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Electrochemical Reduction of Tertiary Nitroalkanes to Amines[1)]

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Electrochemical reduction of tertiary nitroalkanes, 2-substituted-1,1-dimethyl-1-nitroethanes (**1**), was investigated in aqueous buffer solutions. In polarography, **1** with a phenyl group and/or a hydroxyl group at the 2-position showed an ill-defined wave in the weakly acidic and neutral pH region at relatively high negative potentials, in addition to a well-defined wave arising from the reduction of **1** to the corresponding hydroxylamine (**2**). Controlled potential electrolysis of **1** at the potential of the former wave gave the 1,1-dimethylethylamines (**3**) as well as the hydroxylamines **2**. The amines **3** are formed exclusively from **2**, probably *via* the O-protonated form. It is suggested that a phenyl group at the 2-position facilitates the reduction of **2** to **3** by enhancing the adsorption of **2** at the mercury cathode and that a hydroxyl group, while it interferes with the adsorption, assists the reduction by intramolecular hydrogen-bonding to stabilize the O-protonated form of **2**.

Keywords——tertiary nitroalkane; alkylhydroxylamine; electrochemical reduction; polarography; controlled potential electrolysis

Electrochemical reduction of primary and secondary nitroalkanes in aqueous buffer solutions has been suggested to proceed by the mechanism shown in Chart 1,[2)] which is based on the results of controlled potential electrolysis and, with the support of other investigators,[3,4)] has superseded the earlier proposal[5)] that the amine is formed exclusively through the hydroxylamine. In the process II to III, an additional pathway to the amine (V) *via* the iminium ion intermediate (VII) (Chart 2) has also been proposed, mainly because the

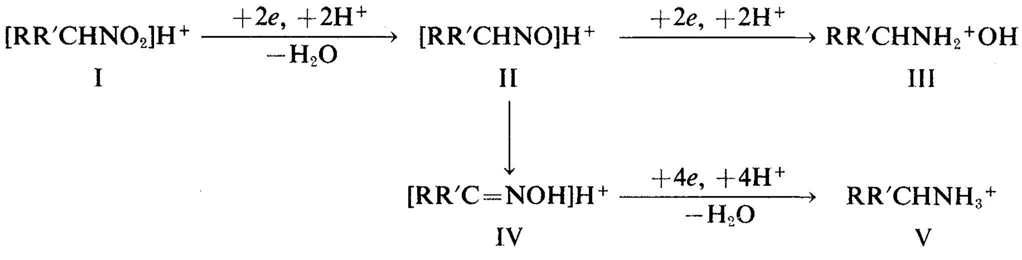


Chart 1

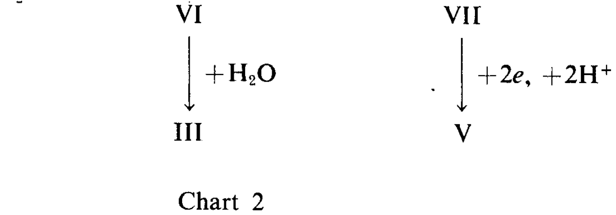


Chart 2

yield of V at a constant pH increased with increasing cathode potential.[2a] The hydroxylamine (III) was not reduced further to the amine (V) under the experimental conditions used.[2a,3] This finding led to the conclusion that tertiary nitroalkanes are not electrochemically reduced to amines, since the corresponding nitroso intermediates (*cf.* II in Chart 1) cannot afford the oxime (IV) and/or the imine (VII) intermediates.[2,6] Although a small amount of *tert*-butylamine ($<3\%$) was produced in the reduction of *tert*-nitrobutane[3,7] and tris-(hydroxymethyl)aminomethane was prepared by constant current electrolysis of the corresponding nitromethane in acid solution,[8] the reduction processes do not seem to have been elucidated in detail. On the other hand, *N*-alkylhydroxylamines have been shown to give ill-defined polarographic reduction waves at considerably negative potentials in weakly acid to neutral solutions.[9,10] Heyrovsky and Vařička[10] ascribed these waves to two parallel electrode processes, reduction of the substrate to the amine and catalytic hydrogen evolution, but this conclusion has not been verified by product identification. Thus, some uncertainty remains as to the possibility that hydroxylamines participate in the reduction of nitroalkanes to amines in addition to the other suggested intermediates (IV and VII).

