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190. Masaichiro Masui, Hiroteru Sayo, and Keiichi Kishi : Controlled Potential Electrolysis. X.[*1] Polarographic Behavior and Electrolytic Reduction Process of Esters of Aliphatic α-Nitrocarboxylic Acids.[*2]

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In the previous paper, the effect of α-substituents on the electrochemical reduction of an aliphatic nitro group was investigated by carrying out the experiment with two nitroindolyl-esters, but the interpretation of the reduction mechanism was not sufficient, partly because of the greater steric effect of the indolyl group compared to the methyl group in 2,2-dinitropropane.[1] The present work extends the above work to more common compounds in order to see the effect more precisely. Ethyl esters of nitroacetic, 2-nitropropionic, 2-nitrobutyric, and 2-nitrovaleric acids were used to study here.

Results and Discussion

Polarography

The four esters showed similar polarographic behaviors in acidic and neutral media (Table I and Fig. 1), developing well defined two waves except at pH 2, where both waves were almost merged into one, particularly in the case of ethyl nitroacetate. In Fig. 1, the plot for pH 2 is shown as that of a combined wave.

$E_{1/2}$ for the first and the second waves are changed with pH at pH 2~7 and pH 4~6, but nearly constant at pH 7~8 and pH 6~8, except that for nitroacetate, respectively.

The total wave height for the two waves is nearly constant in the range between pH 2 and 5, but decreases as pH is raised above the region, being disappeared about pH 9. Ethyl nitroacetate

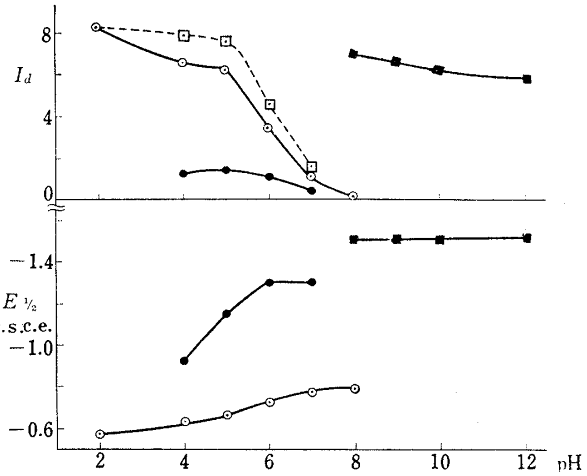

Fig. 1. Relation of $E_{1/2}$ and I_d to pH for Ethyl Nitroacetate in Buffer Solutions containing 5% Ethanol

⊙——⊙ : First wave ●——● : Second wave
⊡……⊡ : Sum of first and second waves
■——■ : Third wave

[*1] Part Ⅸ : J. Chem. Soc., **1963**, 1101.

[*2] A part of this paper was presented at the 9th Symposium on Polarography, Kyoto, October, 1962.

[*3] Toneyama, Toyonaka-shi, Osaka-fu (桝井雅一郎, 佐用博照, 岸 啓一).

1) M. Masui, H. Sayo : J. Chem. Soc., **1961**, 4773.

Table I. Half-wave Potentials and Diffusion Current Constants of α-Nitrocarboxylic Acid Ethyl Esters

pH	Propionate		Butyrate		Valerate	
	$-E_{1/2}$ (V.)	I_d	$-E_{1/2}$ (V.)	I_d	$-E_{1/2}$ (V.)	I_d
2.0	0.55	5.6	0.51	5.5	0.49	5.3
	0.71	2.2	0.66	1.7	0.67	1.8
3.0	0.59	5.4	0.53	5.5	0.49	5.6
	0.78	1.8	0.70	1.6	0.76	1.6
4.0	0.63	5.5	0.58	5.8	0.51	5.6
	0.89	1.8	0.81	1.3	0.83	1.4
5.0	0.68	5.6	0.64	6.2	0.58	5.6
	1.10	1.6	0.96	0.8	1.02	0.9
6.0	0.72	4.2	0.70	5.6	0.64	4.7
	1.37	1.6	1.38	0.8	1.37	0.7
7.0	0.75	1.2	0.74	2.5	0.65	1.6
	1.39	1.2	1.39	1.1	1.38	0.7
8.0	0.76	0.2	0.74	0.5	0.67	0.3
	1.40	0.3	1.40	0.2	1.39	0.2

$5\times10^{-4}M$ solutions containing 5% ethanol and 0.005% gelatin.
All voltages are measured against the saturated calomel electrode.

showed a new wave (a third wave) just before the discharge wave of supporting electrolyte at pH 8~12, whereas the others having a longer carbon chain did not. In that pH range, the esters are assumed to be present in its aci-nitro anion form in the solution because of their relatively low pKa values,[2,3] and the plots for $E_{1/2}$ and I_d *vs.* pH of this wave are not continuous to those for the lower pH region, and the new wave, therefore, may be ascribed to the reduction of an aci-nitro group affected by a great electron withdrawing effect of α-ethoxycarbonyl group. In general, an aci-nitro anion has been believed not to be reducible within the potential range available in normal aqueous buffer solutions. This may probably be the first example reported.

