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Rate Constants for the Gas-Phase Reactions of Methylphenanthrenes with OH as a Function of Temperature

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The rate constants for the gas-phase reactions of phenanthrene, phenanthrene-d_{10}, and 1-, 2-, 3-, and 9-methylphenanthrenes with the hydroxyl radical were measured using the relative rate technique over the temperature range of 323−403 K and at a total pressure of 760 Torr. On-line mass spectrometry was used to monitor the concentrations of reactants as a function of time. The following Arrhenius expressions have been determined for these reactions (in units of cubic centimeters per molecule per second): $(6.46^{+1.77}_{-1.39}) \times 10^{-12} \exp[(477 \pm 89)/T]$ for phenanthrene, $(3.38^{+4.42}_{-1.91}) \times 10^{-12} \exp[(745 \pm 301)/T]$ for phenanthrene-d_{10}, $(0.246^{+0.218}_{-0.115}) \times 10^{-12} \exp[(1420 \pm 242)/T]$ for 1-methylphenanthrene, $(2.54^{+3.57}_{-1.49}) \times 10^{-12} \exp[(964 \pm 322)/T]$ for 2-methylphenanthrene, $(2.97^{+0.69}_{-0.56}) \times 10^{-12} \exp[(926 \pm 77)/T]$ for 3-methylphenanthrene, and $(7.75^{+14.3}_{-5.02}) \times 10^{-12} \exp[(679 \pm 372)/T]$ for 9-methylphenanthrene. The Arrhenius parameters determined here for phenanthrene-d_{10} and 1-, 2-, 3-, and 9-methylphenanthrene are the first to be reported.

Introduction

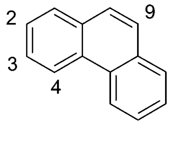
The methylphenanthrenes are semivolatile, polycyclic aromatic hydrocarbons (PAHs) with one methyl group in one of five positions on the phenanthrene skeleton. These compounds occur naturally in coal tar and petroleum, but they are mainly introduced into the ambient environment as byproducts of incomplete combustion.[1−3] In urban areas, vehicle exhaust, especially from diesel-fueled vehicles, is an important source of these compounds.[3−5] For example, a study in the Baltimore Harbor Tunnel (in Baltimore, MD) measured concentrations of methylphenanthrenes in the gas phase of 43 ± 10 ng/m^3 for 1-methylphenanthrene, 8.3 ± 1.9 ng/m^3 for 2-methylphenanthrene, 70 ± 16 ng/m^3 for 3-methylphenanthrene, and 71 ± 16 ng/m^3 for 4- and 9-methylphenanthrenes.[6] These gas-phase concentrations were 2−6 times higher than those in the particle phase.[6] Other studies have reported concentrations of 1-methylphenanthrene in indoor and outdoor air in Los Angeles, CA; Houston, TX; and Elizabeth, NJ of 0.1−8.4, 0.3−12, and 0.4−13 ng/m^3, respectively.[7] The concentration of 1-methylphenanthrene at the entrance and exit of the Lundby Tunnel (in Gothenburg, Sweden) has been reported to be in the range of 3−23 ng/m^3.[8] Methylphenanthrenes are also emitted from wood-burning stoves and fireplaces.[9,10]

Once they enter the atmosphere, methylphenanthrenes are present predominantly in the gas phase at ambient temperatures.[1,2] Thus, the atmospheric fate of these compounds is likely to be controlled by gas-phase reactions with atmospheric oxidants (such as O_3, OH, and NO_3).[11] For these compounds, reactions with OH are likely to be the most important loss process.[12−15] Although several studies have investigated the kinetics of the gas-phase reactions of small PAHs with OH (for example, the rate constants for the reactions of naphthalene, acenaphthalene, phenanthrene, and anthracene with OH are well-known, even in some cases as a function of temperature[16−20]), there have been no kinetic studies of the reactions of OH with methylphenanthrenes, particularly as a function of temperature. Clearly, more kinetic data for the gas-phase reactions of these compounds with OH are needed to help predict the fate of these compounds in the troposphere.

