THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

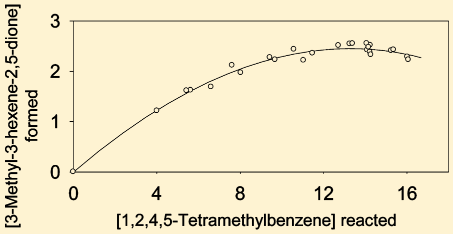
Rate Constants for the Reactions of OH Radicals with 1,2,4,5-Tetramethylbenzene, Pentamethylbenzene, 2,4,5-Trimethylbenzaldehyde, 2,4,5-Trimethylphenol, and 3-Methyl-3-hexene-2,5-dione and Products of OH + 1,2,4,5-Tetramethylbenzene

Sara M. Aschmann, Janet Arey,* and Roger Atkinson*

Air Pollution Research Center, University of California, Riverside, California 92521, United States

S *Supporting Information*

ABSTRACT: Using a relative rate method, rate constants have been measured for the reactions of OH radicals with 1,2,4,5-tetramethylbenzene, pentamethylbenzene, 2,4,5-trimethylbenzaldehyde, 2,4,5-trimethylphenol and 3-methyl-3-hexene-2,5-dione at 298 ± 2 K and atmospheric pressure of air. The rate constants obtained (in units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}) were: 1,2,4,5-tetramethylbenzene, 5.55 ± 0.34; pentamethylbenzene, 10.3 ± 0.8; 2,4,5-trimethylbenzaldehyde, 4.27 ± 0.39; 2,4,5-trimethylphenol, 9.75 ± 0.98; and 3-methyl-3-hexene-2,5-dione, 9.4 ± 1.1. The following first-generation products were identified from the OH + 1,2,4,5-tetramethylbenzene reaction in the presence of NO: biacetyl, methylglyoxal, 3-methyl-3-hexene-2,5-dione, and 2,4,5-trimethylbenzaldehyde. The measured molar formation yields for 3-methyl-3-hexene-2,5-dione and 2,4,5-trimethylbenzaldehyde were 45 ± 9% and 3.3 ± 0.7%, with that for 3-methyl-3-hexene-2,5-dione being extrapolated to low NO_2 concentrations where the OH-1,2,4,5-tetramethylbenzene adducts react only with O_2. Biacetyl appeared to be formed as both a first- and second-generation product, and a first-generation formation yield of 9 ± 3% was derived. The relative formation yield of methylglyoxal was ~0.8 of that for 3-methyl-3-hexene-2,5-dione, indicating that methylglyoxal and 3-methyl-3-hexene-2,5-dione are coproducts. H-atom abstraction from OH + 1,2,4,5-tetramethylbenzene is estimated to account for 3.7 ± 0.8% of the overall OH radical reaction. On the basis of the current understanding of the mechanism of the OH-aromatic adduct + O_2 reaction, the observed formation of biacetyl indicates that some *ipso* addition of OH occurs for OH + 1,2,4,5-tetramethylbenzene.



INTRODUCTION

Aromatic hydrocarbons account for ~20% of nonmethane volatile organic compounds in urban atmospheres.[1] In the troposphere, alkyl-substituted benzenes react with OH radicals, by H-atom abstraction from the C−H bonds of the alkyl substituents and by OH radical addition to the aromatic ring to form OH-aromatic adducts.[1,2] Kinetic data are available for the reactions of OH radicals with a number of aromatic hydrocarbons,[1,2] and kinetic and product studies show that H-atom abstraction accounts for <10% of the overall OH radical reaction for toluene, the xylenes, and the trimethylbenzenes at room temperature and below.[1−4] For these methylbenzenes, the electrophilic OH radical addition pathway therefore dominates at room temperature and below. For alkyl-substituted benzenes, OH radical addition occurs preferentially *ortho-* and *para-* to the substituent alkyl group(s), with the room temperature rate constants for OH radical addition correlating well with the sum of the electrophilic substituent constants, $\Sigma\sigma^{+}$.[5,6]

While there have been numerous kinetic studies of the reaction of OH radicals with benzene, toluene, the xylenes and the trimethylbenzenes[1] and a rate constant for the reaction of OH radicals with hexamethylbenzene has been reported,[7] no published kinetic data are currently available concerning the reactions of OH radicals with the tetramethylbenzenes or pentamethylbenzene. In this work we have measured rate constants at 298 ± 2 K for the gas-phase reactions of OH radicals with 1,2,4,5-tetramethylbenzene and pentamethylbenzene, as well as for 2,4,5-trimethylbenzaldehyde, 2,4,5-trimethylphenol and 3-methyl-3-hexene-2,5-dione, observed or potential reaction products from OH + 1,2,4,5-tetramethylbenzene. In addition, products formed from the OH + 1,2,4,5-tetramethylbenzene reaction in the presence of NO have been investigated, and formation yields of 2,4,5-trimethylbenzaldehyde, methylglyoxal, biacetyl and 3-methyl-3-hexene-2,5-dione obtained.

EXPERIMENTAL METHODS

Experiments were carried out in a ~7500 L volume Teflon chamber at 298 ± 2 K and ~735 Torr of dry purified air. The chamber is equipped with black lamps for irradiation and a Teflon-coated fan to ensure rapid mixing of reactions during introduction into the chamber. OH radicals were generated by the photolysis of CH_3ONO at >300 nm, and NO was present

Received: January 10, 2013
Revised: February 21, 2013
Published: March 18, 2013

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 0.14 min^{-1}.

Rate Constant Measurements. Rate constants for the reactions of OH radicals with 1,2,4,5-tetramethylbenzene, pentamethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol were measured using a relative rate method in which the concentrations of the aromatics and a reference compound were measured in the presence of OH radicals.[8] Under conditions that the aromatic and reference compound are removed by reaction with OH radicals and the aromatic may also undergo dark decay

$$\text{OH} + \text{aromatic} \rightarrow \text{products} \quad (1)$$

$$\text{OH} + \text{reference compound} \rightarrow \text{products} \quad (2)$$

$$\text{aromatic} \rightarrow \text{loss to chamber walls} \quad (3)$$

then

$$\ln\left(\frac{[\text{aromatic}]_{t_0}}{[\text{aromatic}]_t}\right) - k_3(t - t_0) = \frac{k_1}{k_2}\ln\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right) \quad (\text{I})$$

where $[\text{aromatic}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of aromatic and reference compound, respectively, at time t_0, $[\text{aromatic}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t, and k_1, k_2 and k_3 are the rate constants for reactions 1, 2 and 3, respectively. Hence a plot of $\{\ln([\text{aromatic}]_{t_0}/[\text{aromatic}]_t) - k_3(t - t_0)\}$ against $\ln([\text{reference compound}]_{t_0}/[\text{reference compound}]_t)$ should be a straight line of slope k_1/k_2 and zero intercept.

The initial reactant concentrations (molecules cm^{-3}) were: CH_3ONO, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; and aromatic and reference compound, $\sim 2.4 \times 10^{13}$ each. 1,3,5-Trimethylbenzene was used as the reference compound, since its rate constant for reaction with OH radicals is reliably known.[1,2] Irradiations were carried out for up to 9 min, resulting in up to 64, 88, 62, 86 and 70% consumption of the initially present 1,2,4,5-tetramethylbenzene, pentamethylbenzene, 2,4,5-trimethylbenzaldehyde, 2,4,5-trimethylphenol and 1,3,5-trimethylbenzene, respectively. The concentrations of 1,2,4,5-tetramethylbenzene, pentamethylbenzene, 2,4,5-trimethylbenzaldehyde, 2,4,5-trimethylphenol and 1,3,5-trimethylbenzene 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}. During each experiment the following GC-FID analyses were conducted: at least two replicate analyses prior to reaction, one analysis after each of three irradiation periods, and a replicate analysis after the third (and last) irradiation period. Three experiments were conducted for each aromatic compound. Replicate analyses in the dark, after correcting for any dark decays (see below), showed that the measurement uncertainties were typically $\leq 2\%$ for 1,3,5-trimethylbenzene and 1,2,4,5-tetramethylbenzene and $\leq 3\%$ for pentamethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol.

Dark decays were determined by monitoring, over periods of several hours, the concentrations of 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, pentamethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol in the chamber in dry air in the dark. Because of large losses of 2,4,5-trimethylphenol observed in the postreaction replicate analyses (see below), this compound was also monitored in the chamber in the dark in the presence of CH_3ONO and NO_x.

Detection and Quantification of Selected Products from OH + 1,2,4,5-Tetramethylbenzene. Irradiations of CH_3ONO−NO−1,2,4,5-tetramethylbenzene−air and CH_3ONO−NO−1,2,4,5-tetramethylbenzene−1,3,5-trimethylbenzene−air mixtures (the latter being the experiments used to measure the rate constant for OH + 1,2,4,5-tetramethylbenzene) were carried out, with 1,2,4,5-tetramethylbenzene and selected products being measured by GC-FID analyses of gas samples collected onto Tenax solid adsorbent as described above for the kinetic studies. The initial CH_3ONO and NO concentrations (molecules cm^{-3}) were $\sim 2.4 \times 10^{14}$ each or $\sim 4.8 \times 10^{13}$ each, and the initial 1,2,4,5-tetramethylbenzene concentrations were $(2.33-2.76) \times 10^{13}$ molecules cm^{-3}.

