912. *The Polarography of 2 : 2-Dinitropropane.*

By JOHN T. STOCK.

The polarography of 2 : 2-dinitropropane in buffered solutions of constant ionic strength, covering the approximate pH range 1—12, and in 0·1M-sodium hydroxide, has been examined. In alkaline solutions, a well-defined single wave of constant height and of half-wave potential independent of pH is obtained. This reduction wave is attributed to the formation of nitrite and the anion of the *aci*-form of 2-nitropropane. A poorly-defined second wave obtained in acid solutions appears to be due to the reduction of nitrous acid.

ALTHOUGH the polarography of aliphatic mononitro-compounds has received considerable attention [1,2,3] the polarographic behaviour of aliphatic dinitro-compounds has been reported by Radin and DeVries only.[4] These workers examined 1 : 3-dinitropropane, 2 : 2-dinitropropane, 1 : 5-dinitropentane, and 2 : 2-dimethyl-1 : 3-dinitropropane, but restricted their observations to five non-aqueous supporting electrolytes containing lithium chloride. We now report the polarography of 2 : 2-dinitropropane in aqueous buffer solutions of constant ionic strength, covering the approximate pH range 1—12, and in 0·1M-sodium hydroxide (pH ~13). As is clear from Radin and DeVries's results, 2 : 2-dinitropropane gives a much smaller limiting current at a given concentration than the other compounds they examined.

EXPERIMENTAL

Apparatus.—Current–voltage curves were obtained with a Leeds and Northrup Type E Electrochemograph, operated without damping. Data for wave-analysis and determination of half-wave potentials were obtained by manual operation, voltage measurements being checked by a dial-type potentiometer.

The polarographic cell was a 100 ml. tall beaker closed by a rubber stopper bored for the dropping mercury electrode, junction vessel, gas inlet and exit tubes, and microburette. The 12 mm. diameter junction vessel was closed at the lower end with a fine-porosity fritted glass disc and contained 0·5M-potassium chloride to match the level of the cell contents. All potentials were corrected for iR drop and referred to a large saturated calomel electrode, which was connected to the liquid in the junction vessel by an agar-saturated potassium chloride salt bridge. Cell and reference electrode were maintained at 25° ± 0·2°. On open circuit in deoxygenated 0·1M-potassium chloride at 25° the characteristics of the dropping mercury electrodes were (*A*) $m = 1{\cdot}613$ mg. sec.$^{-1}$; $t = 3{\cdot}68$ sec.; (*B*) $m = 1{\cdot}995$ mg. sec.$^{-1}$; $t = 3{\cdot}20$ sec. Most of the work was done with electrode (*B*), numerous checks being made with electrode (*A*).

Absorptiometric measurements were made with 1 cm. cells. in a Beckman model B spectrophotometer.

Reagents.—2 : 2-Dinitropropane (Commercial Solvents Corp.), recrystallised from methanol and maintained just above the m. p. for 1 hr. under vacuum, had m. p. (uncorr.) 53·5°. The material was used as an 0·100M-stock solution in 80% aldehyde-free ethanol.

Acetoxime [5] and 2-nitro-2-nitrosopropane [6] were used as 0·1M-solutions, the former in 80% ethanol and the latter in ether.

Buffer solutions were adjusted to an ionic strength of approximately 0·5 by addition of

[1] DeVries and Ivett, *Ind. Eng. Chem. Anal.*, 1941, **13**, 339; Scott, *J. Ind. Hyg. Toxicol.*, 1943, **25**, 20; Wilson and Hutchinson, *Analyst*, 1947, **72**, 432; Miller, Arnold, and Astle, *J. Amer. Chem. Soc.*, 1948, **70**, 3971; Seagers and Elving, *J. Amer. Chem. Soc.*, 1950, **72**, 3241, 5183; 1951, **73**, 947; DeVries and Bruss, *J. Electrochem. Soc.*, 1953, **100**, 445; Miquel and Condylis, *Bull. Soc. chim. France*, 1955, 236.
[2] Petru, *Coll. Czech. Chem. Comm.*, 1947, **12**, 620.
[3] Stewart and Bonner, *Analyt. Chem.*, 1950, **22**, 793.
[4] Radin and DeVries, *ibid.*, 1952, **24**, 971.
[5] Mann and Saunders, " Practical Organic Chemistry," Longmans, Green and Co., Ltd., London, 1938, 2nd edn., p. 56.
[6] Hammick and Lister, *J.*, 1937, 489.

