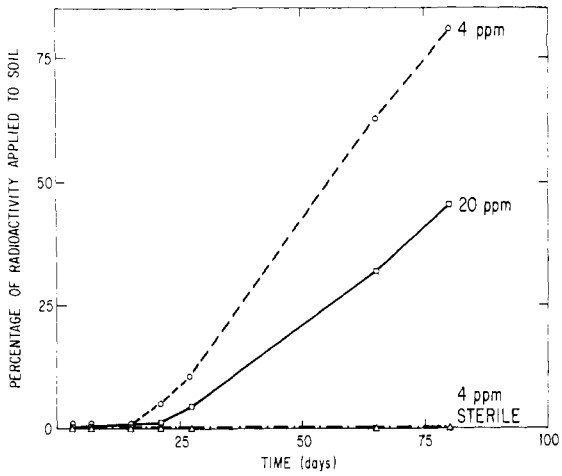

Figure 3. $^{14}CO_2$ evolved from [^{14}C]hexazinone treated Fallsington sandy loam in biometer flasks.

values for hexazinone on Fallsington sandy loam and Flanagan silt loam were 0.2 (slope 0.95) and 1.0 (slope 1.05), respectively. These K values are consistent with data for mobile (Class IV) compounds.

ACKNOWLEDGMENT

The author gratefully acknowledges R. W. Reiser for obtaining and interpreting the mass spectra of the metabolites and G. A. Smith and M. H. Williams for their assistance.

LITERATURE CITED

Bartha, R., Pramer, D., *Soil Sci.* **100**, 68 (1965).
Helling, C. S., *Soil Sci. Soc. Am. Proc.* **35**, 732 (1971a).
Helling, C. S., *Soil Sci. Soc. Am. Proc.* **35**, 737 (1971b).
Helling, C. S., *Soil Sci. Soc. Am. Proc.* **35**, 743 (1971c).
Helling, C. S., Turner, B. C., *Science* **162**, 562 (1968).
Helling, C. S., Kearney, P. C., Martin, A., *Adv. Agron.* **23**, 147 (1971).
Puri, A. N., "Soils, Their Chemistry and Physics", Reinhold, New York, 1949.
Reiser, R. W., Belasco, I. J., Rhodes, R. C., "Identification of Metabolites of Hexazinone by Mass Spectrometry", presented at the ASMS Meeting, Seattle, WA, June 4, 1979.
Rhodes, R. C. Belasco, I. J., Pease, H. L., *J. Agric. Food Chem.* **18**, 524 (1970).
Rhodes, R. C., Jewell, R. A., *J. Agric. Food Chem.* **28**, 303 (1979).
Rhodes, R. C., *J. Agric. Food Chem.* **28**, 306 (1979).

Received for review March 10, 1978. Accepted October 4, 1979.

Photolysis of *N*-Nitrosodi-*n*-propylamine in Water

Donald G. Saunders* and James W. Mosier

The photolysis of the dialkyl nitrosamine *N*-nitrosodi-*n*-propylamine (NDPA) has been studied in lake water and several other aqueous systems. In lake water sunlight photolysis experiments, dissipation of NDPA was significant but variable. Other laboratory studies demonstrated NDPA photodegraded readily in neutral solution and the photodegradation rate was not pH dependent in the 3 to 9 range. The major photoproduct was found to be *n*-propylamine, but the formation of di-*n*-propylamine was also observed.

N-Nitroso-di-*n*-propylamine (NDPA) has been found as a trace contaminant in the herbicide trifluralin (Ross et al., 1977) (TREFLAN, Elanco Products Co., Indianapolis, IN. Trace amounts of NDPA could enter the environment by application of the herbicide to soil. NDPA is readily water soluble [solubility, 10 000 ppm; Mirvish et al. (1976)] and has been shown to move with soil moisture (Saunders et al., 1979), suggesting the chemical might enter natural waters with rainfall runoff.

Though the possibility of water contamination by trace amounts of NDPA exists, no measurable amounts of NDPA in natural waters have been reported. Ross et al. (1978) was unable to detect NDPA in irrigation water taken from a trifluralin-treated field. In work reported by West and Day (1978), no NDPA was found in water samples taken from ponds in areas treated annually with trifluralin for several years. However, because of the potential hazards associated with dialkyl nitrosamines such as NDPA, a study was undertaken to determine the fate of NDPA in water.