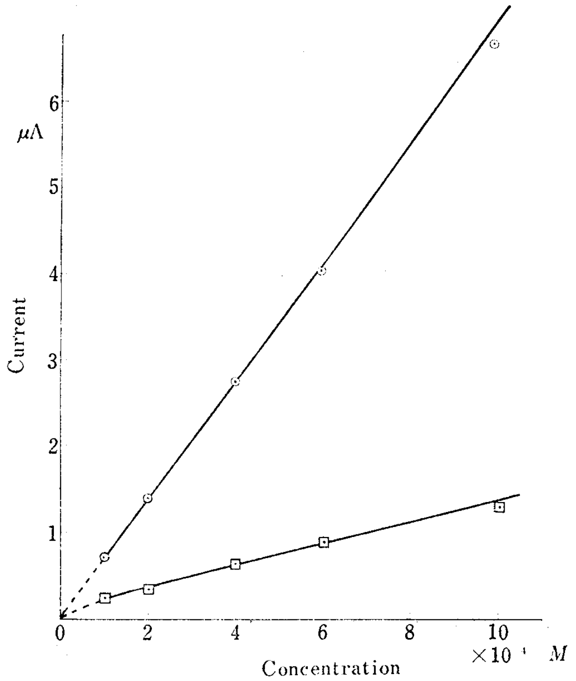

Fig. 2. Limiting Current-Concentration Relations of Ethyl Nitroacetate at pH 5.0

⊙——⊙ : First wave ⊡……⊡ : Second wave

The order of the ease of reduction for the first wave, as seen in Fig. 1 and Table I, is ethyl 2-nitrovalerate>ethyl 2-nitrobutyrate > ethyl 2-nitropropionate > ethyl nitroacetate, hence the order is the same as that reported for α-halocarboxylic acids and their esters.[4,5] In order to interpret their polarographic behaviors, it may be usual to consider both effects from the α-ethoxycarbonyl group that is same for

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[2] H. Ley, A. Hantzch : Ber., **39**, 3154 (1906).
[3] R. G. Pearson, R. L. Dillon : J. Am. Chem. Soc., **75**, 2439 (1953).
[4] I. Rosenthal, C. H. Albright, P. J. Elving : J. Electrochem. Soc., **99**, 227 (1952).
[5] I. Rosenthal, C. S. Tang, P. J. Elving : J. Am. Chem. Soc., **74**, 6112 (1952).

Table II. Effect of Mercury-column Height (h, in cm.) on Limiting Current (i, in μA) of Ethyl 2-Nitrovalerate ($10^{-3}M$, 10% ethanol and 0.005% gelatin)

	h	40	50	60	70
pH 2.0	i_1	4.3	4.8	5.35	5.85
	$i_1 h^{-1/2}$	0.680	0.679	0.691	0.699
	i_2	1.85	2.05	2.20	2.30
	$i_2 h^{-1/2}$	0.292	0.290	0.284	0.274
	$(i_1+i_2) h^{-1/2}$	0.972	0.969	0.975	0.973
pH 4.0	i_1	5.45	6.05	6.65	7.15
	$i_1 h^{-1/2}$	0.862	0.856	0.859	0.855
	i_2	1.7	1.9	2.0	2.0
	$i_2 h^{-1/2}$	0.269	0.269	0.258	0.239
	$(i_1+i_2) h^{-1/2}$	1.131	1.125	1.117	1.094
pH 7.0	i_1	2.15	2.40	2.65	2.85
	$i_1 h^{-1/2}$	0.340	0.339	0.342	0.341
	i_2	1.20	1.30	1.40	1.45
	$i_2 h^{-1/2}$	0.190	0.184	0.181	0.173
	$(i_1+i_2) h^{-1/2}$	0.530	0.523	0.523	0.514

all the above compounds and from the inductive effect of the other α-substituents, R-, but in the present study this is not satisfactory. Electron releasing effect of *n*-alkyl group is greater the larger the size of the group, but the difference is usually almost negligible for those larger than propyl group. The order described above is, therefore, opposite to that expected from the magnitude of the inductive effect of the R, thus this might also be ascribed to such a effect as the free energy of adsorption proposed by Elving, *et al.*[5] for the reduction of α-haloacids and esters. For the aci-nitro anion such effect could be excluded, because the same negative charge on the dropping mercury electrode at the potential should prevent such an adsorption effect, therefore the order may be that expected from the inductive effect, and only the acetic acid derivative having the smallest positive inductive effect of R-, hydrogen, may have reduction potential within the polarographically reducible region.

