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DETERMINING THE RATE CONSTANTS FOR THE GAS-PHASE REACTIONS OF LOW-VOLATILE COMPOUNDS WITH OH RADICAL USING A RELATIVE-RATE METHOD IN CCL₄ LIQUID PHASE-SYSTEM

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[Introduction]

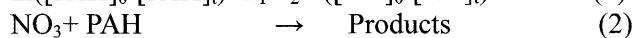
Nitrated polycyclic aromatic hydrocarbons (NPAH) have been found in airborne particles as well as polycyclic aromatic hydrocarbons (PAH). Airborne NPAH such as nitrotriphenylene are believed to be formed by atmospheric reactions of the parent PAH, triphenylene in the presence of nitrogen oxides, especially by those initiated by OH radical or NO₃ radical.¹ Numerous kinetic studies on OH radical-initiated reaction of PAH have been conducted,²⁻⁸ since it is regarded as the major pathway for NPAH formation and atmospheric loss of gas-phase PAH.² On the other hand, it is difficult to determine the rate constants for the gas-phase reactions of semi-, or lower-volatile PAH with four or more aromatic rings using conventional large chamber experiments² or fast-flow discharge methods⁹ because of serious loss of PAH onto the wall of the reaction setup by deposition due to their low vapor pressure. Thus, alternative methods are desired to determine reliable values of the rate constants for the low-volatile compounds. In this study, we conducted a kinetic study on the reactions with NO₃ radical for several kinds of PAH in CCl₄ liquid-phase system for the first time to obtain the rate constants for the NO₃-radical reactions of PAH. Based on the obtained rate constants, the rate constants for the gas-phase OH-radical reactions of triphenylene, which is one of the low-volatile PAH were determined using an empirical correlation between the rate constant ratio for the reactions with OH and with NO₃ radicals.

[Experiments]

N₂O₅ as NO₃ radical source was synthesized by a two-step dehydration of the HNO₃ with P₂O₅.⁹ The prepared N₂O₅ dissolved into CCl₄ solution of each PAH with naphthalene (NA) as a reference substrate, for which the rate constant for the OH-radical reaction has been well established.² The initial concentration of N₂O₅ was ca. 40mmolL⁻¹, and those of PAH were 5-50μmolL⁻¹. Every 30s of the reaction 1mL of the reaction solution was sampled and added to acetaldehyde to scavenge the radicals. PAH in the treated sample solution was determined by conventional reverse-phase HPLC with fluorescence or UV-vis detector.

Ratio of the rate constant to NA was determined for the above PAH and 1-NN in N₂O₅-NO₃-NO₂-CCl₄ system using a relative rate method²⁻⁸ at 273 ± 1K. CCl₄ was employed as a non-polar solvent to make N₂O₅ exist in the form of covalent molecule to generate NO₃ following the equilibrium between molecular N₂O₅, NO₃, and NO₂ (N₂O₅ ↔ NO₃ + NO₂).¹² Under the conditions employed, the reaction with NO₃ radical was the only loss process of the PAH. Hence, the natural logarithm plots of PAH against NA in the concentration at given reaction times within 150s relative to the initial concentration allow one to obtain the rate constant ratio between each PAH and NA following Eqs 1 to 3;

$$\ln([PAH]_0/[PAH]_t) = k_1/k_2 \ln([NA]_0/[NA]_t) \quad (1)$$



Where [PAH]₀ and [NA]₀ are the initial concentrations of PAH and NA, respectively and [PAH]_t and [NA]_t are the corresponding concentrations at reaction time t and k₁ and k₂ are the rate constants for reactions 2 and 3, respectively.

