U. D. C. 545.33 : 547.332

63. Masaichiro Masui and Hiroteru Sayo : Controlled Potential Electrolysis. II.* Studies on Some α,β-Unsaturated Nitro Compounds by Polarography.*

(*Pharmaceutical Faculty, Uuiversity of Osaka***)

Many papers have been published on the polarographic study of aromatic nitro compounds[1~8] and nitroparafflns.[8~14] It is also well known that double bonds are reducible when they are conjugated with other groups and that the reduction is easier when the degree of the conjugation is higher.[15~17]

Recently we were interested in the reduction of the compounds which have a double bond conjugated with a nitro group, R-CH=CH-NO_2 (R=aromatic or aliphatic groups). On the other hand, the necessity of elucidating the machanism of electrolytic synthesis of amino compounds from such compounds has occurred and the study of polarography and controlled potential electrolysis of such compounds were undertaken.

In the present paper, the polarographic study of following compounds are reported. ω-Nitrostyrene (II) which has the most typical aromatic group, R = C_6H_6-; 1-nitro-3-methylbut-1-ene (IV) which has the most typical aliphatic group, R = $(CH_3)_2CH$-; furylnitroethylene (I) which has the intermediate property of the preceding two but rather close to (II); 1-phenyl-2-nitroethane (III) and 1-nitro-3-methylbutan-2-ol (V) were also studied in order to compare with the unsaturated samples. Saturated compound in which R=  is unstable and the pure compound cannot be obtained, that it was not included. (V) has one OH group in the β-position of nitro group, but its effect on the reduction of nitro group is assumed to be negligible, and since the sample was made available, it has been selected.

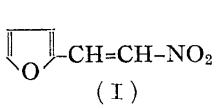
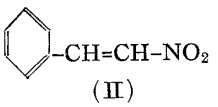
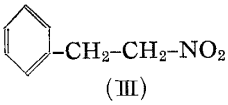
a) Furylnitroethylene Ordinarily it shows two waves; in acidic solutions the first wave is relatively well-defined while the second is not a well-defined wave. The first wave is higher than the second and it attains the maximum height near pH 6. In acidic solutions, the second wave becomes smaller in lower acidity. The first wave is divided into two parts at pH 2, though the latter part is small and combined with the former that they are not clear individually. At pH 6, the two parts coincide and becomes a one wave. Therefore, the height of the first wave described in Table I

* Part I : J. Pharm. Soc. Japan, **75**, 1515(1955).

** Kitatoneyama, Toyonaka, Osaka-fu (桝井雅一郎, 佐用博照).

1) M. J. Astle, W. V. McConnel : J. Am. Chem. Soc., **65**, 35(1943).
2) M. J. Astle, W. P. Cropper : *Ibid.*, **65**, 2395(1943).
3) M. J. Astle, S. P. Stephenson : *Ibid.*, **65**, 2399(1943).
4) M. E. Runner, M. L. Kilpatrick, E. C. Wagner : *Ibid.*, **69**, 1406(1947).
5) S. F. Dennis, A. S. Powell, M. J. Astle : *Ibid.*, **71**, 1484(1949).
6) I. M. Kolthoff, A. Liberti : *Ibid.*, **70**, 1885(1948).
7) D. Stocesova : Collection Czechoslov. Chem. Communs., **14**, 615(1949).
8) Thos. DeVries, R. W. Ivett : Ind. Eng. Chem., Anal. Ed., **13**, 339(1941).
9) P. E. Stewart, W. A. Bonner : Anal. Chem., **22**, 793(1950).
10) W. J. Seagers, P. J. Elving : J. Am. Chem. Soc., **72**, 3241(1950).
11) E. W. Miller, A. P. Arnold, M. J. Astle : *Ibid.*, **70**, 3971(1948).
12) W. J. Seagers, P. J. Elving : *Ibid.*, **72**, 5183(1950).
13) N. Radin, T. DeVries : Anal. Chem., **24**, 971(1952).
14) F. Petru : Collection Czechoslov. Chem. Communs., **12**, 620(1947).
15) H. A. Laitinen, S. W. Cox : J. Am. Chem. Soc., **64**, 1151(1942).
16) H. Adkins, F. W. Cox : *Ibid.*, **60**, 1151(1938).
17) M. Fields, E. R. Blout : *Ibid.*, **70**, 930(1948).