Though dialkyl nitrosamines are readily degraded by light under laboratory conditions (Burns and Alliston, 1971; Polo and Chow, 1976), only limited information on their stability in natural waters is available (Tate and Alexander, 1975). This report is concerned with the stability of NDPA in lake water under natural conditions. Additional laboratory studies were conducted to determine factors affecting the photolysis rate in water as well as to identify and quantify NDPA photolysis products.

Agricultural Analytical Chemistry, Lilly Research Laboratories, Division of Eli Lilly and Company, Greenfield, Indiana 46140.

EXPERIMENTAL SECTION

Chemicals. NDPA was prepared by nitrosation of the amine and purified by vacuum distillation (bp 81 °C at 5 torr). [1-^{14}C]NDPA was obtained from New England Nuclear (Boston, MA). The radiochemical purity was determined to be greater than 98% by thin-layer chromatography and radioautography, and the specific activity was 28.0 μCi/mg.

Di-*n*-propylamine (DPA) (Aldrich Chemical Co., Inc., Milwaukee, WI) and *n*-propylamine (NPA) (MC/B, Norwood, OH) were redistilled prior to use. 2,6-Dinitrofluorobenzene (DNFB) (Eastman Organic Chemicals, Rochester, NY) was used as received. Di-*n*-propyl-2,6-dinitroaniline (DPA-DNFB) and *n*-propyl-2,6-dinitroaniline (NPA-DNFB) were synthesized by the method of Day et al. (1966). Potassium ferrioxalate was prepared according to the method of Hatchard and Parker (1956). *N'*-Hydroxy-*N*-propylpropanimidamide was prepared by reaction of hydroxamoyl chloride with *n*-propylamine.

All samples containing NDPA were handled with extreme care. Undiluted NDPA was stored and handled in a glovebox equipped with a charcoal filter and maintained under negative pressure. All laboratory work with dilute

0021-8561/80/1428-0315$01.00/0

NDPA samples was conducted in a hood with a minimum air flow rate of 150 linear ft/min. Laboratory workers wore heavy rubber gloves. Waste NDPA solutions were decomposed in a hydrogen bromide–acetic acid solution, sealed in a barrel, and buried in a nuclear waste disposal area.

NDPA Hydrolysis. Buffer solutions at pH 3, 6, and 9 were prepared from solutions of 0.1 M citric acid and 0.2 M disodium phosphate using McIlvaine's (1921) formula. Twenty-milliliter portions of the buffers were placed in 20-mL ampules (Kimble Products, Toledo, OH), the ampules were capped with aluminum foil, and the buffer solutions were autoclaved at 121 °C for 20 min.

The buffer solutions were fortified with NDPA by adding 10.0 μL of a 5.40 mg/mL of methanol solution to each ampule. The ampule necks were sealed immediately in a flame.

The solutions were placed in a dark constant temperature room maintained at 51.0 ± 0.5 °C. Ampules were removed from the constant temperature room at intervals of 0, 2, 4, 8, 16, and 32 days after initiation of the experiment. Two ampules at each pH were collected and assayed separately at each sampling time.

NDPA Laboratory Photolysis. Water for the laboratory photochemical studies was redistilled from glass and saturated with air prior to use. Deaerated water was prepared by purging with nitrogen overnight. The buffers at pH 3, 6, and 9 were prepared from solutions of 0.01 M citric acid/sodium hydroxide, sodium acetate/acetic acid, and sodium carbonate/sodium bicarbonate, respectively. Solutions were irradiated in glass 20-mL ampules (Kimble Products, Toledo, OH) which transmitted 39% of the incident radiation at 300 nm but were essentially opaque below 280 nm. Sunlight which reaches the surface of the earth contains no significant radiation below 290 nm (Hirt et al., 1960).

