitroethane and nitrite by electrolysis at a potential on the first-wave plateau was also confirmed in this case as in (a). Acethydroxamic acid oxime, produced by the reduction of the dinitroethane, was also identified by the absorption at 336 mμ and determined to be 0·6 equivalent when the electrolysis was carried out at a potential on the second-wave plateau and in the presence of sulphamic acid to decompose nitrite.

The reduction process of 1,1,1-trinitroethane is, therefore, represented by scheme (4).

$$\text{Scheme (3)} \xrightarrow[\text{at all pH}]{6e} CH_3{\cdot}C(NH{\cdot}OH){:}N{\cdot}OH + NO_2^- \xrightarrow[\text{in alkali}]{2e} CH_3{\cdot}C(NH_2){:}N{\cdot}OH + NO_2^- \quad . \quad (4)$$

Controlled-potential Electrolysis of Tetranitromethane.—Tetranitromethane reacted with electrode mercury at once at any pH, the solution became yellow, and black powder was precipitated on the electrode surface, even though no voltage was applied. The yellow solution showed an absorption band at $\lambda_{\text{max.}}$ 352 mμ which corresponded to that of the *acid*-nitro-form of trinitromethane. The easy removal of one nitro-group is well known.[7] A reaction scheme such as (5) is probable. Therefore electrolysis of tetranitromethane

$$C(NO_2)_4 + 2Hg \longrightarrow C(NO_2)_2{:}NO_2^- + NO_2^- + Hg_2^{++} \quad . \; . \; . \; . \; . \; . \quad (5)$$

itself was impossible, and the electrolysis of the solution was that of the mixture of trinitromethane and nitrite as observed experimentally in neutral and alkaline solutions. The behaviour in acidic media was complicated because of the nitrite reaction.

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[7] Rodd, " Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1951, Vol. I, p. 378.

DISCUSSION

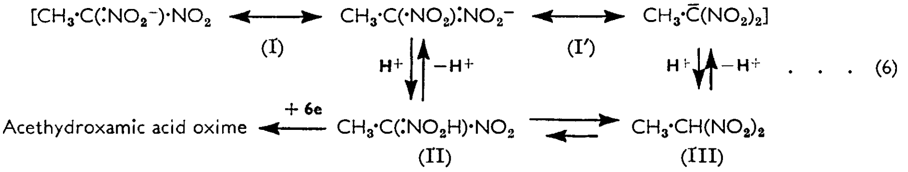
From our study of polynitroalkanes[1,8] the following general rule has been derived governing the electrochemical reduction of *gem*-polynitroalkanes at a mercury cathode.

gem-Polynitro-compounds having at least one hydrogen atom on the carbon attached to the nitro-groups are reduced mainly through conversion of one of the nitro-groups into *aci*-nitro, but the reduction takes place at the nitro-group of the nitro-form without C–N bond fission.

Compounds that have no hydrogen atom on the carbon atom attached to the nitro-groups cannot adopt the *aci*-nitro-form, and reduction is then initiated by fission of a C–N bond to produce nitrite and the *aci*-nitro-form of the nitro-compound having one nitro-group less than the original. The reaction with nitrous acid must often be considered, especially in acid solution. The C–N bond fission takes place at more positive potential as the number of nitro-groups attached to the carbon is increased, but our attempts to find a simple relation between $E_{\frac{1}{2}}$ and substituent constants failed, as did those of Elving and Markowitz for nitroalkanes.[9]

The generalisation holds only for *gem*-polynitroalkanes and not for mononitroalkanes, since the wave height of 2-methyl-2-nitropropane is comparable to that of nitromethane.[10]

The polarograms of *gem*-polynitro-compounds have been understood by considering those obtained from controlled-potential electrolysis. Results obtained by the two methods often exhibit differences, because of large differences in electrode surface area and duration of reaction; the relation of the rates of faradaic and non-faradaic reaction would produce these discrepancies. Thus, consider the second wave of 1,1,1-trinitroethane in acid solution. The production of 1,1-dinitroethane and nitrite by the preceding reduction, the first wave, was explained by the results obtained with the controlled-potential electrolysis, but only one wave, other than that due to nitrite at pH 2, appeared in that region. This discrepancy may well be explained by scheme (6), in which a longer arrow represents larger reaction rate but equal length does not necessarily mean equal rate.



