Oxidation of Hydroxylamine Derivatives. Part 5.[1] Anodic Oxidation of *N*-Hydroxy- and *N*-Alkoxy-ureas

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The anodic oxidation of the ureas EtNH·CO·NR^{1}OR^2 (1)—(5) has been studied by cyclic voltammetry and controlled potential electrolysis in acetonitrile at a glassy carbon electrode. The products of oxidation suggest that (1)—(3) result in cleavage between the carbon of the ethylaminocarbonyl group and the nitrogen of the hydroxyamino-group. Part of the intermediate radical of (3) undergoes disproportionation rather than cleavage of the carbon–nitrogen bond. In the case of (4) and (5), the cleavage of the carbon–nitrogen bond as observed in (1)—(3) is the main reaction route, but the possibility of N–N coupling of the intermediate followed by intramolecular rearrangement cannot be neglected. Oxidations were carried out in both divided and undivided cells.

In our earlier studies on the anodic oxidation of hydroxylamine derivatives,[2] including hydroxamic acid [3] and *N*-hydroxycarbamate,[1] we reported that the cation radicals initially generated at the electrode proceed along different reaction pathways depending on the substituents on the nitrogen and oxygen atoms.

Several *N*-hydroxyureas have been reported to exhibit a beneficial effect in the treatment of leukaemia [4] and also inhibit the growth of transplantable mammary tumours,[5] while many other hydroxyamino-compounds, including *N*-hydroxycarbamates, have been stated to be carcinogenic.[6]

As part of a continuing programme of the study of hydroxyamino-compounds, the anodic oxidation of *N*-hydroxy- and *N*-alkoxy-ureas was investigated. We found that most results can be explained in terms of the reaction of the ethylaminocarbonyl group derived from the first electron-transfer product with nucleophiles present in the system.

Compounds (1)—(10) were examined.

EtNH·CO·NR^1·OR^2

(1) R^1 = R^2 = H
(2) R^1 = Bu^t, R^2 = H
(3) R^1 = Et, R^2 = H
(4) R^1 = H, R^2 = Et
(5) R^1 = H, R^2 = Pr^i
(6) R^1 = H, R^2 = EtNH·CO
(7) R^1 = Bu^t, R^2 = EtNH·CO
(8) R^1 = Et, R^2 = EtNH·CO
(9) R^1 = EtNH·CO, R^2 = Et
(10) R^1 = EtNH·CO, R^2 = Pr^i

RESULTS AND DISCUSSION

Cyclic Voltammetry.—The results of voltammetry on a series of the ureas together with the oxidation products are shown in Table 1. The peak potentials of the first wave are slightly less positive than those for the corresponding hydroxamic acids [3] and *N*-hydroxycarbamates.[1] Substitution of an alkyl group on the hydroxy- or alkoxyamino-nitrogen did not affect the value of E_{p1}, whereas *O*-alkylation makes the potential of E_{p1} more positive as observed in the oxidation of other hydroxyamino-derivatives.[1-3]

In the presence of excess of amine, the *N*-hydroxyureas developed an extra oxidation wave at a lower potential [E_{p1}(excess base)] than E_{p1}. The shape of the extra wave for *O*-substituted derivatives was not well defined and was drawn out over an appreciable potential range, and the potential of the wave was considerably more positive than those of other derivatives. The extra oxidation peak is thought to be derived from the oxidation of a partially ionized form of the *N*-hydroxyureas, as observed in the oxidation of hydroxamic acids [3] and *N*-hydroxycarbamates.[1]

TABLE 1

Cyclic voltammetric data of hydroxy- and alkoxy-ureas and oxidation products in MeCN–0.1M-$NaClO_4$, 25° at a glassy carbon electrode

	E_p [a]				
Compound	E_{p1} (excess base) [b]	E_{p1}	E_{p1} (excess acid) [c]	E_{p2}	E_{p3}
(1)	0.85 (0.30)	1.15	1.47	1.60	(2.55) [d]
(6)		1.60		1.90	
$(EtNH)_2CO$		1.75			
(2)	0.84	1.14	1.45	1.55	2.10
(7)		2.05			
Bu^tNO		1.55			
(3)	0.70	1.15	1.54	2.25	(2.59) [d]
(8)		2.10			
CH_3CO		2.59			
(4)	1.10	1.45	1.60	2.15	
(9)		2.10			
(5)	1.13	1.45	1.63	2.10	
(10)		2.00			

[a] Peak potential, V *vs.* s.c.e. [b] Extra anodic wave appearing on addition of γ-collidine or isopropyl- or ethyl-amine (value in parentheses). [c] Extra anodic wave appearing on addition of excess of perchloric acid. [d] The potential of the wave was sometimes changed by the condition of the electrode surface.