The laboratory irradiation apparatus consisted of four each of FS20T12 fluorescent sunlamps (Westinghouse, Bloomfield, NJ) and F20T12BL fluorescent black lights (General Electric, Cincinnati, OH) mounted vertically in a circle on the inside of an enclosed eight-sided wooden cabinet. This combination of lights produces an ultraviolet spectral energy distribution similar to natural summer sunlight (Hirt et al., 1960). The samples were placed 10 cm from the lamp circle on a 30-cm diameter turntable rotating at 1 rpm inside the irradiation box so that all samples received equal amounts of radiation. The inside of the irradiation apparatus was cooled by an electric blower and remained at 32.0 ± 1.0 °C.

Solutions for photolysis were prepared from a 1.00 mg/mL NDPA solution in water at 1.0, 10.0, and 100.0 μg/mL in water, at 10.0 μg/mL in nitrogen-purged water, and at 10.0 μg/mL in pH 3, 6, and 9 buffers. Twenty milliliters of each solution was pipetted into 14 20-mL ampules, and the ampule necks were sealed in a flame. For the experiments conducted in the absence of oxygen, the head space of the ampule was purged with nitrogen prior to sealing.

Rate experiments were conducted by placing 12 ampules on the turntable in the irradiation apparatus. Two ampules were removed for analysis after 7.5, 15.0, 30.0, 60.0, 90.0, and 120.0 min of irradiation.

Experiments for the determination of photolysis products were conducted in a similar manner except that samples were taken only after 60.0 and 120.0 min of irradiation.

Actinometry. The light intensity incident on the samples was measured during each laboratory photochemical rate experiment using the ferrioxalate chemical actinometer development by Parker (1953). Potassium ferrioxalate (20 mL, 0.088 M) in 20-mL ampules was exposed for 1 min during each experiment. The ferrous ion content of the actinometric solution was determined colorimetrically with phenanthroline. The amount of ferrous ion obtained was converted to light intensity by using the calibrated thermophile data obtained by Hatchard (1956).

NDPA Dissipation in Lake Water. The lake selected for the NDPA dissipation experiments was a 2.5-acre eutrophic lake located near Carthage, IN. The maximum depth was approximately 18 ft and the pH of the water was 7.4. Lake water was collected near the surface and used without filtration. The water transported to the laboratory (experiment 1) was stored in a glass container.

The sample containers for exposure of lake water containing NDPA were 10.0 mm i.d. × 60 cm quartz tubes (experiment 1) or 10.0 mm i.d. × 120 cm glass tubes (experiments 2 and 3) which were closed at the bottom end. The day prior to initiation of experiment 1, a solution of [^{14}C]NDPA (0.11 μCi/40 mL) was prepared in water from the lake at 0.65 μg/mL. Solutions for experiments 2 and 3 were prepared immediately prior to exposure at 10.0 μg/mL (0.76 μCi/80 mL) and 1.0 μg/mL (0.076 μCi/80 mL), respectively, in the lake water. Tubes were loaded by pipetting 40.0 mL (experiment 1) or 80.0 mL (experiments 2 and 3) of fortified solution into each which filled the respective tubes to within 9 cm of the top. All tubes were stoppered and maintained in the dark both before and after exposure.

For exposure, the tubes were secured in a verticle position in full sunlight to a float in the lake. The tubes extended 51 cm (experiment 1) or 111 cm (experiments 2 and 3) into the lake and were adjusted so the water level in the tubes was even with the lake surface. All three experiments were conducted between 8:00 a.m. and 4:00 p.m. on clear days. Experiment 1 was carried out on July 6, 1977; experiments 2 and 3 on July 28, 1978. Two tubes were collected at each sampling time.

Analtyical Procedures. Ampules from the hydrolysis study were opened by fracture of the neck and the contents were decanted into a 250-mL separatory funnel containing 50 mL of 5% aqueous sodium chloride. Each ampule was rinsed with 10 mL of methanol. NDPA was extracted with two 20-mL portions of dichloromethane. The extracts were drained through anhydrous sodium sulfate and collected in a 100-mL volumetric flask. Following dilution to volume, the NDPA content of the solution was determined by gas chromatography.

Aqueous solutions from laboratory photolysis experiments were analyzed without extraction. One milliliter of each aqueous solution was diluted with acetone and analyzed directly by gas chromatography.

