941. Controlled-potential Electrolysis. Part VI.[1] Reductions of 2,2-Dinitropropane.

By MASAICHIRO MASUI and HIROTERU SAYO.

The reduction processes of 2,2-dinitropropane have been studied by controlled-potential electrolysis. In alkaline solution the two-electron reduction to the *aci*-form of 2-nitropropane and nitrite was established by isolation of 2-nitro-2-nitrosopropane. In acid solution the reduction at the plateau potential of the first wave yielded acetoxime and nitrous acid by a four-electron reduction; the uptake at the second wave was 10·6-electrons, the reduction giving ammonia, hydroxylamine, 2-hydroxylamino-propane, and acetoxime. On these bases the reduction processes and the polarograms of 2,2-dinitropropane are discussed.

ONLY Stock[2] has studied the polarographic reduction of 2,2-dinitropropane. He used a small-scale, controlled-potential, electrolytic method for an alkaline solution and found that the reduction wave was due to the reduction to the *aci*-form of 2-nitropropane and nitrite ion, but he merely deduced the mechanisms of the reduction waves in acid solution and gave no evidence in support.

As part of our study of controlled-potential electrolysis of nitro-compounds we applied the method to 2,2-dinitropropane on a fairly large scale and have clarified the reduction processes by isolating the products. Only the result obtained in alkaline solution has agreed with Stock's work.

TABLE 1.

Half-wave potentials and diffusion current constants of 2,2-dinitropropane in buffer solutions containing 10% of ethanol.

pH	2·0 *	4·0 *	6·0	8·0	10·0	12·0
$\pi_{\frac{1}{2}}$ (v)	−0·348	−0·465	−0·488	−0·496	−0·486	−0·499
$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$	4·35	3·87	3·00	3·16	2·94	2·84

Polarography.†—Because of the low solubility of 2,2-dinitropropane in water it was necessary to use ethanol for the more concentrated solutions required. The polarographic behaviour of 2,2-dinitropropane in 10% ethanolic buffer solutions were, therefore, first investigated. The results (Table 1) were almost the same as Stock's, except that the poorly defined second wave (marked *) was overlapped by the reduction wave of hydrogen ion.

Controlled-potential Electrolysis in Alkaline Solution.—Stock's results for alkaline

† All voltages are measured against the saturated calomel electrode.

[1] Part V, *J. Pharm. Soc. Japan*, 1960, **80**, 1256.
[2] Stock, *J.*, 1957, 4532.

solution were confirmed in our experiments on a larger scale. The electrolysed solutions became blue when acidified and the coloured substance was identified as 2-nitro-2-nitroso-propane by isolation in crystalline form. The compound is derived according to reaction (1) which is used as a test for secondary nitroparaffins.[2]

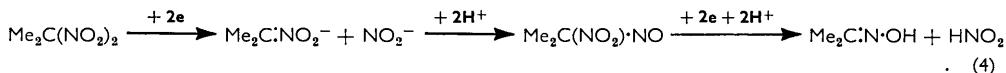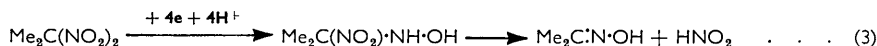$$RR'C=NO \cdot O^- + NO_2^- + 2H^+ \longrightarrow RR'C(NO) \cdot NO_2 + H_2O \quad \ldots \ldots (1)$$

On the other hand, the presence of excess of sodium azide and slow acidification prevented the coloration of the solution, which only showed a single reduction wave of 2-nitropropane.[3] Stock's reaction (2) is thus confirmed.

$$Me_2C(NO_2)_2 + 2e \longrightarrow Me_2C=NO \cdot O^- + NO_2^- \quad \ldots \ldots \ldots (2)$$
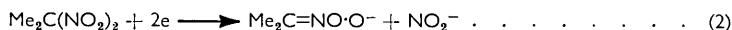
Controlled-potential Electrolysis at a Plateau Potential of the First Wave in Acid Solution.—Electrolysis at $-0 \cdot 55$ v in buffer solutions of pH 2 was slow and consumed four electrons per molecule (Table 2).

