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TECHNICAL REPORT

PHOTOCHEMISTRY OF AQUEOUS NITROGUANIDINE

AD-A203 209

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Prepared for

U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, MD 21010-5401

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Fort Detrick
Frederick, MD 21701-5010

June 1988

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U S ARMY MEDICAL RESEARCH & DEVELOPMENT COMMAND
Fort Detrick
Frederick, MD 21701-5012

88 12

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

AD-A203 200

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release
distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
U.S. Army Biomedical Research and Development Laboratory

6b. OFFICE SYMBOL (If applicable)
SGRD-UBG-O

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS (City, State, and ZIP Code)
Fort Detrick
Frederick, MD 21701-5010

7b. ADDRESS (City, State, and ZIP Code)

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
U.S. Army Toxic and Hazardous Materials Agency

8b. OFFICE SYMBOL (If applicable)
AMXTH-TE-D

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Technical Report 8808

8c. ADDRESS (City, State, and ZIP Code)
Aberdeen Proving Ground
MD 21010-5401

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
62720A	1L163720	D048	

11. TITLE (Include Security Classification)
(U) Photochemistry of Aqueous Nitroguanidine

12. PERSONAL AUTHOR(S)
W. Dickinson Burrows, Ph.D; Mark O. Schmidt; Ralph H. Chyrek; Charles I. Noss, Sc.D.

13a. TYPE OF REPORT
Technical Report

13b. TIME COVERED
FROM Oct 84 TO Sep 86

14. DATE OF REPORT (Year, Month, Day)
1988, June 30

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Nitroguanidine, Guanidine, Nitrosoguanidine, Urea, Dicyandiamide, Photochemistry

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Production of nitroguanidine at Sunflower Army Ammunition Plant (SFAAP), DeSoto, KS, is associated with a number of waste streams with quite different characteristics. Initial studies by the U.S. Army Biomedical Research and Development Laboratory have been directed toward physical chemical treatment of wastewater containing relatively low levels (less than 100 mg/L) of guanidine and nitroguanidine. Ultraviolet photolysis was investigated as an alternative to granular activated carbon adsorption for removal of nitroguanidine.

(1)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
W. Dickinson Burrows, Ph.D.

22b. TELEPHONE (Include Area Code)
(301) 663-2446

22c. OFFICE SYMBOL
SGRD-UBG-O

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE

19. ABSTRACT (Continued)

For an initial nitroguanidine concentration of 50 mg/L, photolysis exhibits zero-order kinetics through complete disappearance, regardless of pH, and the rate is somewhat faster than for other nitramine explosives and propellants, RDX, for example. The products of photolysis became a matter of concern when it was discovered that photo-nitroguanidine is more toxic to aquatic organisms by several orders of magnitude than the parent compound. The principal products from unbuffered nitroguanidine solutions are guanidine, urea and nitrite ion, with lesser quantities of cyanoguanidine, nitrate ion and ammonia, accounting for 80 percent of the carbon and virtually all of the nitrogen. Nitrosoguanidine is a transient intermediate; in separate experiments it was shown to give 90 percent conversion to guanidinium nitrite at a rate slightly faster than for nitroguanidine. All the stable products of unbuffered nitroguanidine photolysis except urea and nitrate ion are known to be much more toxic to aquatic organisms than the parent compound. Photolysis of nitroguanidine at pH 10 proceeds at nearly the same rate as the unbuffered reaction, but the product mix is different; less than 25 percent of nitroguanidine carbon is accounted for as urea, guanidine and cyanoguanidine. Elemental nitrogen is a significant product.

PREFACE

The research reported herein was supported by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, MD, under Project P11 - Treatment of Munition Production Wastes. The Project Officer was Janet Mahannah. This study is part of the U.S. Army Armament, Munitions, and Chemical Command (USAAMCCOM) Pollution Abatement and Environmental Control Technology Program.

High performance liquid chromatography analyses were performed at the U.S. Army Biomedical Research and Development Laboratory (USABRDL) by Ernst E. Brueggemann; all other analyses were carried out under the direction of Dr. Steven H. Hoke. Synthesis and purification of nitrosoguanidine were performed by Alan B. Rosencrance.

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INTRODUCTION

Nitroguanidine, a constituent of triple-base propellant, is presently manufactured at Sunflower Army Ammunition Plant (SFAAP), DeSoto, KS. Although the production facility was designed to operate with no wastewater discharge, it now appears that as much as 400,000 gpd may be generated at the full mobilization production level of 40 tons per day. Reports that nitroguanidine is degraded by ultraviolet (UV) radiation[1] and by sunlight[2] led Noss and Chyrek to investigate UV photolysis and photooxidation as wastewater treatment technologies.[3] The subsequent discovery by van der Schalie that UV-photolyzed nitroguanidine in orders of magnitude more toxic to aquatic organisms than nitroguanidine alone[4] (Table 1) made UV photolysis unsuitable for wastewater treatment and further suggested that discharge of even small quantities of nitroguanidine may be environmentally hazardous. The present study was undertaken to develop a more detailed understanding of the consequences of nitroguanidine photolysis.

TABLE 1. TOXICITIES OF NITROGUANIDINE AND PHOTO-NITROGUANIDINE[a]

	Fathead minnow 96 hr LC50, mg/L	Daphnia 48 hr EC50, mg/L
Nitroguanidine	>2714	>2838
Photo-nitroguanidine	34.5	24.6

a. Reference 4.

EXPERIMENTAL PROCEDURES

EQUIPMENT

Two reactors were employed. The stainless steel reactor, described previously, is 6.6 in (16.8 cm) in diameter and 78 in (2 m) tall, with a useful volume of 38 L.[3] An 80-watt UV lamp (estimated 34-watt output in the UV range) encased in a 1-inch (2.5 cm) quartz tube running vertically through the center of the column emits maximum radiation at a wavelength of 253.7 nm. In the radiation-only mode, reactor contents are mixed by recirculation at ca. 6 L/min. For experiments involving gas collection, the apparatus pictured in Figure 1 was used.[5] Four 40-watt ultraviolet lamps surround a 2-inch (5 cm) quartz sample tube of 1.5 L capacity. Cooling water is circulated from a refrigerated constant temperature bath through a center tube. The apparatus is enclosed in a close-fitting box lined with reflecting foil. Gas is collected in a calibrated bottle at the top.

