

LXXVI.—*The Conditions of Decomposition of Ammonium Nitrite.*

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THE decomposition of ammonium nitrite in aqueous solution has for many years attracted the attention of investigators owing to its simplicity and to the readiness with which the nitrogen gas can be evolved and collected, and the undecomposed nitrite estimated.

Millon (*Ann. Chim. Phys.*, 1847, iii, 19, 255) noticed that a solution of ammonium nitrite can be preserved for several hours at the temperature of boiling water without decomposition if a drop of ammonia solution is added, but the addition of a drop of nitric, hydrochloric, or sulphuric acid produces "une effervescence vive et tumultueuse."

Later, Sorensen (*Zeit. anorg. Chem.*, 1894, 7, 38) made the remarkable observation that large masses of crystalline ammonium nitrite could be made spontaneously explosive by the addition of a trace of tartaric acid, but could be preserved for a month by the addition of a trace of ammonium carbonate. Wegscheider (*Zeit. physikal. Chem.*,

1901, 36, 543) has shown that, on the assumption of an ionic reaction, $\text{NH}_4^+ + \text{NO}_2^- = 2\text{H}_2\text{O} + \text{N}_2$, the addition of the ionic equivalent of salts produces the same acceleration.

Angeli and Boeris (*Atti Real. Accad. Lincei*, 1892, [ii], 1, 870) found that the addition of ammonium salts, on the one hand, and of nitrites, on the other, increases the rate of decomposition, whilst indifferent or neutral salts have no marked influence.

A more recent publication by Arndt (*Zeit. physikal. Chem.*, 1901, 39, 1), induced me to revert to a subject on which I made certain observations some years ago (*Phil. Trans.*, 1888, Series A., 179, 257), as some of his results were in accordance, whilst others were apparently discrepant, with my former work.

While the present investigation was in progress, Blanchard (*Zeit. physikal. Chem.*, 1902, 41, 680) studied the reaction with the view of ascertaining, firstly, which substances act as accelerators, and, secondly, whether subsidiary reactions do not modify the course of the reaction. As regards the first point, this author showed that the action of various acids could be expressed in terms of the ionic equation :

$$V = k(aC_{\text{H}} + bC_{\text{HNO}_2}) + C_{\text{NH}_4} + C_{\text{NO}_2},$$

in which V is the velocity, and k , and C have the usual significance.

As regards the second point, it was proved that there was no evidence of the evolution of oxides of nitrogen unless the reaction was modified by the addition of acid.

These various observations will be alluded to in the sequel, in so far as they have reference to the present inquiry.

Preparation of Solutions of Ammonium Nitrite.

For this purpose, the reaction between ammonium chloride and silver nitrite was selected ; the latter salt was obtained by precipitating purified silver nitrate with sodium nitrite, washing the precipitate of silver nitrite three or four times with cold water, recrystallising from hot water, drying the crystals, first by suction, and then on a porous plate ; all the operations were conducted in such a manner as to avoid as far as possible either contact with organic matter or exposure to direct sunlight. Weighed amounts of the silver nitrite thus prepared were decomposed with equivalent proportions of ammonium chloride in the presence of a small volume of water, the silver chloride filtered off, and the solution, when freed from all turbidity, made up to a known volume.

The concentration of the solution at the outset was determined by a decinormal solution of potassium permanganate, but in any continuous series of observations, the amount of ammonium nitrite undecomposed

was calculated from the evolved volume of nitrogen, corrected to standard pressure and temperature; this latter method is not of the same order of accuracy, as a certain quantity of nitrogen remains in the solution, but it was sufficiently approximate in cases in which the series of observations could not be interrupted.

The acidity or alkalinity of the solutions was determined by very dilute standard solutions of ammonia or sulphuric acid respectively, litmus being used as an indicator.

Method of Working.