When excess of perchloric acid was added, E_{p1} of the hydroxyureas shifted to a more positive potential, [E_{p1}(excess acid)]. The wave at E_{p1}(excess acid) is thought to be derived from protonated hydroxyureas.

The results obtained from the cyclic voltammetric study suggest that the first electron-transfer from the hydroxyureas occurs from electrons on the nitrogen–oxygen system.

As shown in Table 1, the second wave at E_{p2} and the

third wave at E_{p3} are close to the first wave of the corresponding oxidation products.

Controlled Potential Electrolysis and the Oxidation Process.—Controlled potential electrolyses of the hydroxy- and alkoxy-ureas were performed in acetonitrile containing 0.1M-sodium perchlorate using a glassy carbon-plate electrode at the potential of E_{p1} or E_{p1} (excess base). The initial concentration of the starting material was *ca.* 1.0—1.3 $\times$ 10^{-2}M, except where otherwise stated. The results are summarised in Tables 2 and 3.

N-*Ethyl*-N'-*hydroxyurea* (1).—When urea (1) was subjected to electrolysis in a divided cell (Table 2) no compounds containing the ethylaminocarbonyl group

TABLE 2

Products from electrolysis of hydroxy- and alkoxy-ureas in a divided cell

Compound	$E_{app.}$ [a]	n [b]	Products	Yield (%) [c]
(1)	1.15	1.70	$EtNH_2$	95 [d]
			N_2O	62 [h]
			CO_2	*i*
(1) [e]	0.30	1.94	$(EtNH)_2CO$	102
(1) [f]	0.30	1.92	$EtNHCONHPr^i$	97
(2)	1.15	1.08	$EtNH_2$	92 [d]
			Bu^tNO	54
			(2)	50
			CO_2	*i*
(3) [g]	1.15	3.52	$EtNH_2$	79
			MeCHO	71
			N_2O	*i*
			CO_2	*i*
(4)	1.45	0.79	(9)	18 [h]
			$EtNH_2$	54
			EtOH	64
			$EtNHCO_2Et$	19 [h]
			$(EtNH)_2CO$	5 [h]

[a] Applied potential, V *vs.* s.c.e. [b] Coulombs passed per mol of substrate. [c] Mole % based on starting material. [d] See Results and Discussion section. [e] Electrolysis with excess of ethylamine. [f] Electrolysis with excess of isopropylamine. [g] Electrolysis with excess of water. [h] Yield based on mole substrate/0.5 mole product = 100%. [i] Identified but not determined.

were detected in the solution after oxidation. This suggests that an electrolysis intermediate was completely decomposed to ethylaminocarbonyl cation, and this was attacked by water to give ethylamine and carbon dioxide as the conditions became acidic. As shown from cyclic voltammetry with excess of perchloric acid, the proton liberated upon oxidation of the hydroxyurea should protonate the starting urea. Thus the protonated urea (1) is less likely than water to react with the ethylaminocarbonyl cation. The ethylamine produced is also protonated under these conditions.

On the other hand, when the electrolysis of (I) was carried out in an undivided cell in which the electrogenarated proton is reduced to hydrogen at the counter electrode, a somewhat smaller n value was observed and *N*-ethyl-*N*-ethylaminocarbonyloxyurea (6) and *NN'*-diethylurea were obtained as well as ethylamine.

When electrolysis in a divided cell was carried out in the presence of an excess of ethyl- or isopropyl-amine, an n value was *ca.* 2 and almost quantitative amounts of *NN'*-diethylurea or *N*-ethyl-*N'*-isopropylurea, respectively, were obtained.

