chloric acid at 0° to the residue and refluxing for 1 hr gave an additional 20.96 mmol of hydrogen. The total amount of hydrogen evolved was 33.80 mmol, indicating that 4.58 equiv of hydride per mole of oxime ester was consumed in the reduction.

Reduction of O-Acetyl Cyclohexanone Oxime.—From 3.15 g (20.3 mmol) of O-acetyl cyclohexanone oxime[21] and 135.5 mequiv of hydride ion there was obtained 1.2420 g (62.0%) of **cyclohexylamine** and 0.8640 g (94%) of **ethanol** as determined by glpc analysis.

Registry No.—Diborane, 19287-88-8; cyclohexylamine oxalate, 19293-66-4; N-dicyclohexylmethylhydroxylamine, 19293-67-5; N-1,3-diphenyl-2-propylhydroxylamine, 19293-68-6; O-methyl N-methylindole-3-carboxaldehyde oxime, 19293-69-7; O,O'-dimethyl 1,3-diphenyl-1,3-propanedione dioxime, 19293-70-0; O-benzyl heptanal oxime, 19293-71-1; O-methyl 4,4'-dimethoxybenzophenone oxime, 19293-72-2; O-methyl dicyclohexyl ketone oxime, 19293-73-3; O-methyl *p*-dimethylaminobenzaldehyde oxime, 19293-74-4; bis(*p*-methoxyphenyl)methylamine (picrate), 19293-75-5; dicyclohexylmethylamine, 7560-83-0; dicyclohexylmethylamine (phenylthiourea derivative), 19293-50-6; 3-methylamino-1-methylindole (phenylurea derivative), 19293-51-7; 1,3-diphenyl-1,3-propanediamine, 19293-52-8; 1,3-diphenyl-1,3-propanediamine (dipicrate derivative), 19293-53-9.

Acknowledgment.—We wish to extend our appreciation to the Office of Naval Research for support of this work.

---

[21] Z. Czuros, K. Zech, G. Dely, and E. Zuloy, *Acta Chim. Acad. Sci. Hung.*, **1**, 66 (1951).

Electrochemical Dealkylation of Aliphatic Amines

PAUL J. SMITH AND CHARLES K. MANN

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received December 3, 1968

The anodic oxidation of tertiary aliphatic amines in nonaqueous systems has been studied, using tri-*n*-propylamine in acetonitrile as a model. The reaction causes dealkylation to produce secondary amine and aldehyde. The reaction product contains unreactive tertiary and secondary amine salts in a 2:1 ratio. When water is rigorously excluded, elemental nitrogen is a major product. The investigation included 12 amines; effect of unsymmetrical substitution on the dealkylation was studied. Solvents used were tetrahydrofuran, dimethyl sulfoxide, water, ethanol–water, methanol, and 1,2-dimethoxyethane.

The electrochemical reactions of aliphatic amines, unlike aromatic amines, have received relatively little attention. Dapo and Mann[1] examined the oxidation of triethylamine in dimethyl sulfoxide and reported an 80% recovery of triethylammonium salt. Russell[2] proposed that, on oxidation in acetonitrile, it undergoes a one-electron reaction to produce the cation radical which was thought to abstract a hydrogen atom from either the solvent or water to form triethylammonium salt and cyanomethylene or hydroxyl radicals.

An examination of the cyclic voltammetric oxidation of a series of aliphatic amines showed that, although the reactions in every case appeared to be irreversible one-step oxidations, substituent inductive effects could be correlated with voltammetric peak potentials for secondary and tertiary amines.[3] This indicates that the primary site of attack is the nitrogen atom and that abstraction of the first electron is the potential-determining step.

In related work, O'Donnell and Mann[4] have studied the anodic oxidation of aliphatic amides and Barnes and Mann[5] have reported on anodic reactions of aliphatic primary amines. Weinberg and Brown[6] and Smith and Mann[7] have examined the anodic methoxylation of tertiary aliphatic amines.

A detailed investigation of the oxidation of amines by chlorine dioxide has been reported by Rosenblatt and coworkers.[8-10] This chemical oxidation causes dealkylation of a tertiary amine to produce secondary amine and the appropriate aldehyde. As a result of kinetics studies involving isotope substitution, it was concluded that the reaction of tertiary amines involves an electron transfer in the rate-determining step.

