

Estimation of rate constants for gas-phase reactions of  
chrysene, benz[*a*]anthracene, and benzanthrone with OH  
and NO<sub>3</sub> radicals via a relative rate method in CCl<sub>4</sub>  
liquid phase-system

*Takayuki Kameda*<sup>1\*</sup>, *Kohei Asano*<sup>2</sup>, *Hiroshi Bandow*<sup>2</sup> and *Kazuichi Hayakawa*<sup>3</sup>

<sup>1</sup> Graduate School of Energy Science, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501,  
Japan

<sup>2</sup> Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1  
Gakuen-cho, Naka-ku, Sakai 599-8531, Japan

<sup>3</sup> Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi,  
Kanazawa 920-1192, Japan

\* Corresponding author: tkameda@energy.kyoto-u.ac.jp (T. Kameda)

## Abstract

CCl<sub>4</sub> liquid-phase reaction kinetics of polycyclic aromatic compounds (PACs), including chrysene (CHRY), benz[*a*]anthracene (BaA), and benzanthrone (BA), with NO<sub>3</sub> radicals were investigated at 273 K using a relative rate method with naphthalene (NA) as the reference compound. The obtained relative reaction rates of CHRY, BaA, and BA to NA were  $1.76 \pm 0.08$ ,  $2.27 \pm 0.20$ ,  $0.75 \pm 0.01$ , respectively. CHRY, BaA, and BA are semi-volatile PACs with four aromatic rings. They are chemically modified into mutagenic nitropolycyclic aromatic compounds via gas-phase OH or NO<sub>3</sub> radical-initiated reactions. Based on the PACs relative reactivity in the CCl<sub>4</sub> liquid phase-system, the rate constants at 298 K for the gas-phase reaction of CHRY, BaA, and BA with OH radicals and those of CHRY, BaA, and BA with NO<sub>3</sub> radicals were estimated to be (in cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>): CHRY,  $(4.4 \pm 0.3) \times 10^{-11}$  and  $(9.2 \pm 3.2) \times 10^{-28}$  [NO<sub>2</sub>]; BaA,  $(5.3 \pm 0.5) \times 10^{-11}$  and  $(1.3 \pm 0.5) \times 10^{-27}$  [NO<sub>2</sub>]; BA,  $(2.3 \pm 0.1) \times 10^{-11}$  and  $(3.1 \pm 1.1) \times 10^{-28}$  [NO<sub>2</sub>].

**Keywords:** PAH, nitro-PAH, radical-initiated reactions, atmospheric nitration

## 15 **Introduction**

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) are a class of polycyclic aromatic compounds (PACs), most of which exhibit direct-acting mutagenicity or carcinogenicity<sup>1</sup>. They are detected in filtered samples of ambient air<sup>2</sup> or combustion emissions<sup>3</sup>, including diesel exhaust particles<sup>4</sup> and airborne particles<sup>5</sup>. For example, atmospheric 1-nitropyrene (1-NP) is produced during combustion<sup>2, 5</sup>, whereas, 2-nitrofluoranthene (2-NF) is found in higher concentrations in airborne particles<sup>2, 6</sup>, and it is considered a product of atmospheric gas-phase reactions of parent fluoranthene (FLRA) with nitrogen oxides initiated by hydroxyl (OH) radicals or nitrate (NO<sub>3</sub>) radicals<sup>7-9</sup>. Benzanthrone (BA) is a less volatile PAC than FLRA, sublimation pressures at 298 K (*P*<sub>s</sub>(298K)) for BA and FLRA are  $2 \times 10^{-5}$  Pa and  $1.23 \times 10^{-3}$  Pa, respectively<sup>10, 11</sup>. Nevertheless, BA also reacts with OH and NO<sub>3</sub> radicals in the gas phase, resulting in 2-nitrobenzanthrone (2-NBA)<sup>12</sup>. Vapor pressures of chrysene (CHRY) and benz[*a*]anthracene (BaA) are comparable to the vapor pressure of BA, i.e., *P*<sub>s</sub>(298 K) are  $1.2 \times 10^{-6}$  Pa for CHRY and  $2.7 \times 10^{-5}$  Pa for BaA<sup>10</sup>. Thus, CHRY and BaA may also react with OH and NO<sub>3</sub> radicals in the gas phase, resulting in toxic nitro-PAHs. The rate constants for the reactions of BA, CHRY, and BaA with OH or NO<sub>3</sub> radicals, although poorly understood, are important factors, because they may control their nitro-derivatives' concentrations in the atmosphere.

