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CONTROLLED POTENTIAL ELECTROLYSIS[1]—XI

THE REDUCTION OF ETHYL α-NITROISOBUTYRATE AND THE FORMATION OF TRI(2-ETHOXY-CARBONYL-2-PROPYL) HYDROXYLAMINE

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Abstract—Ethyl α-nitroisobutyrate has a four-electron polarographic reduction wave in acid solution, and ethyl hydroxyaminoisobutyrate was confirmed as the reduction product. This may be explained in terms of scheme (2) analogous to scheme (1) proposed for the esters of α-nitrocarboxylic acid with a α-hydrogen. In alkaline solution, the ester has two waves and a similar four-electron reduction product was confirmed at the potential on the second wave, while nitrite ion, *tri(2-ethoxycarbonyl-2-propyl)hydroxylamine*, ethyl isobutyrate and ethyl α-nitrosoisobutyrate were the reduction products of the first wave. Scheme (3) is proposed as a mechanism for the latter reduction.

In order to account for the difference between the two nitro-indolyl-esters[2] in electrochemical reduction, the esters of α-nitrocarboxylic acids containing an α-hydrogen[1a] were investigated and a new reduction mechanism as shown in scheme (1) proposed. In the present work, the electrochemical reduction of ethyl α-nitroisobutyrate having no α-hydrogen, proves that the mechanism proposed is applicable. The α-hydrogen, therefore, plays a decisive role in the electrochemical reduction of an aliphatic nitro group, and determines whether the product is an hydroxylamine or amine. The formation of *tri(2-ethoxycarbonyl-2-propyl)hydroxylamine*, together with its identification and properties were investigated and α-nitroisobutyramide was used as a complementary substance because of its slow rate of hydrolysis.[3]

RESULTS

Polarography. The polarographic behaviour of the ester differs from that of the four esters previously described.[1a] In Fig. 1. the values obtained at 6 min after preparation of the sample solution were used. The ester shows one reduction wave of almost constant wave height at pH 2 $\sim$ 7. The diffusion current constant at pH 2 was only about 80% of the total wave height for ethyl α-nitro-n-valerate. Above pH 7, the first wave decreases its wave height, whereas the second increases in height, but the total wave height does not change significantly until pH 10 is reached. Beyond pH 10, however, the polarographic wave height of the two waves decrease with time more rapidly as is shown in Fig. 1, and above pH 12 no measurement could be taken. The

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[1a] Part X, M. Masui, H. Sayo and K. Kishi, *Chem. Pharm. Bull., Tokyo* **12**, 1397 (1964); [b] A part of this paper was presented at the *10th Symposium on Polarography in Nagoya*, Japan, November (1963).

[2] M. Masui and C. Yijima, *J. Chem. Soc.* 1101 (1963).

[3] M. Masui, H. Sayo and K. Kishi, unpublished data.

kinetic study on the rate of the decrease of the wave height in the alkaline region will be reported later. Since no aci-nitro form is possible for the present ester this can not account for the change of wave heights in the alkaline region. These must, therefore, be due to other factors, such as hydrolysis of the ester or fission of the tertiary nitro group.[4,5] The relation between the limiting current and the mercury column height (Table 1) shows that the waves at pH 2 and 6 and the total wave at pH 8 are diffusion controlled, but the two waves at pH 8 are not.

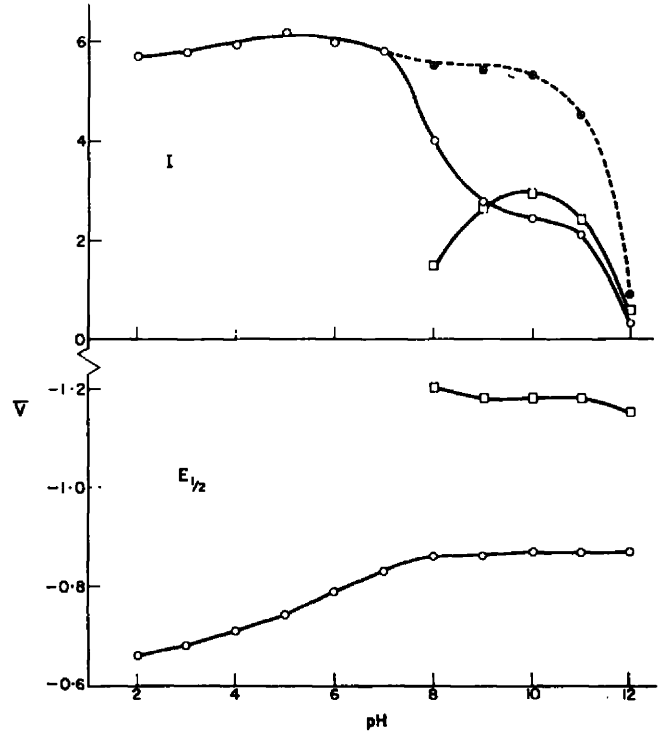

Fig. 1. Relation of $E_{1/2}$ and I for Ethyl α-nitroisobutyrate 5×10^{-4} M soln. containing 5% ethanol and 0·005% gelatin (measured at six minutes after preparing sample solution) ○, first wave; □, second wave; ⊕, sum of the two.