This paper reports the results of polarography and controlled potential electrolysis of 2-substituted-1,1-dimethyl-1-nitroethanes (**1**) in aqueous buffer solutions. On electrolysis of **1a**—**c**, the amines (**3**) as well as the hydroxylamines (**2**) were produced. The reduction process and the effects of the substituents, R^1 and R^2, on the process are discussed. Tertiary nitroalkanes are suitable substrates to examine whether or not the possibility described above is realized.

$R^1R^2CHCMe_2NO_2$	$R^1R^2CHCMe_2NHOH$	$R^1R^2CHCMe_2NH_2$
1	**2**	**3**

	R^1	R^2
a	Ph	H
b	Ph	OH
c	H	OH
d	C_6H_4CN-*p*	OH
e	C_6H_4OMe-*p*	OH
f	Ph	OAc
g	Bu^{tert}	H

Chart 3

Results

Polarography

In Fig. 1 the diffusion current and the half-wave potential are plotted against pH for the nitroethanes **1a**—**c**, **f**, and **g**. The curves for **1d** and **e** are not shown because they are almost superimposable on those for **1b**. The results for **1c** agree well with those reported previously:[11] the decrease in current in alkaline solutions has been attributed to the decomposition of the *β*-hydroxynitroethane in a retroaldol-type reaction. In the case of **1b**, **d**, and **e**,[12] a diminution of the primary wave (1st wave) began at lower pH regions and was accompanied by the appearance of an additional wave (2nd wave) at more negative potentials. For **1b**, the half-wave potential of the 2nd wave coincided with that of benzaldehyde,[13] and formation of the aldehyde under the conditions of the polarographic measurements was confirmed by ultraviolet (UV) spectroscopy and liquid chromatography.

Figure 2 shows a typical polarogram of **1a** at pH 5.48. In addition to the 1st wave described above, a shoulder-like ill-defined wave (extra wave) is discernible. The extra wave, which disappeared on addition of a small amount of gelatine (see Fig. 2), was observed

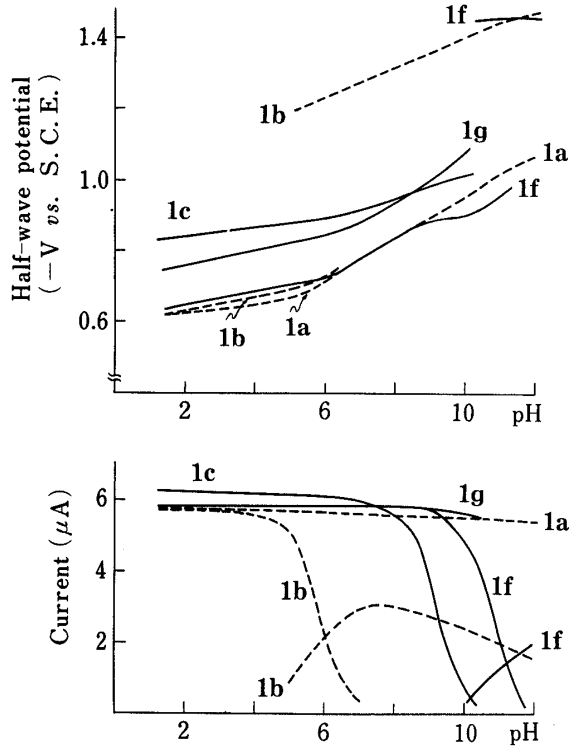


Fig. 1. Half-Wave Potential—pH and Current— pH Curves for **1**

In Britton–Robinson buffer containing 0.1 M KCl and 10% (v/v) ethanol at 30 °C. Concentration of the substrate: **1a**, 0.51; **1b**, 0.50; **1c**, 0.49; **1f**, 0.52; **1g**, 0.51 mM.

