BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (5), 1545—1546 (1979)

The Glow-discharge Reactions of Amines

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(Received July 10, 1978)

Synopsis. The glow-discharge reactions of propylamine, dipropylamine, and *N*,*N*-dimethyl-2-methyl-1-propenylamine were studied. The results show that the primary amines yield $RN=CHR'$ and $RNHCH_2CN$, and that the secondary amines produce $R(R')NCH(R'')CN$. *N*,*N*-Dimethyl-2-methyl-1-propenylamine produces a series of imine and nitrile.

We have already reported that the glow-discharge reactions of butylamine, pyrrolidine, and pyrrole[1] gave characteristic products. In this note, propylamine, dipropylamine, and *N*,*N*-dimethyl-2-methyl-1-propenylamine, whose double bond may be supposed to stabilize the active species produced by a C–N fission, were chosen as the starting materials in order to clarify the glow-discharge reactions of amine derivatives. Their glow-discharge reactions were discussed principally on the basis of detailed product analyses.

Propylamine gave such products as could be deduced from the reaction of butylamine, while dipropylamine gave the same kind of products that could be deduced from the products of pyrrolidine, considered as a typical secondary amine, so it has become apparent that primary and secondary amines gave characteristic products in the discharge field.

N,*N*-Dimethyl-2-methyl-1-propenylamine was prepared by the dehydration of dimethylamine with isobutylaldehyde. From the product analyses, the double bond of enamine may be supposed to stabilize the N-radical produced by the cleavage of the weakest C–N bond in the discharge field, accordingly, several characteristic products were produced. These results will be reported in this note.

Experimental

The propylamine and dipropylamine were obtained from Wako Pure Chemical Industries, Ltd., and were used without further purification. *N*,*N*-Dimethyl-2-methyl-1-propenylamine, which was composed of a fraction with a bp of 87—88 °C/760 mmHg, was prepared according to the ordinary method.[2] The apparatus was a fast-flow system which has been previously described,[3] it was operated in a similar way. The rate of the reactants was adjusted by being controlled the heating of their reservoir. The reaction products were collected in the liquid nitrogen trap.

The principal liquid products were isolated from an appropriate fraction using preparative gas chromatography (Shimadzu GC-2C, Silicone DC 550, 4.5 m, H_2), and were identified by the analyses of their NMR spectra, IR spectra, and mass spectra obtained using GC-MS, and by comparing their retention times with those of the authentic samples in the gas chromatogram. The quantitative analyses of the liquid products were undertaken by comparing the area of the chromatogram using a Shimadzu GC-4BPTF apparatus (4.4 m × 3 mm column packed with 10% and 20% SE-30 on Chromosorb W and Uniport B respectively; oven temp: 30—270 °C; program rate: 10 °C/min; H_2 was used as the carrier gas).

Results and Discussion

N-Propylidenepropylamine, *N*-ethylidenepropylamine, and (propylamino)acetonitrile were produced by the glow-discharge reaction of propylamine. *N*-Propylidenepropylamine and *N*-ethylidenepropylamine are assumed to be formed by the attack of the propyl and ethyl radicals upon the N-atom of propylamine, followed by dehydrogenation. (Propylamino)acetonitrile is supposed to be produced by the reaction of $\dot{C}H_2CN$ with propylamine. It is obvious that these compounds correspond to the reaction products of butylamine.

The results of both reactions under similar conditions are cited in Table 1 in an attempt to deduce a general rule with regard to the behavior of primary aliphatic amines under the influence of the glow discharge. The glow-discharge reactions of $CH_3(CH_3)CHCH_2NH_2$ and $CH_3CH_2(CH_3)CHNH_2$ also gave the products deduced from the above results.

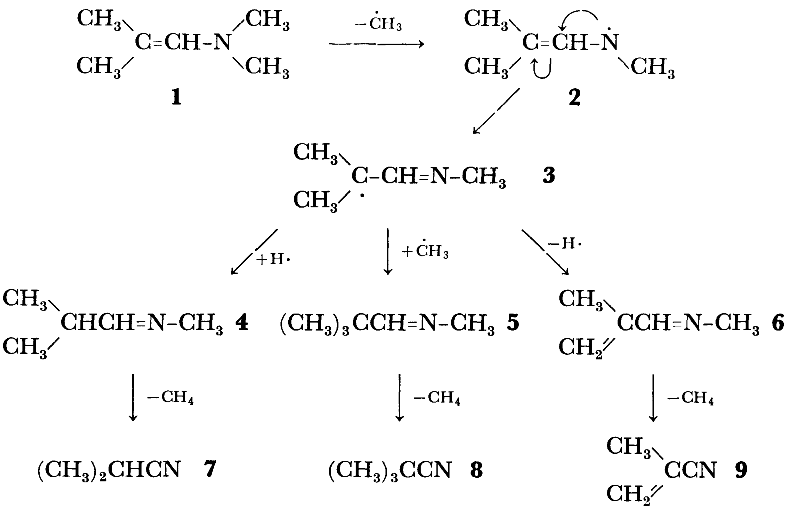
TABLE 1. GENERAL PRODUCTS OF PRIMARY AMINES

	(%)[a]		(%)[a]
n-$PrNH_2$	25.9	*n*-$BuNH_2$	38.8
n-$PrN=CHR$	(35.1)	*n*-$BuN=CHR$	(22.3)
$R=CH_3$	30.5	$R=CH_3$	21.0
$R=CH_2CH_3$	4.6	$R=CH_2CH_3$	tr
		$R=CH_2CH_2CH_3$	1.3
n-$PrNHCH_2CN$	34.3	*n*-$BuNHCH_2CN$	27.7

a) Ratio in the liquid products.

