Reactions of Gas-Phase Phenanthrene under Simulated Atmospheric Conditions

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Rate constants for the gas-phase reactions of phenanthrene with OH radicals, NO₃ radicals, and O₃ have been determined at 296 ± 2 K and atmospheric pressure of air. The rate constants obtained (in cm³ molecule⁻¹ s⁻¹ units) were (1.27 ± 0.23) × 10⁻¹¹ for the OH radical reaction, (1.2 ± 0.4) × 10⁻¹³ for the NO₃ radical reaction under atmospheric conditions, and (4.0 ± 1.0) × 10⁻¹⁹ for the O₃ reaction. These rate constants indicate that the OH radical and NO₃ radical reactions will be the dominant atmospheric lifetime of gas-phase phenanthrene will be ≤ 1 day. Mutagenicity bioassays and chemical analyses of the products of the NO₃ radical reaction and NO_x-air photooxidation of phenanthrene were also conducted.

Introduction

Phenanthrene is an abundant volatile polycyclic aromatic hydrocarbon observed in ambient air (1-10), which exists in the atmosphere almost totally in the gas phase at ~ 298 K (1, 2, 4, 6, 7, 11). The expected atmospheric transformation reactions of gas-phase phenanthrene involve reaction with OH radicals, NO_3 radicals, and O_3 (12). Absolute rate constants for the OH radical reaction have been determined by Lorenz and Zellner (13, 14) over the temperature range 338-748 K using a flash photolysisresonance fluorescence technique, and relative rate constants have been obtained at 298 and 319 K by Biermann et al. (14, 15). However, to date no kinetic data exist for the reactions of phenanthrene with NO_3 radicals or O_3 , although by analogy with the data for naphthalene, 1- and 2-methylnaphthalene, and 2,3-dimethylnaphthalene, the O₃ reaction is expected to be of negligible atmospheric importance (12).

The NO_x-air photooxidation of gas-phase phenanthrene, through the irradiation of CH₃ONO-NO-phenanthreneair mixtures, has been shown to lead to the formation, in low yield, of the direct-acting mutagens 2- and 4-nitro-6H-dibenzo[b,d]pyran-6-one (16, 17). Moreover, chemical analysis and mutagenicity testing of extracts of collected gas- and particle-phase ambient atmospheric samples have shown that, using the microsuspension modification of the Salmonella typhimurium assay, 2-nitrodibenzopyranone is a significant contributor to ambient air direct-acting mutagenicity (16-18).

In this work, we have determined rate constants for the gas-phase reactions of phenanthrene with OH radicals, NO_3 radicals, and O_3 at 296 ± 2 K and atmospheric pressure of air. Additionally, we collected a ~1500-L volume sample from an NO_3 radical reaction and a series of ~350-L volume samples from an NO_3 -air photooxidation of phenanthrene, and we conducted mutagenicity assays and

[†]Also at the Department of Soil and Environmental Sciences, University of California, Riverside, CA 92521. chemical analyses on high-performance liquid chromatographic (HPLC) fractions of extracts from these samples to investigate the formation of mutagenic compounds. The enhanced sensitivity of the bioassay compared to chemical analyses on the HPLC fractions allowed the time-profiles of mutagenic species of various polarities to be obtained during a single photooxidation of phenanthrene.

Experimental Section

All experiments were carried out at 296 ± 2 K and 740 Torr total pressure of air in 6400-6900-L all-Teflon chambers equipped with two parallel banks of black lamps for irradiation. The experimental methods used were generally similar to those described previously (19-21).

