J. Phys. Chem. A **2000,** *104,* 8922−8929

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

Heidi L. Bethel,[†] Roger Atkinson,[*,†,‡,§] and Janet Arey[*,†,‡]

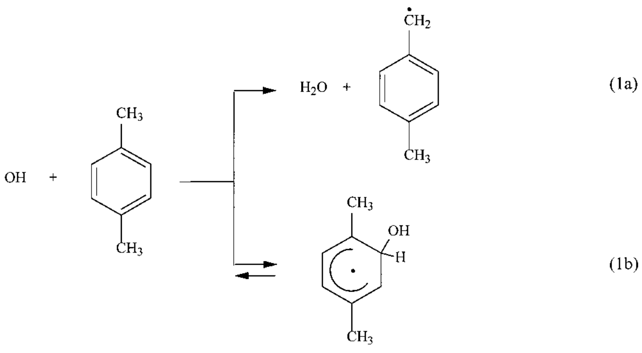
Air Pollution Research Center, University of California, Riverside, California 92521

Received: March 28, 2000; In Final Form: July 26, 2000

Products of the gas-phase reactions of the OH radical with *p*-xylene and 1,2,3- and 1,2,4-trimethylbenzene have been measured by gas chromatography in the presence of varying concentrations of NO_2. Our product analyses show that the ring-cleavage products 2,3-butanedione (from 1,2,3- and 1,2,4-trimethylbenzene) and 3-hexene-2,5-dione (from *p*-xylene and 1,2,4-trimethylbenzene) exhibit a dependence of their formation yields on the NO_2 concentration, with higher yields from the reactions of the OH−aromatic adducts with O_2 than from their reactions with NO_2. Furthermore, our data show that these ring-cleavage products are primary products of the OH−aromatic adduct reactions. Formation yields extrapolated to zero NO_2 concentration should be applicable to ambient atmospheric conditions (provided that there is sufficient NO that peroxy radicals react dominantly with NO), and are from *p*-xylene, *p*-tolualdehyde, 0.0706 ± 0.0042 (independent of NO_2 concentration), 2,5-dimethylphenol, 0.138 ± 0.016 (independent of NO_2 concentration), and 3-hexene-2,5-dione, 0.32 (extrapolated); from 1,2,3-trimethylbenzene, 2,3-butanedione, 0.52 (extrapolated); and from 1,2,4-trimethylbenzene, 2,3-butanedione, 0.10 (extrapolated) and 3-hexene-2,5-dione, 0.31 (extrapolated). Our formation yields of 3-hexene-2,5-dione from *p*-xylene and 1,2,4-trimethylbenzene are similar to those reported for glyoxal from *p*-xylene and of methylglyoxal from 1,2,4-trimethylbenzene and therefore suggest that these are coproducts, as expected from reaction schemes presented here.

Introduction

Aromatic hydrocarbons are important constituents of gasoline fuels,[1−3] vehicle exhaust[1,4] and ambient air in urban areas,[5] typically accounting for ∼20−25% of present-day reformulated gasolines[2,3] and a similar fraction of nonmethane organic compounds in ambient air in urban areas.[5] In the troposphere, aromatic hydrocarbons such as benzene, toluene, xylenes, ethylbenzene, and trimethylbenzenes react essentially only with the hydroxyl (OH) radical.[6−8] These OH radical reactions proceed by H-atom abstraction from the C−H bonds of the alkyl substitutent groups (or, for benzene, from the C−H bonds of the aromatic ring) and by initial addition of the OH radical to the carbon atoms of the aromatic ring,[6−8] as shown for *p*-xylene.