Additionally, for combined gas chromatography−mass spectrometry (GC-MS) confirmation of products, one CH_3ONO−NO−1,2,4,5-tetramethylbenzene−air irradiation and one CH_3ONO−NO−1,2,4-trimethylbenzene−air irradiation were carried out, with initial reactant concentrations (molecules cm^{-3}) of: CH_3ONO and NO, $\sim 4.8 \times 10^{13}$ each; 1,2,4,5-tetramethylbenzene, 2.65×10^{13}; and 1,2,4-trimethylbenzene, $\sim 3.6 \times 10^{13}$. A single irradiation was carried out (3 and 4 min for the 1,2,4,5-tetramethylbenzene and 1,2,4-trimethylbenzene reactions, respectively), and GC-FID analyses of 1,2,4,5-tetramethylbenzene or 1,2,4-trimethylbenzene were carried out as described above. Samples were also collected by exposing a 65 μm polydimethylsiloxane/divinylbenzene solid phase microextraction (SPME) fiber to the chamber contents for 20 min prior to reaction, after reaction, and (for the 1,2,4,5-tetramethylbenzene reaction) after reaction and the sequential addition of 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol to the chamber. The exposed SPME fibers were thermally desorbed and analyzed by GC-MS using an HP-5MS column interfaced to an Agilent 5973 Mass Selective Detector operated in positive chemical ionization mode (PCI GC-MS) with methane as the reagent gas. Samples were also collected after each reaction onto a 5-channel, 400 mm length annular denuder (URG-2000−30B5, URG, Chapel Hill, NC) coated with finely ground XAD-4 resin and, to derivatize carbonyls to their oximes,[9] further coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxyl amine (PFBHA) prior to sampling.[9] Samples were collected from the chamber at 15 L min^{-1} for 60 min directly onto the denuder, the entrance of which extended into the chamber. The denuder samples were extracted as described previously,[9] and the extracts were analyzed by GC-MS as described above, and by GC-FID using a 30 m DB-5 column. Each carbonyl group derivatized to an oxime adds 195 mass units to the compound's molecular weight, and methane-PCI gives characteristic protonated molecules ($[M + H]^+$) and smaller adduct ions at $[M + 29]^+$ and $[M + 41]^+$.[9] Derivatized hydroxycarbonyls also exhibit strong $[M + H - H_2O]^+$ fragment ions.[8,9]

For the analyses of samples collected onto Tenax solid adsorbent, GC-FID response factors for 1,2,4,5-tetramethylbenzene and biacetyl were determined by introducing measured amounts of the chemical into the chamber and conducting several replicate GC-FID analyses. Because of difficulties in quantitatively introducing 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol into the chamber, and the nonavailability of 3-methyl-3-hexene-2,5-dione, GC-FID response factors for these products or potential products were calculated by combining the measured GC-FID response factor for 1,2,4,5-tetramethylbenzene with calculated Effective Carbon Numbers for 1,2,4,5-tetramethylbenzene, 2,4,5-trimethylbenzaldehyde, 2,4,5-trimethylphenol and 3-methyl-3-hexene-2,5-dione, of 10.0, 9.0, 9.0 and 4.9, respectively.[10] Note that this assumes collection and desorption efficiencies for 2,4,5-trimethylbenzaldehyde, 2,4,5-trimethylphenol and 3-methyl-3-hexene-2,5-dione equal to that of 1,2,4,5-tetramethylbenzene.

A single $CH_3ONO-NO-1,2,4,5$-tetramethylbenzene−air irradiation was conducted with analysis by direct air sampling atmospheric pressure ionization tandem mass spectrometry (API-MS/MS), with initial reactant concentrations similar to those for the corresponding experiment carried out with sampling onto the PFBHA-coated denuder and GC-MS analysis (see above), and with two irradiation periods of 1 and 2 min, respectively. API-MS and API-MS/MS analyses were conducted in positive ion mode as described previously.[8]

Formation Yield of 3-Methyl-3-hexene-2,5-dione and its OH Radical Reaction Rate Constant. 3-Methyl-3-hexene-2,5-dione was identified as a major product from OH + 1,2,4,5-tetramethylbenzene by GC-MS analyses of SPME fiber and PFBHA-coated denuder samples (with the latter identification being of its dioximes), and was quantified from GC-FID analyses of samples collected onto Tenax solid adsorbent. Since no rate constant for the reaction of OH radicals with 3-methyl-3-hexene-2,5-dione was available, the approach described by Baker et al.[11] was used to derive the removal rate of 3-methyl-3-hexene-2,5-dione and the formation yield of 3-methyl-3-hexene-2,5-dione from OH + 1,2,4,5-tetramethylbenzene. For the reaction sequence

$$\text{OH} + \text{1,2,4,5-tetramethylbenzene} \rightarrow \alpha\text{3-methyl-3-hexene-2,5-dione} + \text{other products} \tag{4}$$

$$\text{OH} + \text{3-methyl-3-hexene-2,5-dione} \rightarrow \text{products} \tag{5}$$

$$\text{3-methyl-3-hexene-2,5-dione} \rightarrow \text{loss of 3-methyl-3-hexene-2,5-dione} \tag{6}$$

then the concentration of 3-methyl-3-hexene-2,5-dione at time t is given by

$$[\text{3-methyl-3-hexene-2,5-dione}]_t = A(e^{-x} - e^{-Bx}) \tag{II}$$

where α is the formation yield of 3-methyl-3-hexene-2,5-dione from reaction 4, $A = \alpha[\text{1,2,4,5-tetramethylbenzene}]_{\text{initial}}\{k_4[\text{OH}]/(k_5[\text{OH}] + k_6)]\}$, $B = (k_5[\text{OH}] + k_6)/k_4[\text{OH}]$, and x = extent of reaction = $\ln([\text{1,2,4,5-tetramethylbenzene}]_{t_0}/[\text{1,2,4,5-tetramethylbenzene}]_t)$. Hence a fit of eq II to the experimental data leads to values of A and B and hence of α and $(k_5[\text{OH}] + k_6)/k_4[\text{OH}]$.[11]

CHEMICALS

The chemicals used, and their stated purities, were: biacetyl [2,3-butanedione] (99%), 1,2,4-trimethylbenzene (98%), 1,3,5-trimethylbenzene (98%), 1,2,4,5-tetramethylbenzene (98%), pentamethylbenzene (98%) and 2,4,5-trimethylbenzaldehyde (90%), Aldrich; 2,4,5-trimethylphenol (purity not stated), City Chemical; *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (99+%), Alfa Aesar; and NO (≥99.0%), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously.[8,9,12]

RESULTS

Dark Decays. Dark decays were investigated by monitoring the concentrations of the compounds in the chamber in the dark for 2.3−6.6 h. There was no evidence for any dark decay of 1,3,5-trimethylbenzene or 1,2,4,5-tetramethylbenzene, with <2% loss of 1,3,5-trimethylbenzene over 4.8 h and <3% loss of 1,2,4,5-tetramethylbenzene over 6.6 h (corresponding to $k_3 < 1.3 \times 10^{-6}\ \text{s}^{-1}$ in each case). However, pentamethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol did undergo dark decay, with measured decay rates, k_3, in dry purified air of $(2.0 \pm 1.0) \times 10^{-6}\text{s}^{-1}$, $(5.1 \pm 1.0) \times 10^{-6}\ \text{s}^{-1}$ and $(2.3 \pm 0.9) \times 10^{-6}\ \text{s}^{-1}$, respectively, where the indicated errors are two least-squares standard deviations. Over the typical duration of the experiments to measure the OH radical reaction rate constants (~3.0 h from sampling for the last prereaction analysis to sampling for the replicate post-third irradiation analysis), these dark decays correspond to 2.2% and 5.5% loss of pentamethylbenzene and 2,4,5-trimethylbenzaldehyde, respectively.

For 2,4,5-trimethylphenol, replicate postreaction analyses in irradiated $CH_3ONO-NO-2,4,5$-trimethylphenol−1,3,5-trimethylbenzene−air mixtures showed dark decays which were much more rapid than that measured in dry purified air. Accordingly, the dark decay of 2,4,5-trimethylphenol was measured in dry purified air in the presence of CH_3ONO and NO_x (i.e., with initial reactant concentration similar to those used for the kinetic experiments, but with no irradiation). Under these conditions, the dark decay rate of 2,4,5-trimethylphenol was $(1.7 \pm 0.3) \times 10^{-5}\ \text{s}^{-1}$, a factor of 7 faster than in dry air in the absence of CH_3ONO and NO_x. Correcting for this dark decay rate in the presence of CH_3ONO and NO_x resulted in excellent agreement of postreaction replicate analyses of 2,4,5-trimethylphenol in the kinetic experiments. GC-MS analyses of a SPME fiber exposed to 2,4,5-trimethylphenol in the presence of CH_3ONO and NO_x showed the formation of a product of molecular weight 181, presumably 2,4,5-trimethyl-6-nitrophenol or 2,4,5-trimethyl-3-nitrophenol assumed to be formed by heterogeneous reaction of 2,4,5-trimethylphenol with NO_2. Note that NO_2 is formed by thermal oxidation of NO during introduction of NO to the chamber and subsequently in the dark, as well as by NO-to-NO_2 conversion during $CH_3ONO-NO$−air photooxidations of volatile organic compounds from reactions of HO_2 and organic peroxy radicals with NO.[2] The observation that the dark decay rate of 2,4,5-trimethylphenol after irradiation of $CH_3ONO-NO-2,4,5$-trimethylphenol−1,3,5-trimethylbenzene−air mixtures was the same within the experimental uncertainties as in a nonirradiated $CH_3ONO-NO-2,4,5$-trimethylphenol−1,3,5-trimethylbenzene−air mixture suggests that while the dark decay rate of 2,4,5-trimethylphenol was markedly faster in the presence of NO_x (presumably NO_2), it was independent of the gas-phase concentration of NO_x (or NO_2).

Rate Constants for OH Radical Reactions with 1,2,4,5-Tetramethylbenzene, Pentamethylbenzene, 2,4,5-Trimethylbenzaldehyde and 2,4,5-Trimethylphenol. A series of $CH_3ONO - NO -$ aromatic −1,3,5-trimethylbenzene

− air irradiations were carried out, and the data obtained are plotted in accordance with eq I in Figure 1.

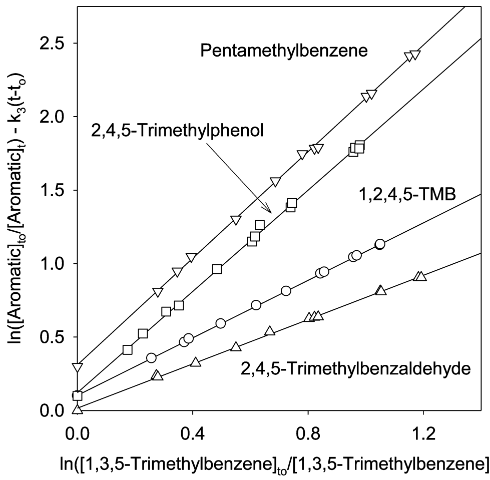


Figure 1. Plots of eq I for the reaction of OH radicals with 2,4,5-trimethylbenzaldehyde, 1,2,4,5-tetramethylbenzene (1,2,4,5-TMB), 2,4,5-trimethylphenol and pentamethylbenzene, with 1,3,5-trimethylbenzene as the reference compound. The measured concentrations of pentamethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol have been corrected for dark decay (k_3) using our measured dark decay rates, with that for 2,4,5-trimethylphenol being the decay rate in the presence of CH_3ONO and NO_x (see text). The data for 1,2,4,5-tetramethylbenzene, 2,4,5-trimethylphenol and pentamethylbenzene have been displaced vertically by 0.10, 0.10, and 0.30 units, respectively, for clarity. Data are from 3 experiments for each aromatic, with GC-FID analyses of samples collected onto Tenax solid adsorbent.

In Figure 1, the measured concentrations of pentamethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol have been corrected for dark decay using our measured dark decay rates, with that for 2,4,5-trimethylphenol being the decay rate in the presence of CH_3ONO and NO_x. Least-squares analyses of the data shown in Figure 1 lead to the rate constant ratios k_1/k_2 listed in Table 1. These rate constant ratios can be placed onto an absolute basis using a rate constant of k_2(OH + 1,3,5-trimethylbenzene) = 5.67 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1},[2] and the resulting rate constants k_1 are also given in Table 1.