The proportionality of the wave height to concentration (Fig. 2) was found to be linear at a concentration less than 4×10^{-3} M for the first wave at pH 2 and the total wave at pH 8, but not linear for either wave at pH 8 below 3×10^{-3} M.

The polarographic behaviour of α-nitroisobutyramide is shown in Fig. 3. Though there is a close resemblance to that of the ester at pH 2 ~ 10, no significant decrease is observed in the wave heights of the first and second wave of the amide even above pH 10. This is because the rate of the decrease in the wave height of the amide in the alkaline region is very slow compared to that for the ester,[3] and in six minutes very little change is observed.

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[4] W. J. Seagers and P. J. Elving, *J. Amer. Chem. Soc.* 72, 3241 (1950).

[5] H. Kleinfeller, *Ber. Dtsch. Chem. Ges.* 62, 1582 (1929).

TABLE 1. EFFECT OF MERCURY-COLUMN HEIGHT (h, IN CM) ON LIMITING CURRENT (i, IN μA) OF ETHYL α-NITROISOBUTYRATE (10^{-3} M 10% ETHANOL AND 0·005% GELATIN)

	h	40	50	60	70
pH 2·0	i	6·85	7·65	8·40	8·95
	$ih^{-1/2}$	1·083	1·082	1·084	1·070
pH 6·0	i	6·90	7·70	8·40	9·05
	$ih^{-1/2}$	1·091	1·089	1·084	1·082
pH 8·0	i_1	4·30	5·00	5·55	6·10
	$i_1h^{-1/2}$	0·680	0·707	0·716	0·729
	i_2	2·20	2·30	2·45	2·55
	$i_2h^{-1/2}$	0·348	0·325	0·316	0·305
	$(i_1 + i_2)h^{-1/2}$	1·028	1·032	1·032	1·034

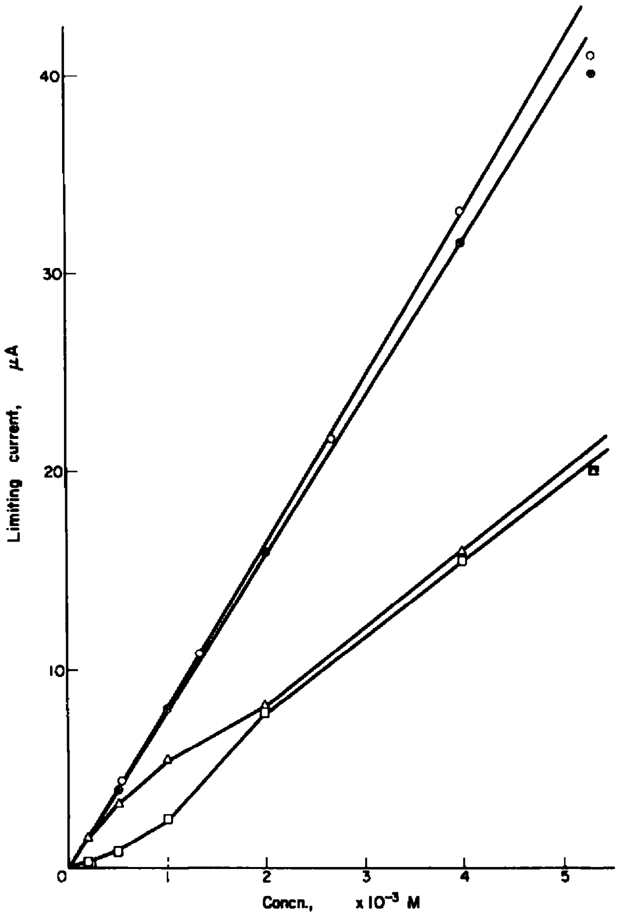

FIG. 2. Limiting current-concentration relations of ethyl α-nitroisobutyrate ○, at pH 2·0; △, first wave at pH 8·0; □, second wave at pH 8·0; ⊕, sum of the two at pH 8·0.