The same types of products have been obtained on oxidation with N-bromosuccinimide,[11] manganese dioxide,[12] and ozone.[13] In several cases, evidence of the formation of enamines has been found. Leonard and Morrow[14] produced stable cyclic enamines by mercuric acetate oxidation of amines. Buckley, *et al.*,[15] trapped enamines formed from simple amines by reaction with quinones to form stable colored compounds. However, enamines produced from amines with simple straight-chain substituents are insufficiently stable to be isolated. They decompose to the secondary amine and the aldehyde.

The present work has involved examination of the reactions of several tertiary and secondary amines in acetonitrile, dimethyl sulfoxide, tetrahydrofuran, and water. The results indicate that the main reaction, in the presence of at least small amounts of water, involves

---

[1] R. F. Dapo and C. K. Mann, *Anal. Chem.*, **35**, 677 (1963).
[2] C. P. Russell, *ibid.*, **35**, 1291 (1963).
[3] C. K. Mann, *ibid.*, **36**, 2424 (1964).
[4] J. F. O'Donnell and C. K. Mann, *J. Electroanal. Chem.*, **13**, 157 (1967).
[5] K. K. Barnes and C. K. Mann, *J. Org. Chem.*, **32**, 1474 (1967).
[6] N. L. Weinberg and E. A. Brown, *ibid.*, **31**, 4058 (1966).
[7] P. J. Smith and C. K. Mann, *ibid.*, **33**, 316 (1968).
[8] D. H. Rosenblatt, A. J. Hayes, Jr., B. L. Harrison, R. A. Streaty, and K. A. Moore, *ibid.*, **28**, 2790 (1963).
[9] D. H. Rosenblatt, L. A. Hull, D. C. Deluca, G. T. Davis, R. C. Weglein, and H. K. R. Williams, *J. Amer. Chem. Soc.*, **89**, 1158 (1967).
[10] L. A. Hull, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, and R. C. Weglein, *ibid.*, **89**, 1163 (1967).
[11] S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 4905 (1957).
[12] H. B. Henbest and M. J. W. Stratford, *ibid.*, 995 (1966).
[13] H. B. Henbest and M. J. W. Stratford, *ibid.*, 711 (1964).
[14] N. J. Leonard and D. F. Morrow, *J. Amer. Chem. Soc.*, **80**, 371 (1958).
[15] D. Buckley, S. Dunstan, and H. B. Henbest, *J. Chem. Soc.*, 4880 (1957).

dealkylation of the starting material to produce secondary amine, aldehyde, and protons.

Results

Constant potential electrolyses have been carried out in acetonitrile–sodium perchlorate solutions at platinum and graphite anodes over a range of potentials from 0.35 to 2.10 V *vs.* the silver reference electrode. Current-time behavior was observed; the number of coulombs of charge passed was measured and reaction products were examined. Tripropylamine was chosen as the initial subject of investigation; on the basis of these results, other amines and other solvents have been studied.

Tripropylamine reaction mixtures which had not been rigorously dried showed continuous decrease of current with time in approximately exponential decay at all potentials. Coulometric n values, the number of faradays of charge per mole of amine taken, amounted to 0.999 ± 0.001 at 1.90 V. This value was not affected by oxygen in the reaction mixture. At potentials of 1.00 V or less, the n value amounted to 0.976, significantly smaller than the value obtained at higher potentials. With oxygen present at low potentials, a considerable decrease in the n value, to around 0.82, was noted.

Results from oxidation of tripropylamine in acetonitrile, without rigorous exclusion of water, *i.e.*, the number of moles of water at least equal to the initial number of moles of amine, are presented in Table I. Products include tripropylammonium ions, dipropylammonium ions, and propionaldehyde. On the average, 93% of the nitrogen in the starting material was accounted for, and in some cases, with a graphite anode, this was as high as 98%. Except when oxygen is present, there is no indication that change of potential affects the yields. When oxygen was present, with either platinum or graphite anodes, N,N-dipropylformamide was recovered in varying yields amounting to a maximum of 17 mol % of the initial amine at 0° in an oxygen-saturated solution. With large amounts of water, yields of various products were unreproducible.

