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Estimation of rate constants for gas-phase reactions of chrysene, benz[*a*]anthracene, and benzanthrone with OH and NO₃ radicals via a relative rate method in CCl₄ liquid phase-system

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Abstract

CCl₄ liquid-phase reaction kinetics of polycyclic aromatic compounds (PACs), including chrysene (CHRY), benz[*a*]anthracene (BaA), and benzanthrone (BA), with NO₃ 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 ± 0.08 , 2.27 ± 0.20 , 0.75 ± 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 NO₃ radical-initiated reactions. Based on the PACs relative reactivity in the CCl₄ 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 NO₃ radicals were estimated to be (in cm³molecule⁻¹s⁻¹): CHRY, $(4.4 \pm 0.3) \times 10^{-11}$ and $(9.2 \pm 3.2) \times 10^{-28}$ [NO₂]; BaA, $(5.3 \pm 0.5) \times 10^{-11}$ and $(1.3 \pm 0.5) \times 10^{-27}$ [NO₂]; BA, $(2.3 \pm 0.1) \times 10^{-11}$ and $(3.1 \pm 1.1) \times 10^{-28}$ [NO₂].

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 carcinogenicity¹. They are detected in filtered samples of ambient air² or combustion emissions³, including diesel exhaust particles⁴ and airborne particles⁵. For example, atmospheric 1-nitropyrene (1-NP) is produced during
20 combustion^{2, 5}, whereas, 2-nitrofluoranthene (2-NF) is found in higher concentrations in airborne particles^{2, 6}, 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 (NO₃) radicals⁷⁻⁹. Benzanthrone (BA) is a less volatile PAC than FLRA, sublimation pressures at 298 K (*Ps*(298K)) for BA and FLRA are 2×10^{-5} Pa and 1.23×10^{-3} Pa, respectively^{10, 11}. Nevertheless, BA also reacts with
25 OH and NO₃ radicals in the gas phase, resulting in 2-nitrobenzanthrone (2-NBA)¹². Vapor pressures of chrysene (CHRY) and benz[*a*]anthracene (BaA) are comparable to the vapor pressure of BA, i.e., *Ps*(298 K) are 1.2×10^{-6} Pa for CHRY and 2.7×10^{-5} Pa for BaA¹⁰. Thus, CHRY and BaA may also react with OH and NO₃ radicals in the gas phase, resulting in toxic nitro-PAHs. The rate constants for the reactions of BA, CHRY, and BaA with OH or NO₃ radicals, although poorly understood, are
30 important factors, because they may control their nitro-derivatives' concentrations in the atmosphere.

OH and NO₃ radical-initiated reactions of polycyclic aromatic hydrocarbons (PAHs) were studied extensively¹³⁻¹⁸. 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 experiments⁸ and fast-flow discharge methods¹⁹, because
35 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 CCl₄ liquid phase-system^{20, 21}. In particular, we obtained several PACs' relative reactivity indices, by reacting them with NO₃ radicals in a CCl₄ liquid phase-system. These indices can be used to predict the reaction rate constants of low-volatile
40 PACs with OH or NO₃ 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 NO₃ radicals based on their reactivity with other PACs in the CCl₄ liquid phase-system.

45 Material and methods

Relative-rate method in the N₂O₅–NO₃–NO₂–CCl₄ liquid phase-system

The gas-phase reactions' rate constants of CHRY, BaA, and BA with OH and NO₃ radicals were predicted using the relative-rate method in a N₂O₅–NO₃–NO₂–CCl₄ liquid phase-system^{20, 21}. Detailed descriptions of this method were provided in the previous reports^{20, 21}. As the source of NO₃ radicals, we used N₂O₅ synthesized by a two-step dehydration of a concentrated HNO₃ aqueous solution with P₂O₅²². The prepared N₂O₅ was dissolved in CCl₄. The N₂O₅–CCl₄ solution was added to a CCl₄ solution of each PAC with stirring. Naphthalene (NA) was used as the reference substrate, because the rate constants of its reactions with OH and NO₃ radicals are well established. The N₂O₅ initial concentration was up to 32 mmol L^{–1}, and the PACs initial concentrations were: 0.5 μmol L^{–1} for FLRA, fluorene (FLRE), 2-methylnaphthalene (2-MNA), NA, phenanthrene (PHE), pyrene (PY), CHRY, BaA, and triphenylene (TP); 1 μmol L^{–1} for BA, acenaphthene (ACE), 1-methylnaphthalene (1-MNA), and 2,3-dimethylnaphthalene (2,3-DMNA); 5 μmol L^{–1} 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 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 N₂O₅–NO₃–NO₂–CCl₄ system using a relative-rate method at 273 ± 1 K. CCl₄ was employed as an aprotic non-polar solvent enabling N₂O₅ to exist as a covalent molecular species to generate NO₃ following equilibrium between molecular N₂O₅, NO₃, and NO₂ (N₂O₅ ⇌ NO₃ + NO₂). Assuming that the reaction with NO₃ 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 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 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 reported rate constants^{13, 14, 17, 18, 23–25}. For the gas-phase NO_3 -reaction, the rate constant of the NO_2 -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., $\log(k_{\text{PAC-NO}_3}/k_{\text{NA-NO}_3}) = 1.27 \cdot \log(k_1/k_2) + 0.09$, correlation coefficient $r = 0.95$, significance level $p < 0.001$] and $k_{\text{PAC-OH}}/k_{\text{NA-OH}}$ [i.e., $\log(k_{\text{PAC-OH}}/k_{\text{NA-OH}}) = 0.78 \cdot \log(k_1/k_2) + 0.07$, $r = 0.97$, $p < 0.001$]²¹. Based on these relationships and the rate 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_3 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_3 or OH radical-initiated reactions of NA [$k_{\text{NA-NO}_3} = (3.66 \pm 1.26) \times 10^{-28} [\text{NO}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{NA-OH}} = (2.39 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]^{18, 26}, 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_3 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 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 factors²⁶.

The tropospheric lifetimes of CHRY, BaA, and BA with respect to the gas-phase reaction with OH and NO_3 radicals (Table 2) are calculated by combining the corresponding reaction rate constants with the ambient atmospheric concentrations (in molecule cm^{-3}) of OH and NO_3 radicals applying a 12-h average daytime concentration of 1.9×10^6 ²⁷ and 5×10^8 ²³, 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_3 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.

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Figure Captions

Figure 1. Plots of Eq (3) for the reaction of NO_3 radicals with CHRY, BaA, and BA in the 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 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 ± 0.08	4.4 ± 0.3	9.2 ± 3.2
Benz[<i>a</i>]anthracene (BaA)	2.27 ± 0.20	5.3 ± 0.5	12.6 ± 4.5
Benzanthrone (BA)	0.75 ± 0.01	2.3 ± 0.1	3.1 ± 1.1

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

^b $[\text{NO}_2]$ and $k_{\text{PAC-NO}_3}$ are given in unit of 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 NO₃ radicals.

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

^a For a 12-h average daytime OH radical concentration of 1.9×10^6 molecule cm⁻³ ²⁷.

^b For a 12-h average NO₃ radical concentration of 5×10^8 molecule cm⁻³ ²³.

^c For a 24-h average NO₂ concentration of 6.91×10^{11} molecule cm⁻³ ²⁸.