Oxidation of Toluene in NO$_\chi$ Free Air: Product Distribution and Mechanism

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ABSTRACT

Product distributions resulting from the oxidation of toluene in air initiated by chlorine atoms, by toluene photolysis, and by hydroxyl radicals were studied at atmospheric pressure in the absence of nitrogen oxides. In the first case only benzaldehyde and benzylalcohol with a ratio of 7.8 ± 1.7 were observed, from which a branching ratio $\alpha = 0.76 ± 0.05$ was derived for the radical propagating pathway of the self-reaction of benzylperoxy radicals. In the second and third case the apparent branching ratio decreased to $\alpha = 0.56 ± 0.07$ and $0.37 ± 0.08$, respectively, indicating the occurrence of additional reactions between benzylperoxy and other peroxy radicals. The major ring retaining products resulting from the reaction of OH with toluene were o-cresol, p-cresol, and methyl-p-benzo-quinone (57.9 ± 12.5% reacted carbon, corrected for secondary losses), in addition to 7.7 ± 1.6% benzaldehyde and benzylalcohol arising from methyl hydrogen abstraction. Formaldehyde, acetaldehyde, glyoxal, methylglyoxal, carbon monoxide, and carbon dioxide were observed as ring cleavage products (25.0 ± 7.2%). Except for CO$_2$, which appears to be an important ring cleavage product only under NO$_x$-free conditions, the distribution of ring cleavage products was similar to that found by Gery et al. (1985) in the presence of NO$_x$. Comparison of experimental data and results from computer simulations show that self-reactions of the hydroxy-methyl-cyclo-hexadienylperoxy radicals are negligible compared to internal rearrangement reactions leading to ring stabilization or ring cleavage. The mechanism of CO$_2$ production appears to require the formation of a Criegee intermediate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The principal sources of toluene in the atmosphere are emissions from automobile traffic [1,2], solvent use [3], and biomass burning [4]. Losses of toluene as well as of other aromatic hydrocarbons in the atmosphere occur predominantly by reaction with the OH radical [5]. In studies of the oxidation pathways of aromatic hydrocarbons under atmospheric conditions toluene has been the preferred test substance (see the summaries by Atkinson [5,6] and Zetzsch

[7]). The majority of these studies were performed in the presence of nitrogen oxides, which may to some extent interfere with the oxidation mechanism. For example, nitrotoluenes are formed as products [8–10]. Accordingly it was of interest to explore the product distribution in the absence of nitrogen oxides.

The reaction of OH with toluene is well known [5–7] to proceed by two pathways: one is hydrogen abstraction from the methyl group (minor), the other is addition of OH to the aromatic ring (dominant). Figure 1 summarizes current knowledge about subsequent processes. Abstraction leads to the formation of the benzyl radical, which adds oxygen to form the benzylperoxy radical. The self-reaction of benzylperoxy is expected to form benzaldehyde and benzylalcohol. In the presence of nitrogen monoxide only the aldehyde and some benzylnitrate is observed [9–11]. The OH-toluene adduct produced by addition of OH to the aromatic ring is unstable and tends to release OH. The decomposition constant at 299 K is 4.8 s^{-1} [12], so that the life time of the adduct is about 0.2 s. However, the addition of either oxygen or nitrogen dioxide to the OH-toluene adduct competes with its decomposition. The rate coefficient for the addition of oxygen is 5.5 × 10^{-16}

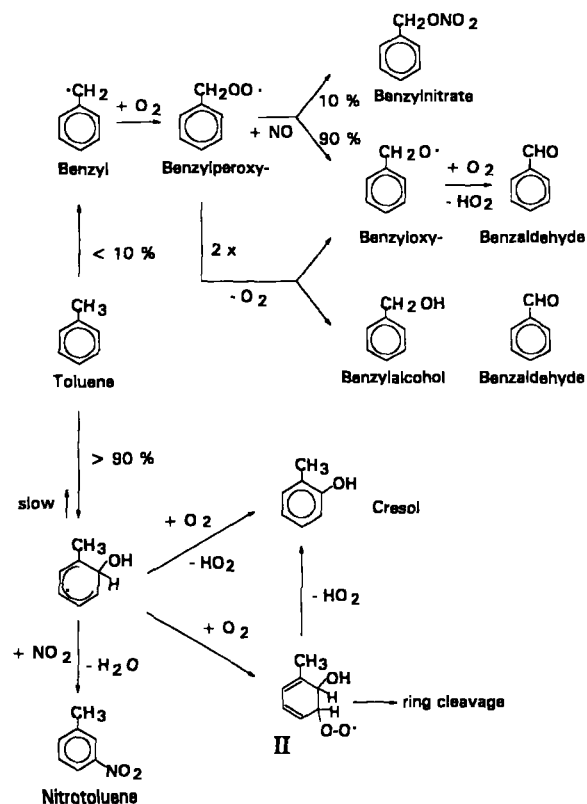cm^3 molecule^{-1} s^{-1}, that for the addition of NO$_2$ is 3.6 × 10^{-11} cm^3 molecule^{-1} s^{-1}, and that for the addition of NO is ≤3 × 10^{-14} cm^3 molecule^{-1} s^{-1} according to Koch et al. [13]. These results supersede earlier data of Zellner et al. [14]. At atmospheric pressure, and in the absence of nitrogen oxides, the addition of oxygen is almost 600 times faster than decomposition of the OH-toluene adduct. NO$_2$ becomes competitive as a stabilizer of the OH-toluene adduct when the NO$_2$ mole fraction reaches about 3 ppm. Under atmospheric conditions, with mole fractions of nitrogen oxides generally smaller than 0.1 ppm, the major initial products from the reaction of toluene with OH thus are expected to be various isomers of the hydroxy-methyl-cyclo-hexadienylperoxy (HM-CHP) radical. The reactions of these radicals are still not well known. The complexes may undergo internal rearrangement resulting in the formation of cresols as well as ring fragmentation or, under laboratory conditions, two HMCHP radicals may react with each other in a manner similar to that of cyclo-hexylperoxy radicals, whose mutual interaction produces cyclo-hexanol and cyclo-hexanone in one channel and cyclo-hexoxyl radicals in another [15]. As shown in Figure 1, oxygen may also abstract a hydrogen directly from the OH-toluene adduct instead of first adding to the ring. This pathway is known as prompt HO$_2$ and cresol formation [7,8]. Whereas cresol formation may occur both by direct H-atom abstraction and/or intramolecular rearrangement of the HMCHP radical, ring cleavage processes mandate the incipient formation of a HMCHP intermediate.

The aim of the present study was to determine the product distribution for the OH induced oxidation of toluene in air in the absence of nitrogen oxides. Chlorine atoms, which do not interact with the aromatic ring, were additionally used to generate benzylperoxy radicals without other peroxy radicals being present. This facilitated the determination of the product distribution arising from the benzylperoxy self-reaction.

EXPERIMENTAL

Apparatus and Experimental Procedures

Toluene oxidations induced by OH radicals were carried out in round glass bulbs of either 2 L or 10 L capacity as described previously [16]. Each bulb was fitted with teflon-stoppered valves and a silicone rubber septum for withdrawing samples. The bulb was first filled with H$_2$O$_2$ withdrawn from the vapor phase over an 80% aqueous solution. The

Figure 1   Identified pathways of toluene oxidation.

H_2O_2 concentration was estimated from a table of H_2O_2/H_2O vapor pressures [17] by extrapolation from temperatures in the range 303–333 K to the temperature used (296 ± 2 K). A gas mixture of toluene in synthetic air was prepared in a static gas handling system and was added to hydrogen peroxide in the bulb to reach a total pressure slightly exceeding atmospheric. Pressures were determined with capacitance manometers.

Hydroxyl radicals were generated photochemically from H_2O_2 by means of 254 nm Hg resonance radiation. The reaction was started by inserting a lit Penray mercury lamp in a quartz finger reaching into the center of the bulb. Specialty quartz was used to block ozone-forming radiation (≤235 nm wavelength). The usual irradiation period was 15 min. Subsequently, the bulb was connected to the sample loop of a gas chromatograph by means of a thin teflon tube pushed toward the center of the bulb through a hole pierced in the septum.

Toluene oxidation induced by reaction with chlorine atoms was carried out in a 400 cm^3 glass cylinder (17 cm length, 5.5 cm diameter), which was filled with air at atmospheric pressure containing about 0.1% of toluene and chlorine each. A XeF Excimer laser provided a 380 mJ (20 ns) pulse of radiation at 351 nm wavelength. About 10% of the energy was absorbed to generate an initial Cl concentration of 3.0×10^{14} atom cm^{-3}. Following irradiation, the glass vessel was connected to the sample loop of the gas chromatograph as described above.

Analyses

Ring-containing products were quantified with a flame ionization detector after separation on a 60 m long capillary column, 0.53 mm i.d., 1.1 μm film thickness (dimethylpolysiloxane, Rtx-1 Restek). The column temperature was raised from 50°C to 220°C in four steps within 32 min. The dominant products eluted within 15 min, however. Mass spectrometry was used to assist in peak identification. Carbon monoxide and carbon dioxide were separated on a column of graphitized molecular sieve at 120°C (isothermal), reduced to methane on a nickel catalyst at 365°C and then detected by flame ionization.