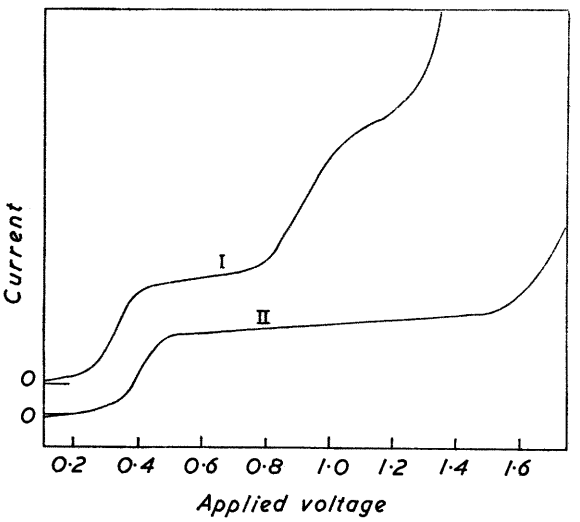
potassium chloride and checked polarographically for absence of reducible impurities. Active constituents were: up to pH 2, hydrochloric acid; [7] pH 2·2—7·8, disodium hydrogen phosphate and citric acid; [8] pH 8—10, boric acid and sodium hydroxide; pH ~11, hydrochloric acid and sodium carbonate; pH ~12, disodium hydrogen phosphate and sodium hydroxide.[7] pH values were measured by a glass electrode calibrated over the pH range 2—12.

Deoxygenation.—Oxygen was removed from a 50 ml. portion of the appropriate buffer by a stream of nitrogen, which was first bubbled through a smaller portion of the same buffer. The desired volume (<1 ml.) of the sample solution was then introduced and deoxygenation continued for a further 5 min. The change in pH caused by this procedure was negligible.

Results and Discussion

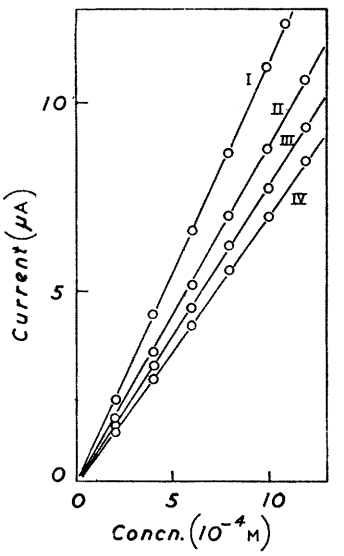
In all solutions 2 : 2-dinitropropane gave a well-defined wave without maxima and reaching full development in the region of −0·5 v (Fig. 1). In acid solution a poorly-defined second wave is also visible, but merges into the decomposition wave of the buffer

Fig. 1. *Polarograms of* 2 × 10^{-4}M-2 : 2-*dinitropropane with electrode A.*



Curve I, pH 2·17; II, pH 6·97.
On the vertical axis, 1 in. corresponds to 3μA.

Fig. 2. *Limiting current–concentration relations.*



Curve I, pH 1·88; II, pH 2·49; III, 3·97; IV, pH 10·18.

solution and thus exhibits no distinct region of limiting current. Since the heights of both waves increase linearly with the square-root of the pressure of mercury at the dropping electrode, they represent diffusion-controlled processes.

Measured at a fixed potential of −0·55 v, the height of the first wave in all solutions increased linearly with the concentration of 2 : 2-dinitropropane (Fig. 2). In acid conditions, however, the height of this wave for a given nitropropane concentration and given capillary characteristics depends markedly on the pH of the solution (curve I, Fig. 3). In alkaline buffers, the wave height becomes virtually independent of pH. Routine determination of 2 : 2-dinitropropane by measurement of the height of the first wave is thus best carried out in alkaline solution. Concentrations in the approximate range 10^{-5}—10^{-3}M are then directly measurable. At a given pH, borate buffers give wave heights a few per cent. greater, and half-wave potentials a few millivolts more negative. than those obtained in phosphate or carbonate buffers.