OH and NO<sub>3</sub> radical-initiated reactions of polycyclic aromatic hydrocarbons (PAHs) were studied extensively<sup>13-18</sup>. However, the rate constants for the gas-phase reactions of semi- and low-volatile PACs (those with four or more aromatic rings) cannot be accurately determined using conventional methods such as large-chamber experiments<sup>8</sup> and fast-flow discharge methods<sup>19</sup>, because they are mainly deposited on the walls of the reaction system due to their low vapor pressures. We established a method for determining the rate constants of the gas-phase reactions of low-volatile organics with OH radicals using a relative-rate technique in CCl<sub>4</sub> liquid phase-system<sup>20, 21</sup>. In particular, we obtained several PACs' relative reactivity indices, by reacting them with NO<sub>3</sub> radicals in a CCl<sub>4</sub> liquid phase-system. These indices can be used to predict the reaction rate constants of low-volatile PACs with OH or NO<sub>3</sub> radicals in the gas phase.

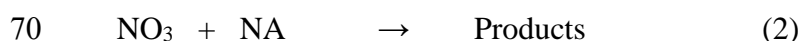
In the present study, we estimate the rate constants of the gas-phase reactions of CHRY, BaA, and BA with OH and NO<sub>3</sub> radicals based on their reactivity with other PACs in the CCl<sub>4</sub> liquid phase-system.

## 45 **Material and methods**

### *Relative-rate method in the N<sub>2</sub>O<sub>5</sub>–NO<sub>3</sub>–NO<sub>2</sub>–CCl<sub>4</sub> liquid phase-system*

The gas-phase reactions' rate constants of CHRY, BaA, and BA with OH and NO<sub>3</sub> radicals were predicted using the relative-rate method in a N<sub>2</sub>O<sub>5</sub>–NO<sub>3</sub>–NO<sub>2</sub>–CCl<sub>4</sub> liquid phase-system<sup>20,21</sup>. Detailed descriptions of this method were provided in the previous reports<sup>20,21</sup>. As the source of NO<sub>3</sub> radicals,  
50 we used N<sub>2</sub>O<sub>5</sub> synthesized by a two-step dehydration of a concentrated HNO<sub>3</sub> aqueous solution with P<sub>2</sub>O<sub>5</sub><sup>22</sup>. The prepared N<sub>2</sub>O<sub>5</sub> was dissolved in CCl<sub>4</sub>. The N<sub>2</sub>O<sub>5</sub>–CCl<sub>4</sub> solution was added to a CCl<sub>4</sub> solution of each PAC with stirring. Naphthalene (NA) was used as the reference substrate, because the rate constants of its reactions with OH and NO<sub>3</sub> radicals are well established. The N<sub>2</sub>O<sub>5</sub> initial concentration was up to 32 mmol L<sup>-1</sup>, and the PACs initial concentrations were: 0.5 μmol L<sup>-1</sup> for FLRA,  
55 fluorene (FLRE), 2-methylnaphthalene (2-MNA), NA, phenanthrene (PHE), pyrene (PY), CHRY, BaA, and triphenylene (TP); 1 μmol L<sup>-1</sup> for BA, acenaphthene (ACE), 1-methylnaphthalene (1-MNA), and 2,3-dimethylnaphthalene (2,3-DMNA); 5 μmol L<sup>-1</sup> for 1-nitronaphthalene (1-NNA). During the reaction, an aliquot of the reaction solution (normally 1 mL) was sampled at 30-sec intervals, and added to 200 μL acetaldehyde to terminate the radical reaction. The remaining PAC was determined through  
60 high-performance liquid chromatograph (HPLC) with either a spectrofluorometric or a UV–vis spectrophotometric detector. The rate constant ratio of each PAC to NA was determined in the N<sub>2</sub>O<sub>5</sub>–NO<sub>3</sub>–NO<sub>2</sub>–CCl<sub>4</sub> system using a relative-rate method at 273 ± 1 K. CCl<sub>4</sub> was employed as an aprotic non-polar solvent enabling N<sub>2</sub>O<sub>5</sub> to exist as a covalent molecular species to generate NO<sub>3</sub> following equilibrium between molecular N<sub>2</sub>O<sub>5</sub>, NO<sub>3</sub>, and NO<sub>2</sub> (N<sub>2</sub>O<sub>5</sub> ⇌ NO<sub>3</sub> + NO<sub>2</sub>). Assuming that the reaction  
65 with NO<sub>3</sub> radicals is the only loss process of the PACs, the natural logarithmic plots of each PAC's concentration against NA at specific reaction times (usually within 150 sec) relative to its initial