The electrolysed solution gave a positive test for nitrite and yielded a yellow precipitate with 2,4-dinitrophenylhydrazine. These solutions did not reduce Fehling's solution until after hydrolysis with boiling dilute sulphuric acid. Neutralisation of the electrolysed solution, removal of the ethanol, and extraction with ether afforded acetoxime, whence two reduction processes, (3) and (4), are inferred.

According to eqn. (3), a four-electron reduction proceeds in one step at the electrode surface, and the product is hydrolysed to acetoxime and nitrous acid. By eqn. (4), the first step is a two-electron reduction to 2-nitropropane and nitrite (as in basic media) then reaction with hydrogen ion to form 2-nitro-2-nitrosopropane, which is reduced in the second step by a two-electron process. If a four-electron reduction, as in eqn. (3), took place, the limiting current of the first wave should be about twice as high in acid as in

$$Me_2C(NO_2)_2 \xrightarrow{+ 4e + 4H^+} Me_2C(NO_2) \cdot NH \cdot OH \longrightarrow Me_2C{:}N \cdot OH + HNO_2 \quad \ldots \quad (3)$$

$$Me_2C(NO_2)_2 \xrightarrow{+ 2e} Me_2C{:}NO_2^- + NO_2^- \xrightarrow{+ 2H^+} Me_2C(NO_2) \cdot NO \xrightarrow{+ 2e + 2H^+} Me_2C{:}N \cdot OH + HNO_2$$
$$\quad \cdot \ (4)$$

alkaline solution and also be diffusion-controlled. But the height of the former is only 1·4 times that of the latter and the effect of mercury-column height on the limiting current does not imply diffusion-control (Table 3).

With reduction in the presence of sulphamic acid (to decompose nitrous acid) the uptake fell to about 3 electrons per molecule; thus some of the nitrous acid produced is consumed in the reduction. Nitrous acid is not reducible at this potential, so that if the reduction proceeds according to eqn. (3), the decomposition of nitrous acid should cause no change in current requirements.

TABLE 2.

Reduction of 2,2-dinitropropane at $-0 \cdot 55$ v at pH 2.

Taken (mg.)	203·0	251·1	369·7
Coulombs reqd. Found	572	710	1062
n, found	3·92	3·93	3·99

According to eqn. (4) the intermediate, 2-nitro-2-nitrosopropane, should be reduced under this condition as produced, because its half-wave potential is $-0 \cdot 05$ v at pH 2. This was proved by the reduction of 2-nitro-2-nitrosopropane, prepared according to Meyer,[3] under the same conditions; acetoxime and nitrous acid were obtained by a two-electron reduction. During electrolysis the solution became blue—the colour of nitro-nitroso-compounds—and again colourless towards the end of the reduction. The time required to complete reduction was always considerably greater than for alkaline solution. These results indicate that the reduction in acid solution is expressed by eqn. (4).

[3] Meyer, *Annalen*, 1875, **175**, 120.

TABLE 3.

Effect of mercury-column height on limiting current of 2,2-dinitropropane.

		40	50	60	70
At pH2	h (cm.)	40	50	60	70
	$i_l(\mu A)$	6·45	7·15	7·80	8·40
	$i_l h^{-\frac{1}{2}}$	1·020	1·011	1·007	1·004
In 0·1N-NaOH	$i_l(\mu A)$	4·20	4·70	5·15	5·55
	$i_l h^{-\frac{1}{2}}$	0·664	0·665	0·665	0·663

Controlled-potential Electrolysis at a Potential beyond the Second Wave in Acid Solution.—
2,2-Dinitropropane consumed about ten electrons per molecule in electrolysis at pH 2
at —1·15 v (see Table 4).

The reduction mixture, when made alkaline and distilled, gave ammonia and with
sufficient boiling sulphuric acid reduced Fe^{3+} to Fe^{2+}; however, it gave only a slight
precipitate with 2,4-dinitrophenylhydrazine. Nitrous acid is reduced under these
conditions to a mixture of hydroxylamine and ammonia in an approximately 4·6-electron
process. There are therefore two reduction processes to be discussed: (*a*) the nitrous
acid produced by the first step is reduced before it reacts with 2-nitropropane so that
2-nitro-2-nitrosopropane is not produced [eqn. (5)], and (*b*) 2-nitro-2-nitrosopropane is
produced by reaction between 2-nitropropane, nitrite, and hydrogen ion, as shown in
eqn. (4), and this is reduced first to acetoxime and nitrous acid and then to hydroxylamine
and ammonia [eqn. (6)].

