KINETIC STUDY OF THE HETEROGENEOUS REACTIONS BETWEEN ADSORBED ANTHRACENE AND OZONE ON ATMOSPHERIC MODEL PARTICLES

Ma J Z, Liu Y C, He H[*]

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Abstract

As ubiquitous persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs) have attracted much attention due to their allergenic, mutagenic, and carcinogenic properties. Thus, it is very necessary to investigate the fate and lifetimes of PAHs in the atmosphere. In this study, the heterogeneous reactions of ozone with anthracene adsorbed on different mineral oxides (SiO_2, α-Al_2O_3 and α-Fe_2O_3) and on Teflon disc were investigated in dark at 293 K. Ozone concentration was kept at constant value (1.18×10^{14} molecules cm^{-3}) during the reaction. Analyses of PAHs samples were performed by a GC-MS. The pseudo-first order rate constants were obtained from the fit of the exponential decay of adsorbed PAH concentrations versus reaction time. The second order rate constants were calculated to be $(1.47 \pm 0.23) \times 10^{-16}$, $(0.99 \pm 0.36) \times 10^{-16}$ and $(0.73 \pm 0.26) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} on SiO_2, α-Al_2O_3 and α-Fe_2O_3, respectively, while the highest second order rate constant between anthracene and O_3 on Teflon disc was estimated to be 4.83×10^{-19} cm^3 molecule^{-1} s^{-1}. The nature of the substrate determined the lifetimes of anthracene in the atmosphere. These results suggest that the reaction of anthracene with O_3 on mineral oxides was much faster than that in gaseous phase, and that mineral oxides can greatly alter the fate of PAHs. They also imply that the role of mineral oxides in the fate of halogenated persistent organic pollutants may be similar to that of PAHs in the atmosphere.

Introduction

Persistent Organic Pollutants (POPs) are chemical substances that persist in the environment, bioaccumulate through the food chains, and pose a risk of causing adverse effects to human health and the environment. POPs are transported across international boundaries far from their sources, even to regions where they have never been used or produced. As ubiquitous POPs, polycyclic aromatic hydrocarbons (PAHs) have attracted much attention due to their allergenic, mutagenic, and carcinogenic properties[1]. PAHs mainly originate from incomplete combustion of fossil fuels (petroleum, natural gas and coal) and biomass burning. The global emission of atmospheric PAHs was roughly estimated to be 0.001-0.02TgC·yr^{-1} and about 90% of PAHs emissions are anthropogenic[2]. Thus it is very necessary to understand the fate and lifetimes of PAHs in the atmosphere.

Once emitted into the atmosphere, PAHs may undergo photodegradation or chemical oxidation by O_3, OH or

---

[*] Corresponding author. Tel: +86-10-62849123; *E-mail address*: honghe@rcees.ac.cn

38 NOx to form degradation products, such as nitro-PAHs, oxy-PAHs, etc., whose carcinogenicity and mutagenicity

39 have been shown to be elevated[3]. Recent laboratory and modeling studies suggest that heterogeneous reactions

40 may be more important than their corresponding gas-phase reactions[4, 5]. However, little is known about the role

41 of substrates in the heterogeneous reaction of PAHs.

42

43 Recently field measurements found that the concentration of PAHs (sum of 16 EPA list PAHs) ranges from 1.0 to

44 85.5 μg/g in the dustfall collected in Tianjin, and from 0.18 to 3.52 μg/g in the sandstorm depositions in Beijing[6,

45 7]. It means that PAHs usually coexist with mineral dust in the real atmospheric particulate matters. Mineral dust,

46 which mainly originates from arid and semi-arid regions with global source strength of about 1000-3000 Tg·yr^{-1},

47 is one of the most important contributor to the loading of atmospheric particle matters[8]. Field observation found

48 that atmospheric PAHs concentration measured using conventional samplers not equipped with an ozone trap can

49 underestimate the PAH concentration by more than 67%[9]. Therefore, it is very significant to investigate the

50 chemical behavior of PAHs on mineral dust. Unfortunately, to our knowledge, it is unknown that how the

51 mineral dust affects the heterogeneous reactions of PAHs with O_3.