Additionally, high performance liquid chromatography (HPLC) was used to determine carbonyl compounds present in the reaction mixture. The concentration and derivatization procedure was similar to one described previously [18]. About half the contents of the reaction bulb was withdrawn through a series of two C18 cartridges (6 cm^3) impregnated with (purified) 1,4 dinitrophenylhydrazine solution.

The second cartridge served to check on the collection efficiency, which for acetaldehyde and benzaldehyde was found to be better than 98%. A third impregnated but unexposed cartridge provided a blank. The derivatization products were eluted with 4 cm^3 acetonitrile and the solution thus obtained was subjected to HPLC with detection by absorption at 365 nm wavelength.

Peak calibration was performed with gaseous as well as liquid samples, as far as possible. Gaseous samples were prepared by successive dilution of gas mixtures based on pressure measurements using capacitance manometers and assuming the ideal gas law to hold. Liquid samples were prepared by dissolving and further diluting small amounts of substances in either isopropanol (gc) or 2 molar hydrochloric acid (HPLC). There was good agreement in most cases, but signals produced by liquid samples were found more reproducible. In particular, there was excellent agreement and nearly 100% recovery when acetaldehyde and benzaldehyde were determined by both gas chromatography and HPLC. Gas mixtures of cresols were difficult to prepare because of low saturation pressures, and the dilution procedure gave a larger scatter. No problems were experienced with cresols in liquid samples. In order to facilitate the analysis of reaction product distributions, standard liquid mixtures containing up to six substances were prepared and used to derive peak response factors relative to toluene in gas chromatography, and relative to benzaldehyde in HPLC. In this way, it was possible to minimize calibration errors to less than 5% of the true concentration.
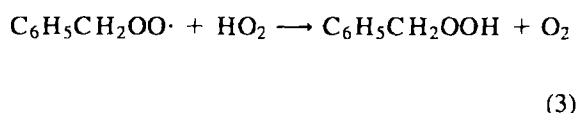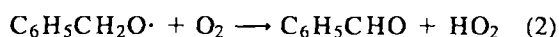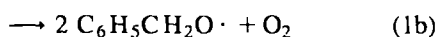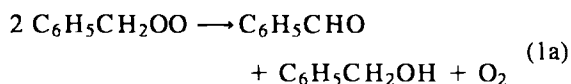
RESULTS

Oxidation of Toluene Initiated by Chlorine Atoms

Experiments with chlorine atoms were carried out because they are expected to react almost exclusively by abstraction of a hydrogen atom from the methyl group of toluene [19]. Indeed, the only products observed in these experiments were benzylalcohol and benzaldehyde, which are the products expected to arise from the self-reaction of benzylperoxy radicals. Up to three laser pulses were applied in each experiment. The concentrations of both benzaldehyde and benzylalcohol rose essentially proportionally with the number of pulses applied to reach mole fractions of about 16 ppm and 2.6 ppm, respectively, after the third pulse. However, the yield of benzylalcohol obtained after the first pulse was quite small and carried a large analytical error. The results from six

experiments were averaged to give 5.42 ± 0.14 ppm per pulse for benzaldehyde and 0.73 ± 0.17 ppm per pulse for benzylalcohol. The average ratio for the two compounds was 7.8 ± 1.7 from all data and 7.3 ± 1.6, if only data from the application of two and three pulses were used.

The interaction of benzylperoxy radicals involves the following reactions

$$2 \, C_6H_5CH_2OO \longrightarrow C_6H_5CHO$$
$$+ \, C_6H_5CH_2OH + O_2 \qquad (1a)$$

$$\longrightarrow 2 \, C_6H_5CH_2O \cdot + O_2 \qquad (1b)$$

$$C_6H_5CH_2O \cdot + O_2 \longrightarrow C_6H_5CHO + HO_2 \qquad (2)$$

$$C_6H_5CH_2OO \cdot + HO_2 \longrightarrow C_6H_5CH_2OOH + O_2$$
$$\qquad (3)$$

the ratio of the rate coefficient for the radical propagating channel to the total rate coefficient for reaction (1) is

$$\alpha = k_{1b}/(k_{1a} + k_{1b})$$
$$= ([C_6H_5CHO] - [C_6H_5CH_2OH]) \qquad (1)$$
$$/([C_6H_5CHO] + [C_6H_5CH_2OH])$$

and can be calculated from the observed yields of benzaldehyde and benzylalcohol as $\alpha = 0.76 \pm 0.05$ from all data, or $\alpha = 0.74 \pm 0.04$, if only data from the application of two or three pulses are used.

Photooxidation of Toluene

The 254 nm radiation employed to generate OH radicals from H_2O_2 is also absorbed by toluene, and precautions must be taken to ensure that photooxidation products do not interfere with products resulting from the reaction of toluene with OH radicals. The absorption cross section of gaseous toluene at 254 nm wavelength was measured at room temperature with a monochromator setup (0.1 nm spectral resolution), an absorption cell of 975 cm path length, and a toluene concentration of 2.85×10^{15} molecule cm^{-3} to be $\sigma = 4.0 \times 10^{-19}$ cm^2 molecule^{-1}. This is comparable to the absorption cross section for H_2O_2 at the same wavelength, which is $\sigma = 7.4 \times 10^{-20}$ [19]. However, the photooxidation of toluene is relatively ineffective, because product quantum yields are small.

The quantum yield for the loss of toluene was determined from the photolysis constant, defined by $k_{phot} = (1/\Delta t)\ln[Tol]_0/[Tol]$, which was obtained by measuring the decrease of toluene concentration [Tol] as a function of time Δt. Initial

concentrations $[Tol]_0$ were varied in the range $(0.2-1) \times 10^{17}$ molecule cm^{-3}, irradiation times ranged from 15 min to 3 h. Five runs were carried out. Each exhibited the expected exponential decrease of toluene concentration with time, but the individual photolysis constants showed an unexpectedly large scatter (within a factor of two). The average value was $k_{phot} = (1.6 \pm 0.5) \times 10^{-5}$ s^{-1}. The quantum yield was calculated from the relation $\Phi = k_{phot}/(I_0 \sigma r V^{-1})$, where $I_0 \approx 3 \times 10^{17}$ photon s^{-1} denotes the photon flux, $r = 8.1$ cm the radius of the reaction vessel, and $V = 2250$ cm^3 its volume. A quantum yield of $\Phi = 0.032 \pm 0.010$ was obtained.

Products that were observed in the absence of H_2O_2 as well as in its presence were benzaldehyde, benzylalcohol, ortho-cresol, para-cresol, methyl-p-benzoquinone, and an unidentified product that will be characterized further below. Photooxidation also produced meta-cresol, which was not observed in the presence of H_2O_2 (see below). The total production rate for these compounds, determined by gas chromatography in conjunction with the measurements of the photolysis constant, was $(2.3 \pm 0.2) \times 10^{-6}$ s^{-1}, on average, as obtained from 12 individual measurements in three runs. This value corresponds to about 15% of total toluene consumption. The majority of products appear to be fragments resulting from ring opening processes. Figure 2 compares chromatograms obtained in the absence and presence of H_2O_2 for similar degrees of toluene conversion to show that photooxidation produces a large number of substances eluting at retention times shorter than 9 min, prior to the elution of toluene. Among the substances identified were acetylene, benzene, furan, methylfuran, furfural, methylfurfural, and pyruvic acid. None of these compounds were found when H_2O_2 was present.

Product concentrations of benzaldehyde, benzylalcohol, and methyl-p-benzoquinone rose linearly with time. The data for o- and p-cresol were more scattered, and in one run an induction period for o-cresol was indicated. The detection of meta-cresol required extended irradiation times ($t \geq 1\frac{1}{2}$ h). Accordingly, a full distribution of ring-retaining products quantified by gas chromatography was possible in only 5 out of 16 analyses. This distribution was: benzaldehyde 0.401 ± 0.017, benzylalcohol 0.127 ± 0.018, o-cresol 0.226 ± 0.020, p-cresol 0.073 ± 0.021, m-cresol 0.018 ± 0.006, methyl-p-benzoquinone 0.098 ± 0.021, and unidentified product 0.078 ± 0.006. Product ratios for ortho-, meta-, and para-cresols were $0.720:0.055:0.225$, or about $14:1:4$. The average ratio for the sum of
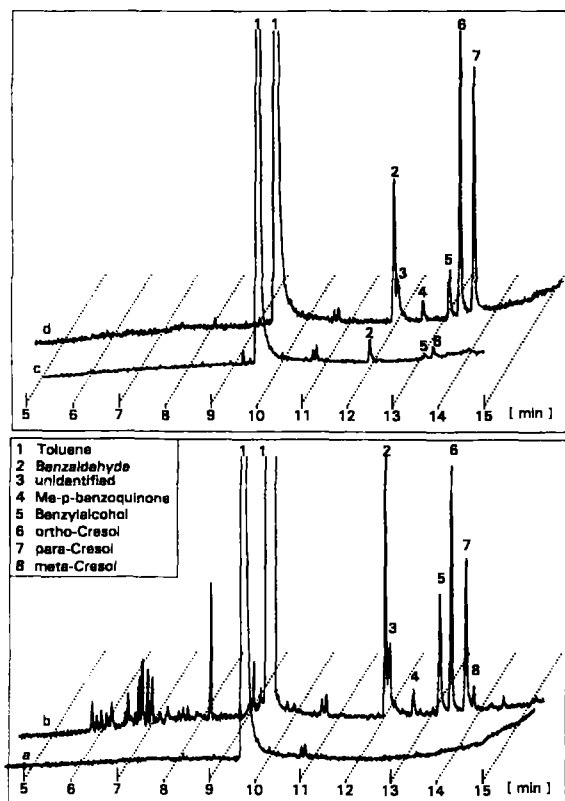
Figure 2 Chromatograms of (a) toluene-air mixture not irradiated; (b) toluene-air mixture irradiated for 2 h; (c) toluene-air mixture irradiated for 15 min; and (d) toluene-H$_2$O$_2$-air mixture irradiated for 15 min. Peak assignment: 1 toluene, 2 benzaldehyde, 3 unidentified, 4 methyl-p-benzoquinone, 5 benzylalcohol, 6 o-cresol, 7 p-cresol, and 8 m-cresol.