The dependence of the wave height on concentration, as seen in Fig. 2, is linear for the first wave at $10^{-4}\sim10^{-3}M$, but the diffusion current constant for the second wave tends to decrease with increasing concentration. The relation between the limiting current and the mercury-column heights (Table II) shows that the first wave at pH 4 and 7 and the total wave at pH 2 and 7 are largely controlled by diffusion, but the other waves, especially the second wave, are clearly not diffusion controlled.

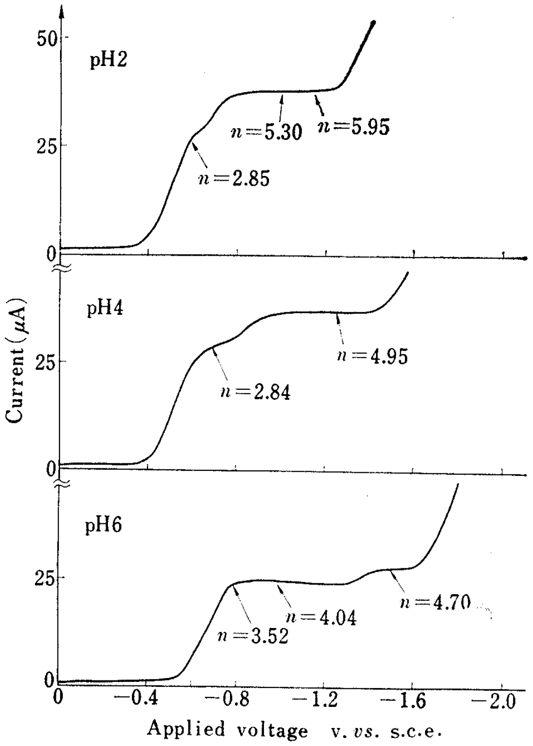

Fig. 3. Polarograms of Ethyl 2-Nitrovalerate (ca. $5\times10^{-3}M$)

n indicates coulometric *n* values.

Controlled Potential Electrolysis

As the polarographic behaviors of the four esters are almost similar in acidic and neutral media, ethyl 2-nitrovalerate was selected as the sample for the macro scale electrolytic study. The results are summarized in Table III

Table III. Controlled Potential Electrolysis of Ethyl 2-Nitrovalerate

pH	Sample taken (mg.)	Applied potential (v.)	Coulombs reqd. (Found)	n (Found)	Identified products
2.0	176.5	−1.15	578	5.95	Norvalin ethyl ester[a]
2.0	105.0	−1.0	307	5.30	Norvalin ethyl ester[a] +Ethyl 2-hydroxyaminovalerate
2.0	175.3	−0.65	278	2.88	Ethyl 2-hydroximinovalerate +Ethyl 2-hydroxyaminovalerate
2.0	170.1	−0.6	267	2.85	Ethyl 2-hydroximinovalerate +Ethyl 2-hydroxyaminovalerate
4.0	178.2	−1.25	486	4.95	Norvalin ethyl ester +Ethyl 2-hydroxyaminovalerate
4.0	179.0	−0.7	277	2.84	Ethyl 2-hydroximinovalerate +Ethyl 2-hydroxyaminovalerate
6.0	176.5	−1.5	458	4.71	Norvalin ethyl ester +Ethyl 2-hydroxyaminovalerate[a]
6.0	177.6	−1.0	368	3.76	Ethyl 2-hydroximinovalerate +Ethyl 2-hydroxyaminovalerate[a]
6.0	175.6	−0.8	341	3.52	Ethyl 2-hydroximinovalerate +Ethyl 2-hydroxyaminovalerate[a]

Each samples were dissolved in 200 ml. buffer solutions containing 10% ethanol.
a) Main product

and Fig. 3.[*4] The coulometric *n* values vary as the applied potential is changed, even if the potential is chosen on the same wave plateau, and the products also vary with the variation of pH and applied potential. These indicate that the reduction process is complex.

