Polarographic Behavior of Nitroammonocarbonic Acids in Aqueous Media. I. Nitrourea*

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The principal organic compounds which possess NO_2 radicals are O-NO_2 compounds (nitric esters), C-NO_2 compounds (nitro compounds) and N-NO_2 compounds (nitramines). Among these compounds, the polarographic behavior of C-NO_2 compounds, especially, of aromatic nitro compounds has been studied considerably. However, the polarographic study published for N-NO_2 compounds, e. g., nitramines, which have a reduction mechanism similar to that of C-NO_2 compounds, was not found, except in the cases of the studies on the electrolytic reduction of nitroguanidine to aminoguanidine[1] and on the polarographic analysis of cyclotrimethylenetrinitramine[2]. Since the reduction mechanism of nitramine which has two N-NO_2 redicals is considered to be more complicated, we studied the polarographic behavior of nitroammonocarbonic acid which has one N-NO_2 radical and is water soluble. Nitrourea was studied at the first stage. However, the result was so complicated that it was impossible to clarify the reduction mechanism. We report here the experimental result mainly.

Experimental

Nitrourea, prepared through the dehydration of urea nitrate by concentrated sulfuric acid[3] below 0°C and purified by recrystallizations from water and afterwards from aceton, had m.p. 155°C (decomp.) (Found: N, 39.97. Calcd. for $CH_3N_3O_3$: N, 40.00%).

The buffer solutions used as the supporting electrolyte are as follows;

pH range	Buffer solution	
1.0....4.7	Walpole	(1N−HCl & 1N−CH_3COONa).
5.2....8.0	Sφrensen	(M/15−KH_2PO_4 & M/15−Na_2HPO_4).
8.0....9.0	〃	(M/20−Borax & N/10−HCl).
9.2...12.0	〃	(M/20−Borax & N/10−NaOH).

The concentration of sample, temperature, sensitivity of galvanometer and the corrected value of shunt, were $1\sim5\times10^{-4}$ mol./l., 25.0 ± 0.1°C, 1.49×10^{-9} amp./mm./m. and 1 : 95.7, respectively. The oxygen gas solved in sample solution was removed by the bubbling stream of purified nitrogen gas, at the rate of $2\sim3$ cc./sec. for twenty minutes, The Heyrovsky-Shikata type polarograph apparatus produced by Yanagimoto Manuf. Co. was used and every polarogram was taken

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[1] K. Sugino and M. Yamashita, *J. Chem. Soc., Japan*, 70, 73 (1949).

[2] W.H. Jones, *J. Am. Chem. Soc.*, 76, 834 (1954).

[3] T.L. Davis, "The Chemistry of Powder and Explosives", John Wiley and Sons, Inc., New York, N. Y (1943), p. 373.

within thirty minutes after the preparation of the sample solution.

Experimental Results and Discussion

1) Effects of pH upon the Half-Wave Potential ($E_{1/2}$) and the Limiting Current (i_l).—The polarographic waves of nitrourea at various pH are shown in Fig. 1.

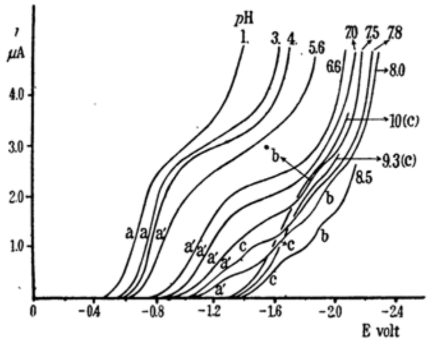

Fig. 1. Polarograms of 1×10^{-4} mol./l. Nitrourea.

Relationships of pH–$E_{1/2}$ (vs. S.C.E.) and of pH–i_l are shown in Fig. 2 and Fig. 3, respectively. The polarographic waves of urea and urea nitrate are not found at any pH under the same condition. It is evident that the above reduction waves are those of N-NO_2 radical. The wave symbolized as the (a) wave at pH 1–3, is the stable wave, and the relationship between concentration and i_l is linear over the range 1–10×10^{-4} mol./l.[4].

