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Electrolytic Reaction of ω -Amino Compounds and Their Acyl Derivatives. IV. The Electrolytic Preparation of the ω -Amino Acids by the Acidic Electrochemical Oxidation of Their Corresponding N-Acetylpolymethylenediamines. (Comparative Studies on the Acidic Electrochemical Oxidation of Simple Diaminoalkanes with Their N-Acetyl Compounds)

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1. Introduction

The author has already shown in previous papers¹⁾ that (a) the terminal aminomethyl groups (I) of simple ω -amino acids or lower primary alkyl amines, were relatively stable to the acidic electrochemical oxidation in sulfuric acid because of the formation of their terminal ω -ammonium groups (II), while, on the contrary, (b) their N-acylation (III) caused to make those derivatives very reactive and be readily oxidized to their corresponding mixed acid imides (IV).

where R are alkyl or ω' -carboxyalkyl groups and R' are methyl or γ -carboxy-n-propyl group.

Based on the principles underlying the above facts, the author tried to establish the electrochemical preparation of simple ω -amino acids either (a) from their corresponding ω -amino alcohols (V) or (b) from their N-acetyl polymethylenediamines (VI) in sulfuric acid using PbO_2 - Pb or Pt anode.

By means of the former (a) method the author already prepared simple α - or ω -amino acids such as γ -amino-n-butyric acid²⁾, and glycine, α -, β -alanine and δ -amino-n-valeric acid³⁾ from δ -amino-n-butyl alcohol and ethanolamine, β -, γ -amino-n-propyl alcohol and ϵ -amino-n-amyl alcohol respectively.

Since there were few studies on these kinds of the electrochemical preparation of ω -amino acids starting from the N-acylpolymethylenediamines, following the principle of the latter (b) method, the author studied on the comparative electrolytic oxidation of the lower diaminoalkanes (ethylene-, propylene-, trimethylene- and hexamethylenediamine) with their N-acetyl derivatives. Thus, from these N-acetyl compounds (VI) the author could prepare electrolytically their corresponding ω -amino acids (VI') in fairly satisfactory yields as follows: glycine (PbO_2 : 64/Pt: 54 mol%), α -alanine (37/21), β -alanine (75/35), ϵ -amino-n-caproic acid (44/50). Conversely, (c) every parent diamines (VII) were stable to these oxidation in sulfuric acid owing to their two terminal ammonium groups (VII').

Reported at the autumn meeting (Sept., 1958 in Shizuoka and Nov., 1959, in Nagoya) of the Tokai Section of the Chem. Soc. of Japan.

The original written in Japanese can be seen in *Denki-Kagaku* **29**, 106 (1961).

(VI)

(VI')

(VII)

(VII')

2. Experimental

A. Preparation of N-Acetyl Derivatives The monoacetylation of diaminoalkanes was carried out by Aspinall's⁴⁾ method (d) as follows: three moles of diamine (IX) were mixed with one mole of ethyl acetate (VIII) and after standing over several days foreign substances were distilled off at reduced pressure, and then N-acetyldiamine (X) was obtained by vacuum distillation of the residual liquid, leaving a small quantity of crystalline N,N'-diacetyl compounds (XI).

(VIII)

(IX)

(X)

(XI)

These results are listed in Table 1.

Table 1 N-Acetyl and N,N'-Diacetylalkylenediamines
(m.p., b.p., Purities of Neutralization, Kjeldahl's Total
Nitrogen Contents and Yields by mol%)

Diamines no. of C-atom (position)	N-Acetylalkylenediamines				N,N'-Diacetyldiamines		
	b.p. °C/mm	neut.- pur. %	T-N%/[calc.]	mol %	m.p. °C	mol %	T-N%/[calc.]
C ₂ (1, 2)	138—9/11 ^a	103.8	21.75*/[27.53]	85	167—9 ^c	4.2	17.27*/[19.43]
C ₃ (1, 2)	131—3/5	100.0	24.75/[24.12]	83	—	—	—
C ₄ (1, 3)	151—2/12 ^b	105.8	24.02/["]	65	—	—	—
C ₆ (1, 6)	183—5/11	97.7	16.82*/[17.70]	30	123—4 ^d	0.5	13.24*/[13.93]

a: 125—30°/5³⁾, b: 130—40°/5, 130°/3⁴⁾, c: 172°⁵⁾ d: 125—5°⁶⁾, * hardly oxidized by the
Kjeldahl decomposition (HgO) of about 4 hours and obtained too lower values.

