

nickel-iron core and 44 Nysa is the largest surviving fragment of a stony mantle.

The Eos and Koronis families are among the best-defined groups (8), but unlike the Nysa group, the Eos family at  $a = 3.01$  A.U. and the Koronis family at  $a = 2.87$  A.U. consist not of one or two large objects plus assorted small chips but rather of a continuum of sizes with the five or ten largest objects having comparable diameters. Both families fall in the outer parts of the belt where the field population, at least for diameters  $> 50$  km, is 85 to 90 percent of type C (5). Neither group seems to contain any classical C objects with  $B - V \sim 0.7$  and  $U - B \sim 0.3$ . The eight measured Koronis members seem to be of the S type, whereas the Eos objects cluster about a point intermediate between the domains of the typical C and S populations. The dispersion in the colors is partially attributable to observational scatter for such faint objects.

The Eos and Koronis family members are generally too small and distant to have been picked up in bright-asteroid surveys. For 208 Lacrimosa in the Koronis family, Morrison (3) has derived, by the method of thermal radiometry, a geometric albedo of 0.14, which puts it firmly in the S class. For 221 Eos itself McCord and Chapman (1) have reported a reflection spectrum of unusual type, showing the ultraviolet dropoff characteristic of ferrous silicates and a weak absorption band near  $0.97 \mu\text{m}$  probably attributable to pyroxene, but without the overall spectral redness that is a signature of free iron in the typical S objects. Apparently Eos consists of a mixture of silicates yet to be specifically identified, probably rather close to chondritic in elemental composition but with no exact analog among known meteorite types.

In any case, both the Eos and Koronis families clearly resulted from the fragmentation of discrete undifferentiated parent bodies and not from random collections of the C-dominated populations in their vicinities.

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principal types are designated C or carbonaceous, identifiable with carbonaceous chondrites and accounting for  $\sim 76$  percent of the population; S or siliceous (16 percent), consisting of ferromagnesian silicates plus iron, and identifiable probably with H chondrites or stony-iron achondrites; and M or metallic (5 percent), identifiable with nickel-iron meteorites or possibly the metal-rich enstatite chondrites.

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## Enhancement of Photochemical Smog by $N,N'$ -Diethylhydroxylamine in Polluted Ambient Air

**Abstract.** A recent proposal for controlling photochemical smog by the addition to ambient air of 0.03 to 0.05 part per million of diethylhydroxylamine (DEHA) is shown to be invalid. The addition of DEHA in the range of 0.05 to 0.5 part per million to ambient air irradiated with sunlight in a dual outdoor environmental chamber caused marked increases in the rates of formation and concentrations of ozone, peroxyacetyl nitrate, and light-scattering particles.

Photochemical smog, formed by the action of solar ultraviolet radiation on polluted ambient air containing hydrocarbons (HC) and oxides of nitrogen ( $\text{NO}_x$ ), is characterized by such undesirable phenomena as the conversion of NO to  $\text{NO}_2$  and the production of  $\text{O}_3$ , peroxyacetyl nitrate (PAN), and light-scattering particles (1). Although strategies for smog control have focused almost exclusively on reducing the emissions of reactive HC and  $\text{NO}_x$  (for example, automobile control devices), the possibility of suppressing photochemical smog by introducing into the atmosphere chemicals known to be free radical "traps" (or smog inhibitors) has been discussed for at least 15 years (2).

The possible use of  $N,N'$ -diethylhydroxylamine [ $(\text{C}_2\text{H}_5)_2\text{NOH}$ ], or DEHA] as an inhibitor has been investigated by Hecklen and his co-workers (3, 4); they recently recommended that DEHA be introduced into polluted urban air at concentrations of about 0.03 to 0.05 part per million (ppm) (5-7). This proposal was based on laboratory experiments conducted with DEHA,  $\text{NO}_x$ , and two olefinic hydrocarbons, ethylene and propylene, at concentrations of several parts per million in  $\text{O}_2$ ; in these experiments DEHA inhibited the conversion of NO to  $\text{NO}_2$  and the formation of  $\text{O}_3$  (3, 4).

According to Hecklen, the advantages of adding DEHA to urban atmospheres rather than using automobile control devices are numerous: DEHA

controls stationary as well as mobile source emissions; the method is projected to be cheaper by at least a factor of 100 than automobile control devices and can provide for the immediate elimination of photochemical smog, whereas it will take at least 10 years to equip all cars with emission control devices (5, 7). For these reasons, this proposal has received attention not only from air pollution control officials and atmospheric scientists (8-10) but also from the general public (11).

Two major questions arise from the proposal to add DEHA to polluted urban atmospheres (7): the possible toxicity of DEHA and its reaction products in ambient air (1, 8), and the validity of extrapolating laboratory results to "real" urban atmospheres. Thus it has been suggested that, even though DEHA might delay the formation of photochemical smog, this would transfer the problem downwind (1, 8).

