

CXL.—*The Action of Nitrous Acid on Amino-compounds. Part I. Methylamine and Ammonia.*

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As has been shown in a previous communication (Taylor, Wignall, and Cowley, J., 1927, 1923), aqueous solutions of nitrous acid can be considerably stabilised if the concentration is below a critical value which depends on the temperature and pressure, and if the solution is covered by a layer of "medicinal paraffin."

A preliminary study of the conditions of interaction of nitrous acid with simple aliphatic amino- and amido-compounds showed that the phenomena were extremely diverse, and thus it was thought essential to investigate the case of methylamine and ammonia where the fewest possible complications are present.

Euler (*Annalen*, 1903, **330**, 280) made the important observation that in 0.05*N*-solution at 40°, methylamine nitrite is stable, but reacts readily with an equivalent of nitrous acid. He attempted to measure the rate of the reaction by the rate of evolution of nitrogen, but his results are inconclusive, largely because of the decomposition of the nitrous acid. Later workers (Neogi, J., 1914, **105**, 1270; Oddo and Cesaris, *Gazzetta*, 1914, **44**, ii, 209) seem to consider that the reaction is essentially the decomposition of the nitrite.

In the case of ammonia, the reaction has been regarded as the decomposition of the nitrite and investigated as such, principally by Arndt (*Z. physikal. Chem.*, 1901, **39**, 64; 1903, **45**, 570) and by Blanchard (*ibid.*, 1902, **41**, 681). The most important results obtained were that ammonium nitrite, although stable in solution at room temperature, decomposes freely at 60°. Arndt suggested that the rate of decomposition was proportional to the product $[\text{NH}_4\text{NO}_2][\text{HNO}_2]$, whilst Blanchard attributed a catalytic effect to the hydrogen ion and suggested that the velocity varied as the product $[\text{H}^+ + \text{HNO}_2][\text{NH}_4^+][\text{NO}_2^-]$. Both followed the reaction by the rate of evolution of nitrogen, and the results of both, especially those from experiments in the presence of excess of mineral acid, were undoubtedly obscured by the spontaneous decomposition of the nitrous acid.

Plimmer (J., 1925, **127**, 2651) performed a few experiments on the action of large excess of nitrous acid on ammonia in the presence of acetic acid; his results indicate that the reaction is complete at 16° in 2½ hours.

Since the rate of gas evolution is an accurate measure of the velocity of reaction only if the solution is continuously and

thoroughly agitated, and since such agitation greatly increases the rate of decomposition of the nitrous acid, the velocity of reaction has been followed by estimating the concentration of undecomposed amine. Further, the initial concentration of nitrous acid was never greater than $0.15N$, *i.e.*, well below the critical concentration ($0.2N$) under the conditions employed.

In a series of preliminary experiments, it was found that ammonia and methylamine show exactly the same type of behaviour towards nitrous acid, the velocity coefficient for the former being a little less than half of that for the latter. Thus methylamine is much more suitable for accurate investigation, since the side reaction, the decomposition of nitrous acid, forms a smaller fraction of the total reaction in any given time.

I. *Methylamine.*

Methylamine free from ammonia could only be obtained by Wallach's method from acetoxime (*Annalen*, 1900, **312**, 175, footnote). The hydrochloride was recrystallised three times from 96% alcohol and its purity established by determining the equivalent of the methylamine against standard sulphuric acid. The methylamine was used as an approximately $0.5N$ aqueous solution of the free base, which kept well in stoppered bottles. Nitrous acid was prepared from pure barium nitrite and sulphuric acid as in the previous communication, no attempt being made to remove the barium sulphate. All experiments were carried out at $25^{\circ} \pm 0.05^{\circ}$; the reaction mixture was covered by a layer of medicinal paraffin, and the stirrer passed through that layer, care being taken to avoid air bubbles being drawn into the solution. Samples of the solution were withdrawn by a pipette from time to time, and run into excess of pure aqueous caustic soda; the methylamine was at once distilled in steam into a known amount of standard acid; the accuracy of the method was found to be about $\pm 0.5\%$.

