

Effects of Inorganic Aerosols on the Gas-Phase Reactions of the Hydroxyl Radical with Selected Aliphatic Alkanes

Sewon Oh* and Jean M. Andino¹⁾

*Division of Civil and Environmental Engineering, Sangmyung University,
Chonan-City, Chungnam, 330-720, Korea*

*¹⁾Department of Environmental Engineering Sciences, University of Florida,
P.O. Box 116540, Gainesville, Florida, 32611-6450, USA*

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Abstract

Effects of inorganic aerosols on the kinetics of the hydroxyl radical reactions with selected aliphatic alkanes have been investigated using the relative rate technique. The relative rates in the absence and presence of aerosols were determined for n-butane, n-pentane, n-hexane, n-octane, and n-decane. p-xylene was used as a reference compound. Inorganic aerosols including $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and NaCl aerosols at two different aerosol concentrations that are typical of polluted urban conditions were tested. Total surface areas of aerosols were 1400 (Condition I) and $3400 \mu\text{m}^2 \text{cm}^{-3}$ (Condition II). Significant changes in the relative rates in the presence of the inorganic aerosols were not observed for the n-butane/·OH, n-pentane/·OH, n-hexane/·OH, n-octane/·OH, and n-decane/·OH reactions versus p-xylene/·OH reaction. These results suggest that the promoting effects depend on the semiconducting property of the aerosols and the nature of the organic compounds.

Key words : OH radical reaction, Relative rates, Inorganic aerosols

1. INTRODUCTION

More than 130 alkanes have been detected in ambient air (Graedel *et al.*, 1986). Alkanes are emitted from various processes including the combustion of fossil fuels or other organic materials. Alkanes were the most abundant nonmethane organic species in the Southern California Air Quality Study (Lurmann *et al.*, 1992), thus the tropospheric chemistry of alkanes is important. Alkanes do not photolyze in the troposphere, and the reaction with O_3 is negligible. The OH radical reac-

tion is generally the dominant daytime loss process of alkanes in the troposphere. The OH radical reactions of alkanes proceed by H-atom abstraction from the C-H bonds, and the reaction sequences for alkanes are known (Atkinson, 2000). In combination with sunlight and oxides of nitrogen, these alkanes react with OH radicals to produce ozone, a major component of photochemical smog in urban areas. Therefore, the accurate rate constants for reactions with the OH radicals are necessary to assess the ozone levels for any given areas.

The reactions of many alkanes with OH radicals have been studied under simulated tropospheric conditions, and the compilations of rate constants appear

* Corresponding author.

Tel : +82-(0)41-550-5310, E-mail : sewonoh@smuc.ac.kr

in Atkinson (1989, 1994, 1997). Air quality modelers have used these chemistry data along with meteorological data, emissions data, and transport mechanisms to assess air pollution control strategies (Dodge, 2000; Seinfeld, 1998). However, these studies have not considered the effects of particulate matters on gas phase reactions. Given the abundance of particles in the troposphere, it is likely that aerosols have catalytic effects on the reaction kinetics of alkanes. However, few studies have been performed to investigate the effects of aerosols on these kinetic constants.

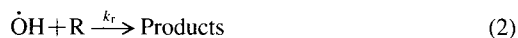
Recent studies of the interaction of TiO₂ aerosols with the OH radical gas-phase reaction with alkanes indicated a significant impact of aerosols on the kinetics of the OH radical/alkane reactions (Behnke *et al.*, 1988, 1987). Also, the impacts of aerosols on the kinetics were more profound with higher carbon alkanes (> C₈). However, a significant impact was not observed with SiO₂ aerosols (Behnke *et al.*, 1988, 1987). Also, in our previous study (Oh and Andino, 2000), a significant impact was not observed for the OH rate constant of n-hexane compared to p-xylene in the presence of ammonium sulfate aerosols. Therefore, studies including large alkanes with various aerosol compositions were needed to determine the effects of aerosols on alkane/·OH reactions. Specific alkanes of concern include n-butane, n-pentane, n-octane, and n-decane. Butane and pentane were identified in the Southern California Air Quality Study as being one of the twenty five most abundant species found in the atmosphere based on the fraction of non-methane carbon (Lurmann *et al.*, 1992). The remaining alkanes are also important constituents of air in urban areas.