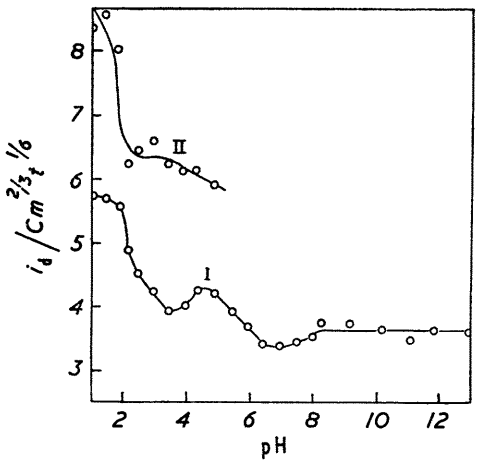
[7] Britton, " Hydrogen Ions," D. van Nostrand Co., New York, 1932, Ch. XII.
[8] Elving, Markowitz, and Rosenthal, *Analyt. Chem.*, 1956, **28**, 1179.

Although accurate measurement is not possible, the height of the second wave for a given concentration appears to be approximately constant, except in strongly acid conditions (curve II, Fig. 3). In the approximate range pH 2—3, the total height of both waves increases linearly with the concentration of 2 : 2-dinitropropane, provided that measurement is made at an appropriately-chosen potential (*e.g.*, −1·15 v at pH 2·2).

Although almost constant in alkaline buffers, the half-wave potential ($E_{\frac{1}{2}}$) of the first wave is somewhat pH-dependent in acid solution (curve I, Fig. 4), but the relation is non-linear. The half-wave potential of the second wave is very sensitive to pH (curve II, Fig. 4).

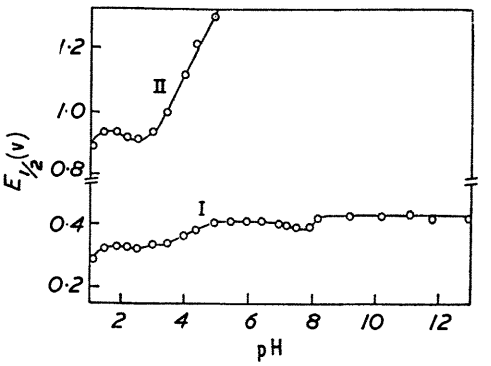
The waves of mononitroparaffins appear at potentials more negative than that required for the full development of the first wave of 2 : 2-dinitropropane. It is thus possible to determine 2 : 2-dinitropropane in the presence of much larger concentrations of mononitroparaffins, as well as in the presence of non-reducible inorganic salts, etc. For example,

FIG. 3. *Diffusion current constant–*pH *relations.*



Curve I, first wave; II, second wave.

FIG. 4. *Half-wave potential–*pH *relations.*



Curve I, first wave; II, second wave.

a few micrograms may be determined to within 5% in the presence of a 100-fold excess of 2-nitropropane.

Although 2 : 2-dinitropropane is polarographically reduced more readily than the lower aliphatic mononitro-compounds, the reduction stage corresponding to the first wave is less complete than that of a mononitro-compound. Thus, at pH 7, the wave height of 2 : 2-dinitropropane is approximately half that of a fresh solution of 2-nitropropane of similar concentration. Since Petru [2] has shown that the principal wave of nitroparaffins involves 4 electrons, the polarographic reduction of 2 : 2-dinitropropane in neutral or alkaline media presumably involves the uptake of 2 electrons. This conclusion is borne out by application of the Ilkovič equation $i_d = 607nD^{\frac{1}{2}}Cm^{2/3}t^{1/6}$ where the terms have their usual significance.[9] Assuming that the 2 : 2-dinitropropane molecule and the 2-nitropropionate ion have the same diffusion coefficient D, we can estimate the latter from the relation $D = 2{\cdot}67 \times 10^{-7}\ \lambda^\circ/z$, where λ° is the equivalent conductance of the ion at infinite dilution and z is its charge.[10] For the 2-nitropropionate ion, λ° is 32 ohm^{-1} equiv.$^{-1}$,[11] giving $D = 0{\cdot}85 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ at 25°. This leads to $n = 2{\cdot}02 \pm 0{\cdot}08$ for the approximately constant wave height in alkaline solutions.