Table I. Polarographic Behavior of Nitro Compounds

pH	 (I) $E_{1/2}$ V.vs. S.C.E.	(I) Id/C × 10^{-3}A/M	 (II) $E_{1/2}$ V.vs. S.C.E.	(II) Id/C × 10^{-3}A/M	 (III) $E_{1/2}$ V.vs. S.C.E.	(III) Id/C × 10^{-3}A/M	$(CH_3)_2CHCH=CHNO_2$ (IV) $E_{1/2}$ V.vs. S.C.E.	(IV) Id/C × 10^{-3}A/M	$(CH_3)_2CHCHCH_2NO_2$ OH (V) $E_{1/2}$ V.vs. S.C.E.	(V) Id/C × 10^{-3}A/M
2.00	−0.14	3.55	−0.13	5.85	−0.60	5.52	−0.34	2.19	−0.75	4.48
							−0.71	—		
	−0.85	—	−0.91	3.34			−0.99	—		
3.00	−0.21	4.61	−0.20	5.51	−0.63	5.30	−0.41	2.16	−0.77	4.43
							−0.75	—		
	−0.89	—	−0.98	3.32			−1.05	—		
4.00	−0.28	4.73	−0.27	5.38					−0.79	4.40
	−0.95	—	−1.08	—						
6.00	−0.38	5.54	−0.36	5.05	−0.67	5.44	−0.59	2.05	−0.84	4.38
							−0.82	—		
	—	—	—	—			—			
9.00	−0.45	1.28	−0.45	—	−0.83	3.59	−0.65	0.60	−0.93	1.22
							−0.90	—		
	−0.89	2.65	—	—			−1.19	—		

takes the largest value at pH 6. When the portion of alcohol becomes larger, the plateaus of the waves are, in general, obscured. As the wave of supporting electrolyte follows immediately after that of the second, determination of the latter height is difficult. In alkaline solutions the wave forms are clear and the height of the second wave in this case is larger than that of the first, but the total wave height is smaller than that in acidic solutions, and becomes smaller at a heigher pH, but this does not extinguish the second wave. The fact is rather close to nitroparaffin than to nitrobenzene.

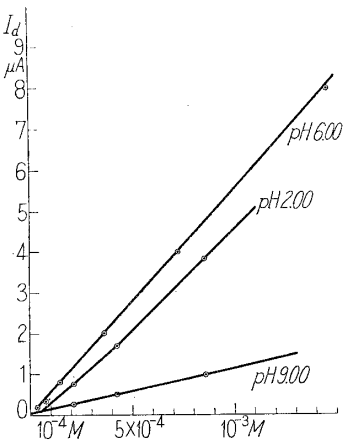


Fig. 1. Relations between Current and Concentration of Furylnitroethylene

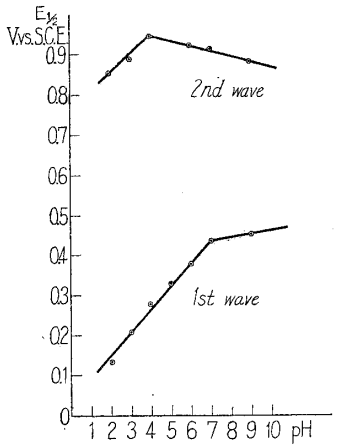


Fig. 2. Half-wave Potential vs. pH for Furylnitroethylene

The relation between the height of the first wave and concentration of the compound is shown in Fig. 1. The best sensitivity and lineality are obtained at about pH 6. The relation between the pH and half-wave potentials is illustrated in Fig. 2. The pH–half wave potential curve of the first wave is linear between pH 2 and 7. Because the wave forms are such that it is difficult to determine their heights, the height of the first wave in acidic solutions described in Table I are determined at positions as to make the graphic method easy and the values may not express the true diffusion current of the first reduction.