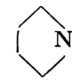
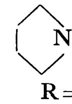
Concerning the cleavage of the secondary amines obtained in the mass spectra, β-fission is very important; also, in the discharge field, the $CH_3CH_2CH_2NH\dot{C}H_2$ formed according to the β-fission of dipropylamine is considered to rearrange to $CH_3CH_2\dot{C}HCN$ accompanying dehydrogenation. The α-fission of dipropylamine formed $CH_3\dot{C}HCN$, and the double β-fission of dipropylamine yielded $\dot{C}H_2CN$. The reactions of these radicals with dipropylamine were supposed to lead to 2-aminonitriles. As the process caused by β-fission is supposed to be a main one, it seems probable that the amount of 2-(dipropylamino)propionitrile is less than that of 2-(dipropylamino)butyronitrile.

The discharge reaction of pyrrolidine also gave a series of 2-(1-pyrrolidinyl)nitrile as the main products; therefore, the formation of such products seems to be a general feature in the glow-discharge reactions of secondary aliphatic amines (see Table 2).



Scheme 1.

Table 2. General products of secondary amines

	(%)[a]		(%)[a]
$(n\text{-Pr})_2NH$	25.4	 NH	19.9
$(n\text{-Pr})_2NCH(R)CN$	(40.8)	 NCH(R)CN	(47.8)
R=H	17.7	R=H	20.4
$R=CH_3$	4.7	$R=CH_3$	16.0
$R=CH_2CH_3$	18.4	$R=CH_2CH_3$	11.4

a) Ratio in the liquid products.

Table 3. Experimental conditions and yields of the liquid products for the glow-discharge reaction of *N*,*N*-dimethyl-2-methyl-1-propenylamine

Reaction condition	Run No. 1	2	3
Anodic current of discharge (mA)	50	65	80
Reactant fed in (g)	3.13	2.54	4.06
Liquid products (g)	3.00	2.07	3.00
% in liquid products			
C_4	0.9	2.0	2.8
$CH_2=CHCN$	3.1	4.7	6.1
CH_3CH_2CN	1.5	2.8	1.1
$CH_2=C(CH_3)CN$	1.2	2.5	4.1
$(CH_3)_2CHCN$	0.4	0.8	1.5
$(CH_3)_3CCN$	0.6	1.7	1.7
$CH_2=C(CH_3)CH=NCH_3$	4.9	5.8	5.6
$(CH_3)_2CHCH=NCH_3$	2.3	1.5	0.9
$(CH_3)_3CCH=NCH_3$	3.1	3.5	1.0
$(CH_3)_2NCH_2CN$	0.5	0.2	1.0
$(CH_3)_2CHCH(CN)N(CH_3)_2$	0.9	1.5	5.0
Others (50 peaks)	5.9	11.2	25.5
$[(CH_3)_2C=CHN(CH_3)_2]$	74.7	61.8	43.7

Thus, the glow-discharge reactions of primary amines gave $RN=CHR'$ and $RNHCH_2CN$, while that of secondary amines gave $R(R')NCH(R'')CN$.

Table 3 shows the results of the glow-discharge reaction of *N*,*N*-dimethyl-2-methyl-1-propenylamine. This table indicates the formation of many kinds of nitrile and imine under the present experimental conditions. The process leading to these products could be reasonably deduced in the following way (see Scheme 1). According to the evaluation of the bond energy of *N*,*N*-dimethyl-2-methyl-1-propenylamine on the basis of the data of Egger and Cocks,[4] the (a) bond in $C=C\text{-}N\overset{(a)}{-}C$ is believed to be the weakest in the molecule. The largest fragment in the mass spectrum of *N*,*N*-dimethyl-2-methyl-1-propenylamine is also M—Me. The N-radical produced by a cleavage of the N-Me bond in the discharge field attacked the neighboring sp^2-carbon, forming an imine, and produced a relatively stable tertiary radical at the β-position. Supposing the existence of this radical in the middle of the way, we can explain the formation of **4**, **5**, and **6**. The doubly-occurring cleavage of the N-Me bonds in the starting enamine, followed by the elimination of hydrogen, leads to **7**, **8**, and **9**. The formation of other identified products, such as propionitrile, acrylonitrile, and hydrogen cyanide, are attributed to the further decomposition of **7**, **8**, and **9**.

Another feature of the discharge reaction of *N*,*N*-dimethyl-2-methyl-1-propenylamine is the formation of *N*,*N*-dimethyl-1-cyano-2-methyl-1-propylamine, produced by HCN addition to the enamine, which occurred during the warming up of the reaction mixture in the trap to room temperature.

References

1) S. Kikkawa, M. Nomura, and N. Hosokawa, *Bull. Chem. Soc. Jpn.*, **50**, 2700 (1977).

2) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **29**, 801 (1964).

3) S. Kikkawa, M. Nomura, and Y. Morita, *J. Synth. Org. Chem. Jpn.*, **34**, 36 (1976).

4) K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, **56**, 1516 (1973).