Identification of products from OH + 1,2,4,5-Tetramethylbenzene. Table 2 lists the products identified from the OH + 1,2,4,5-tetramethylbenzene reaction. Authentic standards of 2,4,5-trimethylbenzaldehyde and biacetyl were available, allowing absolute identification and quantification.

Table 1. Rate Constant Ratios k_1/k_2 or k_5/k_4 and Rate Constants k_1 or k_5 for the Reactions of OH Radicals with 1,2,4,5-Tetramethylbenzene, Pentamethylbenzene, 2,4,5-Trimethylbenzaldehyde, 2,4,5-Trimethylphenol and 3-Methyl-3-hexene-2,5-dione at 298 ± 2 K and Atmospheric Pressure of Air

		10^{11} × k_1 or k_5 (cm^3 $molecule^{-1}$ s^{-1})	
aromatic	k_1/k_2 or k_5/k_4[a]	this work[b]	literature
1,2,4,5-tetramethylbenzene	0.979 ± 0.006	5.55 ± 0.34	
pentamethylbenzene	1.81 ± 0.03	10.3 ± 0.8	
2,4,5-trimethylbenzaldehyde	0.753 ± 0.015	4.27 ± 0.39	
2,4,5-trimethylphenol	1.72 ± 0.04	9.75 ± 0.98	11.7 ± 0.5[c,d] 12.9 ± 0.8[c,e]
3-methyl-3-hexene-2,5-dione	1.70 ± 0.16[f]	9.4 ± 1.1[g]	

[a] Relative to OH + 1,3,5-trimethylbenzene unless noted otherwise. The rate constant ratio involving 3-methyl-3-hexene-2,5-dione is referred to as k_5/k_4. The data for pentamethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol have been corrected for dark decay, using dark decay rates, k_3, of 2.0 × 10^{-6}, 5.1 × 10^{-6} and 1.7 × 10^{-5} s^{-1}, respectively (that for 2,4,5-trimethylphenol being in the presence of CH_3ONO and NO_x; see text). Corrections for dark decays reduced the rate constant ratios k_1/k_2 and rate constants k_1 for pentamethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol by 1%, 6% and 8%, respectively, compared to those obtained neglecting dark decay corrections. The indicated errors are two least-squares standard deviations; the estimated overall uncertainties are ±6% for 1,2,4,5-tetramethylbenzene, ± 7% for pentamethylbenzene, ± 9% for 2,4,5-trimethylbenzaldehyde and ±10% for 2,4,5-trimethylphenol. [b] Placed on an absolute basis using a rate constant for the reaction of OH radicals with 1,3,5-trimethylbenzene of k_2 = 5.67 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1},[2] unless noted otherwise. Unless noted otherwise, the indicated errors are the estimated overall uncertainties (see footnote (a)) and do not include uncertainties in the rate constant k_2. [c] From Bejan et al.,[13] at 298 ± 2 K. [d] Measured relative to OH + isoprene, with the measured rate constant ratio of 1.17 ± 0.05 being placed on an absolute basis using k(OH + isoprene) = 1.00 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.[2,4] [e] Measured relative to OH + 1,3-butadiene, with the measured rate constant ratio of 1.94 ± 0.12 being placed on an absolute basis using k(OH + 1,3-butadiene) = 6.66 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[2] [f] Measured relative to k_4(OH + 1,2,4,5-tetramethylbenzene); see text and Figure 2. The uncertainty is two standard errors of the nonlinear least-squares fit to eq II. [g] Placed on an absolute basis using our measured rate constant for the reaction of OH radicals with 1,2,4,5-tetramethylbenzene of k_4(OH + 1,2,4,5-tetramethylbenzene) = (5.55 ± 0.34) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. The indicated error is the two standard errors in the rate constant ratio combined with the cited uncertainty in the rate constant for OH + 1,2,4,5-tetramethylbenzene.

Other products were identified by GC-MS analysis of SPME fiber samples, GC-MS analysis of extracts of PFBHA-coated denuder samples (i.e., with carbonyls derivatized to their oximes), and by positive ion mode API-MS analysis. Since it was expected that at least some of the products formed from the previously studied OH + 1,2,4-trimethylbenzene reaction[9,14−18] and the OH + 1,2,4,5-tetramethylbenzene reaction would be identical, the products of the two reactions were compared. As detailed in the Supporting Information, the products identified from GC-MS analyses of extracts of PFBHA-coated denuder samples from the OH + 1,2,4,5-tetramethylbenzene reaction were: 2,4,5-trimethylbenzaldehyde, biacetyl (2,3-butanedione), methylglyoxal, 3-methyl-3-hexene-2,5-dione [$CH_3C(O)C(CH_3){=}CHC(O)CH_3$], and a hydroxydicarbonyl of molecular weight 116 attributed to $CH_3C(O)CH(OH)C(O)CH_3$ and/or $CH_3C(O)C(CH_3)(OH)CHO$ and formed as a second-generation product from OH + 3-methyl-3-hexene-2,5-dione (see Supporting Information). As noted in Table 2 and presented in the Supporting Information, the API-MS and API-MS/MS analyses were consistent with the formation of these products (with the exception of methylglyoxal whose $[M + H]^+$ at m/z = 73 would be obscured by a water cluster ion), and in addition indicated the formation of products of molecular weight 100, 112, 142, 182 (tentative) and 227.

GC-MS analyses of samples collected onto SPME fibers from the OH + 1,2,4-trimethylbenzene and OH + 1,2,4,5-tetramethylbenzene reactions (without derivatization) both showed the presence of an identical molecular weight 126

Table 2. Products Identified from the Reaction of OH Radicals with 1,2,4,5-Tetramethylbenzene in the Presence of NO

		observed by		
product molecular weight	product attributed to	GC-MS	API-MS[a]	product quantified by
72	methylglyoxal	yes[b,c]		GC-FID denuder[d]
86	biacetyl	yes[b,c,e]	yes	GC-FID Tenax
100			yes	
112	2,3-dimethyl-1,4-butenedial		yes	
116[f]	$CH_3C(O)CH(OH)C(O)CH_3$ and/or $CH_3C(O)C(CH_3)(OH)CHO$	yes[b,c,f]	yes	GC-FID denuder[d]
126	3-methyl-3-hexene-2,5-dione	yes[b,c,g]	yes	GC-FID Tenax
142			yes	
148	2,4,5-trimethylbenzaldehyde	yes[b,g,h]	yes	GC-FID Tenax
150	2,3,5,6-tetramethylphenol	tentative[i]	tentative[i]	
182			tentative[j]	
227			yes[k]	

[a] See Figure S2 and associated figure caption in the Supporting Information. [b] Observed as its dioxime or (for 2,4,5-trimethylbenzaldehyde) mono-oxime by GC-MS analyses of extract of PFBHA-coated denuder sample (see Supporting Information). [c] Observed in GC-MS analyses of extract of the PFBHA-coated denuder sample of OH + 1,2,4-trimethylbenzene reaction (see Supporting Information). [d] Quantified, relative to 3-methyl-3-hexene-2,5-dione, from GC-FID analysis of their dioximes in the extract of the PFBHA-coated denuder sample. Yield placed on an absolute basis using the quantification of 3-methyl-3-hexene-2,5-dione from GC-FID analyses of samples collected onto Tenax solid adsorbent (without derivatization). [e] Confirmed by retention time matching of dioximes in GC-MS analyses with those of authentic standard introduced into chamber and sampled onto PFBHA-coated denuder. [f] Second-generation product from OH + 3-methyl-3-hexene-2,5-dione (see Supporting Information), consistent with API-MS analyses after 1 and 3 min of reaction which showed that the molecular weight 116 product increased with extent of reaction significantly more rapidly than did 3-methyl-3-hexene-2,5-dione. [g] Observed by GC-MS analysis of sample collected onto SPME fiber. [h] Confirmed by retention time matching in GC-MS analysis of sample collected onto SPME fiber with that of authentic standard introduced into chamber and similarly sampled. [i] Evidence for presence of a minor molecular weight 150 product in SPME GC-MS analysis, but could not be confirmed due to the lack of an authentic standard. In the API-MS analysis, a small peak attributed to $[150 + H]^+$ was present, but no MS/MS analysis was conducted. [j] Also present in prereaction API-MS analysis, and the m/z = 183 signal remained approximately constant relative to that of 1,2,4,5-tetramethylbenzene (i.e., m/z = 134 + 164) during the reaction. This suggests that this molecular weight 182 species was formed in the ion source from 1,2,4,5-tetramethylbenzene (and could have been the unsaturated epoxy-dicarbonyl shown in Scheme 3). [k] Probably a nitrate (see caption to Figure S2, Supporting Information).

product, and this is assigned to the 3-methyl-3-hexene-2,5-dione observed in the extracts of the PFBHA-coated denuder samples. This indicates that 3-methyl-3-hexene-2,5-dione, like 3-hexene-2,5-dione,[17] can be analyzed by GC without prior derivatization. Indeed, GC-FID analyses of samples collected onto Tenax solid adsorbent showed a GC peak with identical retention times from both reactions, attributed to 3-methyl-3-hexene-2,5-dione. As noted in Table 2, 2,4,5-trimethylbenzaldehyde, 3-methyl-3-hexene-2,5-dione and biacetyl were then quantified from GC-FID analyses of samples collected onto Tenax solid adsorbent. Quantification of methylglyoxal relative to 3-methyl-3-hexene-2,5-dione was obtained from GC-FID analyses of their dioximes in the extract of the PFBHA-coated denuder sample, taking into account the differences in the ECNs of the various dioximes[10,18] and secondary reactions of these dicarbonyls with OH radicals (see footnote (f) to Table 3). The resulting methylglyoxal formation yield, relative to the 3-methyl-3-hexene-2,5-dione yield measured by Tenax/GC-FID analysis, is listed in Table 3. The amount of the molecular weight 116 hydroxydicarbonyl attributed to $CH_3C(O)CH(OH)C(O)CH_3$ and/or $CH_3C(O)C(CH_3)(OH)CHO$ which was present (i.e., uncorrected for any wall losses or for photolysis and/or reaction with OH radicals), similarly derived from the GC-FID analyses of the extract of the PFBHA-coated denuder sample, was ~45% of the amount of 3-methyl-3-hexene-2,5-dione calculated to have reacted with OH radicals. The GC-MS analysis of a postreaction SPME fiber showed evidence for minor formation of a tetramethylphenol (see Table 2). There was no conclusive evidence for formation of 2,4,5-trimethylphenol.