Electrolysis of the solution of pH 2 at −1.15 v. consumed six electrons per molecule and gave the ethyl ester of norvalin, thus the nitro group was reduced to amino group by a six-electron process. Except the above one, all electrolysis carried out at either less negative potential or at higher pH gave *n* values smaller than six and mixed products. Higher acid concentration and higher applied potential favoured the production of amine, and under the opposite conditions oxime was yielded predominantly. Between the two extreme conditions, hydroxylamine derivative was always produced. No amine was obtained by the electrolysis at the potential less than that of the second wave.

When the electrolysis was carried out at a potential on the plateau of the first wave, this wave was disappeared of course at the end of the electrolysis, and was not regenerated on standing the solution if it was kept free from oxygen. The second wave, in this case, appeared to remain, but affected in its shape and slightly decreased its wave height; that is, the wave had to be seen as a different one from the original second wave, though having similar $E_{1/2}$. This wave was found to coincide with the reduction wave of ethyl 2-hydroximinovalerate.

Ethyl 2-hydroxyaminovalerate that is a four-electron reduction product was not reducible under the conditions employed in the present study as shown by the followings : Immediately after preparing the solution, the hydroxyamino derivative synthesized showed no or only a very small wave, particularly at low pH, but developed a wave growing and then diminishing with time more quickly as the pH of the solution increased. The rate of the change of the wave height was also affected by the amount of oxygen present. Therefore, the wave developed by the solution of the hydroxyamino derivative is not of its own reduction, but that of the products from the autoxidation[6] or the

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[*4] Essentially the same results were obtained with ethyl nitroacetate.

6) D. H. Johnson, M. A. Rogers, G. Trappe : Chem. & Ind. (London), **1953**, 1032; J. Chem. Soc., **1956**, 1093.

disproportionation[7] of the hydroxyamino derivative. This was further confirmed by the study carried out on several α-hydroxyaminonitrils, which showed a quite similar polarographic behavior to the above compound.

The electrolysis of ethyl nitroacetate in the solution of pH 8 at a potential on the third wave plateau required 4.6 electrons per molecule, and the resulted solution easily reduced Fehling's solution at room temperature, showing the main product was ethyl hydroxyaminoacetate.

Accurate determination of the products in the electrolysed solution was unsucessfull, but the degree of easiness of isolation and detection of the products may be assumed to have semi-quantitative meaning. The following discussion is partly based on the assumption.

Discussion on Scheme (1)

From the results described above, it is clear that the two polarographic waves in acidic medium are not those derived from the reduction of two species existing in equilibrium as in the case of 1,1-dinitroalkane,[8] where one species is more difficultly reducible than the other. Since the ratio of the wave height for the two waves does not coincide with the coulometric n values obtained, and the products from the macro scale electrolysis highly depend on the potential applied, it is also clear that the waves do not simply represent the steps of a reduction. Further, because no abnormal change was observed on the electrocapillary curves, both waves are not a so called adsorption wave. As for the decrease of the diffusion current constant, I_d, with increasing pH, in neutral and alkaline regions, the reason for aliphatic nitro compounds is normally sought in the conversion of the nitro group to the ion of the aci-form. In the present study, the conversion with increasing pH seems also most probable, but there is still another possibility, that is the production of a hardly reducible species, α-nitrocarboxylic acid anion, resulted from the hydrolysis of the ester.*[5] But the latter was denied by the followings : (a) Though the rate of the hydrolysis of common esters under the conditions employed here is too slow to assume the hydrolysis come to completion within ten minutes or so, as this is clearly seen from the reported data[9] and the experiment carried out on ethyl α-nitroisobutyrate,[10] the sample solution subjected to polarography ten minutes after the preparation did not show any change in the wave height with time. (b) Even if the rate of the hydrolysis could be so fast as to complete it within ten minutes, the produced α-nitrocarboxylic acid anion would be decomposed to nitroalkane fairly rapidly.*[6] Because nitromethane, nitroethane, and 1-nitropropane develop a reduction wave having a similar diffusion current constant and $E_{1/2}$ to those corresponding α-nitrocarboxylic acids up to about pH 11, the decrease of wave height with increasing pH should be quite different from those observed by the esters, if the hydrolysis could take place. Really, by the polarography on dipotassium nitroacetate, which showed a quite analogous polarographic behavior with that of nitromethane, the decrease of the wave height was observed above pH 9, and there remained still a little wave even at pH 11. This means that nitroacetic acid causes decarboxylation in the solution, and most of the acid specimen taken are present as nitromethane at the recording of the polarogram. (c) The value of pKa of ethyl nitroacetate is about 5.8,[2,3] whereas that

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*[5] This was questioned by Dr. Zuman at the Symposium.