concentration provide the rate constant ratio between each PAC and NA, according to the following equations:



$$\ln([\text{PAC}]_0/[\text{PAC}]_t) = k_1/k_2 \ln([\text{NA}]_0/[\text{NA}]_t) \quad (3)$$

where  $[\text{PAC}]_0$  and  $[\text{NA}]_0$  are the initial concentrations, and  $[\text{PAC}]_t$  and  $[\text{NA}]_t$  are the concentrations at reaction time  $t$ . The  $k_1$  and  $k_2$  are the rate constants for reactions 1 and 2, respectively.

75 *PACs chemical analysis in the system*

The  $\text{CCl}_4$  solutions containing each PAC were diluted with methanol at appropriate concentrations. An aliquot of each sample solution was analyzed using a Hitachi L-6200 HPLC-system equipped with either a Hitachi F-1050 spectrofluorometric detector or a Hitach L-4200 UV-vis spectrophotometric detector using an Inertsil ODS-3 column (GL science, 3.0 mm i.d.  $\times$  250 mm). The  
80 mobile phase of the analysis system was methanol/water (4/1, v/v).

*Chemicals*

Authentic standards of PACs were obtained from Sigma-Aldrich Co. or Wako Pure Chemical Ind. Ltd. All solvents and other chemicals used were HPLC or analytical grades from Wako Pure  
85 Chemical Ind., Ltd.

**Results and Discussion**

Applying linear regression to the plot of  $\ln([\text{PAC}]_0/[\text{PAC}]_t)$  vs.  $\ln([\text{NA}]_0/[\text{NA}]_t)$ , the slope of the regression line is equivalent to the rate constant ratio  $k_1/k_2$ . The relative rate plots from the experiments  
90 in accordance with Eq (3) are presented in Figs. 1a–1c. Good linear plots with no intercept are obtained, validating the relative rate method as an effective tool to obtain the rate constants ratio for the studied reactions. The  $k_1/k_2$  values for CHRY, BaA, and BA obtained by the least-square analysis and the rate constant ratios for the gas phase OH or  $\text{NO}_3$  radical-initiated reactions of PAC to those of NA ( $k_{\text{PAC-}}$

OH/ $k_{\text{NA-OH}}$  and  $k_{\text{PAC-NO}_3}/k_{\text{NA-NO}_3}$ ) are given in Table 1. These values were obtained by using previously  
95 reported rate constants<sup>13, 14, 17, 18, 23–25</sup>. For the gas-phase NO<sub>3</sub>-reaction, the rate constant of the NO<sub>2</sub>-  
dependent reaction was used as  $k_{\text{PAC-NO}_3}$  (see footnote of Table 1).