PROCEDURES

Samples of nitroguanidine and nitrosoguanidine for rate and product analyses were dissolved in 19 L of deionized water, pumped into the stainless steel reactor and irradiated at ambient temperature, 100-mL aliquots being

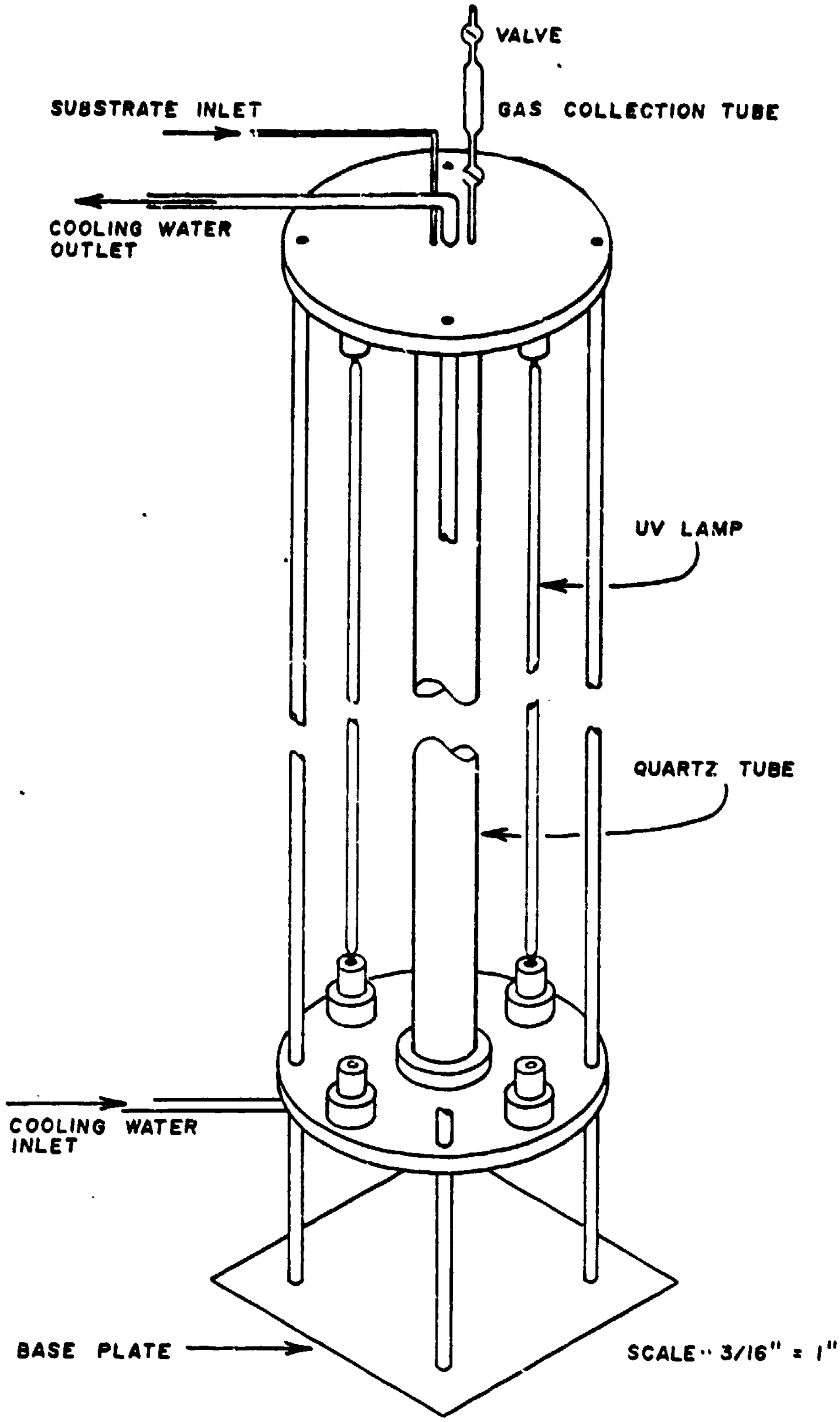


Figure 1. UV Photolysis Apparatus with the Gas Collecting Capability

collected at regular intervals. For buffered samples, 20 g of sodium carbonate and 16 g of sodium bicarbonate were added. Nitroguanidine samples were stirred overnight to assure dissolution; nitrosoguanidine, however, appeared to be unstable in water, particularly at pH 10, and it was essential to initiate photolysis as soon as possible after adding the reagent to water. Nitroguanidine, nitrosoguanidine and cyanoguanidine (dicyandiamide) were determined by HPLC by methods described by Burrows, et al.,[6] while nitrate, nitrite, ammonia nitrogen and guanidine were determined by ion chromatography. Urea was determined by a clinical method which enzymatically converts urea nitrogen to ammonia.[7]

Samples prepared for gas collection were either degassed under vacuum with sonication or were deoxygenated by saturation with nitrogen. The latter method gave the best results. Product analysis was by gas chromatography using a thermal conductivity detector and helium as carrier on a molecular sieve. For nitrogen-saturated samples, gas production was measured directly; for degassed samples a correction was made for the known solubility of nitrogen in water (18 mg/L at 1 atmosphere and 25°C). Buffer proportions were the same as above.

RESULTS AND DISCUSSION

KINETICS

Ultraviolet photolysis of nitroguanidine at 50 mg/L or less is zero order with respect to nitroguanidine through complete disappearance, regardless of pH (Figure 2). As in earlier reports on nitramine photolysis, zero-order behavior is considered a likely consequence of products being relatively transparent.[8,9] Photolysis data for nitroguanidine at initial concentrations in the range of 100 mg/L and above could be fitted to a mixed zero-order, first-order equation as follows:

$$a(C_0 - C)/C_0 + b\ln(C_0/C) = kt$$

$$\text{and} \quad a + b = 1$$

with arbitrary values for coefficients a and b of 0.9 and 0.1, respectively, giving a specific rate constant k of 0.021 min^{-1} for the unbuffered reaction and 0.016 min^{-1} for the reaction at pH 10. The gas collecting apparatus was less efficient, with k equal to ca 0.007 min^{-1} (Table B-1).