The question of the possible toxicity of DEHA and its reaction products has been raised (1, 4-10), but will not be addressed here. We report here on tests of the effectiveness of DEHA as an inhibitor of photochemical smog under closely simulated atmospheric conditions. Our study was conducted in an 80-m<sup>3</sup> dual outdoor environmental chamber constructed from 2-mil FEP Teflon film (12). Two types of experiments were conducted: in three cases we used morning Riverside ambient air and either 0.1

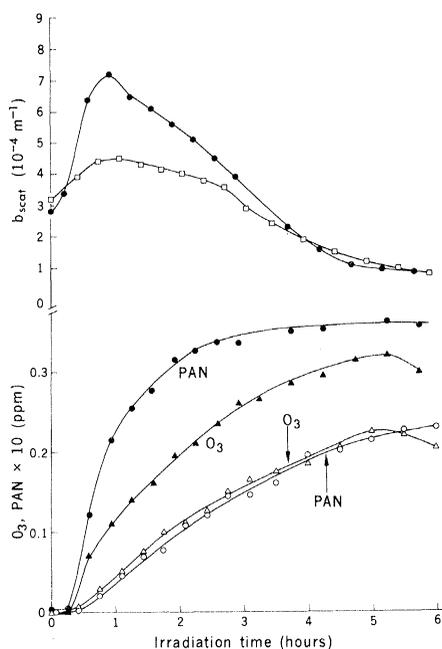


Fig. 1. Concentration-time profiles for  $O_3$ , PAN, and  $b_{scat}$  during simultaneous irradiation of ambient air (open symbols) and ambient air + 0.1 ppm of DEHA (closed symbols) in a dual outdoor smog chamber, 14 October 1976, 1000 to 1600 P.S.T.

ppm of DEHA (experiments 1 and 2) or 2 ppm of DEHA (experiment 3); in five other cases we used morning Riverside ambient air and 0.2 ppm of carbon of a HC surrogate mixture representative of the morning Los Angeles atmosphere (13) to which had been added 0.05 ppm of DEHA (experiment 8), 0.1 ppm (experiments 4 and 7), 0.2 ppm (experiment 5), or 0.5 ppm (experiment 6).

Ambient air conditions and pollutant concentrations at the beginning of the experiments were as follows: the NO concentration ranged from 0.010 to 0.076 ppm,  $NO_2$  from 0.013 to 0.058 ppm, total HC from 1.54 to 3.73 ppm, nonmethane HC from 0.19 to 1.49 ppm, CO from 0.6 to 5.0 ppm,  $O_3$  from 0 to 33 parts per billion (ppb),  $SO_2$  from 0 to 9 ppb, PAN from 0 to 3 ppb, condensation nuclei from  $0.8$  to  $4.1 \times 10^4 \text{ cm}^{-3}$ , relative humidity from 22 to 83 percent, and the aerosol light-scattering coefficient  $b_{scat}$  from  $0.8 \times 10^{-4}$  to  $14.5 \times 10^{-4} \text{ m}^{-1}$ . This range of ambient conditions is typical of the period from 14 October through 25 November 1976, during which our experiments were conducted.

It seemed important to test DEHA from at least two different commercial sources. We obtained DEHA from Aldrich (97 percent pure) and from Penwalt (technical grade) and stored it in the dark at  $4^\circ\text{C}$  prior to use. On the basis of analysis by infrared spectrometry, nuclear magnetic resonance spectrometry, gas chromatography (GC), and mass spec-

trometry, we used the Aldrich DEHA in experiments 1 through 6 without further purification; we purified the Penwalt DEHA by distillation prior to use in experiments 7 and 8. Our results with both commercial sources were identical.

In a typical experiment, the chamber was covered with black plastic film and filled with ambient air (14) to a volume of about  $80 \text{ m}^3$ . The HC surrogate mixture was added in experiments 4 through 8. The chamber was then divided into two compartments of equal volume, and DEHA was added to one of the compartments after dilution with high-purity  $N_2$ . The black cover was then removed, thus exposing the chamber to sunlight. Since in these experiments identical mixtures of polluted air, with and without added DEHA, were subjected to simultaneous solar irradiation (including the same natural changes in light intensity, temperature, and humidity), differences in the time-concentration profiles of the smog parameters measured in the two compartments of the dual outdoor chamber can unambiguously be attributed to the presence of DEHA in one compartment (15).

In a separate series of experiments we established that the loss of DEHA by adsorption on the walls of the chamber was negligible. Furthermore, the initial gas-phase DEHA concentration measured in the chamber was, within experimental precision, that calculated from the known amount of DEHA introduced and the chamber volume. In the same experiment we established that the half-life of 0.5 ppm of DEHA in air in the dark was at least 3 hours (16).

