The Glow-discharge Reactions of Pyrrole, Pyrrolidine, and Butylamine*

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The glow-discharge reactions of pyrrole, pyrrolidine, and butylamine were carried out. Pyrrolidine produces a complex mixture of products, the most prevalent of which is NCH(R)CN (R: H, CH_3, and C_2H_5), and butylamine yielded primarily $CH_3(CH_2)_3N{=}CHR$ (R: CH_3, C_2H_5, and C_3H_7) along with $CH_3(CH_2)_3NHCH_2CN$, whereas pyrrole afforded a mixture of acrylonitrile, crotononitrile, benzene, α-methylpyrrole and β-methylpyrrole, together with large amounts of HCN. The formation of characteristic products, α-(1-pyrrolidinyl) nitrile derivatives with pyrrolidine, and the yield of butylaminoacetonitrile with butylamine can be explained by considering the formation of a resonance-stabilized α-cyanoalkyl radical as the most probable intermediate which attacks a nitrogen atom of pyrrolidine and that of butylamine or which recombines with pyrrolidine-*N*-radical and butylamine-*N*-radical.

Extensive studies of the reaction of organic compounds in a radiofrequency discharge have been carried out.[1-3] There has, however, been little or no attempt to study the discharge reaction of a series of simple amine derivatives. In this paper, the individual reactions of pyrrole, pyrrolidine, and butylamine (three different types of C_4 amine) in a radiofrequency discharge will be reported. These compounds were chosen in an attempt to ascertain the behavior of these three amines under the influence of radiofrequency discharge and to observe the formation of the various products resulting therefrom.

Experimental

The radiofrequency generator was operated at a fixed frequency of 28 MHz, with an output of up to 150 W. The operating pressure in the system was 2.0 Torr through all the runs. The products were collected in a liquid nitrogen trap (−196 °C), as has previously been described.[4]

Analysis. Gas chromatography was employed for quantitative analysis. A Shimadzu GC-4BPTF instrument was used with the following columns: 4.5 m, Silicon SE-30 for the analysis of liquid products (oven temp: 30—270 °C, program rate: 10 °C/min), with H_2 as the carrier gas. The gaseous products were analyzed on a 3-m column packed with silica gel at 150 °C, using N_2 as the carrier gas.

Radiofrequency Decomposition of Pyrrole. Pyrrole vapor was passed through the glow discharge (see Table 1). The major portion of the gas fraction collected in the liquid nitrogen traps was a mixture of ethylene (44.1%), acetylene (31.2%), ethane (20.0%), propylene (0.8%), and propane (0.9%) (Table 1, Run No. 2). Noncondensable products were obtained from the exhaust gas of the vacuum pump connected to the nitrogen traps. Upon gas-chromatographic analysis, they were found to contain only hydrogen and methane (0.21 g; CH_4 22%, H_2 78% in Run No. 2). The fractional distillation of the liquid products collected from several runs and NMR measurements of the resulting fractions showed the presence of hydrogen cyanide (bp 28—29 °C), acetonitrile, propionitrile, acrylonitrile, crotononitrile,[3] benzene, α-methylpyrrole, and β-methylpyrrole. Their mass spectra also confirmed these assignments. The NMR data of these compounds are shown below. Acrylonitrile: NMR (δ ppm in CCl_4): 5.60 (1H, m, $C\underline{H}_3CN$), 5.92 (1H, m, *trans* β-H), 6.10 (1H, m, *cis* β-H). Crotononitrile: NMR (δ ppm in CCl_4): 1.98 (3H, d.d, $C\underline{H}_3CH$), 5.24 (1H, d.q, $C\underline{H}CN$), 6.46 (1H, d.q, $CH_3C\underline{H}$). Benzene: NMR (δ ppm in CCl_4): 7.24 (s, aromatic H). α-Methylpyrrole: NMR (δ ppm in CCl_4): 2.12 (3H, s, CH_3), 5.72 (1H, m, C_3–H), 5.94 (1H, m, C_4–H), 6.34 (1H, m, C_5–$\underline{H}$). β-Methylpyrrole: NMR (δ ppm in CCl_4): 2.07 (3H, s, $C\underline{H}_3$), 5.88 (1H, m, C_4–H), 6.28 (1H, m, C_2–H), 6.40 (1H, m, C_5–H).

