A Novel Technique to Determine the Rate Constants for the Gas-phase Reactions of Low-volatile Compounds with OH Radical Using a Relative-rate Method in CCl$_4$ Liquid Phase-system

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For low-volatile aromatic compounds, a good linear relationship was found between the rate-constant ratio for the liquid-phase reaction with NO$_3$ radical in CCl$_4$ and that for the gas-phase reaction with OH radical when naphthalene was employed as a reference compound. Based on the relationship, the rate constants for the OH radical reaction have been successfully determined for fluoranthene and pyrene, which are important airborne polycyclic aromatic compounds.
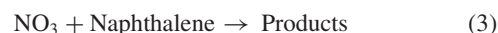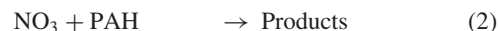
Nitrated polycyclic aromatic hydrocarbons (NPAH) have been found in airborne particles as well as PAH. Some of them such as 1-nitropyrene have also been detected in combustion emissions to be regarded as directly emitted compounds from combustion processes.[1] However, other airborne NPAH such as 2-nitrofluoranthene are believed to be formed by atmospheric reactions of the parent PAH, fluoranthene (FL) in the presence of nitrogen oxides, especially by those initiated by OH radical or NO$_3$ radical.[2] Numerous kinetic studies on OH radical-initiated reaction of PAH have been conducted,[3–9] since it is regarded as the major pathway for NPAH formation and the atmospheric loss of gas phase PAH.[3] 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 experiments[3] or fast-flow discharge methods[10] because of serious loss of PAH onto the wall of the reaction set-up by deposition due to their low vapor pressure. Atkinson and co-workers have reported a number of rate constants for the reaction of moderately volatile PAH and OH or NO$_3$ radicals, which are highly reliable.[2–5,7–9] They have also estimated the rate constants for the reactions of less volatile FL and pyrene (PY), which are major atmospheric PAH to undergo the OH-initiated nitration, using indoor Teflon chambers depending on the product yield.[6] The estimated rate constants reported by them have been widely used to evaluate the atmospheric nitration of FL and PY as a source of atmospheric mutagen. However, rapid wall losses of both the reactants and the products would affect the estimation of the rate constants and bring great difficulties in it. 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 NO$_3$ radical for 9 kinds of PAH and 1-nitronaphthalene (1-NN) in CCl$_4$ liquid-phase system for the first time to obtain the rate constants for the NO$_3$-radical reactions of PAH. Based on the obtained rate constants, the rate constants for the gas-phase OH-radical reactions of low-volatile PAH were determined using an empirical correlation between the rate constant ratio for the reactions with OH and with NO$_3$ radicals. The rate constants of FL and PY with OH radical were determined exhibiting the validity of this method.

N$_2$O$_5$ as NO$_3$-radical source was synthesized by a two-step dehydration of the HNO$_3$ with P$_2$O$_5$.[11] The prepared N$_2$O$_5$ dissolved into CCl$_4$ was added to CCl$_4$ 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.[3] The initial concentration of N$_2$O$_5$ was ca. 40 mmol L^{-1}, and those of PAH were 5–50 µmol L^{-1}. Every 30 s of the reaction, 1 mL 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 N$_2$O$_5$–NO$_3$–NO$_2$–CCl$_4$ system using a relative rate method[3–9] at 273 ± 1 K. CCl$_4$ was employed as a non-polar solvent to make N$_2$O$_5$ exist in the form of covalent molecule to generate NO$_3$ following the equilibrium between molecular N$_2$O$_5$, NO$_3$, and NO$_2$ (N$_2$O$_5$ ⇌ NO$_3$+NO$_2$).[12] Under the conditions employed, the reaction with NO$_3$ 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 150 s relative to the initial concentration allow one to obtain the rate constant ratio between each PAH and NA following Eqs 1 to 3;

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

$$NO_3 + PAH \qquad \rightarrow Products \qquad (2)$$

$$NO_3 + Naphthalene \rightarrow Products \qquad (3)$$

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 k_1 and k_2 are the rate constants for reactions 2 and 3, respectively.

When the plot of $\ln([PAH]_0/[PAH]_t)$ vs $\ln([NA]_0/[NA]_t)$ fitted on a linear regression, the slope of the regression line became equivalent to the rate constant ratio k_1/k_2. Indeed, good straight-line plots in accordance with Eq 1 were obtained for the experimental data for the N$_2$O$_5$–NO$_3$–NO$_2$–PAH–CCl$_4$ system. It clearly shows that the relative rate method in this study was effective to obtain the ratio of rate constants for the reaction of PAH with NO$_3$ radical. The obtained k_1/k_2 values for the PAH by the least-square analysis are given in Table 1. The ratios of the rate constant for the gas phase OH-radical reaction to that of NA ($k_{PAH–OH}/k_{NA–OH}$) are also given in Table 1 for PAH other than FL and PY. These values were obtained by using the report-