Calculations for eqns. (5) and (6) give 10·6 and 8·6 electrons per molecule of 2,2-di-
nitropropane respectively,* since acetoxime was proved experimentally not to be reduced
at this potential. Though the amounts of final products, 2-hydroxyaminopropane,
acetoxime, hydroxylamine, and ammonia, could not be estimated accurately, rough
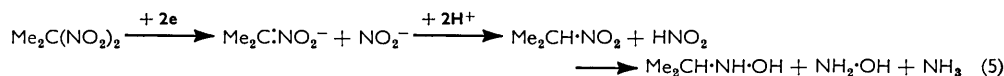
TABLE 4.

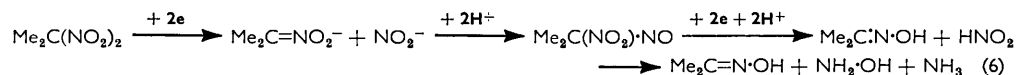Reduction of 2,2-dinitropropane at —1.15 v at pH 2.

Taken (mg.)	39·0	40·3	44·7
Coulombs, reqd. Found	280	294	332
n, found	9·98	10·14	10·31

calculation † for the actual reduction show that only a quarter of the original compound is
reduced according to eqn. (6), whilst the very low yield of acetoxime indicates that the
larger part is reduced according to eqn. (5).

Interpretation of Polarograms in Acid Solutions.—Stock has stated that the increased
height of the first wave in acid solution is due to either the reduction of un-ionized *aci*-
form or the catalytic discharge of hydrogen ions, and that the second wave is due to the

$$Me_2C(NO_2)_2 \xrightarrow{+\ 2e} Me_2C{:}NO_2^- + NO_2^- \xrightarrow{+\ 2H^+} Me_2CH{\cdot}NO_2 + HNO_2$$
$$\longrightarrow Me_2CH{\cdot}NH{\cdot}OH + NH_2{\cdot}OH + NH_3 \quad (5)$$

reduction of nitrous acid to nitrogen, requiring 3-electrons. However, the results of
our controlled-potential electrolysis lead to a different interpretation. They indicate
that the first wave includes a 2-electron reduction of 2,2-dinitropropane to the *aci*-nitro-
propane and nitrite ion which form the nitro-nitroso-compound, some of which is also
reduced. This is why the height of the first wave in acid solution is much greater than
that in alkaline solution (see Table 1). Also the second wave cannot be attributed to a

$$Me_2C(NO_2)_2 \xrightarrow{+\ 2e} Me_2C{=}NO_2^- + NO_2^- \xrightarrow{+\ 2H^+} Me_2C(NO_2){\cdot}NO \xrightarrow{+\ 2e\ +\ 2H^+} Me_2C{:}N{\cdot}OH + HNO_2$$
$$\longrightarrow Me_2C{=}N{\cdot}OH + NH_2{\cdot}OH + NH_3 \quad (6)$$

* 10·6 e = 2 e (2,2-dinitropropane $\longrightarrow$ 2-nitropropane $+NO_2^-$) + 4 e (2-nitropropane $\longrightarrow$ 2-
hydroxyaminopropane) +4·6 e (experimental value for $HNO_2 \longrightarrow NH_2{\cdot}OH + NH_3$):
   8·6 e = 2 e (2,2-dinitropropane $\longrightarrow$ 2-nitropropane $+NO_2^-$) + 2 e (2-nitro-2-nitrosopropane
$\longrightarrow$ acetoxime) +4·6 e (experimental value for $HNO_2 \longrightarrow NH_2{\cdot}OH + NH_3$).
   † From the eqn. $10{\cdot}6a + 8{\cdot}6(1 - a) = 10{\cdot}1$, we obtain $a = 0{\cdot}75$, where a is the proportion following
eqn. (5), and 10·1 is the mean value derived from Table 4.

simple reduction of nitrous acid to nitrogen, but is due to a combination of reductions of (*a*) nitrous acid to hydroxylamine and ammonia, (*b*) nitro-nitroso-compound formed from the *aci*-form of 2-nitropropane, nitrous acid and protons, and (*c*) nitro-form of 2-nitro-propane transformed from its *aci*-form. The rates of formation of nitro-nitroso-compound and of transformation of *aci*-form to nitro-form are rather slow; therefore the diffusion of products into solution from the surface of the electrode makes the height of the second wave smaller than would be expected from consideration of electron consumption, about 10, as measured in controlled-potential electrolysis in which all reducible substances are reduced.