$$\begin{tikzcd}
{[CH_3{\cdot}C({:}NO_2^-){\cdot}NO_2} \arrow[r, leftrightarrow, "(I)"'] & CH_3{\cdot}C({\cdot}NO_2){:}NO_2^- \arrow[r, leftrightarrow, "(I')"'] \arrow[d, shift right, "H^+"'] & {CH_3{\cdot}\bar{C}(NO_2)_2]} \arrow[d, shift right, "H^+"'] \\
\text{Acethydroxamic acid oxime} & CH_3{\cdot}C({:}NO_2H){\cdot}NO_2 \arrow[l, "+6e"'] \arrow[u, shift right, "-H^+"'] \arrow[r, shift left] & CH_3{\cdot}CH(NO_2)_2 \arrow[l, shift left] \arrow[u, shift right, "-H^+"']
\end{tikzcd}$$

(II) (III) . . . (6)

The entity produced by the reduction corresponding to the first wave is system (I), in which the contribution of form (I) to the system is greater than that of (I′).[11,13] Moreover, the addition of a proton to (I) to produce the less-stable form (II) is much faster than addition to (I′) to produce the stable form (III). Thus the more easily reduced (II)[1] predominates at the surface of a dropping-mercury electrode, being reduced quickly at the second wave before its conversion into (III). Therefore no wave due to the reduction of (III) has been observed.

Electrolysis of 1,1,1-trinitroethane at a potential on the first-wave plateau produces the anion which diffuses from the electrode surface into the bulk of the solution. There was sufficient time for the conversion of (II) into (III) when the solution was electrolysed by a mercury-pool electrode and measured by polarography, even if it was carried out soon after the reduction; therefore the height of the first wave in this case was diminished. Though the shape of the second wave in this solution was obscured owing to the presence

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[8] Masui and Sayo, *J.*, 1961, 4773.

[9] Elving and Markowitz, *J. Org. Chem.*, 1960, **25**, 18.

[10] Findeis and DeVries, *J. Amer. Chem. Soc.*, 1958, **80**, 797.

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

[12] Belew and Hepler, *J. Amer. Chem. Soc.*, 1956, **78**, 4005.

[13] Kornblum, Lichtin, Patton, and Iffland, *J. Amer. Chem. Soc.*, 1947, **69**, 307.

of alcohol needed to dissolve the trinitroethane, its appearance was not in doubt. Obviously the amount of dinitroethane (III) produced at the first wave by the dropping-mercury electrode is negligible in the bulk of the solution.

This would be another proof of the generalisation cited by Ingold *et al.*[14]

EXPERIMENTAL

All voltages were measured against the saturated calomel electrode.

Materials.—The potassium salt of trinitromethane, m. p. 98° (decomp.), prepared from atetranitromethane, glycerol, and potassium hydroxide,[15] was used within 3 days of recrystallistion (from water). 1,1,1-Trinitroethane was prepared from the silver salt of trinitromethane and methyl iodide;[16] it had m. p. 56° (from light petroleum). Tetranitromethane was prepared from acetic anhydride and nitric acid;[17] it had b. p. 34—35°/20 mm. Dihydroxyguanidine hydrobromide was prepared from hydroxylamine and cyanogen bromide;[5] it had m. p. *ca.* 95° (decomp.) (from ethanol–ether). Dibenzoyloxyguanidine was obtained from benzoyl chloride and an aqueous solution of hydroxyguanidine prepared from hydroxylamine hydrochloride and cyanamide,[6] m. p. 164—165° (decomp.) (from ethanol). *Benzoylacetamidoxime* was prepared from acetamidoxime hydrochloride and benzoyl chloride; it formed needles, m. p. 124° (decomp.) (from ethanol) (Found: C, 60·6; H, 5·7; N, 15·7. $C_9H_{10}N_2O_2$ requires C, 60·7; H, 5·7; N, 15·7%).

Apparatus and buffer solutions were those described in previous papers except that the potentiostat was modified for use with currents up to about 3 A.

Controlled-potential Electrolysis of Trinitromethane.—(*a*) Potassium salt (37·8 mg.), in buffer solution (200 ml.) of pH 6 (0·1M-KH_2PO_4–Na_2HPO_4, 0·1M-KCl), consumed 219 coulombs, which corresponded to 11·3 electrons per molecule. 20% Sodium hydroxide was added to make the solution pH 12·0 as soon as possible after the finish of the electrolysis, and the ultraviolet absorption spectrum and polarogram were examined.