The H-atom abstraction pathway (1a) generally accounts for ≤10% of the overall OH radical reaction at room temperature and atmospheric pressure.[6,7] The benzyl (or alkyl-substituted benzyl) radicals formed by the H-atom abstraction pathway react in the atmosphere analogously to alkyl radicals,[7,8] and the *p*-methylbenzyl radical formed in reaction 1a reacts in the presence of O_2 and NO (with sufficient NO that organic peroxy radicals react primarily with NO) to form *p*-tolualdehyde (*p*-$CH_3C_6H_4CHO$) and *p*-methylbenzyl nitrate (*p*-$CH_3C_6H_4CH_2ONO_2$).[7,8] The hydroxycyclohexadienyl-type radicals (OH−aromatic adducts) formed by OH radical addition to benzene, toluene, and xylenes (reaction 1b) react with O_2 and NO_2 (but not with NO), with rate constants for the O_2 and NO_2 reactions of $(1.8-20) \times 10^{-16}$ and $(2.5-3.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, respectively, at room temperature.[7,9−11] Hence the dominant reaction of the OH−aromatic adducts in the troposphere (even in polluted urban atmospheres) is with O_2. However, in laboratory studies carried out at elevated NO_x concentrations, the reaction of the OH−aromatic adducts with NO_2 can be significant, and possibly even dominant[12] (for benzene, toluene, and *o*- and *p*-xylene the reactions of the OH−aromatic adducts with O_2 and NO_2 are of equal importance at room temperature and atmospheric pressure of air for NO_2 concentrations of $\sim(3.6-13) \times 10^{13}$ molecules cm^{-3} [9,11,12]). Therefore, the products formed, and their yields, as determined from laboratory product studies may not be applicable to atmospheric conditions.

Numerous product studies of the reactions of OH radicals with benzene, toluene, the xylenes, and trimethylbenzenes have been carried out.[7,8,12−42] However, relatively few of these studies determined product yields under conditions where reaction of the OH−aromatic adducts with O_2 clearly dominated,[12,14,30,31,38,39,41] and product yields have been specifically measured as a function of the NO_2 concentration in only four studies.[12,30,31,40] In this work, we have measured the formation yields of 2,3-butanedione (biacetyl) and/or 3-hexene-2,5-dione

---

[*] Authors to whom correspondence should be addressed.
[†] Also Interdepartmental Program in Environmental Toxicology.
[‡] Also Department of Environmental Sciences.
[§] Also Department of Chemistry.

10.1021/jp001161s CCC: $19.00

from the OH radical-initiated reactions of *p*-xylene and 1,2,3- and 1,2,4-trimethylbenzene, and of *p*-tolualdehyde and 2,5-dimethylphenol from *p*-xylene, as a function of NO_2 concentration.

Experimental Section

The experimental methods used were similar to those described previously.[12,30,31] Experiments were carried out at 298 ± 2 K and 740 Torr total pressure of air (at ~5% relative humidity) in a 7900 L Teflon chamber with analysis by gas chromatography with flame ionization detection (GC-FID) and combined gas chromatography−mass spectrometry (GC-MS). Irradiation was provided by two parallel banks of blacklamps, and the chamber was fitted with a Teflon-coated fan to ensure rapid mixing of reactants during their introduction into the chamber. Hydroxyl radicals were generated in the presence of NO by the photolysis of methyl nitrite in air at wavelengths >300 nm,[12] and NO was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals.

The initial reactant concentrations (in molecules cm^{-3} units) were as follows: CH_3ONO, $(2.2-22.7) \times 10^{13}$; NO, $(2.0-21.2) \times 10^{13}$; NO_2, $(0.12-8.0) \times 10^{13}$; and aromatic hydrocarbons, $(2.22-2.62) \times 10^{13}$ (in all experiments the initial CH_3ONO and NO concentrations were approximately equal). Irradiations were carried out for 3−15 min (*p*-xylene), 1.5−8 min (1,2,3-trimethylbenzene), and 1−8 min (1,2,4-trimethylbenzene), resulting in up to 41%, 53%, and 51% reaction of the initially present *p*-xylene, 1,2,3-trimethylbenzene, or 1,2,4-trimethylbenzene, respectively. The concentrations of the aromatic hydrocarbons and reaction products were measured during the experiments by GC-FID. Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~225 °C onto a DB-1701 megabore column in a Hewlett-Packard (HP) 5710 GC, initially held at 0 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. In addition, gas samples were collected onto Tenax-TA solid adsorbent for GC-MS analyses, with thermal desorption onto a 30 m DB-5MS fused silica capillary column in an HP 5890 GC interfaced to a HP 5970 mass selective detector operating in the scanning mode. GC-FID response factors were determined as described previously.[43] NO and initial NO_2 concentrations were measured using a Thermo Environmental Instruments, Inc., Model 42 $NO-NO_2-NO_x$ chemiluminescence analyzer.