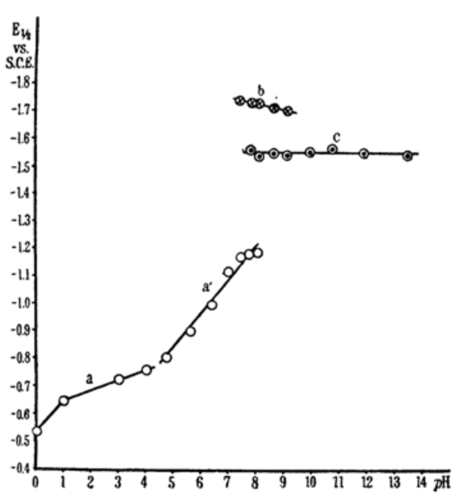

Fig. 2. Relationship between pH and $E_{1/2}$ (vs. S.C.E.)
○ —— (a) and (a′) waves
⊗ —— (b) wave
⊙ —— (c) wave

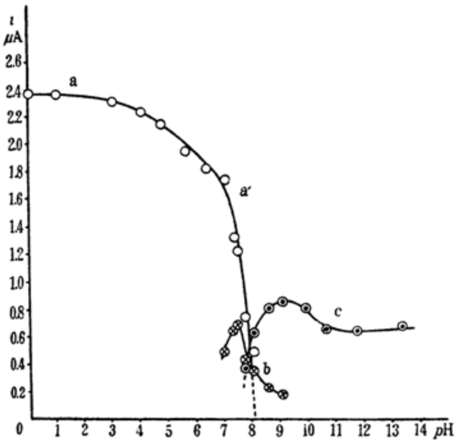

Fig. 3. Relationship between pH and i_l (conc. 1×10^{-4} mol./l.)

The (a′) wave, appeared above pH 3, decreases in its height. The double waves, (a′) and (b), appear above pH 7. Since the $E_{1/2}$ of (b) wave shifts considerably to the reduction potential of supporting electrolyte, it is presumed the polarogram below pH 7 is single wave in its appearance. After the (a′) wave vanishes completely, the trace of (b) wave and the growing (c) wave exist around pH 9. The triple waves are found in range of pH 7.7–8.5. These are considered to be similar to the split polarographic waves reported in the studies of maleic and fumalic acids[5]. Only the (c) wave exists above pH 9.3 stably.

2) Effects of the Height of Mercury Reservoir and of Temperature upon the Limiting Current.—Table I represents the relationship between the effective height of mercury reservoir, h_{eff}, and the limiting current.

TABLE I
DEPENDENCE OF THE EFFECTIVE HEIGHT OF MERCURY RESERVOIR ON THE LIMITING CURRENT OF 1×10^{-4} mol./l. NITROUREA
TEMPERATURE: 25°C

		pH 1.04		pH 5.10		pH 7.01	
h_{eff}	$h_{eff}^{1/2}$	i_l	$i_l/h^{1/2}$	i_l	$i_l/h^{1/2}$	i_l	$i_l/h^{1/2}$
cm.		μa.		μa.		μa.	
57	7.55	3.07	0.41	2.16	0.29	2.12	0.28
47	6.86			1.91	0.28		
37	6.08	2.50	0.41	1.69	0.28	1.74	0.29
32	5.66	2.30	0.41				
27	5.20	2.02	0.39	1.47	0.28	1.39	0.27
22	4.69	1.91	0.41	1.22	0.26	1.23	0.26
17.5	4.18			1.12	0.27	1.04	0.25
15.5	3.94	1.70	0.43				

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[4] K. Namba and K. Suzuki, *Journal of the Industrial Explosives Society*, Japan, 15 171. (1954).