Radiofrequency Decomposition of Pyrrolidine. For 20 min, a 7.7-g portion of pyrrolidine was passed through a radiofrequency glow discharge (Table 2, Run No. 5). The condensable gaseous products consisted of ethylene (62.4%), acetylene (18.9%), propylene (9.6%), ethane (7.6%), and propane (1.5 %), while the noncondensable products were hydrogen and methane. Gas-chromatographic analysis indicated the presence of twelve constituents in the liquid products. A fractional distillation of the reaction mixture isolated acetonitrile, propionitrile, and butyronitrile. Three major unknown compounds were separated by preparative gas chromatography (Shimadzu GC-2C, Silicon DC 550, 4.5 m, H_2). By referring to their NMR spectra, these three compounds were identified 1-pyrrolidinylacetonitrile, 2-(1-pyrrolidinyl)propionitrile, and 2-(1-pyrrolidinyl)butyronitrile respectively.

The analytical data of the identified products were as follows. Acetonitrile: NMR (δ ppm in CCl_4): 1.94 (s, $C\underline{H}_3$-CN). IR: complete superimposable spectrum with an authentic sample. Propionitrile: NMR (δ ppm in CCl_4): 1.26 (3H, t, $C\underline{H}_3CH_2$), 2.32 (2H, q, $C\underline{H}_2CN$). Butyronitrile: NMR[δ ppm in $(CD_3)_2CO$]: 1.00 (3H, t, $C\underline{H}_3CH_2$), 1.62 (2H, m, $CH_3C\underline{H}_2CH_2$), 2.38 (2H, t, $C\underline{H}_2CN$). Pyrrole: NMR (δ ppm in CCl_4): 6.02 (2H, m, β-H), 6.52 (2H, m, α-H). 1-Pyrrolidinylacetonitrile: NMR (δ ppm in $CDCl_3$): 1.86 (4H, m, $C\underline{H}_2C\underline{H}_2$), 2.68 (4H, m, $C\underline{H}_2NC\underline{H}_2$), 3.68 (2H, s, $C\underline{H}_2CN$). IR (cm^{-1}): 2800 (=N–), 2230 (C≡N). MS (*m/e*): 110 (M^+). Found: C, 65.32; H, 9.00; N, 25.15%. Calcd for $C_6H_{10}N_2$: C, 65.42; H, 9.15; N, 25.43%. 2-(1-Pyrrolidinyl)propionitrile: NMR (δ ppm in $CDCl_3$): 1.48 (3H, d, $C\underline{H}_3CH$), 1.83 (4H, m, $C\underline{H}_2C\underline{H}_2$), 2.65 (4H, m, $C\underline{H}_2NC\underline{H}_2$), 3.88 (1H, q, $CH_3C\underline{H}$), IR (cm^{-1}): 2800 (=N–), 2220 (C≡N). MS(*m/e*): 124 (M^+). Found: C, 67.43; H, 9.80; N, 22.60%. Calcd for $C_7H_{12}N_2$: C, 67.70; H, 9.74; N, 22.56%. 2-(1-Pyrrolidinyl)-butyronitrile: NMR (δ ppm in $CDCl_3$): 1.08 (3H, t, $C\underline{H}_3CH_2$), 1.84 (6H, m, $CH_3C\underline{H}_2CH,C\underline{H}_2C\underline{H}_2$), 2.68 (4H, m, $C\underline{H}_2NC\underline{H}_2$), 3.67 (1H, t, $CH_2C\underline{H}CN$). IR (cm^{-1}): 2810 (=N–), 2240 (C≡N). MS (*m/e*) :138 (M^+).

Radiofrequency Decomposition of Butyronitrile. The glow-discharge reaction was carried out by means of a procedure similar to that described above. The condensable gaseous products in Run No. 9 were ethylene (44.2%), acetylene

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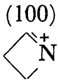
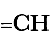
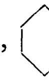
* Organic Reaction Employing the Glow Discharge. VII. Part VI: S. Kikkawa, M. Nomura, and Y. Morita, *J. Syn. Org. Chem. Jpn.*, **34**, 36 (1976).

(7.2%), propylene (15.3%), butene (2.0%), ethane (18.6%), and propane (12.7%).

