GEOPHYSICAL RESEARCH LETTERS, VOL. 31, L15108, doi:10.1029/2004GL020089, 2004

Carbon kinetic isotope effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296 ± 4 K

Rebecca S. Anderson, Richard Iannone,[1] Alexandra E. Thompson,[2] and Jochen Rudolph
Centre for Atmospheric Chemistry and Chemistry Department, York University, Toronto, Canada

Lin Huang
Meteorological Service of Canada, Toronto, Canada

Received 25 March 2004; revised 29 June 2004; accepted 13 July 2004; published 11 August 2004.

[1] The carbon kinetic isotope effects (KIEs) of the room temperature reactions of benzene and several light alkyl benzenes with OH radicals were studied in a reaction chamber at ambient pressure using gas chromatography coupled with online combustion and isotope ratio mass spectrometry (GCC-IRMS). The KIEs are reported in per mil according to ε (‰) = (KIE − 1) × 1000, where KIE = k_{12}/k_{13}. The following average KIEs were obtained, (all in ‰): benzene 7.53 ± 0.50; toluene 5.95 ± 0.28; ethylbenzene 4.34 ± 0.28; *o*-xylene 4.27 ± 0.05, *p*-xylene 4.83 ± 0.81; *o*-ethyltoluene 4.71 ± 0.12 and 1,2,4-trimethylbenzene 3.18 ± 0.09. Our KIE value for benzene + OH agrees with the only reported value known to us [*Rudolph et al.*, 2000]. It is shown that measurements of the stable carbon isotope ratios of light aromatic compounds should be extremely useful to study atmospheric processing by the OH radical. *INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry. **Citation:** Anderson, R. S., R. Iannone, A. E. Thompson, J. Rudolph, and L. Huang (2004), Carbon kinetic isotope effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296 ± 4 K, *Geophys. Res. Lett.*, *31*, L15108, doi:10.1029/2004GL020089.

1. Introduction

[2] Aromatic hydrocarbons can be found in high parts per trillion by volume (pptV) to low parts per billion by volume (ppbV) levels in urban and industrial atmospheres and are emitted into the atmosphere from predominantly anthropogenic sources [*Seinfeld and Pandis*, 1997]. OH-radical oxidations have been established as the primary removal mechanisms for most light aromatic hydrocarbons from the atmosphere and the kinetics of these reactions have been well studied, and are known to contribute to the formation of ozone, photochemical smog and secondary organic aerosol (SOA) [*Atkinson and Aschmann*, 1989; *Calvert et al.*, 2002].

[3] The usefulness of stable carbon isotope measurements of non-methane hydrocarbons (NMHC) has recently been shown to improve insight into atmospheric processes involving NMHC [*Tsunogai et al.*, 1999; *Rudolph and Czuba*, 2000; *Rudolph et al.*, 2000, 2002; *Saito et al.*, 2002; *Rudolph*, 2003; *Rudolph et al.*, 2003; *Thompson et al.*, 2003]. For this, knowledge of the isotopic fractionations associated with the removal mechanisms of NMHC is essential. In this paper, laboratory measurements of the carbon kinetic isotope effects (KIEs) associated with the reactions of C_6–C_9 aromatic hydrocarbons with OH radicals are presented. The KIE for the reaction of benzene with OH radicals has been reported [*Rudolph et al.*, 2000], but to our knowledge, no measurements of OH-reaction KIEs have been reported for any other aromatic compound.

2. Measurement

[4] The KIEs were measured using the technique described by *Anderson et al.* [2003] using Gas Chromatography Combustion Isotope Ratio Mass Spectrometry (GCC-IRMS). Hydrocarbons were injected into a 30 L PTFE reaction chamber to generate concentrations between 25 and 120 ppmV. OH radicals were generated by isopropyl nitrite photolysis in the presence of high parts per million by volume (ppmV) NO. Measurements were made prior to the initiation and during the reaction over total reaction time periods ranging from 11 to 23 hours.

[5] Samples from the reaction chamber were separated on an HP1 column (Agilent Technologies, 60 m, 0.32 mm I.D., 5 μm film thickness). The GC temperature program used in all experiments was: 243 K held for 2.5 min, 4 K min^{-1} to 303 K, 1.5 K min^{-1} to 453 K, held until the last peak eluted. The carrier gas (He, Air Products, 99.995%) was controlled at 1.5 mL min^{-1}. With 0.3 mL min^{-1} of the GC effluent sent to a Saturn 2000 Ion Trap Mass Spectrometer for peak identification, 1.2 mL min^{-1} of the effluent passed through a combustion interface for conversion to carbon dioxide. Approximately 0.4 mL min^{-1} of this went to an isotope ratio mass spectrometer (Finnigan Mat 252) for isotope ratio measurement.