The purpose of this study was to examine the effects of aerosol compositions and concentrations on the kinetics of the OH radical reactions with alkanes. Inorganic salts such as ammonium sulfate, ammonium nitrate, and sodium chloride aerosols were selected, and two different aerosol concentrations typical of polluted urban conditions were tested. Ammonium, sulfate, nitrate, sodium, and chloride typically account for 25~50% of the nonwater atmospheric aerosol mass (Sein-

feld *et al.*, 1994).

2. EXPERIMENTAL METHODS

The experimental methods and apparatus used in this study have been described in detail previously (Oh and Andino, 2000), thus only a brief summary is given here. The relative rate technique (Atkinson *et al.*, 1981) was used to investigate the effects of aerosols on the kinetics of the alkane/·OH reaction. This method relies on the comparison of the rates of disappearance of a "reference" (R) compound with a known OH radical reaction rate constant and a compound of interest, the "sample" (S), with an unknown OH radical reaction rate constant. Hydroxyl radicals react with the reference and sample, and the reactions are governed by individual rate constants k_s and k_r :



Provided that the sole loss process for the reference and reactant is the reaction with OH radicals, the following relationship holds:

$$\ln \left[\frac{S_0}{S_t} \right] = \frac{k_s}{k_r} \ln \left[\frac{R_0}{R_t} \right] \quad (3)$$

The subscripts 0 and t denote time zero and t, respectively. Plots of experimental data for $\ln[S_0/S_t]$ vs. $\ln[R_0/R_t]$ should yield a straight line with a slope of k_s/k_r and an intercept of zero. Thus, knowing k_r , the value of k_s can be calculated using the slope. Compilations of rate constants for many organic compounds exist, and the relative rate method is widely used to determine unknown rate constants (Atkinson, 1989, 1994). However, since all published rate constant data for gas-phase reactions were determined under relatively pristine laboratory conditions, the values for rate constants in the presence of aerosols do not exist. Hence, in this study, the relative rate ($=k_s/k_r$) was used as a measure of the effects of aerosols on the gas-phase reactions. The relative rates of the alkanes and the refer-

ence compound in the absence and presence of aerosols were determined, and changes in the relative rates were used as an indication of the effects of aerosols on the reactions.

Experiments were carried out in 100-liter, 2-mil Tedlar[®] bags (SKC Inc., USA), with irradiation provided by eight 40-watt black lamps (Sylvania F40/350BL, USA). All experiments were performed at room temperature, $298 \pm 2\text{K}$, and atmospheric pressure, ~ 760 Torr. Hydroxyl radicals were generated by the photolysis of methyl nitrite in the actinic region ($\lambda \geq 295$ nm) in the Tedlar[®] bag (Atkinson *et al.*, 1981). The aerosol was generated by atomizing an aqueous solution containing 1 wt % of the inorganic salt using a Collision atomizer (BGI Inc., USA). Ammonium sulfate, ammonium nitrate, and sodium chloride were used as the aerosol base materials for all studies. The aerosol generated was passed through a diffusional dryer and a ⁸⁵Kr charge neutralizer (TSI, Inc., USA) before being admitted to the bag. The bag was typically filled with 80 l of the air/reactant/aerosol mixture. Two different aerosol concentrations typical of polluted urban condition were tested. In order to minimize interferences between reactants and products, the following combinations of alkanes and reference compound were employed: n-octane/n-decane/p-xylene, n-hexane/p-xylene, and n-butane/n-pentane/p-xylene. P-xylene was used as a reference compound since its behavior compared to n-hexane in the presence of ammonium sulfate aerosols had been characterized previously (Oh and Andino, 2000).