Controlled potential electrolysis. The results are summarized in Table 2. The electrolysis at the potentials on the plateau of the first wave and at pH 2 ~ 6 showed a four-electron reduction (n = 4) coulometrically and produced ethyl α-hydroxyaminoisobutyrate. Similar results were obtained at the potentials corresponding to the second wave plateau and pH 8. At the potential on the first wave plateau and pH 8, the coulometric n value was two. During this electrolysis not only the first wave but also the second wave decreased its wave height with time, leaving only a small wave at the end. In this instance, about 0·6 mole equivalent of nitrite ion was detected in the solution by Griess reaction.[6] When the same reduction was carried out on a solution more concentrated than 5 × 10^{-3} M, the solution became cloudy in the course of the electrolysis and finally yielded an oil, which crystallized at room temperature, and analysed for the molecular formula $C_{18}H_{33}O_7N$. The yield was about 32% of the theoretical value based on the assumption that three molecules of the original ester would produce one molecule of $C_{18}H_{33}O_7N$. From the aqueous layer after the filtration of the oil and acidification of the filtrate, a small amount of crystalline ethyl α-nitrosoisobutyrate was isolated by extraction with ether, but because of the small amount and the negligible degree of the absorption of the nitroso derivative, λ_{max} 289 mμ ($\varepsilon = 1900$) of the solution, even immediately after the electrolysis, the nitroso derivative

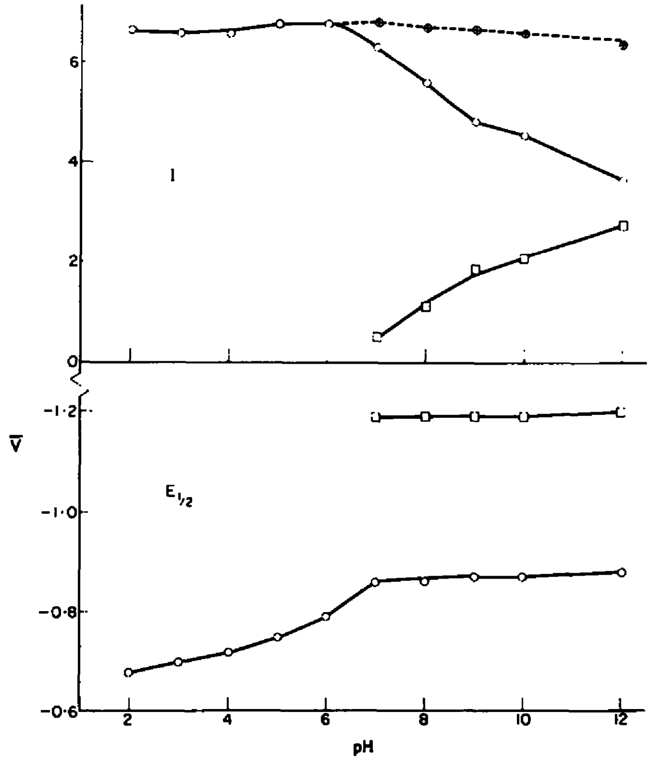

FIG. 3. Relation of $E_{1/2}$ and I for α-nitroisobutyramide 6 × 10^{-4} M soln. containing 5% ethanol and 0·005% gelatin ○, first wave; □, second wave; ⊕, sum of the two.

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[6] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis* (3rd Edition) Vol. II; p. 804. Van Nostrand, New York (1954).

TABLE 2. CONTROLLED POTENTIAL ELECTROLYSIS OF ETHYL α-NITROISOBUTYRATE

pH	Sample (taken, mg)	Applied potential v. *vs* S.C.E.	Coulombs reqd. Found	n Found	Products identified
2·0	200·7	−1·10	476	3·96	Ethyl α-hydroxyaminoisobutyrate[a]
2·0	200·8	−1·15	499	4·15	Ethyl α-hydroxyaminoisobutyrate[a]
4·0	42·4	−1·00	103	4·06	Ethyl α-hydroxyaminoisobutyrate[a]
6·0	97·7	−1·00	227	3·90	Ethyl α-hydroxyaminoisobutyrate[a]
6·0	166·8	−1·20	410	4·14	Ethyl α-hydroxyaminoisobutyrate[a]
8·0	122·1	−1·50	278	3·80	Ethyl α-hydroxyaminoisobutyrate[a]
8·0	99·7	−1·60	245	4·10	Ethyl α-hydroxyaminoisobutyrate[a]
8·0	98·9	−1·00	113	1·91	NO_2^- 0·625eq.,[b] $C_{18}H_{33}O_7N$,[a] (Ethyl α-nitrosoisobutyrate[a])
8·0	365·4	−1·00	423	1·94	NO_2^- 0·594eq.,[b] $C_{18}H_{33}O_7N$,[a] (Ethyl α-nitrosoisobutyrate[a])

Each samples were dissolved in 200 ml buffer solution containing 10% EtOH.

[a] Isolated from the electrolysed solutions. Parenthesis means minor products.

[b] Detected quantitatively from the electrolysed solutions.

was not regarded as the main product. The electrolysed solution had the odour of an ester and yielded ethyl isobutyrate as a by-product. These final products can be attributed to the high reactivity under the conditions of the primary reduction product in the electrolysis. Similar results were obtained for α-nitroisobutyramide.

Chemical and physical properties and controlled potential electrolysis of $C_{18}H_{33}O_7N$. These unidentified crystals (m.p. 43°) obtained from the electrolysis at −1·0 v. and pH 8 could be distilled at 97° (0·1 mm Hg) without decomposition. They were practically insoluble in water, dilute acids and alkalis but very soluble in most organic solvents.