*[6] As the rate constant for the decarboxylation of nitroacetic acid is given by the equation $k_{obs.} = \{[H^+]/([H^+]+K_2)\} \times 0.121\ min^{-1}$ at 23.5°,[11] where K_2 is 1.25×10^{-9}, the half-life is calculated to be 6 min. 26 sec. at pH 8.

7) I. D. Spenser, A. Ahmad : Proc. Chem. Soc., **1961**, 375.

8) M. Masui, H. Sayo : J. Chem. Soc., **1961**, 5325.

9) F. A. Long, M. Paul : Chem. Rev., **57**, 935 (1957).

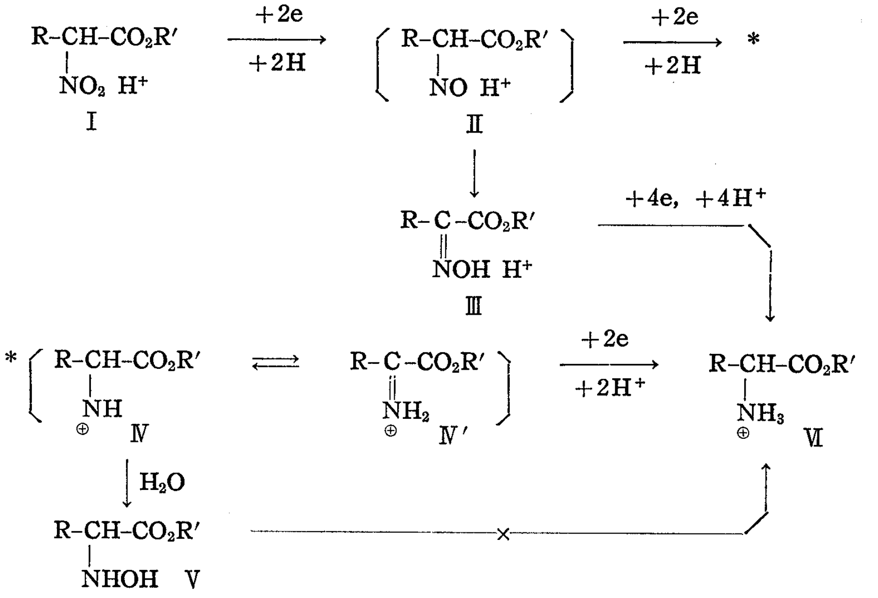
10) This will be reported in near future.

11) H. L. Finkleiner, M. Stiles : J. Am. Chem. Soc., **85**, 616 (1963).

obtained from I_d-pH curve is 6.1. The difference between the two values is reasonable for the recombination reaction of ethyl nitroacetate anion with a proton, $k_{-1}=2.5\times10^6$ L. mole^{-1} min^{-1}.[3)]

The decrease of the wave height in the I_d-pH relation is, therefore, clearly caused by the conversion of an easily reducible nitro form to a hardly reducible aci-nitro anion form, and not by the hydrolysis of the ester group.

By considering those described above, a reaction scheme (1) is proposed for the polarographic reduction of the esters of aliphatic α-nitrocarboxylic acids containing α-hydrogen. In this scheme, the equation is depicted with pre-protonation theory[12)] in mind, but in some conditions a cation radical (IV) is rather expressed as a free radical.



(1)

Generally, in acid solution, a nitro derivative (I) is reduced to a nitroso derivative (II) at first, which is instantaneously farther reduced by a two-electron reduction to the cation or the free radical of hydroxyamino derivative (IV). In the present case, the rate of the transformation of II to III must be considered. If the rate is comparable to that of II→IV, III and IV should be produced simultaneously, and the amount of each product depends on the relative rate. Since α-hydrogen of the ester is more easily released than that of nitroalkanes, as seen from their pKa values, the rate of transformation for the former compound should be more rapid, being faster the larger the concentration of II. With this idea, the results of the controlled potential electrolysis can be understood. III was not reducible at a potential less than the potential corresponding to the second wave, and so accumulated in the bulk of the solution. IV gives hydroxyamino derivative (V) rapidly in the presence of water, but V produced is not reducible any more in the aqueous solution even at a higher applied potential available. To interpret the farther reduction stages, an intermediate like IV', a protonized imine derivative, must be assumed. This structure have an important role in the reduction of common nitro compounds to amine.[10)] By assuming the rates IV → IV' and IV' → IV are the fastest in the scheme, it is possible to believe that the processes to V and VI are also competing with each other at the potential corresponding to the second wave, since the C=N double bond in IV' is fairly easily reducible to give amine (VI) owing to the conjugation effect with the α-ethoxycarbonyl group. A larger amount of VI and a smaller amount of V must be, therefore, yielded with a higher applied potential. This stage IV → IV' may be also