In this study, we have measured the rate constants for the gas-phase reactions of 1-, 2-, 3-, and 9-methylphenanthrene with the OH radical, all as a function of temperature. We have also investigated the kinetics of the reaction of phenanthrene itself and phenanthrene-d_{10} with OH, both as a function of temperature. We used the relative rate technique and on-line mass spectrometry to monitor the concentrations of the reactants. To obtain sufficient reactant in the gas phase, our experiments were conducted at 323−403 K; rate constants at ambient temperature were obtained by extrapolation.

Experimental Section

Chemicals. The chemicals that were used, their stated purities, their *Chemical Abstracts* registry numbers, and their suppliers are as follows: phenanthrene, >99.5%, 85-01-8, and Aldrich; phenanthrene-d_{10}, 98 at. % D, 1517-22-2, and Aldrich; 1-methylphenanthrene, 99.5%, 832-69-9, and ChemService; 2-methylphenanthrene, 98.0%, 2531-84-2, and ChemService; 3-methylphenanthrene, 99%, 832-71-3, and Crescent Chemical; 9-methylphenanthrene, 98.5%, 883-20-5, and Crescent Chemical; 2-methylpropene, 99%, 115-11-7, and Aldrich; and hydrogen peroxide, 50 wt % solution in water, 7722-84-1, and Aldrich. The phenanthrene numbering system is given here:



Experimental Procedures. The experimental apparatus used to measure the rate constants has been described in detail elsewhere.[16,21−26] The reaction system consisted of an ∼190 cm^3

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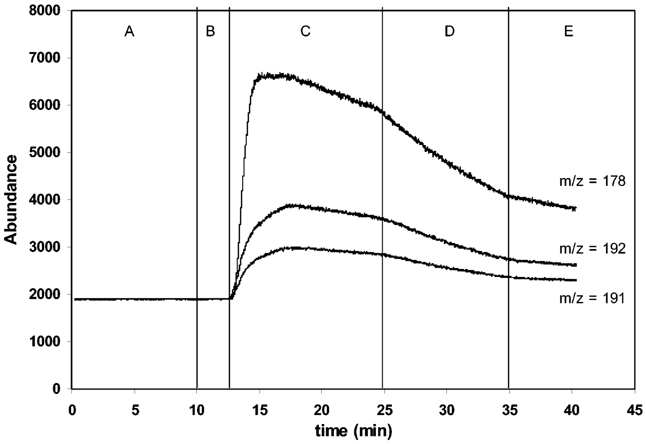


Figure 1. Raw data from a relative rate experiment at 343 K for the reaction of 2-methylphenanthrene (*m/z* 191 and 192) with OH using phenanthrene (*m/z* 178) as a reference compound. The mixture of He and H_2O_2 is supplied to the chamber for 10 min (A), and the valves are closed. The reactant and reference compound are injected at 12.5 min (B). After an equilibration period that lasts until 25 min (C), the UV lamps are turned on and the reaction proceeds until 35 min (D), when the reaction is stopped by turning off the lamps. The signals are stabilized from 35 to 40 min (E), and the mass spectrometer is then turned off.

quartz reaction chamber mounted in a gas chromatographic oven; the chamber was connected to a mass spectrometer with a 75 cm × 100 μm (inside diameter) deactivated, fused silica capillary column (J&W Scientific Inc.). This arrangement allowed us to precisely control the temperature (±0.1 K) of the reaction chamber and to sample the reactant and reference compounds continuously. Helium was used as a diluent gas (99.999%, Gas Tech Inc.) under static conditions at atmospheric pressure. OH radicals were produced *in situ* by the photolysis of hydrogen peroxide.[26] Four 8 W germicidal lamps (General Electric, G8-T5) attached to the door of the GC oven provided UV radiation centered at 254 nm. To generate a sufficient OH radical concentration, a preconcentrated hydrogen peroxide solution was used with an air diffuser, and the radiation was maximized by lining the inside of the GC oven with reflective tape.