[6] For each experiment at least two measurements were made with the reaction chamber in the dark. For these measurements the relative standard deviation of the concentration values was always lower than 3% and the standard deviations of the $\delta^{13}C$ always lower than 0.25‰.

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[1] Now at Institut für Chemie und Dynamik der Geosphäre, ICG-II: Troposphäre, Forschungszentrum Jülich, Jülich, Germany.

[2] Now at Ecosystem Science, University of California, Berkeley, California, USA.

0094-8276/04/2004GL020089

Table 1. Measurements of the Kinetic Isotope Effects for the Reactions of Aromatic Hydrocarbons with OH Radicals at 296 ± 4 K at 760 Torr Total Pressure in Air

Hydrocarbon	ε,[a] ‰	R^2	k,[b] 10^{-12} cm^3 $molecule^{-1}$ s^{-1}
Benzene	9.01 ± 0.34	0.996	1.12 ± 0.23[c]
Benzene	6.29 ± 0.46	0.974	1.21 ± 0.24[d]
Benzene	7.01 ± 0.62	0.962	1.21 ± 0.28[c]
Benzene	7.70 ± 0.87	0.934	1.43 ± 0.30[c]
Benzene	7.62 ± 0.64	0.965	1.10 ± 0.22[c]
Toluene	5.84 ± 0.13	1.000	6.1 ± 1.2[e]
Toluene	5.39 ± 0.22	0.993	5.3 ± 1.1[d]
Toluene	5.88 ± 0.06	0.999	5.8 ± 1.2[d]
Toluene	6.98 ± 0.24	0.993	6.8 ± 1.7[f]
Toluene	6.32 ± 0.23	0.994	6.2 ± 1.3[g]
Toluene	5.29 ± 0.23	0.993	6.2 ± 1.3[e]
Ethylbenzene	4.14 ± 0.14	0.996	6.0 ± 1.5[c]
Ethylbenzene	4.53 ± 0.09	0.998	6.5 ± 1.6[h]
o-Xylene	4.24 ± 0.05	1.000	12.1 ± 3.1[e]
o-Xylene	4.39 ± 0.08	0.998	11.0 ± 2.2[c]
o-Xylene	4.27 ± 0.09	0.998	10.8 ± 2.2[c]
o-Xylene	4.20 ± 0.16	0.989	12.7 ± 2.5[c]
p-Xylene	4.25 ± 0.07	1.000	14.0 ± 3.5[h]
p-Xylene	5.40 ± 0.06	0.999	11.8 ± 2.4[c]
1, 2, 4-Trimethylbenzene	3.18 ± 0.09	0.997	31.0 ± 7.8[f]
o-Ethyltoluene	4.71 ± 0.12	0.996	14.4 ± 3.6[f]

[a] Error given is the uncertainty in the plot of equation (1).

[b] Calculated from relative rate using literature rate constant, uncertainty of the reference compound from *Atkinson and Arey* [2003] and standard error of the relative rate.

[c] Toluene used as reference.

[d] *n*-Octane used as reference.

[e] Benzene used as reference compound.

[f] *p*-Xylene used as reference.

[g] *n*-Heptane used as reference.

[h] *o*-Xylene used as reference.

After initiating the reaction, between three and seven samples were analyzed. All measurements took 1.5 to 2 hours. Except for benzene, with an average 25% depletion due to its slower OH-reaction rate, the hydrocarbon concentrations at the end of the experiment were depleted to <50% of their initial values.

[7] Stable carbon isotope ratios and concentrations were determined from the IRMS traces. Concentrations were derived from the abundance of the ^{12}C atoms in the sample. The relationship between isotope ratio and concentration measurements is described by *Anderson et al.* [2003] as

$$\ln\left({}^{12}C_t/{}^{12}C_0\right) = k_{12}/k_{13}/(1 - k_{12}/k_{13}) \times \ln\left[\left({}^{13}C_t/{}^{12}C_t\right)/\left({}^{13}C_0/{}^{12}C_0\right)\right] \qquad (1)$$

where C_t and C_0 correspond to the abundance of carbon atoms at time *t* and *t* = 0 respectively. Thus, a plot according to equation (1) will yield a straight line with a slope of $k_{12}/k_{13}/(1 - k_{12}/k_{13})$. The KIE, which is the ratio of the rate constants for the species containing only ^{12}C atoms and those containing a ^{13}C atom, k_{12}/k_{13}, is calculated from the slope of a standard linear least squares fit, and the experimental uncertainty for an individual experiment is determined from the uncertainty in the slope.

