

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY]

THE ACTION OF SULFURIC ACID ON NITROGUANIDINE¹

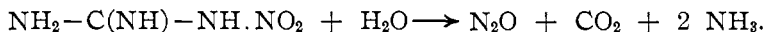
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Nitroguanidine is an especially interesting and valuable explosive for the reasons that it is cool, and that it may be produced cheaply from raw materials the supply of which is inexhaustible. While it has about the same force as 75% dynamite, Vielle's experiments² have shown that its explosion produces a temperature of only 907° as compared with 3161° for 75% dynamite, 3429° for mannite hexanitrate, and 2676° for the nitrocellulose powder of the French. Since dicyandiamide reacts³ with 2 molecules of ammonium nitrate to yield 2 of guanidine nitrate, and since guanidine nitrate on treatment with strong sulfuric acid gives nitroguanidine⁴ in excellent yield, the explosive can be prepared by a short process from atmospheric nitrogen—and the action of sulfuric acid on nitroguanidine is a matter of obvious and immediate interest.

If nitroguanidine is dissolved in cold conc. sulfuric acid and the solution is diluted promptly with water, the material precipitates again. If the solution is allowed to stand, gas bubbles presently begin to come off and the solution after a few days no longer gives any precipitate when diluted with water. The same gas evolution and destruction of nitroguanidine take place more quickly if the solution in strong sulfuric acid is warmed. In view of these facts it is necessary to operate rapidly and at as low a temperature as possible when preparing nitroguanidine from guanidine nitrate by the action of sulfuric acid.

Preliminary experiments showed that the gases contain nitrous oxide and carbon dioxide and that ammonium sulfate remains in the acid liquid—a result which leads us to believe that the decomposition of nitroguanidine by strong acid might be the same as the reported decomposition by strong alkali,⁵ namely, in accordance with the following equation.



We have shown this to be the case by measurements of the amounts of ammonia and of carbon dioxide. These are produced quantitatively

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² Vielle, "Mémorial des Poudres," **11**, 195 (1901).

³ THIS JOURNAL, **43**, 2234 (1921). Compare also Ewan and Young, *J. Soc. Chem. Ind.*, **40**, 109-12T (1921).

⁴ Jousselin, *Compt. rend.*, **88**, 1087 (1879). Pellizzari, *Gazz. chim. ital.*, **21**, II, 406 (1891).

⁵ Franchimont, *Rec. trav. chim.*, **10**, 233 (1891). Thiele, *Ann.*, **270**, 18 (1892).

in accordance with the equation when a solution of nitroguanidine in sulfuric acid is evaporated until fumes come off. The reaction has a possible application as a means of analysis.

Nitroguanidine dissolved in dil. sulfuric acid can obviously not be recovered by the evaporation of the solution. We have determined the solubility of nitroguanidine in sulfuric acid of various concentrations by measurements of the amount of carbon dioxide which is produced when the solutions are evaporated to fuming. We have been able to check these results by digesting known weights of nitroguanidine with dil. sulfuric acid in the thermostat and measuring the loss in weight.

Discussion of Experiments

The nitroguanidine which was used for this work was a sample which had been recrystallized from water to constancy of melting point. When the temperature of the melting-point bath was raised with moderate rapidity, the sample melted sharply at 232° and decomposed at a slightly higher temperature giving off gas and depositing a white solid.

A weighed amount was heated with sulfuric acid, the acid liquid was made slightly alkaline with caustic soda and distilled with steam as in the Kjeldahl determination of ammonia, and the distillate was titrated with standard hydrochloric acid solution. The ammonia which was found, therefore, was the result both of the acid and of the alkaline decomposition, but the fact that ammonia was produced quantitatively only when the sulfuric acid solution had been evaporated to fuming is evidence that the

Wt. of sample G.	Acid Cc.	Materials	Duration of heating Hours	Conditions of heating	NH ₃
					%
0.2638	{ 10 50	{ conc. acid water }	1	Reflux condenser	83.33
0.4271	Same		3	Reflux condenser	68.0
0.6788	{ 15 100	{ conc. acid water }	4	Same	64.1
0.8717	{ 10 1	{ conc. acid water }	2	Fuming in Kjeldahl flask	100.6
0.9664	Same		2	Boiled under reflux	97.0
0.7751	{ 8 5	{ conc. acid water }	2	Same	69.3
1.1484	{ 2 10	{ fuming acid conc. acid }	2	Fuming in flask	99.93
1.5328	{ 2 132	{ fuming acid conc. acid }	2	Not fuming	61.87
2.0712	{ 3 10	{ fuming acid conc. acid }	3	Not fuming	71.31
1.2044	{ 3 8	{ fuming acid conc. acid }	3	Fuming	99.4
1.5941	10	conc. acid	3	Fuming in covered casserole	99.6
1.1484	Same		3	Same	99.93

alkaline decomposition in our experiments was inconsiderable and that the vigor of the sulfuric acid treatment was the determining factor. It was found necessary, when working with conc. sulfuric acid, to start the heating slowly; otherwise small explosions occurred involving possible loss of material. The various experiments are tabulated below, where the conditions under which each experiment was carried out are indicated. The *per cent.* is the amount of ammonia which was found calculated as a fraction of the amount which would be expected in accordance with the above equation. Results were satisfactory in the cases in which the liquid was evaporated to fuming.

Vigorous heating was found to be necessary also for the liberation of all of the carbon dioxide from nitroguanidine. Satisfactory results were obtained by dissolving the sample in dil. sulfuric acid and evaporating until crystals of ammonium sulfate separated from the liquid. Rather elaborate apparatus was necessary in order that no part of it might be attacked by sulfuric acid fumes and in order that sulfuric acid and water might be completely removed from the gases before they reached the tubes for the absorption of carbon dioxide. As the solution became concentrated, it was necessary to continue the heating more slowly in order to avoid a violent evolution of gas.