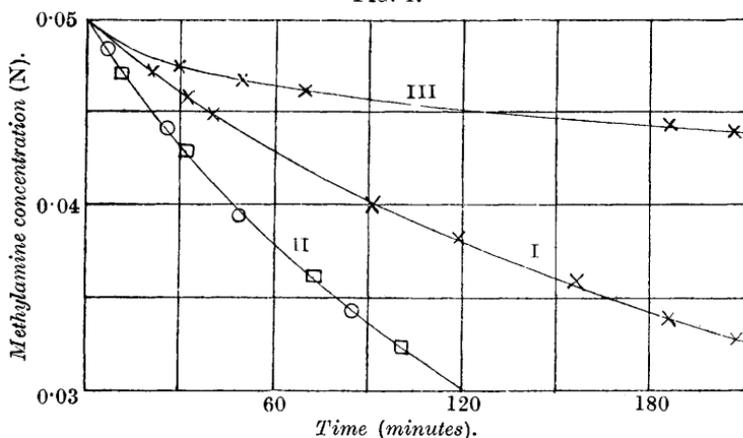
$0.05N$ -*Methylamine* + $0.05N$ -*nitrous acid*. No change in the concentration of methylamine occurred during $2\frac{1}{2}$ hours; this is in agreement with previous workers.

$0.05N$ -*Methylamine* + $0.05N$ -*nitrous acid* + $0.05N$ -*sulphuric acid*. No reaction could be observed during a period of $2\frac{1}{2}$ hours. Euler (*loc. cit.*), with the same concentrations at 40° , found a very slow reaction, but in his experimental data (40 c.c. of gas in 50 hours) he does not state what proportion of the gas was nitric oxide from the decomposition of the nitrous acid. At least half must have been nitric oxide, in which case the concentration of methylamine fell from $0.05N$ to $0.0496N$ in 50 hours.

0.05N-Methylamine + 0.1N-nitrous acid. A fairly rapid reaction occurs. The rate of this was measured repeatedly; some of the results are shown in the figure (Curve I). From the smooth curve drawn through them the values shown in Table I were read.

From the results obtained so far, it is clear that the reaction is one in which methylamine ions, nitrite ions, and free nitrous acid all take part. Estimation of the concentration of nitrous acid from time to time showed that one molecule of nitrous acid disappears for each molecule of methylamine, and not two; thus

FIG. 1.



- Curve I. 0.05N-CH₃·NH₂ + 0.1N-HNO₂.
 Curve II. ○ 0.05N-CH₃·NH₂ + 0.1N-HNO₂ + 0.05N-CH₃·NH₂Cl.
 □ 0.05N-CH₃·NH₂ + 0.1N-HNO₂ + 0.05N-Ba(NO₂)₂.
 Curve III. 0.05N-CH₃·NH₂ + 0.1N-HNO₂ + 0.05N-H₂SO₄.

the reaction velocity, assuming that it varies as the product [CH₃·NH₃⁺][NO₂⁻][HNO₂], should be given by an equation of the form $-dx/dt = kax^2$, where x is the concentration of methylamine (and hence of the nitrite ion) at time t , and a is the initial concentration of methylamine, and hence that of the undissociated nitrous acid, assuming it to be completely undissociated in the presence of the excess nitrite ion. Values of the coefficient k calculated for every 30 minutes are shown in Table I.