3. Results

[8] The reactions of seven different aromatic hydrocarbons with OH radicals were studied in synthetic air at atmospheric pressure. Seven experiments containing between one and four aromatic compounds each, and in some cases additional *n*-alkanes, were performed. The results are summarized in Table 1. To verify that hydrocarbon loss was due solely to reaction with OH radicals, a relative reaction rate analysis was performed for each experiment. A summary is included in Table 1. All *k* values calculated from the relative rate analysis fall into the uncertainty range of the literature rate constants (Table 2). The results for each aromatic hydrocarbon were averaged and compiled in Table 2. The uncertainty reported is the error of the mean = $\sigma \cdot (n - 1)^{-1/2}$ where σ is the 1σ standard deviation of the KIE measurements and *n* is the number of measurements.

[9] Using the data in Table 1, a plot of ε against the number of carbon atoms N_C in the aromatic hydrocarbon was made including the alkene and benzene OH-reaction KIE results from *Rudolph et al.* [2000] (Figure 1). Although the data in Figure 1 show some scatter, which is partly experimental, but may also partly be due to structure specific isotope fractionations, on average the carbon KIEs for the reactions of aromatic compounds are slightly higher than those for alkenes.

4. Discussion and Conclusions

[10] The KIE we found for benzene agrees within the experimental uncertainty with the value of (8.1 ± 0.8)‰ reported by *Rudolph et al.* [2000]. Similar to the findings reported by *Rudolph et al.* [2000] for OH-radical reactions of alkenes and alkanes, we can describe the KIE for the reaction of aromatic KIEs by an inverse dependence on N_C due to the probability of the reaction occurring at the

Table 2. Statistics of the Kinetic Isotope Effect Measurements for the Reactions of Aromatic Hydrocarbons With OH Radicals at 296 ± 4 K

Hydrocarbon	Average ε, ‰	Error of Mean, ‰	95% Confidence Interval, ‰	$k_{experimental}$,[a] 10^{-12} cm^3 $molecule^{-1}$ s^{-1}	$k_{literature}$,[b] 10^{-12} cm^3 $molecule^{-1}$ s^{-1}
Benzene	7.53	0.50	7.09–7.97	1.2 ± 0.1	1.22 ± 0.24
Toluene	5.95	0.28	5.72–6.17	6.1 ± 0.5	5.63 ± 1.13
Ethylbenzene	4.34	0.28	3.96–4.72	6.2 ± 0.3	7.00 ± 1.75
o-Xylene	4.27	0.05	4.23–4.32	11.7 ± 0.9	13.6 ± 3.4
p-Xylene	4.83	0.81	3.70–5.95	12.9 ± 1.5	14.3 ± 3.6
1, 2, 4-Trimethylbenzene[c]	3.18	0.09[d]		31.0 ± 7.8	32.5 ± 8.1
o-Ethyltoluene[c]	4.71	0.12[d]		14.4 ± 3.6	11.9 ± 4.2

[a] Mean *k* calculated using relative rate analysis; uncertainties are 1σ standard deviations for compounds with multiple measurements.

[b] *Atkinson and Arey* [2003].

[c] Confidence interval cannot be calculated as results are available for only one experiment.

[d] Error is uncertainty in the slope of equation (1).

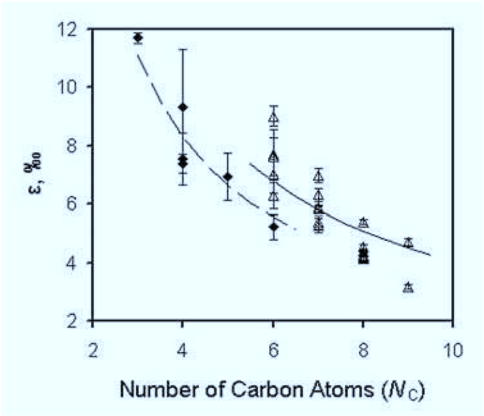

Figure 1. Plot of the KIEs for hydrocarbon reactions with OH radicals against the number of carbon atoms in the hydrocarbon. Triangles are the KIEs for aromatic compounds from this work, with the errors showing the uncertainty from the plot of equation (1). Diamonds show the KIE measurements for alkenes made by *Rudolph et al.* [2000] with 1σ errors of the mean KIE for compounds with multiple measurements, and the experimental uncertainty for compounds with only one KIE measurement. The solid and dashed lines are the N_C^{-1} best-fit curves to the aromatic and alkene data, respectively.