Kinetic Studies. Rate constants for the OH radical and NO_3 radical reactions were determined using relative rate methods in which the disappearance rates of phenanthrene and a reference compound, whose OH radical or NO_3 radical reaction rate constant is reliably known, were monitored in the presence of OH or NO_3 radicals (20, 21). Provided that phenanthrene and the reference compound reacted only with OH radicals or NO_3 radicals, then

$$\ln \left\{ \frac{[\text{phenanthrene}]_{t_o}}{[\text{phenanthrene}]_t} \right\} - D_t = \frac{k_1}{k_2} \left[\ln \left\{ \frac{[\text{reference compound}]_{t_o}}{[\text{reference compound}]_t} \right\} - D_t \right]$$
(I)

where [phenanthrene]_{to} and [reference compound]_{to} are the concentrations of phenanthrene and the reference compound, respectively, at time t_0 ; [phenanthrene]_t and [reference compound]_t are the corresponding concentrations at time t; D_t is the amount of dilution caused by any additions to the chamber during the reactions; and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively:

$$\left.\begin{array}{c} OH\\ NO_3\end{array}\right\}$$
 + phenanthrene ----- products (1)
OH $\right]$

Phenanthrene was introduced into the chambers by flowing a stream of N_2 through a Pyrex tube packed with phenanthrene at room temperature.

Hydroxyl radicals were generated by the photolysis of methyl nitrite (CH₃ONO), and NO was added to the reactant mixtures to avoid the formation of O₃ and NO₃ radicals. Propene was used as the reference compound, and the initial reactant concentrations (in molecule cm⁻³ units) were as follows: CH₃ONO, 2.4×10^{14} ; NO, 2.4×10^{14} ; phenanthrene, $(1.2-1.4) \times 10^{11}$; and propene, 4.8×10^{13} . Irradiations were carried out at 50% of the maximum light intensity for 3–18 min. Phenanthrene and propene were monitored during the experiments by gas chroma-

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tography with flame ionization detection (GC-FID). For propene, gas samples were collected from the chamber in 100-cm³ all-glass, gas-tight syringes and transferred via a 1-cm³ loop and gas-sampling valve onto a 30-m DB-5 megabore column temperature programmed from -50 °C at 8 °C min⁻¹. For phenanthrene, gas samples of 0.69-L volume were collected from the chamber onto Tenax solid adsorbent, with subsequent thermal desorption at 250 °C onto a 15-m DB-5 megabore column held at 40 °C and then temperature programmed at 10 °C min⁻¹. For these experiments, D_t in eq I was zero.

NO₃ radicals were generated by the thermal decomposition of N_2O_5 , and NO_2 or ethane was added to the reactant mixture to investigate the reaction mechanism and to scavenge any OH radicals formed (21-23). 1-Butene was used as the reference compound, and the initial reactant concentrations (in molecule cm⁻³ units) were as follows: phenanthrene, (1.3–2.8) \times $10^{11};$ 1-but ene, 4.8 \times $10^{13};$ NO_2 (when added), $(4.8-24) \times 10^{13}$; or ethane, 2.4×10^{16} . Three to five additions of N_2O_5 [at initial concentrations in the chamber of $(4.9-9.6) \times 10^{12}$ molecule cm⁻³] were made to the chamber during the experiments. The phenanthrene and 1-butene concentrations were measured during the experiments by GC-FID, with 1-butene being analyzed as described above for propene (but with the initial column temperature being -25 °C). For the phenanthrene analyses, gas samples of 0.69-1.54 L volume were collected onto the Tenax solid adsorbent, and for one of the experiments conducted with an initial NO₂ concentration of 4.8×10^{13} molecule cm⁻³, a 1500-L sample was collected from the chamber after the reaction onto two polyurethane foam (PUF) plugs in series for chemical analysis and bioassay testing (see below). For these experiments, D_t = 0.0028 per N₂O₅ addition.

A rate constant for the O_3 reaction was determined by measuring the decay rate of phenanthrene in the presence of an excess concentration of O_3 . Cyclohexane was also added to the reactant mixture to scavenge any OH radicals formed in this system (24, 25). Provided that the only loss process of phenanthrene was by gas-phase reaction with O_3 , then

$$\ln \left\{ \frac{[\text{phenanthrene}]_{t_o}}{[\text{phenanthrene}]_t} \right\} = k_3 [O_3](t - t_o)$$
(II)

where k_3 is the rate constant for reaction 3:

$$O_3$$
 + phenanthrene \rightarrow products (3)