Irradiations with sunlight were conducted over periods of at least 6 hours. The following parameters were monitored in both compartments during the irradiation: temperature, dew point, solar ultraviolet radiation intensity; NO;  $NO_2$  (Bendix chemiluminescent instrument);  $O_3$  (17); CO; HC (flame ionization GC); PAN (electron capture GC);  $SO_2$  (Meloy flame photometric sulfur analyzer); condensation nuclei (Environmental One nuclei counter);  $b_{scat}$  (Meteorological Research, Inc., integrating nephelometer); and aerosol size distribution (Thermosystems, Inc., electrical mobility analyzer and Bausch & Lomb optical particle counter).

When added at initial concentrations of 0.05, 0.1 (Fig. 1), or 0.2 ppm to either ambient air or ambient air doped with the HC surrogate mixture, the DEHA did not inhibit the formation of photochemical smog; in fact, it substantially accelerated the conversion of NO to  $NO_2$  and the production of  $O_3$ , PAN, and light-

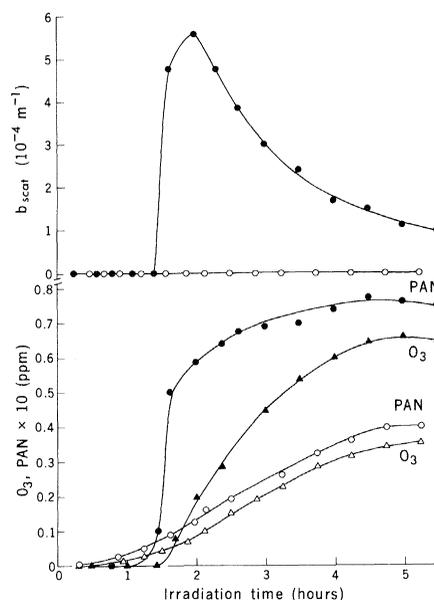


Fig. 2. Concentration-time profiles for simultaneous irradiation of ambient air + 0.2 ppm of carbon of the HC surrogate mixture without DEHA (open symbols) and with 0.5 ppm of DEHA (closed symbols), 1 November 1976, 1000 to 1600 P.S.T.

scattering particles. For example (Fig. 1), the addition of 0.1 ppm of DEHA to ambient air significantly increased the rates of formation and also the concentrations of  $O_3$ , PAN, and light-scattering particles throughout the 6-hour irradiation period.

With 0.5 ppm of DEHA added to ambient air doped with the HC surrogate mixture (experiment 6), an "intermediate" behavior was observed, with inhibition being predominant during the first hour of irradiation. At that point a marked acceleration of smog formation took place, resulting in much higher rates of formation and concentrations of  $O_3$ , PAN, and light-scattering particles than in the compartment lacking DEHA (Fig. 2).

Only at the highest concentration used, 2 ppm, did DEHA effectively inhibit the conversion of NO to  $NO_2$  and the formation of  $O_3$  and PAN in ambient air for the entire 6-hour irradiation period. The compartment without added DEHA exhibited a "normal" behavior, with conversion of NO to  $NO_2$  and formation of  $O_3$ , PAN, and light-scattering particles.

Our results demonstrate that the introduction of 50 to 200 ppb of DEHA to polluted urban atmospheres [that is, the concentrations recommended by Heicklen (5-7), and up to four times these concentrations] would result in a significant increase in the rates of formation and concentration of  $O_3$ , PAN, and light-scattering aerosols, with a corresponding increase in health hazards, visibility deg-

radation, and damage to vegetation. These effects would be observed not only at the time of release of DEHA into the atmosphere but also at least 6 hours downwind from the release sites. In the same way, use of DEHA at 0.5 ppm would greatly exacerbate smog symptoms at locations from 1 hour to at least 5 hours downwind (see Fig. 2). Furthermore, DEHA's odor threshold level (0.5 ppm) prohibits its introduction into polluted atmospheres at concentrations of 0.5 ppm or more (we do not consider here the possible toxicity of DEHA and its reaction products).

Our results confirm that DEHA, at sufficiently high concentrations, acts as an inhibitor of photochemical smog. However, this result cannot be extrapolated to conditions prevailing in ambient polluted atmospheres. Clearly, experimental validation of proposed techniques for the control of photochemical smog by chemical additives must be conducted at ambient pollutant levels.

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14. Ambient air was introduced into the chamber less than 1 hour after the local morning peak of automobile traffic.
15. Control experiments were conducted simultaneously in the two compartments of the chamber with ambient air and the HC surrogate mixture without added DEHA. Identical NO, NO<sub>2</sub>, O<sub>3</sub>, PAN, nuclei, and *b*<sub>scat</sub> profiles were obtained in the two compartments throughout the 6-hour irradiation periods. The possible contamination by reactive species formed in an earlier experiment and adsorbed on the chamber walls was

also investigated. Since DEHA was added to the same compartments in all experiments except experiment 2, one may argue that the observed increase in O<sub>3</sub>, PAN, and *b*<sub>scat</sub> with the addition of DEHA may be due in part to contamination from earlier experiments. We tested this possibility in experiment 2, where DEHA was added to the compartment usually used for ambient air alone, and vice versa. The results of this experiment were in no way different from the results of the other experiments.