b) ω-Nitrostyrene The first wave is not divided into two parts as in the case

of (I) and is well developed, but the second wave is not so distinct. In acidic solutions the height of the first wave is larger than that of the second. Between pH 4 and 6, the second wave is not clear, as the wave of supporting electrolyte follows immediately. In alkaline solutions the wave form is entirely obscured.

c) 1-Phenyl-2-nitroethane In all pH ranges studied, it shows one well-defined wave. The wave heights are almost equal in acidic solutions, but decrease in alkaline solutions. In the solution of pH 6 the probable second wave appears to be present, but was not distinct.

d) 1-Nitro-3-methylbut-1-ene In all pH ranges studied it shows three waves, but in acidic solutions the plateau of each wave is not distinct, so the accurate height of only the first wave can be determined. In the solution of pH 6, the third wave is much obscured, only the first wave being well defined. The wave form is rather clear and the height of the three waves are almost the same in alkaline solutions, but the total height is smaller than that in the acidic solutions.

e) 1-Nitro-3-methylbutan-2-ol It gave almost the same wave form as compound (III), but the half-wave potentials are somewhat heigher than (III) as seen in Table I, and close to those of nitroparaffins.

Experimental

Apparatus—Instrument used was Yanagimoto Polarograph Model PEL-3. Sensitivity of galvanometer was 1.03×10^{-9}A./mm./m. The capillary constant, $m^{2/3}t^{1/6}$, was 1.025. Ordinary cells employing a mercury pool as an anode were used. All experiments were carried out at 25°±0.1°.

Reagents—Furylnitroethylene was prepared and purified by the procedure of Takamoto.[18] The melting point was 75°. ω-Nitrostyrene, m.p. 58~59°, was prepared by the method described.[19] 1-Phenyl-2-nitroethane, colorless oil, $b.p_{14}$ 128~135°, was prepared as follows :

$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!O + C_6H_5\text{-}MgBr \rightarrow C_6H_5\text{-}CH_2\text{-}CH_2\text{-}OH \rightarrow C_6H_5\text{-}CH_2\text{-}CH_2\text{-}Br \rightarrow C_6H_5\text{-}CH_2\text{-}CH_2\text{-}I \rightarrow C_6H_6\text{-}CH_2\text{-}CH_2\text{-}NO_2$$

1-Nitro-3-methylbut-1-ene, $b.p_{13}$ 66~67°, and 1-nitro-3-methylbutan-2-ol, $b.p_2$ 72~74°, were obtained from a private source.

Buffer solutions—The buffer solutions used in the present investigation were prepared according to Britton and Robinson. Measurement of the pH was carried out with Towa-Dempa Glass Electrode pH Meter Model HM-5.

Cell solutions—The weighed sample was dissolved in 10 cc. of pure EtOH, and 1 cc. of the solution was made up to 10 cc. with buffer solution. This solution further contained gelatine 0.01% and KCl 0.1*M*. (shown as the final concentration). Dissolved oxygen was removed satisfactorily by bubbling hydrogen (deoxygenated by bubbling H_2 through an alkaline-pyrogallol solution) through the solution for 10~15 mins. before each run.