O3 concentrations were monitored by ultraviolet absorption using a Dasibi Model 1003 AH ozone monitor and were varied over the range $(8.7-15.6) \times 10^{13}$ molecule cm⁻³. The phenanthrene concentrations were measured by GC-FID, as described above, and by combined gas chromatography/mass spectrometry (GC/MS) with collection of gas samples onto Tenax solid adsorbent and subsequent thermal desorption onto a 60-m DB-5 fused silica capillary column in a Hewlett-Packard (HP) 5890 GC interfaced to a HP 5970 mass selective detector (MSD). Fluorene was also included in these reactant mixtures as a nonreactive tracer compound (26) of fairly similar volatility to phenanthrene (27) to check for wall adsorption problems. The initial phenanthrene, fluorene, and cyclohexane concentrations (molecule cm⁻³ units) were 5.2×10^{11} , 1.3 \times 10¹², and 2.4 \times 10¹⁴, respectively.

In addition to these kinetic studies of the reactions of phenanthrene with OH radicals, NO₃ radicals, and O₃, the presence of anthracene as an isomeric impurity in the phenanthrene allowed an approximate rate constant for the reaction of the OH radical with anthracene to be derived [the initial anthracene concentrations were ~9–10% of the initial phenanthrene concentration, reasonably consistent with the reported solid-phase vapor pressures of phenanthrene and anthracene at 298 K of 1.2×10^{-4} Torr and 6.0×10^{-6} Torr, respectively (27)]. The phenanthrene and anthracene concentrations were monitored during one of the OH radical reactions (see above) by GC/MS using the m/z 178 molecular ion signals from phenanthrene and anthracene.

Product and Mutagenicity Studies. In addition to the kinetic studies described above, an irradiation of a CH₃ONO-NO-phenanthrene-air mixture was carried out under similar conditions to those used in our previous investigation of the formation of mutagenic products from the CH₃ONO-NO-air photooxidations of naphthalene. fluorene, and phenanthrene (19). The sensitivity of the mutagenicity assay allowed several small-volume samples to be taken during a single irradiation. These samples contained insufficient quantities of the mutagenic products to allow quantitative chemical analysis. Phenanthrene in methanol solution was sprayed onto the chamber walls to maximize the amount of phenanthrene in the gas phase within the chamber (19), and the majority of the methanol was removed by flushing the chamber with dry pure air for 30 min. The irradiation was carried out at the maximum light intensity for 18 min, and the initial reactant concentrations (molecule cm⁻³ units) were as follows: CH₃-ONO, 5.5×10^{13} ; NO, 2.0×10^{13} ; and phenanthrene, 1.7 $\times 10^{12}$. The gas-phase phenanthrene concentrations were measured by GC-FID prior to and after the irradiation.

The reaction conditions were similar to those used by Arey et al. (19), except that the irradiation was carried out in nine 2.0-min intervals and gas samples of \sim 350-L volume were collected from the chamber onto a PUF plug over a 0.25-min period after each 2.0-min irradiation period. The PUF plugs were individually extracted with CH₂Cl₂ and fractionated by high-performance liquid chromatography (HPLC) as described by Arey et al. (19), and the nine 9-min HPLC fractions from each PUF collection were subjected to mutagenicity testing with strain TA98, without microsomal activation, using the preincubation modification to the standard plate incorporation test (18, 19). Chamber blanks (from samples collected from CH₃-ONO-NO-air irradiations with the same initial concentrations) and HPLC blanks were also tested as controls.

The PUF plug sample collected after the NO₃ radical reaction with phenanthrene at an initial NO₂ concentration of 4.8×10^{13} molecule cm⁻³ was also solvent extracted and HPLC fractionated, and 50% of each of the HPLC fractions was bioassay tested as described above. Chemical analysis of selected fractions was carried out by GC/MS, using a 60-m DB-5 fused silica capillary column in an HP 5890 GC interfaced to a HP 5790 MSD. Injections were made on-column at 50 °C injector and oven temperature, and after 1 min the oven temperature was temperature programmed to 150 °C at 25 °C min⁻¹ and then to 325 °C at 4 °C min⁻¹. Detection was made in the selective ion monitoring mode using the m/z 241 molecular ion together with the major fragment ions at m/z 183, 167, 155, and 139 for the nitrodibenzopyranones and using the m/z 223



