[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Mechanism of the Decomposition of α-Diethylaminoisobutyronitrile[1]

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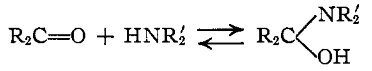
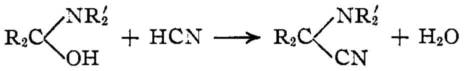
The mechanism for the formation of the α-aminonitriles in acetone and ethanol investigated by Stewart and Li,[2] was postulated as



$$R_2C{=}O + HNR'_2 \rightleftharpoons R_2C(NR'_2)(OH) \quad (1)$$

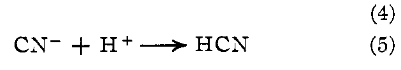


$$R_2C(NR'_2)(OH) + HCN \longrightarrow R_2C(NR'_2)(CN) + H_2O \quad (2)$$

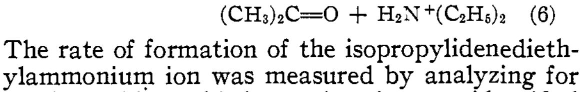
Lapworth, Cocker and Walton[3] had observed earlier that α-diethylaminoacetonitrile decomposed in aqueous solution to form free hydrogen cyanide and presumed that this decomposition proceeded by way of the α-amino alcohol although they did not entirely discount the possibility of the immonium ion, $CH_3{-}CH{=}N^+(C_2H_5)_2$, as the intermediate. Stewart and Cook[4] assumed that the decomposition of α-diethylaminophenylacetonitrile proceeds through the hydrolysis of the nitrile to give the cyanohydrin and the secondary amine as the initial reaction, followed by the decomposition of the cyanohydrin.

Reiber and Stewart[5] isolated the tetraalkyl methylene immonium salts in absolute ethanol by treating the α-aminonitriles with silver nitrate, and then demonstrated that the immonium ion hydrolyzes to the ketone and dialkylammonium ion.

This paper presents a study of the decomposition of α-diethylaminoisobutyronitrile in dilute aqueous solution over a pH range of 0 to 3. The data indicate that at these hydrogen ion concentrations neither the amino alcohol nor the cyanohydrin is involved but that the nitrile decomposes according to the reactions



$$(CH_3)_2C(N^+(C_2H_5)_2H)(CN) \rightleftharpoons (CH_3)_2C(N(C_2H_5)_2)(CN) + H^+ \quad (3)$$



$$(CH_3)_2C(N(C_2H_5)_2)(CN) \xrightarrow{k_4} (CH_3)_2C{=}N^+(C_2H_5)_2 + CN^- \quad (4)$$

$$CN^- + H^+ \longrightarrow HCN \quad (5)$$

$$(CH_3)_2C{=}N^+(C_2H_5)_2 + H_2O \xrightarrow{k_6} (CH_3)_2C{=}O + H_2N^+(C_2H_5)_2 \quad (6)$$

The rate of formation of the isopropylidenediethylammonium ion was measured by analyzing for total cyanide. This immonium ion was identified by determining its rate of hydrolysis to acetone in the same reaction mixture.

Experimental Part

Preparation of the α-Aminonitrile.—The α-diethylaminoisobutyronitrile was prepared by Method II given by Luten,[6] b. p. 79° (24 mm.). Equivalent weights were determined by titration of the nitrile with acid.

Decomposition of α-Diethylaminoisobutyronitrile.—All reagents were of C. P., Reagent or equivalent grade. The nitrile was dissolved in nitric acid solution and the pH was adjusted by adding water. After thorough mixing, the solution was thermostated at 25 ± 0.1°. All reagents were at the temperature of the water-bath before mixing. The pH was determined periodically on an aliquot by means of a Coleman pH Electrometer. The rate of the reaction was determined by withdrawing aliquots and analyzing for cyanide and acetone. Duplicate experiments were carried out.