The compounds with the same retention times as acetonitrile were separated from the reaction mixtures and were identified as such. Butylaminoacetonitrile was separated by preparative gas chromatography and identified on the basis of its NMR spectrum. Two other major components were identified as *N*-ethylidenebutylamine and *N*-butylidenebutylamine[5] by comparing the retention times with authentic samples, and the mass spectra of the individual fraction (obtained by the use of Hitachi RMU-6MG type GC-MS), with authentic sample. Acetonitrile: NMR (δ ppm in $CDCl_3$) 2.01 (s, $\underline{H}_3$CN → $C\underline{H}_3CN$). IR: complete superimposable spectrum with an authentic sample. Butylaminoacetonitrile: NMR (δ ppm in $CDCl_3$): 0.93 (3H, t, $C\underline{H}_3CH_2$), 1,30 (1H, s, $N\underline{H}$), 1.42 (4H, m, $CH_3C\underline{H}_2C\underline{H}_2CH_2$), 2.65 (2H, t, $C\underline{H}_2NH$), 3.48 (2H, s, $NHC\underline{H}_2CN$). IR (cm^{-1}): 3320 ($-\underset{H}{N}-$), 2240 ($C\equiv N$). MS (*m*/*e*): 112 (M^+). Found: C, 63.65; H, 11.01; N, 24.97%. Calcd for $C_6H_{12}N_2$: C, 64.24; H, 10.78; N, 24.98%. *N*-ethylidenebutylamine: MS (*m*/*e*): 99 (M^+), 84 $CH_3CH_2CH_2CH_2\overset{+}{N}\equiv CH$ (67.6), 57 $CH_3CH_2\overset{+\cdot}{N}{=}CH_2$ (54.0), 56 $CH_3CH{=}\overset{+}{N}{=}CH_2$ (100). *N*-Butylidenebutylamine: MS (*m*/*e*)[6]: 127 (M^+), 112 $\overset{+}{N}CH_2CH_2CH_2CH_3$ (12.5), 99 (15.3), 84 $CH_3CH_2CH_2CH{=}\overset{+}{N}{=}CH_2$ (100), 70 $\overset{+}{N}{=}CH_2$ (27.8), 57 $\overset{+}{N}H\dot{C}H_2$ (75.0), 56 $CH_2{=}\overset{+}{N}HCH{=}CH_2$ (75.0). *N*-Propylidenebutylamine: MS (*m*/*e*): 113 (M^+), 98 (7.4), 84 $CH_3CH_2CH_2CH_2\overset{+}{N}\equiv CH$ (100), 71 (38.9), 70 (70.4), 57 (50.0), 56 (92.6).

Results and Discussion

The product distributions with the discharge reactions of pyrrole and pyrrolidine are shown in Tables 1 and 2 respectively, along with the reaction conditions. Under the influence of radiofrequency discharge, pyrrole produced HCN, CH_3CN, C_2H_5CN, $CH_2{=}CHCN$, *trans*-$CH_3CH{=}CHCN$, C_6H_6, α-$CH_3C_4H_4N$, and β-$CH_3C_4H_4N$ as the primary products, whereas pyrrolidine yielded the characteristic products of α-(1-pyrrolidinyl) nitrile, NCH(R)CN (R=H, CH_3, and C_2H_5), in addition to other nitrile derivatives.

First, we will discuss the discharge reaction of pyrrole. In the experiment with a discharge current of 70 mA at 1.23 kV (Run No. 1), the primary products were HCN and crotononitrile. If this discharge reaction is assumed to proceed *via* the radical mechanism suggested in a previous paper,[7] the formation of crotononitrile may be explained by the following scheme, where the initial homolytic fission of C–N bond is accompanied by both the subsequent rotation of the C–C bond and the double-bond shift, leading to crotononitrile.

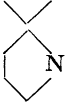
When the discharge current was changed from 70 to 90 mA, the crotononitrile yield decreased among the products while, the yields of HCN and acrylonitrile

Table 1. Experimental conditions and yields of the liquid products for the glow discharge reaction of pyrrole[a]