Figure 1. Plot of eq I for the gas-phase reaction of phenanthrene with the OH radical, with propene as the reference compound.

molecular ion together with the major fragment ions at m/z 193, 176, 165, and 151 for the nitrophenanthrenes. Quantification of the nitrodibenzopyranones was carried out as described by Helmig et al. (17). The nitrophenanthrenes were quantified by external calibration of the integrated signals of the m/z 223, 193, 176, 165, and 151 ions to those of the external standard 9-nitroanthracene, assuming the same response factors for 9-nitroanthracene and the nitrophenanthrenes.

Chemicals. The chemicals used and their stated purities were as follows: fluorene (98%), 9-nitroanthracene (97%), 2-nitro-6*H*-dibenzo[*b*,*d*]pyranone, 3-nitro-6*H*dibenzo[*b*,*d*]pyranone (98%), and phenanthrene (99.5+%), Aldrich Chemical Company; 3-nitrophenanthrene (99.7%), 4-nitrophenanthrene (99%), and 9-nitrophenanthrene (>99%), AccuStandard; cyclohexane (high-purity solvent grade), American Burdick and Jackson; and 1-butene (\geq 99.0%), ethane (\geq 99.0%), propene (\geq 99.0%), and NO (\geq 99.0%), Matheson Gas Products. NO₂ was prepared immediately prior to use by reacting NO with an excess of O₂, and O₃ was prepared as needed by a Welsbach T-408 ozone generator. Methyl nitrite and N₂O₅ were prepared and stored as described previously (28, 29).

Results and Discussion

Kinetic Studies. The experimental data obtained from replicate OH radical reactions of phenanthrene are plotted in accordance with eq I in Figure 1. A good straight-line plot is observed, and a least-squares analysis of these data yields the rate constant ratio $k_1/k_2 = 0.478 \pm 0.047$, where the indicated error is 2 least-squares standard deviations. This rate constant ratio can be placed on an absolute basis by use of a rate constant for the reaction of the OH radical with propene of $k_2 = 2.66 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\pm 15\%)$ at 296 K (14), leading to a rate constant k_1 of

$$k_1(\text{OH} + \text{phenanthrene}) = (1.27 \pm 0.23) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 296 ± 2 K, where the indicated error is 2 least-squares standard deviations combined with the estimated overall uncertainties in k_2 . This rate constant for the OH radical reaction of $k_1 = (1.27 \pm 0.23) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 296 ± 2 K is a factor of 2.7 lower than the previous rate constant of $(3.4 \pm 1.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ measured by Biermann et al. (14, 15) at 298 K (also relative to that



Figure 2. Plots of eq I for the gas-phase reaction of phenanthrene with the NO₃ radical, with 1-butene as the reference compound. Initial NO₂ concentrations (molecule cm⁻³ units) were as follows: (∇) zero, but with 2.4 × 10¹⁶ molecule cm⁻³ of ethane added (see text); (\oplus) 4.8 × 10¹³; (O) 1.2 × 10¹⁴.