52

53 **Materials and Methods**

54 The SiO_2 sample was purchased from Degussa. The α-Fe_2O_3 sample was supplied by Beijing Nanshangle

55 Chemicals Factory. The α-Al_2O_3 sample was prepared from boehmite (AlOOH, Shandong aluminum

56 Corporation) by calcining at 1473K for 3h. Nitrogen Brunauer-Emmett-Teller (BET) physisorption measurement

57 was performed using Micromeritics ASAP 2000 automatic equipment. The specific surface area of these samples

58 was 420.7, 2.74 and 12.65 m^2g^{-1}, respectively. The crystalline for these samples were identified to be amorphous,

59 hematite and corundum by a D/max-RB automatic powder X-ray diffractometer (XRD) using Cu Kα irradiation.

60

61 All solvents were chromatographic grade and used without further purification. Anthracene (99%) was

62 purchased from Acros Organics. Ultrahigh purity N_2 and O_2 were supplied by Beijing AP BEIFEN Gases Inc. O_3

63 was generated by a homemade quartz O_3 generator (UV, 185 and 254nm). The concentration of O_3 was detected

64 by an O_3 monitor (Model 202, 2B Technology).

65

66 Before adsorption of anthracene, SiO_2, α-Al_2O_3 and α-Fe_2O_3 were cleaned three times by ultrasonication in

67 dichloromethane and followed by drying at room temperature. Anthracene was coated on particles by adsorption

68 in the liquid phase. 1.0 g of the cleaned particles was added into 20.0 ml of n-hexane containing 500 μg of

69 anthracene. After homogenization of the mixture, the solvent was slowly evaporated using a rotary evaporator at

70 303K. Finally, the PAHs-coated particles were dried at room temperature for 4 hours. Because the cross section

71 of anthracene molecule was 1 nm^2, the surface coverage of anthracene on these samples was all below

72 monolayer[10]. In order to avoid the photodegradation of adsorbed PAHs, all of the particles in amber glass flasks

73 were stored at 255 K in dark.

74

75 20.0 mg of coated particles were evenly deposited on a Teflon disc (3.39 cm^2), which then were placed in a

76 quartz reactor. In the case of reaction on Teflon disc, 10 μg of anthracene dissolved in CH_2Cl_2 was evenly

77 distributed on the Teflon disc. Before O_3 was introduced into the quartz reactor, $O_2/O_3/N_2$ with a given
78 concentration was flow through another blank reactor. When the concentration of O_3 was stable, the feed gas was
79 switched to the reactor containing adsorbed PAHs for reaction. The reacted particle samples were ultrasonically
80 extracted using 20.0 mL CH_2Cl_2. Then, the extracts were filtered using glass fiber filter which was previously
81 cleaned same as pure mineral oxides. Subsequently, CH_2Cl_2 was evaporated and changed to 1.00 mL n-hexane
82 under a gentle stream of nitrogen gas at 293K. Analyses of PAHs samples were performed by a GC-MS. The
83 column was a HP-5 MS (30m, 0.25mm i.d., 0.25μm film thickness). The concentration of PAHs in solution were
84 measured based on an external standard and the use of calibration curve.

85

86 **Results and Discussion**

87 Prior to the study of anthracene reaction with O_3, in order to clarify that no compound desorption was occurring
88 during the reaction time, blank experiments were performed in the same conditions as those used for the
89 oxidation reactions but without O_3. The results showed that the desorption of anthracene was negligible under
90 our experimental conditions.

91

92 The kinetics data on various substrates were determined by monitoring the loss of anthracene concentration as a
93 function of O_3 ($[O_3] = 1.18 \times 10^{14}$ molecules cm^{-3}) exposure time, which were displayed in Figure 1. The results
94 showed that anthracene concentration on Teflon disc after reacted with O_3 for 900s was not significantly
95 different from the initial concentration. Within our experimental precision, the average error of anthracene
96 concentration is about 5%, thus the smallest rate constant was estimated to be 5.7×10^{-5} s^{-1}. This value represents
97 an upper limit of the pseudo-first-order rate constant for the reaction between anthracene and O_3 on Teflon disc
98 and also represents the rate constant of the gas-phase reaction. However, as shown in Figure 1, degradation of
99 anthracene was very prominent on SiO_2, α-Al_2O_3 and α-Fe_2O_3, and exhibited an exponential behavior. The
100 pseudo-first-order rate constant ($k_{1,obs}$) were obtained by fitting the data (Figure 1) according to equation 1 [11]