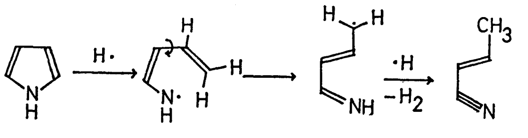
Reaction conditions	Run No.		
	1	2	3
Applied voltage (kV)	1.23	1.50	1.63
Anodic current of discharge (mA)	70	80	90
Reactant fed in (g)	4.6	4.8	4.4
Liquid products (g)	4.1	4.2	3.5
Polymeric materials (g)	0.35	0.42	0.44
Condensable gaseous products (g)	0.11	0.22	0.30
Liquid products (%)			
HCN	5.0	12.5	16.3
CH_3CN	0.7	1.4	2.4
$CH_2{=}CHCN$	1.3	5.2	6.3
CH_3CH_2CN	0.4	1.1	2.0
trans-$CH_3CH{=}CHCN$	3.7	3.2	3.4
C_6H_6	0.2	0.7	1.3
α-$CH_3C_4H_4N$	2.0	2.9	3.3
β-$CH_3C_4H_4N$	1.3	2.1	2.4
Otheres	2.1	4.4	7.8
C_4H_5N	83.3	66.5	54.8
% Conversion	16.7	33.5	45.2

a) Duration of reaction: 20 min.

Table 2. Experimental conditions and yields of the liquid products for the glow discharge reaction of pyrrolidine[a]

Reaction conditions	Run No.			
	4	5	6	7
Applied voltage (kV)	1.33	1.50	1.70	1.95
Anodic current of discharge (mA)	70	80	90	100
Reactant fed in (g)	7.5	7.7	7.7	7.3
Liquid products (g)	6.8	6.5	5.5	4.1
Polymeric materials (g)	0	0	0.01	0.03
Condensable gaseous products (g)	0.4	0.6	1.5	2.3
Liquid products (%)				
HCN	t	t	5.6	32.9
CH_3CN	t	t	3.0	5.9
CH_3CH_2CN	t	t	0.4	2.2
$CH_3CH_2CH_2CN$	1.6	4.3	8.9	9.6
C_4H_5N	0.3	1.0	2.9	5.4
NCH_2CN	1.9	7.4	20.4	7.0
$NCH(CH_3)CN$	3.2	8.6	16.0	9.6
$NCH(C_2H_5)CN$	1.4	4.5	11.0	9.9
Others (20 peaks)	2.9	6.2	11.4	17.6
C_4H_9N	88.6	67.9	19.9	0
% Conversion	11.4	32.1	80.1	100

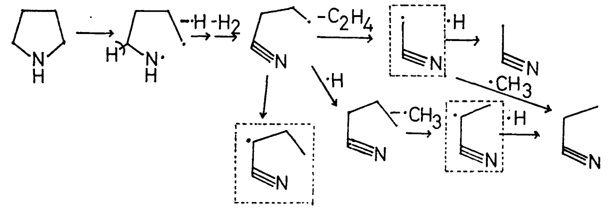
a) Duration of reaction: 20 min.



Scheme 1.

increased. In view of these findings and its chemical structure, the formation of acrylonitrile is considered to proceed by means of the generation of crotononitrile. The fact that no detectable amounts of butyronitrile were found in the reaction mixture suggests that propionitrile was formed not by the hydrogenation of acrylonitrile, but by the recombination of $\cdot CH_2CN$ with the methyl radical. By analogy with the reactions of the atomic hydrogen produced by electric discharge with CH_3CN,[8] it seems likely that hydrogen atoms first attack one of the primary products, crotononitrile, to abstract the CN radical or methyl radical to produce HCN, $CH{\equiv}CH$, and the methyl radical, or CH_4, $CH{\equiv}CH$, and the CN radical, respectively. The formation of $CH{\equiv}CH$ may partly compensate for the energy needed for the above bond cleavage. Accordingly, these cyano and methyl radicals which stem from crotononitrile produce C_2H_6 and CH_3CN *via* recombination. It is evident that the methyl radical formed in the discharge zone also attacks pyrrole to generate α- and β-methylpyrrole.

With the reaction of pyrrolidine, the radiofrequency discharge initiates a homolytic fission of the C–N bond, which is surely the weakest bond[9] in this molecule, accompanied by a subsequent dehydrogenation similar to that described above to deliver various saturated aliphatic nitriles, such as acetonitrile, propionitrile and butyronitrile, that is outlined in the following scheme.



Scheme 2.

