Atmospheric Environment 44 (2010) 3970–3975

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Extent of H-atom abstraction from OH + *p*-cymene and upper limits to the formation of cresols from OH + *m*-xylene and OH + *p*-cymene

Sara M. Aschmann [a], Janet Arey [a,b], Roger Atkinson [a,b,c,*]

[a] *Air Pollution Research Center, University of California, Riverside, CA 92521, USA*
[b] *Department of Environmental Sciences, University of California, Riverside, CA 92521, USA*
[c] *Department of Chemistry, University of California, Riverside, CA 92521, USA*

ARTICLE INFO

Article history:
Received 22 June 2010
Accepted 29 June 2010

Keywords:
Hydroxyl radical
m-Xylene
p-Cymene
4-Methylacetophenone
Cresol
Abstraction

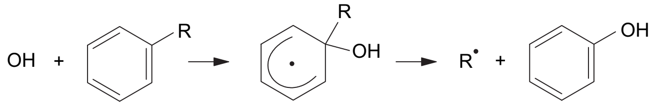
ABSTRACT

Aromatic hydrocarbons are important constituents of vehicle exhaust and of non-methane volatile organic compounds in ambient air in urban areas. It has recently been proposed that dealkylation is a significant pathway for the OH radical-initiated reactions, leading to the formation of phenolic compounds and/or oxepins (Noda, J., Volkamer, R., Molina, M.J., 2009. Dealkylation of alkylbenzenes: a significant pathway in the toluene, *o*-, *m*-, and *p*-xylene + OH reaction. Journal of Physical Chemistry A 113, 9658–9666.). We have investigated the formation of cresols from the reactions of OH radicals with *m*-xylene and *p*-cymene, and obtain upper limits of <1% for formation of each cresol isomer from OH + *m*-xylene and <2% for formation of each cresol isomer from OH + *p*-cymene. In addition, we have measured the formation yield of 4-methylacetophenone (the major product formed subsequent to H-atom abstraction from the $CH(CH_3)_2$ group) in the OH + *p*-cymene reaction to be 14.8 ± 3.2%, and estimate that H-atom abstraction from the CH_3 and $CH(CH_3)_2$ groups in *p*-cymene accounts for 20 ± 4% of the overall OH radical reaction. We also used a relative rate technique to measure the rate constant for the reaction of OH radicals with 4-methylacetophenone to be $(4.50 \pm 0.43) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 297 ± 2 K.

1. Introduction

Aromatic hydrocarbons are important components of polluted ambient air, accounting for ~20% of non-methane volatile organic compounds in urban areas (Calvert et al., 2002). In the atmosphere, aromatic hydrocarbons are removed by reaction with OH radicals, and for alkylbenzenes these reactions proceed by H-atom abstraction from the C-H bonds of the alkyl substituents and by initial OH radical addition to the aromatic ring (Calvert et al., 2002; Atkinson and Arey, 2003). Based on the available kinetic and product data, at room temperature H-atom abstraction accounts for <10% of the overall OH radical reactions for toluene, the xylenes, and the trimethylbenzenes (Atkinson, 1989), and hence the OH radical addition pathway dominates at room temperature and below. In addition to these two pathways, using chemical ionization mass spectrometry Noda et al. (2009) observed ion peaks indicative of dealkylation from the reactions of OH radicals with toluene and *o*-, *m*- and *p*-xylene conducted at 154 ± 4 Torr total pressure, with dealkylation accounting for 5.4 ± 1.2% (as phenol) of the toluene reaction and 4.5 ± 3.2%, 11.2 ± 3.8% and 4.3 ± 3.1% (as cresol) of the *o*-, *m*- and *p*-xylene reactions respectively (Noda et al., 2009). Smith et al. (1998) previously reported <0.1% formation of phenol from toluene at atmospheric pressure, and formation of cresols from the xylenes has not been reported to date. Noda et al. (2009) postulated that dealkylation occurs by either an addition-elimination reaction involving initial addition of OH at an *ipso* position (Scheme 1) or, more likely, by a more complex process as shown for *m*-xylene after addition of OH at the preferred *ortho* position (Scheme 2).