Gas analyses were carried out with a Finnigan-MAT GCQ system (Model 9001 gas chromatography coupled to a mass spectral detector, Finnigan, USA). A 30 m \times 0.25 mm i.d. DB-5ms capillary column (J & W Scientific Co., USA) was used for the gas chromatograph, and split injections of 2 ml of sample were made with a six-port injection valve. The GC column temperature was programmed at 40°C for 90 seconds, then increased at a rate of 30°C min⁻¹ to a final temperature of 150°C. All mass spectral analyses were performed in the positive electron ionization mode. Initial concentra-

Table 1. Initial aerosol characteristics in the bag for aerosol condition I and II.

	I	II
Number		
Median diameter (μm)	0.05	0.07
Concentration ($\# \text{cm}^{-3}$)	6.5×10^4	9.9×10^4
Surface area ^a		
Median diameter (μm)	0.15	0.15
Concentration ($\mu\text{m}^2 \text{cm}^{-3}$)	1400	3400
Mass ^a		
Median diameter (μm)	0.20	0.20
Concentration ($\mu\text{g m}^{-3}$)	42	99

^aConverted assuming aerodynamic particles.

tions for gaseous compounds were typically 30 to 60 ppm of methyl nitrite, 12 to 20 ppm of n-butane, 8 to 10 ppm of n-pentane, 4 to 6 ppm of n-hexane, 1 to 2 ppm of n-octane, 1 to 2 ppm of n-decane, and 1 to 2 ppm of p-xylene, respectively. A 30 m \times 0.25 mm i.d. DB-WAX capillary column (J & W Scientific Co., USA) was used for the gas chromatograph.

Particle size distributions were determined using an electrical aerosol analyzer (EAA, Model 3030, TSI, Inc., USA). Total aerosol surface areas were $1400 \mu\text{m}^2 \text{cm}^{-3}$ (Condition I) and $3400 \mu\text{m}^2 \text{cm}^{-3}$ (Condition II); these values are typical of total atmospheric surface area found in polluted urban areas (Willeke and Whitby, 1975). Initial characteristics of aerosols admitted to the chamber are listed in Table 1. Since only a number concentration can be measured by an EAA, the corresponding surface and mass (volume) concentrations were converted from the number concentration assuming aerodynamic particles. No significant differences in aerosol characteristics were observed between different aerosol base materials. To avoid a change in aerosol characteristics during an experiment, only one irradiation time varying between 1 and 10 minutes was applied for each experiment. The change in aerosol surface area for these time scales was less than 10%. Separate loss studies (Oh and Andino, 2000) showed that the reaction with OH radicals was found to be the dominant loss process for the organics in the Tedlar bag. Other losses (wall interactions, gas-aerosol interac-

tions, and photolysis) were negligible (<5%, total) over time scales identical to those used in this study.

3. RESULTS AND DISCUSSION

3.1 Reactions in the Absence of Aerosols

The relative rates of the OH radical reactions with the alkanes in the absence of aerosols were obtained by linear least-square analyses of two different runs for the following combinations of alkanes and the reference compound: n-butane/n-pentane/p-xylene, n-hexane/p-xylene, and n-octane/n-decane/p-xylene. The data are plotted in accordance with equation (3), and plots are shown in Figure 1 through 3. All plots are good straight lines, and the relative rates (k_s/k_r) are reported in Table 2. Errors represent 95% confidence intervals. Gas-phase "sample" rate constants (k_s) were placed on an absolute basis by using the rate constants (k_r) of OH radical reaction with p-xylene. The rate constant of the p-xylene/OH reaction ($12.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $298 \pm 2\text{K}$) determined in our previous study (Oh and Andino, 2001) was used because the literature rate constants of the p-xylene/OH reaction exhibited a significant degree of scatter (Atkinson, 1989). The resulting rate constants of the alkanes and the recommended values by Atkinson (1997) are listed in Table 2.

Table 2. Gas-phase relative rates (k_s/k_r) and rate constant (k_s) for the reactions of OH radical with the alkanes using p-xylene as a reference compound at room temperature.