The  $k_1/k_2$  ratio correlates well with  $k_{\text{PAC-NO}_3}/k_{\text{NA-NO}_3}$  [i.e.,  $\log(k_{\text{PAC-NO}_3}/k_{\text{NA-NO}_3}) = 1.27*\log(k_1/k_2) + 0.09$ , correlation coefficient  $r = 0.95$ , significance level  $p < 0.001$ ] and  $k_{\text{PAC-OH}}/k_{\text{NA-OH}}$  [i.e.,  $\log(k_{\text{PAC-OH}}/k_{\text{NA-OH}}) = 0.78*\log(k_1/k_2) + 0.07$ ,  $r = 0.97$ ,  $p < 0.001$ ]<sup>21</sup>. Based on these relationships and the rate  
100 constant ratio  $k_1/k_2$  for CHR, BaA, and BA (1.76, 2.27, and 0.75, respectively), the ratios of the rate  
constant for the gas phase NO<sub>3</sub> or OH radical-initiated reactions of these PACs to those of NA ( $k_{\text{PAC-NO}_3}/k_{\text{NA-NO}_3}$  and  $k_{\text{PAC-OH}}/k_{\text{NA-OH}}$ , respectively) can be predicted. Based on the obtained rate constant  
ratios  $k_{\text{PAC-NO}_3}/k_{\text{NA-NO}_3}$  and  $k_{\text{PAC-OH}}/k_{\text{NA-OH}}$  and the known rate constants for the gas phase NO<sub>3</sub> or OH  
radical-initiated reactions of NA { $k_{\text{NA-NO}_3} = (3.66 \pm 1.26) \times 10^{-28}[\text{NO}_2] \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ,  $k_{\text{NA-OH}} =$   
105  $(2.39 \pm 0.10) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ }<sup>18, 26</sup>, the rate constants at room temperature for the gas-phase  
reaction of CHRY, BaA, and BA with OH radicals and those of CHRY, BaA, and BA with NO<sub>3</sub> radicals  
are (in  $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ): CHRY,  $(4.4 \pm 0.3) \times 10^{-11}$  and  $(9.2 \pm 3.2) \times 10^{-28} [\text{NO}_2]$ ; BaA,  $(5.3 \pm 0.5) \times$   
 $10^{-11}$  and  $(1.3 \pm 0.5) \times 10^{-27} [\text{NO}_2]$ ; BA,  $(2.3 \pm 0.1) \times 10^{-11}$  and  $(3.1 \pm 1.1) \times 10^{-28} [\text{NO}_2]$ . The  
indicated errors were based on the standard deviations of the  $k_1/k_2$  ratios from three replicate  
110 measurements and the uncertainty of the rate constants of the reference compound. The obtained rate  
constants of the gas-phase OH reaction using this system for CHRY and BaA agreed closely with  
previously estimated values,  $3.4 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$  and  $5.3 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ,  
respectively, using an empirical relationship between  $k_{\text{PAC-OH}}$  and the Hückel hardness factors<sup>26</sup>.

The tropospheric lifetimes of CHRY, BaA, and BA with respect to the gas-phase reaction with  
115 OH and NO<sub>3</sub> radicals (Table 2) are calculated by combining the corresponding reaction rate constants  
with the ambient atmospheric concentrations (in molecule  $\text{cm}^{-3}$ ) of OH and NO<sub>3</sub> radicals applying a 12-h  
average daytime concentration of  $1.9 \times 10^6$ <sup>27</sup> and  $5 \times 10^8$ <sup>23</sup>, respectively. Indeed, the OH radical  
reaction during daytime is the dominant CHRY, BaA, and BA loss process. Thus, considerable  
atmospheric formation of CHRY, BaA, and BA nitro-derivatives is anticipated from their reaction with

120 OH radicals. The NO<sub>3</sub> radical reaction is less important by 2–3 orders of magnitude than the OH radical  
125 reaction in the atmospheric removal of CHRY, BaA, and BA.

### **Acknowledgments**

This work was supported in part by the Environment Research and Technology Development  
125 Fund (5-1306) of the Ministry of the Environment, Japan and the cooperative research program of  
Institute of Nature and Environmental Technology, Kanazawa University.