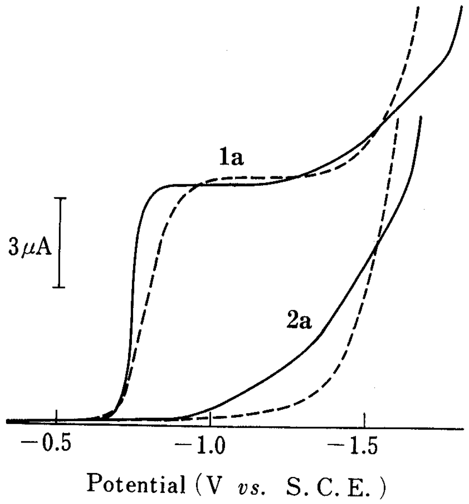


Fig. 2. Polarograms of **1a** (0.58 mM) and **2a** (1.26 mM) at pH 5.48

In Britton–Robinson buffer containing 0.1 M KCl and 10% (v/v) ethanol at 30 °C. Broken lines were obtained in the presence of 0.01% gelatine.

between pH 3 and 6. Similar results were obtained with **1b**, **c**, and **d**, though the pH ranges over which the extra wave appeared were somewhat different from compound to compound. For **1e**, the wave was masked by the reduction of *p*-methoxybenzaldehyde formed by decomposition of the substrate. From the results reported on the polarographic behavior of alkylhydroxylamines[9,10] and from the fact that the nitroethanes **1** are reduced to the corresponding hydroxylamines **2** at the 1st wave (see below), the extra wave can be considered to result from the reduction of **2**. Under the experimental conditions used, the hydroxylamine **2a** showed an ill-defined polarographic wave which also disappeared on addition of gelatine (Fig. 2).[14]

Controlled Potential Electrolysis

Controlled potential electrolysis in acidic and weakly acidic solutions was carried out with the nitroethanes **1a**—**c**, which gave the polarographic extra wave. Typical results obtained at ambient temperatures are summarized in Table I.

Electrolysis of **1** at pH 1.8 and at a potential just below that for hydrogen evolution (−1.15—−1.20 V) consumed about 4 F per mol of the substrate and gave the hydroxylamine **2** as the main product (runs 1—3). On electrolysis at pH 4.2 and at the potential region of the polarographic extra wave, the amines **3** were produced (runs 5—7), while electrolysis at the plateau of the 1st wave gave **2** as the sole product (run 4). Below pH 2, the extra wave can be considered to be masked by the reduction of hydronium ion, so the results of electrolysis at pH 4.2 (see also run 24) suggest that the amine **3** will be formed at pH 1.8 when the electrolysis is performed at a high cathodic potential behind the background current. This was found to be the case (runs 8 and 9). In this case the possibility that a hydrogen molecule or hydrogen atom formed at the electrode acts as the reducing agent can be ruled out. When **1a** in the same

