# Sea-to-Air Transport of Surface Active Material

Abstract. *Fine platinum wires were used to collect airborne particulate matter along the shore in Hawaii. This matter was examined for surface active material and for sea salt. Droplets that rise from the sea in the surf zone appear to carry a highly compressed surface active film.*

Many studies have been made of the air-sea exchange of heat, water vapor, and momentum, and a number have been concerned with the exchange of condensation nuclei (*1, 2*), giant nuclei (*2, 3*), and electric charge (*2, 4*). But few studies have been directly concerned with the exchange of surface active organic material. Attention should be given to this, for organic films on the sea may influence the oceanic production of condensation nuclei, modify the ocean-to-air flux of charged particles (*2*), provide organic ice nucleators (*5*) for supercooled clouds, and contribute to soil nutrients (*6*).

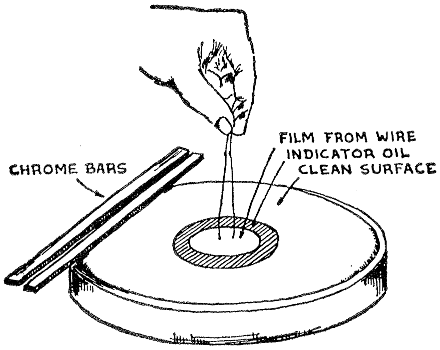

Fig. 1. The method by which the exposed wires are tested for the presence of surface active material.

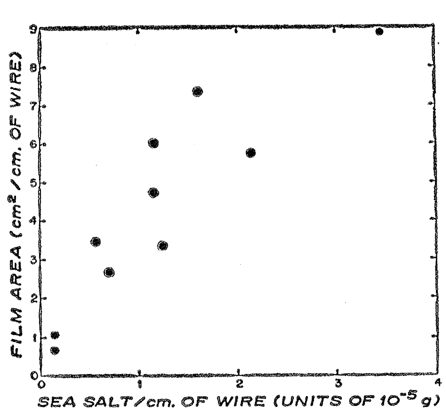

Fig. 2. The area covered by the surface active material at zero surface pressure as a function of the weight of sea salt. The sea salt is presumed to be the carrier of the film.

Evidence of surface active material on the sea can be seen in slicks or windrows. The composition of these surface films has received a great deal of attention (*7*). Most of this organic material must have its source in the dissolved organic matter in the sea (*8*); its transformation into particulate form and transport to the surface is probably brought about by the bubbles that result from breaking waves (*2, 9, 10*). Laboratory studies have shown that when bubbles brust at the surface a portion of the organic material plus sea water is ejected into the atmosphere (*2, 9*).

In the spring of 1962 I was working along the windward shore of the island of Hawaii, about 5 miles (8 km) east of the town of Hilo. The surf was particularly heavy and the water was white with bubbles. When the wind came in from the open sea the air that passed over the shore just downwind from the "white water" contained such a large number of small drops of sea water that it appeared hazy. I was anxious to see how much surface active material was carried by these particles.

The particles were captured by exposing platinum wires to the airflow. The wires (254 $\mu$ in diameter) were strung between two parallel brass rods 15 cm apart and supported by a rectangular wooden block. Knots were placed in each wire about 1 cm from the rods. This simple apparatus was exposed for 30 to 60 minutes to the air just downwind from extensive bubbling zones in the surf. Just prior to exposure the wires were flamed to burn off any organic material; just after exposure a control wire was placed between the rods and treated in the same way. The apparatus was taken back to the laboratory where the control wire and one of the exposed wires were tested for the presence of surface active material.

The indicator oil method (*11*) was used to test for surface active material. A circular glass dish was filled with distilled water (Fig. 1) to a level slightly above the top of the dish. The top of the dish had been ground flat and treated with ferric stearate, which is hydrophobic to water. Two chromium-plated brass bars, also treated with ferric stearate, were used to sweep the water surface free of surface active material. A minute drop of indicator oil (partially oxidized motor oil) was placed on the water. A duplex film, about 2 cm in diameter and of a characteristic interference color, was formed. One of the exposed wires was then slipped off the rods and bent back at the middle until the ends touched. It was carefully dipped into the water at the center of the indicator film until all of the wire between the knots had been immersed. The surface active material from the wire spread out on the surface of the clean water, pushing the indicator film before it. The surface film from the wire could not be seen, but its outer edge was delineated by the indicator film. Because the indicator film showed no change in its interference color it could be concluded that it and the film from the wire were not being subjected to any surface pressure. The major and minor axes of the test film were measured, and the area of the surface film was calculated.

The amount of sea salt picked up by the wires was determined by dipping a second wire into distilled water and then testing for sodium in a flame photometer (*12*). The sodium value was multiplied by 3.25, the ratio of sea salt to sodium in sea water, to obtain the weight of sea salt collected by the wire.

Wires were exposed on 7 days. On two of the days three wires were exposed and two were tested for organic material. At another but similar location about 25 miles (40 km) away one set of wires was exposed. In all cases the surface wind was 2 to 4 m/sec. With but one exception the surface area of the film on the control wire was about 10 percent of that on the exposed wire; this exception gave about 60 percent. The control value was subtracted from the test value. The relationship between salt amount and film area (Fig. 2) suggests that the surface film was being carried by the very small drops that originate at the surface of the sea. The amount of surface active material either on or within the sea is likely to vary from day to day.