On the basis of the n value and product analysis,

TABLE 3

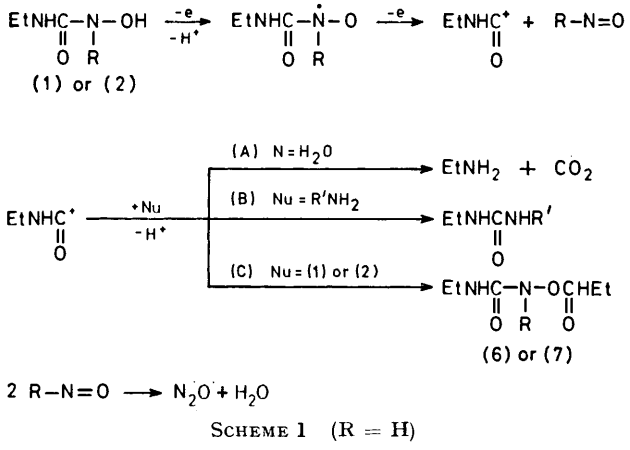
Products from electrolysis of hydroxy- and alkoxy-ureas in an undivided cell

Compound	$E_{app.}$ [a]	n [b]	Products	Yield (%) [c]
(1)	1.15	1.44	(6)	39 [d]
			$(EtNH)_2CO$	12 [d]
			$EtNH_2$	41
(2)	1.15	1.31	(7)	60 [d]
			$EtNH_2$	32
			Bu^tNO	74
			CO_2	*e*
(3)	1.15	1.75	(8)	61 [d]
			(6)	9 [d]
			$EtNH_2$	15
			MeCHO	8
(4)	1.45	0.82	(9)	52 [d]
			EtOH	58
			$EtNH_2$	19
			$EtNHCO_2Et$	Trace
(5)	1.55	1.06	(10)	22 [d]
			Pr^iOH	63
			$EtNH_2$	34
			CO_2	*e*

[a] Applied potential, V *vs.* s.c.e. [b] Coulombs passed per mole of the substrate. [c] Mole % based on starting material. [d] Yield based on mole substrate/0.5 mole product = 100%. [e] Identified but not determined.

Scheme 1 is proposed for the anodic oxidation of (1) and (2).

Routes (A) and (B), and route (C), correspond to two- and one-electron processes, respectively. The n value of 1.70 and the relative amount of the products observed during electrolysis in a divided cell without added amine



SCHEME 1 (R = H)

suggest that almost all the ethylaminocarbonyl cation was hydrolysed *via* route (A). The formation of slightly more ethylamine (95%) than expected is due to partial hydrolysis of protonated (1) under the conditions used both in the electrolysis and the fluorometric determination of the product.[7] The n value of 1.44 and the total yield of the oxidation products (*ca.* 66%, *i.e.*, 39/2 + 12/2 + 41%) (Table 3) suggest that *ca.* 70% of (1) was

oxidized to ethylaminocarbonyl cation, and the remaining (1) was attacked by the ion to give (6). Because the yield of *NN'*-dialkylureas from electrolysis in the presence of excess of amine was almost quantitative, it is reasonable to consider this latter reaction to be responsible for the formation of (6) rather than the similar intramolecular rearrangement of the N–N coupled dimer of the radical EtNHC(O)NRO· as observed in the oxidation of *N*-hydroxycarbamates.[1]

N'-*Ethyl*-N-*hydroxy*-N-*t-butylurea* (2).—The *n* value and the amount of 2-methyl-2-nitrosopropane (Table 2) suggest that about half the starting hydroxyurea (6) was subjected to two-electron oxidation and consequently the remainder remained in the protonated form. Cyclic voltammetry with γ-collidine, examined immediately after completion of the electrolysis, again showed an anodic wave with half the original height at E_{p1}. A higher yield of ethylamine (92%) than that expected on the basis of the *n*-value was also found and was shown to be due to hydrolysis of protonated (6).

In anodic oxidation in an undivided cell, the *n* value increased to 1.31, and (7) together with a decreased amount of ethylamine was obtained (Table 3).