PRODUCTS: UNBUFFERED

Products of unbuffered photolysis are guanidine (Gu), cyanoguanidine (GuCN), nitrite and nitrate ions, urea and ammonia, with nitrosoguanidine (GuNO) as a transient intermediate (Tables 2 and 3), all (except urea) as noted by Noss and Chyrek.[3] Approximately 80 percent of nitroguanidine carbon is accounted for as guanidine, urea and cyanoguanidine (Table 3). The remaining carbon may have been present as cyanamide, which is in equilibrium with cyanoguanidine below pH 7[10] but which is not detectable at the mg/L level by the HPLC method employed.

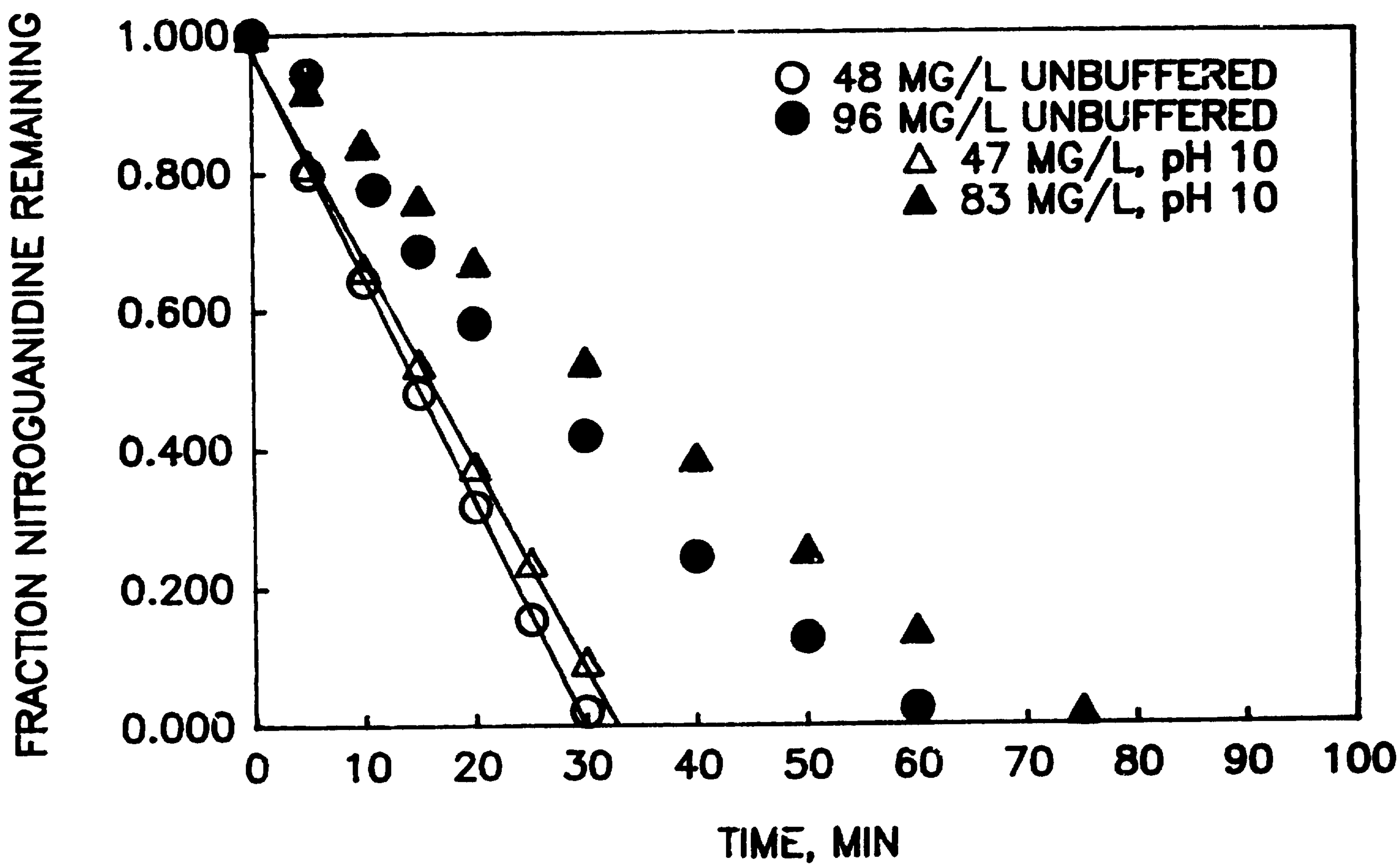


Figure 2. UV Photolysis of Nitroguanidine in 38-L Reactor

TABLE 2. UV PHOTOLYSIS OF NITROGUANIDINE, 48 MG/L, UNBUFFERED[a]

Time min	Equivalent per initial equivalent of nitroguanidine NQ	GuNO	Gu	GuCN	NO_3N	NO_2-N	NH_3-N
0	1.000	<0.003	<0.11	<0.005	<0.16	<0.16	<0.077
5	0.799	0.006	<0.11	0.018	<0.16	<0.16	<0.077
10	0.642	0.012	0.11	0.027	<0.16	0.25	<0.077
15	0.481	0.016	0.18	0.037	<0.16	0.43	<0.077
20	0.317	0.019	0.22	0.047	<0.16	0.46	<0.077
25	0.153	0.017	0.26	0.054	<0.16	0.56	0.077
30	0.020	0.014	0.32	0.082	<0.16	0.67	0.087
40	<0.002	0.007	0.32	0.080	<0.16	0.72	0.085
50	<0.002	0.005	0.32	0.080	<0.16	0.74	0.084
60	<0.002	0.003	0.33	0.081	<0.16	0.78	0.085
72	<0.002	<0.003	0.33	0.081	<0.16	0.74	0.085
90	<0.002	<0.003	0.29	0.081	<0.16	0.74	0.084

a. Data from Table A-1.