Formation Yield of 3-Methyl-3-hexene-2,5-dione and its OH Radical Reaction Rate Constant. Since 3-methyl-3-hexene-2,5-dione is not commercially available, the removal rate of 3-methyl-3-hexene-2,5-dione and its formation yield from OH + 1,2,4,5-tetramethylbenzene were obtained from a fit of eq II to the experimental data. The initial 1,2,4,5-tetramethylbenzene concentrations ranged from (2.48–2.76) × 10^{13} molecules cm^{-3}, and a plot of the measured 3-methyl-3-hexene-2,5-dione concentrations, adjusted to $[\text{1,2,4,5-tetramethylbenzene}]_{\text{initial}} = 2.50 \times 10^{13}$ molecules cm^{-3}, against the extent of reaction, defined as $\ln([\text{1,2,4,5-tetramethylbenzene}]_{t_0}/[\text{1,2,4,5-tetramethylbenzene}]_t)$, is shown in Figure 2. A nonlinear least-squares regression analysis leads to $A = (1.27 \pm 0.22) \times 10^{13}$ molecules cm^{-3} and $B = (1.70 \pm 0.16)$, where the indicated errors are two standard errors, and the solid line in Figure 2 is eq II with these parameters. Replicate postreaction GC-FID analyses showed no evidence for dark decay of 3-methyl-3-hexene-2,5-dione. Furthermore, by analogy with 3-hexene-2,5-dione,[17] it is likely that 3-methyl-3-hexene-2,5-dione photolyzes only slowly, if at all, by black lamps. Hence it is likely that $k_6 \approx 0$, and hence that $B = k_5/k_4 = 1.70 \pm 0.16$ and, combined with k_4(OH + 1,2,4,5-tetramethylbenzene) from Table 1, $k_5 = (9.4 \pm 1.1) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Table 1).

From $A = \alpha[\text{1,2,4,5-tetramethylbenzene}]_{\text{initial}}\{k_4[OH]/(k_5[OH] + k_6)\} = 1.27 \times 10^{13}$ molecules cm^{-3}, the molar formation yield of 3-methyl-3-hexene-2,5-dione from OH + 1,2,4,5-tetramethylbenzene, α, is 35.6%. This formation yield was measured in experiments with initial CH_3ONO and NO concentrations of ~2.4 × 10^{14} molecules cm^{-3} each, and with an average NO_2 concentration during the reactions of 1.02 × 10^{14} molecules cm^{-3} (assuming that $([NO] + [NO_2])$ = constant, as previously derived from computer calculations of irradiated $CH_3ONO-NO-NO_2$–toluene–air mixtures using a

Table 3. First-generation Products Quantified from the Reaction of OH Radicals with 1,2,4,5-Tetramethylbenzene in the Presence of NO

product	$10^{-13} \times [NO_2]_{av}$ (molecules cm^{-3})[a]	molar yield (%)
2,4,5-trimethylbenzaldehyde	9.0–11.9 (10.2)	3.5 ± 0.3[b]
	1.5–2.3 (1.9)	3.8 ± 0.8[b]
	1.5–11.9	3.3 ± 0.7[c]
2,4,5-trimethylphenol	9.0–11.9	<3
3-methyl-3-hexene-2,5-dione	9.0–11.9 (10.2)	35 ± 7[d]
	1.5–2.3 (1.9)	43 ± 8[d]
	0	45 ± 9[e]
methylglyoxal	1.5	35[f]
biacetyl (2,3-butanedione)	1.5–11.9	9 ± 3[g]

[a] Range of average NO_2 concentrations for the experiments conducted. The value in parentheses is the average for those experiments. [b] Indicated errors are two least-squares standard deviations. [c] For the entire data set shown in Figure 5. The indicated error is two least-squares standard deviations combined with the estimated uncertainty in the GC-FID response factor for 2,4,5-trimethylbenzaldehyde relative to that for 1,2,4,5-tetramethylbenzene of ±15% (the yield with two least-squares standard deviation errors is 3.3 ± 0.4%). [d] The 3-methyl-3-hexene-2,5-dione formation yields are 43.2 ± 2.8% and 35.5 ± 1.5% at average NO_2 concentrations of 1.9×10^{13} and 10.2×10^{13} molecules cm^{-3}, respectively, where the errors are two least-squares standard deviations of the slopes of the plots shown in Figure 3. The indicated errors given in the table are the two least-squares standard deviations combined with estimated uncertainties in the GC-FID response factor for 3-methyl-3-hexene-2,5-dione relative to that for 1,2,4,5-tetramethylbenzene of ±15% and in the rate constant ratio $k_4[OH]/(k_5[OH] + k_6)$ of ±10%, corresponding to a ± 8% uncertainty in the maximum value of the multiplicative correction factor F. [e] Yield at low (zero) NO_2 concentration was calculated using eq III. The uncertainty is the estimated overall uncertainty. [f] Derived from GC-FID analyses of the extract of a PFBHA-coated denuder sample, relative to a 3-methyl-3-hexene-2,5-dione formation yield of 43.2% and taking into account the slight differences in the ECNs of the dioximes[10,18] and secondary reaction with OH radicals (using a rate constant for OH + methylglyoxal of 1.3×10^{-11} cm^3 molecule^{-1} s^{-1} [4] and those in Table 1 for 1,2,4,5-tetramethylbenzene and 3-methyl-3-hexene-2,5-dione). Relative to 3-methyl-3-hexene-2,5-dione =1.0, the methylglyoxal formation yield was 0.82 ± 0.06, where the error is two standard deviations from 3 replicate injections. This methylglyoxal yield is not corrected for expected secondary formation of methylglyoxal from OH + 3-methyl-3-hexene-2,5-dione as a coproduct to biacetyl (see text). Correction for secondary formation would result in a methylglyoxal yield relative to that of 3-methyl-3-hexene-2,5-dione of ~0.73 and hence a methylglyoxal yield at 1.5×10^{13} molecules cm^{-3} of NO_2 of ~31%. [g] The biacetyl first-generation formation yields derived from the initial slopes of the second-order regression fits to the data shown in Figure 4 (○) were 9.0 ± 2.5% and 8.3 ± 3.8% at average NO_2 concentrations of 1.9×10^{13} and 10.2×10^{13} molecules cm^{-3}, respectively, where the errors are two least-squares standard deviations. The cited yield is the weighted average with the indicated error being the two least-squares standard deviation combined with estimated uncertainties in the GC-FID response factors for biacetyl and 1,2,4,5-tetramethylbenzene of ±10% and ±5%, respectively. Assumption of 30% biacetyl formation from OH + 3-methyl-3-hexene-2,5-dione leads to the biacetyl concentrations corrected for secondary formation (● in Figure 4), and least-squares analyses of these data results in biacetyl formation yields at average NO_2 concentrations of 1.9×10^{13} and 10.2×10^{13} molecules cm^{-3} of 10.5% and 7.7%, respectively.

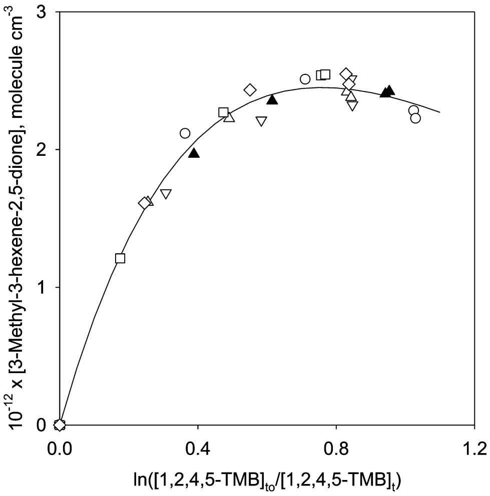


Figure 2. Plot of the amounts of 3-methyl-3-hexene-2,5-dione measured during OH + 1,2,4,5-tetramethylbenzene (1,2,4,5-TMB) reactions against the extents of reaction, defined as ln([1,2,4,5-tetramethylbenzene]$_{t_0}$/[1,2,4,5-tetramethylbenzene]$_t$) [eq II]. The differing symbols refer to the 6 experiments carried out (○, △, ▲, in the presence of 1,3,5-trimethylbenzene; ▽, □, ◇, in the absence of 1,3,5-trimethylbenzene). The solid line is the fit to eq II with $A = 1.27 \times 10^{13}$ molecules cm^{-3} and $B = (k_5[OH] + k_6)/k_4[OH] = 1.70$. 1,2,4,5-Tetramethylbenzene and 3-methyl-3-hexene-2,5-dione were measured from GC-FID analyses of samples collected onto Tenax solid adsorbent (see text).

detailed reaction mechanism[12]). As noted above, experiments were carried out at initial CH_3ONO and NO concentrations of ~2.4×10^{14} and ~4.8×10^{13} molecules cm^{-3} each. Plots of the amount of 3-methyl-3-hexene-2,5-dione formed, corrected for secondary reactions[19] using $k_4[OH]/(k_5[OH] + k_6) = 1.70$, against the amounts of 1,2,4,5-tetramethylbenzene reacted are shown in Figure 3. Excellent straight-line plots are obtained, indicating that the rate constant ratio $k_4[OH]/(k_5[OH] + k_6)$ is appropriate. Least-squares analyses leads to the 3-methyl-3-hexene-2,5-dione formation yields listed in Table 3, together with the average NO_2 concentrations during these two sets of experiments. As may be expected, the 3-methyl-3-hexene-2,5-dione formation yield at an average NO_2 concentration of 1.02×10^{14} molecules cm^{-3} obtained from the plot in Figure 3 (35.5%) is essentially identical to that obtained from the same data using eq II and shown in Figure 2 (35.6%).

Formation Yields of 2,4,5-Trimethylbenzaldehyde, 2,4,5-Trimethylphenol and Biacetyl from OH + 1,2,4,5-Tetramethylbenzene. 2,4,5-Trimethylbenzaldehyde, 2,4,5-trimethylphenol and biacetyl were quantified from GC-FID analyses of samples collected onto Tenax solid adsorbent. Secondary reactions with OH radicals (plus dark decay, where applicable) were taken into account as described previously,[19] using our measured rate constants for 1,2,4,5-tetramethylbenzene, 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylphenol (Table 1) and a rate constant for OH + biacetyl of 2.3×10^{-13} cm^3 molecule^{-1} s^{-1}.[4] The multiplicative correction factors F increase with the rate constant ratio k(OH + product)/k(OH + 1,2,4,5-tetramethylbenzene) and with the extent of reaction,[19] and the maximum values of F were 1.59 for formation of 2,4,5-trimethylbenzaldehyde, 2.25 for any formation of 2,4,5-trimethylphenol, and 1.003 for formation of biacetyl (and hence no corrections for loss to the measured biacetyl concentrations were made).