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[12)] S. G. Mairanovskii: J. Electroanal. Chem., 4, 166 (1962).

considered to be accelerated by proton, because the results of the experiments described above (Table Ⅲ) show that higher proton concentration favour the yield of amine (Ⅵ) rather than V. Eletrolysis at pH 2 with applied potential of −1.15 v. gave substantially amine derivative. The hydrolysis rate of Ⅳ′ is negligibly small compared to the rate of Ⅳ→V and Ⅳ′→Ⅵ, because no appreciable amount of keto ester or ammonium was detected. Really the hydrolysis rate constants for ketimines are less the order of 10^{-1} sec^{-1} at 25°,[13,14] and for the present compounds the value may not exceed much over the value,[14] being the slowest among the stages.

As for the reduction of Ⅲ, the same intermediate like Ⅳ′ should be passed too, because in the reduction of R-CR′=N-Y-R″ the N-Y bond fission occurs in advance to the reduction of the double bond when Y is nitrogen or oxygen.[15,16] Since Ⅲ showed only one wave of a four-electron reduction, the $E_{1/2}$ of the intermediate (Ⅳ′) should be more positive than that of Ⅲ.[16]

If the rate of Ⅳ′→Ⅳ in the scheme is much smaller than that of Ⅳ→Ⅳ′, the amount of Ⅳ′ should be large in the solution when applied potential is not so high as to reduce Ⅳ′, and hence the hydrolysis of the ketimine may not be neglected like the case of the reduction of testosterone propionate oxime,[15] in which two two-electron reduction waves were reported. But it is necessary, in general, to assume that the equilibrium between 〉CH-N〈 ⇄ 〉C=NH must be well to the right for the more easily reducible nitro compounds. This assumption appears very important in the interpretation of the reduction of nitro compounds. Nitro compounds which can easily produce amino derivatives by polarographic reduction, such as *p*-nitroaniline,[17,18] *p*-nitrophenol,[19-21] and other hydroxy substituted nitrobenzene,[22] are found that they can take quinoid-imine form more easily than those more hardly give aminoderivatives, such as nitrobenzene.[23] For aliphatic series, tertiary nitro compounds which can not take corresponding imino type having C=N double bond in any reduction intermediate have been reported not to give amino derivatives.[10,24]

From these considerations it may be deduced for aliphatic nitro compounds having α-substituents of large electro negativity to have a great tendency to take imino form favouring reduction to amine. In order to reduce aromatic and aliphatic nitro compounds to amines, it seems necessary to take a C=N double bond at the nitro nitrogen just prior to yield amines.

There are several papers assuming fairly rapid dehydration of an aromatic hydroxyamino intermediate to a quinoid imine prior to yield an amine by the electrode reduction of a nitro or nitroso group,[21,25] but it is clear from our results that the dehydration mechanism is not applicable for the above esters and must be displaced by the stage Ⅳ→Ⅳ′. Because there have given no experimental evidence for the dehydration, there may still be a necessity of considering the kinetic stage for the reduction of *p*-nitrophenol, *et al.* on the bases of a direct transformation as 〉CH-N〈 ⇄ 〉C=NH.

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13) J. B. Cloke: J. Am. Chem. Soc., **51**, 1174 (1929).
14) J. B. Culbertson: *Ibid.*, **73**, 4818 (1951).
15) H. Lund: Acta Chem. Scand., **13**, 249 (1959).
16) M. Masui, H. Ohmori: This Bulletin, **12**, 877 (1964).
17) O. D. Schreve, E. C. Markham: J. Am. Chem. Soc., **71**, 2993 (1949).
18) W. Kemula, Z. Kublik: Nature, **182**, 793 (1958); Bull. de L'Acad. Polom. des Sciences, **6**, 653 (1958).
19) M. J. Astle, W. V. McConnell: J. Am. Chem. Soc., **65**, 35 (1943).
20) J. Pearson: Trans. Faraday Soc., **44**, 692 (1948).
21) D. Stocesova: Collection Czechoslov. Chem. Communs., **14**, 615 (1949).
22) M. J. Astle, S. P. Stephenson: J. Am. Chem. Soc., **65**, 2395, 2399 (1943).
23) I. M. Kolthoff, J. J. Lingane: "Polarography," p. 748, Interscience Publishers, New York, 1952.
24) M. Masui, C. Yijima: J. Chem. Soc., **1963**, 1101.
25) G. S. Alberts, I. Shain: Anal. Chem., **35**, 1859 (1963); L. Holleck, R. Schindler: Z. Elektrochem., **60**, 1138 (1956).