Experiments aimed at determining the rate constants as a function of temperature were conducted using the following steps (see Figure 1). Before the start of each experiment, helium was flushed through the reaction chamber for 40 min. The helium was then directed through the hydrogen peroxide solution, and the mixture of He and H_2O_2 was introduced into the chamber for 10 min. The experiments were started by closing the valves attached to the reaction chamber to isolate the gas flows and by turning on the mass spectrometer, which had been adjusted to monitor the *m/z* values of interest. The reactant and reference compounds were injected into the chamber after 2−3 min, and a waiting period of 10−13 min was initiated to ensure mixing of the reactants and to establish a good baseline. After this waiting period, the UV lamps were turned on to initiate the reaction with OH. 2-Methylpropene was used as the reference compound for measuring the rate constants of phenanthrene with OH, and phenanthrene was then used as the reference compound for measuring the rate constants of phenanthrene-d_{10} and the four methylphenanthrenes. Solutions were prepared by dissolving exact amounts of the phenanthrenes in CCl_4 to give a concentration of 6 μg/μL; CCl_4 was selected because it is essentially nonreactive to OH radicals.[15] Aliquots of this solution (0.5−1 μL) were injected into the reaction chamber, which resulted in gas-phase reactant concentrations of 5−10 × 10^{13} molecules/cm^3. 2-Methylpropene was stored in 125 mL glass vessels and injected into the chamber with a 25 μL gastight syringe (Hamilton) to give a concentration of 5−10 × 10^{13} molecules/cm^3.

TABLE 1: Masses (*m/z* values) of Reactants and Reference Compounds Monitored in the Kinetic Experiments

compound	*m/z* values
2-methylpropene	56 (M^+)
phenanthrene	89 (M^{2+}), 176 ($M - H_2^+$), 178 (M^+)
phenanthrene-d_{10}	94 (M^{2+}), 187 ($M - H^+$),[a] 188 (M^+)
1-methylphenanthrene	191 ($M - H^+$), 192 (M^+)
2-methylphenanthrene	191 ($M - H^+$), 192 (M^+)
3-methylphenanthrene	191 ($M - H^+$), 192 (M^+)
9-methylphenanthrene	191 ($M - H^+$), 192 (M^+)

[a] This ion is monitored for this compound because of the presence of ~15 mol % $C_{14}D_9H$ as an impurity in $C_{14}D_{10}$. This ~15 mol % gives an overall isotopic impurity of ~2 at. %.

The reaction was initiated by turning on the UV lamps, and it was allowed to proceed for 10−15 min. After the lamps were turned off, the signal stabilized at a lower level, which was measured for 5 min, and the mass spectrometer was then turned off. The reaction chamber was flushed with helium, and the oven temperature was increased and stabilized for the next run. The raw data were treated as described below to produce relative rate plots for all combinations of reference and reactant *m/z* values. A linear regression was used for each plot, and the slopes from these regressions were averaged to give a measured rate constant ratio ($k_{\mathrm{reac}}/k_{\mathrm{ref}}$). The experimental sequence is illustrated in Figure 1, which shows raw data for an experiment with 2-methylphenanthrene using phenanthrene as the reference compound.

Analytical Procedures. The reactants and reference compounds were monitored by on-line electron-impact mass spectrometry using a Hewlett-Packard 5989A mass spectrometer operating in the selected ion monitoring mode. The mass spectrometer was set to monitor several masses (*m/z* values) of the reactants and reference compounds. These *m/z* values were selected in an effort to avoid overlaps with each other and with masses of potential transformation products. Preliminary experiments aimed at investigating the overlaps of these masses were conducted by following the experimental approach previously described by Khamaganov and Hites[25] and by Gill and Hites.[26] The analytical conditions obtained from the preliminary experiments result in a systemic error of <5% for our rate constant measurements. Table 1 shows the *m/z* values of the reactants and reference compounds, obtained from the preliminary experiments, which were used to monitor the concentrations of these compounds in each kinetic experiment.