[9] Kolthoff and Lingane, " Polarography," Interscience Publishers, Inc., New York, 2nd edn., Vol. I, p. 63.

[10] *Idem, op. cit.*, p. 52.

[11] " International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, pp. 259 and 264.

That the reduction of 2 : 2-dinitropropane in alkaline solution involves the uptake of two electrons per molecule was confirmed by coulometric electrolysis [12] in 50 ml. of previously-deoxygenated 0·1M-sodium hydroxide. The stirred mercury-pool cathode was maintained at $-0{\cdot}85 \pm 0{\cdot}03$ v and a coulometer similar to that of Lingane and Small [13] was used. Results are summarised in Table 1.

Since the half-wave potential in the alkaline region is almost independent of pH, it

TABLE 1. *Reduction of 2 : 2-dinitropropane in 0·1M-sodium hydroxide.*

2 : 2-Dinitropropane taken (mmoles) ...	0·05	0·10	0·15	0·20	0·25
Coulombs reqd. Found and (calc.) ...	10·0 (9·7)	19·4 (19·3)	29·7 (29·0)	38·9 (38·6)	48·2 (48·3)
Nitrite found (mmoles)	0·05	0·09	0·16	0·20	0·24
Relative " acetone " reaction	0·5	1·0 *	1·2	2·2	2·5

* Arbitrarily assigned unit intensity.

is unlikely that hydrogen ions are directly involved in the electrode process. It is possible that the reduction product is 2-nitro-2-nitrosopropane, formed according to

$$Me_2C\begin{matrix}NO_2\\NO_2\end{matrix} + H_2O + 2e^- \longrightarrow Me_2C\begin{matrix}NO\\NO_2\end{matrix} + 2OH^- \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Pearson and Evans [14] inferred that such substances are formed during the electrolysis of nitroparaffins between platinum electrodes, and Bahner [15] has shown that, in alkaline solution, 2-nitropropane gives rise to some 2 : 2-dinitropropane at a platinum anode. In a pH 12 buffer, the polarographic reduction of 2-nitro-2-nitrosopropane commenced at a potential of approximately zero and the wave height decreased with time. In acid buffers the much more stable wave height increased linearly with the concentration of 2-nitro-2-nitrosopropane. This easily-reduced compound is therefore not the product sought.

Another stoicheiometric possibility is

$$Me_2C(NO_2)_2 + 2e^- \longrightarrow Me_2C{:}NO^- + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this connection, acetoxime gave no reduction wave in any of the buffers and, in alkaline solutions of sodium salts, nitrate is not polarographically reducible.[16] Further, acetoxime (or its anion) is stable in alkaline solution. However, aliquot portions of the coulometric solutions gave no reaction for nitrate [17a] but yielded strong and reproducible positive results in the 1-naphthylamine–sulphanilic acid test for nitrite.[17b] Determined absorptiometrically by this test, the yield of nitrite was one mole per mole of 2 : 2-dinitropropane taken [Table 1, rows (i) and (iii)]. Blanks containing unreduced 2 : 2-dinitropropane or acetoxime gave negligible results. Presumably the electrode reaction is of the form:

$$Me_2C(NO_2)_2 + 2e^- \longrightarrow [Me_2C{\cdot}NO_2]^- + NO_2^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

After acidification with hydrochloric acid, portions of the coulometric solutions containing the reduction products gave no immediate reaction with 2 : 4-dinitrophenylhydrazine; a slight turbidity on standing suggested the formation of a carbonyl compound. Aliquot parts of the coulometric solutions were therefore diluted to 5 ml. with water, and 5 ml. of 50% v/v sulphuric acid were added to each. Each mixture was gently heated for 5 min., then 3 ml. were distilled off and collected at a rate of 0·2 to 0·3 ml. per min. The distillates all gave a positive acetone reaction with alkaline salicylaldehyde.[18,19]

[12] Lingane, " Electroanalytical Chemistry," Interscience Publishers, Inc. New York, 1953, p. 368.
[13] *Idem, op. cit.*, p. 353.
[14] Pearson and Evans, *Trans. Amer. Electrochem. Soc.*, 1943, **84**, 173.
[15] Bahner, *Ind. Eng. Chem.*, 1952, **44**, 317.
[16] Kolthoff and Lingane, *op. cit.*, p. 533.
[17] " Standard Methods for the Examination of Water, Sewage, and Industrial Wastes," American Public Health Association, Inc., New York, 1955, (*a*) p. 149; (*b*) p. 153.
[18] Csonka, *J. Biol. Chem.*, 1916, **26**, 209.
[19] Thomson, *J. Soc. Chem. Ind.*, 1946, **65**, 121.