Pyrrolidine produces, unlike pyrrole, the characteristic products of α-(1-pyrrolidinyl)nitrile derivatives, whose yields amount to 47.8%, on the basis of the converted pyrrolidine (Run No. 6). The product distribution indicates that, with anodic currents of 70, 80, and 90 mA (Run No. 4, 5, and 6), α-(1-pyrrolidinyl) nitriles are the main products, while small amounts of acetonitrile, propionitrile and butyronitrile are detected which are the alternative constituents of the α-(1-pyrrolidinyl) nitrile derivatives. These findings strongly suggest that pyrrolidine reacts with the resonance-stabilized α-cyanoalkyl radicals[10] to produce α-(1-pyrrolidinyl) nitrile. In this case it appears that α-cyanoalkyl radicals such as $\cdot CH_2CN$, $CH_3\dot{C}HCN$, and $CH_3CH_2\dot{C}HCN$ are not re-formed from the corresponding nitriles by the abstraction of a hydrogen atom, but are generated by the initial radical fission of the C–N bond of pyrrolidine, followed by dehydrogenation subsequent migration to a more stable radical, and the elimination of ethylene, ultimately forming an acetonitrile radical. Scheme 2 shows this, together with the production of saturated nitriles. In Scheme 2, the first-stage intermediate, $\cdot CH_2CH_2CH_2CN$, may rapidly abstract a hydrogen atom to yield butyronitrile, because it is an unstable primary radical. This route competes with another rearrangement leading to a more stable α-radical. Such an idea is supported by the fact that the amounts of butyronitrile were appreciable relative to the trace amounts of acetonitrile and propionitrile produced under rather mild conditions (Run No. 4 and Run No. 5).

Concerning the formation of α-(1-pyrrolidinyl) nitrile derivatives, two possible mechanisms may be considered; one is the recombination of the α-cyanoalkyl radical with the pyrrolidine-*N*-radical, and the other is the electrophilic attack of the α-cyanoalkyl radical towards the basic nitrogen atom of pyrrolidine, accompanied by the subsequent release of the H atom.

Table 3. Experimental conditions and yields of the liquid products for the glow discharge reaction of butylamine[a)]

Reaction conditions	Run No 8	9	10
Applied voltage (kV)	1.60	1.95	2.25
Anodic currrent of discharge (mA)	70	85	100
Reactant fed in (g)	4.2	4.8	3.7
Liquid products (g)	3.7	4.2	2.3
Polymeric materials (g)	0.04	0.05	0.07
Condensable gaseous products (g)	0.3	0.4	0.9
Liquid products (%)			
CH_3CN	0.6	0.4	2.8
$CH_3CH_2CH_2CH_2N{=}CHCH_3$	9.4	15.4	21.0
$CH_3CH_2CH_2CH_2N{=}CHCH_2CH_2CH_3$	3.8	2.8	1.3
$CH_3CH_2CH_2CH_2NHCH_2CN$	0.6	2.5	27.7
Others (13 peaks)	2.5	3.3	8.4
$CH_3CH_2CH_2CH_2NH_2$	83.0	75.6	38.8
% Conversion	17.0	24.4	61.2

a) Duration of reaction: 10 min.

The product distribution and the reaction conditions with butylamine are shown in Table 3. The reaction mixture was found to contain acetonitrile, *N*-butylidenebutylamine, *N*-ethylidenebutylamine, and butylaminoacetonitrile, together with other unidentified products. In this case, the probable mechanism of butylaminoacetonitrile formation is considered to be the same as that for the formation of α-(1-pyrrolidinyl) nitrile derivatives in the discharge reaction of pyrrolidine; *e.g.*, α-acetonitrile radical resulting from ethylene-elimination and the dehydrogenation of butylamine either attacks a nitrogen atom of butylamine or combines with the butylamine-*N*-radical, forming butylaminoacetonitrile. *N*-Butylidenebutylamine is assumed to be formed by the recombination of intermediate radicals, $CH_3CH_2CH_2\dot{C}HNH_2$ and $CH_3CH_2CH_2CH_2\dot{N}H$, followed by the elimination of ammonia whose formation was confirmed in this experiment.

An inspection of Table 3 shows that the combined yield of $CH_3CH_2CH_2CH_2N{=}CHCH_3$ and $CH_3CH_2CH_2CH_2N{=}CHCH_2CH_2CH_3$ increases almost linearly with the anodic currents of discharge (70, 85, and 100 mA). As the release of the ethyl radical from the latter to yield $CH_3CH_2CH_2CH_2N{=}CHCH_2\cdot$ seems to be an energetically preferred process, so the latter produced may be easily converted to $CH_3CH_2CH_2CH_2N{=}CHCH_3$ under these discharge conditions. Therefore, the formation of $CH_3CH_2CH_2CH_2N{=}CHCH_3$ may be supposed to be contingent upon the prior generation of CH_3CH_2-$CH_2CH_2N{=}CHCH_2CH_2CH_3$.

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