for the reaction of the OH radical with propene). However, the present rate constant is consistent with the absolute rate constants measured by Lorenz and Zellner (13, 14) of $(1.56 \pm 0.20) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 338 \text{ K}, (1.61 \pm 1.56) \text{ s}^{-1} \text{ at } 338 \text{ K}, (1.61 \pm 1.56) \text{ s}^{-1} \text{ at } 338 \text{ K}, (1.61 \pm 1.56) \text{ s}^{-1} \text{ s}^{-1} \text{ at } 338 \text{ K}, (1.61 \pm 1.56) \text{ s}^{-1} \text{ s}^{-1} \text{ at } 338 \text{ K}, (1.61 \pm 1.56) \text{ s}^{-1} \text$ $(0.20) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 355 \text{ K}, (1.91 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 355 \text{ K}, (1.91 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 355 \text{ K}, (1.91 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 355 \text{ K}, (1.91 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 355 \text{ K}, (1.91 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ s}^{-1} \text{ at } 355 \text{ K}, (1.91 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ s}^{-1}$ $10^{-11} \,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ at 387 K, and $(1.20 \pm 0.17) \times 10^{-11}$ cm^3 molecule⁻¹ s⁻¹ at 399 K. The present rate constant and those of Lorenz and Zellner (13, 14) suggest that the rate constant for the OH radical reaction with phenanthrene increases slightly with increasing temperature over the range 296-399 K, with a least-squares analysis of these rate constants leading to $k_1 = 2.3 \times 10^{-11} \text{ e}^{-150/T} \text{ cm}^3$ molecule⁻¹ s⁻¹ over this temperature range. It is also possible that the rate constant is essentially temperatureindependent over this temperature range, with a value of $(1.5 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Although only approximate, a rate constant ratio of k_1 -(OH + anthracene)/ k_1 (OH + phenanthrene) = 1.0 ± 0.5 was derived from the GC/MS analyses of two samples collected during one of the OH radical reactions with phenanthrene. This rate constant ratio then leads to

 $k_1(\text{OH} + \text{anthracene}) = (1.3 \pm 0.7) \times$

 $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

at 296 ± 2 K, a factor of 8.6 lower than the rate constant obtained by Biermann et al. (14, 15) at 325 ± 1 K. Our present, though obviously limited, data for anthracene strongly suggest that the rate constant obtained by Biermann et al. (15) is erroneously high, as we have also shown to be the case for phenanthrene.

The experimental data obtained from the NO₃ radical reactions are plotted in accordance with eq I in Figure 2. It can be seen that, while reasonable straight-line plots are obtained at a given initial NO₂ concentration, the slopes of these plots, k_{obs}/k_2 , increase with increasing NO₂ concentration. A plot of k_{obs}/k_2 , obtained by least-squares analysis of data such as those shown in Figure 2, against the NO₂ concentration is shown in Figure 3. The linear increase in the rate constant with increasing NO₂ concentration indicates that one reaction pathway involves NO₃ radical addition to the aromatic rings to form an NO₃phenanthrene adduct, which can either thermally decompose back to reactants or react with NO₂ to form products,

as observed previously for the NO₃ radical reactions with naphthalene, 1- and 2-methylnaphthalene, 2.3-dimethylnaphthalene, and acenaphthene (22). However, Figure 3 shows that the plot of k_{obs}/k_2 against NO₂ concentration has an intercept significantly different from zero. This non-zero intercept was verified by conducting an experiment with no initially present NO_2 , which exhibited a positive initial slope of the plot of eq I (Figure 2), in contrast to the behavior observed for the NO₃ radical reactions with naphthalene (22, 30), 2-methylnaphthalene (22), and dibenzo-p-dioxin (21) for which the initial slopes of plots of eq I were essentially zero in the absence of initially added NO₂. This observation shows that the NO₃ radical reaction with phenanthrene must also involve a reaction channel that is independent of the NO_2 concentration. This situation is similar to that for acenaphthene (22) and suggests that this reaction pathway may involve NO₃ radical addition to the 9,10- >C=C< bond to yield a thermally stable NO₃-phenanthrene adduct. A leastsquares analysis of the data shown in Figure 3 leads to an intercept of 9.90 \pm 0.50 and a slope of (5.89 \pm 0.40) \times 10⁻¹⁴ cm³ molecule⁻¹, where the indicated errors are 2 leastsquares standard deviations.