The presence of an ester group was clearly visible in the IR spectrum. In the investigation on the hydrogen bonding of methanolic O—H (0·01 M) to the compound (0·015 M) in carbon tetrachloride, the free O—H stretching frequency showed two shifts, $\Delta\nu = 87$ and 212 cm^{-1}. The former seems to be due to the hydrogen bonding to the ester oxygen, because the value 212 cm^{-1} seems too high to be ascribed to the hydrogen bonding to such weakly basic oxygen as that of the ester group.[7] The compound was reducible polarographically in acidic media containing 20% of ethanol and 0·003% of Triton X-100; the half wave potentials were −0·80 v. (in 1 N–HCl), −0·91 v. (in 0·1 N–HCl), −1·09 v. (at pH 2), −1·17 v. (at pH 3) and −1·25 v. (at pH 4). In the preparative controlled potential electrolysis of the compound at −1·05 v. in 0·1 N–HCl, *di(2-ethoxycarbonyl-2-propyl)amine* and ethyl α-hydroxyisobutyrate were isolated as the products of a two-electron reduction. As to the structure of the compound, (A) and (B) may be proposed on the assumption that it was formed from three nitroso intermediates with two of their NO groups missing.

$$\underset{(A)}{(Me_2C{\cdot}CO_2C_2H_5)_3N^+{-}O^-} \qquad \underset{(B)}{(Me_2C{\cdot}CO_2C_2H_5)_2N{\cdot}O{\cdot}(Me_2C{\cdot}CO_2C_2H_5)}$$

(A) is a N-oxide and (B) is a hydroxylamine derivative. IR spectra of the compound did not give any definite clue to identification, as there are several strong bands near the region where N-oxides develop characteristic strong absorptions.

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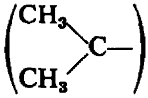
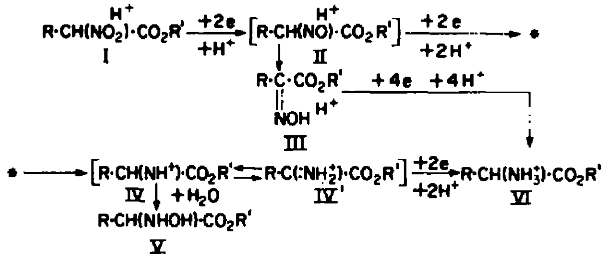
[7] E. D. Becker, *Spectrochimica Acta* 17, 436 (1961).

Some N-oxides have been reported to be converted to trialkylhydroxylamines when heated in aqueous sodium hydroxide solution,[8] but under the present conditions this conversion is not likely to occur. N-oxides, in general, show stronger basicity than trialkylhydroxylamines and are soluble in mineral acids but not in organic solvents. The $\Delta\nu_{O-H}$ for the hydrogen bonding between methanolic O—H and pyridine N-oxide has been reported to be 285 cm^{-1}.[9] N-oxides and trialkylhydroxylamines, reduced chemically to tertiary amines,[10] and a mixture of secondary amines and alcohols[8] respectively. The NMR spectrum of the compound in carbon tetrachloride referenced to tetramethylsilane as an internal standard gave two quartets (J = 7·2 c/s.) at τ = 5·96 and 6·00 (—CH$_2$—), two singlets at τ = 8·51 and 8·57  $\left(\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!\!>C—\right)$, and a triplet (J = 7·1) at τ = 8·71 (CH$_3$—); these and the integrated intensity of the peaks favour the structure (B).

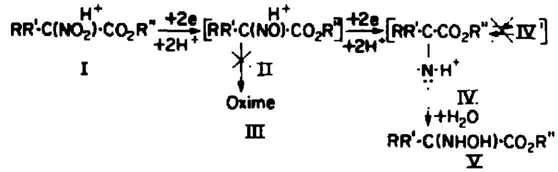
Tri(2-ethoxycarbonyl-2-propyl)hydroxylamine prepared from ethyl azobisisobutyrate and nitric oxide according to the method used for the preparation of tri(2-cyano-2-propyl)hydroxylamine[11] was identical with the above compound as shown by analysis, mixed m.p., and IR spectrum.

DISCUSSION

Scheme (1) proposed for the electrochemical reduction of the esters of α-nitrocarboxylic acids containing an α-hydrogen, assumed the presence of an imidonium ion intermediate (IV) or an imido intermediate[12] and a very rapid IV $\rightleftarrows$ IV′ instead of the dehydration accepted for some phenylhydroxylamine intermediates in the reduction of aromatic nitro or nitroso compounds.[13] The scheme (2) shows that the same mechanism as scheme (1) is applicable to ethyl α-nitroisobutyrate in both acid and neutral media.