benzaldehyde and benzylalcohol to that of the cresols was 1.71 ± 0.35, indicating that the photolysis of toluene generates benzylperoxy radicals in excess of that of other ring-retaining radicals. The ratio of benzaldehyde to benzylalcohol was 3.72 ± 0.78. The corresponding value for α, the branding ratio for the radical propagating channel of the self-reaction of benzylperoxy radicals, would be α = 0.56 ± 0.07, if one assumes that other reactions do not interfere. The value is smaller than that obtained when benzylperoxy radicals were produced by reaction with chlorine atoms.

Toluene Oxidation Initiated by OH Radicals

The photolysis constant observed for toluene photo-decomposition was by an order of magnitude smaller than that for OH formation from photolysis of H$_2$O$_2$, which in 2 L vessels was estimated as about 1.6 × 10^{-4} s^{-1}.

Accordingly, it was sufficient to work with a toluene concentration somewhat smaller than that of H$_2$O$_2$ in order to largely suppress the photolysis of toluene in the presence of H$_2$O$_2$. Most experiments were performed with toluene/H$_2$O$_2$ concentration ratios of 0.6–0.7. Under these conditions the toluene photolysis products contributed about 4% to the yield of ring-retaining products. The largest contribution from toluene photolysis occurred in the case of benzaldehyde; this compound required a correction of its yield in the order of 10%. In working with an excess of H$_2$O$_2$ the OH radicals were not completely scavenged by toluene, and losses due to their reaction with H$_2$O$_2$ had to be tolerated. From the known rate coefficients for both reactions ($k_{(OH+Tol)}$ = 6.4 × 10^{-12} and $k_{(OH+H2O2)}$ = 1.7 × 10^{-12}, units: cm^3 molecule^{-1} s^{-1}) we calculated that OH radicals react to about 75% with toluene, and to 25% with H$_2$O$_2$ under our conditions. Additional losses of OH radicals occurred due to reactions with products (see below).

Ten runs were carried out in 2 L bulbs, and an additional 5 runs in 10 L bulbs. In the first case the mole fractions of toluene and H$_2$O$_2$ in air were kept at about 800 and 1200 ppm, respectively, and the irradiation time was 15 min. In the second case the mole fraction of toluene was varied between 975 and 1380 ppm, that of H$_2$O$_2$ was varied between 1700 and 2280 ppm, and the [H$_2$O$_2$]/[Tol] ratio was varied between 1.4 and 1.7. In these experiments, in order to achieve a comparable degree of conversion, the irradiation period was partly increased to 30 min. The evolution of products with time was essentially linear for irradiation periods up to 20 min in 2 L bulbs and up to 40 min in 10 L bulbs. Table I compares averaged distributions of products determined by gas chromatography in both series of runs to show that the size of the reaction bulb has no influence on the product distribution. It was further verified that [H$_2$O$_2$]/[Tol] mixtures were stable in the dark (no product evolution), and that the product composition

Table I Relative Yields of Products Determined by Gas Chromatography in Bulbs of 2 L and 10 L Volume

Compound	2 L Bulb[a]	10 L Bulb[b]
Benzaldehyde	0.087 ± 0.013	0.082 ± 0.020
Benzylalcohol	0.041 ± 0.007	0.040 ± 0.008
o-Cresol	0.561 ± 0.041	0.563 ± 0.027
p-Cresol	0.192 ± 0.031	0.201 ± 0.029
Me-p-Benzoquinone	0.075 ± 0.016	0.055 ± 0.018
Unknown Substance	0.056 ± 0.011	0.059 ± 0.016

[a] Average of 10 runs.
[b] Average of 5 runs.

after irradiation did not change with time for at least 2 h. The amounts of products never reached values approaching saturation pressures; and there was no indication that wall adsorption of condensable products played any appreciable role.

The major products observed in all experiments by means of gas chromatography were benzaldehyde, benzylalcohol, o-cresol, p-cresol (but not m-cresol), and methyl-p-benzoquinone. In addition, an unidentified peak of a ring-retaining compound occurred at a retention time slightly exceeding that of benzaldehyde (see Fig. 2). The mass spectrum of the unidentified compound is shown in Figure 3 together with the spectra for benzaldehyde and methyl-p-benzoquinone. The mass spectrum of the unidentified compound resembled that of methyl-p-benzoquinone, although the peak at 82 daltons was missing; the parent peak was weak and occurred at 124 rather than 122 daltons as for methyl-p-benzoquinone. Tentatively, we have assigned the gc peak to 3-methyl-4-hydroxy-2,5 cyclohexadienone. A response factor similar to that for benzaldehyde was used to assess the contribution from the unknown compound to the total product yield.

Five runs were performed, in which carbonyl compounds that were difficult to analyze by means of gas chromatography were extracted from the gas mixture for analysis by HPLC. In another five runs, an analysis was carried out for CO and CO_2. The consumption of toluene was also determined in each run, and this quantity was used to estimate absolute product yields defined by $\Delta[prod]/\Delta[Tol]$. Individual

Figure 3 Mass spectra of (top) benzaldehyde; (center) unidentified compound, peak No. 3 in Figure 2; and (bottom) methyl-p-benzoquinone.

product yields were averaged and the results are shown in Table II. The first column of this table presents the mole fraction distribution of products within each class of substances: ring-retaining compounds, small carbonyl compounds, and CO and CO_2. The second column shows absolute yields derived for each of the three classes of compounds relative to toluene consumption (percent of reacted carbon). The third column presents the contribution of each quantified product to the total product yield. The fourth column shows yields obtained after correction for losses by secondary reactions with OH radicals (see below).

While Table II describes the most complete set of data obtained under similar experimental conditions, additional runs were performed with analysis only of ring-retaining products to explore the effect of changing the $[Tol]/[H_2O_2]$ ratio. An increase of this ratio to values exceeding unity decreased the yield of cresols compared with benzaldehyde due to the increasing importance of toluene photolysis. Decreasing the ratio to $[Tol]/[H_2O_2] \approx 0.2$ did not result in significant changes in product yields. For example, the average yields of ortho- and para-cresols in % reacted carbon for $[Tol]/[H_2O_2] = 0.45$ obtained in four runs were 19.2 ± 6.7 and 5.9 ± 2.7, respectively, whereas the average for $[Tol]/[H_2O_2] = 0.67 \pm 0.7$ in 25 runs (including those used here for presentation) was 25.6 ± 10.8 and 8.8 ± 3.4, respectively. The data may indicate a slight increase of yield with increasing $[Tol]/[H_2O_2]$ ratio, but the differences are statistically not significant.

The extent of toluene conversion was about 6%, on average. Individual values for the yield of ring-retaining products generally varied between 40% and 80%, two extreme values were 31% and 116%. The average yield obtained using all data in Table VI except the two extremes was 56.0 ± 12.3 percent. Inclusion of the two extreme values would have raised the yield only slightly (to 58.4 ± 20.6 percent), but the statistical variance would have increased considerably. The total yield for the carbonyl compounds was 12.0 ± 4.4 percent, and that for the carbon oxides was 13.0 ± 3.2 percent. The yield of quantified products thus amounted to a total of 81 ± 20 percent. A total yield of 81% suggests that most, though not all, of the products were accounted for. The relatively large range of error is mainly due to keeping the degree of toluene conversion small, which caused larger errors in its determination.