The ammonium nitrite solutions were placed in distillation flasks of 75 to 90 c.c. capacity, the volume used being such that when the thermometer was introduced, and the contents heated to the required temperature, the level of the liquid was nearly up to the side-delivery tube, and thus evaporation from a large surface avoided. My experience, however, coincided with that of Arndt, which was that the water formed by the reaction approximately counterbalanced the loss by evaporation. The flasks were closed with rubber plugs through which the thermometer passed, and the side limb connected by stout rubber tubing with a capillary tube drawn out so as to deliver small bubbles (about 75 per c.c.) of nitrogen. In most experiments, a standard volume of 4 to 5 c.c. was collected for each observation; if the evolution of gas was more rapid, 10 c.c., if less rapid, then 2 and even 1 c.c. of gas were collected.

In all cases, V/T represents volume of gas in c.c. collected in time expressed in minutes.

Three thermometers were used, all graduated in one-tenths of a degree, two of these instruments ranged from 50° to 103°, and one from 0° to 20°; one of the former (1°=13 mm.) had been calibrated by Gay Lussac's method, the boiling point error determined, and the readings reduced to the hydrogen scale, the other was compared with it within the temperature interval; the last (1°=15 mm.) had also been calibrated by the same method, its freezing point error determined, and the readings also reduced to the hydrogen scale.

The water-bath, used for the purpose of heating, consisted of a tin vessel containing water, the temperature of which was controlled by a Reichert's regulator; inside this vessel was placed a calorimeter made of copper and tin, and consisting of three chambers filled with water, in the innermost of which the decomposition flask was placed, the surrounding water being stirred by a stream of fine bubbles of carbon dioxide from a Kipp's apparatus. The whole was closed with a lid furnished with suitable apertures.

In a control experiment, the temperature in the decomposition

flask, when filled with water only, was found to remain constant within $\pm 0.1^\circ$ for several hours, but in actual working there was a gradual rise of about 0.2° at the earlier stage, due to the heat evolved by the decomposition of ammonium nitrite. The value of this, according to the determination of Thomson (*Prakt. Chem.*, 1880, [ii], 21, 449) is 71770 cal. per molecular proportion of salt, but according to Berthelot it equals 80400 cal. In certain experiments, a rise, in others a fall, of temperature was produced by the addition of certain reagents; these, when observed, were compensated as speedily as possible.

The whole apparatus, with the distillation flask empty, was heated up *slowly* until the required temperature was reached; then the ammonium nitrite solution, which had been heated up *quickly* to nearly the same temperature in another flask, was introduced, the rubber plug with the thermometer pressed in, and when the temperature had become constant, observations were commenced, the gas evolved in the meanwhile being collected and measured.

The Course of the Reaction.

The decomposition of the ammonium nitrite starts slowly at first, as observed many years ago by Harcourt,* owing to the retention of the nitrogen gas, then quickly reaches a maximum; from this point, it decreases in accordance with the law of mass action for a uni-molecular reaction.

If V be the volume in c.c. of nitrogen evolved in time T , then

$$\log V/T(n) = \log V/T - n \log \text{const.} \quad . \quad . \quad . \quad (1),$$

for which n is the number of observations from the commencement.

The above equation can be transformed into the usual form:

$$\log A/A - = aT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

The values in Series I, p. 740, were obtained in a set of observations made at a temperature of 65° ; $\log \text{const.} = 0.0080$.

The differences between the observed and calculated values, which rarely exceed 2 per cent., are mainly due to slight variations of temperature, since a rise or fall produces two errors in the same direction, firstly, an increase or decrease in the velocity of decomposition, and secondly, an expansion or contraction in the solution which causes more or less gas to be expelled.

The values in Series II, p. 740, were obtained in another series of

* Blanchard (*loc. cit.*, *supra*) records a similar observation, apparently without being aware that it had been noted previously.

SERIES I.

No. of observation.	Value V/T found.	Value V/T calc.	No. of observation.	Value V/T found.	Value V/T calc.
—	1.369	—	9	1.134	1.155
1	1.353	1.344	10	1.118	1.138
2	1.345	1.319	11	1.087	1.118
3	1.311	1.295	12	1.068	1.097
4	1.273	1.271	13	1.079	1.078
5	1.251	1.249	14	1.030	1.057
6	1.196	1.226	15	1.040	1.038
7	1.203	1.202	16	1.009	1.020
8	1.184	1.182	17	0.940	1.001

observations in which benzoic sulphinide ("saccharin") had been added, which produced a considerable acceleration :

SERIES II.