A possible reaction sequence is shown in Scheme 1. Based on Scheme 1

$$k_{obs} = k_{add} + \{k_a(k_c[NO_2] + k_d[O_2])/(k_b + k_c[NO_2] + k_d[O_2])\}$$
(III)

where k_{add} , k_a , k_b , k_c , and k_d are the rate constants for reactions (add), (a), (b), (c), and (d), respectively, and (add) refers to the NO₃ radical addition to the 9,10-double bond. Our experimental data showing a linear dependence of the measured rate constant with NO₂ concentration indicate that $k_b \gg k_c[NO_2]$ and $k_b \gg k_d[O_2]$, as is the case for naphthalene, 1- and 2-methylnaphthalene, 2,3-dimethylnaphthalene, and acenaphthene (22). Equation III then simplifies to

$$k_{\rm obs} = k_{\rm add} + k_{\rm a} (k_{\rm c} [\rm NO_2] + k_{\rm d} [\rm O_2]) / k_{\rm b}$$
 (IV)

and the slope of the plot shown in Figure 3 is then k_ak_c/k_bk_2 . Our observation of a reaction in the absence of NO₂ then suggests that the NO₂-independent reaction pathway is either reaction (add) with $k_{obs} = k_{add}$ or that reaction (add) is insignificant but k_d is sufficiently large so that

Scheme 1



Figure 3. Plot of the slopes, k_{obs}/k_2 , obtained from plots such as those shown in Figure 2 against the NO₂ concentration.

 $k_{\rm obs} = k_{\rm a}k_{\rm d}[O_2]/k_{\rm b}$. Our present data cannot distinguish between these alternatives (which are not mutually exclusive). From the intercept/slope ratio of the plot of the data shown in Figure 3, a rate constant ratio of $k_{\rm d}/k_{\rm c}$ = 3.3×10^{-5} is obtained, if $k_{\rm add}$ is insignificant. This rate constant ratio is 2 orders of magnitude higher than those derived for the reactions of O₂ and NO₂ with the NO₃dibenzo-*p*-dioxin and NO₃-naphthalene adducts (21, 31), suggesting (but not proving) that reaction pathway (add) occurs and that this pathway is responsible for the observed rate constant at zero NO₂ concentration. This suggestion is reinforced by the observation of a reaction of phenanthrene with O₃ (see below).

Using a rate constant for the reaction of the NO₃ radical with 1-butene of 1.19×10^{-14} cm³ molecule⁻¹ s⁻¹ (±30%) at 296 K (32) leads to values of $k_{add} = (1.2 \pm 0.4) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ and $k_a k_c / k_b = (7.0 \pm 2.2) \times 10^{-28}$ cm⁶ molecule⁻² s⁻¹ at 296 ± 2 K, where the indicated errors include the uncertainties in k_2 . (Alternatively, $k_a k_d [O_2] / k_b = 1.2 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ and $k_a k_d / k_b = (2.4 \pm 0.8) \times 10^{-32}$ cm⁶ molecule⁻² s⁻¹ at 296 ± 2 K.) The value of $k_a k_c / k_b$ for phenanthrene of 7×10^{-28} cm⁶ molecule⁻² s⁻¹ at room temperature is comparable to the corresponding rate constant ratios for naphthalene, 1- and 2-methylnaphthalene, 2,3-dimethylnaphthalene, and acenaphthene, which range from 3.6×10^{-27} cm⁶ molecule⁻² s⁻¹ for



acenaphthene (33). Under typical ambient atmospheric conditions, the NO₂ concentrations are $<6 \times 10^{12}$ molecule cm⁻³, and hence the effective rate constant under atmospheric conditions is that measured at essentially zero NO₂ concentration of 1.2×10^{-13} cm³ molecule⁻¹ s⁻¹ at 296 \pm 2 K.

Phenanthrene was observed to react in the presence of $(8.7-15.6) \times 10^{13}$ molecule cm⁻³ of O₃, with 31% reacting over 2.7 h for 8.7 × 10¹³ molecule cm⁻³ of O₃ and 70% reacting over 4.6-4.9 h for 1.56×10^{14} molecule cm⁻³ of O₃. Within the analytical uncertainties, no decay of phenanthrene in the dark in the absence of O₃ was observed over 2.9 h. The fluorene concentrations showed an initial decrease with no obvious further decay, within the analytical uncertainties of ~5%, under these conditions. The phenanthrene decay rates, -d ln[phenanthrene]/dt, are plotted against the O₃ concentration in Figure 4, and it can be seen that the GC-FID and GC/MS analyses were in good agreement. A least-squares analysis of these data lead to a rate constant of

$$k_3(O_3 + \text{phenanthrene}) = (4.0 \pm 1.0) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 296 \pm 2 K, where the indicated error is an estimated overall uncertainty based on the 2 least-squares standard deviations in the individual phenanthrene decay rates of 12-29% and the low phenanthrene decay rates measured.