Wt. of sample G.	Acid Cc.	Materials	Duration of heating Hours	Conditions of heating	CO ₂ %
0.3028	{ 10 5	{ conc. acid water	1/2	Boiled slowly	93.9
0.2815	Same		1/4	Same	55.0
0.7906	{ 20 10	{ conc. acid water	1/3	Same	54.0
0.8500	{ 30 5	{ conc. acid water	3	Same	97.77
*2.6994	{ 4 2.5	{ conc. acid water	1 1/2	Boiled until crystals appeared	99.47
*1.9735	Same		Same	Same	99.93
1.9593	Same		Same	Same	99.95
1.7374	Same		Same	Same	99.90
1.4489	Same		Same	Same	100.11

In the two experiments which are marked with a star, 0.4 g. of potassium permanganate was added in the expectation that it would hasten the decomposition of the nitroguanidine. It was found however to be without material effect.

Samples of nitroguanidine were digested with sulfuric acid of various concentrations (the specific gravity was determined) in a well-regulated thermostat at 25° for periods of at least 3 days. A measured volume of the saturated solution was then removed, and nitroguanidine was determined in it by weighing the carbon dioxide which it evolved when heated

as described above. Similar experiments were carried out with samples digested, with frequent shaking, in ice water for at least 3 days. Results are shown in the following table.

Sulfuric acid		Nitroguanidine (g.) per 100 cc. of solution	
Sp. gr.	%	at 0° G.	at 25° G.
1.092	13.2	...	0.3418
1.120	17.0	0.2498	0.6162
1.132	18.5	0.4438	0.8988
1.160	22.2	0.5324	1.357
1.187	25.6	0.5822	1.909
1.219	29.7	1.107	2.815
1.269	35.6	...	5.348
1.355	45.4	5.368	10.81

In order to check these results another set of determinations was made by a different method. An excess of nitroguanidine, previously dried to constant weight and weighed, was placed in each of seven 250cc. glass-stoppered narrow-mouth bottles; 150cc. portions of dil. sulfuric acid of known specific gravity were introduced into the bottles, and the bottles were shaken in the thermostat at 25° for 10 hours. The contents of each bottle was filtered immediately through a weighed Gooch crucible, drained as much as possible, carefully washed with 25 cc. of ice water, dried to constant weight at 100° and weighed. The solubility of the nitroguanidine was calculated on the basis of the amount which was left undissolved. Another series was carried out in the same way except that the bottles after removal from the thermostat were kept in ice water for 2 days with frequent shaking. These experiments were made in duplicate. The results tabulated below are the means of two determinations.

Sulfuric acid		Nitroguanidine per 100 cc. of solution	
Sp. gr.	%	at 0° G.	at 25° G.
1.12	17.0	0.447	0.700
1.13	18.3	0.495	0.920
1.15	20.9	0.664	1.280
1.18	24.8	0.755	1.800
1.22	29.8	1.506	2.714
1.26	34.6	...	5.451
1.349	44.7	6.956	11.129

In the accompanying graph the values obtained by determination of carbon dioxide are indicated by crosses while those obtained by difference of weight before and after treating with solvent are indicated by black dots. It appears that the two methods give substantially the same result.

The mean curves are plotted. Reading from them we obtain the following figures for the solubility of nitroguanidine in sulfuric acid of various

concentrations. The values for pure water, determined by the usual method, are included for purposes of comparison.

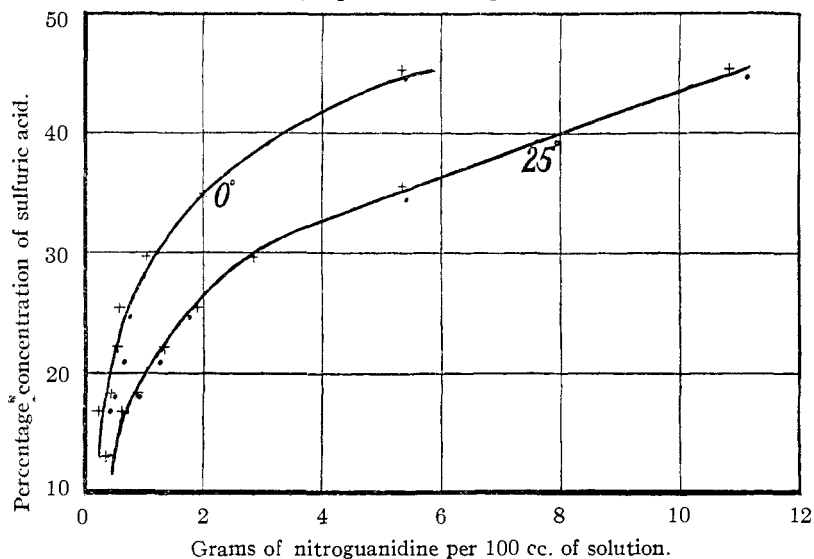


Fig. 1.—Solubility of nitroguanidine in sulfuric acid of various concentrations.

Conc. of sulfuric acid used	Nitroguanidine per 100 cc. of solution	
	at 0° C.	at 25° C.
45	5.8	10.9
40	3.4	8.0
35	2.0	5.2
30	1.3	2.9
25	0.75	1.8
20	0.45	1.05
15	0.30	0.55
0	0.12	0.42

Summary

Nitroguanidine is decomposed quantitatively by hot conc. sulfuric acid, half of its nitrogen appearing as ammonia and all of the carbon as carbon dioxide. By taking advantage of this reaction to determine the solubility of nitroguanidine in sulfuric acid of various concentrations, results have been obtained which check with those determined by the more direct method.

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