Determination of Cyanide.—The total cyanide (CN^- + HCN) in each aliquot was determined by the precipitation of silver cyanide in 1 *M* nitric acid, allowing two minutes for the complete precipitation. The excess silver ion was determined in the filtrate by the Volhard method. It was shown that the silver ion reacted directly with the α-aminonitrile under these conditions to the extent of 2% in the two minutes, thus necessitating a correction factor which was applied in all cases. In addition, this direct reaction produces a small amount of silver cyanide in the filtrate which causes a fading end-point. A permanent end-point at which all of the silver cyanide had been converted to silver thiocyanate was obtained within three to five minutes with vigorous agitation.

Determination of Acetone.—The acetone formed was determined by titrating the hydrogen ion released in five minutes by the formation of the oxime in the reaction

$$(CH_3)_2C{=}O + H_3N^+OH \rightleftharpoons (CH_3)_2C{=}NOH + H_2O + H^+ \quad (7)$$

A factor of 1.05 to correct for the incomplete reaction between acetone and the hydroxylammonium ion as determined by Marasco[7] was verified experimentally. Both the aliquot containing acetone and the hydroxylamine hydrochloride solution (1%) were adjusted to the methyl orange end-point (pH about 3.5) before mixing. Loss of acetone by volatilization was minimized by adjusting the pH of the aliquot in a closed flask.

A preliminary experiment in which the α-diethylaminoisobutyronitrile was added directly to an excess of a 1% solution of hydroxylamine hydrochloride, and the reaction mixture was maintained at the methyl orange end-point by adding standard alkali, demonstrated that a direct reaction occurs between the nitrile and the hydroxylammonium ion. One-half of the theoretical amount of hydrogen ion was liberated in seventy-eight minutes as compared to approximately ten hours for the formation of one-half the theoretical amount of acetone from this nitrile at the same pH. An additional factor which causes high results in the acetone determination is the rapid decomposition of the nitrile by local concentration of alkali during the adjustment to a pH of 3.5 from more acid solution. Both of these factors were compensated for by analyzing the first aliquot within five minutes, assuming negligible acetone formation, and using it as a correction blank.

Results and Discussion

The data obtained for cyanide formation were analyzed by means of the first order rate equation

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[1] Presented before the Division of Organic Chemistry at the 115th Meeting of the American Chemical Society at San Francisco, March 28, 1949.

[2] Stewart and Li, THIS JOURNAL, **60**, 2782 (1938).

[3] Lapworth, Cocker and Walton, *J. Chem. Soc.*, 440 (1930).

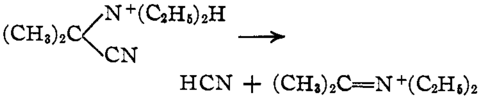
[4] Stewart and Cook, THIS JOURNAL, **50**, 1973 (1928).

[5] Reiber and Stewart, *ibid.*, **62**, 3026 (1940).

[6] Luten, *J. Org. Chem.*, **3**, 588 (1939).

[7] Marasco, *Ind. Eng. Chem.*, **18**, 701 (1926).

for reaction (8), a net reaction including (3) through (5).



$$(CH_3)_2C\begin{matrix}\nearrow N^+(C_2H_5)_2H \\ \searrow CN\end{matrix} \longrightarrow HCN + (CH_3)_2C{=}N^+(C_2H_5)_2 \quad (8)$$

The first order rate law was adhered to for at least 90% of the reaction at each hydrogen ion concentration studied as evidenced by the typical run shown in Table I. The rate proved to vary inversely with the hydrogen ion concentration. The calculated values for the half-life and the rate constant for reaction (8) at various pH's are given in Table II.

TABLE I

CYANIDE FORMATION FROM $(C_2H_5)_2N^+H—C(CH_3)_2—CN$ IN NITRIC ACID AT A pH OF 0.10 AND AT 25 ± 0.1°

Time, minutes	Cyanide formed, mole/liter	$(C_2H_5)_2N^+H—C(CH_3)_2—CN$ unreacted, mole/liter
0	0	0.0600
70	0.0041	.0559
210	.0125	.0475
504	.0254	.0346
666	.0311	.0289
952	.0393	.0207
1540	.0490	.0110
2010	.0535	.0065
2780	.0568	.0032
3480	.0580	.0020
4435	.0594	.0006
5985	.0597	.0003