Plots of the amounts of biacetyl and 2,4,5-trimethylbenzaldehyde formed against the amounts of 1,2,4,5-tetramethylben-

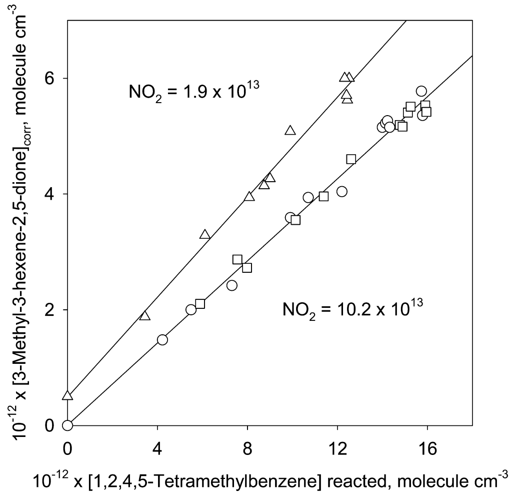


Figure 3. Plots of the amounts of 3-methyl-3-hexene-2,5-dione formed, corrected for secondary reactions (see text), against the amounts of 1,2,4,5-tetramethylbenzene reacted with OH radicals at average NO_2 concentrations of (△) 1.9 × 10^{13} molecules cm^{-3} and (○, □) 10.2 × 10^{13} molecules cm^{-3} (the NO_2 concentrations (molecules cm^{-3}) are noted in the figure) ○, 3 experiments carried out in the presence of 1,3,5-trimethylbenzene; □, △, 3 experiments each, carried out in the absence of 1,3,5-trimethylbenzene. The 3-methyl-3-hexene-2,5-dione data at an average NO_2 concentrations of 1.9 × 10^{13} molecules cm^{-3} have been displaced vertically by 5 × 10^{11} molecules cm^{-3} for clarity. 1,2,4,5-Tetramethylbenzene and 3-methyl-3-hexene-2,5-dione were measured from GC-FID analyses of samples collected onto Tenax solid adsorbent.

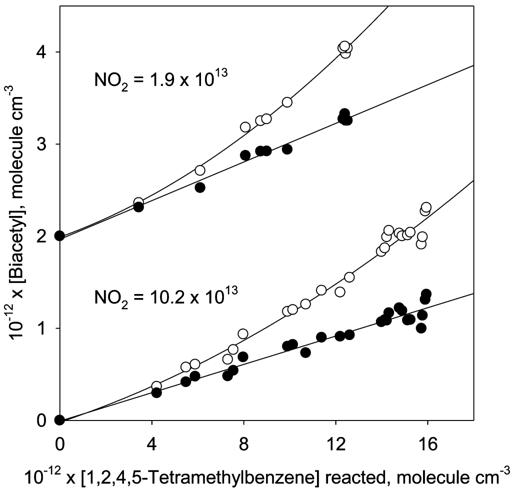


Figure 4. Plots of the amounts of biacetyl formed against the amounts of 1,2,4,5-tetramethylbenzene reacted with OH radicals at average NO_2 concentrations of 1.9 × 10^{13} molecules cm^{-3} and 10.2 × 10^{13} molecules cm^{-3} (the NO_2 concentrations (molecules cm^{-3}) are noted in the figure) ○, measured biacetyl concentrations, with the solid curves being second-order regression fits; ●, measured biacetyl concentrations corrected for secondary formation of biacetyl from OH + 3-methyl-3-hexene-2,5-dione in 30% yield, with $[\text{biacetyl}]_{\text{corr}} = [\text{biacetyl}]_{\text{measured}} - 0.3([\text{3-methyl-3-hexene-2,5-dione}]\ \text{reacted})$. The biacetyl data at an average NO_2 concentrations of 1.9 × 10^{13} molecules cm^{-3} have been displaced vertically by 2.0 × 10^{12} molecules cm^{-3} for clarity. 1,2,4,5-Tetramethylbenzene and biacetyl were measured from GC-FID analyses of samples collected onto Tenax solid adsorbent.

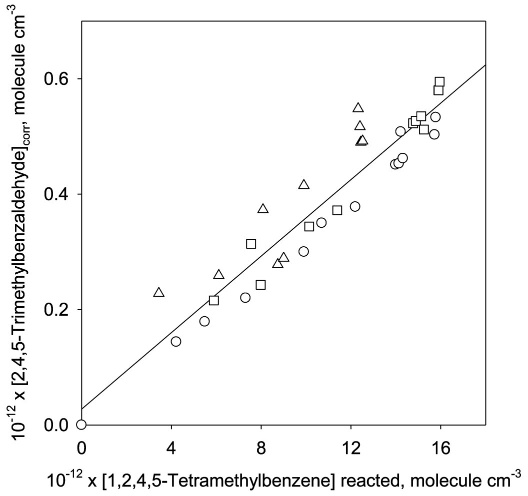


Figure 5. Plot of the amounts of 2,4,5-trimethylbenzaldehyde formed, corrected for reaction with OH radicals (see text), against the amounts of 1,2,4,5-tetramethylbenzene reacted with OH radicals at average NO_2 concentrations of (△) 1.9 × 10^{13} molecules cm^{-3} and (○, □) 10.2 × 10^{13} molecules cm^{-3}. ○, 3 experiments carried out in the presence of 1,3,5-trimethylbenzene; □, △, 3 experiments each, carried out in the absence of 1,3,5-trimethylbenzene. 1,2,4,5-Tetramethylbenzene and 2,4,5-trimethylbenzaldehyde were measured from GC-FID analyses of samples collected onto Tenax solid adsorbent.

zene reacted from irradiated CH_3ONO–NO–1,2,4,5-tetramethylbenzene–air and CH_3ONO–NO–1,2,4,5-tetramethylbenzene–1,3,5-trimethylbenzene–air mixtures are shown in Figures 4 (biacetyl) and 5 (2,4,5-trimethylbenzaldehyde). In Figure 4, the measured biacetyl concentrations are shown as the open circles, and the biacetyl yields increased with the extent of reaction and second-order regression fits are shown by the curved lines in Figure 4. It is therefore apparent that biacetyl is formed as both a first-generation product and as a second-generation product (almost certainly from OH + 3-methyl-3-hexene-2,5-dione; see Supporting Information). The initial slopes of the plots to the measured biacetyl data (the data shown as the ○ symbols in Figure 4) obtained from the second-order regression fits are listed in Table 3. As also shown in Figure 4, correcting the measured biacetyl concentrations for secondary formation from OH + 3-methyl-3-hexene-2,5-dione in a 30% molar yield (data shown by the ● symbols in Figure 4) leads to good straight-line plots with slopes similar to the initial slopes of the uncorrected data. Formation of biacetyl in ∼30% yield from OH + 3-methyl-3-hexene-2,5-dione is compatible with the simultaneous formation of ≥45% of $CH_3C(O)CH(OH)C(O)CH_3$ and/or $CH_3C(O)C(CH_3)(OH)CHO$.

The 2,4,5-trimethylbenzaldehyde formation yield obtained from least-squares analyses of the data shown in Figure 5 is given in Table 3. Note that the amounts of 2,4,5-trimethylbenzaldehyde present were low (≤4.3 × 10^{11} molecules cm^{-3}), resulting in significant experiment-to-experiment variability. However, as noted in Table 3, the 2,4,5-trimethylbenzaldehyde formation yields at average NO_2 concentrations of 1.9 × 10^{13} and 10.2 × 10^{13} molecules cm^{-3} were indistinguishable within the experimental uncertainties. As noted above, no evidence was obtained from GC-MS analyses for the formation of 2,4,5-trimethylphenol, and an upper limit to its formation yield of <3% was derived based on the areas of a peak in the GC-FID analyses of Tenax samples at the retention time of 2,4,5-trimethylphenol.

DISCUSSION

Rate Constants for OH Radical Reactions. These are the first reported rate constants for the reaction of OH radicals with 2,4,5-trimethylbenzaldehyde and 3-methyl-3-hexene-2,5-dione. Our rate constant for OH + 2,4,5-trimethylphenol is 17−24% lower than the rate constants measured by Bejan et al.,[13] who used a similar relative rate method with isoprene and 1,3-butadiene as the reference compounds. This is reasonable agreement considering the occurrence of wall losses in both studies (stated to account for 20−28% of the measured total loss rate in the Bejan et al.[13] study compared to 7−14% in the present study), and the present observation of a markedly higher dark loss rate in the presence of CH_3ONO and NO_x which was not mentioned by Bejan et al.[13] Our rate constants for 1,2,4,5-tetramethylbenzene and pentamethylbenzene agree well with those presented in graphical form by Alarcon et al.[20,21] Our rate constant for OH + 3-methyl-3-hexene-2,5-dione is a factor of 1.6−2.3 higher than those we have measured for the reactions of OH radicals with *cis*- and *trans*-3-hexene-2,5-dione,[22] consistent with the 3-position methyl group enhancing the reactivity of 3-methyl-3-hexene-2,5-dione compared to 3-hexene-2,5-dione.[6]

Our present rate constants for 1,2,4,5-tetramethylbenzene, pentamethylbenzene and 2,4,5-trimethylphenol, together with the room temperature rate constants for the overall reactions of OH radicals with benzene,[2] toluene,[2] the xylenes,[2] the trimethylbenzenes[2] and hexamethylbenzene,[7] are plotted in Figure 6 in the form $\log_{10}k$ against the sum of the electrophilic substituent constants, $\Sigma\sigma^+$ (see reference 6 for details of how the values of $\Sigma\sigma^+$ are calculated). There is a reasonable correlation between $\log_{10}k$ and $\Sigma\sigma^+$, as expected for an electrophilic reaction, and the least-squares regression fit to the data plotted is shown as the dashed line in Figure 6. While the rate constants plotted should really be those for OH radical addition, H-atom abstraction accounts for <10% of the overall reaction for benzene, toluene, the xylenes, the trimethylbenzenes and 1,2,4,5-tetramethylbenzene and hence the use of the overall reaction rate constants instead of the addition rate constants makes no significant difference (the difference would be the size of the symbols in Figure 6, or less). The correlation proposed by Atkinson[23] and Kwok and Atkinson[6] from a regression analysis of 66 aromatic compounds, of $\log_{10}k = -11.71 - 1.34\Sigma\sigma^+$ (with k being the rate constant for OH radical addition to the aromatic ring, in cm^3 $molecule^{-1}$ s^{-1} units), is shown by the solid line in Figure 6.