The measured consumption of toluene $\Delta[Tol] = [Tol]_o\{1 - \exp(-k_{OH+Tol}[OH]_{ss}\Delta t)\}$ can be used to estimate the mean OH concentration during an
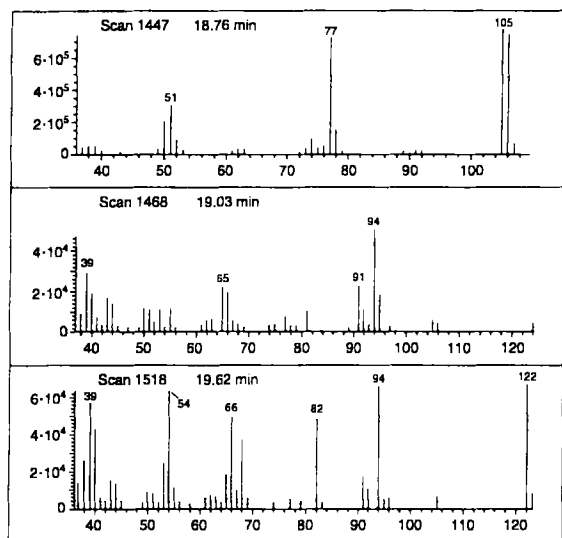
Table II Oxidation of Toluene Initiated by OH: Average Mole Fraction Distribution for Three Classes of Products; Percent Reacted Carbon for Each Class and for Individual Products

Product	Mole Fraction (%) For Each Class of Products	Product Distribution (% Reacted Carbon)		
		Total for Each Class of Products	Individual Products	Corrected for Secondary Losses[a]
Benzaldehyde	8.8 ± 1.2	ring-retaining	4.94 ± 1.06	5.3 ± 1.1
Benzylalcohol	4.2 ± 0.7		2.33 ± 0.50	2.4 ± 0.5
o-Cresol	54.6 ± 2.2	0.56 ± 0.12	30.58 ± 6.55	38.5 ± 8.3
p-Cresol	19.8 ± 2.3	n = 13	11.10 ± 2.38	14.4 ± 3.1
m-Cresol	–		≤0.4	–
Me-p-Benzoquin.	6.9 ± 1.7		3.89 ± 0.83	5.0 ± 1.1
Unknown Subst.	5.7 ± 1.2		3.16 ± 0.64	4.1 ± 0.9
Formaldehyde	32.9 ± 10.4		2.06 ± 0.69	2.2 ± 0.7
Acetaldehyde	8.9 ± 0.7	0.12 ± 0.04	1.10 ± 0.37	1.2 ± 0.4
Glyoxal	31.3 ± 5.5	n = 5	3.87 ± 1.29	4.1 ± 1.4
Me-Glyoxal	26.9 ± 5.5		4.96 ± 1.65	5.5 ± 1.8
CO	31.1 ± 5.6	0.130 ± 0.032	4.04 ± 0.99	3.5 ± 1.0
CO$_2$	68.9 ± 5.6	n = 5	8.96 ± 2.21	8.7 ± 2.2
Total Yield			81.0 ± 19.2	95.0 ± 23.5
Δ[Prod]/Δ[Tol]			81.0 ± 19.8	

[a]Losses due to reaction with OH radicals.

experiment from

$$[OH]_{av} = (k_{OH+Tol}\Delta t)^{-1} \log\{1 - [Tol]/[Tol]_0\}$$

(2)

For runs carried out with the 2 L bulb the OH concentration was calculated as $[OH]_{av} \approx (1.25 \pm 0.5) \times 10^7$ molecule cm^{-3} (average from ten runs). Alternatively, one can calculate the steady-state concentration of OH from the known light flux, the absorption cross sections of hydrogen peroxide and toluene, and the rate coefficients for the reactions of OH with H_2O_2 and toluene from the expression

$$[OH]_{ss} = 2(k_{H2O2}[H_2O_2] + k_{Tol}[Tol])^{-1}(\Delta I V^{-1})$$
$$\sigma_{H2O2}(\sigma_{H2O2}[H_2O_2] + \sigma_{Tol}[Tol])^{-1}$$

(3)

where

$$\Delta I = I_0\{1 - \exp - (\sigma_{H2O2}[H_2O_2] + \sigma_{Tol}[Tol])r\}$$

The value obtained was $[OH]_{ss} \approx (2.5 \pm 2) \times 10^7$ molecule cm^{-3}, about twice that calculated from the observed loss of toluene. Consumption of H_2O_2 concentration with time cannot have been responsible for the lower OH concentration, because less than 10% of H_2O_2 was calculated to have been consumed during the 15 min irradiation period. The discrepancy may partly be due to the uncertainty associated with determining the H_2O_2 partial pressure in the presence of water vapor, so that the H_2O_2 concentration may have been smaller than estimated. However,

secondary reactions of OH radicals with products also may have contributed to a lower steady-state OH concentration, and it is therefore of interest to estimate the extent to which such losses occurred.

Rate coefficients k_{Prod} for reactions of OH with the product compounds shown in Table II are known in most cases. To correct for losses due to secondary reactions we have applied the expression

$$\Delta[Prod]/\Delta[Tol]$$
$$= f\frac{k_{Tol}\{\exp(-k_{Tol}[OH]\Delta t) - \exp(-k_{Prod}[OH]\Delta t)\}}{(k_{Prod} - k_{Tol})\{1 - \exp(-k_{Tol}[OH]\Delta t)\}}$$

(4)

were $\Delta[Prod]/\Delta[Tol]$ is the observed yield and f is the corrected yield calculated for $[OH] = 1.26 \times 10^7$ molecule cm^{-3}. Rate coefficients (units: 10^{-12} cm^3 molecule^{-1} s^{-1}) were largely taken from Atkinson [5]: toluene 6.4, benzaldehyde 12.9, benzylalcohol 7 (assumed), o-cresol 42, p-cresol 47, methyl-p-benzoquinone 47 (assumed), unknown 47 (assumed), formaldehyde 10, acetaldehyde 15.8, glyoxal 11.4, methylglyoxal 17.2, carbon monoxide 0.24 (Atkinson et al. [21]). The last column of Table II gives product yields corrected for losses due to secondary reaction with OH radicals. Losses of products due to photodecomposition may also have occurred, but these were not accounted for. Most affected by the correction are the yields of the cresols, whereas those of the carbonyl compounds are changed by less than 10%. For the carbonyl

compounds the differences between corrected and uncorrected yields can be used to estimate the amount of carbon oxides generated by reaction with OH, which produces CO from formaldehyde, glyoxal (twice) and methylglyoxal, and CO_2 from acetaldehyde and methylglyoxal. Thus, for the products CO and CO_2 the correction results in a reduction of the yield rather than a gain. The reaction of OH with acetaldehyde and methyglyoxal also results in the formation of a methyl radical, which is oxidized to formaldehyde. This was also taken into account. The differences between corrected and uncorrected yields for all products sums to a total of 14% of reacted toluene, which must be added to that of the observed yield. The percentage of OH radicals lost by secondary reactions is higher, because on a mole per mole basis the yield of carbonyl compounds is greater than that shown in column 3 of Table II, which is based on the amount of reacted toluene. We thus estimate that the consumption of OH radicals is 17% greater than it would be, if losses by secondary reactions were entirely negligible.

In a few runs the irradiation period was extended to one hour, and a search was made for products that may have resulted from secondary reactions. None of the products expected were found, in particular we did not detect hydroxy-benzaldehyde, dihydroxy-toluene isomers, and methyl-benzohydroquinone, all compounds eluting later than the cresols. The addition products that occurred eluted at times earlier than toluene and must be fragments resulting from ring cleavage. It was not possible, however, to differentiate between true products arising from the reaction of toluene with hydroxyl radicals and products originating from the photooxidation of toluene.

The ratio of benzaldehyde and benzylalcohol observed in individual runs is 2.19 ± 0.41, on average. This is smaller than the values observed either in the photooxidation of toluene or in experiments with chlorine atoms. Table III compares values for the benzaldehyde/benzylalcohol ratio obtained from the three types of experiments. The comparison includes branching ratios k_{1a}/k_{1b} and $\alpha = k_{1b}/(k_{1b} + k_{1b})$ calculated from eq. (1) with the assumption that

reactions (1) and (2) proceed without interference from other reactions. The last line of Table III gives the ratio for the sum of cresols to that of benzaldehyde and benzylalcohol. The ratio may serve as an indicator for the rate of formation, relative to that of benzylperoxy, of peroxyradical sites located at the aromatic ring. The covariance of this ratio k_{1a}/k_{1b} suggests that interaction of benzylperoxy radicals with peroxy radicals generated by OH addition to the aromatic ring, or with peroxy radicals derived from subsequent ring opening, is largely responsible for the shift in the ratio of benzaldehyde to benzylalcohol formation. The possibility of a reaction of benzyloxy radicals with hydrogen peroxide, which would have changed the ratio of benzaldehyde to benzylalcohol, was considered. In a number of experiments the H_2O_2 concentration was varied. In nine runs with an average H_2O_2 concentration of 2.9×10^{16} molecule cm^{-3}, the branching ratio ranged from 0.26 to 0.47 with an average $\alpha = 0.36 \pm 0.08$; three runs with $[H_2O_2] = 4.3 \times 10^{16}$ molecule cm^{-3} gave $\alpha = 0.36 \pm 0.04$, on average; two additional runs with $[H_2O_2] = 5.8 \times 10^{16}$ molecule cm^{-3} gave $\alpha = 0.33 \pm 0.02$. The similarity of results argues against the occurrence of a rapid reaction of benzyloxy radicals with H_2O_2 in competition with oxygen.