## References

1. Durant, J. L., W. F. Busby, A. L. Lafleur, B. W. Penman, and C. L. Crespi. "Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols." *Mutat. Res.* 371 (1996): 123-157.
2. Bamford, H.A., and J.E. Baker. "Nitro-polycyclic aromatic hydrocarbons and sources in urban and suburban atmospheres of the Mid-Atlantic region." *Atmos. Environ.* 37 (2003): 2077-91.
3. Schuetzle, D., T. J. Riley, T. J. Prater, T. M. Harvey, and D. F. Hunt. "Analysis of nitrated polycyclic aromatic hydrocarbons in diesel particulates." *Anal. Chem.* 54 (1982): 265-271.
4. Schuetzle, D. "Sampling of vehicle emissions for chemical analysis and biological testing." *Environ. Health Perspect.* 47 (1983): 65-80.
5. Feilberg, A., M. W. B. Poulsen, T. Nielsen, and H. Skov. "Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark." *Atmos. Environ.* 35 (2001): 353-366.
6. Kameda, T., K. Inazu, Y. Hisamatsu, N. Takenaka, and H. Bandow. "Determination of atmospheric nitro-polycyclic aromatic hydrocarbons and their precursors at a heavy traffic roadside and at a residential area in Osaka, Japan." *Polycyclic Aromat. Compd.* 24 (2004): 657-666.
7. Arey, J., B. Zielinska, R. Atkinson, A. M. Winer, T. Ramdahl, and J. N. Pitts. "The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO<sub>x</sub>." *Atmos. Environ.* 20 (1986): 2339-45.
8. Atkinson, R., J. Arey, B. Zielinska, and S. M. Aschmann. "Kinetics and nitro-products of the gas-phase OH and NO<sub>3</sub> radical-initiated reactions of naphthalene-d<sub>8</sub>, Fluoranthene-d<sub>10</sub>, and pyrene." *Int. J. Chem. Kinet.* 22 (1990): 999-1014.
9. Atkinson, R., and J. Arey. "Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of atmospheric mutagens." *Environ. Health Perspect.* 102 (1994): 117-126.
10. Allen, J. O., N. M. Dookeran, K. Taghizadeh, A. L. Lafleur, K. A. Smith, and A. F. Sarofim. "Measurement of Oxygenated Polycyclic Aromatic Hydrocarbons Associated with a Size-Segregated Urban Aerosol." *Environ. Sci. Technol.* 31 (1997): 2064-70.