TABLE I. Results of Controlled Potential Electrolysis[a] of **1**

No.	Compound (amount/mmol)	pH	$-Ec$[b]	F/mol[c]	Yield (%) of **2**	Yield (%) of **3**	Remarks[d]
1	**1a** (1.05)	1.8	1.20	4.4	90	None	A
2	**1b** (0.60)	1.8	1.15	4.3	84	None	A
3	**1c** (0.23)	1.8	1.20	4.0	95	None	A
4	**1a** (0.60)	4.2	1.30	4.4	98	None	A
5	**1a** (0.61)	4.2	1.65	7.1	28	62	A
6	**1b** (1.00)	4.2	1.65	6.3	None	75	A
7	**1c** (0.23)	4.2	1.65	5.5	64	25	A
8	**1a** (0.69)	1.8	1.65	—	None	79	B
9	**1b** (0.61)	1.8	1.65	—	7	69	B
10	**1a** (0.50)	4.2	1.65	5.4	43	40	A, G 0.01%
11	**1a** (0.58)	4.2	1.65	4.5	62	14	A, G 0.05%
12	**1b** (0.58)	4.2	1.65	6.7	34	43	A, G 0.01%
13	**1b** (0.58)	4.2	1.65	5.5	54	17	A, G 0.03%
14	**1a** (0.58)	4.2	1.65	—	72	None	B, Pt cathode
15	**1a** (0.50)	4.2	1.65	4.9	80	5	B, GC[e] cathode
16	**1a** (1.18)	4.2	1.65	—	73	None	B, Ti cathode
17	**1a** (1.18)	4.2	1.65	—	70	10	B, Ni cathode
18	**1a** (0.63)	4.2	1.65	—	39	31	B, Pb cathode
19	**1a** (1.18)	4.2	1.65	—	37	37	B, Cu cathode
20	**1a** (0.63)	4.2	1.65	—	20	40	B, Zn cathode
21	**1a** (0.59)	4.0	1.45	4.2	92	3	C
22	**1a** (0.59)	4.0	1.45	5.0	41	38	C
23	**1a** (0.59)	4.0	1.45	5.6	9	65	C
24	**1a** (0.59)	4.0	1.35	5.6	85	10	C
25	**1a** (0.59)	4.0	1.65	5.6	Trace	87	C

a) Electrolysis conditions, see Experimental.
b) *Ec*, cathode potential (V *vs.* S.C.E.).
c) Amount of electricity consumed.
d) Unless othewise specified, Hg was used as the cathode. A, the electrolysis was discontinued when the current had decreased close to the background value; B, when the nitroethane **1** disappeared in the solution; C, when the indicated amount of electricity (the 5th column) had been consumed. G, in the presence of the indicated amount of gelatine.
e) Glassy carbon.

medium was electrolyzed at a platinum electrode at 1.20 V, vigorous hydrogen evolution was observed, but formation of **3a** was not detected.

The effects of other factors such as added gelatine, cathode materials, total amount of electricity, and electrode potential on the product distribution were examined. The yield of the amines **3** decreased with the amount of gelatine (runs 10—13) in accordance with the polarographic results (Fig. 2). The effectiveness of cathode materials for the formation of **3** was $\mathrm{Hg}>\mathrm{Zn}\gtrsim\mathrm{Cu}\gtrsim\mathrm{Pb}>\mathrm{Ni}>$ glassy carbon $\gtrsim$ Pt and Ti (runs 5 and 14—20), which is essentially the same order as that reported in the reduction of nitrocyclohexane, a secondary nitroalkane, to cyclohexylamine in strong acid solution.[15] The results obtained by varying the amount of electricity consumed (runs 21—23) strongly suggest that the amine **3** is formed *via* the hydroxylamine **2**. However, the yield of **3** was dependent on the cathode potential even at a constant amount of electricity (runs 23—25), indicating that the process producing the polarographic extra wave is not a simple reaction.

From the results of electrolysis of **1a** and **b** at pH 4.2 (runs 5 and 6), it can be seen that the hydroxy group of **1b** has some favorable effects on the amine formation. This point became clearer on electrolysis of the nitroethanes and the corresponding hydroxylamines (**2a** and **b**) under more strictly controlled conditions as shown in Table II. Typical current–time curves