Computer Simulations

As outlined in the introduction, the reaction of toluene with OH is rapidly followed by addition of oxygen to the primary products. These consecutive reactions lead to the formation of benzylperoxy radicals with 7–10% probability, and HMCHP radicals with 90–93% probability. The self-reaction of benzylperoxy radicals could be isolated experimentally and the partitioning of products was determined. Peroxy radicals resulting from OH addition to the ring also are expected to react with each other and with benzylperoxy radicals. In addition they may undergo rearrangement leading on the one hand to the formation of a cresol and the release of a hydroperoxy radical, and on the other hand to ring cleavage and the corresponding products. The Harwell FACSIMILE

Table III Product Ratios and Branching Ratios for Reaction (1) Calculated for Different Experimental Conditions

| Ratio	Oxidation Induced by Cl Atom	Photooxidation of Toluene	Oxidation Induced by OH Radical
[Bzald]/[Bzalcohol]	7.82 ± 1.66	3.72 ± 0.78	2.14 ± 0.38
k_{1a}/k_{1b}	0.32 ± 0.07	0.81 ± 0.20	1.86 ± 0.58
$k_{1b}/(k_{1a} + k_{1b})$	0.76 ± 0.04	0.56 ± 0.07	0.37 ± 0.08
Σ[Cresol]/[Bzald + Bzalcohol]	0	0.61 ± 0.07	6.14 ± 1.35

computer program [22] was used to simulate these reactions and to determine the extent to which mutual interactions of peroxy radicals are consistent with the experimental data.

The dominant sites of OH addition are the ortho and para positions. Addition at the meta-position is a minor pathway; in order to facilitate the computations, addition at the meta-position was neglected. A possible addition at the ipso-position also was neglected. Even with this simplification it was still necessary to take into account the existence of five isomeric HMCHP radicals. Their structures are shown in Figure 4. We may classify these peroxy radicals as secondary or tertiary depending on whether or not the peroxy group is accompanied by a hydrogen atom on the same carbon atom. Figure 5 shows examples for pathways and products expected to result from self-reactions of secondary and tertiary peroxy radicals. Secondary peroxy radicals are modeled to behave similar to cyclo-hexylperoxy radicals, that is their self-reaction is assumed to produce an alcohol and a ketone in one channel and an alkoxyl radical in a second channel. The second pathway would be the only one available for the self-reaction of tertiary peroxy radicals. Note from Figure 5 that the hydroxyketone is expected to rearrange to form dihydroxytoluene, whereas the dihydroxy-intermediate is expected to split off water and form a cresol. The hydroxy-methyl-cyclo-hexadienyloxy radicals are assumed to undergo ring cleavage only. A detailed description of products resulting from ring cleavage was not included in the reaction scheme.

Table IV summarizes reactions and rate coefficients used in the computer simulations. The rate coefficient for the self-reaction of benzylperoxy radicals was taken from Nozière et al. [23] and combined
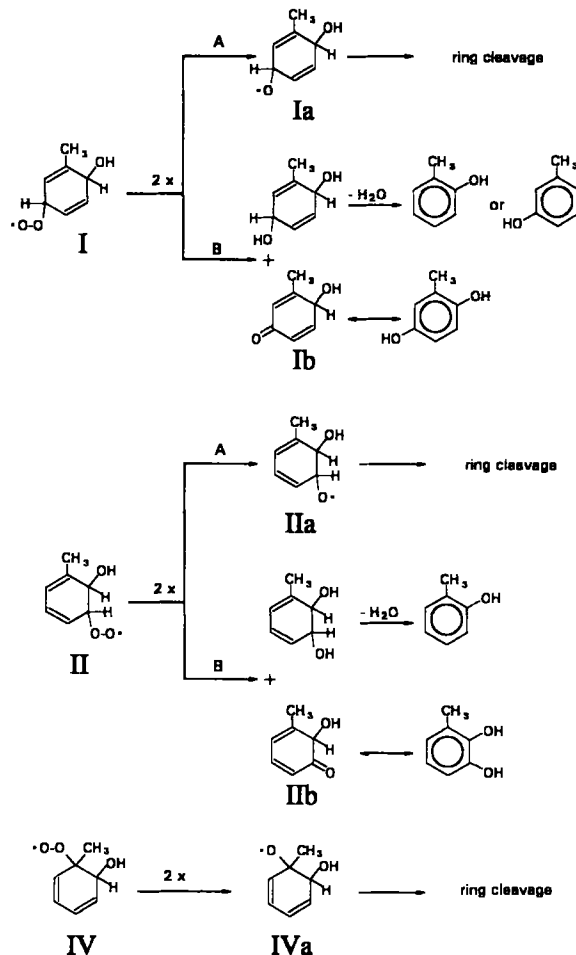
Figure 5 Examples of reactions and products expected from self-reactions of hydroxy-methyl-cyclo-hexadienylperoxy radicals.

Figure 4 Ortho- and para-isomers of the hydroxy-methyl-cyclo-hexadienylperoxy radical.

with the present value for the branching ratio. The rate coefficient for the self-reaction of secondary peroxy radicals and the associated α value were assumed to be similar to those for the reaction between cyclo-hexylperoxy radicals [15]. The rate coefficient for the self-reaction of tertiary peroxy radicals was assumed to be similar to that for t-butylperoxy radicals [15]. The rate coefficient for the cross combination reaction involving primary and tertiary peroxy radicals was taken to be similar to that between methylperoxy and t-butylperoxy radicals [15]. The following parameters were treated as variables: rate coefficient and branching ratios for the cross combination reaction involving primary and secondary peroxy radicals; the rate coefficient for the release of hydroperoxy and formation of cresol from rearrangement of HMCHP radical; and the rate coefficient ring cleavage of this intermediate. The values of these three parameters were adjusted until the calculated product distribution

Table IV   Reactions and Rate Coefficients used for Computer Simulations

Reactions		k^a
H_2O_2	$\rightarrow OH + OH$	3.0×10^{-5b}
$OH + H_2O_2$	$\rightarrow H_2O + HO_2$	1.7×10^{-12}
$OH + HO_2$	$\rightarrow H_2O + O_2$	7.0×10^{-11}
$HO + HO_2$	$\rightarrow H_2O_2 + O_2$	2.5×10^{-12}
HO_2	$\rightarrow$ losses	$10\ s^{-1}$
$OH + Tol\ (+O_2)$	$\rightarrow R_1O_2 + H_2O$	6.4×10^{-13}
$OH + Tol\ (+O_2)$	$\rightarrow o\text{-}R_2O_2$	2.83×10^{-12}
$OH + Tol\ (+O_2)$	$\rightarrow p\text{-}R_2O_2$	1.01×10^{-12}
$OH + Tol\ (+O_2)$	$\rightarrow o\text{-}R_3O_2$	1.41×10^{-12}
$OH + Tol\ (+O_2)$	$\rightarrow p\text{-}R_3O_2$	5.1×10^{-13}
$R_1O_2 + R_1O_2$	$\rightarrow$ bzald + bzalcohol + O_2	1.98×10^{-12}
$R_1O_2 + R_1O_2$	$\rightarrow$ 2 bzald + 2 HO_2	5.62×10^{-12}
$R_1O_2\ HO_2$	$\rightarrow R_1O_2H + O_2$	8.0×10^{-12}
R_1O_2H	$\rightarrow$ bzald + OH	3.0×10^{-5b}
$o\text{-}R_2O_2 + o\text{-}R_2O_2$	$\rightarrow o$-cresol + DHT + O_2	2.3×10^{-14}
$o\text{-}R_2O_2 + o\text{-}R_2O_2$	$\rightarrow$ ring cleavage products + O_2	1.9×10^{-14}
$p\text{-}R_2O_2 + p\text{-}R_2O_2$	$\rightarrow p$-cresol + DHT + O_2	2.3×10^{-14}
$p\text{-}R_2O_2 + p\text{-}R_2O_2$	$\rightarrow$ ring cleavage products + O_2	1.9×10^{-14}
$o\text{-}R_2O_2 + p\text{-}R_2O_2$	$\rightarrow o$-cresol + DHT + O_2	1.15×10^{-14}
$o\text{-}R_2O_2 + p\text{-}R_2O_2$	$\rightarrow p$-cresol + DHT + O_2	1.1×10^{-14}
$o\text{-}R_2O_2 + p\text{-}R_2O_2$	$\rightarrow$ ring cleavage products + O_2	1.9×10^{-14}
$o\text{-}R_3O_2 + o\text{-}R_3O_2$	$\rightarrow$ ring cleavage products + O_2	2.5×10^{-17}
$p\text{-}R_3O_2 + p\text{-}R_3O_2$	$\rightarrow$ ring cleavage products + O_2	2.5×10^{-17}
$o\text{-}R_3O_2 + p\text{-}R_3O_2$	$\rightarrow$ ring cleavage products + O_2	2.5×10^{-17}
$o\text{-}R_2O_2 + R_1O_2$	$\rightarrow$ bzald + o-cresol + O_2	2.7×10^{-13}
$o\text{-}R_2O_2 + R_1O_2$	$\rightarrow$ bzalcohol + DHT + O_2	2.7×10^{-13}
$o\text{-}R_2O_2 + R_1O_2$	$\rightarrow$ bzald + HO_2 + ring cleavage products	3.6×10^{-13}
$p\text{-}R_2O_2 + R_1O_2$	$\rightarrow$ bzald + p-cresol + O_2	2.7×10^{-13}
$p\text{-}R_2O_2 + R_1O_2$	$\rightarrow$ bzalcohol + DHT + O_2	2.7×10^{-13}
$p\text{-}R_2O_2 + R_1O_2$	$\rightarrow$ bzald + HO_2 + ring cleavage products	3.6×10^{-13}
$o\text{-}R_3O_2 + R_1O_2$	$\rightarrow$ bzald + o-cresol + O_2	7.0×10^{-16}
$o\text{-}R_3O_2 + R_1O_2$	$\rightarrow$ ring cleavage products + O_2	2.3×10^{-15}
$p\text{-}R_3O_2 + R_1O_2$	$\rightarrow$ bzald + p-cresol + O_2	7.0×10^{-16}
$p\text{-}R_3O_2 + R_1O_2$	$\rightarrow$ ring cleavage products + O_2	2.3×10^{-15}
$o\text{-}R_2O_2$	$\rightarrow o$-cresol + HO_2	$0.192\ s^{-1}$
$o\text{-}R_2O_2$	$\rightarrow$ ring cleavage products	$0.128\ s^{-1}$
$p\text{-}R_2O_2$	$\rightarrow p$-cresol + HO_2	$0.192\ s^{-1}$
$p\text{-}R_2O_2$	$\rightarrow$ ring cleavage products	$0.128\ s^{-1}$
$o\text{-}R_3O_2$	$\rightarrow o$-cresol + HO_2	$0.192\ s^{-1}$
$o\text{-}R_3O_2$	$\rightarrow$ ring cleavage products	$0.128\ s^{-1}$
$p\text{-}R_3O_2$	$\rightarrow p$-cresol + HO_2	$0.192\ s^{-1}$
$p\text{-}R_3O_2$	$\rightarrow$ ring cleavage products	$0.128\ s^{-1}$
$o/p\text{-}R_2O_2 + HO_2$	$\rightarrow o/p\text{-}R_2O_2H + O_2$	1.0×10^{-12}
$o/p\text{-}R_2O_2 + HO_2$	$\rightarrow o/p\text{-}R_3O_2H + O_2$	1.0×10^{-12}
$o/p\text{-}R_3O_2$	$\rightarrow OH$ + ring cleavage products	3.0×10^{-5b}
$o/p\text{-}R_2O_2$	$\rightarrow OH$ + ring cleavage products	3.0×10^{-5b}
$OH +$ bzald	$\rightarrow$ products	1.4×10^{-11}
$OH +$ bzalcohol	$\rightarrow$ products	7.0×10^{-12}
$OH + o$-cresol	$\rightarrow$ products	4.3×10^{-11}
$OH + p$-cresol	$\rightarrow$ products	4.7×10^{-11}