[5] P. J. Elving and I. Rosenthal, *Anal. Chem.*, 26, 1454 (1954).

		pH 7.99				
		(a)		(b)		(c)
h_{eff}	$h^{1/2}_{\text{eff}}$	i_l	$i_l/h^{1/2}$	i_l	$i_l/h^{1/2}$	i_l
cm.		μa.		μa.		μa.
57	7.55	0.545	0.072	0.650	0.086	0.437
47	6.86	0.509	0.074	0.562	0.082	0.437
37	6.08	0.481	0.079	0.495	0.081	0.408
32	5.66	0.452	0.080	0.437	0.077	0.437
27	5.20	0.422	0.081	0.373	0.072	0.437
22	4.69	0.399	0.085	0.335	0.072	0.408
17	4.12	0.378	0.092	0.282	0.069	0.408

The fact that the limiting current at pH 1.05, 5.10 and 10.68 are proportional to $h^{1/2}$ means that these currents are controlled by the diffusion process; whilst the limiting current of the split polarographic wave such as the (c) wave at pH 7.99 is independent of the effective height of the mercurry reservoir, i.e., it can be concluded that the limiting current of the split wave shows the characteristics of kinetic current.

The relationships between the temperature and the limiting current at pH 2.20 and 5.20 is shown in Table II. Since the decomposition of nitrourea is acceralated in proportion to the increase of both temperature and pH, particularly in alkaline[4], it is impossible to obtain the above relationship except in the case of comparatively strong acidic media where nitrourea is actually stable.

TABLE II

INFLUENCE OF THE TEMPERATURE ON THE LIMITING CURRENT OF 1×10^{-4} mol./l. NITROUREA

pH 2.20			pH 5.20	
t, °C	i_l, μa.	Temp. coeff., %	t, °C	i_l, μa.
22.8	2.28	av. 1.30	26.4	2.15
26.7	2.42		36.3	2.42
36.3	2.78		44.0	2.22
45.0	3.08		51.9	1.98
54.7	3.44			

The temperature coefficient of the limiting current is about 1.30% per degree at pH 2.20 and it is almost equal to that of the diffusion current. At pH 5.20, it was impossible to account for the temperature coefficient in sake of the decomposition which induced the decrease of height in the limiting current despite the increase of temperature.

3) Calculation of the Electron Number for Reduction (n).—Since the reduction process of nitrourea in alkaline media seems to be kinetically controlled, it is not reasonable to calculate n in such a region, by assuming a proper diffusion coefficient (D) in the Ilkovič equation. Therefore, we only calculated n in the range of pH 1–3, where nitrourea is considered stable. We could not find out the proper value of the anion such as $NH_2{\cdot}CO{\cdot}NH{\cdot}COO^-$, the molecular size and weight of which are almost similar to those of nitrourea. The anion we chose was that of malonamic acid, $NH_2{\cdot}CO{\cdot}CH_2{\cdot}COO^-$, whose electroconductivity in infinite dilution was 35.5 Ω^{-1} cm^2 [6]. Inserting this value into the equation: $D_0 = 2.67\times10^{-7}\ \lambda_i^0/Z$ cm^2 sec^{-1} (where λ_i^0 is the electroconductivity of ion in infinite dilution and the ionic value of ionized substance (Z) is 1), we obtained 9.49×10^{-6} cm^2 sec^{-1} for the D_0 value. The calculated n's through this method, were 5.25 and 5.22 at pH 1.04 and 3.05, respectively (where $m^{2/3}$ is 1.98 mg./sec. and $t^{1/6}$ are 1.20 sec. in both cases).

Assuming the mechanism of reduction of nitrourea with five electrons, we must suppose the tetrazane compound such as that shown in the following formula

$$2NH_2{\cdot}CO{\cdot}NH{\cdot}NO_2 + 10H^+ + 10e$$
$$= NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 + 4H_2O$$

However, such tetrazane compound would be too unstable to exist. Further investigation on this problem by means of another direct method such as the controlled potential electrolysis will be necessary.

Summary

1) The relationship of pH–$E_{1/2}$ (vs. S.C.E.) and of pH–i_l of nitrourea under the dropping mercury electrode was studied.

2) It is presumed from the experiment on the effect of the effective height of the mercury reservoir and of temperature upon i_l that i_l will follow the diffusion law in acidic solution.

3) The electron number consumed for reduction was calculated by assuming the diffusion coefficient.

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[6] Randolt - Börnstein, "Physikalisch - Chemische, Tabellen", Eg. III, Verlag von Julius Springer, Berlin (1936), S. 2044.