Compound	Relative rates (k_s/k_r) ^a	Rate constants ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	
		This work ^{a,b}	Recommended ^c
n-butane	0.19 ± 0.02	2.5 ± 0.3	2.44 ± 0.49
n-pentane	0.31 ± 0.02	4.0 ± 0.3	4.00 ± 0.80
n-hexane	0.53 ± 0.02	6.8 ± 0.3	5.45 ± 1.36
n-octane	0.70 ± 0.03	9.0 ± 0.4	8.71 ± 1.74
n-decane	0.93 ± 0.03	12.0 ± 0.4	11.2 ± 2.80

^aErrors represent 95% confidence intervals.

^bObtained by using $k_r(\text{p-xylene}) = 12.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ determined in the previous study (Oh and Andino, 2001).

^cFrom Atkinson *et al.* 1997.

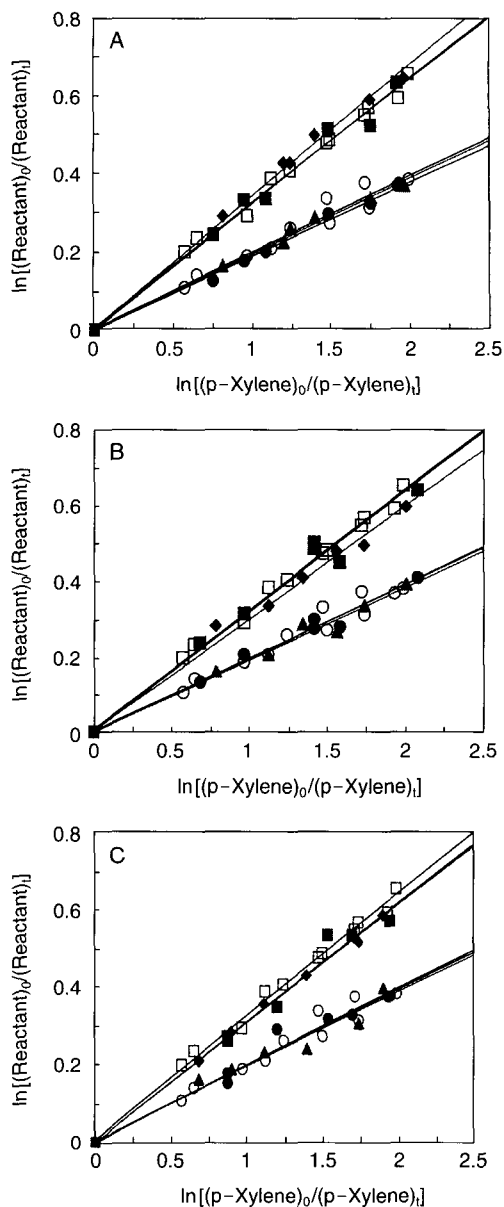


Fig. 1. Plots of $\ln[(\text{Reactant})_0/(\text{Reactant})_t]$ vs. $\ln[(\text{p-Xylene})_0/(\text{p-Xylene})_t]$ in the absence of aerosols (\circ : n-butane, \square : n-pentane) and the presence of aerosols (\bullet : Aerosol condition I, \blacktriangle : Aerosol condition II for n-butane and \blacksquare : Aerosol condition I, \blacklozenge : Aerosol condition II for n-pentane). The lines represent linear least squares fit to the data. Plot A represents data in the presence of $(\text{NH}_4)_2\text{SO}_4$ aerosols. Plot B represents data in the presence of NH_4NO_3 aerosols. Plot C represents data in the presence of NaCl aerosols.

