Experimental Study of Intermediates from OH-Initiated Reactions of Toluene

M. J. Molina,*,† R. Zhang,‡ K. Broekhuizen,† W. Lei,‡ R. Navarro,† and L. T. Molina†

Department of Earth, Atmospheric, and Planetary Sciences and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Meteorology, Texas A&M University, College Station, TX 77843

Aromatic hydrocarbons constitute a significant fraction of the total volatile organic compounds (VOCs) in urban and regional atmospheres.[1,2] The primary source is emission from automobiles and other fuel-based vehicles as well as from various industrial activities. Their atmospheric oxidation is largely initiated by attack from the hydroxyl radical, OH.[1] The toluene-OH reaction results in OH addition to the aromatic ring approximately 90% of the time and H-atom abstraction from the methyl group about 10% of the time. The abstraction pathway results in the formation of benzyl radicals, which then form benzyl peroxy radicals by addition of O_2. Subsequently, these radicals react with NO, leading to the formation of aromatic benzylaldehyde and benzyl nitrate. The carbonyl compound formed can further react with OH and O_2, and the peroxy radical produced leads to the formation of carboxylic acids, thus propagating the radical chain reactions.

The addition pathway results in the formation of methyl hydroxycyclohexadienyl radical (the adduct). Most of the ring retaining and fragmentation species of the photooxidation of toluene are a result of reactions of the adduct. Laboratory studies indicate that the adduct reacts with NO_2 with an estimated room temperature rate constant of 3×10^{-11} cm^3 molecule^{-1} s^{-1}.[2,3] The reaction of the adduct with O_2 has a lower estimated rate constant of 1.8×10^{-16} cm^3 molecule^{-1} s^{-1} at room temperature.[1,3,5] Also, instead of reaction with NO, the aromatic peroxy radicals are speculated to cyclize, forming bicyclic radicals. This process is followed by addition of another O_2 molecule and subsequent ring fragmentation.[6]

There is considerable uncertainty concerning the mechanism of the toluene oxidation reactions initiated by OH. Few direct experimental studies are available on the chemistry of the intermediate radicals. Laboratory data on the detection of aromatic intermediates in the gas phase has been reported only by Fritz et al.[4] and Knispel et al.;[3] their work involves UV absorption by the OH-benzene adduct, whose spectrum apparently displays a broad band around 270−340 nm. Most experimental data concerning the reactions after the initial OH attack involve the identification of the stable products formed, which include cresols, nitrotoluenes, benzyl nitrate, glyoxal, methylglyoxal, and peroxyacetyl nitrate (PAN).[1] In this work we present the first laboratory study to monitor directly with mass spectrometry the aromatic intermediate radicals formed in the OH-initiated reactions of toluene. We also report ion−molecule reaction rate constants for these radicals using various positive and negative reagent ions.

The experimental method employed in this study is similar to that used previously in our laboratory for chemical kinetics studies of elementary gas-phase reactions.[7,8] We employed a fast-flow reactor coupled to chemical ionization mass spectrometry (CIMS) detection, using both positive and negative reagent ions. The CIMS apparatus was fit with an electrostatic ion guide recently developed in our laboratory.[9] The detection sensitivity of the CIMS system was generally in the range from 10^7 to 10^8 molecule cm^{-3} with a S/N ratio of unity for a one second integration time. OH radicals were generated by passing a small amount of H_2O or H_2 through a microwave discharge. An excess amount of ozone was added downstream of the discharge cavity to scavenge the H atoms and to convert them to OH. Alternatively, OH was generated by the reaction of H-atoms with NO_2 or of F-atoms with H_2O. The OH radical was detected in the negative ion mode using SF_6^- as the reagent ion. The OH concentration was calibrated by converting it to HNO_3, followed by independent calibration of the HNO_3 with the mass spectrometer, as done previously in our laboratory.[10] The initial concentrations of OH in the flow reactor were typically in the range from 5×10^9 to 7×10^{10} molecule cm^{-3}. Commercially available toluene (99.5%) was introduced into the flow reactor by passing N_2 through a toluene bubbler at 0 °C. The concentrations of toluene in the flow reactor were in the range from 7×10^{11} to 8×10^{12} molecule cm^{-3} and were at least a factor of 10 higher than the OH concentration to ensure pseudo-first-order conditions.