An irradiation of a *cis*-3-hexene-2,5-dione (2.20×10^{13} molecules cm^{-3})−air mixture was also carried out in the presence of 3.5×10^{15} molecules cm^{-3} of cyclohexane (to scavenge any OH radicals formed) at the same light intensity as used for the product studies, for up to 12 min to investigate the importance of photolysis of *cis*-3-hexene-2,5-dione during the $CH_3ONO-NO-$aromatic hydrocarbon−air irradiations.

The chemicals used, and their stated purities, were as follows: cyclohexane (high purity solvent grade), American Burdick and Jackson; 2,3-butanedione (biacetyl) (99%), 2,5-dimethylphenol (99+%), *p*-tolualdehyde (97%), 1,2,3-trimethylbenzene (90%), 1,2,4-trimethylbenzene (98%), and *p*-xylene (99+%), Aldrich Chemical Co.; and NO (≥99.0%), Matheson gas Products. Methyl nitrite was prepared as described by Taylor et al.[44] and stored at 77 K under vacuum. A synthesized sample of *cis*-3-hexene-2,5-dione was kindly donated by Drs. Harvey E. Jeffries and Kenneth G. Sexton of the University of North Carolina at Chapel Hill.

Results

A series of $CH_3ONO-NO-p$-xylene−air, $CH_3ONO-NO-$1,2,3-trimethylbenzene−air, and $CH_3ONO-NO-$1,2,4-trimethylbenzene−air irradiations were carried out with varying initial CH_3ONO and NO concentrations (ranging from $\sim 2.2 \times 10^{13}$ to $\sim 2.2 \times 10^{14}$ molecules cm^{-3} each). As noted above, NO and initial NO_2 concentrations were monitored by a chemiluminescence analyzer and, because methyl nitrite and organic nitrates are measured by this $NO-NO_2-NO_x$ analyzer as "NO_2", the NO_2 concentrations during the experiments were estimated assuming that ([NO] + [NO_2]) = constant during the irradiations.[30,31] This has been shown by computer model calculations of these systems[30] and is consistent with the overall photolysis of methyl nitrite: $CH_3ONO + h\nu\ (+ O_2) \rightarrow HCHO + OH + NO_2$ followed by $OH + NO_2\ (+ M) \rightarrow HNO_3\ (+ M)$. For each experiment, the average NO_2 concentration, $[NO_2]_{av}$ was calculated from $[NO_2]_{av} = (\sum_{i=1}^{n}[NO_2]_i)/n$.[30,31]