^{13}C atom: ε (‰) = (40.6 ± 1.4)·N_C^{-1} with an R^2 value for the linear least-squares fit of 0.651. However, the deviations of the individual KIEs from the curve and the differences between compounds of identical carbon number but different structure indicate that the dependence on N_C^{-1} is simply a first approximation.

[11] From Figure 1, it is evident there is a different relationship between the KIEs for the OH reaction with alkene and aromatic hydrocarbons, with a higher average KIE for aromatics with equal numbers of carbon atoms from C_6–C_8. The curve for the alkene KIEs was determined using the alkene KIEs in *Rudolph et al.* [2000] and an ethene KIE provided by *R.S. Anderson* (18.6 ± 2.9)‰ (unpublished data, 2004) as ε (‰) = (34.1 ± 1.0)·N_C^{-1}, with an R^2 value of 0.966. Unfortunately a direct comparison of KIEs for compounds with identical carbon numbers is limited to benzene since no OH-reaction KIEs have been measured for alkenes larger than C_6.

[12] A particularly interesting application of stable isotope ratio measurements of NMHC is the possibility to determine the average photochemical age, $t_{av}[OH]_{av}$ of a NMHC which has been demonstrated by *Thompson et al.* [2003]. This is done by measuring the isotope ratios δ_z of an individual hydrocarbon z if OH-radical photo-oxidation is the dominant process and the isotope ratio of the emissions $^0\delta_z$ is known [*Rudolph and Czuba*, 2000]:

$$t_{av}[OH]_{av} = \frac{\delta_z - {}^0\delta_z}{k_z \cdot \varepsilon_z} \tag{2}$$

[13] The usefulness of (2) will depend on the magnitudes of the KIE and k as well as on the uncertainties of the isotope ratios. Using the error of the right-hand side of (2) $\Delta(t_{av}[OH]_{av})$, it is possible to define a minimum detectable photochemical age $(t_{av}[OH]_{av})_{min} = \Delta(t_{av}[OH]_{av})$, which depends on the uncertainties (Δ) of the variables in (2). The following equation can be used for any significance level n, as long as the denominator is positive. For simplicity we will use in the following discussion a 1σ significance level ($n = 1$).

$$(t_{av}[OH]_{av})_{min} = n\sqrt{\frac{\Delta^2\delta_z + \Delta^2\,{}^0\delta_z}{(k_z \cdot \varepsilon_z)^2 - n^2(\Delta k_z \cdot \varepsilon_z)^2 - n^2(k_z \cdot \Delta\varepsilon_z)^2}} \tag{3}$$

[14] *Rudolph et al.* [2002] report source isotope ratios, $^0\delta$, for transport related sources of saturated and aromatic hydrocarbons at −27.7‰ (S.D. 1.7‰, error of the mean, 0.2‰). Alkene source isotope ratios from *Rudolph et al.* [2002] are reported at −25.3‰ (S.D. 1.9‰, error of the mean 0.4‰). State-of-the-art techniques allow measurements with uncertainties in the range of 0.5‰ to 1‰ for atmospheric concentrations in the range of 0.1 ppbC [*Rudolph et al.*, 1997], which can easily be converted into a volume mixing ratio for any given compound (Table 3). Using (3) with published rate constants and KIEs and their uncertainties, KIEs from this work and R. S. Anderson (unpublished data, 2004), $(t_{av}[OH]_{av})_{min}$ for different NMHC were calculated (Table 3).

[15] The average photochemical age which can be calculated from (2) is the average of the time the observed molecules spend in the atmosphere, that is the average time span between emission and observation multiplied by the average OH-radical concentration for this time interval. A conversion from photochemical age to average physical age will obviously depend on the average OH-radical concentration. For our considerations we use the global average 10^6 radicals cm^{-3}, but for situations with higher or lower OH-radical concentrations the physical time spans given in Table 3 must be modified according to the relevant average OH-radical concentration.

