

Photodecomposition of 1-Naphthaleneacetic Acid

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Aqueous solutions of 1-naphthaleneacetic acid (sodium salt) decomposed rapidly in sunlight or under ultraviolet irradiation in the laboratory. A photoreactor was used to simulate exposure to sunlight and to trap the intermediate photolysis

products which then were separated and purified by gas chromatography. 1-Methylnaphthalene, 1-naphthalenemethanol, 1-naphthaldehyde, 1-naphthoic acid, and phthalic acid were identified, but only the two acids were stable to light.

The effect of sunlight and laboratory ultraviolet (UV) light on pesticides recently has received increasing attention. The results of such investigations are of major importance to a clear understanding of the environmental fate of these compounds and to improvement of their practical application.

1-Naphthaleneacetic acid (NAA), in the form of ammonium or alkali-metal salts, is a plant growth regulator useful in nursery practice, induction of flowering in pineapple, thinning of olives and apples, and inhibition of preharvest fruit drop. Similar to many pesticides, NAA was shown to decompose upon exposure to energetic (2537 Å) UV light (Mitchell, 1961; Luckwill and Lloyd-Jones, 1962), and the report of Leeper *et al.*, (1962) that sunlight was the rate-controlling factor in the evolution of ¹⁴CO₂ from carbonyl-labeled NAA applied to leaf surfaces also suggested that photolysis might be significant under practical conditions. In view of the demonstrated photodecarboxylation of NAA (Luckwill and Lloyd-Jones, 1962) as well as the analogous indole-3-acetic (Melchior, 1957) and phenylacetic (Crosby, 1966) acids, the present research was conducted to determine the photochemical fate of NAA salts in aqueous solution.

EXPERIMENTAL

Materials. 1-Naphthaleneacetic acid was recrystallized twice from aqueous methanol, m.p. 132.0° to 132.5° C. 1-Naphthalenemethanol was prepared in quantitative yield by reduction of 1-naphthaldehyde with sodium borohydride in tetrahydrofuran at room temperature (Fieser and Fieser, 1967). Other standards were commercial products purified by recrystallization or gas chromatography (GLC). Methyl esters were prepared by reaction of the corresponding acids with ethereal diazomethane.

Irradiation. A preparative-scale photoreactor which closely simulated the effects of sunlight was employed for laboratory irradiations (Crosby, 1969; Crosby and Tang, 1969). Air was conducted to the bottom of the 2-liter reaction chamber at 6 ml. per minute; nitrogen was employed in anaerobic experiments.

A similar reactor (Figure 1) was used to isolate neutral photolysis products as they were formed. The irradiated solution could be circulated, by means of a gas-lift (A), from the bottom of the reaction chamber (B) (General Electric F8T5BL lamp) to an extraction chamber (C) in which a water-immiscible solvent such as benzene rapidly removed the soluble photo-

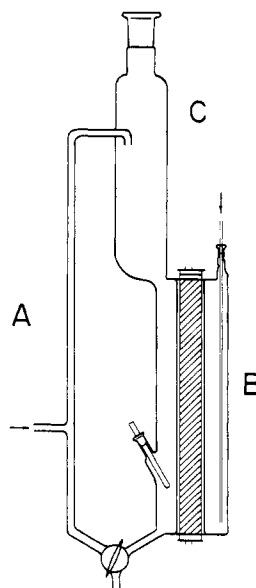


Figure 1. Photoreactor (B) equipped with a gas lift (A) for continuous extraction (C)

products and held them away from further exposure to light. Anionic compounds were returned to the reactor for further irradiation.

Sunlight irradiation was carried out at midsummer in Davis, Calif., in borosilicate glass baking dishes. Alternatively, a 2-liter round-bottomed quartz flask equipped with a water-cooled condenser occasionally was employed when danger of sample contamination existed.

An aqueous solution (1200 ml.) containing 100 mg. per liter of NAA sodium salt was irradiated for the desired period, usually 3 hours in the preparative reactor or 1 day in sunlight, at 30° to 40° C. The resulting brown, fluorescent solution (pH 7.5 to 8.0) was extracted with three portions of ethyl ether, and the combined neutral extracts were washed with a small volume of water, dried (MgSO₄), and evaporated to small volume. The aqueous phase was acidified to pH 2 and extracted in the same way.

Separation and Identification of Photoproducts. GLC employed an Aerograph Model 202 instrument equipped with a thermal conductivity detector, a 5-foot × 1/4-inch O.D. stainless steel column packed with 4% SE-30 silicone gum on 60- to 80-mesh Chromosorb G at 150° C., and a nitrogen flow rate of 50 ml. per minute. As it eluted, each compound was collected in a glass capillary tube for purification by rechromatography. Infrared spectra (KBr disk and/or thin-film, Perkin-Elmer Model 337 spectrometer) formed the basis for characterization, and identities were confirmed by IR spectra, GLC retention times, and cochromatography with authentic standards.