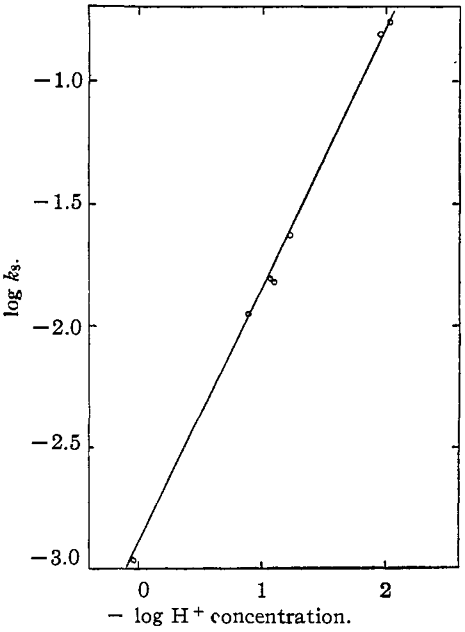


FIG. 1.—Relation between k_8 and H$^+$ concentration.

TABLE II

CYANIDE FORMATION FROM $(C_2H_5)_2{}^+NH—C(CH_3)_2—CN$ IN AQUEOUS SOLUTION AT 25°

Initial concn. of $(C_2H_5)_2N^+H—C(CH_3)_2—CN$, mole/liter	pH	H$^+$ concn., moles/liter	$t^1/_2$, minutes	$k \times 10^1$ min.$^{-1}$	$k_4 \times 10^{-4}$ min.$^{-1}$
0.0600	0.1	1.09	635	0.0109	5.93
.0600	0.99	0.129	61.8	.112	7.23
.0600	1.15	.0863	43.8	.158	6.82
.0300	1.18	.0805	45.8	.153	6.16
.0600	1.31	.0598	29.3	.237	7.08
.0598	2.01	.0110	4.5	1.54	8.44
.1196	2.08	.00924	4.0	1.73	7.89
.0598	3.06	....	...[a]	....	..

[a] Too fast to follow.

The specific rate constant for the formation of the cyanide ion from the nitrile by reaction (4) was calculated in the following manner. Assuming a first order reaction for (4), the rate would be

$$d(CN^-)/dt = k_4((C_2H_5)_2N—C(CH_3)_2—CN) \quad (A)$$

Since the method of analysis measures both the CN$^-$ and the HCN, the rate of appearance of total cyanide was considered to be a measure of the rate of formation of CN$^-$ by reaction (4). The concentration of the nitrile can be determined from equation (B), the expression for the equilibrium constant for reaction (3).

$$K_a = \frac{((C_2H_5)_2N—C(CH_3)_2—CN)(H^+)}{((C_2H_5)_2N^+H—C(CH_3)_2—CN)} \quad (B)$$

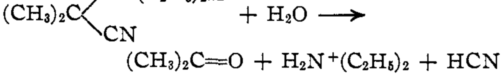
Substituting in equation (A)

$$d(CN^-)/dt = \frac{k_4K_a}{(H^+)}((C_2H_5)_2N^+H—C(CH_3)_2—CN) \quad (C)$$

At constant hydrogen ion concentration, the term $k_4K_a/(H^+)$ will be a constant and will be equal to k_8 which was calculated for reaction (8) and is listed in Table II.

$$k_4 = k_8(H^+)/K_a \quad (D)$$

Since no value for the activity coefficient of the α-diethylammoniumisobutyronitrile ion was available, the pH as measured was converted to hydrogen ion concentrations using approximate activity coefficients for nitric acid.[8] The specific rate constant, k_4, was calculated from equation (D) and is listed in Table II for each experiment. The value of 2 × 10^{-8} for K_a, the acidic dissociation constant for the α-diethylammoniumisobutyronitrile ion, was calculated from the experimentally determined pK_a value at the 50% titration point in a very rapid titration of the ion with standard alkali. If the mechanism proposed is correct, the linear relationship betwen k_8 and hydrogen ion concentration should have a slope of 1.00. A plot of log k_8 and minus the log of hydrogen ion concentration is shown in Fig. 1 and the slope is 1.04. This is a reasonable check in view of the experimental difficulties at the extremes of the pH range studied. The net reaction



$$(CH_3)_2C\begin{matrix}\nearrow N^+(C_2H_5)_2H \\ \searrow CN\end{matrix} + H_2O \longrightarrow (CH_3)_2C{=}O + H_2N^+(C_2H_5)_2 + HCN \quad (9)$$