Product and Mutagenicity Studies. GC/MS analysis of the O₃ reaction products sampled onto Tenax solid adsorbent showed the presence of 2,2'-diformylbiphenyl, indicating that the O₃ reaction occurs at the 9,10->C==C< bond, as may be the case for the NO₃ radical reaction (see Discussion above). These indications that the O₃ and NO₃ reactions (at least partially for the NO₃ reaction) proceed by reaction at the 9,10- >C==C< bond suggest that phenanthrene behaves as a substituted biphenyl, with a cyclohexa-fused ring. This situation is then analogous to the NO₃ radical and O₃ reactions with acenaphthylene, which proceed by addition to the >C==C< bond in the cyclopenta-fused ring (22).

GC/MS analysis of the NO₃ radical reaction products showed the presence of 2-nitrodibenzopyranone



with a calculated yield of 0.002%, in HPLC fraction 6, and all five nitrophenanthrenes, with formation yields of the 1-, 2-, 3-, 4-, and 9-nitrophenanthrenes of 0.03%, 0.002%, 0.002%, 0.004%, and 0.10%, respectively, in HPLC fraction 4. The identifications of the nitrophenanthrene isomers were based on retention time matching of the 3-, 4-, and 9-nitrophenanthrene standards available and the prediction by Robbat et al. (34) that 1-nitrophenanthrene elutes just after 9-nitrophenanthrene on a similar column (SE-52). We obtained an elution order of 4-, 9-, 1-, 3-, and 2-nitrophenanthrene, while Robbat et al. (34) predicted that 2-nitrophenanthrene should elute prior to 3-nitrophenanthrene.



Figure 4. Plot of the phenanthrene decay rate against the O_3 concentration. Analyses of gas-phase phenanthrene carried out by (O) GC-FID and (\bullet) GC/MS.



Figure 5. Mutagrams obtained from mutagenicity analyses of extracts of samples collected after reaction of phenanthrene with the NO_3 radical, with an initial NO_2 concentration of 4.8 \times 10¹³ molecule cm⁻³ (bottom) and after 18-min irradiation of a CH₃ONO–NO–phenanthrene–air mixture (top).

The formation of 2-nitrodibenzopyranone and the nitrophenanthrenes was consistent with the mutagenicity profile (mutagram) which showed mutagenicity in HPLC fractions 4 (the nitro-PAH-containing fraction) and 6 (the nitrodibenzopyranone-containing fraction) (Figure 5). The overall nitrophenanthrene yield of 0.13% obtained here is consistent with the upper limit of <1% reported by Arey et al. (35), although only four nitrophenanthrenes (including 9-nitrophenanthrene) were observed by Arey et al. (35) in similar abundance. The formation of 9-nitrophenanthrene may be ascribed to electrophilic nitration by the nitric acid, formed in the CH₃ONO-NOair irradiation during sampling. The yield of 2-nitrodibenzopyranone of $\sim 0.002\%$ from the NO₃ radical reaction with phenanthrene at 4.8×10^{13} molecule cm⁻³ of NO₂ is less than those previously derived by Helmig et al. (17) from product analyses of irradiated CH₃ONO-NO-phenanthrene-air mixtures. This observation indi-



Figure 6. Time dependence of the mutagenicity in fractions 4 and 6 during the irradiation of a $CH_3ONO-NO$ -phenanthrene-air mixture.

cates that the NO₃ radical reaction with phenanthrene is not a dominant source of nitrodibenzopyranones in the previous chamber experiments nor in the ambient atmosphere (17).