Temperature = 61.8° . $\log \text{const.} = 0.0248$.

No. of observation.	Value V/T found.	Value V/T calc.	No. of observation.	Value V/T found.	Value V/T calc.
—	5.986	—	11	3.350	3.326
1	5.885	5.825	12	3.050	3.141
2	5.561	5.561	13	2.870	2.947
3	5.274	5.252	14	2.833	2.803
4	5.083	4.961	15	2.675	2.647
5	4.857	4.698	16	2.467	2.500
6	4.525	4.441	17	2.293	2.361
7	4.260	4.180	18	2.134	2.230
8	4.018	3.948	19	1.944	1.989
9	3.840	3.729	20	1.843	1.847
10	3.589	3.522	21	1.728	1.758

In the above series, the errors are of about the same order as in the preceding, so that whether the decomposition proceeds on its normal course or is accelerated, the same equation holds good.

Effect of Ammonia and its Derivatives.

Arndt (*loc. cit. supra*) in the course of his investigations confirmed the older observation of Millon that the addition of free ammonia prevents, or hinders, according to the quantity added, the evolution of nitrogen from an aqueous solution of ammonium nitrite, and that even the addition of 1/800th part of ammonia reduces the rate by nearly two-thirds.

Some years ago (Trans., 1883, 43, 370), in the course of experiments on the rate of decomposition of ammonium nitrate, it was observed that a fragment of litharge added to a considerable mass of fused salt (about 100 grams) completely stopped the evolution of nitrous oxide, and the same result was obtained when ammonia gas was bubbled into the fused salt. The former experiment serves as a good lecture demonstration.

In order to ascertain whether ammonia liberated by the addition of a basic oxide would in like manner prevent the evolution of nitrogen from ammonium nitrite, an experiment was conducted as follows: a solution of the salt containing 2.24 grams in 70 c.c. (0.5 molecular) was heated for the purpose of determining the rate of decomposition, then 0.028 gram of lime was dropped in, which would liberate 0.017 gram of ammonia, and additional observations were recorded:

SERIES III.

Temperature 70.7—70.9°.

Before addition of lime.		After addition of lime.	
No. of observation.	Value V/T .	No. of observation.	Value V/T .
1	1.572	8	0.0639
2	1.493	9	0.0281
3	1.477	Reaction stopped	
4	1.398		
5	1.343		
6	1.274		
7	1.186		

The ammonium nitrite originally present amounted to 2.2400 grams and 0.1468 gram was decomposed in the first part of the experiment, hence 2.0932 grams were present when the lime was added. This amount corresponds with 0.5569 gram of ammonia, of which only 0.0170 gram, or 3.06 per cent., was liberated by the lime.

It is thus evident that 3 per cent. of liberated ammonia, which remained dissolved in the solution at first impeded and then practically stopped the evolution of nitrogen, for even in the last observation nearly 36 minutes were required for the evolution of 1 c.c. of nitrogen.

A similar result was obtained with litharge, namely, the liberation of 1/9th of the total combined ammonia, this amount, which is equivalent to 1/350th of the total mass of ammonium nitrite, reduced the rate of evolution to 33 per cent. of its original value at the mean temperature 58.9°. Arndt found that 1/800th part of free ammonia

reduced the value to the same extent, but did not give temperature or other conditions of experiment.

In studying the effect produced by derivatives of ammonia, the liquids or solutions of solids were in all cases added by raising the rubber plug of the decomposition flask, dropping in a definite fraction of 1 c.c. by means of a 1 c.c. pipette graduated in 1/100ths, stirring with the thermometer, and then replacing the plug. As this operation only required a few seconds, the alteration of temperature was insignificant, and the time selected was that at which the rate of evolution of nitrogen had just passed its maximum value, the mean being taken of the observations before, during, and immediately after this point.

Amines.

1. *Trimethylamine*, 33 per cent. solution, sp. gr. 12/12 = 0.9434. Ammonium nitrite present on adding the base = 2.0573 grams; weight of trimethylamine added = 0.036 gram. Mean temperature = 66.5°. Mean value of V/T before addition of trimethylamine = 1.561, after addition = 0.129. Thus the addition of 1.56 per cent. of trimethylamine reduces the rate of evolution of nitrogen to 8.2 per cent.