TABLE I.

t (mins.).	x .	k (min. ⁻¹).	k corr. (min. ⁻¹).	t (mins.).	x .	k (min. ⁻¹).	k corr. (min. ⁻¹).
0	0.0500	—	—	120	0.0381	1.04	1.12
30	0.0461	1.13	1.15	150	0.0361	1.03	1.13
60	0.0427	1.14	1.18	180	0.0343	1.02	1.13
90	0.0402	1.08	1.15				Mean 1.14

The values of k fall slowly with time, a behaviour which could be foreseen, because the concentration of free nitrous acid is not constant, but falls slowly owing to its spontaneous decomposition. A correction can be applied for this effect; from the measurements of the nitrous acid concentration during the reaction, the rate of its decomposition was found to be slightly greater than the rate for pure nitrous acid (0.05*N*) decomposing undisturbed beneath a layer of paraffin. In the previous communication it was shown that this rate agrees roughly with the unimolecular law; hence the equation for the reaction can be written more accurately

$$- dx/dt = kx^2ae^{-Kt} \dots \dots \dots (1)$$

where K is the velocity coefficient of the nitrous acid decomposition. The value of K was found in a blank experiment in the same flask, using nitrous acid alone, to be 1.22×10^{-3} min.⁻¹. Integrating, expanding, and neglecting powers of K higher than the first, we have

$$k = \frac{a-x}{a^2x} \cdot \frac{1}{t - \frac{K}{2}t^2} \dots \dots \dots (2)$$

Values of k thus corrected (k corr.) are given in Table I; their constancy is as good as can be expected; inclusion of higher powers of K has no influence on their value. Hence the mean value of the velocity coefficient at 25° can be taken as 1.14 (normality⁻²; min.⁻¹).

Influence of Potassium Chloride.—Measurements were made with methylamine and nitrous acid at the same concentrations in the presence of 0.05*N*-potassium chloride and 0.2*N*-potassium chloride; the potassium chloride was pure, the same sample having been used in certain electrometric determinations (Taylor and Bomford, J., 1924, 125, 2016). The velocity is diminished; values of k calculated from (2) are given in Table II.

TABLE II.

KCl normality	0	0.05	0.2
k corr. (min. ⁻¹)	1.14	1.02	0.79

Only one experiment was carried out at each concentration. The effect of the added salt obviously belongs to the class of phenomena discussed by Brönsted (*Z. physikal. Chem.*, 1922, 102, 169), Bjerrum (*ibid.*, 1924, 108, 82), and Christiansen (*ibid.*, 1924, 113, 35). It was measured here because an estimate of the magnitude of the effect is required later.

Influence of Excess of Methylamine Ion or of Nitrite Ion.—If the above hypothesis is correct, the velocity should be equally acceler-

ated by addition of either a methylamine salt or a soluble nitrite. Measurements were made with the same concentrations of methylamine and nitrous acid together with 0.05*N*-methylamine hydrochloride, and also with 0.05*N*-barium nitrite (pure). The equation should take the form $-dx/dt = kax(a+x)e^{-Kt}$, giving

$$k = \frac{1}{a^2\left(t - \frac{K}{2}t^2\right)} \cdot \log_e \frac{a+x}{2x}.$$

The velocity was found to be the same in both cases; results are shown in the figure (Curve II), and values of k in Table III.

Since the reaction is faster, the rate of spontaneous decomposition of the nitrous acid is increased, because it depends on the rate of passage of gas bubbles through the solution; hence if the same value of K is taken as before, the values of k diminish with time, as is shown in the table. If a somewhat greater value be taken for K , *viz.*, 1.8×10^{-3} , k is reasonably constant and is shown as k_2 corr. (The value of K for 0.05*N*-nitrous acid in the same flask unprotected by paraffin was about 5×10^{-3} min.⁻¹) Hence the mean value of the velocity coefficient is 1.02; this must be compared with the value in the presence of 0.05*N*-potassium chloride, since the added salt will increase the ionic strength and in this way depress the velocity. The agreement is good.

TABLE III.

t (min.).	x .	k_1 corr.	k_2 corr.
0	0.0500	—	—
30	0.0431	1.01	1.02
60	0.0379	0.99	1.01
90	0.0338	0.98	1.01
120	0.0302	0.98	1.02

Influence of Nitrous Acid.—One experiment was performed with 0.05*N*-methylamine and 0.15*N*-nitrous acid. On the above hypothesis the velocity coefficient should be 2×1.14 , since the concentration of free nitrous acid is doubled; the value found was 2.22 (min.⁻¹).