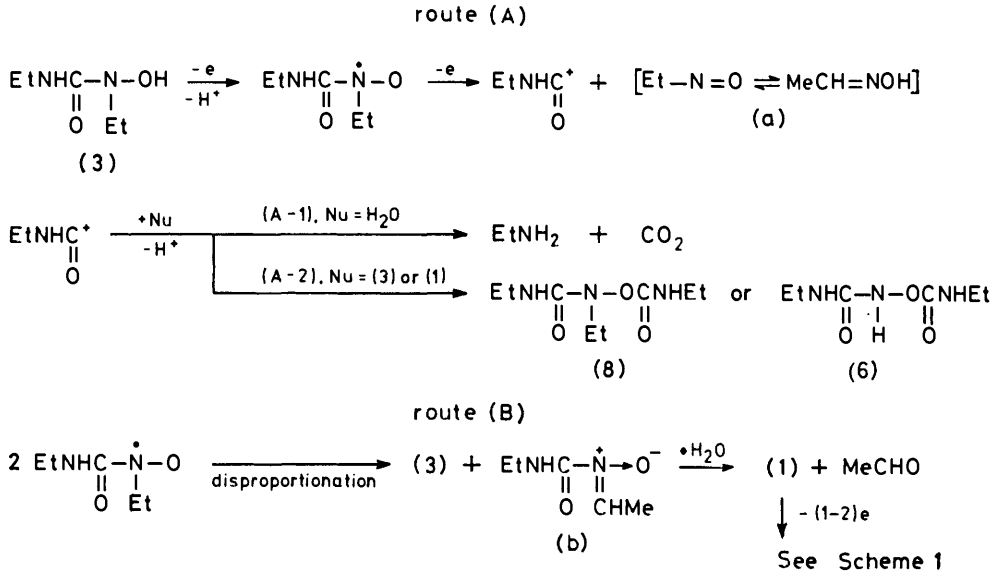
The products and their relative amounts indicate that the mechanism for the anodic oxidation of (2) is essentially identical with that of (1) except that the reaction of ethylaminocarbonyl cation with (2) increased, and the reaction with ethylamine was not observed.

NN'-*Diethyl*-N-*hydroxyurea* (3).—When (3) was subjected to anodic oxidation in a divided cell as above, the results fluctuated from run to run, and gave an *n* value of *ca.* 2—3 and 16—19% of acetaldehyde, ethylamine (*ca.* 50%), and considerable amounts of nitrous oxide. The cyclic voltammogram of the solution with γ-collidine after electrolysis showed that some (3) remained in the protonated form.

On the basis of the previous studies on hydroxamic acids[3] and hydroxycarbamates,[1] the formation and hydrolysis of an intermediate nitrone (b) (see Scheme 2) should occur after the first electron-transfer [route (B)], and the rate of the reaction should be affected by the amount of water present as a contaminant in acetonitrile. Then the electrolysis was performed with excess (1.25% v/v) of water. Under these conditions, the *n* value increased to nearly four and acetaldehyde (*ca.* 70%), ethylamine (*ca.* 80%), and considerable amounts of nitrous oxide and carbon dioxide were obtained (Table 2).

In oxidation in an undivided cell, the *n* value and the yields of ethylamine and acetaldehyde were noticeably reduced and (8) and (6) were obtained (Table 3).

We failed to detect the expected products, nitroso-



SCHEME 2

ethane[3] and/or acetaldoxime (a), by u.v. and gas chromatographic detection, respectively.

From the *n* value and the distribution of the oxidation products, Scheme 2 is proposed for the anodic oxidation of (3). As shown in Scheme 2, routes (A-1, Nu = H_2O), [A-2, Nu = (3) or (1)], and (B) correspond to two-, one-, and three- to four-electron processes, respectively. An over 70% yield of acetaldehyde, an *n* value of 3.5, and the formation of nitrous oxide observed for electrolysis in a divided cell shows that under the acidic conditions the larger part of the intermediate EtNHC(O)NEtO· undergoes disproportionation *via* route (B) and the remainder is subjected to further oxidation. Since nitrosoethane and acetaldoxime were not detected, the oxidation of protonated hydroxylamines does not occur at the potentials required to produce an *n* value of nearly four.