The dealkylation pathway proceeding as shown in Scheme 1 becomes thermochemically more favorable as the leaving-group changes from H to methyl to isopropyl. Thus, the overall reaction OH + benzene → phenol + H is calculated to be slightly endothermic ($\Delta H = 0.4$ kcal mol^{-1}), while the overall reactions OH + toluene → phenol + •CH_3 and OH + isopropylbenzene →



Scheme 1. Dealkylation through an addition-elimination reaction after initial *ipso* addition of OH (R = alkyl), leading to formation of *m*-cresol from OH + *m*-xylene and of *p*-cresol from OH + *p*-cymene.

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[*] Corresponding author at: Air Pollution Research Center, University of California, Riverside, CA 92521, USA. Tel.: +1 (951) 827 4191.
E-mail address: ratkins@mail.ucr.edu (R. Atkinson).

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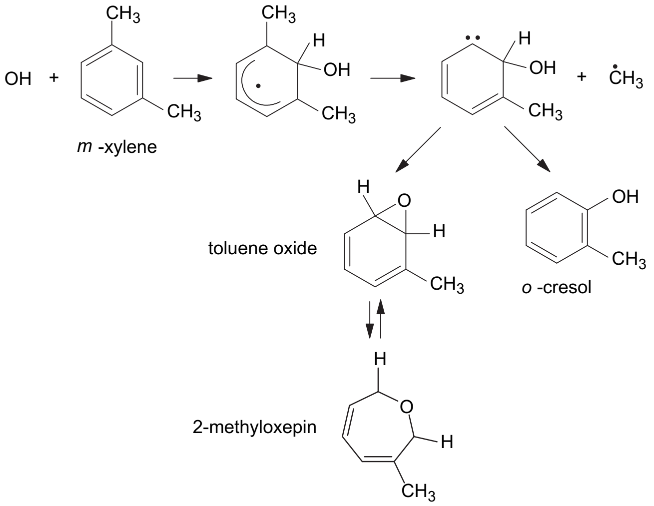
doi:10.1016/j.atmosenv.2010.06.059



Scheme 2. Proposed pathways leading to formation of *o*-cresol and/or toluene oxide/2-methyloxepin from OH + *m*-xylene (Noda et al., 2009).

phenol + •CH(CH$_3$)$_2$ are increasingly exothermic, with calculated values of $\Delta H = -8.9$ and -12.2 kcal mol^{-1}, respectively (NIST, 1994; IUPAC, 2010). While theoretical calculations show that formation of phenol + H from the OH + benzene reaction is of no importance at room temperature and below (Lay et al., 1996), is it possible that elimination of alkyl groups from the OH-aromatic adducts can occur, more so for alkyl = isopropyl.

In this work, we have investigated the formation of cresols from the OH radical-initiated reactions of *m*-xylene (the xylene isomer reported by Noda et al. (2009) as having the highest fraction of dealkylation) and *p*-cymene (4-isopropyltoluene or 1-methyl-4-(1-methylethyl)benzene). In addition, since H-atom abstraction from the C-H bonds of the isopropyl substituent in *p*-cymene is expected to lead mainly to formation of 4-methylacetophenone (see Scheme 3 and Discussion), we have measured the formation yield of 4-methylacetophenone from the OH + *p*-cymene reaction and the rate constant for OH + 4-methylacetophenone.

2. Experimental methods

Experiments were carried out in a ~7000 L volume Teflon chamber at 297 ± 2 K and ~735 Torr of dry pure air. The chamber is equipped with black lamps for irradiation and a Teflon-coated fan to ensure rapid mixing of reactants during introduction into the chamber. OH radicals were generated by the photolysis of CH_3ONO at >300 nm, and NO was added to suppress formation of O_3 and hence of NO_3 radicals. All irradiations were carried out at a light intensity corresponding to an NO_2 photolysis rate of 0.137 min^{-1}.