Table II. Results of Controlled Potential Electrolysis[a] of **1** and **2**

No.	Compound (amount/mmol)	pH	F/mol[b]	Time/h[c]	Yield (%) of **2**	**3**
26	**1a** (0.25)	4.0	4.0	1.1	90	4
27	**1a** (0.25)	4.0	6.0	3.6	10	70
28	**2a** (0.25)	4.0	2.0	2.6	30[d]	57
29	**1b** (0.25)	4.0	4.0	0.8	74	Trace
30	**1b** (0.25)	4.0	6.0	2.0	21	78
31	**2b** (0.25)	4.0	2.0	1.4	18[d]	75
32	**2a** (0.25)	6.7	2.0	6.1	70[d]	26
33	**2b** (0.25)	6.7	2.0	3.4	45[d]	39

[a] The electrolysis was carried out at a cathode potential of −1.55 V *vs.* S.C.E., at 30 °C, with the same electrolysis cell: the amount of Hg used for the cathode was 3.0 ml.

[b] The electrolysis was discontinued when the indicated amount of electricity had been consumed.

[c] Time required to consume the electricity given in the 4th column.

[d] Amount of the starting material recovered.

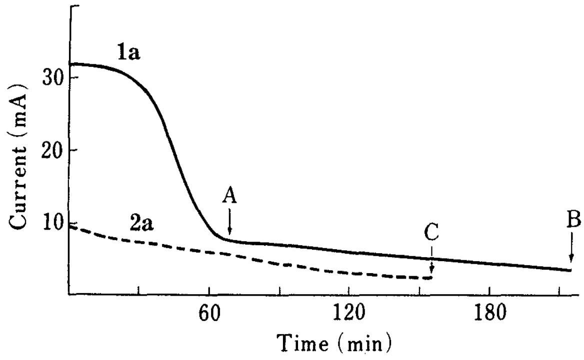


Fig. 3. Current–Time Curves in the Controlled Potential Electrolysis of **1a** (Run 27 in Table II) and **2a** (Run 28)

Arrows A, B, and C represent the points at which 4.0, 6.0, and 2.0 F per mol of the substrate have been consumed, respectively.

observed under the defined conditions are illustrated in Fig. 3. The hydroxy group apparently accelerates the process **2** to **3** (runs 27, 28, and 30—33), while its effect on the process **1** to **2** seems to be small (runs 26 and 29).

Discussion

The results of controlled potential electrolysis indicate that the polarographic 1st wave of the tertiary nitroethanes **1** corresponds simply to reduction of the substrates to the hydroxylamines **2** (see runs 1—4), and that reduction to the amines **3** takes place only in the potential region of the extra wave and proceeds almost exclusively *via* the hydroxylamines, at least in macro-scale electrolysis.

In the polarographic reduction of *N*-alkylhydroxylamines, the N-protonated substrate was assumed to undergo electron transfer.[10] Then, since the hydroxylamines **2** will be fully protonated[16] below pH 5 and the protonation is considered to occur at the nitrogen atom, reduction of **2** in weakly acidic solutions is expected to give a diffusion-controlled two-electron polarographic wave. If the process is accompanied by catalytic hydrogen evolution,[10] the wave will be enhanced further. However, the observed extra wave in the polarography of **1** is ill-defined and very small as compared to the 1st wave, and **2** did not show a clear reduction wave below pH 6,[14] indicating that in the reduction of **2** one or more chemical reactions to form an electroactive species must precede the electron transfer. The pathway shown in Chart 4 seems to be compatible with the results obtained in the present