(1)



(2)

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[8] R. F. Kleinschmidt and A. C. Cope, *J. Amer. Chem. Soc.* **66**, 1929 (1944).

[9] H. Shindo, *Chem. Pharm. Bull., Tokyo* **7**, 791 (1959).

[10] E. Ochiai, M. Ishikawa and S. Katada, *Yakugaku Zasshi* **63**, 307 (1944).

[11] B. Gingras and W. A. Waters, *J. Chem. Soc.* 1920 (1954).

[12] R. A. Abramovitch and B. A. Davis, *Chem. Rev.* **64**, 149 (1964).

[13] D. Stocesova, *Coll. Czech. Chem. Comm.* **14**, 615 (1949); L. Holleck and R. Shindler, *Z. Elektrochem.* **60**, 1138 (1956).

In the case of ethyl α-nitroisobutyrate, the nitroso derivative (II) produced by a first two-electron reduction can not be converted to an oxime (III) because it contains no α-hydrogen, and hence II is further reduced to an imido intermediate (IV) at the potential; for the same reason, since IV can not take an imino form; it reacts with water to yield an hydroxyamino derivative (V), which no longer can be reduced at the mercury electrode and, therefore, no amine is produced. The many examples reported in the literature show that for aliphatic and aromatic nitro compounds the presence of an α-hydrogen or the formation of a C=N double bond between α-carbon and nitro-nitrogen, are essential in the electrochemical reduction of a nitro group to amine. These facts suggest the presence of an easily reducible imino form (IV′). One or more double bonds conjugated with the imino bond would render the reduction to amine easier. We now believe this to be important in the electrochemical reduction of nitro compounds.

In the alkaline region the results are more complicated. The reduction at a potential on the crest of the first wave seems to produce unstable primary intermediates which rapidly produce various compounds as secondary products. If the electrode process proposed for the nitro reduction in acidic or neutral media[14] is also applicable in alkaline solution, the scheme may be

$$\mathrm{RNO_2} \xrightarrow{+e} \mathrm{RNO_2}^{\dot{-}} \xrightarrow{+e} \mathrm{RNO_2}^{2-} \xrightarrow{+H_2O} \mathrm{RNO} + 2\mathrm{OH}^-$$

$$\mathrm{RNO} \xrightarrow[+H_2O]{+2e} \mathrm{RNHOH}$$

Therefore a product from a two-electron reduction at the first wave should be a nitroso derivative. Chemically synthesized ethyl α-nitrosoisobutyrate dimerizes rapidly and only the dimer is isolated. This dimer is stable at room temperature even in alkaline solution, being dissociated partially to the monomer at 70 ∼ 80° to develop a blue colour which is stable for 1 ∼ 2 hr, but is rapidly decomposed above 90°. Since if ethyl α-nitrosoisobutyrate is formed it is stable, the decomposition of a part of the reduction intermediate or product should occur before the stable nitroso derivative is formed. There are two possibilities (i) and (ii):

$$\mathrm{RNO_2}^{\dot{-}} \rightarrow \mathrm{R}\cdot + \mathrm{NO_2}^- \qquad \text{(i)}$$

$$\mathrm{RNO_2}^{2-} \rightarrow \mathrm{R}^- + \mathrm{NO_2}^- \qquad \text{(ii)}$$

where $\mathrm{R} = (\mathrm{CH_3})_2\mathrm{C{\cdot}CO_2C_2H_5}$

In the case of (i) the trialkylhydroxylamine should be formed by a radical reaction, but in (ii) by a ionic reaction. If the trialkylhydroxylamine could be formed through the ionic process, not only R^- and nitroso derivative but also R^+ should be needed; otherwise N,N-dialkylhydroxylamine rather than the trialkylhydroxylamine should be produced. Even if R^+ is produced by a process like $2\mathrm{RNO} \rightarrow 2\mathrm{R}^+ + \mathrm{N_2O_2}^{2-}$, it is not likely that the $\mathrm{R_2NOR}$ is the product of the reaction of R^- and R^+ with RNO in the bulk of the solution. On the other hand, several papers have reported that trialkylhydroxylamines are formed from alkyl radicals and nitrosoalkanes. Gingras and Waters[11] stated that a compound of $\mathrm{C_{12}H_{18}ON_4}$ was formed by a reaction between 2-cyano-2-propyl radical and nitric oxide or α-nitrosoisobutyronitrile, and the compound was considered to be tri(2-cyano-2-propyl)hydroxylamine from the fact that

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[14] M. Suzuki and P. J. Elving, *Coll. Czech. Chem. Comm.* **25**, 3202 (1960).