101
$$\frac{[PAH]_t}{[PAH]_0} = \frac{[PAH]_{plateau}}{[PAH]_0} + \frac{[PAH]_0 - [PAH]_{plateau}}{[PAH]_0} \times \exp\left(-k_{1,obs} \times t\right) \tag{1}$$

102 where $[PAH]_t$ is the concentration of adsorbed PAH at a given time, $[PAH]_0$ is the initial concentration of
103 adsorbed PAH, $[PAH]_{plateau}$ is the concentration of adsorbed PAH at the plateau shown in Figure 1, and $k_{1,obs}$ is the
104 apparent rate constant of the pseudo-first-order reaction.
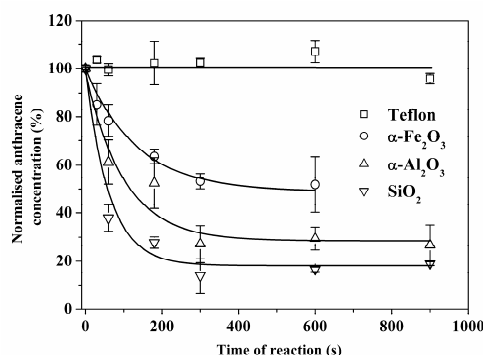
105
106 Figure 1. Representative anthracene decays observed on various substrates at 293 K ($[O_3] = 1.18 \times 10^{14}$ molecules

3

107   cm^{-3}). The data points and error bars represent the means and standard deviations (±1s.d.) of the triplicate
108   analysis performed at every time.

110   The $k_{1,obs}$ were calculated to be $(1.73\pm0.27)\times10^{-2}$, $(1.16\pm0.42)\times10^{-2}$ and $(0.86\pm0.31)\times10^{-2}$ s^{-1} on SiO$_2$, α-Al$_2$O$_3$
111   and α-Fe$_2$O$_3$, respectively. The unreacted fraction of anthracene was about 20%, 30% and 55% on SiO$_2$, α-Al$_2$O$_3$
112   and α-Fe$_2$O$_3$, respectively. Perraudin et al.[11] has studied the reactions of anthracene with O$_3$ on different types of
113   silica. Under the similar concentration of O$_3$ and the initial surface coverage of anthracene, they measured the
114   rate constants to be from 0.9×10^{-2} to 1.8×10^{-2} s^{-1}. The rate constant on silica measured by us is well agreement
115   with their results within experimental uncertainties. They also reported that the degradation of 13 studied PAHs
116   reached a plateau on graphite and silica [5]. The plateau was found to be dependent on the specific surface area of
117   particle samples, and a plateau was not observed for the samples with higher specific surface area. In our results,
118   the plateau was also related to the specific surface area of the particle sample as shown in Figure 1. However,
119   Kwamena et al.[9] observed the presence of the plateau at both high and low anthracene surface coverage, which
120   suggested that the anthracene on the surface was not being deposited as a smooth, uniform layer, but more likely
121   as clumps or islands under their conditions even in a submonolayer regime. Therefore, the plateau can be
122   ascribed to a complex gas-solid reaction that depends upon the extent of the multilayering of the PAH sample,
123   and the extent that oxidized species hinder the oxidation of the subsurface material[11]. However, Kwamena et al.[12]
124   found that the rate constants were not affected by the surface coverage in the submonolayer regime. Thus, the
125   difference of $k_{1,obs}$ on SiO$_2$, α-Al$_2$O$_3$ and α-Fe$_2$O$_3$, can be ascribed to the difference of the nature of substrate. The
126   second order rate constants were calculated by dividing pseudo-first-order rate constants by the reactant
127   concentration, and are shown in table 1.