TABLE 3. UV PHOTOLYSIS OF NITROGUANIDINE, 96 MG/L, UNBUFFERED[a]

Time min	Equivalent per initial equivalent of nitroguanidine NQ	GuNO	Gu	GuCN	NO_3-N	NO_2-N	NH_3-N	Urea
0	1.000	<0.001		<0.003	<0.05	<0.02	0.036	
5	0.943	0.003	0.24	0.013	<0.05	0.06	0.040	
11	0.776	0.008	0.06	0.017	<0.05	0.19	0.053	
15	0.686	0.011	0.10	0.026	<0.05	0.24	0.056	
20	0.581	0.014	0.12	0.035	<0.05	0.35	0.063	
30	0.418	0.019	0.18	0.050	<0.05	0.56	0.077	
40	0.244	0.020	0.26	0.059	0.06	0.71	0.092	
50	0.126	0.017	0.32	0.068	0.09	0.94	0.108	
60	0.024	0.010	0.38	0.073	0.09	0.99	0.115	0.29
75	<0.001	0.004	0.40	0.094	0.17	1.06	0.115	
90	<0.001	0.003	0.40	0.096	0.15	1.13	0.115	
107	<0.001	0.001	0.42	0.094	0.15	1.13	0.115	
120	<0.001	<0.001	0.42	0.097	0.10	1.41	0.114	0.28

a. Data from Table A-2.

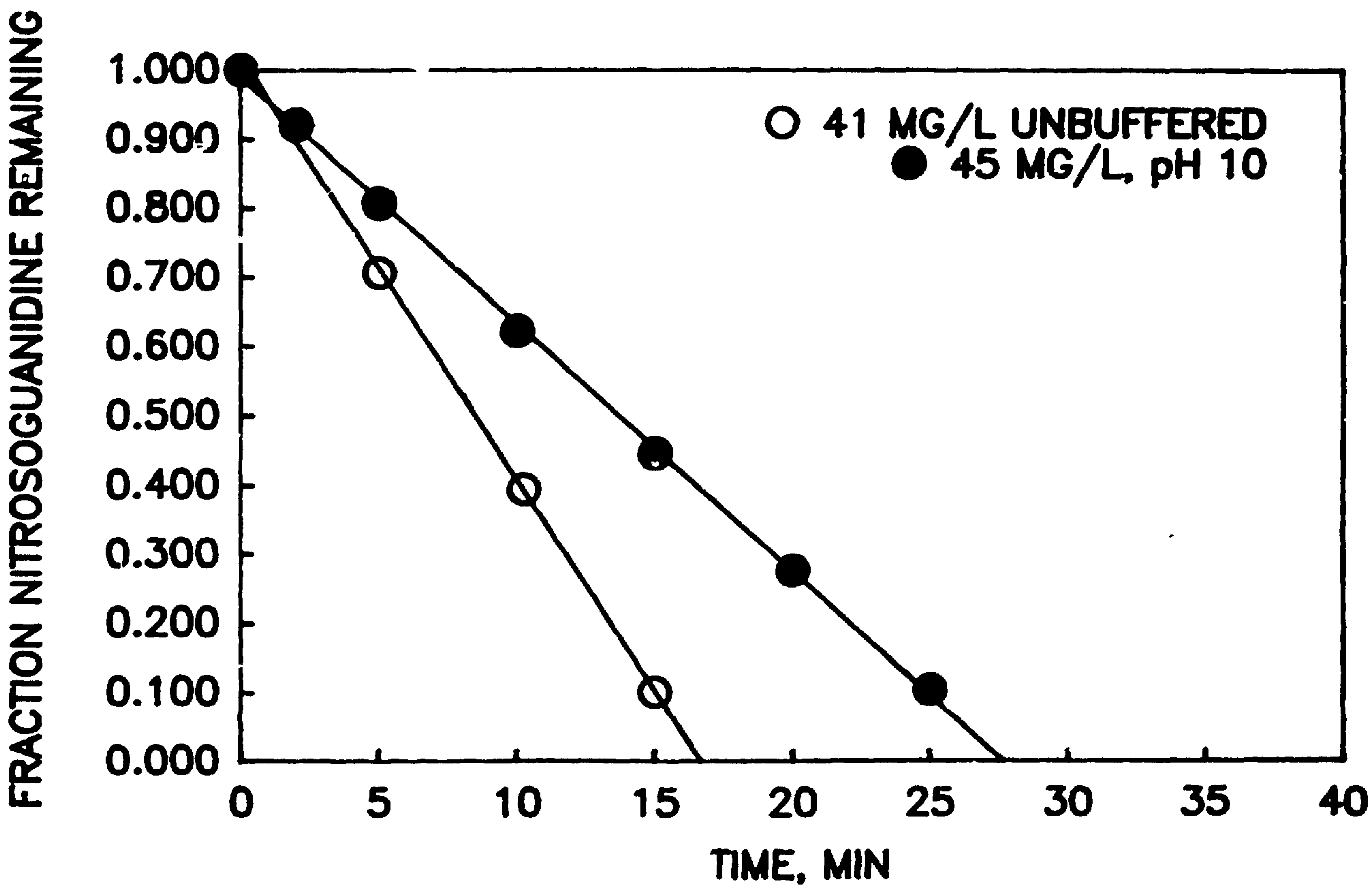
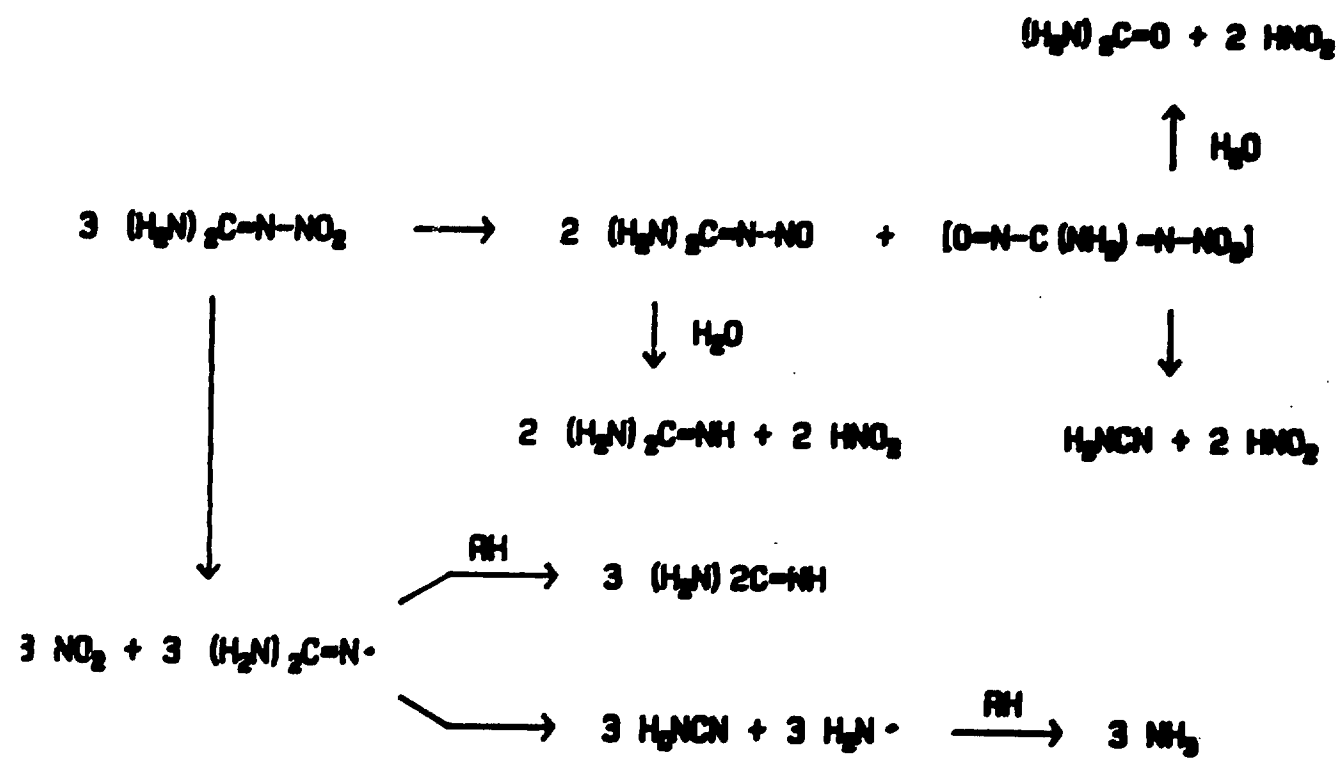