[a]Units: cm^3 molecule^{-1} s^{-1} unless otherwise indicated; abbreviations: R_1O_2 = benzylperoxy; R_2O_2 = secondary peroxy; R_3O_2 = tertiary peroxy; bzald = benzaldehyde; bzalcohol = benzylalcohol; and DHT = dihydroxy-toluene.
[b]Decomposition by photolysis.

resembled the observed one. Table IV includes the parameter values required to obtain this result.

Table V provides a comparison of calculated and observed product distributions. Three points must be emphasized: one is that the postulated interaction of benzylperoxy with other peroxy radicals can explain the reduction in the ratio of benzaldehyde to benzylalcohol compared to that found when chlorine atoms were used to generate benzylperoxy radicals. The ratio is determined largely by the interaction between benzylperoxy and secondary peroxy radicals. The contribution of the reaction between benzylperoxy and tertiary peroxy radicals is relatively unimportant in this regard. The second point concerns the postulated formation of dihydroxy-toluenes as indicated in Figure 5. These products have not been observed; the detection limit was less than 2% of reacted toluene, whereas a yield of about 5% was predicted by the computer simulation. It is possible that enolization of the aromatic hydroxo-keto-compound (Ib in Fig. 5) to form p-dihydroxy-toluene is not particularly efficient, and that the unidentified product (peak No. 3 in Fig. 2) corresponds to this product from the self-reaction of secondary peroxy radicals. If this were the case, the predicted and observed yields would

be in reasonable agreement. We also have not had any indication for the formation of hydroxy-methyl-cyclo-hexadienyl-hydroperoxides. They probably are unstable against a split-off of water with methyl-p-benzoquinone being one of the possible products. The computer simulation shows that the postulated self-reaction of secondary peroxy radicals must be fairly unimportant. Its contribution to the formation of both cresols and ring cleavage products is less than about 10%. This leads to the third conclusion, namely that the predominant fate of the HMCHP radical is internal rearrangement leading to ring retaining stable products such as cresols and methyl-p-benzoquinone, and ring cleavage products such as methylglyoxal, CO, and CO$_2$. Both secondary and tertiary peroxy radicals contribute about equally in these pathways. The associated rate coefficients shown in Table IV combine to a total of 0.32 s^{-1} for both pathways of internal rearrangement. The value must be viewed in relation to the rate coefficient used for the self-reaction of secondary peroxy radicals. In the kinetic equation, the term for the latter reaction involves the square of the concentration of secondary peroxy radicals, whereas the term for the rearrangement reaction contains the first power of this concentration.

Table V Comparison of Results: Computer Simulation, Experimental Data, and Data from Gery et al. [9] and Bierbach et al. [27]

Product	Percent Reacted Carbon			
	Calculated	Observed	Gery et al.	Bierbach et al.[a]
Benzaldehyde	5.4	5.0 ± 1.0	12.2 ± 2.9[b]	7.1 ± 1.8
Benzylalcohol	2.3	2.3 ± 0.5	–	+
Benzylhydroperoxide	1.2-	–	–	1.2 ± 0.3
o-Cresol	30.0	30.6	24.6 ± 4.5	+
			(30.4 ± 6.6)[c]	
p-Cresol	10.9	11.1	5.4 ± 2.7	+
			(8.8 ± 4.1)[d]	
m-Cresol	–	≤0.4	0.8 ± 0.4	+
			(3.1 ± 1.2)[e]	
Me-p-Benzoquinone	–	3.9 ± 0.1	4.5 ± 0.7	–
Dihydroxytoluene	4.9	≤2	–	–
HMCHOOH[f]	6.7	–	–	–
Formaldehyde		2.1 ± 0.7	1.4 ± 0.1	2.3 ± 0.6
Acetaldehyde		1.1 ± 0.4	–	–
Glyoxal	ring cleavage	3.9 ± 1.3	2.5 ± 0.1	3.7 ± 0.9
Me-Glyoxal	31.1	4.9 ± 1.6	4.0 ± 1.6	4.4 ± 1.1
CO		4.0 ± 0.9	3.0 ± 0.8	2.7 ± 1.4
CO$_2$		9.0 ± 2.2	–	3.5 ± 1.8
Total	92.5	81 ± 20	72 ± 17	

[a]Species detected but not quantified are indicated by a plus sign.
[b]Includes about 10% of benzylnitrate.
[c]o-cresols = [o-cresol] + 2-hydroxy-nitrotoluene] + (2/3)[m-nitrotoluene] + (2/3)[3,5,-dinitrotoluene].
[d]p-cresols = [p-cresol] + [4-hydroxy-nitrotoluene] + (1/3)[m-nitrotoluene] + (1/3)[3.5-dinitrotoluene].
[e]m-cresols = [o-nitrotoluene] + [p-[nitrotoluene].
[f]Hydroxy-methyl-cyclo-hexadienyl-hydroperoxides.

Accordingly, a change of the rate coefficient for the self-reaction by one order of magnitude would change that for the rearrangement reaction by a factor of only about three. It is probable that the rearrangement process is much faster, and in this case the mutual reactions of HMCHP radicals would be entirely negligible. In addition, a part of the rearrangement process, namely that leading to ring cleavage, may give rise to other peroxy radicals, which can also enter into either self-reactions or reactions with other peroxy radicals, among them benzylperoxy. This case was not explored by computer calculations in view of the still speculative nature of the reaction mechanisms involved.

DISCUSSION

The present results for the reaction of OH with toluene indicate that $(7.7 \pm 1.6)\%$ of the reaction proceeds by hydrogen abstraction from the methyl group. The value was obtained after corrections for the contribution of toluene photolysis products and losses due to secondary reactions of OH with benzaldehyde and benzylalcohol. Good agreement exists with results reported earlier by other investigators: Gery et al. [9] found 13 ± 4, Atkinson et al. [10] 7.3 ± 1.0, both groups in the presence of NO_x; Knispel et al. [12] and Zetzsch et al. [7] determined the rate coefficients for the abstraction and addition pathways separately and found values between 6.3% and 8% for the abstraction channel; Goumri et al. [24] determined the relative fluorescence yields for benzyl radicals formed in the reactions of toluene with OH and Cl in helium and reported a ratio of $(6 \pm 2)\%$. It is possible that the yield of the hydrogen abstraction pathway obtained here is underestimated because benzylhydroperoxide, which would have escaped detection, may have been formed by the relatively rapid reaction between benzylperoxy and hydrogenperoxy radicals.