Discussion

Nitro compounds without a double bond conjugated with nitro group

They show a well-defined reduction wave and their half-wave potentials are analogous to those of nitroparaffins. 1-Phenyl-2-nitroethane presents somewhat lower values than the others, probably because of the effect of benzene. The slopes of the pH-half wave potentials of the two compounds in acid media have a value of about 0.2 v./pH, so it is equal to that of nitroparaffin. The decrease of the wave height in alkaline solutions is also considered because of the formation of aci form. Except for the fact that the second wave, which should appear in the solution of pH 4.5~9.0 in the case of simple nitroparaffins, was not distinct as the wave of supporting electrolyte following immediately, all behaviors were much analogous to the simple nitroparaffins. Therefore, the reduction should be considered as the four-electron reduction to N-alkyl-

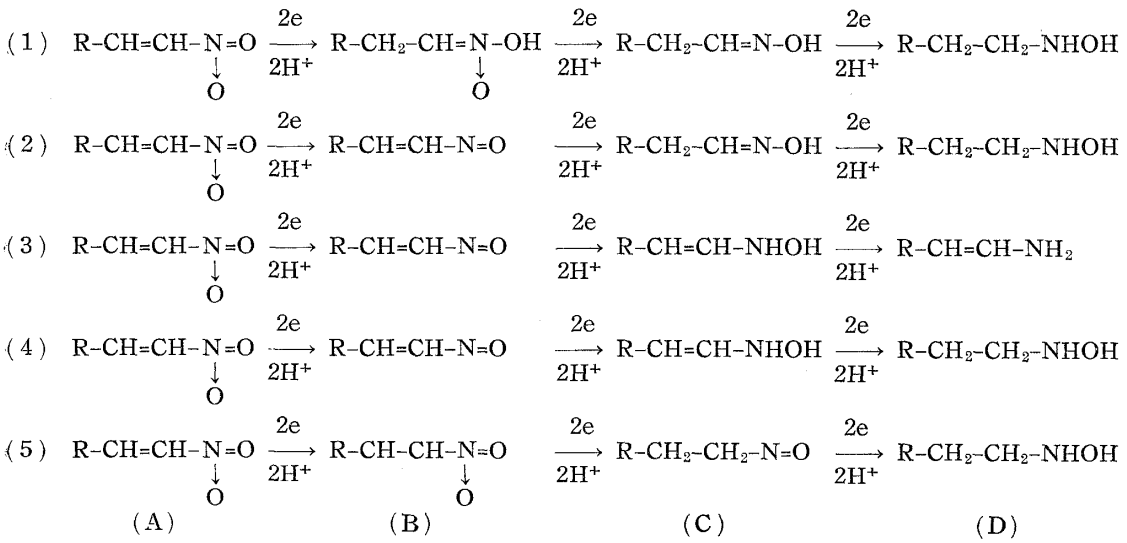
18) R. Takamoto : J. Pharm. Soc. Japan, **48**, 136(1928).
19) Org. Syntheses, Coll. Vol. I, 405.

hydroxylamine as in the case of simple nitroparaffins.

Nitro compounds with a double bond conjugated with nitro group

Considering the variations of wave forms and their heights accompanying the variation of pH and also those of nitro compounds reported to date, it may be proper to consider that the reduction of the doule bond as well as the nitro group may have taken place. The slope of pH–half wave potential plots against the first wave in acid medium, about 0.06 v./pH, was of the same value as that of nitrobenzene[7] and was in good agreement with the theoretical value of 0.059 v./pH at 25°. The fact that the half-wave potential of nitro group has shifted to a more positive value when it is conjugated with a double bond is in agreement with the fact that the half-wave potential of aromatic nitro compounds is more positive than that of nitroparaffins. It is also seen in Table I that the half-wave potential was more positive if aromaticity of R was higher. The reduction curves of these three are somewhat different from the difference between their R as shown above, and (I) shows the intermediate form of (II) and (IV). Now, considering that the dimensions of (II) and (III) are almost of the same order, their diffusion constant may be assumed to be equal. Therefore, if their value of Id/C is equal, when the same capillary is used and the determination is carried out under the same conditions, the number of electrons involved in the reduction must be equal. Actually, in acid media, the value of Id/C of (III) and that of the first wave of (II) are almost equal. Therefore, the first wave of (II) can be considered to be four-electron reaction and the second wave, two. In the same manner, the three waves of (IV) have almost the same wave height and the Id/C of the first wave is almost one-half of that of (V), so that the reaction is considered to be two-electron and the total reaction to be six-electron. As the diffusion constants of (I) and (II) can be assumed as not largely different, from the comparison of the values of their Id/C at pH 6 (the reason for selecting the value at pH 6 should be apparent from the above), it may be seen that six-electron reduction, as a total reduction, composed of three two-electron reductions also takes place in this case.