Data Treatment. The data were first corrected by subtracting the background signal from all data points; this was ~1900 in Figure 1. The data were then smoothed using a five-point moving average. Because the chamber leaked slightly during the experiment (see sections C and E of Figure 1), the rate of this leak was established (by curve fitting) from the latter part of these data. In the case of the data shown in Figure 1, we used the period from 18 to 24 min for this curve fitting. Data during the "light-on" period (section D in Figure 1) were corrected to eliminate this systematic effect by adding values extrapolated from the curve fit of section C. Some of the decrease during section C could also be due to "dark" reactions between H_2O_2 and the phenanthrenes, but these also would be corrected with the procedure outlined here. The corrected data from section D (see Figure 1) were then used to calculate the rate constants as follows:

TABLE 2: Rate Constants and Arrhenius Parameters of the Reference Compounds Used in This Research

reference compound	$10^{11}k$ (298 K) (cm^3 molecule^{-1} s^{-1})	$10^{12}A$ (cm^3 molecule^{-1} s^{-1})	$-E_a/R$ (K)
2-methylpropene[27]	5.14	9.47	504
phenanthrene[a]	3.20	6.46	477

[a] See line 3 of Table 4 and Figure 2.

The kinetic rate constants were calculated by the relative rate technique assuming the simultaneous losses of the reactant and reference compound as described in reactions 1 and 2:

$$\text{reactant} + \text{OH} \xrightarrow{k_{\text{reac}}} \text{products} \qquad (1)$$

$$\text{reference} + \text{OH} \xrightarrow{k_{\text{ref}}} \text{other products} \qquad (2)$$

where k_{reac} is the rate constant of the reactant and k_{ref} is the rate constant of the reference compound. The concentrations of the reactant and the reference compound at any time t can be calculated by the relative rate equation

$$\ln\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_{\text{reac}}}{k_{\text{ref}}}\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \qquad (3)$$

where $[\text{reactant}]_0$ and $[\text{reference}]_0$ are the initial concentrations of the reactant and reference compound and $[\text{reactant}]_t$ and $[\text{reference}]_t$ are their concentrations at time t, respectively. A plot of $\ln([\text{reactant}]_0/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_0/[\text{reference}]_t)$ gives a slope equal to the rate constant ratio ($k_{\text{reac}}/k_{\text{ref}}$), from which k_{reac} can be calculated using a known value of k_{ref} at the temperature of the experiment. Table 2 shows the k_{ref} values of the reference compounds used in this study as a function of temperature. The temperature-dependent rate constants of 2-methylpropene are well-known,[27] and those of phenanthrene were measured using 2-methylpropene as a reference compound in this study. The rate constants of phenanthrene were then used as the reference for the measurement of those of the methylphenanthrenes and of phenanthrene-d_{10}.

Results and Discussion

The rate constant ratios for the reactions of the six target compounds with OH radical are summarized as a function of temperature in Table 3. These ratios were obtained by averaging the slopes of the relative rate plots for all combinations of reactant and reference compound masses and are listed with errors representing the 95% confidence limits of the averaged values. The Arrhenius parameters [pre-exponential factor (A) and activation energy (E_a)] were determined by a linear regression of the natural logarithms of the measured rate constants versus the corresponding reciprocal values of the absolute temperatures of the reactions. The rate constants of the target compounds at 298 K (room temperature) were then extrapolated using this Arrhenius relationship. The Arrhenius parameters and rate constants obtained in this study are shown in Table 4 along with their standard errors. The Arrhenius parameters for phenanthrene as reported by other researchers are also listed for comparison.

Reaction of Phenanthrene with OH. The phenanthrene experiment was conducted to validate the experimental approach used in this study. For example, H_2O_2 has been used as an OH source for the reaction of biogenic hydrocarbons,[26] but it has not been used as an OH source for its reactions with PAH. Figure 2 shows an Arrhenius plot of our measured rate constants for the reaction of phenanthrene with OH; this figure also shows rate constants from other researchers for comparison. The solid line is the least-squares fit of all data (including that of Brubaker and Hites[16] and Biermann et al.[28] but excluding that of Lorenz and Zellner[17] and Kwok et al.[18]) to the Arrhenius expression. Figure 2 shows that our results are in good agreement with the literature. We should point out that the rate constants reported by Lorenz and Zellner[17] were from experiments conducted at low pressure (10^{-3} atm), but the others were conducted at atmospheric pressure. The Arrhenius parameters for the line

