NOMENCLATURE

B = Constant in Tait equation
B' = Constant in dielectric constant equation
C = Constant in Tait equation
C' = Constant in dielectric constant equation
c = Concentration
E = Constant in Equation 4
J = Constant in Equation 4
P = Pressure
S = Constant in Equation 4
W = Walden product
ϵ = Dielectric constant
ϵ_1 = Dielectric constant at 1 atm
η = Viscosity
Λ = Equivalent conductance
Λ_0 = Limiting equivalent conductance
ρ = Density
ρ_1 = Density at 1 atm

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ORGANIC SECTION

Recovery of Guanidine from Nitroguanidine in Concentrated Sulfuric Acid

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Solvolysis of nitroguanidine in sulfuric acid was studied with specific reference to the amount of guanidine that could be recovered. Experiments were made at three concentrations of sulfuric acid with acetamide, urea, salicylic acid, and urethane as nitric acid scavengers, with excess nitric acid, and with sulfuric acid alone. Removal of nitric acid by scavengers increased the recovery of guanidine.

The main use of nitroguanidine is as an ingredient in gun propellants because of its unique ability to lower combustion temperature—i.e., minimize gun barrel erosion—and reduce flash with little or no loss of power.

Nitroguanidine is usually manufactured by nitration of guanidine in concentrated sulfuric acid solution from which guanidine is not recovered. The data in this paper indicate that an economical method for the recovery of guanidine from nitroguanidine is feasible and that the information presented may be of use in the degradation and reclamation problems associated with industrial pollution of such compounds.

The nitration of guanidine in concentrated aqueous acid solution has been previously studied with special emphasis on the mechanism of the reverse reaction—i.e., denitration (*2*-*9*). Evans et al., claimed a process for the recycling of guanidine in spent guanidine nitrating acid, but the guanidine was not recovered (*5*). Recovery of the guanidine by treatment of nitroguanidine with strong acids to convert it to guanidine and nitric acid was found unsatisfactory by Simkins et al., because nitric acid was found to react with guanidine-forming urea, carbon dioxide, and oxides of nitrogen (*8*, *9*).

This paper presents the effect of nitric acid scavengers on the solvolysis of nitroguanidine in sulfuric acid and the recoverability of guanidine from such a solution. The recovery of guanidine was improved by shifting the equilibrium that exists between guanidine and nitroguanidine toward guanidine by addition of compounds that preferentially react with nitric acid.

In Table I (expt. 1) the data exhibit a minimum value for the percent recovery of guanidine from nitroguanidine with no additive, at the 80.7% sulfuric acid concentration. Other laboratories have also demonstrated a minimum in the percent denitration of nitroguanidine over the range 70 to 90% sulfuric acid (*2*). The complete recovery of guanidine could be achieved by addition of compounds such as salicylic acid and urethane which are capable of rapid and complete reaction

Table I. Influence of Additives on Recovery of Guanidine from Solvolysis of Nitroguanidine in Concentrated Sulfuric Acid