2. *Ethylamine*, 33 per cent. solution.—Ammonium nitrite present, on adding the base = 2.3493 grams; weight of base added = 0.0303 gram. Mean temperature = 59.5°.

Mean value of V/T before addition = 0.859; observations after addition = (i) 0.154, (ii) 0.046, and then evolution of gas practically came to an end.

3. *Amylamine*, 28 per cent. solution.—Ammonium nitrite present on adding the base = 2.1936 grams; weight of base added = 0.028 gram. Mean temperature = 63.6°.

Mean value of V/T before addition.	Values of V/T after addition.			
	No.		No.	
1.274	1	0.486	4	0.158
	2	0.235	5	0.129
	3	0.267		

In this case, a more gradual reduction of the velocity was observed, the final rate being 10 per cent. of the original value.

4. *Aniline* (recently redistilled).—Ammonium nitrite present on adding the base = 1.6928 grams; weight of base added = 0.052 gram. Mean temperature = 64.5°. Mean value of V/T before addition

=1.008, observations after addition = (i) 0.348, (ii) 0.14, (iii) 0.083. Thus the addition of 3 per cent. of aniline reduces the value to 8/100ths; at the conclusion of the experiment, the base, originally suspended in the liquid, had completely dissolved.

5. *Benzylamine*.—Ammonium nitrite present on adding the base = 2.3402 grams; weight of base added = 0.0987 gram. Mean temperature = 64.9°.

Mean value of V/T before addition.	Value of V/T after addition.			
	No.		No.	
1.591	1	0.314	3	0.061
	2	0.090	4	0.048

Thus, the addition of 4.2 per cent. benzylamine reduced the rate to 3/100ths of its former value, and then the rate became too slow for observation.

6. *α -Picoline* (recently redistilled).—Ammonium nitrite present on adding the base = 2.0294 grams; weight of base added = 0.0952 gram. Mean temperature = 64.4°.

Mean value of V/T before addition.	Value of V/T after addition.			
	No.		No.	
1.319	1	0.811	4	0.235
	2	0.378	5	0.234
	3	0.240		

Thus the addition of 4.7 per cent. of picoline reduced the rate to 18/100ths of its former value, at which point it remained nearly constant.

The foregoing results show that paraffinoid, benzenoid, and pyridine bases either reduce the rate of, or completely stop the decomposition of ammonium nitrite in aqueous solution.

Hydrazines.

1. *Phenylhydrazine*.—Ammonium nitrite present on adding the base = 2.1524 grams; weight of base added = 0.1099 gram. Mean temperature = 65.1°. Mean value of V/T before addition = 1.266; the evolution of gas stopped almost at once.

2. *Diphenylhydrazine* or *Hydrazobenzene*.—Ammonium nitrite present on adding the base = 2.1849 grams; 0.5 c.c. of a saturated solution of base added. Mean temperature = 64.5°.

Mean value of V/T before addition.	Values of V/T after addition.			
	No.		No.	
1.210	1	0.518	6	0.428
	2	0.459	7	0.429
	3	0.431	8	0.434
	4	0.419	9	0.432
	5	0.419		

In this case, a reduction to 346/1000ths was observed, but at that point the rate remained constant during a considerable period.

Oximes.

1. *Acetaldoxime*.—Ammonium nitrite present on adding the acetaldoxime = 2.2766 grams; acetaldoxime added = 0.2892 gram. Mean temperature = 65.2°.

Mean value of V/T before addition.	Value of V/T after addition.			
	No.		No.	
1.689	1	1.183	4	0.260
	2	0.815	5	0.209
	3	0.429		

2. *α-Benzaldoxime*.—Ammonium nitrite present on adding the benzaldoxime = 2.0487 grams; benzaldoxime added = 0.1844 gram. Mean temperature = 64.1°.

Mean value of V/T before addition.	Value of V/T after addition.			
	No.		No.	
1.161	1	1.214	6	0.625
	2	1.070	7	0.510
	3	0.976	8	0.445
	4	0.843	9	0.332
	5	0.765	10	0.242

3. *β -Benzaldoxime*.—Ammonium nitrite present on adding the benzaldoxime = 1.8849 gram; benzaldoxime added = 0.188 gram. Mean temperature = 64.7°.