The lake water samples from experiment 1 were poured into 100-mL volumetric flasks. The tubes were rinsed with 20 mL of methanol to complete the transfer and the flasks were diluted to volume with 5% aqueous sodium chloride. A 2.0-mL portion was subjected to liquid scintillation counting. The remainder was transferred to a 250-mL separatory funnel and was extracted and analyzed as described above for the hydrolysis solutions.

The lake water samples from experiments 2 and 3 were quantitatively transferred to 100-mL volumetric flasks using deionized water to rinse the glass tubes. Following dilution to volume, a 1-mL aliquot was subjected to liquid scintillation counting. An additional 1 mL was diluted with acetone and analyzed directly by gas chromatography.

NDPA was measured by gas chromatography–mass spectrometry (GC–MS) using a single ion detection me-

thod. The instrument was an LKB 9000 (LKB Inc., Bromma, Sweden) equipped with a 1.8 m × 3.0 mm i.d. glass column packed with 5% Carbowax 20M on 80/100 mesh Chromosorb W-HP. The instrument parameters were as follows: column temperature, 130 °C; injector temperature, 155 °C; separator temperature, 150 °C; ion source temperature, 290 °C; trap current, 60 μA; electron energy, 20 eV; helium flow, 29 mL/min; single ion, *m/e* 130. NDPA eluted in 1.8 min, and the detection limit was about 0.025 ng.

The analyses for NPA and DPA were performed on the aqueous photolysis solutions using a method similar to that developed by Day et al. (1966). A 10.0-mL portion of each solution was placed in a 125-mL boiling flask. Four milliliters of borate buffer (2.5 g of $Na_2B_4O_7 \cdot 10H_2O$ in 100 mL of water) and 2 mL of DNFB reagent (0.75 mL in 50 mL of dioxane) were added, and the flask was stoppered and placed in a 60 °C water bath for 20 min. Two millilters of 2 N sodium hydroxide was then added to destroy the excess DNFB reagent and the flask was returned to the water bath for an additional 30 min. After cooling, the derivatives were extracted into 50.0 mL of toluene in the boiling flask.

The NPA-DNFB and DPA-DNFB content of the toluene layer was determined by gas chromatography on a Hewlett-Packard Model 402 (Avondale, PA) equipped with an electron-capture detector and a 1.2 m × 3.0 mm i.d. glass column packed with 5% XE-60 on 80/100 Chromosorb W-HP. The carrier gas was 90:10 argon/methane at a flow rate of 30 mL/min and the column temperature was 215 °C, the injection port temperature 270 °C, and the detector temperature 260 °C. Retention times for DPA-DNFB and NPA-DNFB were 1.5 and 2.2 min, respectively. DPA-DNFB and NPA-DNFB were quantitated by peak height, and their response to the detector was determined to be linear over the concentration range utilized.

The efficiencies of the analytical methods for NDPA, DPA, and NPA were determined by analyzing solutions containing known amounts of each compound. The recoveries ranged from 75.0 to 93.0%, and all results were corrected for the recovery efficiency.

Radiochemical Measurements. Radiochemical determinations on solutions were made with a Packard Model 3380 Tri-Carb liquid scintillation counter (Packard Instrument Co., Downers Grove, IL). Aqueous or aqueous–methanol samples were dissolved in a scintillation fluid prepared by dissolving 35 g of PPO (2,5-diphenyloxazole), 1.75 g of dimethyl-POPOP {1,4-bis[2-(4-methyl-5-phenyloxazolyl)]benzene}, and 278 g of naphthalene in 496 mL of toluene, 1490 mL of dioxane, and 1490 mL of ethyleneglycol monomethyl ether. All samples were counted for 5 or 10 min, and the counting efficiency was determined by [^{14}C]toluene internal standardization.