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[Results]

Good straight-line plots in accordance with eq 1 are obtained from the experimental data of the NO₃-NO₂-PAH-reference compound reactions. The rate constant ratios k_1/k_2 determined by the least-square analysis in this study are given in Table 1. Table 1 also shows the ratios of the gas phase reaction rate constants of PAH to that of NA with OH radicals ($k_{\text{PAH-OH}}/k_{\text{NA-OH}}$) as reported in literatures. A plot of $k_{\text{PAH-OH}}/k_{\text{NA-OH}}$ against the rate constant ratios k_1/k_2 obtained in this work is shown in Figure 1. Proportionality, between $k_{\text{PAH-OH}}/k_{\text{NA-OH}}$ and k_1/k_2 seems also attained in this plot with one exception, and the value of the slope is 0.79. In this study, we use the latest reported rate constant for the OH radical reaction with phenanthrene of $k_{\text{Phenanthrene-OH}} = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ measured by Kwok et al. (1994). However, the previously measured rate constant of $k_{\text{Phenanthrene-OH}} = (3.4 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ is a factor of 2.6 higher,⁴ and using this value, the point for phenanthrene becomes in good agreement with the straight line obtained in this work. The two rate constant values for the phenanthrene and OH radical reaction are both from the same group using the same experimental technique, the relative rate method, but by the different analysis method for PAHs examined. The cause of the discrepancy is uncertain (no explanation has been made on this discrepancy in their latter paper),³ and it is noteworthy that the currently recommended rate constant of the gas-phase OH radical reaction with phenanthrene, $1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 296 K, seems still open to discussion judging from the present result. By using the rate constant ratio k_1/k_2 for triphenylene and the values of the slopes described above, the rate constants of the reaction of triphenylene with OH radical in the gas-phase at room temperature can be first estimated to be $(7.86 \pm 1.12) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

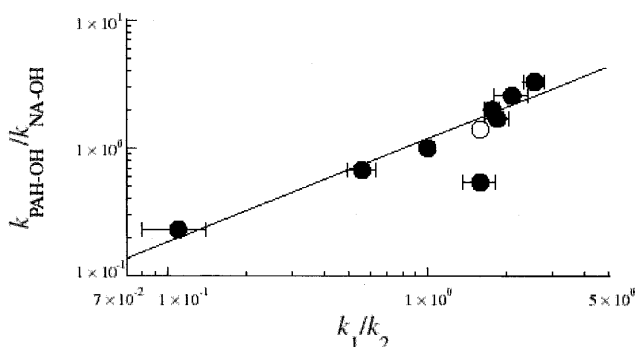


Figure 1 Plot of the rate constant ratio $k_{\text{PAH-OH}}/k_{\text{NA-OH}}$ against k_1/k_2 obtained in this study. Open circle indicates the data point for phenanthrene calculated using $k_{\text{phenanthrene-OH}}$ value reported by Biermann et al.⁴ This point is excluded from the calculation of the fitting.

Table 1 Ratios of rate constant k_1/k_2 obtained and the rate constants of $k_{\text{PAH-OH}}$ for the gas-phase reaction of corresponding PAH with OH radicals

Compound	k_1/k_2	$k_{\text{PAH-OH}} \times 10^{11a}$	$k_{\text{PAH-OH}}/k_{\text{NA-OH}}^g$
Naphthalene	1.00	2.39	1.00
1-Methylnaphthalene	1.85	4.09	1.70
2-Methylnaphthalene	1.77	4.86	2.00
2,3-Dimethylnaphthalene	2.11	6.15	2.57
Acenaphthene	2.57	8.0 ^b	3.30
Fluorene	0.56	1.6 ^c	0.67
Phenanthrene	1.59	1.3 ^d	0.54
1-Nitronaphthalene	0.11	0.54 ^e	0.23
Triphenylene	0.22	0.79 ^f	

^aGiven in unit of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; Taken from Reference 7 with exceptions as indicated. ^bTaken from Reference 8. ^cTaken from Reference 6. ^dTaken from reference 3. ^eTaken from reference 2. ^fObtained in this study. ^gCalculated using $k_{\text{PAH-OH}}$ values in this table.

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