Influence of Sulphuric Acid.—Addition of a strong acid should repress the reaction, since in its presence the concentration of nitrite ion must be smaller. Some experiments carried out by Mr. J. F. Cowley showed that with 0.1*N*-methylamine and 3 equivalents of nitrous acid in the presence of 4.2*N*-sulphuric acid there was no change in the methylamine concentration in a period of 16½ hours at 25.5°.

The above hypothesis as to the reaction was confirmed by

measurements at 25° with 0.05*N*-methylamine, 0.1*N*-nitrous acid, and 0.05*N*-sulphuric acid, which are shown in Curve III of the figure. At the start the mixture contains essentially methylamine ions, sulphate ions, nitrite ions, and nitrous acid; as the reaction proceeds methylamine disappears and highly dissociated sulphuric acid is formed; hence the hydrogen-ion concentration rises, the nitrite ion concentration falls, and the reaction becomes slower and slower. At time *t* the concentration of the hydrogen ions can be taken as (*a* - *x*), and that of the undissociated nitrous acid as (*a* + *x*); thus if the dissociation constant of nitrous acid is *C*, $[\text{NO}_2'] = C(a + x)/(a - x)$. Hence the equation for the reaction should be $-dx/dt = kCx(a + x)^2/(a - x)$, whence, integrating between the times *t*₁ and *t*₂,

$$kC = \left(\frac{1}{a} \log_e \frac{x_1}{x_2} \cdot \frac{a + x_2}{a + x_1} - \frac{2}{a + x_2} + \frac{2}{a + x_1} \right) \frac{1}{t_2 - t_1} \quad (3)$$

The expression obviously cannot be integrated back to time 0, since it only holds when the concentration of free sulphuric acid is appreciable. Values of *kC* calculated from (3) vary between 2×10^{-4} and 4×10^{-4} (min.⁻¹); the variation arises from three causes: (i) The reaction is proceeding very slowly in the region where the expression holds; (ii) expression (3) is extremely sensitive to small inaccuracies in the values of *x*₁ and *x*₂; (iii) no allowance is made for the spontaneous decomposition of nitrous acid.

Nevertheless, since *k* has been shown to be 1.14, the calculation gives a value for *C* which agrees in order of magnitude with that determined by Blanchard, 4×10^{-4} , and by Schumann, 4.5×10^{-4} (Landolt-Börnstein "Tabellen," 5th Edn.).

II. Ammonia.

The reaction with ammonia was not examined in any detail. The following experimental facts were established: (i) Ammonia (0.05*N*) at 25° does not react with one equivalent of nitrous acid, but reacts with two, the velocity coefficient being of the order of 0.48 (normality⁻²; min.⁻¹). (ii) The velocity is lowered by addition of mineral acids and of potassium chloride. (iii) The velocity is accelerated equally by equivalent quantities of either ammonium chloride or barium nitrite.

Hence there is little doubt that the same mechanism is involved and that the velocity varies as the product $[\text{NH}_4^+][\text{NO}_2'][\text{HNO}_2]$, agreeing with the conclusions of Arndt; Blanchard's expression is erroneous and his attribution of a catalytic effect to the hydrogen ion obviously arose from adding small amounts of strong acid to

solutions of ammonium nitrite, whereby free nitrous acid was formed.

The results obtained may have one of two meanings. Either the reaction involves the two ions and a molecule of nitrous acid, or, since the concentration of any form of undissociated amine nitrite is proportional to the product of the concentrations of its ions, the actual reacting molecules may be undissociated molecules of amine nitrite and those of nitrous acid. The results suggest that the best conditions for converting an aliphatic amine into the alcohol are to use large excess of nitrous acid and to avoid the presence of mineral acids in the solution.

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