In the light of those discussed above, the polarographic waves may be ascribed to the electrode reductions as follows; the first wave to I→II→IV, and the second wave to IV'→VI and III→VI. The process of III→VI seems a subsidiary reaction, as seen from the relative wave heights for the first and the second waves. Because the second wave includes the subsidiary reaction and is affected by both rates of the reactions (II)→(III) and [(IV) ⇄ (IV')], the kinetic nature of the wave is well understood.

Experimental

Materials——Ethyl nitroacetate (b.p$_{25}$ 105～107°) was prepared from dipotassium nitroacetate obtained from nitromethane and KOH by the method of Feuer.[26] Ethyl 2-nitropropionate (b.p$_4$ 66～67°, n_D^{20} 1.4210 (1.4209[27])), ethyl 2-nitrobutyrate (b.p$_4$ 74°, n_D^{20} 1.4234 (1.4233[27])). and ethyl-2-nitrovalerate (b.p$_4$ 80～81°, n_D^{20} 1.4269 (1.4266[27])) were prepared by the reaction between the corresponding ethyl α-bromoalkylcarboxylate and sodium nitrite in the presence of phloroglucin in N,N-dimethylformamide.[27] Ethyl 2-hydroxyaminovalerate (b.p$_3$ 71°, *Anal.* Calcd. for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; N, 8.69. Found : C, 51.78; H, 9.22; N, 8.85.) was prepared from 2-hydroxyaminovaleric acid[28] and EtOH saturated with dry HCl gas. It reduced Fehling's solution easily at room temperature. α-Hydroxyaminonitrils were prepared from propylaldoxime, butyraldoxime and heptaldoxime according to the known method.[28,29] Ethyl 2-hydroximinovalerate, prepared by reaction between diethyl propylmalonate and butylnitrite,[30] had b.p$_3$ 107° and m.p. 48°. Norvalin ethyl ester (b.p$_3$ 50°) was prepared by the esterification of norvalin with EtOH in the presence of anhyd. hydrogen chloride.

Britton-Robinson type buffer solution were used for polarographic analysis, but the following solution were used for the controlled potential electrolysis : pH 2, 0.2M H_3PO_4-NaOH; pH 4, 0.1M citric acid-NaOH; pH 6, 0.1M KH_2PO_4-Na_2HPO_4 : pH 8, 0.1M $Na_2B_4O_7$-HCl. All solutions contained 0.1M KCl as an additional supporting electrolyte.

General Procedure for Polarographic Analysis——Sample solutions were prepared by pipetting 0.5 ml. of a stock solution (0.01M) of the ester prepared in EtOH into a 10 ml. volumetric flask, adding 0.05 ml. of 1% gelatin solution, and filling the flask to the calibration mark with a buffer solution. The final solution contained $5 \times 10^{-4}M$ of the ester. The cell used was of the conventional cylinder type having a mercury pool electrode as anode. The cell was maintained at 25±0.1°. Oxygen was removed from all cell solutions by bubbling for 5 min. with N_2 which had previously been bubbled through the vanadyl sulfate solution contacted with zinc amalgam. Polarograms were recorded 10 min. after preparation of sample solution. After the polarographic analysis the potential of mercury pool anode was determined against saturated calomel electrode.

General Procedure for Controlled Potential Electrolysis——1～2 mmoles of the ester dissolved in 20 ml. of EtOH was added to 180 ml. of pre-electrolysed buffer solution, and the mixed solution was electrolysed at a settled cathode potential until the current diminished to the background value. The amount of electricity required for the electrolysis was measured by graphical integration of a current *vs.* time plot. The electrolysed solution was concentrated to about 50 ml. under reduced pressure, neutralized to an appropriate pH value, and extracted with ether after saturation with NaCl. Evaporation of ether after drying with anhyd. Na_2SO_4 gave products, which were purified by distillation under reduced pressure or recrystallization. Identification of the products was carried out on them or on their derivatives by mixed melting with a supposed authentic sample, IR spectrum, and organic elemental analysis.