Thin-Layer Chromatography. Thin-layer chromatography was conducted on silica gel 0.25-mm plates (E. Merck, Darmstadt, Germany) using dichloromethane/methanol/ammonium hydroxide (80:20:1, v/v/v) as the developing solvent. NDPA (rf = 0.75) and DPA (rf = 0.25) were detected by radioautography. NPA (rf = 0.07) was detected by UV absorption after treatment with spray reagent (0.2 g of malonic acid and 0.1 g of salicyaldehyde in 100 mL of ethanol) and heating at 120 °C for 15 min. The oxime (I) (rf = 0.59) was detected by UV absorption.

RESULTS AND DISCUSSION

Hydrolysis. Tate and Alexander (1975) found NDPA did not degrade in lake water incubated at 30 °C for 108 days. They concluded NDPA was not susceptible to microbiological degradation.

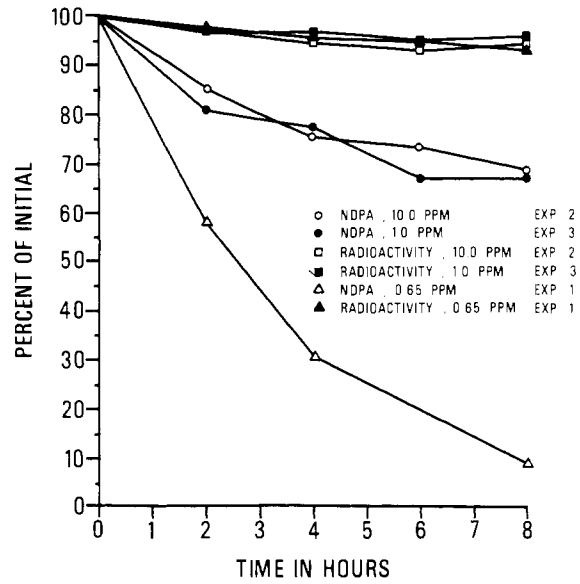

Figure 1. Photolysis of [^{14}C]NDPA in lake water.

The results of the chemical hydrolysis study also demonstrate the stability of NDPA. Even at the elevated temperature of 51 °C, no degradation of NDPA was detected during the 32-day study at any pH. It is probable that NDPA will not degrade in water in the absence of light.

Lake Water Photolysis. The results of the lake water sunlight photolysis experiments are presented graphically in Figure 1. Each data point represents the average results from two tubes. The ^{14}C concentration in the water remained constant throughout each experiment, indicating that no significant amounts of radioactivity were lost by volatilization. The NDPA rapidly degraded in all three experiments. Experiments 2 and 3 were conducted simultaneously and indicate that concentration (in the 1–10 ppm range) had no effect on the NDPA photolysis rate. The results from experiment 1, when compared to those from experiments 2 and 3, suggest NDPA photolysis occurred more rapidly closer to the lake surface (the tubes in experiment 1 were one-half the depth of those used in experiments 2 and 3). However, variation in experimental conditions such as sunlight intensity and water turbidity could also have accounted for the observed difference.

Laboratory Photolysis. The photolysis of various dialkylnitrosamines has been studied by several investigators. Chow (1967) observed that dialkylnitrosamines were rapidly photodegraded in the presence of acid but were stable in neutral solution. Burns and Alliston (1971) studied the photolysis of di-*n*-butylnitrosamine in aqueous solution and observed degradation at all pH's (range of 0.7 to 9.2) studied but also observed degradation was more rapid at low pH. Polo and Chow (1976) observed that dimethylnitrosamine photodegraded in solution up to pH 10 but also found that the rate at pH 10 was about one-tenth that observed at pH 1. The latter two studies indicated the photolysis occurred via first-order kinetics with tendencies toward zero-order kinetics at higher concentrations.

The results of the present NDPA laboratory photolysis rate study are presented graphically in Figures 2 and 3. The data from all experiments, when plotted on a logarithmic scale, resulted in linear relationships, indicating the photolysis proceeded by first-order kinetics. No tendencies toward zero-order kinetics were noted. Statistical analysis of the data revealed the rates of photolysis were identical within experimental error at all concen-