acetone was produced by the hydrolysis with sulphuric acid. When we attempted to prepare α-nitroisobutyronitrile by the oxidation of α-hydroxyaminoisobutyronitrile with potassium permanganate, we found that colourless crystals (m.p. 80°) were produced when the amount of $KMnO_4$ was insufficient. As the crystals analysed for $C_{12}H_{18}ON_4$ and the IR spectrum had the same absorption peaks as those reported by Gingras and Waters for their compound, both compounds are thought to be identical. The NMR spectrum of the compound (in $CDCl_3$) showed two singlets at $\tau = 8{\cdot}18$ and 8·23, which have an intensity ratio of 2:1, and hence the compound is believed to be a trialkylhydroxylamine as Gingras and Waters suggested. More recently, Hoffman *et al.* have reported the formation of tri-*t*-butylhydroxylamine in the reduction of *t*-nitrobutane with metalic sodium in glyme.[15] The NMR spectrum to the hydroxylamine derivative in carbon tetrachloride showed two singlets of 2:1 relative intensity at $\tau = 8{\cdot}75$ and 8·83, by which its structure was deduced. Further we found that tri(2-ethoxycarbonyl-2-propyl)hydroxylamine was also formed by a reaction between 2-ethoxycarbonyl-2-propyl radical and nitric oxide. From these observations, it would seem a radical process is the more likely as the electrolytic process that produced the trialkylhydroxylamine.

Assuming that the electrolysis reaction includes a radical process, scheme (3) is proposed for the electro-chemical reduction of the ester at a potential on the crest of the first wave in the region where two waves are observed.

$$
\begin{array}{l}
RNO_2 \xrightarrow{+e} [RNO_2^{\cdot -}] \xrightarrow{+e} [RNO_2^{2-}] \xrightarrow{+H_2O} RNO + 2OH^- \\
\qquad\qquad (i) \downarrow (M) \qquad\qquad (ii) \downarrow (N) \\
\qquad\qquad [R\cdot] + NO_2^- \qquad [R^-] + NO_2^- \\
\qquad\qquad\qquad\qquad\qquad\quad \xrightarrow{+H_2O} RH + OH^- \\
2[R\cdot] + RNO \longrightarrow R_2NOR \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3) \\
2RNO \rightleftarrows (RNO)_2 \\
(iii)\ [R\cdot] + H_2O \longrightarrow RH + [\cdot OH] \\
\qquad\qquad\qquad\qquad\qquad\qquad \xrightarrow{+e} OH^- \\
\qquad\qquad\qquad\qquad\qquad\qquad \text{or} \\
\qquad\qquad\qquad\qquad\qquad\qquad \longrightarrow H_2O_2 \xrightarrow{+2e} OH^-
\end{array}
$$

where $R = (CH_3)_2C{\cdot}CO_2C_2H_5$ and [ ] indicates an assumed intermediate which could not be observed experimentally.

The life time of a certain aliphatic nitro anion radical generated electrochemically in aqueous alkaline solution has been reported to be the order of several tenths of a second[16] and that of *t*-nitrobutane anion radical in glyme was found to be 0·66 sec,[15c] so that the anion radical (M) may be considered to be fairly stable under the conditions. If the applied potential is not sufficiently high to make the process (M) → (N) instantaneous, the more stable the radical R· is, the more likely is the process (i). This process is only part of the whole reaction, as (M) can take another electron to yield (N) at the

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[15a] A. K. Hoffmann and A. T. Henderson, *J. Amer. Chem. Soc.* **83**, 4671 (1961); [b] A. K. Hoffmann, W. G. Hodgson and W. H. Jura, *Ibid.* **83**, 4675 (1961); [c] A. K. Hoffmann, W. G. Hodgson, D. L. Maricle and W. H. Jura, *Ibid.* **86**, 631 (1964); [d] A. K. Hoffmann, A. M. Feldman, E. G. Gelblum and W. G. Hodgson, *Ibid.* **86**, 639 (1964).

[16] L. H. Piette, P. Ludwig and R. N. Adams, *J. Amer. Chem. Soc.* **84**, 4212 (1962).

electrode potential, and (N), in turn, reacts with water to give RNO and OH^-. Some of the RNO molecules react with R· at the surface of the electrode to yield R_2NOR and others convert to the stable dimer, $(RNO)_2$. In addition to these reactions, a reaction like (ii) needs be postulated in order to explain the estimated amount of nitrite ion (0·6 mole equivalent). If all of NO_2^- is assumed to result from reaction (i), R· should be 0·6 mole equivalent as well. From the amount of the trialkylhydroxylamine produced, the amount of R· consumed in the production of the trialkylhydroxylamine is calculated to be about 0·33 mole equivalent, accordingly, 0·27 mole equivalent of R· should react with each other and with water. But the fact that we failed to detect the dimerized product, diethyl tetramethylsuccinate suggests that the amount of R· does not exceed the amount needed for the formation of trialkylhydroxylamine. This means that the yield of R_2NOR is controlled by R· rather than RNO, and only the excess of RNO is converted to its dimer. Thus the probability of the reaction (iii) is small. We must, therefore, consider that a part of the nitrite ion and ethyl isobutyrate are produced by another route, and hence reaction (ii) is rationalized. This reaction is not common, and could not be verified experimentally, although it does fit the facts. A reaction between R· and RNO_2^-, as considered by Hoffmann *et al.* is not likely to occur, because under the conditions the concentration of RNO_2^- at the electrode is too low.