	Reactants		Original analyses[a]		Final Analyses after 4 hr at 75°C[a]						
Expt. no.	Nitroguanidine (NGu) (0.28 molal solutions) and additives	H_2SO_4 wt %	NGu	Nitric acid	NGu[b]	Nitric acid	Guanidine	Carbon dioxide	Urea	Mass balance[c]	% Guanidine recov
1	Nitroguanidine alone	70.6	0.2784	0.0099	0.1346	0.1460	0.1490	0.0035	0.0000	99.6	51.7
		80.7	0.2604	0.0269	0.1218	0.0063	0.0850	0.0640	0.0041	95.7	29.5
		89.8	0.2418	0.0417	0.0000	0.0000	0.1180	0.1229	0.0404	99.3	40.9
2	Nitroguanidine plus acetamide	70.6	0.2768	0.0111	0.1144	0.1618	0.1696	0.0016	0.0000	99.4	58.8
		80.7	0.2566	0.0429	0.1470	0.0032	0.0863	0.0568	0.0059	98.7	29.9
		89.8	0.2632	0.0238	0.0000	0.0000	0.1424	0.1114	0.0298	98.7	49.4
3	Nitroguanidine plus urea	70.6	0.2777	0.0095	0.0759	0.0667	0.2219	0.1281	0.1420	98.7	76.9
		80.7	0.2494	0.0408	0.0257	0.0008	0.2488	0.2513	0.0528	100.0	86.3
		89.8	0.2509	0.0245	0.0000	0.0000	0.2127	0.2214	0.1296	100.0	73.8
4	Nitroguanidine plus urethane	70.6	0.2807	0.0064	0.0000	0.0000	0.2861	0.2629	0.0000	99.6[d]	99.2
		80.7	0.2489	0.0207	0.0000	0.0000	0.2590	0.2340	0.0000	95.9[d]	89.8
		89.8	0.2658	0.0236	0.0000	0.0000	0.2159	0.2141	0.0271	74.6[d]	74.9
5	Nitroguanidine plus salicylic acid	70.6	0.2479	0.0375[d]	0.0000	0.1009[e]	0.2202	0.1408	0.0000	77.2[d]	76.4
		80.7	0.2373	0.0528[d]	0.0000	0.2748[e]	0.2797	0.0178	0.0000	96.4[d]	97.0
		89.8	0.0000	0.2873[d]	0.0000	0.2863[e]	0.2797	0.0079	0.0000	97.4[d]	97.0
6	Nitroguanidine plus nitric acid	70.6	0.2902	0.2872	0.2104	0.3507	0.0729	0.0081	0.0000	100.4	25.3
		80.7	0.2815	0.2951	0.1643	0.1714	0.0024	0.1125	0.0000	99.2	0.8
		89.8	0.2854	0.2852	0.0000	0.0000	0.0000	0.2873	0.0000	100.6	0.0

[a] Molal units used. [b] Includes all nitro compounds. [c] Based on carbon compounds. [d] Based on guanidine recovery. [e] Nitrosalicylic acid.

with nitric acid (Table I, expts. 4 and 5). Addition of nitric acid (Table I, expt. 6) was found to bring about complete decomposition of nitroguanidine and guanidine at 89.8% sulfuric acid.

EXPERIMENTAL

The apparatus consisted of a train of gas-washing bottles with fritted cylinders, fitted with ball and socket joints. Helium was used to maintain positive pressure on the system. The first two bottles, which were placed in a constant temperature bath, contained 95% sulfuric acid (to wash the helium) and the reaction mixture in that order. The remaining two bottles which contained 10% sodium hydroxide solution were placed on the outside of the bath.

In a typical experiment, sufficient nitroguanidine was dissolved in 70.6% sulfuric acid at 20°C to make an approximately 0.28 molal solution. Part of the solution was held at 20°C for analysis (constant time period used for all experiments) and a known weight of the remainder was placed in the second gas washing bottle through which helium was bubbled. The reaction bottle was held at 75 ± 0.2°C for 4 hr during which time any evolved carbon dioxide was trapped by the two bottles outside the temperature bath containing sodium hydroxide solution. At the end of the reaction period, the reaction mixture was quenched and analyzed for nitric acid, nitroguanidine, urea, and guanidine (*1*, *10*). The sodium hydroxide solutions were analyzed for carbon dioxide. This experiment was repeated in 80.7 and 89.8% sulfuric acid which contained the same quantity of nitroguanidine. Similar experiments were carried out, but with the addition of equimolal quantities of acetamide, urea, salicylic acid, urethane, and nitric acid. The value for the percent guanidine recovered varied not more than ±2% when the experiments were replicated.

Guanidine could be separated from the reaction mixture by the following procedure: The reaction mixture was poured over 300 grams of crushed ice and neutralized to a pH of between 5 and 6 with barium hydroxide solution. The barium hydroxide was dissolved in sufficient distilled water to make the total neutralized product have a volume of about 1200 ml. The barium sulfate was filtered and washed by slurrying with two portions of 1200 ml of distilled water. The combined filtrates were evaporated to about 100 ml by warm air (35–40° C). Undissolved nitroguanidine, if present, was filtered off and the filtrate analyzed for guanidine by the American Cyanamid Co. method (*1*). Total nitroguanidine was determined by potentiometric titration with ferrous sulfate in sulfuric acid or by the transnitration of salicylic acid (*10*).

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