TABLE 3: Summary of the Average Measured Rate Constant Ratios, $k_{\text{reac}}/k_{\text{ref}}$, for the Reactions of OH with Phenanthrene, Phenanthrene-d_{10}, and Methylphenanthrenes

T (K)	$k_{\text{reac}}/k_{\text{ref}}$	T (K)	$k_{\text{reac}}/k_{\text{ref}}$	T (K)	$k_{\text{reac}}/k_{\text{ref}}$
		Phenanthrene[a]			
358	0.606 ± 0.035[b]	368	0.601 ± 0.099	378	0.607 ± 0.035
363	0.585 ± 0.051	373	0.539 ± 0.048	383	0.567 ± 0.026
368	0.664 ± 0.099	378	0.585 ± 0.051	383	0.597 ± 0.026
		Phenanthrene-d_{10}[c]			
323	1.078 ± 0.018	363	1.033 ± 0.017	373	1.303 ± 0.055
343	1.179 ± 0.120	368	1.123 ± 0.065	373	1.003 ± 0.091
353	1.207 ± 0.028	368	1.111 ± 0.068	383	0.836 ± 0.155
358	1.219 ± 0.112				
		1-Methylphenanthrene[c]			
363	0.505 ± 0.064	378	0.422 ± 0.005	393	0.380 ± 0.066
368	0.469 ± 0.027	383	0.462 ± 0.064	398	0.436 ± 0.073
373	0.510 ± 0.014	388	0.443 ± 0.023	403	0.393 ± 0.072
		2-Methylphenanthrene[c]			
338	1.702 ± 0.077	358	1.769 ± 0.036	393	1.466 ± 0.122
343	1.387 ± 0.021	383	1.533 ± 0.157	398	0.943 ± 0.073
348	1.520 ± 0.041	383	1.536 ± 0.001		
353	1.591 ± 0.154	388	1.577 ± 0.046		
		3-Methylphenanthrene[c]			
353	1.652 ± 0.025	363	1.556 ± 0.049	378	1.511 ± 0.122
358	1.599 ± 0.002	368	1.615 ± 0.001	383	1.494 ± 0.125
363	1.551 ± 0.029	373	1.526 ± 0.147	388	1.442 ± 0.098
		9-Methylphenanthrene[c]			
333	2.479 ± 0.164	353	1.959 ± 0.001	368	2.547 ± 0.047
343	2.209 ± 0.010	358	1.976 ± 0.050	373	2.119 ± 0.064
348	1.838 ± 0.066	363	2.067 ± 0.076	373	1.953 ± 0.048

[a] The reference compound was 2-methylpropene. [b] The errors represent 95% confidence intervals. [c] The reference compound was phenanthrene.

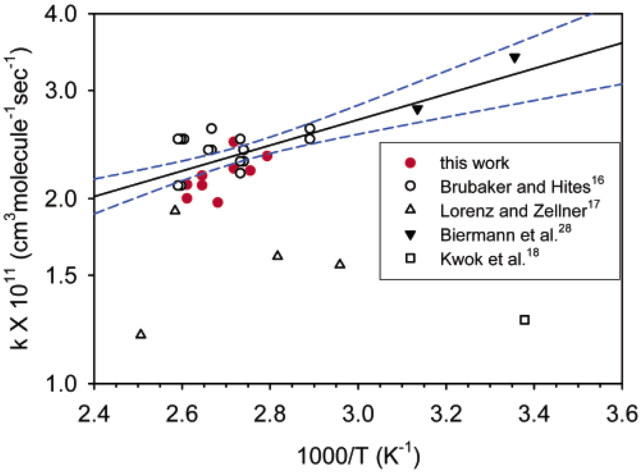


Figure 2. Measured rate constants for the reaction of phenanthrene with OH obtained in this study and from other researchers. The line is the linear regression of all measured values except those of Lorenz and Zellner[17] and Kwok et al.[18] The dashed lines are the 95% confidence limits of this regression. The correlation coefficient (r) of the regression is 0.713.