Figure 3. UV Photolysis of Nitrosoguanidine in 38-L Reactor



Scheme 1. Pathways for Photolysis of Nitroguanidine

Ultraviolet photolysis of nitrosoguanidine, which is also zero order but slightly faster than nitroguanidine photolysis (Figure 3), yields almost 90 percent of its carbon as guanidine (Table 4). This strongly suggests that nitrosoguanidine is an intermediate in a major pathway to guanidine from nitroguanidine. A simple explanation for the products observed involves photodecomposition through alternative pathways: (1) disproportionation of nitroguanidine to nitrosoguanidine and an oxidized intermediate, and (2) homolysis of the nitroguanidine N-N bond (Scheme 1). The relatively small quantities of nitrate ion and ammonia detected indicate that the first pathway is more important. (The first pathway predicts that four moles of nitrite ion will be produced for every three moles of nitroguanidine photolyzed, as observed in Table 3; however, it does not predict the excess of nitrite from nitrosoguanidine photolysis reported in Table 4. We are unable to explain this discrepancy.)

TABLE 4. UV PHOTOLYSIS OF NITROSOGUANIDINE, 41 MG/L, UNBUFFERED[a]

Time	Equivalent per initial equivalent of nitrosoguanidine					
min	GuNO	Gu	GuCN	NO_3-N	NO_2-N	NH_3-N
0	1.000	<0.11	<0.005	<0.16	<0.16	<0.011
2	0.919	<0.11	<0.005	<0.16	0.17	<0.011
5	0.706	0.21	0.015	<0.16	0.46	<0.011
10.25	0.394	0.52	0.032	<0.16	0.90	0.053
15	0.100	0.80	0.050	<0.16	1.24	0.064
20	0.004	0.90	0.060	<0.16	1.47	0.056
25	<0.002	0.89	0.061	<0.16	1.49	0.054
30	<0.002	0.89	0.059	<0.16	1.42	0.053
40	<0.002	0.88	0.063	<0.16	1.47	0.048
50	<0.002	0.89	0.063	<0.16	1.47	0.045
60	<0.002	0.85	0.062	<0.16	1.27	0.056
90	<0.002	0.88	0.061	<0.16	1.33	0.043

a. Data from Table A-5.

PRODUCTS: BUFFERED TO pH 10

Ultraviolet photolysis of nitroguanidine at pH 10 is only slightly slower than unbuffered photolysis (Figure 2), but the product distribution is quite different (Tables 5 and 6). The maximum level of nitrosoguanidine is no more than one third that observed before, and no more than 23 percent of the nitroguanidine carbon can be accounted for as guanidine, cyanoguanidine and urea. (Note that at this pH all cyanamide would be present as cyanoguanidine.[10]) An unusual discovery was that as much as 23 mole percent of elemental nitrogen could be isolated from the buffered reaction, compared with none for the unbuffered reaction. Ammonium nitrite is photochemically converted to elemental nitrogen, but this bimolecular reaction is too slow to account for the production of nitrogen from nitroguanidine, as shown in Table B-3.

TABLE 5. UV PHOTOLYSIS OF NITROGUANIDINE, 47 MG/L, pH 10[a]

Time min	Equivalent per initial equivalent of nitroguanidine NQ	GuNO	GuCN	NO_3-N	NO_2-N	Urea
0	1.000	<0.003	<0.005	<0.16	<0.16	
5	0.811	0.003	<0.005	<0.16	<0.16	
10	0.661	0.005	<0.005	<0.16	0.22	
15	0.524	0.006	<0.005	<0.16	0.35	
20	0.375	0.006	0.012	<0.16	0.46	
25	0.237	0.004	0.016	<0.16	0.56	
30	0.092	<0.003	0.022	<0.16	0.68	
40	<0.002	<0.003	0.033	<0.16	0.60	
50	<0.002	<0.003	0.035	<0.16	0.62	
62	<0.002	<0.003	0.036	<0.16	0.59	
75	<0.002	<0.003	0.035	<0.16	0.55	
90	<0.002	<0.003	0.035	<0.16	0.63	0.19

a. Data from Table A-3.