On the other hand, results of electrolysis in an undivided cell shows that the lesser part of EtNHC(O)-NEtO· undergoes disproportionation *via* route (B) and the major portion is further oxidized to ethylamino-

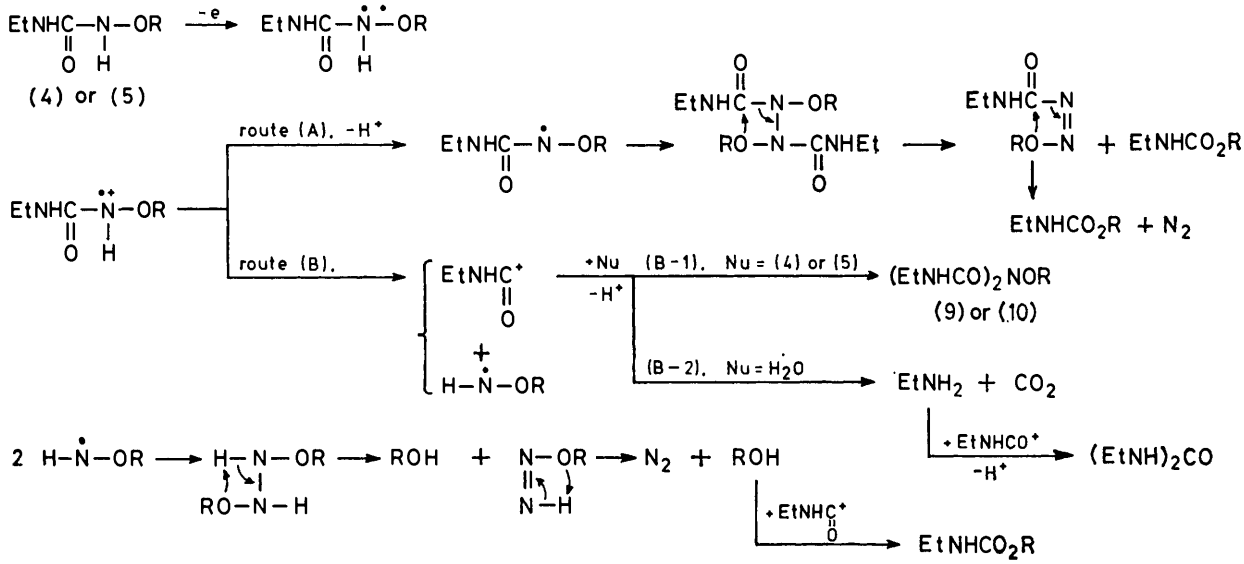
carbonyl cation, and the cation reacts with (3), water, and (1) to form (8), ethylamine, and (6), respectively.

N-Alkoxy-N'-ethylureas.—*N-Ethoxy-N'-ethylurea* (4). When (4) was electrolysed in a divided cell, the *n* value was *ca.* 0.8 and a biuret (9), ethylamine, ethanol, ethyl *N*-ethylcarbamate, and *NN'*-diethylurea were obtained. Upon electrolysis in an undivided cell the yield of (9) increased and that of ethylamine decreased, though the *n* value and the yield of ethanol were almost unchanged.

N-Ethyl-N'-isopropoxyurea (5). The electrolysis of (5) in an undivided cell also gave (10) and *n* value of *ca.* 1. The smaller yield of (10) than of (9) in the above case may be due to the larger steric effect of the propyl than of the ethyl group during the reaction of the ethylaminocarbonyl group with the nitrogen of the alkoxyurea.

On the basis of the *n* value, the products, and their relative yields, Scheme 3 is proposed for the anodic oxidation of (4) and (5). In the electrolysis of alkoxyureas, the expected products, a hydrazine derivative as obtained in the electrolysis of alkoxycarbamates,[1] was not obtained, but because of the similarity of the structures with those reported for N–N coupling,[1,7] this possibility cannot be excluded.

As shown in Scheme 3, routes (A) and (B-2), and route (B-1), correspond to one- and a half-electron processes, and oxygen and the conditions used for electrolysis. The reaction of the intermediate, ethylaminocarbonyl cation, with the nucleophiles present is worthy of note.



SCHEME 3

respectively. The results obtained suggest that the intermediate EtNHC(O)$\dot{\dot{N}}$H(OR) gives the products in the main *via* route (B). The fact that the electrolysis of (4) gave (9) even in a divided cell indicates that it is a weaker base than (1)—(3) as the latter three are not attacked by ethylaminocarbonyl cation because of protonation under these conditions.