TABLE 4: Summary of All Measurements of k_{reac}[a]

reactant	temperature range (K)	$10^{12}A$ (cm^3 molecule^{-1} s^{-1})	$-E_a/R$ (K)	$10^{11}k_{\mathrm{reac}}$ (298 K)[b] (cm^3 molecule^{-1} s^{-1})	ref
phenanthrene	338−492	1.02	1021 ± 318	3.14 ± 2.06	Atkinson[15]
	346−386	14.2	192 ± 168	2.71 ± 1.17	Brubaker and Hites[16]
	298−386	$6.46^{+1.77}_{-1.39}$[c]	477 ± 89[c]	3.20 ± 1.23[c]	this work
phenanthrene-d_{10}	323−383	$3.38^{+4.42}_{-1.91}$	745 ± 301	4.12 ± 5.67	this work
1-methylphenanthrene	363−403	$0.246^{+0.218}_{-0.115}$	1420 ± 242	2.88 ± 3.05	this work
2-methylphenanthrene	338−398	$2.54^{+3.57}_{-1.49}$	964 ± 322	6.45 ± 9.49	this work
3-methylphenanthrene	353−388	$2.97^{+0.69}_{-0.56}$	926 ± 77	6.64 ± 2.21	this work
9-methylphenanthrene	333−373	$7.75^{+14.3}_{-5.02}$	679 ± 372	7.57 ± 13.3[d]	this work

[a] The errors indicated represent one standard error. [b] The values reported here at 298 K were calculated on the basis of the Arrhenius parameters reported by the authors. The standard error of the rate constant at 298 K (s_k) is given by the equation $s_k = \sqrt{e^{(2E_a)/(RT)}[s_A^2 + s_{E_a/R}^2(A/T)^2]}$, where s_A is the average standard error of the pre-exponential factor, $s_{E_a/R}$ is the standard error of the activation energy, and $T = 298$ K. [c] The values were calculated using the data of this work, Brubaker and Hites,[16] and Biermann et al.;[28] see Figure 2. [d] The regression of this Arrhenius plot is significant with only 90% confidence.

shown in Figure 2 are also shown in Tables 2 and 4, and these values were used as the reference rate constants for the other compounds studied here.

The Arrhenius parameters obtained in this study are between the values recommended by Atkinson[15] and those obtained by Brubaker and Hites[16] (see Table 4). The rate constant of phenanthrene at 298 K extrapolated by the Arrhenius relationship was similar to those measured by other research groups with the exception of that of Kwok et al., which was much smaller than our result. These results indicate that the experimental conditions we used for the phenanthrene experiment can be used for the other kinetic experiments (for example, H_2O_2 can be used as an OH source for these reactions) and that the kinetic parameters for phenanthrene obtained from Figure 2 can be used to determine the rate constants for the reactions of phenanthrene-d_{10} and methylphenanthrenes with OH.

We observed a negative temperature dependence for the reaction of phenanthrene with OH, which is similar to the observations of others for the reaction of OH with other aromatic compounds.[11] The primary mechanism for this reaction is likely to be OH addition, producing an OH−phenanthrene adduct. Although this adduct may react with both O_2 and NO_2, reaction with O_2 to generate stable products is expected to dominate under atmospheric conditions.[11] Because the rate constant for this reaction is likely to be at the high-pressure limit under the conditions of these experiments, the negative temperature dependence is probably due to the increased rate of unimolecular dissociation of the collisionally stabilized adduct at higher temperatures.[11]

Reaction of Phenanthrene-d_{10} with OH. The phenanthrene-d_{10} experiment was conducted in the temperature range of 323−383 K in an effort to identify the isotope effect on the degradation kinetics of phenanthrene. The temperature dependence of the measured rate constants of phenanthrene-d_{10} is shown in Figure 3, and the Arrhenius parameters are given in Table 4. A negative temperature dependence was also observed for this reaction. The pre-exponential factor and activation energy of phenanthrene-d_{10} obtained by the regression are statistically indistinguishable from those of phenanthrene, and the rate constants at 298 K are approximately the same. The lack of a significant primary isotope effect is consistent with an OH addition mechanism as opposed to a hydrogen (or in this case deuterium) abstraction mechanism.[29]