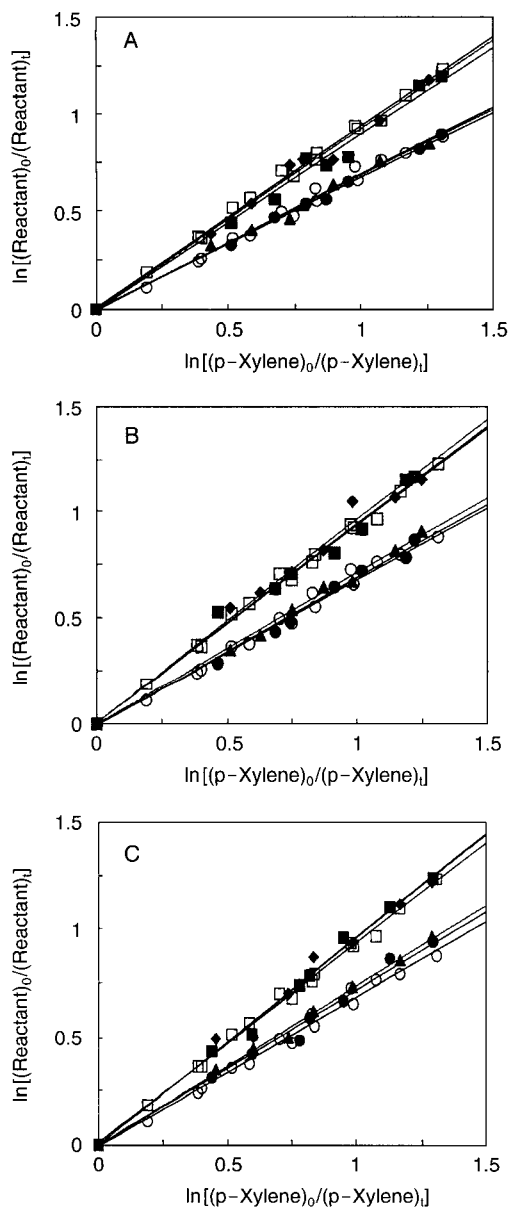


Fig. 2. Plots of $\ln[(\text{Reactant})_o/(\text{Reactant})_i]$ vs. $\ln[(p\text{-Xylene})_o/(p\text{-Xylene})_i]$ in the absence of aerosols (\circ : *n*-octane, \square : *n*-decane) and the presence of aerosols (\bullet : Aerosol condition I, \blacktriangle : Aerosol condition II for *n*-octane and \blacksquare : Aerosol condition I, \blacklozenge : Aerosol condition II for *n*-decane). The lines represent linear least squares fit to the data. Plot A represents data in the presence of $(\text{NH}_4)_2\text{SO}_4$ aerosols. Plot B represents data in the presence of NH_4NO_3 aerosols. Plot C represents data in the presence of NaCl aerosols.