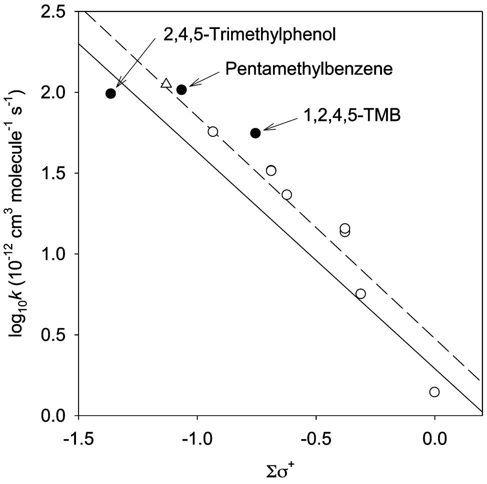


Figure 6. Plot of $\log_{10}k$ against the sum of the electrophilic substituent constants, $\Sigma\sigma^+$, where k is the overall rate constant for reaction of OH radicals with a series of aromatic hydrocarbons and 2,4,5-trimethylphenol (see text). ○, benzene, toluene, *o*-, *m*- and *p*-xylene, and 1,2,3-, 1,2,4- and 1,3,5-trimethylbenzene, with 298 K rate constants from Atkinson and Arey[2] or (the limiting high-pressure rate constant for OH + benzene) Atkinson;[3] ●, 1,2,4,5-tetramethylbenzene (1,2,4,5-TMB), pentamethylbenzene and 2,4,5-trimethylphenol, with the rate constants measured here (Table 1); and △, hexamethylbenzene, with the room temperature rate constant from Berndt and Böge.[7]

For the restricted series of aromatic compounds represented in Figure 6, the rate constants predicted from the least-squares regression line are uniformly a factor of 1.6 higher than those predicted from the correlation proposed by Atkinson and Kwok[6] and Atkinson[23] from use of a much larger database. This is within the factor of 2 uncertainty of the structure−reactivity predictions,[6] and within two least-squares standard deviations of the fit to the data shown in Figure 6 (which is a factor of 1.74 at $\Sigma\sigma^+ = 0.0$).

Products and Mechanism of OH + 1,2,4,5-Tetramethylbenzene. As shown in Scheme 1, the initial reaction of OH radicals with 1,2,4,5-tetramethylbenzene is expected[1−3] to proceed by H-atom abstraction from the substituent CH_3 groups and by addition to the aromatic ring to form two isomeric OH-aromatic adducts. Because of the symmetric nature of 1,2,4,5-tetramethylbenzene, H-atom abstraction from the CH_3 groups forms the 2,4,5-trimethylbenzyl radical, and the subsequent reactions of this radical in the presence of NO are shown in Scheme 2, leading to the formation of 2,4,5-trimethylbenzaldehyde together with a lesser amount of 2,4,5-trimethylbenzyl nitrate via reactions 7a, 7b and 8.

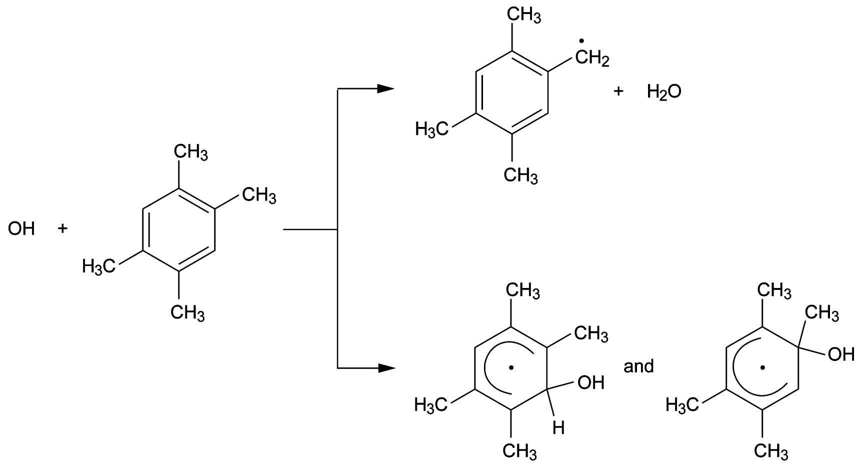
$$(CH_3)_3C_6H_2CH_2OO^\bullet + NO \rightarrow (CH_3)_3C_6H_2CH_2O^\bullet + NO_2 \tag{7a}$$

$$(CH_3)_3C_6H_2CH_2OO^\bullet + NO \rightarrow (CH_3)_3C_6H_2CH_2ONO_2 \tag{7b}$$

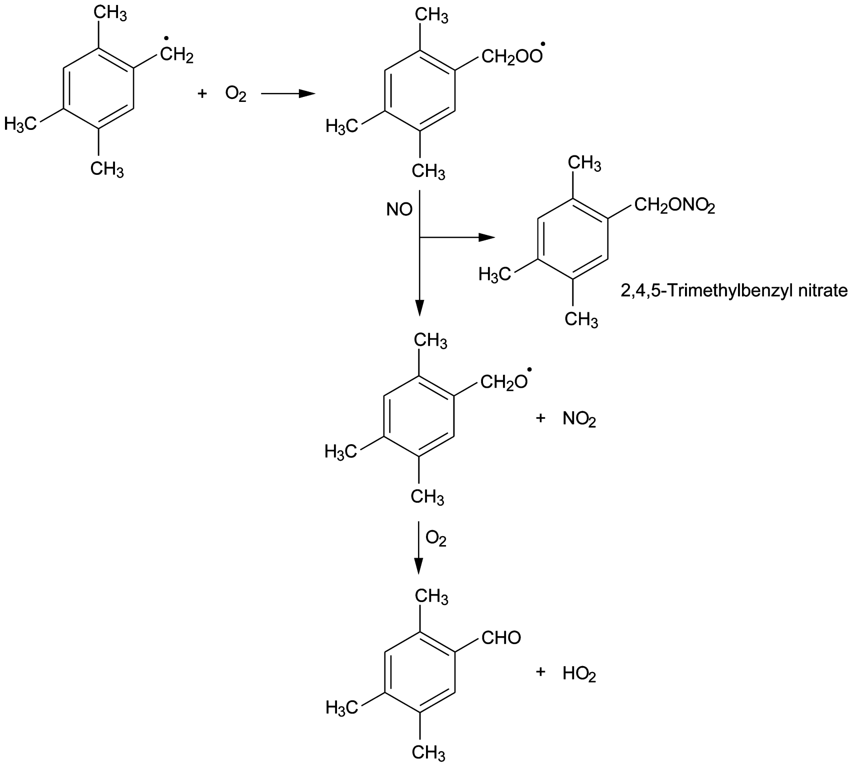
$$(CH_3)_3C_6H_2CH_2O^\bullet + O_2 \rightarrow (CH_3)_3C_6H_2CHO + HO_2 \tag{8}$$

While 2,4,5-trimethylbenzaldehyde was observed and quantified, 2,4,5-trimethylbenzyl nitrate was not observed (the lack of an authentic standard hindered analysis). However, rate constant ratios k_{7b}/k_7 [$= k_{7b}/(k_{7a} + k_{7b})$] can be derived from previously reported product yields for formation of benzyl nitrate and benzaldehyde from OH + toluene ($k_{7b}/k_7 = 0.11 \pm 0.04$[24] and 0.12 ± 0.03[12]), and methylbenzyl nitrates and tolualdehydes from the OH + *o*-, *m*- and *p*-xylene reactions (k_{7b}/k_7 = 0.23 ± 0.10, 0.16 ± 0.08 and 0.10 ± 0.03, respectively[25]). Using a weighted average of $k_{7b}/k_7 = 0.12$ (with an estimated uncertainty of ±50%), then the yield of 2,4,5-trimethylbenzyl nitrate from OH + 1,2,4,5-tetramethylbenzene is estimated to be 0.4 ± 0.2%. Combined with the 2,4,5-trimethylbenzaldehyde yield of 3.3 ± 0.7%, this results in an estimated fraction of the overall OH + 1,2,4,5-tetramethylbenzene reaction proceeding by H-atom abstraction from the CH_3 groups of 3.7 ± 0.8%. This corresponds to a partial rate constant for H-atom abstraction per CH_3 substituent group in 1,2,4,5-tetramethylbenzene of $(5.1 \pm 1.2) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 ± 2 K, a factor of ~1.5 higher than the H-atom abstraction rate constant in the OH + toluene reaction at 298 K.[4]