The products identified and quantified by GC-FID and GC-MS in this work (by matching of GC retention times and mass spectra with those of authentic standards) were *p*-tolualdehyde, 2,5-dimethylphenol, and 3-hexene-2,5-dione from *p*-xylene, 2,3-butanedione from 1,2,3-trimethylbenzene, and 2,3-butanedione and 3-hexene-2,5-dione from 1,2,4-trimethylbenzene. These reaction products also react with OH radicals and carbonyls may also photolyze.[6−8,45] Photolysis of *cis*-3-hexene-2,5-dione in the presence of cyclohexane (to scavenge any OH radicals present) showed a <3% loss of 3-hexene-2,5-dione over a 12 min irradiation period. However, in agreement with previous studies,[29,45] cis/trans photoisomerization occurred with conversion of 12% of the cis isomer to the trans isomer over the 12 min irradiation period employed. Because we observed ~10% trans isomer to be initially present (possibly formed by cis/trans isomerization during the thermal desorption and analysis procedure), we choose to sum the cis and trans isomer products and report them as "3-hexene-2,5-dione". We have recently shown that the photolysis rate of 2,3-butanedione in the Teflon chamber under the conditions used in this work is $(1.25 \pm 0.56) \times 10^{-3}\ min^{-1}$, where the indicated error is two least-squares standard deviations.[46] For the ≤8 min irradiation times employed in the 1,2,3- and 1,2,4-trimethylbenzene reactions (where 2,3-butanedione was observed as a product), this corresponds to a 1.0 ± 0.5% loss of 2,3-butanedione due to photolysis which is within the analytical uncertainties and hence neglected. Corrections for the OH radical reactions with the products were calculated as described previously,[47] using rate constants at 298 K (in units of $10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$) of *p*-xylene, 14.3;[7] 1,2,3-trimethylbenzene, 32.7;[7] 1,2,4-trimethylbenzene, 32.5;[7] *p*-tolualdehyde, 17.3 (estimated[48]); 2,5-dimethylphenol, 80.0;[6] 2,3-butanedione, 0.238;[7] and 3-hexene-2,5-dione, 60 (based on the literature rate constants for the cis and trans isomers of 6.3×10^{-11} and $5.3 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$, respectively,[7,45] and using the fractions of cis and trans isomers typically observed during the reactions). The multiplicative correction factors, F, increase with the rate constant ratio $k(OH + \text{product})/k(OH + \text{aromatic hydrocarbon})$ and with the extent of reaction.[47] The maximum values of the multiplicative factors F were as follows: for the *p*-xylene reactions, 1.38 for *p*-tolualdehyde, 3.44 for 2,5-dimethylphenol, and 2.69 for 3-hexene-2,5-dione; for the 1,2,3-trimethylbenzene reactions, <1.01 for 2,3-butanedione; and for the 1,2,4-trimethylbenzene reactions, <1.01 for 2,3-butanedione and 1.92 for 3-hexene-2,5-dione. Because of the negligible amount of photolysis of the diketones, no corrections for photolysis were made, nor were corrections made for the OH radical reaction with 2,3-butanedione.

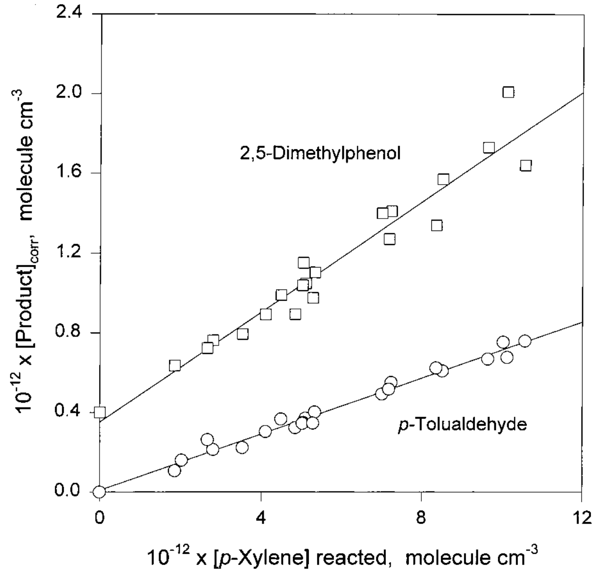


Figure 1. Plots of the amounts of *p*-tolualdehyde and 2,5-dimethylphenol formed, corrected for reaction with the OH radical (see text), against the amounts of *p*-xylene reacted with the OH radical. The entire data set, obtained at average NO_2 concentrations varying in the range (0.90−8.16) × 10^{13} molecules cm^{-3}, are shown in these plots. The data for 2,5-dimethylphenol have been displaced vertically by 4.0 × 10^{11} molecules cm^{-3} for clarity.