[16] While (3) allows a straightforward calculation of the lowest detectable physical ages, the upper end of photochemical ages that may be studied using stable carbon isotope ratio measurements of NMHC is less clearly defined. Obviously, photochemical aging will be combined with a decrease in concentration, partly due to chemical removal, partly due to mixing and dilution and at some point the concentrations will no longer be sufficient for stable isotope ratio measurements. This time span may vary considerably depending on initial NMHC concentration, atmospheric lifetime of the studied NMHC and the specific conditions of dispersion of the air mass. Table 3 includes an overview of urban concentrations, minimum concentrations for the measurements of stable carbon isotope ratios and an estimate of upper end of time scales, which can be studied using individual NMHC. As a rough guideline we use the assumption that the effect of dispersion on NMHC concentration is about the same as the chemical loss.

[17] We can sort the NMHC listed in Table 3 into approximately three groups: (i) alkenes excluding ethene, useful for studies on timescales ranging from approximately an hour to one or two days, (ii) alkylbenzenes and ethene, for timescales between a few hours and several days, and (iii) alkanes and benzene, for time scales between a few days and several weeks. Most of the compounds will allow studies over a range of a factor of 5–10 and thus are very promising probes for photochemical aging. The exceptions

Table 3. Time Scales Relevant for Photochemical Age Determination of Selected Light Hydrocarbons in the Atmosphere

Hydrocarbon	Minimum Detectable Photochemical Age,[a,b] s OH radicals cm^{-3}	Minimum Average Physical Age,[c] days	Average Tropospheric Lifetime,[b,c] days	Estimated Minimum Concentration for Stable Carbon Isotope Ratio Measurement, ppbV	Typical Urban Mixing Ratios, ppbV	Estimated Upper End of Time Scales for Studies of Photochemical Age,[d] days
Ethene	1.33E + 10	0.15	1.4	0.05	0.7–168[e]	2–5.5
Propene	6.46E + 09	0.07	0.44	0.03	0.1–39[e]	0.2–1.6
Isoprene	2.91E + 09	0.03	0.12	0.02	0.1–2[e]	0.1–0.3
1-Butene	8.64E + 09	0.10	0.37	0.03	0.2–7[e]	0.4–1
p-Xylene	2.69E + 10	0.31	0.81	0.01	0.3–30[e,f]	1.3–3
o-Xylene	3.15E + 10	0.36	0.85	0.01	0.4–6[e]	1.5–2.6
Toluene	5.41E + 10	0.63	2.0	0.01	2–39[e]	5–8
Ethylbenzene	6.04E + 10	0.70	1.7	0.01	1.1[g]	4
Benzene	1.97E + 11	2.3	9.5	0.02	0.9–26[e]	19–35
Propane	4.84E + 11	5.6	11	0.03	0.4–221[e]	13–47
n-Hexane	3.31E + 11	3.8	2.2	0.02	1.8[g]	5

[a] Based on the KIEs from *Rudolph et al.* [2000], R. S. Anderson (unpublished data, 2004) and this work.

[b] Rate constants from *Atkinson and Arey* [2003].

[c] Based on average OH-radical concentration of 10^6 radicals cm^{-3}.

[d] Considerations behind the estimates are explained in the text.

[e] *Finlayson-Pitts and Pitts* [2000].

[f] Combined mixing ratio range for *m*- and *p*-xylene.

[g] *Seinfeld and Pandis* [1997].

are the heavier (>C_5) alkanes, mainly due to their small KIEs and often low atmospheric concentrations.

[18] In summary, the KIE measurements for aromatic compounds presented here indicate that measurements of stable carbon isotope ratios of these compounds will be suitable for studying photochemical processing in the troposphere at timescales ranging from less than one day to several weeks. Furthermore, the only relevant removal mechanism for aromatic compounds is reaction with the OH radical, which avoids uncertainties and ambiguities in the interpretation of photochemical ages derived from stable carbon isotope ratio measurements.

[19] **Acknowledgments.** The authors sincerely thank D. Ernst and A. Chivulescu from the Meteorological Service of Canada for technical support and standard preparation. This research was supported financially by the Natural Science and Engineering Research Council of Canada.

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R. S. Anderson and J. Rudolph, Centre for Atmospheric Chemistry, 002 Steacie Science and Engineering Library, York University, 4700 Keele Street, Toronto, ON, M3J 1P3, Canada. (rebeccah@yorku.ca; rudolphj@yorku.ca)

L. Huang, Meteorological Service of Canada, 4905 Dufferin Street, Toronto, ON, M3H 5T4, Canada.

R. Iannone, Institut für Chemie und Dynamik der Geosphäre, ICG-II: Troposphäre, Forschungszentrum Jülich, Jülich, Germany.

A. E. Thompson, Ecosystem Science, University of California, Berkeley, CA, USA.