An interesting question that can be raised about Fig. 2 is the relation between the film and the surface area of the drops that carried the film. Knowing the amount of salt collected by the wire, I was able to compute the total surface area of the drops. I assumed that the drops were of sea water concentration and that the frequency distribution of drop size was the same as that found behind the surf in Florida (*13*). I found in each of the samples of Fig. 2 that the area of surface active material at zero surface pressure was from 4 to 11 times the total surface area of the drops that carried the material. This suggests that the drops carry a compressed film when they leave the surf zone.

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13. A. H. Woodcock, D. C. Blanchard, C. G. H. Rooth, *ibid.*, p. 159. I have calculated that the efficiency of collection of the wire at the windspeeds that were observed, 2 to 4 m/sec, exceeded 70 percent for drops greater than 4 μ in radius. It was only about 5 percent for drops of 1-μ radius. But this is of little concern since about 98 percent of the mass of the droplet spectrum is in drops greater than 4 μ in radius. These drops were estimated to be in concentrations of the order of 100 per cubic centimeter.
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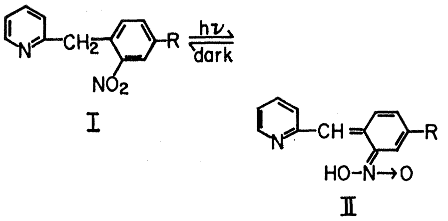
## Photoisomerism: A Colorless Photoinduced Intermediate of o-Nitrobenzylpyridine

Abstract. *Exposure to light of* o-*nitrobenzylpyridines at −185°C yields a long-lived colorless intermediate which is converted to a colored isomer on warming.*

Recently several investigators have reported on the photochromic behavior of substituted nitrobenzylpyridines (I) (*1*) and related compounds (*2*) having in common a nitro group ortho to an $R_3CH$ group. When these compounds are exposed to light a colored isomer is formed, with a lifetime that depends upon structure and physical state. The formation of the colored isomer (II) has been interpreted as a tautomeric shift, I ⇌ II:



During studies on the photochromic behavior of these compounds incorporated in solid plastic matrices, we observed upon irradiation at −185°C that the usual color formation did not occur; but when the plastic discs were allowed to warm somewhat in the dark the colored isomer did develop. When the disc was recooled at this point, bleaching did not occur. On further warming, but at a temperature still below room temperature, the color slowly faded and the original colorless disc remained.

These observations provide evidence for the formation of a long-lived, colorless, photoinduced species at −185°C, which then changes to the colored isomer II on warming; on further standing it reverts to the original colorless form I.

The following experiments were designed to show the existence of the colorless intermediate. The photochromic compounds, 2-(2,4-dinitrobenzyl)-pyridine and 2-(2-nitro-4-cyanobenzyl)pyridine, were prepared (*1*) and purified by repeated crystallization from ethanol. A mixture of diethyl ether, isopentane, and absolute ethanol (EPA) (5 : 5 : 2 by volume) at room temperature was used as the solvent; this gave an optically clear glass at −185°C. A concentration of $2.64 \times 10^{-4}M$ 2-(2-nitro-4-cyanobenzyl)pyridine was used in the EPA glass.

Polymethyl methacrylate (PMMA) discs were prepared by polymerizing methyl methacrylate monomer containing the photochromic compound in solution. The discs contained 0.050 mole of the dinitro compound per liter, or 0.054 mole of the cyano-derivative per liter.

Potassium bromide discs were prepared by grinding 0.30 g of spectroscopic grade KBr with 0.24 mg of 2-(2,4-dinitrobenzyl)pyridine and pressing in the usual manner.

Dinitrobenzyl pyridine was incorporated in polyvinyl alcohol (PVA) by adding an alcohol solution of the pyridine derivative to an aqueous solution of polyvinyl alcohol and filtering through a fine sintered-glass filter. The clear filtrate was evaporated on a quartz disc, and a clear film was obtained.

Irradiations were performed in a cryostat (*3*). The sample discs were mounted as windows on a 2.5-cm sample cell against a reference disc of similar material but which contained no photochromic compound. All exposures were made at −185°C except when otherwise stated. The samples were exposed to an unfiltered quartz mercury lamp (*4*) for 5-second periods, followed by 15-second dark periods to minimize heating (Figs. 1 and 2).

After exposure, the cryostat was quickly transferred to the sample compartment of a spectrophotometer (*5*), and the absorption spectra were measured. The temperature of the sample disc was then slowly raised, and development of the colored isomer was recorded continuously at its wavelength maximum. Measurements of temperature were made by a copper-constantan thermocouple inserted in a well drilled into the disc. The spectrum was recorded (Figs. 1 and 2) when the color intensity reached a maximum; further warming resulted in a gradual discharge of the color.

The absorption spectra of 2-(2,4-dinitrobenzyl)pyridine incorporated in polyvinyl alcohol before and after color formation is shown in Fig. 1. When the irradiated sample was gradually warmed, a band developed at 585 mμ and reached a maximum intensity at −91°C, as shown in the third curve. No fading of color was measurable at this temperature during a 2-hour period, probably because of the extremely slow rate of the back reaction. However, at temperatures above −91°C the band at 585 mμ began to fade.

In Fig. 2, the colored forms are shown in the visible region for 2-(2,4-dinitrobenzyl)pyridine in KBr and in

Table 1. Absorption maxima of colored form of irradiated benzylpyridine derivatives.

| Matrix | Absorption (mμ) | | | |
|---|---|---|---|---|
| | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\lambda_4$ |
| | | *$NO_2$* | | |
| PMMA | 567 | | | |
| PVA | 585 | 260 | | |
| KBr | 610 | | | |
| | | *C≡N* | | |
| PMMA | 580 | 450 | 405 | |
| EPA | 590 | 450 | 405 | 225 |