TABLE 6. UV PHOTOLYSIS OF NITROGUANIDINE, 83 MG/L, pH 10[a]

Time min	Equivalent per initial equivalent of nitroguanidine NQ	GuNO	Gu	GuCN	Urea
0	1.000	<0.001	0.006	<0.003	
5	0.920	0.003	0.007	<0.003	
10	0.842	0.005	0.010	<0.003	
15	0.760	0.007	0.012	<0.003	
20	0.670	0.008	0.014	0.004	
30	0.525	0.008	0.020	0.007	
40	0.386	0.007	0.026	0.009	
50	0.254	0.005	0.033	0.013	
60	0.136	0.003	0.046	0.016	0.16
75	0.018	<0.001	0.046	0.019	
90	0.002	<0.001	0.046	0.022	
109	<0.001	<0.001	0.046	0.022	
120	<0.001	<0.001	0.050	0.022	0.16

a. Data from Table A-4.

About 40 percent of the carbon from buffered photolysis of nitrosoguanidine (compared with more than 90 percent for unbuffered photolysis) can be accounted for as urea, guanidine and cyanoguanidine (Table 7). The low yields of guanidine from photolysis of nitroguanidine and nitrosoguanidine may be due to the strongly basic nature of guanidine;[11] at high pH the driving force of protonation is lacking. Although oxidized nitrogen is well accounted for, we are unable to explain the low recovery of carbon from photolysis of these compounds. Carbon dioxide and derivatives thereof are unlikely, since the known photolysis products are hydrolytically stable at pH 10.

TABLE 7. UV PHOTOLYSIS OF NITROSOGUANIDINE, 45 MG/L, pH 10[a]

Time	Equivalent per initial equivalent of nitrosoguanidine				
min	GuNO	Gu[b]	GuCN	NO_2-N	Urea[c]
0	1.000		<0.005	0.28	
2	0.921		<0.005	0.31	
5	0.806		<0.005	0.39	
10	0.622		<0.005	0.48	
15	0.446		0.012	0.60	
20	0.275		0.013	0.71	
25	0.103		0.015	0.83	
30	0.028		0.017	0.88	
40	0.001		0.021	0.90	
50	<0.002		0.023	0.91	
60	<0.002	0.15	0.024	0.91	0.22

a. Data from Table A-9.
b. Estimated from data in Table A-8.
c. Estimated from data in Table A-7.

PHOTO-NITROGUANIDINE TOXICITY

All the identified photolysis products of nitroguanidine (except urea[12]) are more toxic to aquatic organisms than the parent compound, as shown in Table 8. However, only nitrite ion is present at a level high enough to account for the greatly enhanced toxicity of photo-nitroguanidine. The concentration of nonionized ammonia, e.g., would be well below the LC50 at pH 8, the condition used by van der Schalie.[4] Of course, synergistic effects cannot be excluded. The US Environmental Protection Agency has declined to recommend restrictive criteria for nitrite, arguing that "concentrations of ... nitrite that would exhibit toxic effects on warm or cold water fish could rarely occur in nature."[13] The half-life for sunlight photolysis of nitroguanidine in natural waters is estimated to be 1-2 days, depending on season and latitude,[2,14] which suggests that wastewater discharged to a moving body of water would present a hazard to aquatic life only if nitroguanidine levels substantially exceeded the current SFAAP NPDES Permit limit of 25 mg/L.

TABLE 8. ACUTE TOXICITY OF NITROGUANIDINE PHOTOLYSIS PRODUCTS

Chemical/Target	Exposure hr	Endpoint	Concentration mg/L
Guanidinium nitrate[a]			
Fathead minnow	96	LC50	690
Daphnia magna	48	EC50	70.2
Ammonia (nonionized)			
Fathead minnow[b]	96	LC50	0.75-3.4
Daphnids[c]	48	EC50	123-189
Nitrite (as NO_2)			
Rainbow trout[d]	96	LC50	0.6-1.3
Channel catfish[d]	96	LC50	13.7
Fathead minnow[e]	96	LC50	2.2-2.99
Daphnia magna[f]		"threshold"	18-66
Cyanoguanidine[g]			
Rainbow trout(?)	48	LC50	*ca*. 6

a. Reference 15
b. Reference 16
c. Reference 17
d. Reference 18
e. Reference 19
f. Reference 20
g. Reference 21

SUMMARY AND CONCLUSIONS

1. Nitroguanidine is readily degraded in water by ultraviolet light and by natural sunlight. The end products of UV photolysis in unbuffered waters are guanidine, urea, cyanoguanidine and nitrite ion, with lesser quantities of nitrate ion and ammonia. Nitrosoguanidine, which is even more readily photolyzed, is an intermediate in a major pathway to guanidine. Eighty percent of the carbon from nitroguanidine and virtually all of the oxidized nitrogen can be accounted for.

2. At pH 10, photolysis of nitroguanidine and nitrosoguanidine is slightly slower, but the product distribution is different. Less than 25 percent of nitroguanidine carbon can be accounted for as guanidine, cyanoguanidine and urea. Gaseous nitrogen is a significant product.

3. Photolyzed nitroguanidine has been shown by others to be much more toxic to aquatic life than nitroguanidine, but given the photolytic half-life of 1-2 days for nitroguanidine in natural waters, and considering the dilution that would take place in that timeframe, it is highly unlikely that wastewaters discharged to a body of moving water could present a hazard to aquatic life unless the nitroguanidine levels substantially exceeded the present NPDES daily average limit of 25 mg/L for Sunflower Army Ammunition Plant.

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APPENDIX A

DATA FOR PHOTOLYSIS EXPERIMENTS IN 38 L STAINLESS STEEL REACTOR

TABLE A-1. UV PHOTOLYSIS OF NITROGUANIDINE, UNBUFFERED

Time min	NQ[a] mg/L	GuNO mg/L	Gu[b] mg/L	GuCN mg/L	NO_3-N mg/L	NO_2-N mg/L	NH_3-N mg/L	pH
0	47.90	<0.100	<3	<0.100	<1	<1	<0.5	7.8
5	38.27	0.256	<3	0.342	<1	<1	<0.5	7.7
10	30.759	0.497	3.3	0.726	<1	1.6	<0.5	7.3
15	23.042	0.657	4.8	1.017	<1	2.8	<0.5	7.2
20	15.172	0.754	5.9	1.277	<1	3.0	<0.5	6.3
25	7.314	0.699	7.2	1.480	<1	3.6	0.5	5.7
30	0.944	0.564	8.6	1.597	<1	4.3	0.56	4.8
40	<0.100	0.267	8.7	1.541	<1	4.6	0.55	4.7
50	<0.100	0.198	8.7	1.554	<1	4.8	0.54	4.7
60	<0.100	0.107	8.9	1.562	<1	5.0	0.55	
72	<0.100	<0.100	8.9	1.564	<1	4.8	0.55	
90	<0.100	<0.100	8.0	1.569	<1	4.8	0.54	4.7

a. Prepared from 0.95 g of nitroguanidine in 19 L of water.
b. Guanidine reported as guanidine, not as nitrogen.