Mean value of V/T before addition.	Value of V/T after addition.			
	No.		No.	
1.082	1	1.038	6	0.418
	2	0.913	7	0.367
	3	0.817	8	0.224
	4	0.689	9	0.182
	5	0.528		

4. *Acetoxime*.—Ammonium nitrite present on adding the acetoxime = 1.8791 gram; acetoxime added = 0.113 gram. Mean temperature = 63°.

Mean value of V/T before addition.	Value of V/T after addition.			
	No.		No.	
0.843	1	0.764	4	0.312
	2	0.672	5	0.198
	3	0.505		

The action of the above oximes is in all cases generally the same, being neither so effective nor so complete as in the case of the amines and hydrazines. The reduction apparently does not proceed in accordance with any simple equation, and it is probable that the reaction is also complicated.

Amides.

1. *Acetamide*, recrystallised four times previous to use. Ammonium nitrite present on adding acetamide = 1.8068 grams; weight of acetamide added = 0.1 gram. Mean temperature = 64.2°.

Mean value of V/T before addition.	Value of V/T after addition.			
	No.		No.	
1.190	1	1.375	5	1.383
	2	1.378	6	1.350
	3	1.340	7	1.327
	4	1.376	8	1.191

The addition of 5.5 per cent. of acetamide thus causes a temporary increase in the reaction, and the rate remains constant for some period of time, probably as the result of two opposing causes; on the one hand, the accelerating effect of the amide, and on the other, the diminution of mass. A repetition of the experiment with a larger quantity of acetamide gave a precisely similar result.

2. *Butyramide* (recently recrystallised). Ammonium nitrite present on adding the butyramide = 2.012 grams; weight of butyramide added = 0.1 gram. Mean temperature = 63.8°.

Mean value of V/T before addition.	Value of V/T after addition.			
	No.		No.	
1.386	1	1.493	4	1.345
	2	1.389	5	1.248
	3	1.325	6	1.211

3. *Benzamide* dissolved in alcohol so as to form a saturated solution, of which 0.5 c.c. was added. Mean temperature = 65.9°.

Mean value of V/T before addition.	Value of V/T after addition.		
	No.	Found.	Calc. log. const. = 0.0140.
1.702	1	1.575	—
	2	1.539	1.522
	3	1.507	1.474
	4	1.423	1.427
	5	1.375	1.381
	6	1.308	1.338
	7	1.293	1.295
	8	1.209	1.268

From these results it appears that benzamide neither accelerates nor retards the reaction, as the rate of decomposition after its addition is in accordance with the equation given above.

4. *Urea*. Ammonium nitrite present on adding urea = 1.8944 grams; weight of urea added = 0.1 gram. Mean temperature = 63.1°.

Mean value of V/T before addition.	Value of V/T after addition.		
	No.	Found.	Calc. log. const. = 0.022.
0.840	1	0.803	—
	2	0.768	0.768
	3	0.704	0.730
	4	0.693	0.694
	5	0.658	0.660
	6	0.641	0.637
	7	0.602	0.597

Urea, like benzamide, neither accelerates nor retards the reaction.

Imides.

Of the imides sufficiently soluble in water to be applicable for this investigation, only one, namely, benzoic sulphinide or "saccharin," was tried, and a saturated aqueous solution was made.

Ammonium nitrite present on adding "saccharin" = 2.2237 grams ; "saccharin" added = 0.125 gram. Mean temperature = 61.8°.

Value of V/T before addition = 1.050 ; immediately after addition, = 5.060, subsequently rising after three observations to 5.946 and then to 5.986, from which point the rate decreased uniformly, the remaining observations being given in Series II (*vide supra*). It appears, therefore, that the addition of this imide immediately increases the rate of evolution of nitrogen by 5—6 times its value before addition, and although the reaction proceeds according to the law of mass, yet even after a large part of the ammonium nitrite had been decomposed, the accelerating effect still continued.