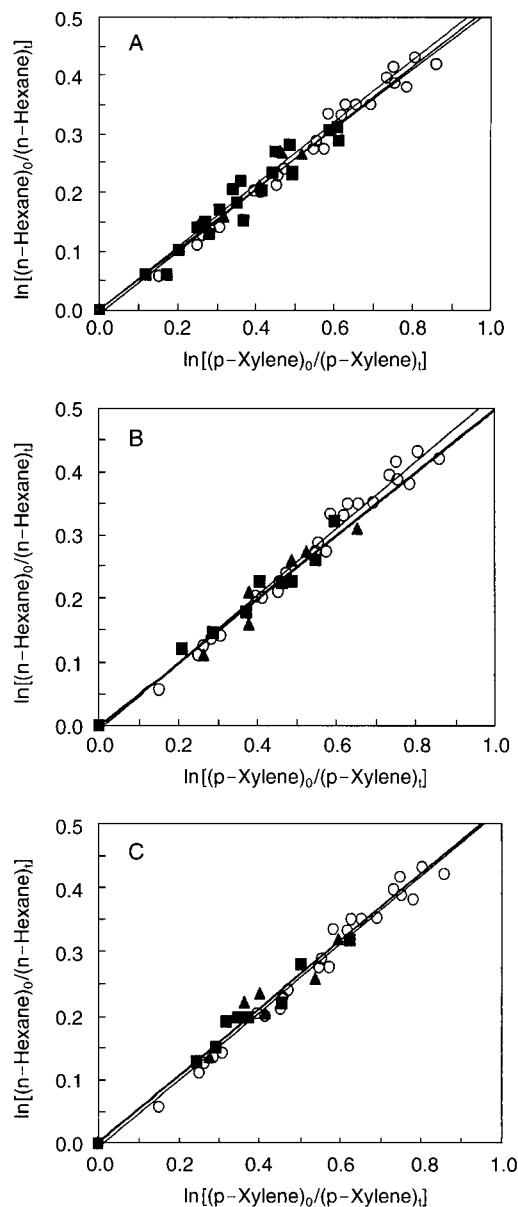


Fig. 3. Plots of $\ln[(n\text{-Hexane})_o/(n\text{-Hexane})_i]$ vs. $\ln[(p\text{-Xylene})_o/(p\text{-Xylene})_i]$ in the absence of aerosols (\circ) and the presence of aerosols (\blacksquare : Aerosol condition I, \blacktriangle : Aerosol condition II) of the following aerosol compositions: (A) $(\text{NH}_4)_2\text{SO}_4$; (B) NH_4NO_3 ; (C) NaCl . The lines represent linear least squares fit to the data.

Considering overall uncertainties in the recommended rate constants, the observed gas-phase rate cons-

Table 3. Relative rates of the alkane/ · OH reactions versus the p-xylene/ · OH reaction in the absence and presence of aerosols for aerosol conditions I and II.

Compound	Relative rates ^a					
	n-butane	n-pentane	n-hexane	n-octane	n-decane	
In the absence of aerosols	0.19 ± 0.02	0.31 ± 0.02	0.53 ± 0.02b	0.70 ± 0.03	0.93 ± 0.03	
In the presence of aerosols						
(NH ₄) ₂ SO ₄	I	0.19 ± 0.01	0.32 ± 0.02	0.51 ± 0.02	0.68 ± 0.01	0.90 ± 0.04
	II	0.19 ± 0.01	0.34 ± 0.01	0.53 ± 0.03	0.69 ± 0.02	0.92 ± 0.04
NH ₄ NO ₃	I	0.19 ± 0.01	0.32 ± 0.02	0.50 ± 0.03	0.69 ± 0.02	0.94 ± 0.04
	II	0.19 ± 0.01	0.30 ± 0.01	0.50 ± 0.04	0.72 ± 0.02	0.96 ± 0.04
NaCl	I	0.20 ± 0.01	0.31 ± 0.02	0.52 ± 0.02	0.73 ± 0.03	0.97 ± 0.02
	II	0.19 ± 0.02	0.30 ± 0.01	0.51 ± 0.04	0.74 ± 0.02	0.96 ± 0.04

^aErrors represent 95% confidence intervals.

tants of the alkanes using p-xylene as a reference compound are generally in good agreement with the recommended values. As shown in Table 2, the observed rate constants of the n-butane/ · OH reaction and n-pentane/ · OH reaction are in excellent agreement with the recommended values. The observed and recommended rate constants of the n-butane/ · OH reaction are $2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $2.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The observed and recommended rate constant of the n-pentane/ · OH reaction are identical at $4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For n-hexane, the observed rate constant is 25% higher than the recommended value, but within the overall uncertainty reported in the literature. The observed rate constants for n-octane and n-decane are 3% and 7% higher than the recommended values, and are within the reported overall uncertainties. Thus, our data fall within the acceptable ranges of published rate constants, thereby validating the relative rate technique used in this study.

3. 2 Reactions in the Presence of Aerosols

The relative rates of the reactions of the OH radical with the alkanes in the presence of inorganic aerosols were determined at two aerosol concentrations. Ammonium sulfate, ammonium nitrate, and sodium chloride were tested. The total surface area of aerosols were $1400 \mu\text{m}^2 \text{ cm}^{-3}$ and $3400 \mu\text{m}^2 \text{ cm}^{-3}$ for aerosol conditions I and II, respectively. Plots of $\ln[(\text{Alkane})_0/$

$(\text{Alkane})_t]$ vs. $\ln[(\text{p-Xylene})_0/(\text{p-Xylene})_t]$ for the purely gas-phase condition as well as for aerosol conditions I and II are shown in Figures 1 through 3. The experimentally determined relative rates are listed in Table 3.