It should be noted that the nitroso derivative is not reduced at the potential, but becomes the stable dimer. In general, as the half-wave potential of nitroso derivatives is much more positive than the corresponding nitro derivatives, no nitroso wave is observed in the polarographic reduction of nitro compounds, and the nitroso intermediate is immediately reduced to hydroxylamine derivatives at the potential. The reason why the nitroso derivative is not reduced but changed at once at the potential to its dimer is not known, although the presence of an electronegative substituent, ethoxycarbonyl, at the α-carbon may be an explanation because a similar split in the polarographic wave is observed only with compounds $(CH_3)_2C(NO_2)\cdot X$ where X is $—CO_2R$, $—CONH_2$ or $—C{\equiv}N$, but not if X is CH_3.[17]

In the scheme, only the process giving R· consumed in the reaction with RNO is a one-electron process and the others are ultimately two-electron processes, so that the total electrons consumed per molecule is calculated to be about 1·8,[18] if we can assume the yield of the trialkylhydroxylamine is 33%, which is a reasonable value for the actual yield of 30 ~ 35%. The slightly larger n values, 1·9 ~ 2·0, found by the macro electrolysis are ascribable to the reduction of some of the nitroso derivative, because when the concentration of the nitroso derivative is high, the initial potential of the reduction moves to the more positive region. Under this condition, a trace of a hydroxyamino derivative was detected by a Fehling test at room temperature on the evaporated solution.

The reason why no tri(2-ethoxycarbonyl-2-propyl)hydroxylamine was produced by the electrolysis carried out at the potential on the plateau of the second wave at pH 8 will be clear from the above discussion, that is, because the rates of (M) → (N) and further RNO → RNHOH are very fast at the potential.

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[17] Comparisons for the *t*-nitrocompounds each with an ethoxycarbonyl, cyano and alkyl group at the α-carbon atom will be reported in near future.

[18] $2e \times 0{\cdot}78 + 1e \times 0{\cdot}22 = 1{\cdot}78e$.

In order to confirm the radical process experimentally, the electrolysis was carried out in the presence of methyl methacrylate, acrylonitrile or *p*-aminodimethylaniline which are known to be strong radical traps, but the effect of the radical traps was not found in the yield of the trialkylhydroxylamine. This appears to suggest that the reaction is not through a radical process, but when we think of the unavoidably low concentration (2% by weight) of the radical traps because of their low solubility in the system, we should rather interpret the result as follows: the alkyl radical can exist only at the surface of the mercury electrode reacting with the very active radical trap that is, electrolytically produced RNO, but can not exist long enough to react with the added radical traps in the bulk of the aqueous solution.

EXPERIMENTAL

Materials. Ethyl α-nitroisobutyrate was prepared from ethyl α-bromoisobutyrate and sodium nitrite,[19] b.p. 46 ~ 48° (1 mm), n_D^{20} 1·4200 (lit. 1·4197[19]); ethyl α-nitrosoisobutyrate was prepared from α-hydroxyaminoisobutyrimidoethyl ether dihydrochloride and chlorine gas,[20] m.p. 89° (dec) from ethanol; ethyl α-hydroxyaminoisobutyrate was prepared from α-hydroxyaminoisobutyrimidoethyl ether dihydrochloride,[20] b.p. ca. 80° (5 mm); α-nitroisobutyramide was prepared by acid hydrolysis of α-nitroisobutyronitrile,[20] m.p. 117° (dec) (lit. 117° ~ 118°[20]) from ether; ethyl azobisisobutyrate was prepared by hydrolysis of the imidoether prepared from azobisisobutyronitrile and hydrogen chloride.[21] All compounds synthesized except the last gave correct analysis. Those obtained from commercial sources were of the highest purity available (R. G. etc.), but most of them were examined for their impurity polarographically.

Apparatus. NMR spectra were recorded on a Varian A-60 spectrometer operating at 60 Mc. Tetramethylsilane was used as an internal standard and all chemical shifts are expressed on the τ-scale. For the measurement of $\Delta\nu_{O-H}$ a Nihonbunko DS402G IR spectrophotometer was used. A 10 mm cell was used. The instruments and the buffer solutions used for polarographic study and others were the same as those described in a previous paper.[1a]

Procedure. General procedures for the electrolysis including polarography were the same as those described in a previous paper. Potentials were measured against a saturated calomel electrode.