EXPERIMENTAL

Apparatus.—Current–voltage curves were obtained with Yanagimoto type PEL-3 and GR-3 galvarecorder in a constant-temperature bath at 25° ($\pm 0.1°$). The capillary characteristics were $m = 0.937$ mg. sec.$^{-1}$, $t = 3.68$ sec., $m^{\frac{2}{3}} t^{\frac{1}{6}} = 1.194$. The macro-electrolyses were carried out by using a Yanagimoto potentiostat type VE, model 3. The electrolysis cell used was of Lingane–Jones type, with a mercury cathode surface of about 50 cm.^{2} The total quantity of electricity passed was measured by graphical integration of the plots of current against time.

Reagents.—2,2-Dinitropropane was prepared by chromic acid oxidation [4] of 2-nitro-2-nitrosopropane, which was prepared from 2-nitropropane and sodium nitrite. After purification by distillation it had b. p. 70°/10 mm., m. p. 53°.

Buffer solutions used for polarographic analysis were of Britton–Robinson type containing 0.1M-potassium chloride as additional supporting electrolyte. pH values were measured by a Toa Dempa glass electrode pH meter HM-5.

Oxygen was removed by a stream of nitrogen.

Reduction of 2,2-Dinitropropane in 0.1N-*Sodium Hydroxide.*—The compound (400 mg.) was reduced at -0.75 v in a mixture of 0.1N-sodium hydroxide (360 ml.), potassium chloride (1.5 g.), and ethanol (40 ml.). The electrolysed solution was acidified with dilute hydrochloric acid and extracted with ether, and the extract dried (Na_2SO_4). Evaporation gave a residue which was washed with cold ether to give 2-nitro-2-nitrosopropane, m. p. 76° (decomp. in sealed tube) (Found: C, 30.9; H, 5.4. Calc. for $C_3H_6N_2O_3$: C, 30.5; H, 5.1%).
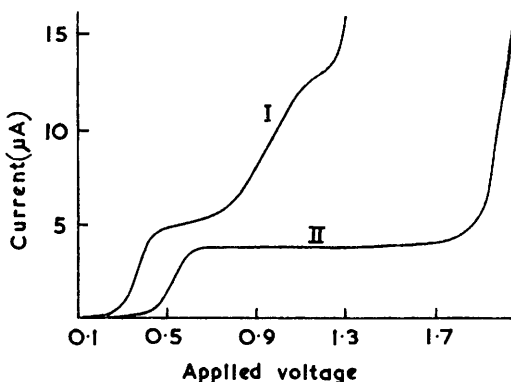
Polarograms of 10^{-3}M-2,2-dinitropropane.

Curve I, pH 2.0; curve II, pH 12.0.

Reduction of 2,2-Dinitropropane at pH 2.—(*a*) This compound (200 mg.) was reduced at -0.55 v in a mixture of 0.1M-phosphoric acid (270 ml.), adjusted to pH 2 with sodium hydroxide, potassium chloride (1.1 g.), and ethanol (30 ml.). Products from two runs were combined and neutralized with 10% sodium hydroxide. Ethanol was distilled off and the residue was extracted with ether after being saturated with sodium chloride. Removal of ether and storage of the residue in a vacuum desiccator overnight gave acetoxime, m. p. 60° (2,4-dinitrophenyl-hydrazone, m. p. 128°).

(*b*) The compound (40 mg.) was reduced at -1.15 v as described above, but nitrogen was introduced on the surface of the solution to prevent loss of nitrous acid from the solution.

Reduction of Nitrous acid in a Solution at pH 2.—Sodium nitrite (23.5 mg.) was reduced

4 Born, *Ber.*, 1896, **29**, 93.

as described in (*b*) above. From the reduction mixture hydroxylamine (64%) was evaluated potentiometrically by use of ferric iron and potassium dichromate, and ammonia (33%) was determined by titration.

SCHOOL OF PHARMACY, UNIVERSITY OF OSAKA, JAPAN.