Conclusion.—The anodic oxidation of the title compounds takes various reaction pathways as shown in Schemes 1—3 depending on the substituents on nitrogen

EXPERIMENTAL

Materials.—The hydroxyureas (1)—(3) and alkoxyureas (4) and (5) were prepared by the reaction of ethyl isocyanate with the corresponding hydroxylamine in ether at 0—10°.[8] Compounds (1) and (4) were purified by silica gel chromatography with elution by chloroform–methanol (10 : 1 v/v) and were recrystallized from ether–light petroleum. *N-Ethyl-N'-hydroxyurea* (1) had m.p. 123—125° (Found: C, 34.85; H, 7.8; N, 26.65. $C_3H_8N_2O_2$ requires C, 34.6; H, 7.75; N, 26.9%). *N-Ethoxy-N'-ethylurea* (4) had m.p. 43—45° (Found: C, 45.4; H, 9.2; N, 21.65. $C_5H_{12}N_2O_2$ requires C, 45.45; H, 9.15; N, 21.1%), δ($CDCl_3$) 1.15 and 1.25 (6 H, 2 × t, *J* 7 Hz, $NHCH_2CH_3$ and OCH_2CH_3), 3.28 (2 H, quint, *J* 7 Hz, $NHCH_2CH_3$), 3.85 (2 H, q, *J* 7 Hz, OCH_2CH_3), 5.75br (1 H, $NHCH_2CH_3$), and 8.0br (1 H, ONHCO). Compounds (2), (3), and (5) were purified by recrystallization from ether–n-hexane. *N'-Ethyl-N-hydroxy-N-t-butylurea* (2) had m.p. 57—59° (Found: C, 52.1; H, 10.0; N, 17.7. $C_7H_{16}N_2O_2$ requires C, 52.45; H, 10.05; N, 17.5%), δ(CD_3CN) 1.05 (3 H, t, *J* 7 Hz, CH_2CH_3), 1.31 (9 H, s, CMe_3), 3.12 (2 H, quint, *J* 7 Hz, $CONHCH_2CH_3$), 5.80—6.40 (1 H, NH), and 7.14 (1 H, s, OH). *NN'-Diethyl-N-hydroxyurea* (3) had m.p. 54—55° (Found: C, 45.3; H, 9.1; N, 21.45. $C_5H_{12}N_2O_2$ requires C, 45.45; H, 9.15; N, 21.2%). *N-Ethyl-N'-isopropoxyurea* (5) had m.p. 83—85° (Found: C, 48.85; H, 9.65; N, 19.35. $C_6H_{14}N_2O_2$ requires C, 49.3; H, 9.65; N, 19.15%), δ(CD_3CN) 1.09 and 1.20 (9 H, t and d, *J* 7 Hz, CH_2CH_3 and $CHMe_2$), 3.18 (2 H, quint, *J* 7 Hz, $NHCH_2CH_3$), 3.89 (1 H, sept, *J* 6 Hz, $CHMe_2$), 6.05br (1 H, $NHCH_2CH_3$), and 7.88 (1 H, s, ONHCO).

Commercial reagent grade acetaldoxime was used without further purification. Nitrous oxide was purchased from Nishio Kogyo. 2-Methyl-2-nitrosopropane was prepared according to the method of Stowell.[9] Commercial reagent

grade *NN'*-diethylurea was recrystallized from ether–ethanol. N-*Ethyl*-N'-*isopropylurea* was prepared by the reaction of ethyl isocyanate with 1 mol. equiv. of isopropylamine in ether and recrystallized from ether–ethanol, m.p. 153—155° (Found: C, 55.25; H, 11.1; N, 21.5. $C_6H_{14}N_2O$ requires C, 55.350 H, 10.85; N, 21.5%), δ($CDCl_3$) 1.11 and 1.14 (9 H, t and d, *J* 7 Hz, CH_2CH_3 and $CHMe_2$), 3.18 (2 H, quint, *J* 7 Hz, $NHCH_2CH_3$), 3.86 (1 H, m, *J* 7 Hz, $-CHMe_2$), and 4.80—5.70 (2 H, NH).

