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Anodic Oxidation of Amines. VIII.[1] Oxidation of Ethane-1,2-diamines

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Anodic oxidation of ethylenediamines (ethane-1,2-diamines) was investigated by cyclic voltammetry and controlled potential electrolysis in aqueous carbonate buffer (pH 10) at a glassy-carbon electrode. The first wave of the diamines is developed at a lower potential than that of the corresponding β-alkanolamines. Among the oxidative bond cleavages, the relative amount of (α)C–(β)C bond fission is larger than that observed for β-alkanolamines and oxidative deamination is only observed after the (α)C–(β)C bond fission. A scheme for the reaction processes is proposed.

Keywords——ethane-1,2-diamine; anodic oxidation; (α)C–(β)C bond fission; C–N bond fission; carbonate buffer; glassy-carbon electrode

The anodic oxidation of an ethylenediamine (ethane-1,2-diamine) derivative was studied in connection with the anodic oxidation of aliphatic tertiary amines by Lindsay Smith *et al.*[2] The oxidation was conducted in methanol–water (30% v/v) containing sodium perchlorate and hydroxide. Formaldehyde was detected after the electrolytic oxidation of *N,N,N′,N′*-tetraethyl-ethane-1,2-diamine, but they did not determine the quantity of formaldehyde and did not detect the presence of acetaldehyde and the other expected products.

A recent study of the anodic oxidation of several different types of β-alkanolamines, $R^1R^2C(OH)CR^3R^4NR^5R^6$, performed in an aqueous carbonate buffer of pH 10 at a glassy-carbon electrode,[1] revealed that both the (α)C–(β)C and the C–N bonds are cleaved, and the substituents R^1—R^4 affect the oxidation potential of the first wave and the relative amounts of the bond cleavages.

In the present study, we performed the anodic oxidation of derivatives of ethylenediamine, *i.e.*, amines with an amino nitrogen in place of an oxygen of β-alkanolamines, and investigated the influence of the amino group on the anodic oxidation.

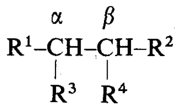
Results and Discussion

Cyclic Voltammetry

Cyclic voltammetric data for the ethylenediamines and the corresponding β-alkanolamines[1] measured in carbonate buffer of pH 10 at a glassy-carbon electrode are shown in Table I.

The ethylenediamines showed two or three oxidation waves and the oxidation potential of the first wave was less anodic than that of the corresponding β-alkanolamines, except for **3**.[1] The lower oxidation potential can be attributed to i) the larger electron-donating capacity of a diethylamino group than of a hydroxy group at the β-carbon and ii) stabilization of the radical by a through-bond interaction between the two nitrogens.[2,3] In contrast, the first wave of the amine **3**, which possesses both a phenyl group and a methyl groups on the α and β

TABLE I. Cyclic Voltammetric Data for Ethylenediamines and β-Alkanolamines at pH 10



$$R^1-\underset{\displaystyle R^3}{\overset{\alpha}{\mathrm{C}}\mathrm{H}}-\underset{\displaystyle R^4}{\overset{\beta}{\mathrm{C}}\mathrm{H}}-R^2$$

	R^1	R^2	R^3	R^4	E_{p1}[a]	i_{p1}[b]
	H	H	OH	NEt_2	0.70	1033
1	H	H	NEt_2	NEt_2	0.50	1028
	CH_3	H	OH	NEt_2	0.70	984
2	CH_3	H	NEt_2	NEt_2	0.40	988
	C_6H_5	CH_3	OH	NMe_2 (±-*erythro*)	0.55	809
	C_6H_5	CH_3	NMe_2	OH (Mixture)[c]	0.78	
3	C_6H_5	CH_3	NMe_2	NMe_2 (±-*threo*)	0.75	832

a) Volt *vs.* SCE.
b) Peak current of first wave in μA, mM^{-1}, cm^{-2}, $\mathrm{V}^{-1/2}$.
c) Mixture of ±-*erythro* and ±-*threo* isomers.[1]

positions, respectively, develops at a 200 mV more anodic potential than that of the corresponding β-alkanolamine.[1] This is probably because the greater steric hindrance around the nitrogens inhibits close approach of the amine to the electrode surface, and the effect should be larger than the electron-donating effect of another diethylamino group to the reaction center. In the case of **2**, it is quite difficult to decide which nitrogen is oxidized first, because the oxidation potentials of the nitrogens may not be very different. In the case of **3**, however, the first electron transfer may be considered to take place from the nitrogen of the R^3 group, since the E_{p1} value (0.78 V) is considerably higher than that of **2** (0.40 V), and a similar trend of potential values was observed in the oxidation of *N*-methylephedrine (0.55 V) and *N*-methylisoephedrine (0.78 V), in which electron transfer from the nitrogen attached on the carbon α to the phenyl group is more difficult. The values of E_{p1} shown in Table II indicate that a larger electron-donating effect of the β-substituent makes the E_{p1} value lower.