Absorptiometric comparison showed that the intensity of the reaction was approximately proportional to the amount of 2 : 2-dinitropropane initially present [Table 1, rows (i) and (iv)]. Other aliquot parts similarly distilled formed immediate precipitates with 2 : 4-dinitrophenylhydrazine. Paper chromatography [20,21] showed that the precipitates were mixtures of the 2 : 4-dinitrophenylhydrazones of acetone and acetaldehyde. The acetone derivative was separately eluted and confirmed by mixed m. p.

The production of acetone suggests that the anion $[Me_2C{:}NO_2]^-$ is that of the *aci*-form of 2-nitropropane.[22] Support for this conclusion was obtained by dissolving 2-nitropropane in 0·1M-sodium hydroxide, then distilling portions of the solution with sulphuric acid. The distillates behaved similarly to those obtained from the coulometric solutions. Petru [2] has shown that, in alkaline buffers, the wave heights of nitroparaffins diminish with time, and attributes this to the conversion of the molecular form into the anion of the *aci*-form, which is not polarographically reducible.

In acid solutions, the minimum at about pH 4 in the wave height–pH curve (Fig. 3, curve I) suggests that competing reductions may be involved. However, the half-wave potential–pH curve (Fig. 4, curve I) does not support this. Further, a linear plot of $\log i/(i_d - i)$ against potential [23] was obtained for all the solutions examined, the slope being almost independent of pH (Table 2). Since the polarographic reduction of 2 : 2-dinitropropane, like that of other nitro-compounds,[2] is probably irreversible, no significance is attached to the magnitude of the slope. Reduction of the un-ionised *aci*-form $Me_2C{:}NO_2H$ or catalytic discharge of hydrogen ions may account for the increased wave height in acid solutions. Since the half-wave potential of 2-nitropropane is given by $-E_{\frac{1}{2}} = 0{\cdot}658 + 0{\cdot}037\text{pH}$,[3] the increased wave height cannot be attributed to reduction of this substance formed by rearrangement of the *aci*-form.

TABLE 2. *Analysis of first wave of* 2 : 2-*dinitropropane* ($c = 2 \times 10^{-4}$M).

pH	1·48	3·44	5·44	6·40	11·80
Reciprocal of slope	0·065	0·062	0·066	0·068	0·069

In the region pH 2·5—5, the height of the second wave is about that required for a 3-electron reduction and the half-wave potential of about −1·0 v changes by approximately 0·20 v per pH unit. This suggests that the second wave is due to the reduction of nitrous acid, for which Keilin and Otvos [24] give

$$HNO_2 + 3H^+ + 3e^- \longrightarrow \tfrac{1}{2}N_2 + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

According to them, the wave occurs at about −1·0 v. The increased height in strongly acid solution may be due to the superimposition upon the nitrous acid wave of waves due either to the reduction of the *aci*- or the nitro-form of 2-nitropropane or intermediate reduction products, or to the catalytic discharge of hydrogen ions.

The author thanks Dr. M. E. Morgan for the chromatographic separation and identification of the 2 : 4-dinitrophenylhydrazones, and acknowledges support by the U.S. Navy Department. Bureau of Ordnance. The 2 : 2-dinitropropane was a gift from the Commercial Solvents Corporation.

CHEMISTRY DEPARTMENT, UNIVERSITY OF CONNECTICUT,
STORRS, CONNECTICUT, U.S.A. [*Received, May 10th*, 1957.]

[20] Jackson and Morgan, *J. Dairy Science*, 1954, **37**, 1316.
[21] Morgan and Anderson *ibid.*, 1956, **39**, 253.
[22] Johnson and Degering, *J. Org. Chem.*, 1943, **8**, 10.
[23] Kolthoff and Lingane, *op. cit.*, p. 193.
[24] Keilin and Otvos, *J. Amer. Chem. Soc.*, 1946, **68**, 2665.