Most experiments were carried out with sodium perchlorate as the supporting electrolyte. However, the following were also used: silver nitrate, calcium perchlorate, magnesium perchlorate, tetraethylammonium perchlorate, lead perchlorate, potassium perchlorate, and tetramethylammonium tetrafluoroborate. Results were substantially independent of the identity of the supporting electrolyte except that no reaction at all occurred with lead perchlorate and with magnesium perchlorate. Platinum anodes were used in most of the work; however, substitution of spectrographic graphite anodes made no difference except in the recoveries of propionaldehyde, which were consistently higher with graphite than with platinum anodes.

To study the role of water in this reaction, careful precautions were taken to achieve water concentrations at the level of 5 mol % of starting amine or less. The results, presented in Table II, were quite different from those obtained with moderate amounts of water present. Specifically, yields of tripropylammonium ions, dipropylammonium ions, and propionaldehyde were reduced to approximately 65, 10, and 5%, respectively. About 25% of the original amine nitrogen was recovered as nitrogen gas. A significant and variable yield of nonvolatile, presumably polymeric material, was formed.

In addition to tripropylamine, a number of other tertiary amines was examined. The results, presented in Table III, are generally comparable with those obtained for tripropylamine. The exceptions are trimethylamine, for which no dealkylation was observed, and triallylamine, which formed an insoluble deposit on the anode that prevented the reaction from going to completion.

In addition to acetonitrile, methanol, water, dimethyl

TABLE I

PRODUCTS OF OXIDATION OF TRIPROPYLAMINE IN ACETONITRILE

Potential[a]	n	% Pr_3NH^+ [b]	% $Pr_2NH_2^+$ [b]	% EtCHO[b]	O_2 present	Anode
1.00	0.82	65	15		Yes	Pt
1.90	0.999	70	Present[c]		Yes	Pt
0.50	0.976	70	22	15	No[d]	Pt
0.55	0.965	74	22		No	Pt
0.55[e]	0.973	68	20		No	Pt
0.55[f]	0.980	72	22		No	Pt
0.55[g]	0.960	71	22		No	Pt
0.80	0.85	71	26	27	Yes	Graphite
1.00[h]	0.97	77	33	15	Yes	Pt
1.00[h]	1.05	87	10	15	Yes	Pt
1.00[h]	0.80	54	53	48	Yes	Pt
1.00[i]	0.68				Yes	Pt
1.00[j]	0				Yes	Pt
1.00[k]	0.81, 0.77				Yes	Pt
1.20[l]	0				Yes	Pt
1.00[m]	0.85				Yes	Pt
1.00[n]	0.83, 0.90				Yes	Pt
0.60[o]	0.98	70	17	*c*	No	Pt
0.40	0.85	58	26	27	Yes[p]	Graphite
0.50	0.84				Yes[q]	Graphite

[a] Volts *vs.* Ag/$AgNO_3$ (0.10 *M*). [b] Mole per cent of starting amine. [c] Qualitatively detected by glpc. [d] Solutions degassed. [e] Reaction at 0°. [f] Reaction at 25°. [g] Reaction at 50°. [h] Solvent, 10% water. [i] $Ca(ClO_4)_2$ (0.10 *M*). [j] $Mg(ClO_4)_2$ (0.10 *M*). [k] Et_4NClO_4. [l] $Pb(ClO_4)_2$ (0.10 *M*). [m] $KClO_4$ (0.05 *M*). [n] $AgNO_3$ (0.2 *M*). [o] Me_4NBF_4. [p] $HCONPr_2$ (2%). [q] $HCONPr_2$ (5%).

TABLE II

TRIPROPYLAMINE OXIDATION PRODUCTS IN DRY ACETONITRILE

Potential	n	% Pr_3NH^+[b]	% $Pr_2NH_2^+$[b]	% EtCHO[b]	% H_2O[b]	% N_2[b]	Anode
0.50	0.86	65	11		0.7		Pt
1.25	0.82	61	13	7	0.7		Pt
0.80	0.96				5.1	25	Pt
0.80	1.00				c	9	Pt
0.80	0.91				c		Graphite

[a] Volts *vs.* Ag/AgNO$_3$ (0.10 *M*). [b] Mole per cent of starting amine. [c] Less than 5%.