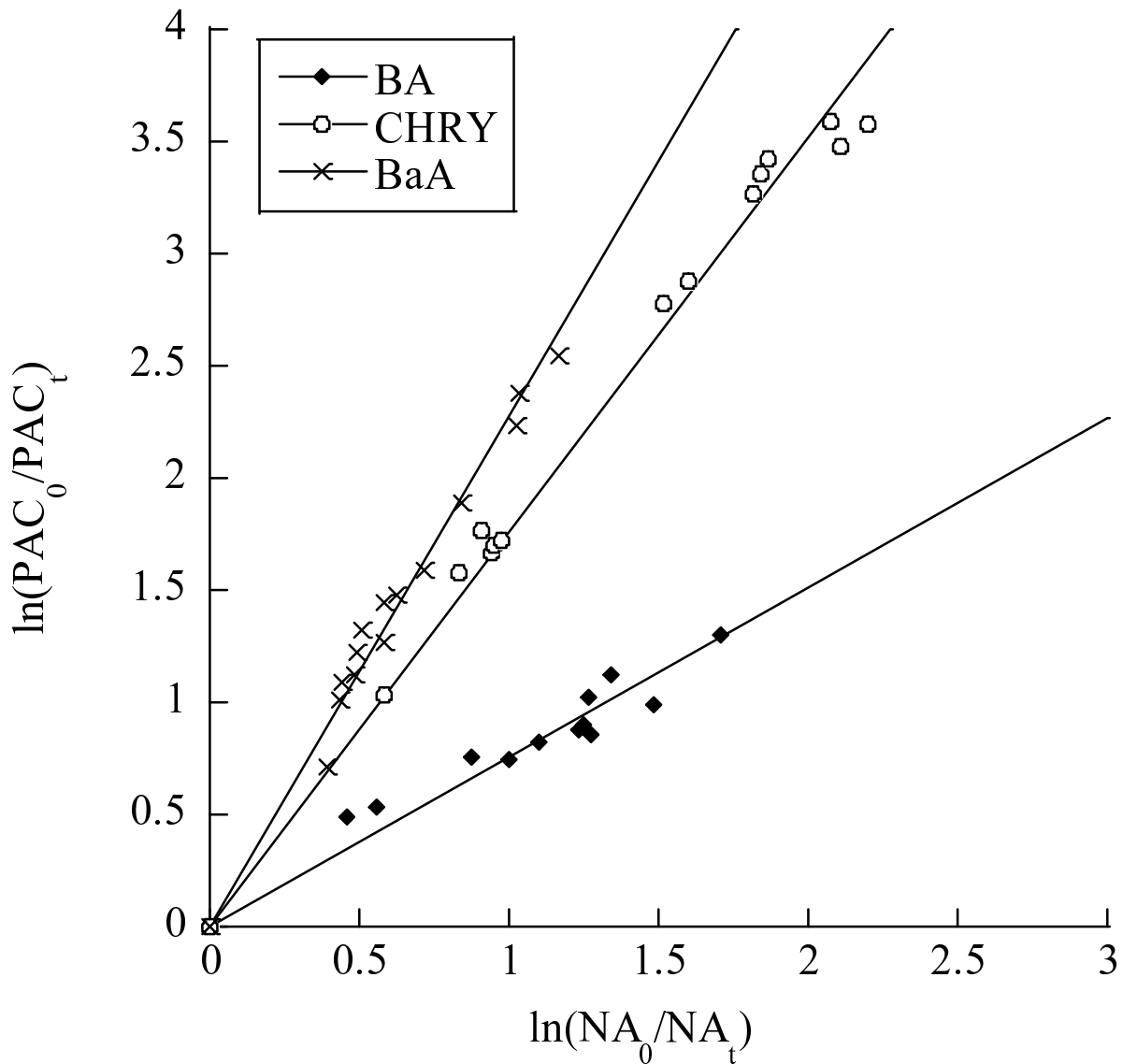


11. Sonnefeld, W. J., W. H. Zoller, and W. E. May. "Dynamic coupled-column liquid-chromatographic determination of ambient-temperature vapor pressures of polynuclear aromatic hydrocarbons." *Anal. Chem.* 55 (1983): 275-280.
12. Phouongphouang, P. T., and J. Arey. "Sources of the atmospheric contaminants, 2-nitrobenzanthrone and 3-nitrobenzanthrone." *Atmos. Environ.* 37 (2003): 3189-99.
13. Atkinson, R. "Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. J. Phys." *Chem. Ref. Data, Monogr.* 1 (1989): 1-246.
14. Kwok, E. S., R. Atkinson, and J. Arey. "Kinetics of the gas - phase reactions of indan, indene, fluorene, and 9,10-dihydroanthracene with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub>." *Int. J. Chem. Kinet.* 29 (1997): 299-309.
15. Sasaki, J., S. M. Aschmann, E. S. Kwok, R. Atkinson, and J. Arey. "Products of the Gas-Phase OH and NO<sub>3</sub> Radical-Initiated Reactions of Naphthalene." *Environ. Sci. Technol.* 31 (1997): 3173-79.
16. Brubaker, W. W., and R. A. Hites. "OH Reaction Kinetics of Polycyclic Aromatic Hydrocarbons and Polychlorinated Dibenzo- p -dioxins and Dibenzofurans." *J. Phys. Chem. A* 102 (1998): 915-921.
17. Reisen, F., and J. Arey. "Reactions of Hydroxyl Radicals and Ozone with Acenaphthene and Acenaphthylene." *Environ. Sci. Technol.* 36 (2002): 4302-11.
18. Phouongphouang, P. T., and J. Arey. "Rate Constants for the Gas-Phase Reactions of a Series of Alkyl-naphthalenes with the OH Radical." *Environ. Sci. Technol.* 36 (2002): 1947-52.
19. Finlayson-Pitts, B. J., M. J. Ezell, and C. E. Grant. "Temperature dependence of the hydroxyl + nitrosyl chloride (ClNO) reaction: evidence for two competing reaction channels." *J. Phys. Chem.* 90 (1986): 17-19.
20. Kameda, T., K. Asano, K. Inazu, Y. Hisamatsu, N. Takenaka, and H. Bandow. "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<sub>4</sub> Liquid Phase-system." *Chem. Lett* 34 (2005): 758-759.