Table 2 Ethylenediamine and Its N-Acetyl Derivatives

		Ethylenediamine	N-Acetyletthylenediamine	
anode		PbO ₂	PbO ₂	Pt
concentration in 2N H ₂ SO ₄		0.245 M/1	0.42	0.37
temperature, C°		18—19	17—18	17—19
voltages, V		2.45—2.55	2.45—2.5	2.85—3.0
oxidizabilities (F/mo.e) NH ₂ -N/Total-N %	(2)	12.5	23.0	35.0
	(4)	18.0	—	52.0
	(6)	—	55.5(5F)	59.0
	(8)	29.0	—	—
Glycine, mol %		—	64.0	54.0

B. Electrolysis and Results The comparative electrochemical oxidation of diaminoalkanes with their N-acetyl derivatives in 2*N* sulfuric acid were carried out by the similar methods as previously reported¹⁾, using PbO₂ - Pb or Pt anode and Pb cathode under the conditions as follows: C.D. 2A/dm² (PbO₂) or 4A/dm² (Pt), 6-9 F/mole, at room temperature, in undivided cells. The degrees of oxidation of these electrolytes were determined by the NH₃-N/Total-N (Kjeldahl) per centages at 2, 4, 6 and 8 F/moles, respectively. The electrolytes oxidized were treated by the same methods as those in the last report⁷⁾ and each amino acid was isolated as the insoluble substance from the alcoholic washings of the final residues.

These results are summarized in Tables 2, 3, 4 and 5, and the oxidizabilities of these compounds are presented in Figs. 1, 2, 3 and 4, respectively, by the curves on which their NH₃ - N/T - N values are plotted against the current quantities used (Faradays per mole).

Table 3 Propylenediamine and Its α -N-Acetyl Compound

		Propylenediamine	α -N-Acetylpropylenediamine	
Anode		PbO ₂	PbO ₂	Pt
concentration in 2 <i>N</i> H ₂ SO ₄		0.47 M/l	0.13	0.25
temperature, °C		23-31	23-24	22.5-24.5
voltages, V		3.0-3.2	2.9-3.0	3.1-3.2
oxidizabilities (F/mole) NH ₃ -N/Total-N %	(2)	—	35.1	25.2
	(4)	27.8 (3.3F)	53.3	45.6
	(3)	39.3 (4.7F)	65.7	57.2
α -Alanine	mol %	—	37.3	21.0
	m.p.	Vol. Acid 10.7 mol %	n.d. 258-9°/[275-30°]	
Kjeldahl-N		(Acet.a. ?)	15.72%/[15.71]	

Table 4 Trimethylenediamine and Its N-Acetyl Compound

		Trimethylenediamine	N-Acetyltrimethylenediamine	
anode		PbO ₂	PbO ₂	Pt
concentration in 2 <i>N</i> H ₂ SO ₄		0.157 M/l	0.125	0.153
temperatures, C°		13—21	22—24	22—24
voltages, V		3.0—3.05	2.8—3.0	2.8—3.2
oxidizabilities (F/mole) NH ₃ -N/Total-N %	(2)	4.8 (3F)	43.0 (3F)	—
	(4)	—	—	40.0 (4.4F)
	(3)	14.3	52.5	—
	(8)	18.0	—	63.4
β -Alanine	mol %		75.4	34.6
	m.p.		193—7°/[197—30°]	
Kjeldahl-N			15.81%/[15.71]	