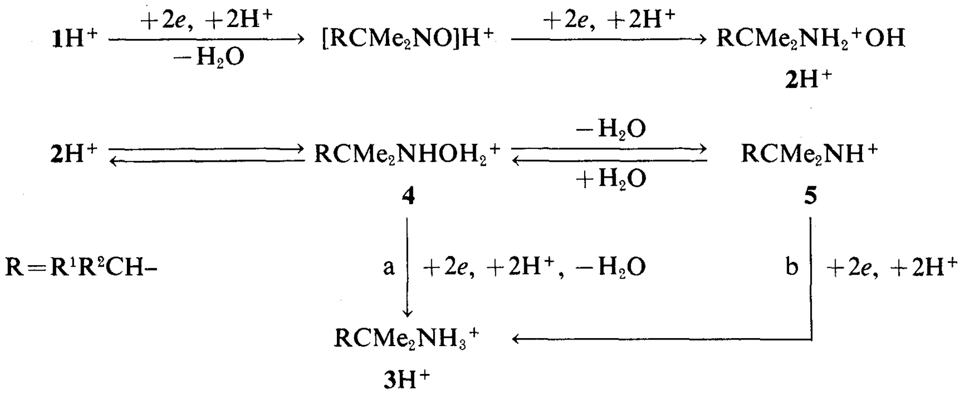


Chart 4

study.

Since an O-protonated hydroxylamine is much less stable than its N-protonated counterpart,[17] the equilibrium between **4** and **2**H^+ will lie far to the left, and the reduction of **4** will give an ill-defined kinetic current in polarography and a drawn-out current–time curve (Fig. 3) in the controlled potential electrolysis. An intermediate nitrenium ion such as **5** has been suggested in the reduction of *p*-hydroxylaminoisobutylbenzene to the corresponding amine.[18] However, paths a and b in Chart 4 are not sharply differentiated because the latter can be considered as a limiting case of the former as to the timing of expulsion of the water molecule.

The effects of cathode potential on the product distribution (Table I, runs 23—25) suggest that at least one more electrode reaction is occurring in parallel with the process **2** to **3** in the potential region of the extra wave. Although we have no unambiguous evidence, hydrogen evolution catalyzed by the protonated hydroxylamine **2**H^+ and/or **4** seems plausible.[10] The yields of the amine **3** at various electrodes (Table I, runs 5 and 14—20) can be correlated with the hydrogen overvoltage of the electrode materials. As seen in the results of electrolysis at pH 1.8 (runs 8 and 9), concurrent hydrogen evolution from hydronium ion and/or buffer acid has little effect on the amine formation. Thus, the lower yield of **3** at an electrode with lower hydrogen overvoltage can be ascribed to the consumption of the protonated hydroxylamine by the catalytic process in preference to its reduction to the amine.

When the cathodic behavior of **1a**—**c** and **g** is compared, it can be seen that phenyl and hydroxyl groups on the carbon β to the nitro group facilitate the reduction of **2** to **3**. Compound **1g**, which lacks both groups, did not show the extra wave in polarography, the yield of **3c** is apparently lower than that of **3b** (Table I, runs 6 and 7),[19] and the formation of **3b** from **2b** is faster than that of **3a** from **2a** (Table II). The electrocapillary curves of hydroxylamines **2a**—**c** (Fig. 4) suggest that the phenyl group enhances the adsorption of the protonated hydroxylamine at the mercury surface[20] while the hydroxyl group interferes with it. The lifetime of **4** and/or **5** (Chart 4) must be very short, and hence these species will be reduced to the amine **3** only when they are formed at the electrode surface. It is expected that a strongly adsorbed hydroxylamine will have a good chance of being reduced and that a surface-active substance will inhibit the amine formation (see Table I, runs 5—7 and 10—13).

The hydroxyl group, though it interferes with the adsorption, can assist the amine formation as illustrated in Chart 5. The interaction (A) represents a stabilization of the O-protonated hydroxylamine **4b** by six-membered ring intramolecular hydrogen-bonding. Similar hydrogen-bonding in the N-protonated form **2b**H^+ requires an unstable eclipsed conformation (B). Consequently, the equilibrium concentration of the electroactive form of the hydroxylamine will be increased. Hydrogen-bonding such as (C) raises the possibility of