The oxidation products (6)—(10) were prepared separately by the reaction of ethyl isocyanate with 1 mol. equiv. of (1)—(5), respectively, in ether or 1,4-dioxan containing potassium carbonate. N-*Ethyl*-N'-*ethylaminocarbonyloxyurea* was purified by silica gel column chromatography with elution by chloroform–methanol (19 : 1 v/v) and was recrystallized from ether–light petroleum, m.p. 103—104° (Found: C, 41.1, H, 7.55; N, 23.75. $C_6H_{13}N_3O_3$ requires C, 41.15; H, 7.5; N, 24.0%), δ(CD_3CN) 1.07 and 1.10 (6 H, 2 × t, *J* 7 Hz, CH_2CH_3), 3.17 (4 H, quint, *J* 7 Hz, $NHCH_2CH_3$), 5.50—6.40 (2 H, CONHEt), and 7.98 (1 H, CONHOCO). N'-*Ethyl*-N-*ethylaminocarbonyloxy*-N-t-*butylurea* (7) was purified by silica gel column chromatography with elution by methanol–chloroform (1 : 40 v/v) and was recrystallized from ether, m.p. 158—160° (Found: C, 51.8; H, 9.15; N, 18.15. $C_{10}H_{21}N_3O_3$ requires C, 51.95; H, 9.15; N, 18.15%), δ(CD_3CN) 1.03 and 1.08 (6 H, 2 × t, *J* 7 Hz, CH_2CH_3), 1.31 (9 H, s, CMe_3), 3.12 (4 H, quint, *J* 7 Hz, CH_2CH_3), and 5.60—6.60 (2 H, NH). NN'-*Diethyl*-N-*ethylaminocarbonyloxyurea* (8) was recrystallized from ether–light petroleum, m.p. 93—95° (Found: C, 47.2; H, 8.55; N, 20.45. $C_8H_{17}N_3O_3$ requires C, 47.25; H, 8.45; N, 20.7%), δ($CDCl_3$) 1.00—1.30 (9 H, m, 3 × CH_2CH_3), 3.05—3.76 (6 H, m, *J* 7 Hz, 3 × CH_2CH_3), 6.25br (1 H, NH), and 6.69br (1 H, NH). N-*Ethoxy*-N'-*ethyl*-N-*ethylaminocarbonylurea* (9) was purified by silica gel column chromatography with elution by chloroform–methanol (20 : 1 v/v) and was distilled under reduced pressure, b.p. 108—112° at 0.02 mmHg (Found: C, 47.65; H, 8.25; N, 20.8. $C_8H_{17}N_3O_3$ requires C, 47.25; H, 8.45; N, 20.7%), δ(CD_3CN) 1.14 and 1.27 (9 H, 2 × t, *J* 8 Hz, 2 × $NHCH_2CH_3$ and OCH_2CH_3), 3.28 (4 H, quint, *J* 8 Hz, $NHCH_2CH_3$), 4.05 (2 H, quart, *J* 8 Hz, OCH_2CH_3), and 7.55br (2 H, $NHCH_2CH_3$). N'-*Ethyl*-N-*ethylaminocarbonyl*-N-*isopropoxyurea* (10) was purified by silica gel column chromatography and was distilled under reduced pressure. The oil obtained solidified upon cooling, m.p. 62° (Found: C, 50.05; H, 8.8; N, 19.8. $C_9H_{19}N_3O_3$ requires C, 49.75; H, 8.8; N, 19.35%), δ(CD_3CN) 1.10 and 1.22 (12 H, t and d, *J* 7 Hz, CH_2CH_3 and $CHMe_2$), 3.18 (4 H, quint, *J* 7 Hz, 2 × CH_2CH_3), 4.26 (1 H, sept, *J* 6 Hz, $CHMe_2$), and 6.80—7.65 (2 H, NH).

Cyclic Voltammetry.—Cyclic voltammetry was performed with the apparatus described previously.[1] The electrode system consisted of a glassy carbon indicator electrode, a glassy carbon counter electrode, and a saturated calomel reference electrode (s.c.e.). Measurements were made at 25 ± 0.05° with substrate concentration of *ca.* 5mM and with a scanning rate of 0.05 V s^{-1}. The concentration of the supporting electrolyte, sodium perchlorate, was *ca.* 0.1M.