As described in the previous study (Oh and Andino 2000), significant changes in the relative rates of the n-hexane/ · OH reaction versus the p-xylene/ · OH reaction were not observed in the presence of aerosols for the aerosol compositions and concentrations considered. As shown in Table 3, no significant effects on the kinetics of OH radical reactions with n-butane, n-pentane, n-octane or n-decane were observed for the aerosol compositions and concentrations considered. The relative rates of the n-butane/ · OH reaction, n-pentane/ · OH reaction, n-octane/ · OH reaction and n-decane/ · OH reaction versus the p-xylene/ · OH reaction in the absence and presence of aerosols were identical, within the error limits. The results indicate that (NH₄)₂SO₄, NH₄NO₃, and NaCl aerosols do not promote the alkane/ · OH reactions as compared to the p-xylene/ · OH reaction for n-butane, n-pentane, n-hexane, n-octane, and n-decane. These results are quite different from those determined by Behnke *et al.* (1988, 1987). Behnke *et al.* (1988, 1987) used TiO₂ particles, which, when exposed to UV generate OH radicals because of the semiconducting nature of TiO₂. Since (NH₄)₂SO₄, NH₄NO₃, and NaCl aerosols do not have semiconducting properties, it is likely that addi-

tional OH radicals were not generated at the particles' surfaces. Benke *et al.* (1987) also did not observe an enhancement of the alkane (n-butane, n-pentane, n-hexane, n-octane, and n-nonane)/ · OH reaction in the presence of SiO₂. Silicon dioxide particles are not capable of generating surface OH radicals. These results support the idea that the semiconducting property of the aerosol is the factor that determines the promoting effects on the alkane/ · OH reactions.

In our previous study (Oh and Andino, 2002), interactions between cations in aerosol particles and the organic compounds were considered as the process influencing the promotion of the 1-propanol/ · OH reaction in the presence of aerosols. To address this issue, possible interactions between aerosols and alkanes are considered. Since the interaction between cations in aerosol particles and the organic compounds is electrostatic (Inoue *et al.*, 1998), the interaction strength depends on the polarity of the gas-phase organic compound. Thus, the polarity of the gas-phase organic compounds should be considered. Aliphatic alkanes are non-polar compounds and the dipole moments of the alkanes are zero (Dean, 1992). Thus, there are no permanent partial negative charges in the molecules to interact with cations in aerosol particles. Consequently, promotion of the alkane/ · OH reaction due to an interaction between aerosol ions and gas-phase compounds is not feasible for the alkanes studied. Thus, no significant changes in the relative rates of the alkane/ · OH reactions versus the p-xylene/ · OH reaction were observed in the presence of non-semiconducting aerosols. The results suggest that the polarities of the gas-phase compounds were also important factors to consider when examining the organic/ · OH reaction in the presence of aerosols. Furthermore, the results indicate that the alkane/ · OH reactions (for >C₃ alkanes) in the troposphere will not be affected by inorganic aerosols which are major constituents of the tropospheric aerosols (i.e. non-semiconducting aerosols containing NH₄⁺, SO₄²⁻, NO₃⁻, Na⁺, and Cl⁻).

4. CONCLUSIONS

The effects of aerosols on the · OH rate constant of several alkanes were investigated using (NH₄)₂SO₄, NH₄NO₃, and NaCl aerosols. N-butane, n-pentane, n-hexane, n-octane, and n-decane were tested with p-xylene as a reference compound. Significant changes in the relative rates of the n-butane/ · OH, n-pentane/ · OH, n-octane/ · OH, and n-decane/ · OH reactions versus the p-xylene/ · OH reaction were not observed for aerosol concentrations I and II. These results indicate that the inorganic aerosols might not promote the alkane/ · OH reactions, and the promoting effects depend on the semiconducting property of the aerosols and the nature of the organic compounds. However, more studies under the presence of organic aerosols are needed to understand the effects of tropospheric aerosols on the alkane/ · OH reactions, since organic aerosols are major constituents of tropospheric aerosols. These results will validate the accuracy of current air quality models that are using the rate constants determined in the conditions ignoring effects of the tropospheric aerosols on organic/ · OH reactions.

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