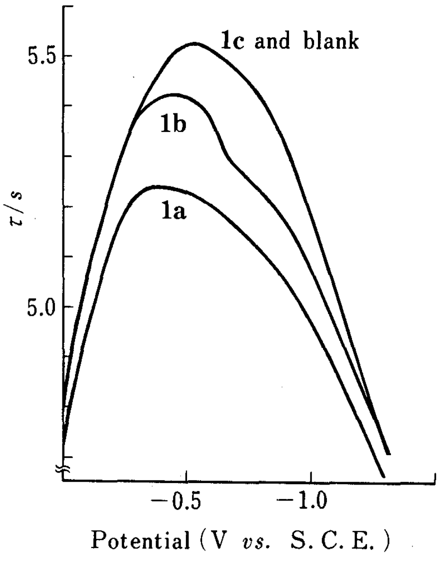
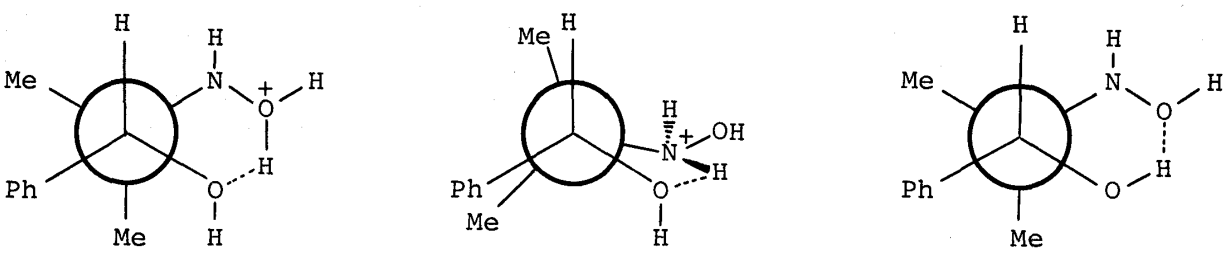


Fig. 4. Electrocapillary Curves for **1a**—**c** at pH 4.40

In 0.2 M citrate buffer containing 0.1 M KCl and 40% (v/v) ethanol at 30 °C. Concentration of the substrates, 8.2 mM.



A B C

Chart 5

intramolecular general acid-catalyzed electron transfer to the unprotonated and/or the N-protonated hydroxylamine. However, while similar assistance can also be considered in the reduction of the parent nitroethane **1** to **2**, the effect of the hydroxy group seems to be small (Table II, runs 26 and 29; see also the half-wave potentials of **1a** and **b** in Fig. 1) as observed in the case of β-hydroxynitrobutanes.[11,21] The intramolecular hydrogen-bonding between nitro and hydroxyl groups in β-hydroxynitroalkanes has been proved to be weak.[22]

In conclusion, an alkylhydroxylamine can be an intermediate in the electrochemical reduction of a nitroalkane to the corresponding amine in addition to the other suggested intermediates,[1-3] and any factor which enhances the adsorption of the hydroxylamine at the electrode surface or increases the stability of the O-protonated form of the hydroxylamine is expected to increase the contribution of the pathway *via* the hydroxylamine.

Experimental

Materials——The nitroethanes **1** were prepared by known methods (**1a**, ref. 23; **1b**, **d**, and **e**, ref. 24; **1c**, ref. 25; **1g**, ref. 26; **1f**, by acetylation of **1b** with acetic anhydride and pyridine), and gave the expected analytical and spectroscopic results (**1b** and **d**—**f** are racemates). Chemicals used for preparing buffer solutions were of reagent grade and were used without further purification. For the electrochemical experiments, ethanol was distilled from 2,4-dinitrophenylhydrazine and deionized water was used throughout.

Polarography——Polarograms were obtained with a Yokogawa type POL-11 polarograph essentially as described previously.[1] The capillary constant of the dropping mercury cathode was $m^{2/3}t^{1/6} = 1.584\,\mathrm{mg}^{2/3}\,\mathrm{s}^{-1/2}$ in 0.1 M KCl at open circuit. Britton–Robinson buffer solutions containing 10% (v/v) ethanol and 0.1 M KCl were used as the basic media.