TABLE A-2. UV PHOTOLYSIS OF NITROGUANIDINE, UNBUFFERED

Time min	NQ[a] mg/L	GuNO mg/L	Gu[b] mg/L	GuCN mg/L	NO_3 mg/L	NO_2 mg/L	NH_3-N mg/L	Urea[b] mg/L
0	95.978	<0.100		<0.100	<3	<1	0.46	
5	90.548	0.274	0.93	0.517	<3	2.4	0.52	
11	74.471	0.685	2.45	0.677	<3	8.1	0.69	
15	65.887	0.865	4.01	1.024	<3	10.0	0.73	
20	55.752	1.145	4.50	1.371	<3	15.0	0.82	
30	40.144	1.561	7.12	1.926	<3	24.0	1.00	
40	23.447	1.653	10.26	2.273	3.4	30.0	1.19	
50	12.046	1.385	12.48	2.620	5.4	40.0	1.39	
60	2.347	0.813	14.94	2.828	5.1	42.0	1.49	7.45
75	<0.100	0.363	15.68	3.660	9.6	45.0	1.49	
90	<0.100	0.220	15.68	3.730	8.4	48.0	1.49	
107	<0.100	0.116	16.17	3.643	8.4	48.0	1.49	
120	<0.100	<0.100	16.17	3.744	5.7	60.0	1.47	7.15

a. Prepared from 2.0 g of nitroguanidine in 19 L of water.
b. Guanidine and urea reported as guanidine or urea nitrogen.

TABLE A-3. UV PHOTOLYSIS OF NITROGUANIDINE, BUFFERED TO pH 10

Time min	NQ[a] mg/L	GuNO mg/L	Gu[b] mg/L	GuCN mg/L	NO_3-N mg/L	NO_2-N mg/L	pH	Urea[c] mg/L
0	46.940	<0.100		<0.100	<1	<1	10.1	
5	38.046	0.133		<0.100	<1	<1	10.1	
10	31.032	0.218		<0.100	<1	1.4	9.9	
15	24.602	0.243		<0.100	<1	2.2	9.9	
20[d]	17.593	0.220		0.228	<1	2.9	10.0	
25	11.133	0.149		0.312	<1	3.5	10.1	
30	4.339	<0.100		0.413	<1	4.3	10.2	
40	<0.100	<0.100		0.628	<1	3.8	10.2	
50	<0.100	<0.100		0.665	<1	3.9	10.2	
62	<0.100	<0.100		0.675	<1	3.7	10.1	
75	<0.100	<0.100		0.666	<1	3.5	10.1	
90	<0.100	<0.100		0.667	<1	4.0	10.0	2.4

a. Prepared from 0.95 g of nitroguanidine in 19 L of water
b. Guanidine not measured.
c. Urea reported as urea nitrogen.
d. Sample yellow.

TABLE A-4. UV PHOTOLYSIS OF NITROGUANIDINE, BUFFERED TO pH 10

Time	NQ[a]	GuNO	Gu[b]	GuCN	NO_3-N[c]	NO_2-N[c]	Urea[d]
0	82.78	<0.100	0.20	<0.100			
5	76.16	0.202	0.25	<0.100			
10	69.66	0.355	0.32	<0.100			
15	62.89	0.478	0.41	<0.100			
20	55.438	0.551	0.48	0.136			
30	43.438	0.564	0.68	0.237			
40	31.961	0.460	0.87	0.315			
50[e]	21.026	0.325	1.09	0.426			
60[e]	11.275	0.193	1.50	0.527			3.5
75[e]	1.245	<0.100	1.53	0.649			
90[e]	0.150	<0.100	1.54	0.750			
109	<0.100	<0.100	1.55	0.750			
120	<0.100	<0.100	1.66	0.744			3.5

a. Prepared from 2.0 g of nitroguanidine in 19 L of water.
b. Guanidine reported as guanidine nitrogen.
c. Nitrate and nitrite not measured.
d. Urea reported as urea nitrogen.
e. Sample yellow

TABLE A-5. UV PHOTOLYSIS OF NITROSOGUANIDINE, UNBUFFERED

Time min	NQ mg/L	GuNO[a] mg/L	Gu[b] mg/L	GuCN mg/L	NO_3-N mg/L	NO_2-N mg/L	NH_3-N mg/L	pH
0	<0.100	40.533	<3	<0.100	<1	<1	<0.7	7.7
2	<0.100	37.269	<3	<0.100	<1	1.1	<0.7	7.6
5	<0.100	28.600	5.7	0.287	<1	3.0	<0.7	7.4
10.25	<0.100	15.960	14.0	0.617	<1	5.8	0.34	7.1
15	<0.100	4.034	21.7	0.970	<1	8.0	0.41	6.4
20	<0.100	0.157	24.5	1.170	<1	9.5	0.36	6.4
25	<0.100	<0.100	24.3	1.178	<1	9.6	0.35	6.3
30	<0.100	<0.100	24.2	1.145	<1	9.2	0.34	6.2
40	<0.100	<0.100	23.9	1.222	<1	9.5	0.31	6.1
50	<0.100	<0.100	24.2	1.228	<1	9.5	0.29	6.2
60	<0.100	<0.100	23.2	1.202	<1	8.2	0.35	4.1
75	<0.100	<0.100	24.0	1.189	<1	8.6	0.28	5

a. Prepared from 0.97 g Of nitrosoguanidine in 19 L of water.
b. Guanidine reported as guanidine.

TABLE A-6. UV PHOTOLYSIS OF NITROSOGUANIDINE, UNBUFFERED

Time min	GuNO[a] mg/L	GuCN mg/L
0	45.68	<0.10
2	41.43	<0.10
5	33.57	<0.10
10	20.64	<0.10
15	6.39	0.23
20	0.11	0.53
27	<0.10	0.70
35	<0.10	0.78
45	<0.10	0.90
60	<0.10	1.00
75	<0.10	1.12

a. Prepared from 0.95 g of nitrosoguanidine in 19 L of water.