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(8) "Int. Crit. Tables," Vol. VII, p. 239.

was first used for analyzing data obtained from the acetone analyses. A linear relationship between the log of the α-diethylammoniumisobutyronitrile ion concentration and time, that is, the first order rate law required by this equation, existed only at the *p*H of 2 and 3. The rate constants are given in Table III.

TABLE III

ACETONE FORMATION FROM $(C_2H_5)_2N^+H—C(CH_3)_2—CN$ IN AQUEOUS SOLUTION AT 25°

Initial concn. of $(C_2H_5)_2N^+H—C(CH_3)_2—CN$	*p*H	$t^1/_2$ minutes	$k_9 \times 10^4$ min.$^{-1}$
0.1196	1.95	960	7.2
.0598	2.05	890	7.9
.0598	3.06	8.25	8.4

At these hydrogen ion concentrations, the rate of reaction (8) is sufficiently rapid (Table II) that the maximum concentration of the intermediate, the immonium ion, builds up very rapidly. Consequently, the first order reaction actually measured was the hydrolysis of the immonium ion, reaction (6).

At a *p*H of 1 and 0, the rate of formation of the immonium ion by reaction (8) is slow (Table II). Since the formation of acetone from the immonium ion is the second of two slow consecutive first order reactions, an analysis of the data on the basis of the net reaction, reaction (9), using the first order rate equation should not show a linear relationship between the log of the α-diethylammoniumisobutyronitrile ion concentration and time. An initial slow rate of formation of acetone was evidenced experimentally. This lag was appreciably greater at a *p*H of 0 as would be expected since the rate of formation of the immonium ion is tenfold slower than at a *p*H of 1. The rate constant, k_6, for the second of these two slow consecutive first order reactions, the formation of acetone by the hydrolysis of the immonium ion, was calculated to be between 11×10^{-4} and 14×10^{-4} min.$^{-1}$ at a *p*H of 0.1. This value is somewhat higher than would be predicted from the values in Table III, but the agreement is reasonably good.

As mentioned previously, Reiber and Stewart[5] isolated the isopropylidenediethylammonium ion as the iodide salt. They determined the rate of hydrolysis of this ion in acid solution to form acetone and the diethylammonium ion. The rate constants they calculated for the first order reaction

$$(CH_3)_2C=N^+(C_2H_5)_2 + H_2O \xrightarrow{k_{10}} (CH_3)_2C=O + H_2N^+(C_2H_5)_2 \quad (10)$$

are given in Table IV.

TABLE IV

HYDROLYSIS OF $(CH_3)_2C=N^+(C_2H_5)_2$ AT 25°[a]

Concn. of immonium ion, *M*	Reaction medium	$t^1/_2$, minutes	$k_{10} \times 10^4$ minutes^{-1}
0.05	0.01 *N* HCl	828	8.3
.05	0.001 *N* HCl	780	9.0

[a] Data from Reiber and Stewart.[5]

The close correlation between the rates of acetone formation from isopropylidenediethylammonium iodide (Table IV) and from α-diethylammonium isobutyronitrile ion (Table III) clearly demonstrates that the immonium ion, $(CH_3)_2C=N^+(C_2H_5)_2$, is the compound intermediate in the formation of acetone from α-diethylaminoisobutyronitrile in aqueous acid solution.

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Summary

The decomposition of α-diethylaminoisobutyronitrile at a *p*H of 0 to 3 has been shown to proceed through two consecutive first order reactions and the intermediate is the immonium ion rather than the α-amino alcohol or cyanohydrin.

At the *p*H of 0 to 1 both reactions are slow and the rate constant for the hydrolysis of the immonium ion has been calculated.

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