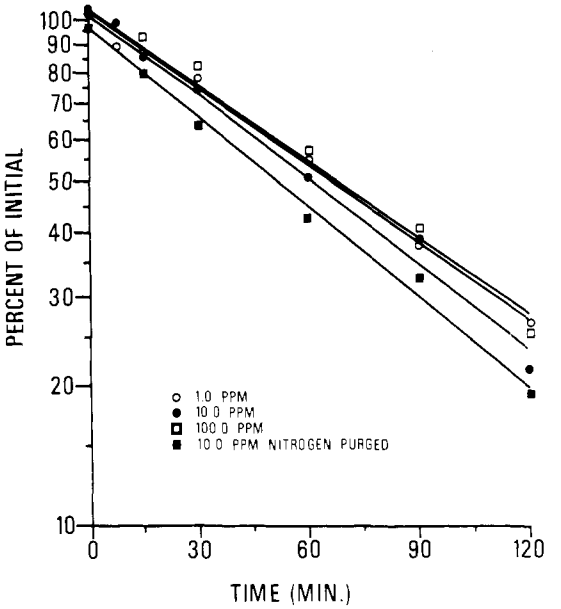

Figure 2. Photolysis of NDPA in distilled water in the laboratory irradiation apparatus.

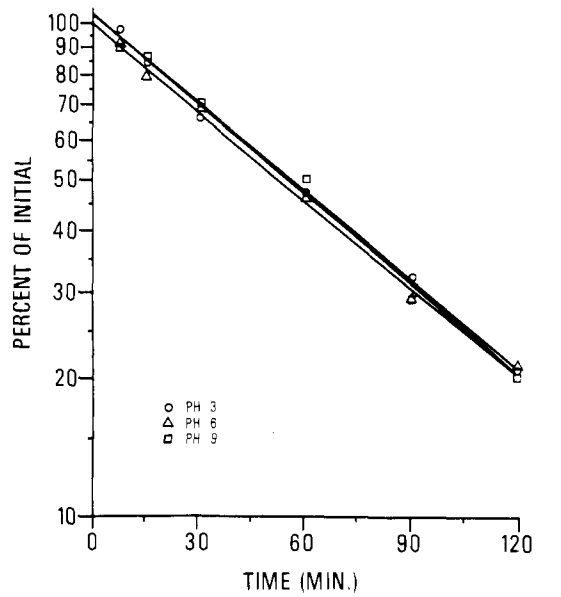

Figure 3. Photolysis of NDPA in pH 3, 6, and 9 buffers in the laboratory irradiation apparatus.

trations (Figure 2) and pH levels (Figure 3). The lack of a concentration effect and no indication of zero-order kinetics indicate the experiments were conducted with sufficiently dilute solutions such that only a small fraction of the light was absorbed. The data obtained under oxygen-deficient conditions (Figure 2) demonstrates that oxygen has no great effect on the photolysis rate. The results obtained in different buffer solutions (Figure 3) indicate the photolysis rate is independent of pH within the range investigated. This lack of a pH effect on the photolysis rate does not support the data obtained by other investigators with other dialkylnitrosamines.

The results of the actinometric measurements conducted during the laboratory photolysis studies verify that little variation in the light source intensity occurred during the photolysis rate experiments. The average light intensity was found to be 524 $\mu W/cm^2$, and no corrections were made for varying light intensity.

Aqueous Photolysis Products. The mechanism of dialkynitrosamine photolysis in aqueous acid has been

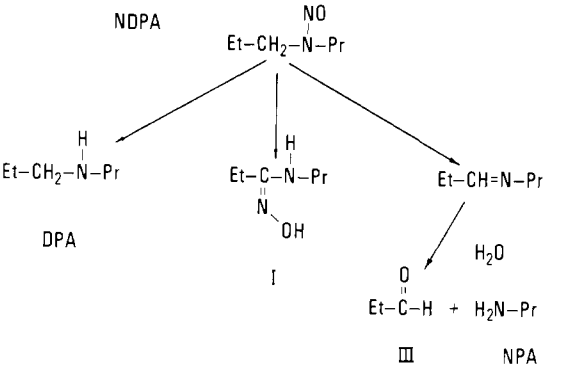

Figure 4. Prosposed scheme for photolysis of NDPA in neutral solution.