The branching ratio for the radical propagating channel in the self-reaction of benyzlperoxy radicals, $\alpha = 0.76 \pm 0.04$, is higher than that reported recently by Nozière et al. [23], who also used Cl atoms to generate benzylperoxy radicals but infrared spectroscopy for product analysis. Their value as given in the text is $\alpha = 0.4$; however, the percentage yields of benzaldehyde (41 ± 4) and benzylalcohol (15 ± 3) suggest $\alpha = 0.46 \pm 0.11$. These authors also determined $(18 \pm 4)\%$ of the products to occur as benzylhydroperoxide. Although this compound does not enter directly in the determination of the branching ratio, it may have affected our data, if

benzylhydroperoxide, which was not determined, had decomposed in the inlet system of the gas chromatograph to form benzaldehyde. The present result therefore represents an upper limit. The apparent value of the branching ratio is considerably reduced following a change of experimental conditions, that is in the photooxidation of toluene and in the reaction with OH radicals. We attribute this effect to interference by reactions of benzylperoxy with other peroxy radicals. The results from computer simulations show that this is indeed a realistic interpretation of the data, even though the reaction mechanism used may require additions. Consequently, the true value of the branching ratio must be at least 0.56 ± 0.07, the value derived from the toluene photooxidation experiments, in order that the apparent branching ratio can be reduced to 0.37 ± 0.08, when benzylperoxy is produced by reaction of toluene with OH radicals.

Ortho- and para-cresols are major products observed in the present study of the OH initiated oxidation of toluene in NO_x-free air. Their combined yield is 41.7% of reacted toluene, or 52.9% after correction for losses due to secondary reactions with OH radicals. The results from the computer simulations indicated that the cresols are formed from the HMCHP radicals mainly by internal hydrogen abstraction and release of HO_2, or via prompt cresol formation, which was not included as a pathway in the computer calculations. Gery et al. [9], who worked with nitrous acid as a photochemical source of OH radicals, found that cresols were largely present as hydroxy-nitrotoluenes, presumably as a result of secondary reactions of cresols with nitrous acid. The (uncorrected) combined yields of cresols amounted to 24.6% o-cresol and 6.2% m- and p-cresol, on average. This corresponds to about 75% of the combined yield observed here. Atkinson et al. [10] who generated OH photochemically from methylnitrite and worked with lower concentrations of nitrogen oxides, reported yields of 20.4% o-cresol and 4.8% m- and p-cresol. In this case, a correction was applied for losses due to secondary reactions with OH radicals. Similar or somewhat smaller cresol yields were observed in earlier studies (e.g., Atkinson et al. [25] and Leone et al. [26]).

Nitrotoluenes are significant products in the presence of NO_2. They are understood to arise largely from the attachment of NO_2 to the toluene-OH adduct and consecutive release of water (see Fig. 1). This process would produce m-nitrotoluene from the ortho- and para-OH-toluene adducts, and ortho- and para-nitrotoluene from the m-OH-toluene adduct. Atkinson et al. [10] showed that the yield of m-nitrotoluene is essentially proportional

to the concentration of NO$_2$. Their yield of m-nitrotoluene for a NO$_2$ concentration of about 2.5 × 10^{14} molecule cm^3 was about 6%. If this is added to the yield of cresols, one obtains 31% yield for the sum of ring-retaining products from the OH-toluene adduct. Gery et al. [9] observed 7.4% m-nitrotoluene, 0.47% 3,5-dinitrotoluene, 0.8% o-nitrotoluene, and 2.3% p-nitrotoluene. For the present accounting purpose, we have apportioned 2/3 of m-nitrotoluene (plus 3,5-dinitrotoluene) to result from the ortho-OH-toluene adduct and 1/3 from the para-OH-toluene adduct, and we have added the corresponding yields to that of ortho- and para-cresols to obtain a total of 30.5% and 8.8%, respectively. The 3.1% yield of ortho- and para-nitrotoluenes were taken to represent the products resulting from meta-OH-toluene. The total sums to (42.4 ± 9.4)% for the combined yield of cresols and nitrotoluenes, which is similar to the yield for cresols observed here.

The percentage mole fraction distribution of ortho-, meta-, and para-cresols observed here is approximately 73:1:26, if the upper limit yield derived for m-cresol is adopted. Gery et al. [9] reported average ratios about 81:2:17. Kenley et al. [8], who had studied toluene oxidation at pressures lower than atmospheric, estimated 75:11:14. Atkinson et al. [10] did not distinguish between m- and p-cresols and reported a mole ratio 81:19 for ortho- and meta- plus para-cresol. This comparison suggests that in the absence of nitrogen oxides more p-cresol is formed at the expense of m-cresol (and o–cresol). However, the distribution of cresols may be influenced by the formation of nitrotoluenes. If the isomers of nitrotoluene are also taken into account, we estimate from the results of Gery et al. [9], with the help of the yields cited above, the ratios 72:7:21. whereas Kenley et al. [8] calculated the ratios 81:5:14. From the data of Atkinson et al. [10] we further estimate the ratios 73:7:20. Comparison with our own ratios (73:1:26) suggests again that in the absence of nitrogen oxides more ring-retaining products are formed in the para- than in the meta-position. If it can be confirmed that 5–7% of OH addition to toluene occurs in the meta-position, then the m-hydroxy-methyl-cyclo-hexadienyl radical must undergo reactions that direct the OH group toward the para-position.

The ratios of o-, m-, p-cresols observed in the photooxidation of toluene, which were approximately 72:6:22. are in better agreement with the above literature data.

Unfortunately, the mechanism of cresol formation associated with toluene photooxidation is not clear. It is possible that OH radicals are formed as interme-

diate products, and that these are responsible for the cresols. Since the major product, the benzyl radical, arises from elimination of a hydrogen atom, a large yield of HO$_2$ radicals is expected. Recombination of HO$_2$ produces H$_2$O$_2$. Its photolysis, in turn, would lead to the formation of OH. From the data given in the results section we estimate that the rate of OH production from this source is much too small to explain the yield of cresols observed. The difference in the distributions of cresol isomers in the two types of experiments thus remains unexplained.

Bierbach et al. [27] have recently studied toluene oxidation in a 1.08 m^3 chamber with OH produced by 254 nm photolysis of H$_2$O$_2$ under otherwise similar conditions as ours. Although formation of all three possible cresol isomers was identified, only the yields for o-cresol were reported (relative to that of benzaldehyde assumed to occur with 7% yield). Yields observed in the absence of NO$_x$ generally were less than 10% of reacted carbon, but the yields rose when NO$_2$ was added. Atkinson and Aschmann [28] produced OH radicals from the dark reaction of ozone with either propene or α pinene and found the cresol yield from the reaction of OH with toluene (about 1 ppm) to be 0.123 in the absence of NO$_x$, increasing to 0.160 for an average NO$_2$ concentration of 1.7 × 10^{14} molecule cm^{-3}. The results of the present study obviously are in conflict with these data, but we are unable to identify the origin of the discrepancy.

Glyoxal and methylglyoxal were observed in the present study with a total yield of (9.6 ± 3.2)% reacted carbon (corrected for losses by secondary reactions) and a mole ratio 1.13 ± 0.14. This result compares well with yields and mole ratios reported previously from experiments conducted in the presence of NO$_x$: 5.5% and 1.07 (Shepson et al. [29]), 10.3% and 1.07 (Bandow et al. [30]), 7.3% and 0.94 (Gery et al. [9]), 9.5% and 0.76 (Tuazon et al. [31]), and 13.5% and 1.13 (Dumdei et al. [11]). The similarity of results suggest that ring fragmentation is not dramatically affected by the presence of nitrogen oxides. With regard to other products, Gery et al. [9] have made a more extensive analysis than other authors, and their average product yields are included in Table V for comparison with the present results to show that their yields and ours are similar also for methyl-p-benzoquinone, formaldehyde, and carbon monoxide.

Table V includes also yields for several ring fragmentation products observed by Bierbach et al. [27] under NO$_x$-free conditions. In contrast to the discordant results for the cresols mentioned above, the yields for formaldehyde, glyoxal, and methyl glyoxal are in excellent agreement with our own data.

Bierbach et al. [27] also reported the production of CO and CO_2, although their yields were somewhat smaller than those obtained here. The total yield of identified ring cleavage products was 44.7% of reacted carbon, with formic acid (12.9%) being a major product and acetylene (0.7%) and ketene (0.5%) minor ones. In the present study, acetylene was observed to arise only in the photooxidation of toluene, not in the OH initiated oxidation.

It was frequently assumed (see for example Dumdei et al. [11] and Atkinson et al. [32]) that HMCHP radicals react with NO in a manner similar to other organic peroxy radicals (such as benzylperoxy, see Fig. 1) to produce NO_2 and an alkoxyl radical. The cyclic hydroxy-alkoxyl radicals thus formed are the same as those shown in Figure 5 as products Ia, IIa, and IVa, which are expected to undergo primarily ring cleavage. As a consequence, more ring cleavage products are expected to occur in the presence of NO compared with NO-free conditions. While the comparatively greater yield of cresols observed here for NO-free conditions appears to support this concept, the similarity of yields for the ring cleavage products formaldehyde, glyoxal, methylglyoxal, and CO provides evidence against it. However, the greater yield of cresols may partly be due to the prompt formation of cresols and HO_2 following direct abstraction of hydrogen of oxygen. The results of our computer calculations show that the self-reaction of HMCHP radicals is insufficient to account for the observed amount of ring cleavage products, and that a major part of ring cleavage must proceed via internal rearrangement of the HMCHP radical. If the rate constant for the reaction of NO with HMCHP had a magnitude similar to that of reactions between NO and other alkylperoxy radicals (about 10^{-11} cm^3 molecule^{-1} s^{-1}, Atkinson et al. [10]), a rate constant of the order of 250 s^{-1} would be required for the internal conversion process to be competitive with the reaction with NO. The rate constant for the rearrangement process estimated here is about 0.3 s^{-1}. This is a lower limit value, however. The true value may be much greater, although it should not exceed about 2.5×10^3 s^{-1}, which is an upper limit determined by the rate constant for the interaction of oxygen with the OH-toluene adduct. While it is clear that the problem cannot be settled until the rate coefficients for the reactions discussed are better known, the present data suggest that the reaction of HMCHP radicals with NO does not compete with internal rearrangement and ring cleavage reactions of this radical.