Apparatus——Those used for IR spectrum, polarography, pH measurement and controlled potential electrolysis are same as those described in the previous paper.[1]

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Summary

Polarographic reduction mechanism of aliphatic ethyl nitrocarboxylates was investigated. The decrease of the wave height in alkaline region was ascribed to the conver-

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[26] H. Feuer, H.B. Hass, K.S. Warren : J. Am. Chem. Soc., **71**, 3078 (1949).
[27] N. Kornblum, R.K. Blackwood, J.W. Powers : *Ibid.*, **79**, 2507 (1957).
[28] W. Miller, J. Plöchl : Ber., **26**, 1552 (1893).
[29] C.D. Hurd, J.M. Longfellow : J. Org. Chem., **16**, 761 (1951).
[30] R.H. Barry, W.H. Hartung : *Ibid.*, **12**, 460 (1947).

sion of the nitro form to aci-nitro anion rather than the ester hydrolysis. Only ethyl nitroacetate developed a wave for the aci-nitro anion. The coulometric *n* values and the products obtained, combined with the polarographic results, suggest the scheme (1) as the most probable reduction mechanism. The production of amine is only possible through C=N double bond formation, but not through hydroxyamino derivatives as usually suggested.

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191. Zen-ichi Horii, Chuzo Iwata, Ichiya Ninomiya, Nobuhiko Imamura, Masayoshi Ito, and Yasumitsu Tamura: Studies on Ergot Alkaloids and Its Related Compounds. X.[*1] Condensation of Cyclic Ketones and 3-Methylaminopropionates.

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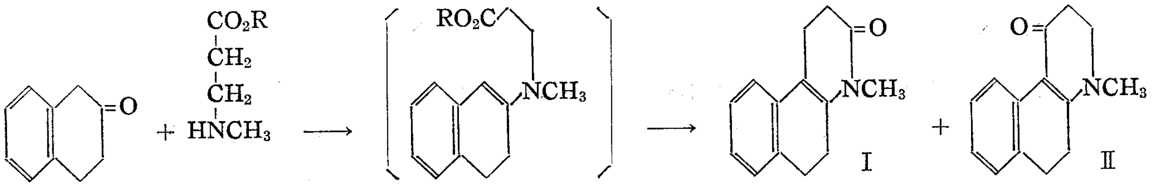
In 1958, Nelson and his coworkers[1] carried out the condensation of 2-tetralone and methyl 3-methylaminopropionate and assigned the structure of the sole product as 4-methyl-3,4,5,6-tetrahydrobenzo[*f*]quinolin-1(2*H*)-one (II). Later in 1962,[2] we applied their procedure to the reactions between a variety of cyclic ketones and the 3-methylaminopropionates and formulated the structures of the major products as III, IX, X, XVIII'~XXI' and XXIII~XXV on the basis of the Nelson's conclusion. However, it has recently been found by the joint work[3] of Nelson's and our groups that the structure of the major product from 2-tetralone and methyl 3-methylaminopropionate should be 4-methyl-1,2,5,6-tetrahydrobenzo[*f*]quinolin-3(4*H*)-one (I) instead of II and, further, that compound (II) is also formed, although a very small amount, in the reaction.[*1] These results prompted us to reinvestigate our previous work[2] in order to make necessary corrections on the structures of the reaction products and, at the same time, to elucidate the course of this type of the reaction.



Reaction of Cyclohexanone and Ethyl 3-Methylaminopropionate

A mixture of equimolar amounts of cyclohexanone and ethyl 3-methylaminopropionate was heated under reflux for 50 hours as in the previous paper.[2] The products were purified by fractional distillation, followed by column chromatography on alumina, giving 1-methyl-2,3,5,6,7,8-hexahydro-4(1*H*)-quinolone (III) in 53% yield, along with small

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[*1] Part IX: Yakugaku Zasshi, **85**, 1220 (1964).

[*2] Toneyama, Toyonaka, Osaka-fu (堀井善一, 岩田宙造, 二宮一弥, 今村信彦, 伊藤允好, 田村恭光).

1) N. A. Nelson, J. E. Ladbury, R. S. P. Hsi: J. Am. Chem. Soc., **80**, 6633 (1958).

2) Z. Horii, C. Iwata, Y. Tamura: This Bulletin, **10**, 940 (1962).

3) Z. Horii, C. Iwata, Y. Tamura, N. A. Nelson, G. H. Rasmusson: J. Org. Chem., **29**, 2768 (1964).