TABLE A-7. UV PHOTOLYSIS OF NITROSOGUANIDINE, BUFFERED TO pH 10

Time min	NQ mg/L	GuNO[a] mg/L	Gu[b] mg/L	GuCN mg/L	NO_3-N mg/L	NO_2-N mg/L	Urea[c] mg/L	pH
0	<0.100	34.749		<0.100	<1	<1		10.3
2	<0.100	33.159		<0.100	<1	<1		10.3
5	<0.100	28.504		<0.100	<1	1.9		10.3
10	<0.100	21.918		<0.100	<1	3.6		10.3
15	<0.100	16.036		<0.100	<1	4.7		10.3
20	<0.100	10.102		<0.100	<1	7.0		10.3
25	<0.100	4.612		0.5358	<1	8.2		10.3
30	<0.100	1.127		0.4172	<1	8.6		10.4
40	<0.100	<0.100		0.5735	<1	9.1		10.3
50[d]	<0.100	<0.100		0.5757	<1	9.1		10.3
60	<0.100	<0.100		0.6261	<1	9.3		10.3
75	<0.100	<0.100		0.6183	<1	8.6	3.1	10.2

a. Prepared from 0.95 g of nitrosoguanidine in 19 L of water.
b. Guanidine not measured.
c. Urea reported as urea nitrogen.
d. Sample yellow.

TABLE A-8. UV PHOTOLYSIS OF NITROSOGUANIDINE, BUFFERED TO pH 10

Time min	GuNO[a] mg/L	Gu[b] mg/L	GuCN mg/L
0	24.46		<0.10
2	24.43		<0.10
5	16.21		0.35
10	8.69		0.44
15	3.15		0.46
20	2.47		0.48
27	<0.10		0.51
35	<0.10		0.50
45	<0.10		0.51
60	<0.10		0.51
76	<0.10	3.25	0.51

a. Prepared from 0.95 g of nitrosoguanidine in 19 L of water
b. Guanidine reported as guanidine nitrogen.

TABLE A-9. UV PHOTOLYSIS OF NITROSOGUANIDINE, BUFFERED TO pH 10

Time min	GuNO[a] mg/L	Gu[b] mg/L	GuCN mg/L	NO_2-N mg/L	Urea[c] mg/L
0	45.002		<0.100	2.01	
2	41.430		<0.100	2.19	
5	36.272		<0.100	2.77	
10	27.994		<0.100	3.41	
15	20.067		0.259	4.33	
20	12.367		0.288	5.09	
25	4.632		0.326	5.95	
30	1.276		0.370	6.29	
40	0.032		0.440	6.44	
50	<0.100		0.497	6.48	
60	<0.100		0.522	6.53	0.0

a. Prepared from 1.0 g of nitrosoguanidine in 19 L of water.
b. Guanidine analysis by fluorescence method unsatisfactory.
c. Urea reported as urea nitrogen.

APPENDIX B

DATA FOR PHOTOLYSIS EXPERIMENTS IN GAS COLLECTING APPARATUS

TABLE B-1. UV PHOTOLYSIS OF NITROGUANIDINE, BUFFERED TO pH 10

Time hrs	NQ mg/L	GuNO mg/L	GuCN mg/L	NO_3-N mg/L	NO_2-N mg/L
0	923.385	<0.100	<0.100	ND[a]	ND[a]
0.5	724.480	7.500	0.844	ND[a]	ND[a]
1	381.909	11.167	2.205	1.6	85
1.5	333.520	9.855	4.044	2.0	108
2	274.470	10.094	7.293	2.7	158
2.5	213.982	9.548	8.869	3.0	200
3	148.465	7.463	13.393	3.3	177
4	34.648	2.475	16.431	4.3	222
5	2.732	<0.100	18.691	4.3	261
6	<0.100	<0.100	18.897	4.3	302
7	<0.100	<0.100	18.132	4.3	237
8	<0.100	<0.100	19.336	4.4	221
9	<0.100	<0.100	16.986	4.3	199
10	<0.100	<0.100	17.493	4.5	215
11	<0.100	<0.100	17.697	5.1	211
12	<0.100	<0.100	17.259	4.9	213
13	<0.100	<0.100	17.758	5.5	203
14	<0.100	<0.100	17.291	5.8	222
15	<0.100	<0.100	17.787	5.8	211
16	<0.100	<0.100	19.051	5.9	212
17	<0.100	<0.100	20.726	6.2	199
18	<0.100	<0.100	19.607	6.3	181
19	<0.100	<0.100	20.134	6.2	183
20	<0.100	<0.100	20.288	6.7	195
21	<0.100	<0.100	20.337	6.8	166
22	<0.100	<0.100	19.862	7.1	163
23	<0.100	<0.100	20.365	6.6	190

a. ND = Below detection limits.

TABLE B-2. UV PHOTOLYSIS OF NITROGUANIDINE, BUFFERED TO pH 10

	Run 9[a]	Run 10[a]	Run 11[b]
NQ initial, mg/L	1267	1140	1130
NQ final, mg/L	37.7	0.74	3.08
pH initial	10.25	10.0	10.25
pH final	9.76	9.95	10.00
Vol gas collected, mL	78	42	100
Correction for N_2 solubility, mL	27	27	
Total gas, mL	105	69	100
Percent N_2 in gas	96.5	93.5	93.6
Temperature, °C	25	25	25

a. Sample initially degassed.
b. Sample presaturated with nitrogen.

TABLE B-3. UV PHOTOLYSIS OF AMMONIUM NITRITE[a]

Time hr	NO_2-N mg/L	NH_3-N mg/L	Gas collected mL
0	70	70	0
24			35
55			75
81	47	35	100

a. Prepared as 0.005 M $NaNO_2$, 0.005 N $(NH_4)SO_4$ and 0.1 M $NaHCO_3$.

APPENDIX C

GLOSSARY OF TERMS

Gu	guanidine
GuCN	cyanoguanidine (dicyandiamide)
GuNO	nitrosoguanidine
HPLC	high performance liquid chromatography
NPDES	National Pollution Discharge Elimination System
NQ	nitroguanidine
SFAAP	Sunflower Army Ammunition Plant
UV	ultraviolet

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