TABLE III

OXIDATION PRODUCTS OF OTHER AMINES IN ACETONITRILE

Compound	Potential[a]	n	% tertiary[b]	% secondary[b]	% aldehyde[b]
Dicyclohexylethylamine	1.00	0.97	38	22,[c] 2.5[d]	e
Cyclohexyldiethylamine	1.00	0.76	50	22,[d] 1[f]	e
	1.00[g]		37	9,[d] 1[f]	6[h]
Tribenzylamine	1.31	0.94	69	25	36
Tri-*n*-butylamine	1.20	0.95	62	20	16
Trimethylamine	0.70		98	0	0
	0.80		100	0	0
	1.00[i]		56	0	0
Allyldiethylamine	1.00	0.87	57	18[f]	
N-Methyldibenzylamine	0.90	0.87	60	24	34[j]
N,N-Dimethylbenzylamine	0.80	0.65[k]	51	11,[l] 11[m]	16[n]
Ethyldiisopropylamine	0.85	0.89	62	22[o]	p
Di-*n*-propylamine	1.40[i]	0.89		70[q]	
	1.30	0.88		61	0
	1.30	0.90		68	0

[a] Volts *vs.* AgNO$_3$ (0.10 *M*). [b] Mole per cent of starting amine. [c] Dicyclohexylamine. [d] Cyclohexylethylamine. [e] Acetaldehyde present. [f] Diethylamine. [g] Approximately same number of moles of water and amine. [h] Acetaldehyde. [i] Water content 5 mol % of amine. [j] Benzaldehyde. [k] Precipitate formed when sample added. [l] Methylbenzylamine. [m] Dimethylamine, estimated from benzaldehyde recovery. [n] Benzaldehyde and formaldehyde present. [o] Diisopropylamine. [p] Acetaldehyde present, acetone absent. [q] N_2 (22%) recovered; $PrNH_2$ shown to be present.

TABLE IV

PRODUCTS FROM REACTIONS IN SOLVENTS OTHER THAN ACETONITRILE

Compound	Solvent	Potential, V	n	% tertiary[a]	% secondary[a]	% aldehyde[a]
Tripropylamine	30% EtOH–H_2O[b]	1.00[c]	0.85	72	18	
	Tetrahydrofuran[b]	1.00[d]	0.69	70	10	10
	Dimethyl sulfoxide[b]	0.80[e]	0.95	80	0	
Triethylamine	Water[f]	0.88[g]	0.93	50	35	20
	Water[f]	1.00[g]	0.98	47	27	28
	Water[f]	1.00[g]		54	40	44
N-Methyldibenzylamine	Methanol[b]	0.50[h]		61	18[i]	j
Tripropylamine	Dimethoxyethane[b,k]	0.80[l]	1.06	65	10[m]	
Triallylamine	Water		0.93	93		

[a] Mole per cent of starting amine. [b] Pt anode. [c] Aqueous sce. [d] Ag/AgNO$_3$ (0.10 *M*)–MeCN/NaClO$_4$ (0.05 *M*)–THF. [e] Ag/AgNO$_3$ (0.10 *M*)–MeCN/NaClO$_4$ (0.25 *M*)–DMSO. [f] Graphite anode. [g] Ag/AgNO$_3$ (0.10 *M*)–MeCN/NaClO$_4$ (0.25 *M*)–H$_2$O. [h] Ag/AgNO$_3$ (0.10 *M*)–MeOH. [i] Dibenzylamine plus a small yield of N-methylbenzylamine. [j] Small amount of benzaldehyde present. [k] Water content 5 mol % of starting amine. [l] Ag/AgClO$_4$ (0.005 *M*)–DME. [m] Also recovered 24% N$_2$.

sulfoxide, and dimethoxyethane were used as solvents. Results are presented in Table IV. In general, the products of amine oxidation are not greatly affected by changes in solvent. One point of difference was that there appeared to be no dealkylation when the reaction was run in dimethyl sulfoxide. Reactions run in water showed widely varying yields from one experiment to the next.

The behavior of dipropylamine was investigated in acetonitrile, both with and without precautions concerning water content. In either case, the *n* value was 0.90 and about 70% of starting amine was recovered as dipropylammonium ion. In dry electrolyses, nitrogen gas and propylamine were also detected. They were produced in variable amounts. Probably the water content, the exact potential setting used, and the duration of the experiment caused the variations noted.