As six-electron reduction may be considered to take place, all the possible reduction processes will be as follows :



In the case of (II), for example, from considering the molecular structure and $E_{1/2}$ of the first wave, there is no doubt that the first wave is due to the reduction concerned with the nitro group. In process (1), 1,4-addition takes place at first and produces (B), in which the nitro group is in the so-called aci form and this does not seem correct. In the polarographic reduction of ordinary nitro groups, they produce

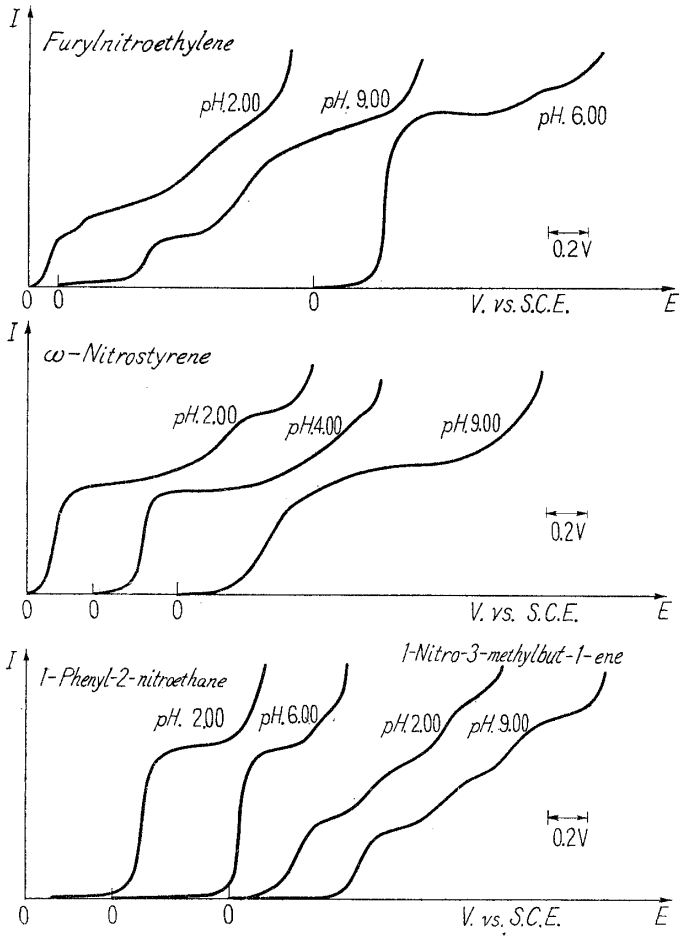


Fig. 3.

Some Polarogaphic Waves of Nitro Compounds

nitroso groups by two-electron and the reduction of nitroso compounds immediately takes place, since the half-wave potentials of the nitroso groups in general are more positive than those of nitro groups. In the present case, however, the 1, 4-addition process in the course of (B)→(C) in (2) must also be considered. Process (5) has a logically inconsistent fact, because if the reduction of the double bond takes place, it is a two-electron reduction and the successive reduction must be due to the aliphatic nitro group, which is the reduction of (III). Then, if the process is not a 1, 4-addition the reduction process must be (3) or (4). Process (3) is exactly the same as that of nitrobenzene; process (4) is also the same as that of nitrobenzene until (C) is produced, but the process (C)→(D), the reduction of a C=C double bond, is thought to be impossible at the half-wave potential as indicated in Table I. Therefore, except for process (2), process (3) may have the highest possibility, but the fact that the value of half-wave potential of the first wave is more positive while that of the second wave is more negative than those of nitrobenzene, is difficult to understand. Moreover, the behavior of the second waves, especially of (I) and (IV)(in the case of (IV), it corresponds to the third wave), is different from the simple nitro groups. The change of solution pH from acidic to alkaline does not extinguish the second wave. From these facts, it may be proper to consider that there must be some differences between the reduction process of α,β-unsaturated nitro compounds and simple nitro compounds and process (3) may also be not correct for the reduction process of the α,β-unsaturated nitro compounds. The remaining one, process (2), has not any logically inconsistent facts and therefore, it may become the most reliable process.