Nearly identical peak currents for **1** and 2-diethylaminoethanol suggest that the electron transfer involved in the first wave occurs at only one of the two diethylamino nitrogens of **1**.

The second wave of **1** cannot be ascribed to one of the oxidation products, **4**, unlike that observed in the oxidation of simple aliphatic amines.[4]

Controlled Potential Electrolysis

The ethylenediamines with two dimethylamino or diethylamino groups and the β-alkanolamine **6** were electrolyzed potentiostatically in the buffer of pH 10 with a glassy-carbon plate electrode (Table III).

When electrolysis was continued until the current decreased to nearly zero, 4—4.5 Faradays (***F***) per mol of the diamines was consumed, and this means that further oxidation of some of the primary oxidation products occurred. The electrolysis was, therefore, halted when *ca.* 2 ***F***/mol of the diamines had been consumed. As shown in Table III, the mode of the oxidative bond fission, as a whole, seems to be similar to that of β-alkanolamines,[1] but small differences are apparent: i) the yields of the products derived from (α)C–(β)C bond cleavage are slightly larger than those from β-alkanolamines, and ii) α-aminoketone, a product of (α)C–N bond fission, is not detected, whereas in the oxidation of 2-ethylaminoethanol, a trace amount of glycolaldehyde is detected.[1] The amounts of formaldehyde, benzaldehyde and acetaldehyde suggest that the substituent on the α or β carbons increases the rate of (α)C–(β)C

TABLE II. Cyclic Voltammetric Data for Ethylenediamines

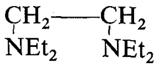
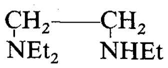
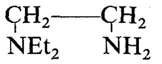
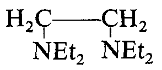
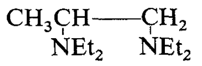
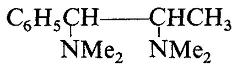
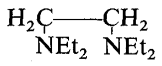
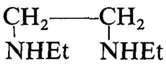
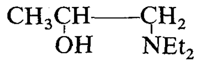
Compds.		E_{p1} (V *vs.* SCE)
1	 $\underset{\mathrm{NEt_2}}{\mathrm{CH_2}}-\underset{\mathrm{NEt_2}}{\mathrm{CH_2}}$	0.50
4	 $\underset{\mathrm{NEt_2}}{\mathrm{CH_2}}-\underset{\mathrm{NHEt}}{\mathrm{CH_2}}$	0.62
5	 $\underset{\mathrm{NEt_2}}{\mathrm{CH_2}}-\underset{\mathrm{NH_2}}{\mathrm{CH_2}}$	0.75

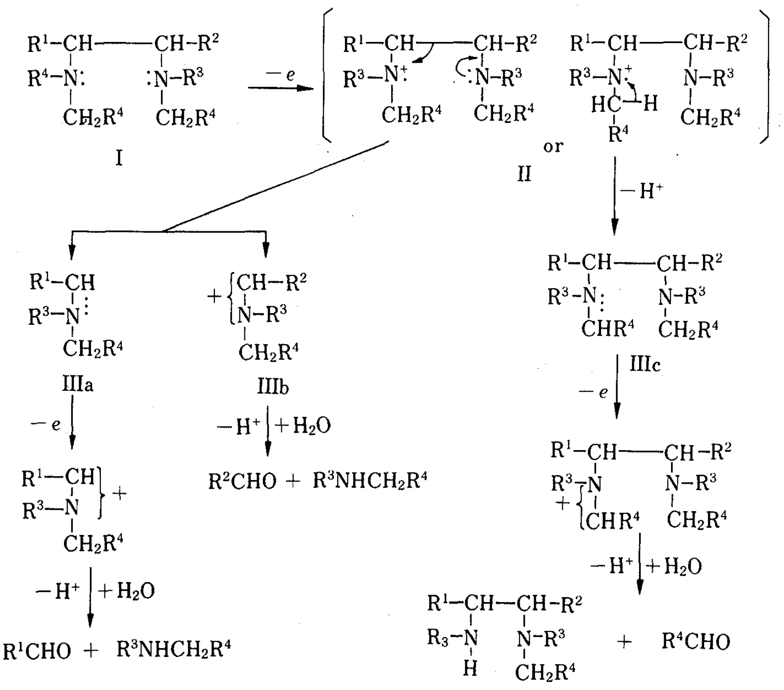
TABLE III. Anodic Oxidation Products from Ethylenediamines and a β-Alkanolamine