Discussion

General Reaction Scheme.—In considering a reaction scheme for the model compound, salient points from the experimental results that must be accommodated include involvement of the nitrogen atom in the initial electron transfer, which is rate determining; formation of secondary amine, aldehyde, and protons; and the coulometric *n* of 0.97 electrons per molecule of amine taken. The steps outlined in eq 1–6 are suggested. These provide for an initial transfer of one electron to the anode to form a cation radical **1** which is probably very short lived, losing a proton to leave the neutral radical **2**. This can either undergo

$$(C_3H_7)_3N \xrightarrow{-e^-} \underset{\mathbf{1}}{(C_3H_7)_3N\cdot^+} \qquad (1)$$

$$\mathbf{1} \xrightarrow{-H^+} \underset{\mathbf{2}}{(C_3H_7)_2\ddot{N}\dot{C}HC_2H_5} \quad (2)$$

$$\mathbf{2} \xrightarrow{-e^-} (C_3H_7)_2\ddot{N}\overset{+}{C}HC_2H_5 \longleftrightarrow \underset{\mathbf{3}}{(C_3H_7)_2\overset{+}{N}{=}CHC_2H_5} \quad (3)$$

$$\mathbf{2} \longrightarrow (C_3H_7)_3N + \underset{\mathbf{4}}{(C_3H_7)_2\ddot{N}CH{=}CHCH_3} \quad (4)$$

$$\mathbf{3} + H_2O \longrightarrow (C_3H_7)_2NH + C_2H_5CHO + H^+ \quad (5)$$

$$\mathbf{4} + H_2O \longrightarrow (C_3H_7)_2NH + C_2H_5CHO \quad (6)$$

further anodic oxidation in step 3 or can disproportionate in step 4. The possibility of **2** undergoing dimerization or reaction with the solvent or with water was considered. The data in Table I show that about 90% of the starting amine has been recovered as protonated secondary and tertiary amines, making it impossible for dimerization to be an important process when some water is present. No evidence of dimerized products was found, even in small amounts. The role of water is discussed below. Both reaction paths, disproportionation or direct oxidation of radical **2**, give the same coulometric results and produce the same products.

Since the amines are the strongest bases in the system, they are protonated as the reaction proceeds. It is possible that the secondary amine is protonated as it is formed; another possibility is that it may undergo further reaction at the anode before being protonated. If it is protonated as it is formed, the over-all reaction is given in eq 7. This makes n equal to 1.000 and

$$2(C_3H_7)_3N + H_2O \xrightarrow{-2e^-} (C_3H_7)_2NH_2^+ + C_2H_5CHO + (C_3H_7)_3NH^+ \quad (7)$$

gives 50 mol % each of tripropylammonium salt, dipropylammonium salt, and propionaldehyde, which is not in accordance with experimental results. If it is assumed that a substantial amount of the secondary amine undergoes oxidation before being protonated, as an extreme, all of the protons produced in the initial dealkylation steps would be accepted by unreacted tertiary amine. The over-all reaction would then be that shown in eq 8. According to the stoichiometry of

$$3(C_3H_7)_3N + H_2O \xrightarrow{-2e^-} (C_3H_7)_2NH + C_2H_5CHO + 2(C_3H_7)_3NH^+ \quad (8)$$

eq 8, the yield of tripropylammonium salt is 67 mol % of the starting amine and neutral dipropylamine is a product. However, it has been ascertained that the recovery of electrolyzed dipropylamine is incomplete, amounting to 70%, with an n value of 0.90 under both wet and dry conditions. If these results are used empirically to modify the stoichiometry of eq 8, the expected recoveries will be 67% tripropylammonium ion, 33% propionaldehyde, and 23% dipropylammonium ion, with an n value of 0.97. Actual experimental results follow: n, 0.97; tripropylammonium salt, 67–72%; dipropylammonium salt, 20–22%; aldehyde, 15%. The experimental values for n and for amine salt recoveries agree reasonably well with the predicted values; that for propionaldehyde is low. This is discussed below.