In the present study, therefore, we have presumed that the reduction in acid medium would progress through the process (2).

The authors are indebted to Prof. K. Takiura and Dr. T. Kametani for valuable suggestions and encouragements. The authors also wish to thank Mr. Y. Sanno for gifts of samples.

Summary

The polarographic behavior of α,β-unsaturated nitro compounds was studied by comparison with corresponding saturated nitro compounds and the reduction process were considered. The electrode reaction in acid medium was presumed to be a six-electron reduction and its process to be as follows :

$$R\text{-}CH{=}CH\text{-}NO_2 \xrightarrow[2H^+]{2e} R\text{-}CH{=}CH\text{-}N{=}O \xrightarrow[2H^+]{2e} R\text{-}CH_2\text{-}CH{=}N\text{-}OH \xrightarrow[2H^+]{2e} R\text{-}CH_2\text{-}CH_2\text{-}NHOH$$

(Received March 22, 1956)

U. D. C. 545.37 : 547.538.141

64. Masaichiro Masui, Hiroteru Sayo, and Yukio Nomura : Controlled Potential Electrolysis. III.[1] Controlled Potential Electrolysis of ω-Nitrostyrene.

(*Pharmaceutical Faculty, University of Osaka**)

In the previous paper[1] α,β-unsaturated nitro compounds were studied by polarography, comparing with the corresponding saturated nitro compounds, and it was presumed that they would undergo six-electron reduction at electrode and the process in acid medium might be expressed by the following equation :

$$R\text{-}CH{=}CH\text{-}NO_2 \xrightarrow[2H^+]{2e} R\text{-}CH{=}CH\text{-}N{=}O \xrightarrow[2H^+]{2e} R\text{-}CH_2\text{-}CH{=}N\text{-}OH \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}NHOH \quad \ldots\ldots(1)$$

In the present series of experiments, we studied the controlled potential coulometric analysis and controlled potential electrolytic preparation of the reduction intermediates of ω-nitrostyrene and determined the number of electrons, n, involved in the electrode reaction and reduction process.

Determination of the Number of Eloctrons, n

To determine the n value, a controlled potential coulometric analysis with counter millicoulometer was applied. The results are shown in Table I. From these results it is evident that the first wave of ω-nitrostyrene in acid medium is a four-electron and the second two-electron reduction. The first wave of 1-phenyl-2-nitroethane in

Table I. Determination of the Number of Reduction Electrons

pH	EtOH present (%)	Cathode potential vs. S.C.E.	Sample taken (mg.)	Electricity required (coulombs)	Number of electrons
ω-nitrostyrene					
2.00	1	0.40	0.92	2.45	4.12
2.00	1	1.00	0.75	3.03	6.25
50% AcOH	1	0.40	0.92	2.50	4.20
6.00	1	0.60	0.75	1.83	3.77
1-phenyl-2-nitroethane					
2.00	1	0.90	0.92	2.28	3.88
6.00	1	1.00	0.92	2.16	3.67

* Kitatoneyama, Toyonaka, Osaka-fu (桝井雅一郎, 佐用博照, 野村幸雄).

1) Part II : This Bulletin, **4**, 332(1956).

2) M. Masui, H. Sayo : J. Pharm. Soc. Japan, **75**, 1515(1955).