Table I. NDPA Aqueous Photolysis Photoproducts

solution	time of exposure, min	% of initial NDPA			total material balance
		NDPA	DPA	NPA	
distilled water	0	100.0	0	0	100.0
	60	49.0	10.0	38.0	97.0
	120	22.0	24.0	47.0	93.0
pH 3	0	100.0	0	0	100.0
	60	44.0	2.0	49.0	95.0
	120	22.0	5.0	72.0	99.0
pH 6	0	100.0	0	0	100.0
	60	45.0	3.0	50.0	98.0
	120	23.0	5.0	68.0	96.0
pH 9	0	100.0	0	0	100.0
	60	47.0	1.0	52.0	100.0
	120	23.0	2.0	73.0	98.0

thoroughly discussed (Polo and Chow, 1976; Chow, 1967). A complete discussion of the mechanism of the photolysis of NDPA in neutral solution is beyond the scope of this paper. However, a possible NDPA photodecomposition scheme indicating probable photoproducts is shown in Figure 4.

The presence of the NDPA photolysis products suggested by Figure 4 were confirmed in a preliminary aqueous photolysis study. DPA and NPA were detected by TLC but the oxime (I) was not observed in the sample. The oxime would be formed by nucleophilic attack of HNO on the imine (II) (Chow, 1973). The low NDPA concentrations and relatively neutral solutions utilized here may not have resulted in sufficient HNO concentration for this to occur. If the imine (II) is the precursor to NPA, propionaldehyde should also be produced during NDPA photolysis. Propionaldehyde was qualitatively detected in the photolysis solution by gas chromatography–mass spectrometry which lends additional support to the scheme in Figure 4.

The results of the NDPA photolysis rate studies in which the amounts of NPA and DPA formed were determined are presented in Table I. NPA was the major photolysis product at all pH levels studied. Small amounts of DPA were found in all solutions with the highest level being detected when photolysis was carried out in distilled water. The presence of the buffering salts apparently favors the pathway to NPA, though the NPA and DPA product distribution was not affected by pH.

The pathways outlined in Figure 4 apparently account for all of the photolytic dissipation of NDPA. The data in Table I indicate the NPA and DPA determinations account for all degraded NDPA.

The presence of NPA as the major photolysis product is important when considering the potential amount of nitrosamine introduced into the environment. Ayanaba and Alexander (1974) observed that *N*-nitrosodimethyl-

amine was formed in samples of sewage and lake water treated with its precursors, dimethylamine and nitrite. Thus, the formation of NDPA from DPA could conceivably result from renitrosation in the environment. However, the corresponding nitrosation of NPA, if it should occur, would result in the formation of an unstable diazonium salt rather than an alkyl nitrosamine.

ACKNOWLEDGMENT

The authors thank K. H. Fuhr and J. E. Gray for the synthesis of reference chemicals, R. P. Basson for aid in conducting statistical analysis, and E. W. Day for the synthesis of NPA-DNFB and assistance in the preparation of the manuscript.

LITERATURE CITED

Ayanaba, A., Alexander, M., *J. Environ. Qual.* **3**, 83 (1974).
Burns, D. T., Alliston, G. V., *J. Food Technol.* **6**, 433 (1971).
Chow, Y. L., *Can. J. Chem.* **45**, 53 (1967).
Chow, Y. L., *Acc. Chem. Res.* **6**, 354 (1973).
Day, E. W., Golab, T., Koons, J. R., *Anal. Chem.* **38**, 1053 (1966).
Hatchard, C. G., Parker, C. A., *Proc. R. Soc. London, Ser. A* **235**, 518 (1956).
Hirt, R. C., Schmitt, R. G., Searle, N. D., Sullivan, A. P., *J. Opt. Soc. Am.* **50**, 706 (1960).
McIlvaine, T. C., *J. Biol. Chem.* **49**, 183 (1921).
Mirvish, S. S., Issenberg, P., Sornson, H. C., *J. Natl. Cancer Inst.* **56** 1125 (1976).
Parker, C. A., *Proc. R. Soc. London, Ser. A* **220**, 104 (1953).
Polo, J., Chow, Y. L., *J. Natl. Cancer Inst.* **56**, 997 (1976).
Ross, R. D., Morrison, J., Rounbehler, D. P., Fan, S., Fine, D. H., *J. Agric. Food Chem.* **25**, 1416 (1977).
Ross, R. D., Morrison, J., Fine, D. H., *J. Agric. Food Chem.* **26**, 455 (1978).
Saunders, D. G., Mosier, J. W., Gray, J. E., Loh, A., *J. Agric. Food Chem.* **27**, 584 (1979).
Tate, R. L., Alexander, M., *J. Natl. Cancer Inst.* **54**, 327 (1975).
West, S. D., Day, E. W., *J. Agric. Food Chem.* **27**, 1075 (1979).