2.1. Rate constant for OH + 4-methylacetophenone

The rate constant was measured using a relative rate method in which the concentrations of 4-methylacetophenone and a reference compound (*n*-octane in this case, its OH radical reaction rate constant being reliably known) were measured in the presence of OH radicals.

$$\text{OH} + \text{4-methylacetophenone} \rightarrow \text{products} \tag{1}$$

$$\text{OH} + n\text{-octane} \rightarrow \text{products} \tag{2}$$

Providing that 4-methylacetophenone and *n*-octane reacted only with OH radicals, then,

$$\ln\left(\frac{[\text{4-methylacetophenone}]_{\text{to}}}{[\text{4-methylacetophenone}]_t}\right) = \frac{k_1}{k_2}\left[\ln\left(\frac{[n\text{-octane}]_{\text{to}}}{[n\text{-octane}]_t}\right)\right] \tag{I}$$

where $[\text{4-methylacetophenone}]_{\text{to}}$ and $[n\text{-octane}]_{\text{to}}$ are the concentrations of 4-methylacetophenone and *n*-octane, respectively, at time t_o, $[\text{4-methylacetophenone}]_t$ and $[n\text{-octane}]_t$ are the corresponding concentrations at time *t*, and k_1 and k_2 are the rate constants for reactions (1) and (2), respectively. Hence a plot of ln $([\text{4-methylacetophenone}]_{\text{to}}/[\text{4-methylacetophenone}]_t)$ against ln $([n\text{-octane}]_{\text{to}}/[n\text{-octane}]_t)$ should be a straight line of slope k_1/k_2 and zero intercept.

The initial reactant concentrations (molecule cm^{-3}) were: CH_3ONO, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; and 4-methylacetophenone and *n*-octane, $\sim 2.4 \times 10^{13}$ each. Irradiations were carried out for up to 30 min, resulting in up to 23% and 36% consumption of the initially present 4-methylacetophenone and *n*-octane, respectively. The concentrations of 4-methylacetophenone and *n*-octane were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, and subsequently thermally desorbed onto a 30 m DB-1701 megabore column, temperature programmed from −40 °C at 8 °C min^{-1}.

2.2. Formation of selected products from OH + m-xylene and OH + p-cymene

Irradiations of CH_3ONO − NO − *m*-xylene -air and CH_3ONO − NO − *p*-cymene − air mixtures were carried out, resulting in up to 27% and 35% consumption of the initially present *m*-xylene or *p*-cymene, respectively. Gas samples were collected prior to and during the reactions onto Tenax solid adsorbent, with subsequent thermal desorption and GC-FID analysis. For the *m*-xylene reactions, a 30 m DB-1701 megabore column was used for the GC-FID analyses, while for the *p*-cymene reactions concurrent GC-FID analyses were carried out using both 30 m DB-1701 and 30 m DB-5 megabore columns. Additionally, in one *p*-cymene experiment, analyses were carried out by exposing a 65 μm poly-dimethylsiloxane/divinylbenzene solid phase microextraction (SPME) fiber to the chamber contents for typically 10 min, (a) prior to reaction, (b) after reaction and (c) after reaction and the addition of 4-methylacetophenone and *m*-cresol to the chamber. The exposed SPME fibers were then thermally desorbed and analyzed by GC-MS using a DB-5 column interfaced to an Agilent 5975 Mass Selective Detector operated in positive chemical ionization mode with methane as the reagent gas.

GC-FID response factors and retention times for *m*-xylene, *p*-cymene, *o*-, *m*- and *p*-cresol, 4-methylacetophenone and *p*-tolualdehyde were determined by introducing known amounts of authentic standards into the chamber and carrying out replicate analyses. In addition, $\sim 8.4 \times 10^{10}$ molecule cm^{-3} of *o*-, *m*- and *p*-cresol were added separately to the chamber after the reactions were complete, with additional GC-FID analyses being carried out.

2.3. Chemicals

The chemicals used, and their stated purities, were: *o*- cresol (99+%), *m*-cresol (99+%), *p*-cresol (99+%), *p*-cymene (99%), 4-methylacetophenone (95%), *n*-octane (99+%), *p*-tolualdehyde (97%) and *m*-xylene (99+%), Aldrich; and NO (≥99.0%), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously (Atkinson et al., 1989, 1991).