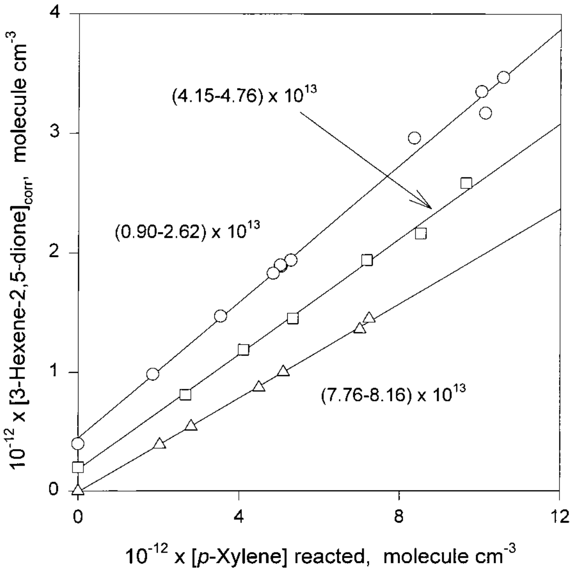


Figure 2. Plots of the amounts of 3-hexene-2,5-dione formed, corrected for reaction with the OH radical (see text), against the amounts of *p*-xylene reacted with the OH radical at differing average NO_2 concentrations (in molecules cm^{-3} units). The data at $[NO_2]_{av}$ = (4.15−4.76) × 10^{13} and (0.90−2.62) × 10^{13} molecules cm^{-3} have been displaced vertically by 2.0 × 10^{11} and 4.0 × 10^{11} molecules cm^{-3}, respectively, for clarity.

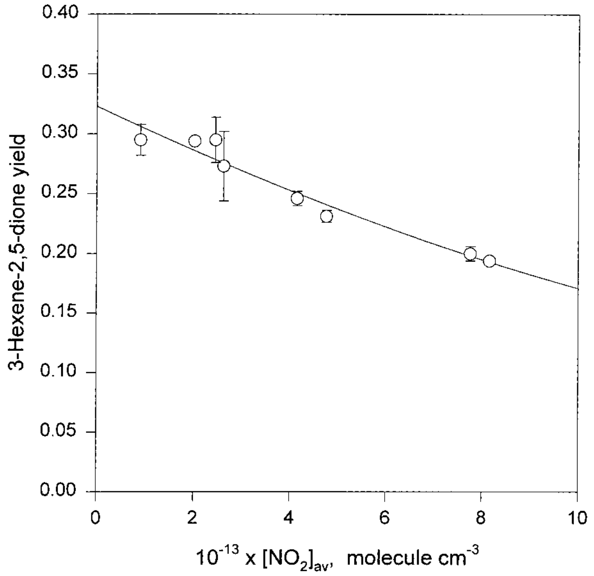


Figure 3. Plot of the 3-hexene-2,5-dione formation yields from the OH radical-initiated reaction of *p*-xylene against the average NO_2 concentration, $[NO_2]_{av}$.

***p*-Xylene.** GC-MS and GC-FID analysis of irradiated CH_3ONO−NO−*p*-xylene−air mixtures showed the formation of *p*-tolualdehyde, 2,5-dimethylphenol, and 3-hexene-2,5-dione (cis and trans, with the trans/cis ratio increasing with the extent of reaction probably due to cis,trans photoisomerization as observed in the photolysis experiment). Plots of the amounts of *p*-tolualdehyde and 2,5-dimethylphenol formed, corrected for reaction with the OH radical, against the amounts of *p*-xylene reacted are shown in Figure 1, and analogous plots for the formation of 3-hexene-2,5-dione are shown in Figure 2. Within the experimental uncertainties, no dependence of the *p*-tolualdehyde or 2,5-dimethylphenol formation yields on the NO_2 concentration was observed. However, for 3-hexene-2,5-dione the formation yield decreased with increasing NO_2 concentration, as shown in Figure 3. The formation yields of the products identified and quantified are given in Table 1.