Received for review June 1, 1979. Accepted October 19, 1979.

Determination of Daminozide Residues on Foods and Its Degradation to 1,1-Dimethylhydrazine by Cooking

William H. Newsome

Daminozide was determined by alkaline hydrolysis to dimethylhydrazine. The dimethylhydrazine was recovered by distillation, derivatized with pentafluorobenzoyl chloride, and determined by GLC. Recoveries from several commodities fortified from 0.10 to 40 ppm were generally greater than 80%. 1,1-Dimethylhydrazine was determined in apples by extraction with 0.01 N HCl, chromatography on a cation-exchange resin, and derivatization with pentafluorobenzoyl chloride. The resulting 1,1-dimethyl-2,2-bis(pentafluorobenzoyl)hydrazine was cleaned up on a silicic acid and quantitated by GLC. Recoveries averaged 88% from 0.10 to 12 ppm. Daminozide was found to decompose to dimethylhydrazine when boiled in apple homogenate. The amount of decomposition increased with the duration of boiling from 10 to 60 min and with the amount of daminozide from 5 to 30 ppm.

Daminozide (succinic acid 2,2-dimethylhydrazide) is a plant growth regulator registered for use on several crops including apples, peaches, grapes, plums, and tomatoes. It is water soluble and readily translocated to all parts of the plant. With apples, the recommended preharvest interval is 60–70 days and significant residues persist for over 100 days (Edgerton and Greenhalgh, 1966; Edgerton et al., 1967). Long persistence of daminozide residues has also been observed in cherries (Ryugo, 1965).

Daminozide has been implicated in the production of tumors when fed as a 2% solution in the drinking water of mice (Toth et al., 1977). The possibility also exists that hydrolysis of daminozide would yield 1,1-dimethylhydrazine, itself a carcinogen in mice (Roe et al., 1967).

Methods for the determination of daminozide in foods involve hydrolysis in strong alkali and distillation of the resulting dimethylhydrazine (Edgerton et al., 1967). The dimethylhydrazine is determined with a colorimetric reagent either directly (Edgerton et al., 1967; Lane, 1967) or after oxidation to formaldehyde (Lynch, 1969). No methods have been reported in the literature for the determination of free dimethylhydrazine in foods although it has been determined in tobacco (Schmeltz et al., 1977). Since colorimetric methods are insufficiently specific for regulatory purposes and since it was necessary to determine whether free dimethylhydrazine occurred in foods, the following method was developed. It is based on the derivatization of dimethylhydrazine with pentafluorobenzoyl chloride and subsequent determination of the derivative by GLC with electron-capture detection.

Food Research Division, Bureau of Chemical Safety, Food Directorate, Department of National Health and Welfare, Tunney's Pasture, Ottawa, Ontario K1A 0L2, Canada.

EXPERIMENTAL SECTION

Materials. 1,1-Dimethylhydrazine was purchased from Aldrich Chemical Co., Milwaukee, WI, and was labeled as being 95% pure. A stock standard solution containing 1 mg/mL was prepared in 1 N HCl. Working standards containing 0.5 and 5.0 μg/mL were prepared by dilution of the stock in 0.01 N HCl.

Succinic acid 2,2-dimethyl hydrazide (Daminozide) was obtained from Aldrich Chemical Co.

Cation-exchange resin, Dowex 50W × 8, 100–200 mesh (Sigma Chemical Co., St. Louis, MO), was purified before use by washing with alkali and acid as described previously (Newsome, 1974). Ion-exchange columns containing 3 mL

0021-8561/80/1428-0319$01.00/0