	Compds.	$E_{\mathrm{app.}}$[a]	n[b]	Products	Yields (%)[c] Mean (limit)
1	 $\mathrm{H_2}\underset{\mathrm{NEt_2}}{\mathrm{C}}-\underset{\mathrm{NEt_2}}{\mathrm{CH_2}}$	0.50	1.66—1.70	HCHO	29 (4)
				$NHEt_2$	29 (5)
				CH_3CHO	73 (4)
				4	75 (6)
2	 $\mathrm{CH_3}\underset{\mathrm{NEt_2}}{\mathrm{CH}}-\underset{\mathrm{NEt_2}}{\mathrm{CH_2}}$	0.40	1.52—1.76	HCHO	44 (4)
				CH_3CHO	86 (12)
				$NHEt_2$	86 (6)
3	 $\mathrm{C_6H_5}\underset{\mathrm{NMe_2}}{\mathrm{CH}}-\underset{\mathrm{NMe_2}}{\mathrm{CHCH_3}}$	0.75	2.01—2.06	C_6H_5CHO	76 (4)
				CH_3CHO	68 (6)
				$NHMe_2$	168 (4)
				HCHO	14 (0.3)
1	 $\mathrm{H_2}\underset{\mathrm{NEt_2}}{\mathrm{C}}-\underset{\mathrm{NEt_2}}{\mathrm{CH_2}}$	0.50	4.0	HCHO	55 (4)
				$NHEt_2$	52 (2)
				NH_2Et	11 (0.7)
				CH_3CHO	115 (7)
				4	15 (2)
				5	9 (4)
				 $\underset{\mathrm{NHEt}}{\mathrm{CH_2}}-\underset{\mathrm{NHEt}}{\mathrm{CH_2}}$	44 (4)
6	 $\mathrm{CH_3}\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{NEt_2}}{\mathrm{CH_2}}$	0.70	1.73—1.78	HCHO	23 (2)
				CH_3CHO	88 (3)
				$NHEt_2$	30 (1)

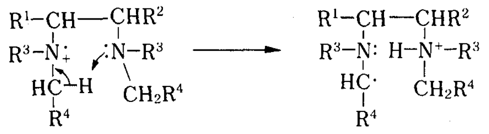
a) Applied potential in volts *vs.* SCE.
b) Faradays passed per mol of the amines.
c) Mol. % of starting amines.

bond fission in the order $H < Me$ (or Et) $< C_6H_5$, and this is similar to the order observed in the oxidation of β-alkanolamines.[1] The production and subsequent decomposition of α-aminoketones in the anodic oxidation could not be completely ruled out, because an α-aminoketone, diethylaminoacetophenone, was found to be decomposed upon being stirred in the buffer of pH 9 to give diethylamine, benzoic acid and unidentified compounds. The dependence of the total and relative amounts of oxidation products on the ammount of electricity consumed, however, strongly suggests that nearly all of the products are derived from the electrolysis and not from auto-oxidation or hydrolysis of the starting amine and the primary oxidation products. When 4 *F* of electricity per mol of **1** had been passed, further oxidative dealkylation of the other tertiary amino group was observed.

The following scheme is proposed.



The oxidation products of the electrolysis show that cleavage of the (α)C–(β)C bond becomes greater as the stability of the intermediates (IIIa) and (IIIb) increases. At present, it is not clear why deprotonation from one of the α carbons is completely suppressed. A possible explanation is that the electron-donating effect of the β amino group assists cleavage of the (α)C–(β)C bond in the manner shown in II of the scheme, and the six-membered transition state shown below may also assist deprotonation from one of the carbons, so that deprotonation from the other α carbon is negligible.