As an indication that dipropylamine may be undergoing oxidation, as suggested above, the ultraviolet (uv) absorption spectrum of the tripropylamine reaction mixture shows a peak at 320 mμ. A peak at the same wavelength, but five to ten times as intense is observed when dipropylamine is electrolyzed. It is possible that this may be caused by a relatively small yield of a condensation product in the dipropylamine reaction.

Two reactions which, if competitive with the main scheme, would cause reduction of the secondary amine yield and increase in the tertiary amine yield are shown in eq 9 and 10.

$$\mathbf{1} + H_2O \longrightarrow (C_3H_7)_3NH^+ + OH\cdot \quad (9)$$

$$\mathbf{1} + CH_3CN \longrightarrow (C_3H_7)_3NH^+ + \cdot CH_2CN \quad (10)$$

The possibility that reaction 9 acts as a major source of protons to such an extent that the mechanism consists of steps 1, 2, and 9 in parallel with steps 1, 2, and 3 was considered. This would involve formation of significant amounts of hydroxyl radicals which presumably would form hydrogen peroxide. It was ascertained that these concentrations of hydrogen peroxide could be detected by cyclic voltammetry and were in fact absent at the end of an electrolysis. Oxygen gas, though detectable in much smaller quantities than would be produced by this scheme, was entirely absent. Similarly, there was no indication of tripropylamine oxide in significant quantities. However, we cannot exclude the possibility that this reaction occurred to a small extent. Reaction 10 like reaction 9 could be a major source of protons; however, it would lead to products characteristic of cyanomethylene radicals. In the anodic oxidation of amides,[4] succinonitrile was produced and attributed to dimerization of cyanomethylene radicals. It was sought in the products of all amine reactions examined, but was found only in the case of triallylamine oxidation. To achieve a significant reaction of triallylamine, it was necessary to operate at such high potentials that the solvent and perchlorate may have been involved in the reaction. If cyanomethylene radicals dimerize head to tail, the resulting ketenimine would be expected to be found ultimately as an amide. With oxygen excluded, no amide could be detected by infrared (ir) spectroscopy.

When yields derived from the reaction scheme are compared with experimental results, the major discrepancy is in the aldehyde recovery. Several factors may be operating. Although aldehyde in acetonitrile is unreactive at a platinum anode, the yields have been consistently smaller at platinum than at graphite. This may be caused by an electrocatalytic oxidation of aldehyde in the presence of small amounts of water. Such an oxidation would have no effect on the coulometric results, since the process of generating platinum oxide to react with aldehyde also produces protons which would make an equivalent amount of starting amine unreactive. In addition to electrocatalytic reaction of aldehyde, it is probable that condensation in the basic reaction solution occurs. We suggest that both these factors are important.

Throughout the discussion, it has been assumed that a sufficient supply of water was available to react as indicated and that it did in fact serve as the source of oxygen in the dealkylation. Other possible oxygen sources are dissolved oxygen and the perchlorate-supporting electrolyte. To determine the effect of dissolved oxygen, reactions were run with oxygen gas deliberately introduced. The result was a decrease in the value of n to 0.75 and a decrease in the recovery of tripropylammonium salt. N,N-Dipropylformamide was isolated from these reaction mixtures. This is presumed to be the result of reaction of oxygen with **2**, the product of step 2. Both manganese dioxide[12] and ozone[13] have been found to produce N,N-dialkylformamides from tertiary amines. An amino alcohol, indicated in eq 11 with tri-*n*-butylamine, was a suggested

$$(C_4H_9)_3N \xrightarrow[MnO_2]{O_3 \text{ or}} (C_4H_9)_2NCH(OH)C_3H_7 \longrightarrow HCON(C_4H_9)_2 + C_2H_5CHO \quad (11)$$

intermediate. With dissolved oxygen excluded in electrochemical reactions, no formamide is formed, but dealkylation, leading to aldehyde, does take place. Oxygen was routinely excluded from most reactions run in the course of this work. The possibility that perchlorate serves as an oxygen source was checked by substituting tetramethylammonium tetrafluoroborate for sodium perchlorate. The reaction products were not significantly changed, showing that perchlorate is not involved and indicating that water, the only reasonable remaining source of oxygen, is responsible.