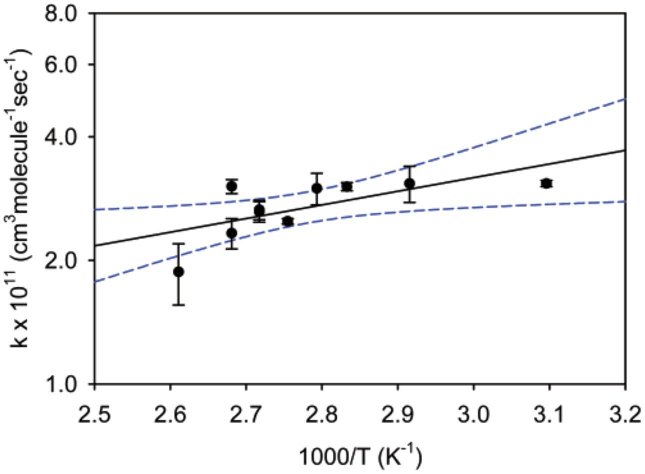


Figure 3. Measured rate constants for the reaction of phenanthrene-d_{10} with OH. The line is the regression of measured values; the dashed lines are the 95% confidence limits of the regression. The correlation coefficient (r) of the regression is 0.669.

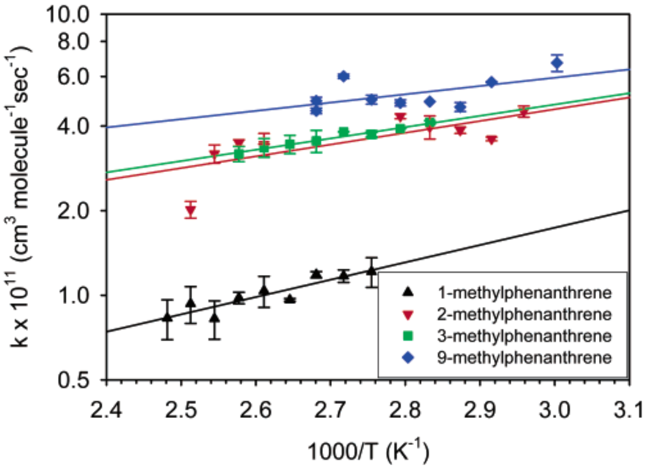
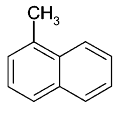
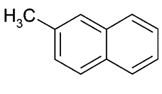


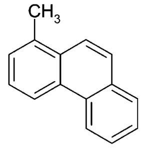
Figure 4. Measured rate constants for the reactions of 1-, 2-, 3-, and 9-methylphenanthrene with OH. The solid lines are the linear regressions of measured values; the correlation coefficients are 0.913, 0.734, 0.978, and 0.579, respectively.

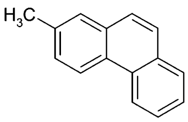
Reactions of Methylphenanthrenes with OH. The kinetic experiments with 1-, 2-, 3-, and 9-methylphenanthrenes were conducted in the temperature range of 333−403 K to investigate the effect of one methyl group on the OH reaction kinetics. The measured rate constants for the reactions of these four methylphenanthrenes with OH are plotted as a function of temperature in Figure 4, and the Arrhenius parameters are given in Table 4. The extrapolated rate constants at 298 K of the methylphenanthrenes were approximately twice those of phenanthrene, except for that of 1-methylphenanthrene, which was similar to that of phenanthrene. 1-Methylphenanthrene also had the lowest pre-exponential factor (by a factor of ~20) and the highest activation energy (by a factor of ~2) of all the compounds we studied. All of the measured rate constants for the reactions of the methylphenanthrenes with OH decreased with increasing reaction temperature as previously shown for phenanthrene and phenanthrene-d_{10}, again suggesting an OH addition mechanism.