(*b*) Potassium salt (75·5 mg.), in buffer solution (200 ml.) of pH 2·0 (0·1M-H_3PO_4–NaOH, 0·1M-KCl), required 381 coulombs, corresponding to $n = 9·9$. 20% Sodium hydroxide was used to make the solution pH 12·0.

(*c*) 704 Coulombs were consumed by the potassium salt (102·7 mg.); this corresponded to $n = 13·4$. Soon after the completion, 10% hydrochloric acid was added to make the solution about pH 9, with ice cooling, and the solution was shaken vigorously with benzoyl chloride (1·5 g.) and sodium hydrogen carbonate (10 g.). The precipitate was collected at pH 10—11, dried, and crystallised from ethanol, giving material, m. p. 164—165° (decomp.), identical (mixed m. p. and infrared spectrum) with Adams's dibenzoyloxyguanidine.

Controlled-potential Electrolysis of Trinitroethane.—(*a*) (*i*) 1,1,1-Trinitroethane (195·6 mg.), dissolved in ethanol (20 ml.), was added to buffer solution of pH 12·0 (180 ml.) and electrolysed at $-0·3$ v at $<3°$. 225 Coulombs ($n = 1·97$) were required. Nitrite was estimated[18] as 0·97 equivalent, and the 1,1-dinitroethane produced as 0·99 equivalent (by the absorption at 382 mμ). Acidification of the solution with 10% hydrochloric acid, distillation under reduced pressure, addition of the calculated amount of potassium hydroxide to the distillate, and evaporation of the yellow solution to dryness under reduced pressure gave the potassium salt of 1,1-dinitroethane as yellow crystals, m. p. *ca.* 151° (decomp.) (from water). The infrared spectrum was identical with that of Wieland and Sakellarios's authentic sample.[19]

(*ii*) The compound (103·4 mg.), dissolved as above, was electrolysed at $-1·7$ v. It consumed 582 coulombs; $n = 9·64$. The electrolysed solution was evaporated at 40° to about 100 ml. under reduced pressure, then treated with benzoyl chloride (1 g.) at 10—15°. Saturation of the treated solution with sodium chloride, extraction with ether, drying (Na_2SO_4) and evaporation of the ether gave needles, m. p. 124° (from ethanol–benzene and then ethanol), which were identical (mixed m. p. and infrared spectrum) with the sample prepared from acetamidoxime hydrochloride.

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[14] Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, p. 565; Catchpole, Hughes, and Ingold, *J.*, 1948, 8.

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[16] Hantzsch and Rinckenberger, *Ber.*, 1899, **32**, 636.

[17] Liang, *Org. Synth.*, 1941, **21**, 105.

[18] Snell and Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., New York, 1954, Vol. II, p. 804.

[19] Wieland and Sakellarios, *Ber.*, 1919, **52**, 904.

(*b*) (*i*) The compound (196·0 mg.), dissolved in ethanol (20 ml.) and the buffer solution of pH 6·0 (180 ml.), consumed 231 coulombs ($n = 2{\cdot}02$) at −0·2 v and yielded 1,1-dinitroethane and nitrite.

(*ii*) The compound (33·0 mg.), dissolved as above, required 155 coulombs ($n = 8{\cdot}04$) at −1·0 v. The amount of acethydroxamic acid oxime produced was estimated to be about 0·1 equivalent by measuring the absorption at 336 mμ at pH 12.

(*c*) (*i*) The compound (197·0 mg.), dissolved in ethanol (20 ml.) and buffer solution of pH 2·0 (180 ml.), consumed 235 coulombs ($n = 2{\cdot}04$) at −0·1 v. The presence of 1,1-dinitroethane and nitrite was confirmed as above.

(*ii*) The compound (66·05 mg.), dissolved in ethanol (20 ml.), was added to the buffer solution of pH 2·0 (180 ml.) containing sulphamic acid (0·5 g.), and subjected to electrolysis. 261 Coulombs ($n = 6{\cdot}37$) were consumed. The amount of acethydroxamic acid oxime produced was found to be about 0·6 equivalent.

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