The influence of water was investigated by performing reactions in systems on which extraordinary precautions were taken to exclude water. It was possible to reduce the amount of water in a reaction mixture to less than 5 mol % of starting amine. When this was done, it had a very noticeable effect on the reaction. Yields of tripropylammonium salt, dipropylammonium salt, and aldehyde were reduced. A significant fraction of amine nitrogen was recovered as gaseous nitrogen. Unlike "wet" reactions, a significant and variable fraction of the hydrocarbon portion of starting amine was recovered as a nonvolatile, presumably polymeric, material.

We interpret this to indicate that water is involved in reactions from which it is not rigorously excluded, that, if it were quantitatively excluded, a different reaction would occur. Recovery of reduced yields of secondary amine and very much reduced yields of aldehyde is thought to indicate that reactions 5 and 6 are being substantially blocked by the limited availability of water.

Although no exhaustive study of the dry reaction has been undertaken, some observations will be offered. The reaction in the absence of water caused degradation to form elemental nitrogen and a polymeric material, which suggests that a complex fragmentation process may take place. The possibility that the solvent might be involved was investigated by performing the reaction in rigorously dry dimethoxyethane. The results, given in Table IV, were quite similar to those obtained in acetonitrile, indicating that amine, rather than the solvent, is the probable source of nitrogen when the reaction is run in acetonitrile.

In the absence of water, it is difficult to suggest a plausible dealkylation mechanism, especially one that yields elemental nitrogen. Presumably, reactions 1–4 would be unaffected by removal of water. However, if this occurs, **3** would probably not be subject to further reaction, but would be present in the reaction products until the cell was opened, after which the remaining step of reaction 5 would occur. Examination of the products shows that this is not the case. With water excluded, reactions 1, 2, and 4 would produce **4.** The enamine, a weaker base than the corresponding saturated compound, would be oxidized, although probably at a smaller rate than that of the saturated amine. The product of this reaction apparently is subject to fragmentation, possibly resulting in formation of radical intermediates with the unshared electron on the nitrogen atom. Dimerization of this radical would produce a substituted hydrazine, which could be expected to be degraded to elemental nitrogen by anodic oxidation.[16]

Unsymmetrical Amines.—Results of oxidation of trialkylamines, presented in Table III, are generally similar to those for tripropylamine; however, examination of the products of oxidation of unsymmetrically substituted amines shows that dealkylation is not a random process. Cyclohexyldiethylamine, dicyclohexylethylamine, and ethyldisopropylamine lose mainly the ethyl group. N,N-Dimethylbenzylamine and N-methyldibenzylamine lose more of the benzyl groups than would be expected on a statistical basis. Allyldiethylamine loses mainly the allyl group.

Considering the reaction scheme presented, the N-methylbenzylamines would react through steps similar to 1, 2, 3, and 5, since an enamine is impossible. It is reasonable to expect that the benzyl group would be lost in preference to the methyl group, because the greater stability of the benzylic radical would tend to cause its formation to be favored. The same argument can be applied to the case of allyldiethylamine. In these examples, experimental results are in accord with the expected stabilities of the radicals.

This is not true, however, for the examples involving cyclohexyl or isopropyl groups. Preferential loss of these groups because of the greater stability of the corresponding tertiary radical, compared with a secondary radical, would be expected, but the reverse is observed. In these cases, the additional possibility of reaction *via* the enamine in steps 1, 2, 4, and 6 exists; on the basis of information presently available, a definite distinction cannot be made. From the voltammetric data,[3] it would appear that step 1 is rate determining. Therefore it is possible that sequences involving either steps 2 and 3 or steps 2 and 4 could occur so rapidly as to constitute a concerted process. In that event, it is possible that formation of the more stable tertiary radical, corresponding to **2** in eq 2, in a concerted process involving its disproportionation, results in a slower over-all rate for the sequence than when the less stable secondary radical is formed. The higher rate of the sequence involving the less stable radical would lead to the observed product. A similar rationale can be offered for the sequence 2–3, if it is postulated that the less stable radical would be oxidized more readily than the more stable radical. The observed products might also be accounted for by postulating that, for a concerted process involving steps 2 and 3, the necessity for planarity at the iminium group would favor its formation in the ethyl group rather than in the cyclohexyl or the isopropyl groups.