Table 5 Hexamethylenediamine and Its N-acetyl- and N,N'-diacetyl Compounds

		Hexamethylene- diamine+AcOH	N-Acetylhexamethylene-diam.		N,N'-Diacetylhexa- methylenediamine	
anode		PbO ₂	PbO ₂	Pt	PbO ₂	Pt
concentration in 2N H ₂ SO ₄		0.24 M/l	0.23	0.17	0.15	0.136
temperature, C°		11—15	15—5	14—15	17—22	18—20
voltages, V		2.6—7	2.45—6	2.7—3.0	2.5—8	3.0—3.2
oxidizabilities (F/mole) NH ₃ -N/Total-N %	(2)	—	39.2	22.7	—	—
	(4)	11.8	49.2	—	54.5 (3.8F)	43.8
	(3)	—	51.0	43.5	—	57.7 (3F)
	(8)	27.2	53.4	50.0	80.0 (9F)	83.1 (10F)
ε-Amino-n- caproic acid	mol %	little*	44.0	50.0	51.0**	33.0**
	m.p.	*(Succinic a.) 182—3°	193—9°/[197—8]		**(Adipic a.) 144—7°/[148—9]	
Kjeldahl-N		—	9.70/9.72%		Titration by 0.1N NaOH 0.0955 g : 13.01 cc/[13.20]	

e. Toyo Raiyon's sample, [N,10.60%, calculated from C₆H₁₄NO₂].

From these results it is considered that α , ω -diaminoalkanes (ethylene-, trimethylene- and hexamethylenediamine) are fairly resistant to electrochemical oxidation in sulfuric acid as presented by their relative lower slope curve of their oxidation rate in Figs. 1, 3 and 4, respectively. But, owing to its secondary amino group, propylenediamine (Fig. 2) is a little more easily oxidized than the other three α , ω -diaminoalkanes having two terminal primary amino groups. On the contrary, the N-acetyl- or N,N'-diacetyldiamines are always very readily oxidized to produce their corresponding ω -amino or dicarboxylic acids as shown by their sharp ascending oxidizability curves.

3. Conclusion

Thus, it is concluded that the electrochemical oxidation of the N-acetylpolymethylenediamines is one of the satisfactory methods of the electrolytic preparation of ω -amino acids. This investigation was supported in part by a research grant from Ministry of Education in 1958 and 1959.

Fig. 1 Oxidizability of ethylenediamine (E.D.) and N-acetyletylenediamine (AC-E.D.)

Fig. 2 Oxidizability of propylenediamine (P.D.) and α -N-acetylpropylenediamine (AC-P.D.)

Fig. 3 Oxidizability of trimethylenediamine (T.D.) and N-acetyltrimethylenediamine (Ac-T.D.)

Fig. 4 Oxidizability of hexamethylenediamine mixed with acetic acid (Hx.D+Ac) and N-acetyl (Ac-Hx.D.), N,N'-diacetylhexamethylenediamine (Ac-Hx-Ac),

(Received Jan. 8, 1960)

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Studies on the Negative Plate of Nickel Cadmium Alkaline Batteries.

III. The Overpotential in Solid Phase of the Cadmium Electrode in Alkaline Electrolyte

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Our study^{1), 2)} on the mechanism of the discharge of cadmium electrode in alkaline electrolyte has shown that the reaction process may be considered as occurring in the slow and quick ones. The former was reasonably explained on the basis of that the primary product (CdO or $\text{Cd}(\text{OH})_2$) reacts with the electrolyte and redeposits as $\text{Cd}(\text{OH})_2$. In this paper consideration is given of the electrochemical aspects of the quick process.

Experimental methods The method for preparing the electrode and measuring the overpotential was similar to that in the previous work¹⁾. Rapid potential changes were measured by a cathode-ray oscillograph with an accuracy of 1 mV, (vertical axis) and 8 μ sec. (horizontal axis) and a mechanical oscillograph. The electrolyte employed in this work was saturated with purified nitrogen and soluble cadmium salt.

Results It has been observed that the potential changes caused by the slow process occur between 10 or 20 seconds and 5 minutes after interrupting current. The values of the overpotentials in this process are hardly varied by the different current densities, and are small as compared with the total.

Representative shapes of potential changes caused by the quick process are shown in Figs. 1a, and 1b.