16. These experiments were conducted in another chamber with Teflon and plexiglass walls housing a Fourier-transform infrared spectrophotometer with a base path of 22 m and a total optical path of 1.1 km. The DEHA concentration was measured on the basis of its known absorptivity at 931 cm<sup>-1</sup>.

17. Ozone was measured with a chemiluminescent instrument calibrated by the ultraviolet photometry method (W. Simmons, filing sheet amending Section 70200, "Table of standards applicable statewide," of Title 17 of the California Administrative Code, Sacramento, 15 May 1975).

18. We thank P. Johnson for help in carrying out the experiments. We thank Dr. E. Tuazon, Dr. A. Winer, and R. Easton for carrying out the DEHA half-life measurements described in (16). This work was supported in part by NSF Research Applied to National Needs (RANN) grant ENV73-02904-A03. Initial results of this study were presented at the NSF RANN 2 meeting, Washington, D.C., 7 to 9 November 1976.

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## High-Frequency $P_n$ Phases Observed in the Pacific at Great Distances

**Abstract.** *Earlier observations of a seismic waveguide in the northwestern Pacific with a velocity of 8.3 kilometers per second to distances of approximately 30° are complemented by suggestions of a possible waveguide with a velocity of 7.8 kilometers per second to distances well in excess of 30°.*

The high-frequency  $P_n$  waveguide in the mantle underlying the northwestern Pacific is characterized by velocities of about 8.3 km/sec and frequencies as high as 6 hertz to distances of 30° (*l*). Waveguides with similar velocities (8.1 to 8.3 km/sec) have been found in other regions of the earth (2), with observations out to 35.07° for continental travel paths (3) and to 37.84° for oceanic travel paths (4). Recently, however,  $P_n$  arrivals for distances greater than 30° in both the North and northwestern Pacific were found (4) to have significantly lower apparent velocities (approximately 7.9 km/sec) than the  $P_n$  arrivals with velocities of 8.3 km/sec or 8.1 to 8.3 km/sec. Suggested interpretations were that low signal-to-noise ratios prevented the observation of the actual first arrival corresponding to the 8.3-km/sec energy or that an additional waveguide was present. The second interpretation implies that the slower waveguide, although masked by phases from the faster waveguide at distances less than 30°, is actually more efficient, resulting in the observation of 7.9-km/sec arrivals at distances greater than 30° and the corresponding absence of 8.3-km/sec arrivals.

The suggestion of a second waveguide prompted a reexamination of existing earthquake data (seismograms and hydrophone recordings from Midway, Wake, and Hawaii; seismograms from Ponape and Easter islands) for travel paths in the Pacific. Thus far, a total of 23 suspected waveguide phases have been found for travel paths generally in excess of 30° (5). Travel paths and a travel time curve for these phases are shown in Figs. 1 and 2, respectively. The travel

time curve [ $T = X/(7.76 \pm 0.18) - 15.7 \pm 11.7$ , where  $T$  is the observed travel time in seconds and  $X$  is the epicentral distance in kilometers] is based on all but two of the data points in Fig. 2; these data points (at distances of 33.88° and 68.42°) represent poorly recorded phases at Easter Island. The travel time curve (Fig. 2) for  $P_n$  arrivals observed at distances of less than 30° illustrates the differences between the curves for the 8.3- and 7.8-km/sec phases. Sample seismograms and hydrophone power level recordings are shown in Fig. 3. [The generally higher apparent velocities (that is,  $X/T$ ) of Fig. 3 relative to the value of 7.76 km/sec determined from Fig. 2 are a result of the large negative intercept ( $-15.7$  seconds) of the travel time curve. This intercept may not be statistically significant because it has a large standard deviation ( $\pm 11.7$  seconds).]

Occasionally, depending on epicentral distances and focal depths, arrival times of the suspected waveguide phases correspond to the expected arrival times of either  $PP$  (a wave reflected once from the surface),  $PPP$  (a wave reflected twice from the surface), or  $PcP$  (a wave that bounces off the core) phases, or scattered precursors of these phases. These phases and their precursors are generally characterized by short wavetrains, consisting of only a few cycles with periods longer than their first-arriving  $P$  phase, and the phases suspected here as being guided arrivals are generally characterized by wavetrains of extremely long duration (a common characteristic of guided waves) and frequencies higher than that of the  $P$  phase (frequencies higher than 3 hertz are gen-