A positive ion spectrum of the OH-toluene reaction products is shown in Figure 1(a), using O_2^+ as reagent ions. The prominent peak at *m/e* 92 corresponds to the parent mass of toluene ($C_7H_8^+$). The next highest peak at *m/e* 109 corresponds to the OH-toluene adduct produced by the following ion−molecule reaction:

$$C_7H_8OH + O_2^+ \rightarrow C_7H_8OH^+ + O_2 \qquad (1)$$

We are not aware of any previous rate constant measurements involving this radical cation. Several experiments were carried out to verify that the ions detected at *m/e* 109 were indeed attributable to the OH-toluene adduct, rather than being produced by secondary ion−molecule reactions. First, we observed that the signal at *m/e* 109 disappeared either when the toluene flow was stopped or when the microwave discharge for generating OH ceased. Second, we followed the evolution of the *m/e* 109 signal as the injector was successively pulled upstream to increase the reaction time. The results show that this signal rises (Figure 2b) in accordance with OH disappearance (Figure 2a). We should point out that the mass spectrometer signals depend only on the mass of ions without discrimination between isomers, although ab initio calculations indicate that the most energetically favored structure is that resulting from OH addition at the ortho position.[6]

To study the intermediates formed in the O_2-OH-toluene system, we added O_2 to the flow reactor at concentrations on the order of 10^{16} molecule cm^{-3}; several mass peaks appeared in the negative ion spectra, using SF_6^- as the reagent ion (Figure 1b). We attribute the mass peaks at *m/e* 123 and 141 to the formation of the benzyl peroxy radical and of the peroxy radical corresponding to the OH-toluene adduct, according to the following

† Massachusetts Institute of Technology.
‡ Texas A&M University
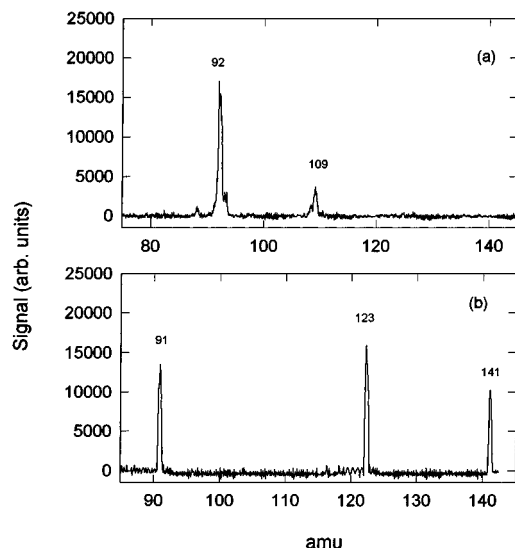(1) Atkinson, R. *J. Phys. Chem. Ref. Data, Monogr.* **1994**, *2*, 1.
(2) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; John Wiley & Sons: New York, 1997.
(3) Knispel, R.; Koch, R.; Siese, M.; Zetsch, C. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1375.
(4) Fritz, B.; Handwerk, V.; Preidel, M.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 343.
(5) Perry, R. A.; Atkinson, R.; Pitts, J. N. *J. Phys. Chem.* **1977**, *81*, 296.
(6) Andino, J. M.; Smith, J. N.; Flagan, R.; Goddard, W. A.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 10967.

(7) Seeley, J. V.; Jayne, J. T.; Molina, M. J. *Int. J. Chem. Kinet.* **1993**, *25*, 571.
(8) Seeley, J. V.; Meads, R. F.; Elrod, M. J.; Molina, M. J. *J. Phys. Chem.* **1996**, *100*, 4026.
(9) Zhang, R.; Molina, L. T.; Molina, M. J. *Rev. Sci. Instrum.* **1998**, *69*, 4002.
(10) Lipson, J.; Elrod, M. J.; Beiderhase, T. W.; Molina, L. T.; Molina, M. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2665.
(11) Harrison, A. G. *Chemical Ionization Mass Spectrometry*, 2nd ed.; CRC Press: Roca Raton, FL, 1992.
(12) Streit, G. E. *J. Chem. Phys.* **1982**, *77*, 826.

Figure 1. Mass spectra (a) for the OH-toluene reaction using O_2^+ as the reagent ion and (b) for the O_2-OH-toluene reaction using SF_6^- as the reagent ion. In b, the mass spectrum taken when the microwave discharge for generating OH was turned off has been subtracted from the original spectrum.

Table 1. Rate Constants of Ion−Molecule Reactions with O_2^+ or SF_6^- Reagent Ions for Intermediates Formed in Toluene Oxidation Reactions[a]

| charge- or electron-transfer reaction	k (cm^3 molecule^{-1} s^{-1})
$C_7H_8OH + O_2^+ \rightarrow C_7H_8OH^+ + O_2$	$(9.6 \pm 1.6) \times 10^{-10}$
$C_7H_7O_2 + SF_6^- \rightarrow C_7H_7O_2^- + SF_6$	$(1.5 \pm 0.6) \times 10^{-10}$
$C_7H_8OHO_2 + SF_6^- \rightarrow C_7H_8OHO_2^- + SF_6$	$(3.7 \pm 0.9) \times 10^{-9}$

[a] All rate constants were measured at 298 ± 2 K and 7 Torr. The uncertainty represents the scatter in the measurements at one standard deviation.