Controlled-potential Electrolysis.—Electrolyses were performed with a Hokuto Denko HA 101 potentiostat. Electrolysis in a divided cell was carried out with 100 ml of anodic solution in a H-type cell. The anodic compartment was separated with a sintered glass disc and methylcellulose plug containing *ca.* 1M-sodium perchlorate. A vessel (60-mm diameter × 90-mm length) containing 100 ml of electrolyte was used for electrolyses in the undivided cell. A glassy carbon plate, 40 mm × 25 mm, was used for the anode. The reference electrode was an aqueous saturated calomel electrode with an agar plug. The solution was stirred with a magnetic stirrer. The quantity of electricity consumed was measured with a Hokuto Denko HF-102 coulometer. The initial concentrations of the ureas and of sodium perchlorate were 1—1.5 × 10^{-2} and 0.1M, respectively.

Product Analyses.—(a) *Products from oxidation of* (1): (6), NN'-*diethylurea, and ethylamine.* After completion of the electrolysis, the solvent was evaporated under reduced pressure and the residue was separated from sodium perchlorate by extraction with chloroform. The extract was evaporated to dryness and the residue was subject to silica gel t.l.c. with chloroform–methanol (8 : 1 v/v) as eluant. *NN'*-Diethylurea and (6) had R_F values of 0.85 and 0.70, respectively. These compounds were isolated by silica gel column chromatography and were identified by comparing their i.r. and n.m.r. spectra with those of authentic samples. Quantitative analysis was performed on a t.l.c. analyser (Iatron Laboratories model TH-10) with an aluminium oxide chromarod (Chromarod A) using 1 μl of condensed solution from electrolysis and the chromarod was chromatographed with chloroform as eluant. Ethylamine was analysed as its sulphonamide.[10]

(b) *Products from oxidation of* (2): (7) *and* 2-*methyl*-2-*nitrosopropene.* Compound (7) was isolated from the electrolysed solution and its structure was identified and the yield determined in a similar manner as described for (6). 2-Methyl-2-nitrosopropane was estimated by measuring the absorption in the visible light region, $\lambda_{max.}$ (CH_3CN) 745 nm (ε 44.4).

(c) *Products from oxidation of* (3): (8), (1), *and acetaldehyde.* Compounds (1) and (8) were isolated from the electrolysed solution and were determined as described for (1). Acetaldehyde was estimated by g.l.c. using 0.5 μl of electrolysed solution with an internal standard. A stainless steel column (2 m × 3 mm) packed with PEG 20M (Nishio Kogyo) was used at 80° in a JEOL JGC 20K chromatograph.

(d) *Products from oxidation of* (4): (9), *ethanol, and ethyl* N-*ethylcarbamate.* Compound (9) was isolated from the electrolysed solution and was purified by distillation under reduced pressure, then determined in a similar manner as described for (1). Ethyl *N*-ethylcarbamate and ethanol were estimated by g.l.c. packed with PEG 20M and maintained at 170 and 180°, respectively.

(e) *Products from oxidation of* (5): (10) *and isopropyl alcohol.* Compound (10) was isolated from the electrolysed solution and was purified by distillation under reduced pressure, b.p. 112—128° at 0.02 mmHg, and determined in a similar manner as described for (6). The yield of isopropyl alcohol was determined by g.l.c. packed with PEG 20M and maintained at 80°.

(f) *Other products.* *N*-Ethyl-*N'*-isopropylurea produced on oxidation of (1) in the presence of an excess of isopropylamine was extracted with chloroform. Evaporation of chloroform gave an amorphous precipitate. The precipitate was recrystallized from ether and was identified by comparing its n.m.r. spectrum with that of an authentic sample. Quantitative analysis of the urea was performed on a t.l.c analyser in a similar manner as described for (6). Quantitative and qualitative analyses of nitrous oxide were done

by g.l.c. using a stainless steel column packed with molecular sieves 5A and maintained at 150°.[11] Carbon dioxide was identified by g.l.c. using dry ice–acetonitrile as an authentic sample with the conditions for analysis used for nitrous oxide.

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