For the reaction samples collected from the CH₃ONO-NO-phenanthrene-air irradiation, mutagenicity was observed mainly in fractions 4 and 6, and the mutagram after 18-min irradiation is shown in Figure 5. The timemutagenicity profiles of HPLC fractions 4 and 6 are shown in Figure 6, which shows that the fraction 4 mutagenicity initially decreases with time and then levels off after ~ 10 min irradiation, while the fraction 6 mutagenicity increases slowly with irradiation time until \sim 16–18 min, during which time the mutagenicity increases very rapidly. We have shown, both previously (19) and above, that with the HPLC fractionation procedure used here the mutagenic nitroarenes elute in fraction 4 and that the mutagenic nitrodibenzopyranones elute in fraction 6. Furthermore, our previous chemical and mutagenicity analyses of the photooxidations of naphthalene and fluorene (19) showed that the nitronaphthalenes and nitrofluorenes accounted for 75-90% of the measured mutagenicities in fraction 4, and similar analyses of the photooxidation of phenanthrene showed that 2-nitrodibenzopyranone accounted for the majority of the mutagenicity in fraction 6 (16). In the discussion below, we therefore assume that the fraction 4 mutagenicity is due to the nitrophenanthrenes and that the fraction 6 mutagenicity is due to 2-nitrodibenzopyranone.

The rate of decrease in the nitrophenanthrene-containing fraction 4 mutagenicity over the irradiation time of 2-10 min has a time scale similar to the methyl nitrite photolysis lifetime of ~ 6 min in this chamber. This suggests that the nitrophenanthrene (or other mutagenic product) is formed from the OH radical-initiated reaction of phenanthrene and photolyzes rapidly, with a photolysis lifetime of $\sim 1-2$ min or less

OH + phenanthrene $\rightarrow \rightarrow \alpha$ nitrophenanthrene nitrophenanthrene + $h\nu \rightarrow$ products

where α is the yield of nitrophenanthrenes. We have previously shown that 1-nitronaphthalene, 2-methyl-1nitronaphthalene, and 2-, 7-, and 8-nitrofluoranthene all photolyze in the gas phase under black lamp irradiation with photolysis lifetimes of a few minutes (36-38).

As noted above, similar phenanthrene photooxidations reported by Helmig et al. (16, 17) showed that the fraction 6 mutagenicity can be attributed to 2-nitrodibenzopyra-

none. The rapid increase in the mutagenicity of this fraction at the end of the experiment suggests that 2-nitrodibenzopyranone is not a primary product of the OH radical reaction with phenanthrene. This is in agreement with the conclusions of Helmig et al. (17) from a comparison of chamber and ambient air data for 2-nitrodibenzopyranone. Thus, the data presented in Helmig et al. (17) lead to an estimated 2-nitrodibenzopyranone formation yield from phenanthrene from ambient atmospheric data of \sim 1–2% and from laboratory chamber data of $\leq 0.1\%$ (using our present rate constant for the OH radical reaction with phenanthrene). Furthermore, the product data from the NO₃ radical reaction with phenanthrene show that this reaction is not the source of the 2-nitrodibenzopyranone observed in the CH₃ONO-NOphenanthrene-air irradiations of Helmig et al. (17). Thus, the data of Helmig et al. (17) and those shown in Figure 6 are consistent with 2-nitrodibenzopyranone being a second-generation product of the phenanthrene-OH radical reaction.

Atmospheric Lifetime and Fate of Phenanthrene. Using the rate constants determined here for the OH radical, NO₃ radical, and O₃ reactions with phenanthrene and estimated ambient concentrations of OH radicals, a 12-h daytime average of 1.6×10^6 molecule cm⁻³ (39); NO₃ radicals, a 12-h nighttime average of 5×10^8 molecule cm⁻³ (33); and O₃, a 24-h average of 7×10^{11} molecule cm⁻³ (40), then the dominant atmospheric loss of phenanthrene is calculated to be by daytime reaction with OH radicals, with a lifetime of 1.1 day, and by nighttime reaction with NO₃ radicals, with a lifetime of 5 h. The calculated overall lifetime is then ≤ 1 day and depends on the nighttime NO₃ radical concentrations, which the limited measurement data indicate to be highly variable (33). The O₃ reaction is of negligible importance as an atmospheric loss process.

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