Macro scale controlled potential electrolysis–Ethyl α-nitroisobutyrate

(i) This ester (200·7 mg) was dissolved in EtOH (20 ml) and added to about 180 ml of pH 2 buffer solution prepared from 0·1 M KCl and 0·1 M H_3PO_4 and NaOH which had previously been electrolysed. Electrolysis at −1·1 v. was continued for 1·5 hr, by which time the current had decreased to its background value. Electricity passed was 476 coulombs (n = 3·96). The electrolysed solution was evaporated to about 40 ml under red. press. Addition of Na_2CO_3 to make the solution weakly alkaline, extraction with ether after saturating the solution with NaCl, evaporation of the ether layer dried with anhydrous Na_2SO_4, and distillation of the residue at 5 mm Hg and 100° (temp of oil bath) gave a colourless liquid, which was identical in IR spectrum with chemically synthesized ethyl α-hydroxyaminoisobutyrate.

(ii) An analogous procedure was used for the other electrolyses except those carried out at pH 8 and −1·00 v. The resultant solution was always acidic when evaporated.

(iii) Electrolysis of this ester (365·4 mg) at −1·0 v. in 200 ml of a pH 8 buffer solution (0·1 M-$Na_2B_4O_7$ + HCl and 0·1 M KCl) containing about 10% EtOH was continued for 2 hr and 10 min, by which time the current had decreased to its background value. Electricity passed was 423 coulombs (n = 1·94). During the electrolysis the solution became cloudy and precipitated on heavy oil at the end of the run. Separation of the oil and distillation at 0·1 mm Hg and 130° (oil bath temp) gave a thick colourless syrup, which crystallized after standing at room temp; m.p. 43°; the same crystals were obtained from the run on much larger scale (1·32 g of this ester) by distillation of the colourless syrup at 0·1 mm Hg and 97°. (Found: C, 57·43; H, 8·71; N, 3·84; mol. wt., 361 (Rast). $C_{18}H_{33}O_7N$

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[19] N. Kornblum, R. K. Blackwood and J. W. Powers, *J. Amer. Chem. Soc.* **79**, 2507 (1957).

[20] O. Piloty and B. G. Schwerin, *Ber. Dtsch. Chem. Ges.* **34**, 1863 (1901).

[21] T. Theil, *Liebigs Ann.* **290**, 1 (1896).

requires: C, 57·58; H, 8·86; N, 3·73%; mol. wt., 375·45.) The IR spectrum (nujol) showed absorption at 1721 (v.s.), 1274 (s.), 1160 (v.s.), 1028 (s.), 959 (m.), 918 (w.), 863 (m.) and 766 (m.) cm^{-1}.

Tri(2-ethoxycarbonyl-2-propyl)hydroxylamine. This compound (360·7 mg) was dissolved in 20 ml EtOH and added to the mixture (140 ml) of 0·1 M HCl and 40 ml EtOH which had previously been electrolysed at −1·05 v. Electrolysis at −1·05 v. was continued for 7 hr, by which time the current had decreased from 88 to 1 m amp. The starting solution became clear at the end of the run. Electricity passed was 187 coulombs (n = 2·02). (a) Half of the electrolysed solution was brought to pH 4 with 10% NaOH solution. Evaporation to about 20 ml and extraction of the solution with ether after washing with ether and making it pH 10, yielded a colourless oil from the ether extract. The oil was distilled at 1 mm Hg and 80 ~ 90° (bath temp). (Found: C, 58·85; H, 9·43. $C_{12}H_{23}O_4N$ requires: C, 58·75; H, 9·45%.) The IR spectrum (film) showed absorptions at 3350 (w.), 1720 (v.s.), 1500 (w.), 1360 (m.), 1230 (s.), 1205 (s.), 1140 (v.s.), 1090 (m.), 1020 (s.), 935 (w.), 915 (w.), 855 (m.), 840 (w.), 765 (m.) and 750 (w.) cm^{-1}. Its hydrochloride was obtained as needles in vacuum desiccator, but as it was too hygroscopic to purify, but was added to an ethanolic solution of hydrogen hexachloroplatinate to give a platinichloride as red–orange prisms, m.p. 180° from EtOH. (Found: C, 32·19; H, 5·32; N, 3·02. $(C_{12}H_{23}O_4N)_2 \cdot H_2PtCl_6$ requires: C, 32·01; H, 5·37; N, 3·11%.) This platinchloride was easily soluble in water and hot EtOH, but not in cold EtOH. The oil was also converted into a picrate (yellow prisms), m.p. 124·5° from water. Found: C, 45·56; H, 5·52. $C_{12}H_{23}O_4N \cdot C_6H_3O_7N_3$ requires: C, 45·57; H, 5·52%), which was easily soluble in EtOH and hot water, but only slightly soluble in cold water. (b) Another half of the electrolysed solution was made to pH 10 with 10% sodium hydroxide solution and evaporated to dryness on a water bath. The residue washed with ether was dissolved in 10% HCl aq, and the solution extracted with ether. Evaporation of the ether gave needles, which after purification by sublimation, m.p. 79°. The IR spectrum of the needles was identical with that of α-hydroxyisobutyric acid (R. G. supplied by Tokyo Kasei.).

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