129   Table 1. Second order rate constants and atmospheric lifetimes of anthracene

Samples	k_2 (cm^3 molecule^{-1} s^{-1})	τ [O$_3$]=25ppb	τ [O$_3$]=500ppb
SiO$_2$	$(1.47\pm0.23)\times10^{-16}$	3.07h	9.2min
α-Al$_2$O$_3$	$(0.99\pm0.36)\times10^{-16}$	4.56h	13.7min
α-Fe$_2$O$_3$	$(0.73\pm0.26)\times10^{-16}$	6.19h	18.6min
Teflon disc	$<4.83\times10^{-19}$	>935h	>2810min

135   Then, the atmospheric lifetimes (τ) of anthracene due to the reaction with O$_3$ can be calculated according to
136   equation 2[13]

137
$$\tau = \frac{1}{k_2[O_3]} \tag{2}$$

138   where k_2 is the second order rate constants and assuming that the heterogeneous reaction of anthracene with O$_3$ is
139   the only degradation process occurring in the atmosphere.

141   As shown in Table 1, the lifetimes of anthracene due to the reaction with O$_3$ on SiO$_2$, α-Al$_2$O$_3$, and α-Fe$_2$O$_3$ were
142   calculated to be 9.2 min, 13.7 min and 18.6 min in highly polluted areas ([O$_3$]= 1.23×10^{13} molecules cm^{-3}); and
143   to be 3.07 h, 4.56 h and 6.19 h in cleaned areas ([O$_3$]=6.15×10^{11} molecules cm^{-3}), respectively. However, the
144   lifetimes of anthracene due to the reaction with O$_3$ on Teflon disc were calculated to be longer than 2810 min in

4

145 highly polluted areas; and to be longer than 935 h in cleaned areas. These results suggest that the reaction of
146 anthracene with O_3 on mineral oxides was much faster than that in gaseous phase and highlights the importance
147 of the nature of the substrates for the reaction of anthracene with O_3 on mineral oxides. The reactions on mineral
148 dust may be an important sink of PAHs in highly polluted regions. Therefore, the mineral dusts should be
149 considered into accurately models for estimation the reactive fate of PAHs in the atmosphere. These results also
150 imply that the behavior of other persistent organic pollutants, such as halogenated persistent organic pollutants
151 on mineral dusts need to be investigated in future work.
152

157

158 **References**
159 1. Finlayson-Pitts B. J. and Pitts Jr J. N. *Scicence* 1997; 276: 1045.
160 2. Perraudin E., Budzinski H. and Villenave E. *Atmos. Environ.*2005; 39: 6557.
161 3. Pitts Jr J. N., Van Cauwenberghe K. A., Grosjean D., Schmidt J. P., Fritz D. R., Belser Jr W. L., Knudson G. B.
162 and Hynds P. M. *Science* 1978; 202: 515.
163 4. Kwamena N. O. A., Clarke J. P., Kahan T. F., Diamond M. L. and Donaldson D. J. *Atmos.Environ.*2007; 41:
164 37.
165 5. Kwamena N. O. A., Staikova M. G., Donaldson D. J., George I. J. and Abbatt J. P. D. *J. Phys. Chem. A* 2007;
166 111:11050.
167 6. Wu S. P., Tao S., Xu F. L., Dawson R., Lan T., Li B. G. and Cao J. *Sci. Total Environ.*2005; 345: 115.
168 7. Fu S., Li K., Xia J. X. and Xu X. B. *Bull. Environ. Contam. Toxicol.*2009; 82: 162.
169 8. Dentener F. J., Carmichael G. R., Zhang Y., Lelieveld J. and Crutzen P. J. *J. Geophys. Res.* 1996; 101: 22869.
170 9. Goriaux M., Jourdain B., Temime B., Besombes J. L., Marchand N., Albinet A., Leoz-Garziandia E. and
171 Wortham H. *Environ. Sci. Technol.* 2006; 40: 6398.
172 10. Kwamena N. O. A., Earp M. E., Young C. J. and Abbatt J. P. D. *J. Phy. Chem. A* 2006; 110: 3638.
173 11. Perraudin E., Budzinski H. and Villenave E. *J. Atmos. Chem.* 2007; 56: 57.
174 12. Kwamena N. O. A., Thornton J. A. and Abbatt J. P. D. *J. Phy. Chem. A* 2004; 108: 11626.
175 13. Pflieger M., Goriaux M., Temime-Roussel B., Gligorovski S., Monod A. and Wortham H. *Atmos. Chem.*
176 *Phys.* 2009; 9: 2215.
177
178
179

5