Experimental

Materials——Commercial *N,N,N',N'*-tetraethylethylenediamine (**1**) was converted into the oxalate and recrystallized from ethanol–water. mp 152—162 °C. *Anal.* Calcd for $C_{14}H_{28}N_2O_8$: C, 47.72; H, 8.01; N, 7.95. Found: C, 47.48; H, 8.05; N, 7.98. *N,N,N'*-Triethylethylenediamine (**4**), *N,N*-diethylethylenediamine (**5**) and *N,N'*-diethylethylenediamine were purchased from Aldrich Chemical Co. 1-Diethylamino-2-propanol (**6**) was prepared by diethylaminolysis of propylene oxide, converted into the oxalate and recrystallized from ethanol–ether. mp 88—91 °C. *Anal.* Calcd for $C_9H_{19}NO_5$: C, 48.86; H, 8.66; N, 6.33. Found: C, 48.74; H, 8.96; N, 6.23. δ (CCl_4): 1.00 (9H, m, Me × 3), 2.10—2.80 (6H, m, $-CH_2-$ × 3), 3.53 (1H, m, $>\underline{C}H-OH$), 3.99 (1H, s, $-OH$). 1,2-Di-(diethylamino)-propane (**2**) was prepared by the reaction of diethylamine and 1-diethylamino-2-chloropropane at room temperature. The distillate (69—86 °C/14 mmHg) was converted into the oxalate and recrystallized from ethanol–tetrahydrofuran (THF). mp 101—107 °C. *Anal.* Calcd for $C_{15}H_{30}N_2O_8 \cdot 1/5H_2O$: C, 48.69; H, 8.28; N, 7.57. Found: C, 48.79; H, 8.39; N, 7.50. δ (CCl_4): 0.98 (15H, t, Me × 5), 2.37 (11H, m, $-CH_2-$ × 5 and $-OH$). 1-Diethylamino-2-chloropropane was prepared by chlorination of (**6**) according to the literature.[5] ($\pm$)-*threo*-1,2-Di(dimethylamino)-1-phenylpropane (**3**) was prepared by the reaction of 1-chloro-1-phenyl-2-dimethylaminopropane with dimethylamine at room temperature for 50 h, then converted into the oxalate and recrystallized from ethanol. The assignment of the *erythro*- and *threo*- isomers of (**3**) was based on the nuclear magnetic resonance (NMR) spectra.[6] mp 125—128 °C. *Anal.* Calcd for $C_{17}H_{26}N_2O_8 \cdot 2/5H_2O$: C, 51.88; H, 6.86; N, 7.12. Found: C, 52.12; H, 6.77; N, 7.09. δ (CCl_4): 0.66 (3H, d, $J=4.5$ Hz,

–CH–C$\underline{H}_3$), 2.09 (6H, s, –CH(Me)N$\underline{Me}_2$), 2.25 (6H, s, –CH(C_6H_5)N$\underline{Me}_2$), 3.20 (1H, m, >C$\underline{H}$Me), 4.10 (1H, d, J= 8 Hz, >C$\underline{H}C_6H_5$), 7.15 (5H, m, –C_6H_5). 1-Chloro-1-phenyl-2-dimethylaminopropane was prepared by chlorination of (±)-*N*-methylephedrine. **2** and **3** were very hygroscopic.

Products Analysis——(a) Amines: Triethylamine was analyzed as its sulfonamide$^{7)}$ in the same manner as described previously. Diethylamine was analyzed spectrophotometrically as its sulfonamide$^{7)}$ and also as its carbamate by gas liquid chromatography (GLC).$^{8)}$ Dimethylamine was determined as its carbamate by GLC.$^{8)}$ *N,N*-Diethylethylenediamine, *N,N'*-diethylethylenediamine and triethylethylenediamine were determined spectrometrically as their sulfonamide. (Dabsyl method)$^{9)}$

(b) Aldehydes: Formaldehyde was determined by the method of Tanenbaum and Bricker.$^{10)}$ Acetaldehyde was determined by GLC (with ethanol as an internal standard) using a stainless steel column (2 m × 3 mm i.d.) packed with Ethofat 60/25 and maintained at 50 °C. Benzaldehyde was determined by GLC (with *N*-ethylacetamide as an internal standard) on a stainless steel column (2 m × 3 mm i.d.) packed with PEG 20M and maintained at 170 °C.

Apparatus and Procedures——(a) Cyclic Voltammetry: Cyclic voltammetry was carried out at 25 ± 0.05 °C with a substrate concentration of *ca.* 5 mM and a sweep rate of 0.05 V s^{-1} using the same apparatus and system as previously described.$^{1)}$

(b) Controlled Potential Electrolysis: The anolytes (*ca.* 1×10^{-2} M substrate in 0.1 M carbonate buffer) were electrolyzed at a glassy-carbon plate electrode (1 cm × 3 cm) with mechanical stirring on the same apparatus as previously described.$^{1)}$ The quantity of electricity consumed during electrolysis was measured with a Hokuto Denko HF-102 coulombmeter.

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