We can compare these results to those of alkylnaphthalenes. As expected, the addition of a methyl group to naphthalene has an activating effect for the addition of OH and increases the rate constant of this reaction by about a factor of 2 ($k_{298} = 2.42 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for naphthalene, $k_{298} = 4.09 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 1-methylnaphthalene, and $k_{298} = 4.86 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 2-methylnaphthalene).[20] We also observe a factor of ~2 increase for the reactivities of 2-, 3-, and 9-methylphenanthrene compared to phenanthrene itself (see Table 4). It is not yet clear why 1-methylphenanthrene is not similarly activated by its methyl group. We note, however, that 1-methylnaphthalene is less reactive than 2-methylnaphthalene, which is similar to what we observe for 1- and 2-methylphenanthrene (see Table 4).


1-methylnaphthalene


2-methylnaphthalene


1-methylphenanthrene


2-methylphenanthrene

Unfortunately, the temperature dependences of the rate constants for the alkylnaphthalene + OH reactions are not known; thus, we cannot compare the pre-exponential factors and the activation energies to the measurements reported here.

Atmospheric Residence Times. Table 5 shows the calculated residence times of phenanthrene and the four methylphenanthrenes due to the reactions with OH in the atmosphere. The residence times of these reactants were calculated using the estimated rate constants at 298 K along with an assumed atmospheric OH concentration (9.7×10^5 cm^{-3}, the global OH concentration averaged over 24 h).[30] Given the errors of these estimates, all of these compounds have approximately the same atmospheric residence times, namely, ~3–9 h. These residence times are smaller than those of fluorene (22 h), fluoranthene (26 h), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (24–130 h), hexachlorocyclohexanes (96–120 days), and hexachlorobenzene (940 days) as reported by Brubaker and Hites.[16,24] This suggests that phenanthrene and the methylphenanthrenes are more likely to degrade quickly due to reactions with OH and, thus, are less likely to be transported long distances through the atmosphere than these other compounds.

TABLE 5: Atmospheric Residence Times of Phenanthrene and Methylphenanthrenes Due to Reactions with OH

reactant	atmospheric lifetime (h)
phenanthrene	9.0 ± 3.5
1-methylphenanthrene	9.9 ± 11
2-methylphenanthrene	4.4 ± 6.5
3-methylphenanthrene	4.3 ± 1.4
9-methylphenanthrene	3.8 ± 6.7

For comparison, we have also calculated the atmospheric residence times of phenanthrene due to the reactions with O_3 during the day and with NO_3 during the night. We assumed three different O_3 concentrations (30 ppbv in remote areas, 85 ppbv in rural areas, and 250 ppbv in urban areas)[31] and three different NO_3 concentrations (8 pptv in remote areas, 80 pptv in rural areas, and 350 pptv in urban areas).[32] We used published rate constants for the reactions of phenanthrene with O_3 (4×10^{-19} cm^3 molecule^{-1} s^{-1})[18] and NO_3 (1.20×10^{-13} cm^3 molecule^{-1} s^{-1}).[18] The atmospheric residence times of phenanthrene at the different ozone concentrations were 840, 300, and 100 h, respectively, which are much longer than for the reaction with OH calculated in this study. This indicates that phenanthrene is primarily removed from the troposphere during the day by OH reactions even in urban areas with high ozone levels. In contrast, the residence times of phenanthrene due to reactions with NO_3 are 12, 1.2, and 0.3 h at the remote, rural, and urban locations, respectively. This result indicates that removal due to reactions with NO_3 at night is much faster than removal due to OH reactions during the day at most locations. These results for phenanthrene are similar to those reported by Kwok et al.,[18] who based their calculations on a much lower OH radical reaction rate constant.

At present, rate constants for the reactions of the methylphenanthrenes with O_3 and NO_3 are not known. However, by analogy with the reactions of phenanthrene with atmospheric oxidants,[16,18] we suggest that reactions of the methylphenanthrenes with OH and NO_3 would dominate the tropospheric removal of these compounds during the day and night, respectively. The measurement of rate constants for the reactions of the methylphenanthrenes with O_3 and NO_3 is warranted.

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