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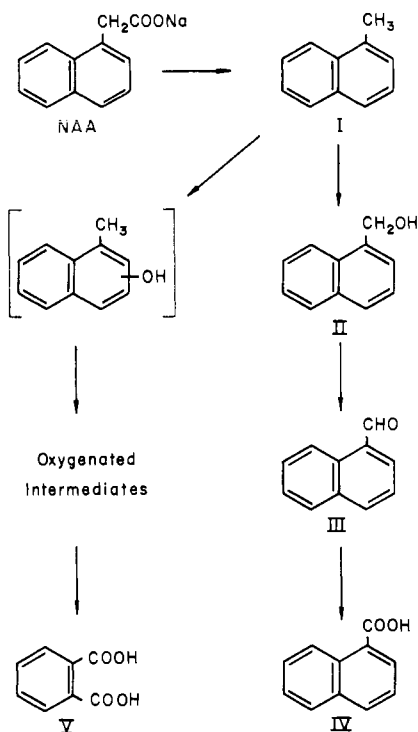


Figure 2. Products of NAA photolysis

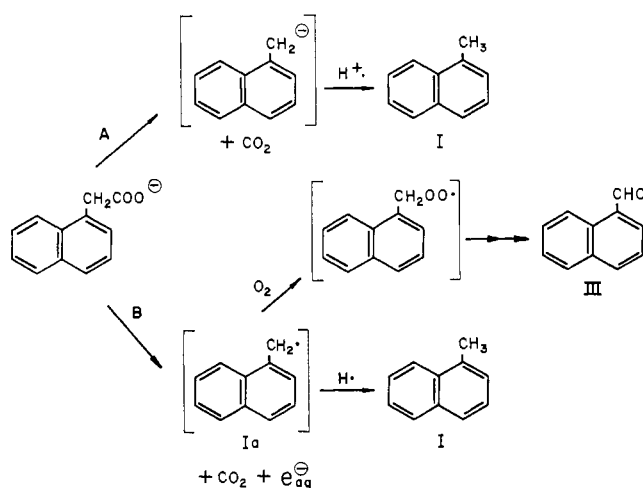


Figure 3. Mechanisms of NAA photolysis

Table I. Products of NAA Photolysis^a

Product	Weight Proportion
NAA	100
I	7
II	43
III	65
IV	9
V	8

^a Initial concn. 100 mg. per liter, 3 hours in reactor.

Thin-layer chromatography (TLC) utilized glass plates coated with a 0.5-mm. thickness of Brinkmann Silica Gel G containing zinc silicate phosphor, with benzene-methanol-acetic acid (20:2:1 by volume) as developing solvent. Detection depended upon fluorescence or light absorption under 2537 Å light.

RESULTS AND DISCUSSION

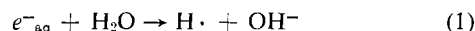
NAA solutions decomposed rapidly in light. The neutral fraction contained three major constituents (GLC retention times 2.3, 4.8, and 5.6 minutes) whose properties coincided with those of 1-methylnaphthalene (I), 1-naphthalenemethanol (II), and 1-naphthaldehyde (III), respectively. The methylated acidic fraction also contained three constituents identified as the methyl esters of 1-naphthoic (7.2 minutes, IV) 1-naphthaleneacetic (9.8 minutes), and *o*-phthalic (3.7 minutes, V) acids. Three hours in the reactor or 8 hours in sunlight produced the product ratios shown in Table I; 4 days of sunlight exposure converted NAA completely to V and a small amount of IV.

Each photolysis product (100 p.p.m.) was exposed in turn to 7 hours of sunlight. I produced II and III in a 1:10 ratio; II formed only III; and III gave only IV. IV remained stable in sunlight or in the reactor for up to 6 hours. Irradiation of NAA under nitrogen produced only I. Thus, I represents the key photolysis intermediate, and its oxidation to II, III, and IV follows the sequence shown in Figure 2 similar to that observed in the photolysis of phenylacetic acids (Crosby and Leitis, 1969).

These results correspond to those of Kawasaki *et al.* (1963), in which oxidation of I by oxygen under high pressure at 260° C. produced III, IV, and (principally) V. Under similar conditions, the formation of 1-naphthol (Kamneva and Simonenko, 1965), 1-methyl-3,4-naphthoquinone, hydroxy-naphthoic and naphthoquinonecarboxylic acids, and hemimellitic acid (Kawasaki *et al.*, 1963) also was observed. Although TLC revealed many acidic and phenolic intermediates during NAA photolysis in the present experiments, none were obtained in sufficient quantity for identification; no 1-naphthol was ever detected. However, their presence preceding the stable V indicates the existence of a second major route of decomposition (Figure 2).

I could be formed from NAA by two different mechanisms (Figure 3), one (A) ionic (Margerum *et al.*, 1965) and the other (B) free-radical (Joschek and Grossweiner, 1966). Present data favor reaction B for three reasons: (1) Under nitrogen, I formation was essentially independent of pH, as expected for B. A should be pH-dependent at these low H⁺ concentrations; (2) NAA, $\lambda_{\text{max}}^{\text{abs}}$ 272, 282, 292 (shoulder) m μ ., can absorb so little energy from sunlight (minimum λ 290–300 m μ .) that the rapid formation of I via A would not be expected. Absorption of energy for B, however, can take place at much longer wavelengths (Joschek and Grossweiner, 1966); (3) Removal of photolysis products as they formed showed that I was produced rapidly in nitrogen; the reaction was slow in air, the short-term products being only I, II, and III in approximate ratio of 1:10:30. These results may be explained on the basis of a predominant reaction of the organic radical Ia with oxygen (Figure 3) which can give rise to III (and II) by well-known routes (Walling, 1957).

In the absence of oxygen, hydrogen atoms formed by reaction of hydrated electrons with water (Equation 1) (Anbar,



1965), could combine with Ia to give I. Mechanism A does not explain the early photolysis products.

The rapid destruction of NAA in sunlight may explain the inconsistency of field results observed in most applications; climate, shading, and even the hour of application would affect the extent of photolysis. Plants appear to be unaffected by phthalic acid at low concentrations, but 1-naphthoic acid has been reported to have herbicidal (Jones, 1946) and abscis-

sion-inducing (Singh, 1956; Petruccioli, 1966) properties. The transient intermediates probably are unimportant toxicologically, although some absorption by fruit might be possible; the stable, terminal naphthoic and phthalic acids present a very low order of mammalian toxicity (Patty, 1963).

Note added in proof: Similar results have been reported by Watkins (1969).

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