21. Kameda, T., K. Inazu, K. Asano, M. Murota, N. Takenaka, Y. Sadanaga, Y. Hisamatsu, and H. Bandow. "Prediction of rate constants for the gas phase reactions of triphenylene with OH and NO<sub>3</sub> radicals using a relative rate method in CCl<sub>4</sub> liquid phase-system." *Chemosphere* 90 (2013): 766-771.
22. Bandow, H., M. Okuda, and H. Akimoto. "Mechanism of the gas-phase reactions of C<sub>3</sub>H<sub>6</sub> and NO<sub>3</sub> radicals." *J. Phys. Chem.* 84 (1980): 3604-08.
23. Atkinson, R. "Kinetics and Mechanisms of the Gas-Phase Reactions of the NO<sub>3</sub> Radical with Organic Compounds." *J. Phys. Chem. Ref. Data* 20 (1991): 459-507.
24. Lee, W., P. S. Stevens, and R. A. Hites. "Rate Constants for the Gas-Phase Reactions of Methylphenanthrenes with OH as a Function of Temperature." *J. Phys. Chem. A* 107 (2003): 6603-08.
25. Phouongphouang, P. T., and J. Arey. "Rate Constants for the Gas-Phase Reactions of a Series of Alkyl-naphthalenes with the Nitrate Radical." *Environ. Sci. Technol.* 37 (2003): 308-313.
26. Calvert, J.G., R. Atkinson, K.H. Becker, R.M. Kamens, J.H. Seinfeld, T.J. Wallington, and G. Yarwood, 2002. *The mechanisms of atmospheric oxidation of the aromatic hydrocarbons*. (New York: Oxford University Press, 2002).
27. Prinn, R. G., R. F. Weiss, B. R. Miller, J. Huang, F. N. Alyea, D. M. Cunnold, P. J. Fraser, D. E. Hartley, and P. G. Simmonds. "Atmospheric Trends and Lifetime of CH<sub>3</sub>CCl<sub>3</sub> and Global OH Concentrations." *Science* 269 (1995): 187-192.
28. Keyte, I. J., R. M. Harrison, and G. Lammel. "Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons – a review." *Chem. Soc. Rev.* 42 (2013): 9333-91.

## Figure Captions

**Figure 1.** Plots of Eq (3) for the reaction of  $\text{NO}_3$  radicals with CHRY, BaA, and BA in the  $\text{CCl}_4$  liquid-phase system.



**Table 1:** Rate constant ratios  $k_1/k_2$  obtained in this study.  $k_{\text{PAC-OH}}$  and  $k_{\text{PAC-NO}_3}$  are rate constants for the gas phase reactions of corresponding PACs with OH radicals and  $\text{NO}_3$  radicals, respectively.

Compound	$k_1/k_2$	$10^{11}k_{\text{PAC-OH}}^{\text{a}}$	$10^{28}[\text{NO}_2]^{-1}k_{\text{PAC-NO}_3}^{\text{b}}$
Chrysene (CHRY)	$1.76 \pm 0.08$	$4.4 \pm 0.3$	$9.2 \pm 3.2$
Benz[ <i>a</i> ]anthracene (BaA)	$2.27 \pm 0.20$	$5.3 \pm 0.5$	$12.6 \pm 4.5$
Benzo[ <i>a</i> ]anthrone (BA)	$0.75 \pm 0.01$	$2.3 \pm 0.1$	$3.1 \pm 1.1$

<sup>a</sup> Given in unit of  $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ .

<sup>b</sup>  $[\text{NO}_2]$  and  $k_{\text{PAC-NO}_3}$  are given in unit of  $\text{molecules cm}^{-3}$  and  $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , respectively.

**Table 2:** Calculated lifetimes of the compounds studied with respect to gas-phase reaction with OH and NO<sub>3</sub> radicals.

	Lifetime Due to Reaction with	
	OH (h) <sup>a</sup>	NO <sub>3</sub> (day) <sup>b, c</sup>
Chrysene (CHRY)	3.3	36
Benz[ <i>a</i> ]anthracene (BaA)	2.8	27
Benanthrone (BA)	6.4	108

<sup>a</sup> For a 12-h average daytime OH radical concentration of  $1.9 \times 10^6$  molecule cm<sup>-3</sup> <sup>27</sup>.

<sup>b</sup> For a 12-h average NO<sub>3</sub> radical concentration of  $5 \times 10^8$  molecule cm<sup>-3</sup> <sup>23</sup>.

<sup>c</sup> For a 24-h average NO<sub>2</sub> concentration of  $6.91 \times 10^{11}$  molecule cm<sup>-3</sup> <sup>28</sup>.