ion−molecule reactions:

$$C_7H_7O_2 + SF_6^- \rightarrow C_7H_7O_2^- + SF_6 \qquad (2)$$

$$C_7H_8OHO_2 + SF_6^- \rightarrow C_7H_8OHO_2^- + SF_6 \qquad (3)$$
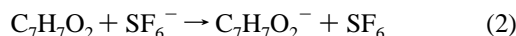
It is unlikely that these two mass peaks resulted from the ion−molecule reactions of O_2^- with the two radicals because O_2 has a smaller electron affinity (0.44 ev)[11] than that of SF_6.[12] Indeed, we did not observe any O_2^- signal in the presence of high concentrations of O_2 in the flow tube when SF_6^- was used as the reactant ion. Figure 1b also shows a prominent peak at *m/e* 91, corresponding most likely to the benzyl anion ($C_7H_7^-$). Since the electron affinity of the benzyl radical is in the range from 0.4 to 0.9 ev,[13] smaller than that of SF_6, this peak could not be linked to the formation of the benzyl radical. On the other hand, Bronstead base reagent ions such as OH^- or F^- are known to react efficiently with toluene to form this radical ion.[11] Also, benzyl radicals formed by thermal decomposition of bibenzyl have been detected previously using electron impact ionization.[14] In the case of the OH-toluene adduct, O_2 addition at the meta position has been shown to be energetically the most favored.[6] In addition, this aromatic peroxy radical may cyclicize, forming a bicyclic radical. However, in light of the relatively short resident time that the intermediate radicals experience in our fast-flow reactor, this process might not be important in our system.

We have determined the ion−molecule reaction rate constants for 1−3. The results are summarized in Table 1. The rate constants for the ion−molecule reactions were obtained by estimating the ion−molecule reaction time Δt and the concentration of the
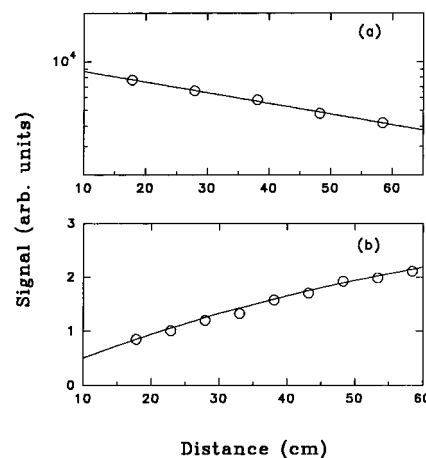
Figure 2. (a) OH signal and (b) OH-toluene adduct signal (normalized) as a function of injector position. The solid curves are from model calculations (see text). Experimental conditions are the following: $P = 14$ Torr, $[OH]_0 = 4.8 \times 10^{10}$ molecule cm^{-3}, and $[C_7H_8]_0 = 5.1 \times 10^{12}$ molecule cm^{-3}.

intermediate [A], using the relation $k = S_A/(S_B[A]\Delta t)$, where S_A and S_B are the signal intensities of the intermediate and the reagent ion, respectively. Using a similar approach, we measured a rate constant of $(1.2 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the reaction of NO_2 with SF_6^-, in good agreement with the literature value.[11] The intermediate radical concentrations from the toluene reactions have been obtained using a simple computer model and rate constants available in the literature for the relevant reactions.[1] The uncertainty in Table 1 includes only the random error; we estimate a systematic error of $\pm 50\%$, considering the sources of error in the measurements and modeling of the toluene reactions.

On the basis of the direct observation of the toluene-OH adduct, we are able to obtain kinetics information for the reaction between toluene and OH. In Figure 2a the OH decay (solid curve) corresponds to an effective bimolecular rate constant of 5.2×10^{-12} cm^3 molecule^{-1} s^{-1}. We have simulated the observed production of the OH-toluene adduct with a computer model that included appropriate reactions in our laboratory system, to extract a rate constant for this reaction. The model input included the initial concentrations of OH and other precursors. The rate constants for reactions relevant to our system were taken from the recommendations given by Atkinson[2] and by DeMore et al.[15] The solid line in Figure 2b represents the best fit to the observed production rate of the OH-toluene adduct; we infer an effective bimolecular rate constant of 4.7×10^{-12} cm^3 molecule^{-1} s^{-1}. The difference between the rate constant obtained from the OH decay and that based on the adduct appearance is $\sim 10\%$, which corresponds to the branching ratio between OH abstraction and addition. Both rate constants agree well with previous laboratory results.[1,16]

We have shown that the CIMS method provides an efficient way to study intermediate radicals formed in the OH-initiated reactions of toluene and that this technique can be used to investigate the kinetics and mechanisms of reactions of aromatic hydrocarbons in urban and regional atmospheres.

(13) Bohme, D. K.; Young, L. B. *Can. J. Chem.* **1971**, *49*, 2918.
(14) Pottie., R. F.; Lossing, F. P. *J. Am. Chem. Soc.* **1961**, *83*, 2634.

(15) DeMore, W. B.; Sander, S. P.; Howard, C. J.; Ravishankara, A. R.; Golden, D. M.; Kolb, C. E.; Hampson, R. F.; Kurylo, M. J.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; JPL Publication 97-4, NASA, 1997.
(16) Bourmada, N.; Devolder, P.; Sochet, L. R. *Chem. Phys. Lett.* **1988**, *149*, 339.