Although CO has been observed previously in toluene oxidation (Gery et al. [9], Dumdei et al. [11],

and Atkinson et al. [32]), it has usually been assumed to result from secondary reactions of products such as glyoxal or methylglyoxal. The present data indicate, however, that only a small fraction of CO is due to secondary reactions. CO_2 has not been reported to arise in the presence of NO_x but it has recently been observed by Bierbach et al. [27] in the absence of NO_x. The present data suggest that both CO and CO_2 are to a large extent primary reaction products that originate directly from ring cleavage. The fact that peroxyacetyl nitrate is found as a product in the presence of NO_x (e.g., Dumdei et al. [11] and Atkinson et al. [32]) is evidence for the formation of the acetylperoxy radical, CH_3CO. In the absence of NO_x this radical is well known to oxidize toward CO_2 and formaldehyde [15]. If CO_2 were formed mainly by this route, CO_2 and HCHO should be produced in equal yields. The present results show that at most about 2% CO_2 can be formed in this way. The remaining 6–7% must be formed via a different route. At least 30% but probably not more than 45% of the reaction leads to ring fragmentation. Thus, approximately one CO_2 molecule must be formed per reacted toluene molecule undergoing ring cleavage. This requires that during the ring cleavage process a peroxy group must rearrange toward a Criegee-type radical, which subsequently decomposes toward CO_2 and other products. The currently accepted pathway of ring cleavage (Atkinson et al. [32]) involves an oxygen bridging mechanism, followed by the addition of a second oxygen molecule as shown in Figure 6. The new peroxy group is usually assumed to lose an oxygen atom by reaction with
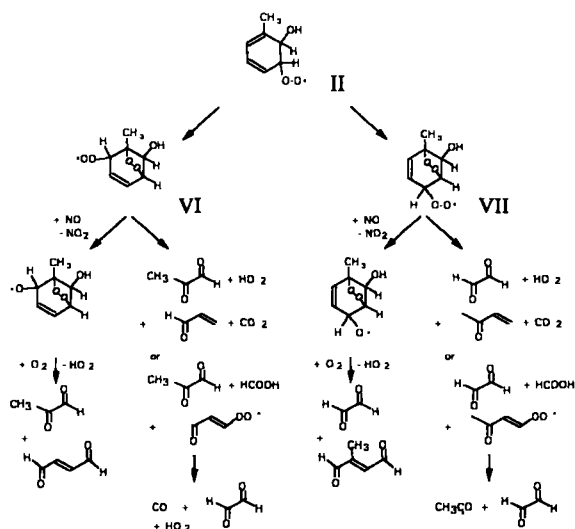
Figure 6   Possible ring fragmentation pathways resulting in the formation of CO_2 and CO.

Table VI Experimental Conditions and Product Yields (ppm Mole Fractions) for the Reaction of OH with Toluene

Initial Conditions	2 L Bulb										10 L Bulb				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Toluene [ppm]	744.8	882.0	749.0	802.0	747.0	752.0	749.0	877.0	992.0	536.0	1014.0	1252.0	975.0	1383.0	1383.0
H2O2 [ppm]	1139	1240	1118	1163	1163	1201	1142	1116	1198	745	1703	1705	1692	2277	2277
Reaction time [s]	1200	900	900	900	900	900	900	900	900	900	1800	1800	1800	1020	1020
Conversion Toluene [%]	14.07	6.37	9.58	4.82	5.65	7.03	11.1	4.88	4.28	9.29	2.61	3.03	3.46	3.39	1.54
Conversion Toluene [ppm]	104.8	56.2	71.8	38.7	42.2	52.9	83.1	42.8	42.5	49.8	26.5	37.9	33.7	46.9	21.3
Products															
Benzaldehyde	8.8	3.4	3.3	3.0	3.0	2.6	2.7	3.0	2.4	2.6	2.5	2.7	2.0	2.0	1.9
Benzylalcohol	3.5	1.2	1.2	1.6	1.4	1.3	1.2	1.4	1.2	0.9	1.0	1.2	0.9	0.9	0.9
o-Cresol	56.5	13.5	17.7	14.7	17.1	13.9	14.0	13.5	12.9	14.7	10.6	11.1	9.2	13.6	14.5
p-Cresol	17.2	2.9	7.1	5.7	6.3	4.1	6.0	4.6	3.8	5.8	3.0	4.7	3.0	4.7	5.9
Methyl-p-Benzoquinone		2.6	2.4	1.7	2.5	2.3	1.7	1.8	2.0	1.8	1.4	0.9	1.4	1.2	1.2
Unknown Product No. 3		0.8	2.1	1.6	1.7	1.1	1.8	1.4	1.0	1.7	0.7	1.7	0.9	1.3	1.5
Sum Ring Retaining Products	86.0	24.5	33.9	28.2	32.0	25.4	27.5	25.8	23.2	27.6	19.2	22.4	17.4	23.5	25.9
Formaldehyde				3.5	6.6	4.3	7.0	4.6							
Acetaldehyde				1.0	3.0	0.8	1.9	1.3							
Glyoxal				3.5	11.8	2.0	7.6	4.9							
Methylglyoxal				3.1	9.1	1.5	6.5	5.0							
CO											8.3	8.5	8.5	12.3	12.3
CO2											19.2	14.1	14.9	35.4	35.3
Sum Products	86.0	24.5	33.9	39.4	62.5	34.0	50.5	41.7	23.2	27.6	46.7	44.9	40.8	71.3	73.5

Table VII Experimental Conditions and Product Yields (ppm Mole Fractions) for the Photolysis of Toluene

Initial Conditions	1							2						3		
Toluene [ppm]	811							922						976		
Conversion Toluene [%]	9.3	10.2	13	14.8	15.8	17.5	17.9	0.04	0.35	5.18	3.18	6.09	6.07	3.6	2.1	9.2
Conversion Toluene [ppm]	75.5	82.5	106	120	128	142	145	0.37	3.23	47.8	29.3	56.1	56	35.3	20.7	89.4
Reaction Time [s]	900	1800	2700	3600	4500	5580	6540	1500	2820	4200	5700	7260	8700	1500	3000	6900
Product																
Benzaldehyde	0.62	1.44	2.16	2.73	3.37	3.81	4.27	1.42	2.8	4.23	5.42	6.59	8.41	1.97	3.26	5.26
Benzylalcohol	0.11	0.43	0.59	0.71	0.93	0.98	1.23	0.41	0.87	1.31	1.95	2.33	2.78	0.29	0.92	1.69
o-Cresol	0.32	0.89	1.41	1.77	2.07	2.41	2.44	0.76	1.56	1.92	3.27	3.77	3.83	0.71	1.87	2.29
p-Cresol	0.05	0.26	0.6	0.62	0.77	0.99	0.91	0	0.24	0.25	0.79	1.06	1.1	0	0.23	0.21
m-Cresol	0	0	0	0	0	0.25	0.25	0	0	0	0.18	0.25	0.27	0	0	0
Methyl-p-Benzoquinone	0	0	0	0.76	0.47	0.76	0.76	0	0.6	1.01	1.67	1.82	2.2	0	1.14	1.85
Unknown Product No. 3	0	0	0.33	0.46	0.7	0.76	0.9	0.23	0.46	0.72	1.1	1.15	1.47	0	0.65	0.83
	1.1	3.02	5.09	7.05	8.31	9.71	10.5	2.82	6.53	9.44	14.2	16.7	19.8	2.97	8.07	12.1

NO. The resulting alkoxyl radical is assumed to undergo decomposition. This concept has led to the proposal that equivalent amounts of methylglyoxal and butenedial or glyoxal and methylbutendial are simultaneously produced (Bandow et al. [30]). Generally, however, the butenedials were detected in less than the required amounts [11,29]). In the absence of NO, the secondary peroxy radicals VI and VII in Figure 6 are expected to be similarly unstable as the peroxy radicals shown in Figure 4. Decomposition of both peroxy radicals VI and VII would generate a Criegee radical, which undergoes further fragmentation leading at least partly to the formation of CO$_2$. Dialdehydes other than glyoxal were not detected by the derivatization method employed in the present study. Acroleine and methylvinylketone are conceivable coproducts of CO$_2$ resulting from decomposition of the Criegee radical. Neither product was detected, however. If they were formed, their yields would have been insufficient to counterbalance CO$_2$ production. Formic acid may also be formed from the decomposition of the Criegee radical, if a hydrogen atom is transferred to the Criegee group from another site. In this case an allyl radical would ensue, which would add oxygen to undergo further oxidation. Figure 6 shows conceivable products. The results of the present study clearly cannot define the details of the ring cleavage mechanism, but the results show that the presence of NO$_x$ is not a prerequisite for the occurrence of ring fragmentation.

APPENDIX

Tables VI and VII of raw data used for evaluation.

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