In considering the two proposed schemes, oxidation of

---

[16] D. M. King and A. J. Bard, *J. Amer. Chem. Soc.*, **37**, 419 (1965).

the radical (steps 1, 2, 3, and 5) and disproportionation to the enamine (steps 1, 2, 4, and 6), it is interesting to note that one compound examined, trimethylamine, although oxidized at the anode, did not undergo dealkylation. Trimethylamine is also one of the compounds for which enamine formation is impossible. Other compounds studied, the benzylmethylamines, are similarly incapable of forming enamines, but did undergo dealkylation. However, these compounds can react *via* the notably stable benzyl radical intermediate. This suggests that enamine formation is involved in dealkylation of simple aliphatic amines.

Experimental Section

Experimental Apparatus.—Electrolyses were performed with a conventional electronic potentiostat; current was integrated with a gas coulometer. H-type electrolysis cells fitted with ground joints to permit exclusion of atmospheric contamination were used. Unless otherwise noted, the reference electrode was a silver wire in contact with a 0.10 *M* $AgNO_3$ solution in acetonitrile which made contact, *via* an asbestos fiber sealed into Pyrex, with a solution of the supporting electrolyte in a guard tube which was similarly in contact with the solution in the anode compartment. Potentials are expressed relative to the reference electrode actually used, in all cases.

Reagents.—Tripropylamine was treated with benzoyl chloride, distilled under reduced pressure and stored over NaOH. No impurities were initially detectable by glpc. At the end of the work, this sample still assayed more than 98% pure. Other amines were the best grade available, generally with less than 2% impurities.

Acetonitrile was prepared by the procedure previously described.[17] Tetrahydrofuran and dimethoxyethane were distilled from lithium aluminum hydride immediately before use and were protected from atmospheric contamination. Reagent grade dimethyl sulfoxide was distilled under reduced pressure.

Sodium perchlorate was recrystallized from ethanol–water, dried under vacuum at 150°, and stored under vacuum over P_2O_5. Other reagents were reagent grade, generally used as received.

Electrolysis Procedure.—Supporting electrolyte and solvent were mixed in a reservoir fitted with joints to attach to the electrolysis cell and with tubulation to attach to a vacuum line. Solutions were degassed by, typically, three sequences of freezing and pumping with a mechanical pump. They were stored under an atmosphere of purified nitrogen or helium. Electrolysis cells were filled from the reservoir without contact with the atmosphere. Preelectrolysis was run at a potential about 0.1 V more anodic than that used for the reaction. Preelectrolysis typically involved less than 1% of the coulombs taken by the subsequent reaction. Electrolyses were carried on until no further decrease in current was noted. This required from 1 to 3 hr; residual currents were typically 0.2–0.5% of starting currents.

Reactant was introduced by syringe after preelectrolysis and samples of solutions and head space were similarly taken for analysis. Reaction currents were often recorded automatically. Reaction concentrations were generally in the range of 5–50 m*M;* supporting electrolyte concentration was in the range of 0.10–0.25 *M*.

Removal of Water.—Acetonitrile was dried by percolation through a 0.5 in. × 1 m bed of 3A molecular sieves directly into the solvent reservoir. All glassware was baked at 150° under vacuum prior to use. Supporting electrolyte was transferred to the reservoir, after which it was evacuated and held at 200° for several hours. By this process, water assays of the anode solution when the reaction was being run would reliably be down to 0.25 m*M*. Water assay in acetonitrile was done by glpc on Porapak Q at 175°.

Product Analyses.—Amines were generally determined by shaking the reaction mixture with NaOH and chromatographing as previously described.[18] Succinonitrile and N,N-dipropylformamide were similarly chromatographed. In all cases, unknowns were compared with valid samples. In some cases, uv absorption spectra of the volatile fraction of reaction products was used as a means of quantitative analysis for aldehydes. Nuclear magnetic resonance spectra were taken in CCl_4, CD_3CN, or $CDCl_3$ solutions, or neat, using a Varian A-60 spectrometer.

Registry No.—Tripropylamine, 102-69-2.

Acknowledgment.—The authors wish to acknowledge financial support from the National Institutes of Health through Grant G. M. 10064.

---

[17] J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

[18] J. F. O'Donnell and C. K. Mann, *ibid.*, **36**, 2097 (1964).