Scheme 1



Scheme 2

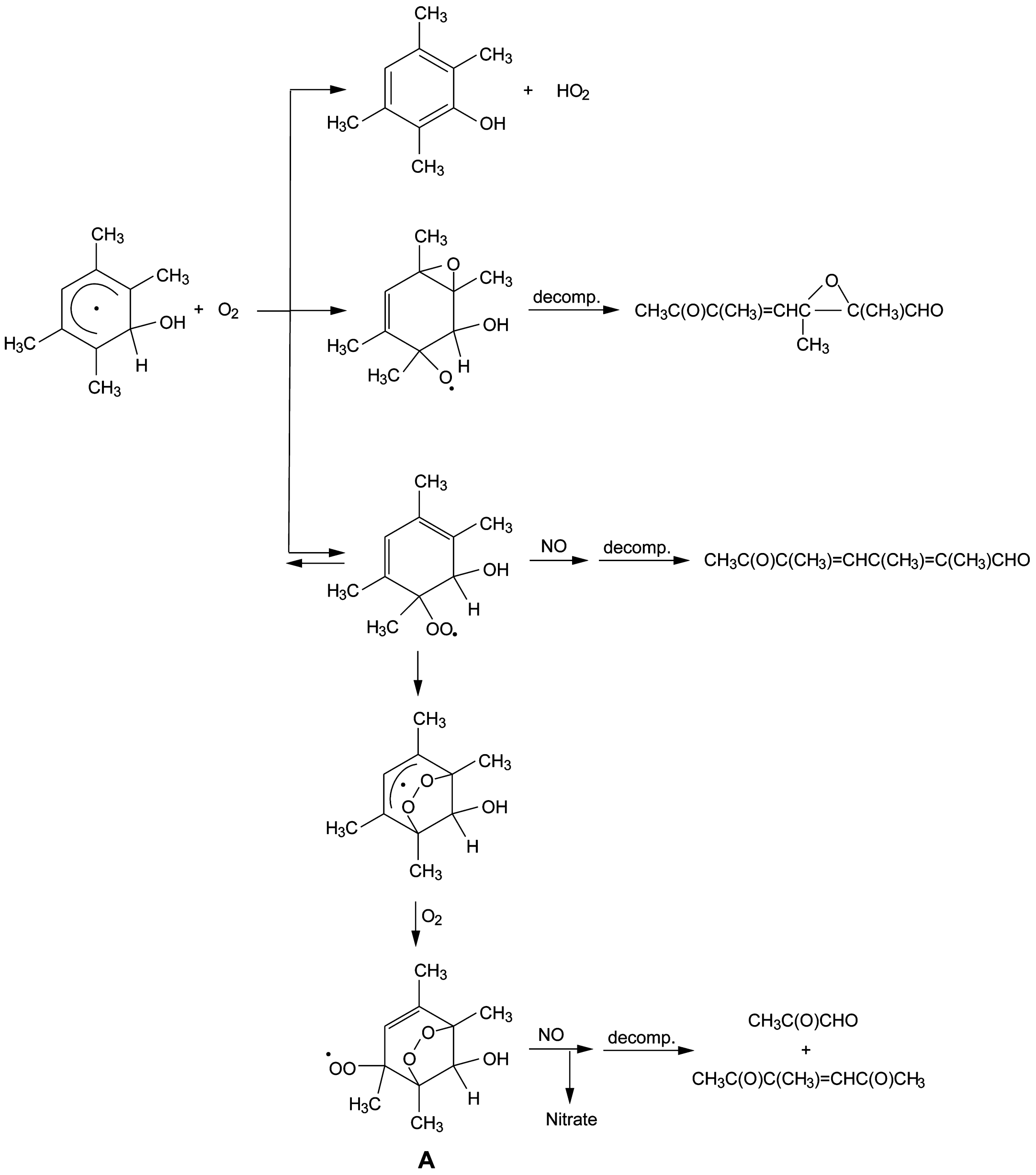


2,4,5-Trimethylbenzaldehyde

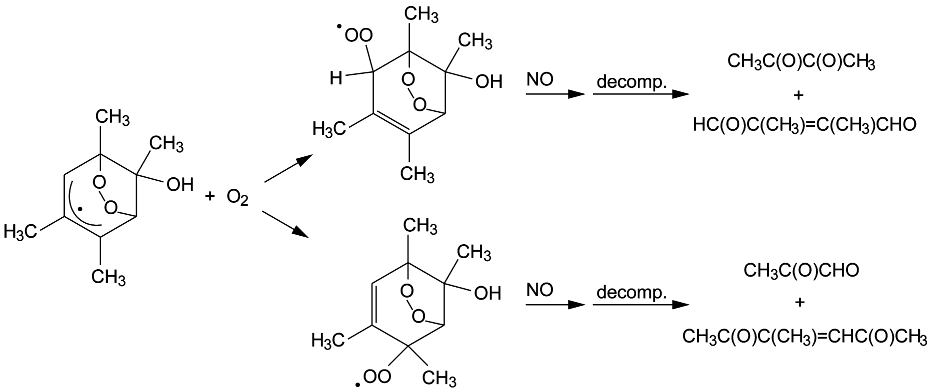
Because of symmetry, only two OH-aromatic adducts can be formed, after OH radical addition to the 1- (or 2-, 4- or 5-) position (*ipso* addition) and after addition to the 3- (or 6-) position (Scheme 1). The OH-aromatic adducts can react with O_2 and NO_2,[26] with the reaction with O_2 dominating for atmospheric conditions.[18,26] Based on literature studies,[18,27−35] the reactions of OH-aromatic adducts with O_2 appear to proceed as shown in Scheme 3 for the adduct formed after OH radical addition at the 3- (or 6-) position.

At low NO concentrations, this OH-1,2,4,5-tetramethylbenzene adduct is predicted to form 2,3,5,6-tetramethylphenol, an unsaturated epoxy-1,6-dicarbonyl, 3-methyl-3-hexene-2,5-dione + methylglyoxal, and the bicyclic nitrate formed from the minor channel of the bicyclic peroxy radical (**A** in Scheme 3) + NO reaction.[34] At higher NO concentrations, reaction of NO with the OH-1,2,4,5-tetramethylbenzene-$O_2^{\bullet}$ peroxy radical may lead to formation of a diunsaturated 1,6-dicarbonyl (Scheme 3). While lack of a standard precluded identification and quantification of 2,3,5,6-tetramethylphenol, formation yields of di- or trimethylphenols from the OH + *m*-xylene, *p*-xylene and 1,2,4- and 1,3,5-trimethylbenzene reactions are relatively low,[16,17] ranging from ∼2% for 1,2,4-trimethylbenzene to 13% for *p*-xylene. The product yields listed in Table 3 indicate that the methylglyoxal and 3-methyl-3-hexene-2,5-dione yields at 1.9 × 10^{13} molecules cm^{-3} NO_2 are similar (to within a factor of 1.2−1.4; see footnote f to Table 3) and hence suggest that methylglyoxal and 3-methyl-3-hexene-2,5-dione are coproducts. While 2,3-dimethyl-1,4-butenedial, the expected coproduct to

Scheme 3



Scheme 4



biacetyl (Scheme 4), was not observed by GC analyses, this is consistent with previous analyses of extracts of PFBHA-coated denuder samples from OH radical-initiated reactions of *o*-xylene and 1,2,4-trimethylbenzene where 2,3-dimethyl-1,4-butenedial was also not observed (noting that for these reactions 2,3-dimethyl-1,4-butenedial was not the only potential coproduct to glyoxal (*o*-xylene reaction) or methylglyoxal (1,2,4-trimethylbenzene reaction)).[9] As noted in Table 2, API MS and MS/MS analyses showed evidence for a minor product (relative to 3-methyl-3-hexene-2,5-dione, see Figure S2, Supporting Information) attributed to 2,3-dimethyl-1,4-butenedial.

The formation yield measured here for 3-methyl-3-hexene-2,5-dione increased with decreasing NO_2 concentration, as previously observed for formation of 1,2-dicarbonyls and unsaturated 1,4-dicarbonyls from other aromatic hydrocarbons.[17,18] Assuming that 1,2-dicarbonyls and unsaturated 1,4-dicarbonyls are formed only from the reaction of OH-aromatic adducts with O_2[18]

$$\text{OH-aromatic} + O_2 \rightarrow Y\,\text{dicarbonyl} + \text{other products} \tag{9}$$

$$\text{OH-aromatic} + NO_2 \rightarrow \text{products} \tag{10}$$

then

$$\text{dicarbonyl yield} = fYk_9[O_2]/(k_9[O_2] + k_{10}[NO_2]) \tag{III}$$

where k_9 and k_{10} are the rate constants for reactions 9 and 10, respectively, f (= 0.96) is the fraction of the overall OH radical reaction proceeding by OH radical addition to form the OH-aromatic adducts, and Y is the yield of the dicarbonyl being considered from reaction 9. Extrapolation of our measured 3-methyl-3-hexene-2,5-dione yields given in Table 3 to NO_2 concentrations applicable to ambient atmospheres (effectively, extrapolation to $[NO_2] = 0$) using eq III results in the formation yield fY also listed in Table 3. The NO_2 concentration at which $k_9[O_2] = k_{10}[NO_2]$ is calculated to be 3.6×10^{14} molecules cm^{-3} from the 3-methyl-3-hexene-2,5-dione data (i.e., a mixing ratio of 15 parts-per-million NO_2), of generally similar magnitude to the corresponding NO_2 concentrations at which the OH-*m*-xylene and OH-1,3,5-trimethylbenzene adduct plus O_2 and NO_2 reactions are of equal importance in air.[18,26]

The products observed and quantified here, using the 3-methyl-3-hexene-2,5-dione (extrapolated to zero NO_2 concentration) and biacetyl yields for formation of 3-methyl-3-hexene-2,5-dione plus methylglyoxal and of biacetyl plus its expected coproduct 2,3-dimethyl-1,4-butenedial, respectively, account for 57% of the overall reaction pathways and products formed from OH + 1,2,4,5-tetramethylbenzene under conditions where the OH-1,2,4,5-tetramethylbenzene adducts react with O_2. The remaining products are expected to include bicyclic nitrates, 2,3,5,6-tetramethylphenol and epoxides such as that shown in Scheme 3, with the yields of the bicyclic nitrates and 2,3,5,6-tetramethylphenol being expected to be low.[16,17,34] The lack of observation of measurable concentrations of 2,4,5-trimethylphenol shows that dealkylation via an addition−elimination reaction does not occur to any significant extent, as previously observed for the OH + *m*-xylene and OH + *p*-cymene reactions.[36]

Of particular interest is that OH radical addition to the 3- (or 6-) position leads only to the 1,2-dicarbonyl + unsaturated 1,4-dicarbonyl combination 3-methyl-3-hexene-2,5-dione + methylglyoxal (Scheme 3). As shown in Scheme 4, the analogous reactions of the bicyclic radical formed after OH radical addition to the 1- (or 2, 4- or 5-) position leads to either 3-methyl-3-hexene-2,5-dione + methylglyoxal or 2,3-dimethyl-1,4-butenedial + biacetyl.

Thus, if the combinations of 1,2-dicarbonyl + unsaturated 1,4-dicarbonyl formed by the mechanism shown in Schemes 3 and 4 are correct, formation of biacetyl from OH + 1,2,4,5-tetramethylbenzene shows that initial OH radical addition to the equivalent 1-, 2-, 4- and 5-position carbon atoms in the aromatic ring, bonded to methyl substituent groups, does occur and that addition of OH radicals to the four equivalent *ipso* positions accounts for $\geq(9 \pm 3)\%$ of the overall reaction. This conclusion then supports the kinetic analyses of OH radical decays following the pulsed formation of OH radicals in the presence of trimethylbenzenes, tetramethylbenzenes and pentamethylbenzene recently reported by Bohn and Zetzsch[37] and Alarcon et al.[20,21] In these studies, triexponential decays were observed,[20,21,37] consistent with the formation of two (or more) OH-aromatic adducts, and for OH + 1,3,5-trimethylbenzene, the tetramethylbenzenes, and pentamethylbenzene thus implies the occurrence of *ipso* addition.[20,21,37] Obviously, *ipso* addition must also occur in OH + hexamethylbenzene,[26,38] and the room temperature rate constant for OH + hexamethylbenzene[7] is consistent with the reaction proceeding primarily by OH addition to the aromatic ring (Figure 6). Recently, Loison et al.[38] have used a discharge-flow reactor with mass spectrometric detection and observed both the OD-hexamethylbenzene adduct and the pentamethylbenzyl radical, and concluded that H-atom abstraction from OH + hexamethylbenzene accounts for 11.1 ± 3.6% of the overall reaction at 298 K.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1 and S2 and reporting the results of GC-MS analyses of extracts from PFBHA-coated denuder samples from OH + 1,2,4-trimethylbenzene and OH + 1,2,4,5-tetramethylbenzene reactions, the API-MS analysis of OH + 1,2,4,5-tetramethylbenzene, and a discussion of the reaction mechanisms of OH + 3-hexene-2,5-dione and OH + 3-methyl-3-hexene-2,5-dione. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*J.A.: e-mail janet.arey@ucr.edu; telephone (951) 827-3502.
R.A.: e-mail ratkins@mail.ucr.edu; telephone (951) 827-4191.