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

Compound	k_1/k_2	$k_{PAH-OH} \times 10^{11a}$	k_{PAH-OH}/k_{NA-OH}^g
Naphthalene	1.00	2.39	1.00
1-Methylnaphthalene	1.85 ± 0.19	4.09	1.70
2-Methylnaphthalene	1.77 ± 0.12	4.86	2.00
2,3-Dimethylnaphthalene	2.11 ± 0.30	6.15	2.57
Acenaphthene	2.57 ± 0.24	8.0^b	3.30
Fluorene	0.56 ± 0.07	1.6^c	0.67
Phenanthrene	1.59 ± 0.23	1.3^d	0.54
1-Nitronaphthalene	0.11 ± 0.03	0.54^e	0.23
Fluoranthene	1.21 ± 0.13	2.8 ± 0.2^f	
Pyrene	2.40 ± 0.29	4.8 ± 0.5^f	

[a]Given in unit of cm^3 molecule^{-1} s^{-1}; Taken from Reference 8 with exceptions as indicated. [b]Taken from Reference 9. [c]Taken from Reference 7. [d]Taken from reference 4. [e]Taken from reference 3. [f]Obtained in this study. [g]Calculated using k_{PAH-OH} values in this table.

ed rate constants.[3,4,7–9] It is not fantastic to expect an excellent correlation between the rate constant ratio for the reaction of PAH and reference NA with NO$_3$ (k_1/k_2) and that with OH (k_{PAH-OH}/k_{NA-OH}) since the reactions of PAH with both radicals are the addition reaction with negligible activation energy and the difference in cross section will be the only important factor which affects the difference in reactivity between NO$_3$ and OH under the condition employed. The relative cross section of NO$_3$ radical to OH radical should be constant in this case. The rate constants for the gas-phase reactions of unsaturated aliphatic hydrocarbons with NO$_3$ radical have been reported to correlate linearly with those for the reactions with OH radical.[13] In this study, we obtained such a relationship for PAH between the gas-phase and the liquid-phase systems experimentally for the first time as shown in Figure 1. For instance, the obtained plot of k_{PAH-OH}/k_{NA-OH} against k_1/k_2 showed that there is a linear relationship between $\log(k_{PAH-OH}/k_{NA-OH})$ and $\log(k_1/k_2)$ except for one data point for phenanthrene (PH). The value of the slope was obtained to be 0.79 by a non-parametric fitting for linear regression. Although the data set is obtained in CCl$_4$, no significant difference in relative rate among PAH is expected between the gas-phase and the liquid-phase systems since the difference between the two systems in this study is not originated from the factors dependent on the kind of the reactant but from the activity of the reactant; i.e. the effective concentration of the reactant in CCl$_4$ should be the same for all PAH employed.

We adopted the latest rate constant for OH reaction of PH (k_{PH-OH}/cm^3 molecule^{-1} s^{-1}) of 1.3×10^{-11}.[4] However, anoth-

Figure 1. Plot of the rate constant ratio k_{PAH-OH}/k_{NA-OH} against k_1/k_2 obtained in this study. Open circle indicates the data point for phenanthrene calculated using k_{PH-OH} value reported by Biermann et al.[5] This point is excluded from the calculation of the fitting.

er reported k_{PH-OH} of 3.4×10^{-11} is larger.[5] Although this disagreement has not been discussed, the latter k_{PH-OH} gave better agreement with the regression (open circle in Figure 1). The important finding in terms of atmospheric chemistry of PAH is that the linear relationship between $\log(k_{PAH-OH}/k_{NA-OH})$ and $\log(k_1/k_2)$ makes determination of the rate constant for OH reactions of PAH possible by using k_1/k_2 and the slope of the regression line. The obtained rate constant (cm^3 molecule^{-1} s^{-1}) for FL of $(2.8 \pm 0.2) \times 10^{-11}$ was between reported values (1.1–5.0×10^{-11}).[6,14] That for PY of $(4.8 \pm 0.5) \times 10^{-11}$ agreed with previously reported one (5.0×10^{-11}).[6]

This study demonstrates that the relative rate method in nonpolar liquid-phase system is effective to determine the rate constants for the atmospheric radical reactions of PAH, which have low-vapor pressure. Recently, nitro derivatives of very low-volatile PAH such as triphenylene[15] have been reported as important atmospheric mutagen. A source of such NPAH should be the atmospheric nitration initiated by the radicals. Hence, to determine the rate constants for the reactions of low-volatile PAH is crucial to elucidate the contribution of atmospheric reactions to the mutagenicity of the air. The method proposed in this study is a promising way to determine the rate constants regardless the vapor pressure of the reactant.

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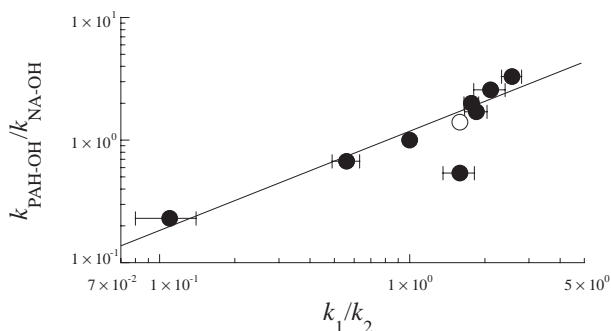15 S. Ishii, Y. Hisamatsu, K. Inazu, and K. Aika, *Chemosphere*, **44**, 681 (2001).