The results detailed above may be summarised as follows: amines, hydrazines, and oximes retard or completely stop the decomposition of ammonium nitrite; amides produce either a slight or temporary acceleration; whilst imides produce a considerable acceleration, without, however, altering the law to which the reaction can be referred. It is not proposed to offer any explanation of these several phenomena; the first and third come within the general category of catalysis, but neither a name nor a classification can be considered to be an explanation.

The Formation of Ammonia or Acid.

Arndt, who prepared the ammonium nitrite in solution by the decomposition of barium nitrite with ammonium sulphate, observed

that such solutions became alkaline after a certain time, a result which he attributed to the formation of ammonia. He writes: "Bei einigen Stundenlang dauernden Messingsreihen was es mir aufgefallen dass in der Ammoniumnitritlösung Spuren von Ammoniak frei geworden waren, die der Lösung alkalische Reaction verstehen."

It is somewhat difficult to understand this observation, having regard to the statement by the same writer that even such a small quantity as 1/800th part of free ammonia reduces the rate to nearly one-third (compare *supra*); further, most solutions of ammonium salts become acid when heated.

In order to examine this point, ammonium nitrite solutions (prepared from silver nitrite), which generally contained a trace of free acid, were titrated with a very dilute solution of ammonia, then heated for different periods of time and again titrated. The amount of salt present before and after the experiment was estimated by potassium permanganate, and hence the percentage decomposition ascertained. The results are given in the following table:

Acids in parts per 10,000.		Percentage decomposition.
Before.	After.	
6.6	6.6	4.9
0.3	0.3	10.31
1.3	1.0	13.53
0.2	0.2	59.63
trace	trace	66.88

From the above results, there does not appear to be any indication of the formation of ammonia, and in the last two observations the reaction was continued for several hours.

Presence of Barium Sulphate and Finely-divided Particles.

As mentioned above, Arndt prepared the ammonium nitrite solutions from barium nitrite and ammonium sulphate *in situ*, and he stated that the presence of the finely-divided, precipitated barium sulphate made no difference in the rate of evolution of nitrogen. In my previous experiments (*loc. cit.*), I observed that the addition of silica and pumice to a solution when heated and evolving gas, caused a temporary increase in the rate of evolution; precipitated barium sulphate, although not tried in this particular decomposition, was found to be an effective material in other cases.

As the observations of Arndt and myself appear to be discrepant, this point was examined incidentally. Finely-divided barium sulphate was prepared by treating, at the ordinary temperature, a solution of recrystallised barium chloride (1 litre = 0.1 BaCl₂) with a solution of recrystallised copper sulphate having an equivalent concentration. The precipitate was washed by decantation only until free from impurities, other than a negligible trace of chloride; it was then ignited in a platinum crucible, rubbed up in an agate mortar, and finally sifted through fine muslin. In order to examine the degree of fineness, the particles were examined under a microscope with a magnification of 1000 diameters, and their average diameter found to be 1–2 μ . Without entering fully into the details of the experiments, it need only be stated that, on the one hand, the addition of this precipitate to a solution evolving gas caused a temporary increase in the rate of the evolution, the effect being quite transitory; on the other hand, in a comparative experiment in which two solutions, one without and the other with, barium sulphate were heated side by side, it was found that at first the evolution of gas was more rapid from the solution containing the precipitate, but subsequently the rates of evolution became equal. The barium sulphate, therefore, merely produces an alteration in the quantity of nitrogen gas stored within the solution.

The main points of the present communication may be summarised as follows:

(1) The decomposition of ammonium nitrite into nitrogen and water proceeds according to the general law

$$\log A/A-x = aT,$$

whether in the presence or absence of an accelerator.

(2) This decomposition is either impeded or stopped by ammonia liberated in the solution by the addition of metallic oxides; it is also similarly affected by amines and hydrazines, and to a less degree by oximes.

(3) The decomposition is temporarily accelerated by amides of the paraffin series, but other amides are ineffective.

(4) Benzoic sulphinide, the only imide tried, produced a considerable acceleration.

(5) Solutions of ammonium nitrite, prepared from silver nitrite and ammonium chloride, do not become alkaline in the course of decomposition.

I have to express my obligations to Mr. H. C. Buck for assistance in the course of this investigation.