Present Address

J.A.: Also Department of Environmental Sciences, University of California, Riverside, California 92521.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the U.S. Environmental Protection Agency (Grant R833752) for supporting this research. While this work has been supported by this Agency, the results and content of this publication do not necessarily reflect the views and opinion of the Agency. J.A. thanks the University of California Agricultural Experiment Station for partial salary support. The authors thank Prof. Cornelius Zetzsch and Dr. Paulo Alarcon (Atmospheric Chemistry Research Laboratory, University of Bayreuth, Germany) for discussions that prompted this study.

REFERENCES

(1) Calvert, J. G.; Atkinson, R.; Becker, K. H.; Kamens, R. M.; Seinfeld, J. H.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*; Oxford University Press: New York, 2002.

(2) Atkinson, R.; Arey, J. Atmospheric Degradation of Volatile Organic Compounds. *Chem. Rev.* **2003**, *103*, 4605−4638.

(3) Atkinson, R. Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds. *J. Phys. Chem. Ref. Data* **1989**, *Monograph 1*, 1−246.

(4) IUPAC, 2013. *Evaluated Kinetic Data for Atmospheric Chemistry*. IUPAC Subcommittee for Gas Kinetic Data Evaluation, http://www.iupac-kinetic.ch.cam.ac.uk.

(5) Zetzsch, C. *Predicting the Rate of OH-Addition to Aromatics using σ^+-Electrophilic Substituent Constants for Mono- and Polysubstituted Benzene*. Presented at 15th Informal Conference on Photochemistry, Stanford, CA, June 27−July 1, 1982.

(6) Kwok, E. S. C.; Atkinson, R. Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds using a Structure-Reactivity Relationship: An Update. *Atmos. Environ.* **1995**, *29*, 1685−1695.

(7) Berndt, T.; Böge, O. Rate Constants for the Gas-Phase Reaction of Hexamethylbenzene with OH Radicals and H Atoms and of 1,3,5-Trimethylbenzene with H Atoms. *Int. J. Chem. Kinet.* **2001**, *33*, 124−129.

(8) Aschmann, S. M.; Arey, J.; Atkinson, R. Kinetics and Products of the Reactions of OH Radicals with Cyclohexene, 1-Methyl-1-cylohexene, *cis*-Cylooctene, and *cis*-Cyclodecene. *J. Phys. Chem. A* **2012**, *116*, 9507−9515.

(9) Arey, J.; Obermeyer, G.; Aschmann, S. M.; Chattopadhyay, S.; Cusick, R. D.; Atkinson, R. Dicarbonyl Products of the OH Radical-Initiated Reaction of a Series of Aromatic Hydrocarbons. *Environ. Sci. Technol.* **2009**, *43*, 683−689.

(10) Scanlon, J. T.; Willis, D. E. Calculation of Flame Ionization Detector Relative Response Factors using the Effective Carbon Number Concept. *J. Chromatogr. Sci.* **1985**, *23*, 333−340.

(11) Baker, J.; Arey, J.; Atkinson, R. Rate Constants for the Gas-Phase Reactions of OH Radicals with a Series of Hydroxyaldehydes at 296 ± 2 K. *J. Phys. Chem. A* **2004**, *108*, 7032−7037.

(12) Atkinson, R.; Aschmann, S. M.; Arey, J.; Carter, W. P. L. Formation of Ring-Retaining Products from the OH Radical-Initiated Reactions of Benzene and Toluene. *Int. J. Chem. Kinet.* **1989**, *21*, 801−827.

(13) Bejan, I.; Schürmann, A.; Barnes, I.; Benter, T. Kinetics of the Gas-Phase Reactions of OH Radicals with a Series of Trimethylphenols. *Int. J. Chem. Kinet.* **2012**, *44*, 117−124.

(14) Bandow, H.; Washida, N. Ring-Cleavage Reactions of Aromatic Hydrocarbons Studied by FT-IR Spectroscopy. III. Photooxidation of 1,2,3-, 1,2,4-, and 1,3,5-Trimethylbenzene in the NO_x-Air System. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2549−2555.

(15) Tuazon, E. C.; Mac Leod, H.; Atkinson, R.; Carter, W. P. L. α-Dicarbonyl Yields from the NO_x-Air Photooxidations of a Series of Aromatic Hydrocarbons in Air. *Environ. Sci. Technol.* **1986**, *20*, 383−387.

(16) Smith, D. F.; Kleindienst, T. E.; McIver, C. D. Primary Product Distributions from the Reaction of OH with *m*-, *p*-Xylene, 1,2,4- and 1,3,5-Trimethylbenzene. *J. Atmos. Chem.* **1999**, *34*, 339−364.

(17) Bethel, H. L.; Atkinson, R.; Arey, J. Products of the Gas-Phase Reactions of OH Radicals with *p*-Xylene and 1,2,3- and 1,2,4-Trimethylbenzene: Effect of NO_2 Concentration. *J. Phys. Chem. A* **2000**, *104*, 8922−8929.

(18) Nishino, N.; Arey, J.; Atkinson, R. Formation Yields of Glyoxal and Methylglyoxal from the Gas-Phase OH Radical-Initiated Reactions of Toluene, Xylenes, and Trimethylbenzenes as a Function of NO_2 Concentration. *J. Phys. Chem. A* **2010**, *114*, 10140−10147.

(19) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. Alkyl Nitrate Formation from the NO_x-Air Photooxidations of C_2-C_8 *n*-Alkanes. *J. Phys. Chem.* **1982**, *86*, 4563−4569.

(20) Alarcon, P.; Bohn, B.; Zetzsch, C. *Rate Constants for the Reaction of OH with Durene (1,2,4,5-Tetramethylbenzene), Leading to Two Types of Adducts: Ortho und Ipso*. Presented at 22nd International Symposium on Gas Kinetics, Boulder, CO, June 18−22, 2012.

(21) Alarcon, P.; von Buttlar, J.; Bohn, B.; Koch, R.; Knispel, R.; Siese, M.; Witte, F.; Zetzsch, C. *Reversible Reactions of OH with Methylated Benzenes: Contribution of Ipso Adducts*. Presented at 22nd International Symposium on Gas Kinetics, Boulder, CO, June 18−22, 2012.

(22) Aschmann, S. M.; Nishino, N.; Arey, J.; Atkinson, R. Kinetics of the Reactions of OH Radicals with 2- and 3-Methylfuran, 2,3- and 2,5-Dimethylfuran, and *E*- and *Z*-3-Hexene-2,5-dione, and Products of OH + 2,5-Dimethylfuran. *Environ. Sci. Technol.* **2011**, *45*, 1859−1865.

(23) Atkinson, R. Atmospheric Lifetimes of Dibenzo-*p*-dioxins and Dibenzofurans. *Sci. Total Environ.* **1991**, *104*, 17−33.

(24) Hoshino, M.; Akimoto, H.; Okuda, M. Photochemical Oxidation of Benzene, Toluene, and Ethylbenzene Initiated by OH Radicals in the Gas Phase. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 718−724.

(25) Atkinson, R.; Aschmann, S. M.; Arey, J. Formation of Ring-Retaining Products from the OH Radical-Initiated Reactions of *o*-, *m*-, and *p*-Xylene. *Int. J. Chem. Kinet.* **1991**, *23*, 77−97.

(26) Koch, R.; Knispel, R.; Elend, M.; Siese, M.; Zetzsch, C. Consecutive Reactions of Aromatic-OH Adducts with NO, NO_2 and O_2: Benzene, Naphthalene, Toluene, m- and p-Xylene, Hexamethylbenzene, Phenol, m-Cresol and Aniline. *Atmos. Chem. Phys.* **2007**, *7*, 2057−2071.

(27) Klotz, B.; Sørensen, S.; Barnes, I.; Becker, K. H.; Etzkorn, T.; Volkamer, R.; Platt, U.; Wirtz, K.; Martín-Reviejo, M. Atmospheric Oxidation of Toluene in a Large-Volume Outdoor Photoreactor: In Situ Determination of Ring-Retaining Product Yields. *J. Phys. Chem. A* **1998**, *102*, 10289−10299.

(28) Volkamer, R.; Platt, U.; Wirtz, K. Primary and Secondary Glyoxal Formation from Aromatics: Experimental Evidence for the Bicycloalkyl-Radical Pathway from Benzene, Toluene, and *p*-Xylene. *J. Phys. Chem. A* **2001**, *105*, 7865−7874.

(29) Volkamer, R.; Klotz, B.; Barnes, I.; Imamura, T.; Wirtz, K.; Washida, N.; Becker, K. H.; Platt, U. OH-Initiated Oxidation of Benzene. Part I. Phenol Formation under Atmospheric Conditions. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1598−1610.

(30) Klotz, B.; Volkamer, R.; Hurley, M. D.; Sulbaek Andersen, M. P.; Nielsen, O. J.; Barnes, I.; Imamura, T.; Wirtz, K.; Becker, K.-H.; Platt, U.; Wallington, T. J.; Washida, N. OH-Initiated Oxidation of Benzene. Part II. Influence of Elevated NO_2 Concentrations. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4399−4411.

(31) Glowacki, D. R.; Wang, L.; Pilling, M. J. Evidence of Formation of Bicyclic Species in the Early Stages of Atmospheric Benzene Oxidation. *J. Phys. Chem. A* **2009**, *113*, 5385−5396.

(32) Birdsall, A. W.; Andreoni, J. F.; Elrod, M. J. Investigation of the Role of Bicyclic Peroxy Radicals in the Oxidation Mechanism of Toluene. *J. Phys. Chem. A* **2010**, *114*, 10655−10663.

(33) Birdsall, A. W.; Elrod, M. J. Comprehensive NO-Dependent Study of the Products of the Oxidation of Atmospherically Relevant Aromatic Compounds. *J. Phys. Chem. A* **2011**, *115*, 5397−5407.

(34) Elrod, M. J. Kinetic Study of the Aromatic Bicyclic Peroxy Radical + NO Reaction: Overall Rate Constant and Nitrate Product Yield Measurements. *J. Phys. Chem. A* **2011**, *115*, 8125−8130.

(35) Nehr, S.; Bohn, B.; Wahner, A. Prompt HO_2 Formation Following the Reaction of OH with Aromatic Compounds under Atmospheric Conditions. *J. Phys. Chem. A* **2012**, *116*, 6015−6026.

(36) Aschmann, S. M.; Arey, J.; Atkinson, R. 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. *Atmos. Environ.* **2010**, *44*, 3970−3975.

(37) Bohn, B.; Zetzsch, C. Kinetics and Mechanism of the Reaction of OH with the Trimethylbenzenes − Experimental Evidence for the Formation of Adduct Isomers. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13933−13948.

(38) Loison, J.-C.; Rayez, M.-T.; Rayez, J.-C.; Gratien, A.; Morajkar, P.; Fittschen, C.; Villenave, E. Gas-Phase Reaction of Hydroxyl Radical with Hexamethylbenzene. *J. Phys. Chem. A* **2012**, *116*, 12189−12197.