Controlled Potential Electrolysis——The electrolysis was carried out with a Hokuto Denko HA-101 potentiostat/galvanostat connected with a Hokuto Denko HF-102 coulometer and a Toa-Dempa EPR-2TB electronic recorder. An H-type electrolysis cell was used: the cathode compartment was separated with an agar plug and a sintered glass disk. In the electrolysis at a cathode other than mercury, a plate (*ca.* 3 x 5 cm) of the particular material was employed as the electrode. The buffer systems used for the catholyte were: pH 1.8, 0.2 M phosphate; pH 4.0—4.5, 0.2 M citrate; pH 6.0—7.0, 0.2 M phosphate. All solutions contained 0.1 M KCl as an additional supporting electrolyte. The anolyte was a saturated solution of Na_2SO_4. A typical electrolysis procedure is as follows. A weighed amount of the nitroethane **1** was added, with 20 ml of ethanol, to a pre-electrolyzed mixture of 60 ml of the buffer solution and 20 ml of ethanol, and the solution was electrolyzed at a set cathode potential. The electrolysis was discontinued when (A) the current diminished to the background value, (B) the nitroethane **1** disappeared in the electrolysis solution, or (C) a pre-determined amount of electricity had been consumed, depending upon the electrolysis conditions (see Tables I and II). During the electrolysis (including the pre-electrolysis) a stream of nitrogen was bubbled through the catholyte. When necessary, the electrolysis was interrupted and the pH of the solution—measured with a pre-equipped glass electrode—was readjusted with hydrochloric acid.

Identification and Determination of Products——The ethanol in the electrolysis solution was removed under reduced pressure. When the hydroxylamines **2a**—**c** were the main products, the resulting solution was neutralized with $NaHCO_3$ and extracted with ether. After being dried with Na_2SO_4, the extract was evaporated under reduced pressure and the residue was identified by comparison with authentic samples.27) In the case of the amines **3a**—**c**, the aqueous phase from the ether extraction described above was made alkaline with NaOH and extracted with ether. The extract was treated similarly to give the amines, which were identified by comparison with authentic samples.23,24,28) Determination of the products was performed in the above ether extracts. Compounds **2a**, **2b**, **3a**, and **3b** were determined by gas liquid chromatography (GLC) after being derivatized with trifluoroacetic anhydride.29) The hydroxylamine **2c** was treated with formaldehyde30) and the resulting nitrone was determined by UV spectroscopy. The amine **3c** was determined as the corresponding 1-dimethylaminonaphthalene-5-sulfonamide.31)

References and Notes

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12) In the case of **1f**, the decrease of the 1st wave in basic media is due to the hydrolysis of the ester, as observed in the polarography of 2-nitro-1-butyl acetate (ref. 21), followed by the retroaldol-type reaction.
13) Another product of the reaction is 2-nitropropane, which should give a polarographic reduction wave in the potential range covered. However, the immediate product of the reaction will be the anion of 2-nitropropane, and the absence of such a polarographic wave suggests that the product is converted to the unionized form of aci-nitropropane which is polarographically inactive [ref. 11 and E. W. Miller, A. P. Arnold, and M. J. Astle, *J. Am. Chem. Soc.*, **70**, 3971 (1948)].
14) A freshly prepared sample of the hydroxylamine was used for the measurements. No well-defined wave, as reported for methylhydroxylamine (ref. 5), was obtained. However, two well-defined waves gradually developed when the solution was allowed to stand in contact with air. These waves are similar to those reported for the autoxidation products of alkylhydroxylamines [D. H. Johnson, M. A. T. Rogers, and G. Trappe, *J. Chem. Soc.*, **1956**, 1093]. Above pH 8 the waves appeared clearly even when the measurement was performed within 10 min after preparation of the sample solutions.

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