As shown in Table 2, our present formation yield for *p*-tolualdehyde of 7.06 ± 0.42% is in general agreement with previous literature values[25,31,41] which are in the range 7.0−10.3% (Becker and Klein[29] have also reported a *p*-tolualdehyde yield obtained in the presence of NO_x of 10%, but few experimental details were reported). Our present and previous[31] studies show that within the experimental errors the *p*-tolualdehyde formation yield is independent of the NO_2 concentration over the range (0.9−24) × 10^{13} molecules cm^{-3}. This is anticipated, because in the presence of NO the *p*-methylbenzylperoxy radical formed after O_2 addition to the *p*-methylbenzyl radical reacts with NO to form either the *p*-$CH_3C_6H_4CH_2\dot{O}$ radical plus NO_2 (reaction 2a) or *p*-methylbenzyl nitrate (reaction 2b), with the *p*-$CH_3C_6H_4CH_2\dot{O}$ radical reacting with O_2 (reaction 3) to form *p*-tolualdehyde.[7,8]

$$CH_3C_6H_4CH_2O\dot{O} + NO \rightarrow CH_3C_6H_4CH_2\dot{O} + NO_2 \qquad (2a)$$

$$CH_3C_6H_4CH_2O\dot{O} + NO \rightarrow CH_3C_6H_4CH_2ONO_2 \qquad (2b)$$

$$CH_3C_6H_4CH_2\dot{O} + O_2 \rightarrow CH_3C_6H_4CHO + HO_2 \qquad (3)$$

While the *p*-$CH_3C_6H_4CH_2\dot{O}$ radical is also expected to react with NO_2 to form *p*-methylbenzyl nitrate (reaction 4)

$$CH_3C_6H_4CH_2\dot{O} + NO_2 \rightarrow CH_3C_6H_4CH_2ONO_2 \qquad (4)$$

rate constants for reactions 3 and 4 for alkoxy radicals formed from alkanes are ∼(8−10) × 10^{-15} and ∼3 × 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively.[7] Assuming similar rate constants for the corresponding reactions of the *p*-$CH_3C_6H_4CH_2\dot{O}$ radical, at an NO_2 concentration of 2.4 × 10^{14} molecules cm^{-3} reaction 4 is calculated to contribute 12−15% of the *p*-$CH_3C_6H_4CH_2\dot{O}$ radical loss processes.

Our 2,5-dimethylphenol formation yield is in reasonable agreement with the previous data of Atkinson et al.[31] and Smith et al.,[41] given the high reactivity of 2,5-dimethylphenol and the

TABLE 1: Products Identified and Quantified, and Their Formation Yields, from the OH Radical-Initiated Reaction of *p*-Xylene in the Presence of NO[a]

$10^{-13}[NO_2]_{av}$ (molecules cm^{-3})	3-hexene-2,5-dione	*p*-tolualdehyde	2,5-dimethylphenol
0.90−8.16		0.0706 ± 0.0042	0.138 ± 0.016
0.90	0.295 ± 0.013		
2.02	0.294 ± 0.003		
2.45	0.295 ± 0.019		
2.62	0.273 ± 0.029		
4.15	0.246 ± 0.006		
4.76	0.231 ± 0.005		
7.76	0.200 ± 0.006		
8.16	0.194 ± 0.001		

[a] Indicated errors are two least-squares standard deviations. The estimated uncertainties in the GC-FID response factors for *p*-xylene and the products are ±5% each.

corrections necessary for secondary reactions in this and our previous[31] studies. Formation of 2,5-dimethylphenol has also been reported by Becker and Klein[29] in the presence of NO_x and by Becker et al.[32] and Bierbach et al.[33] in the absence of NO_x, but few experimental details were reported (for example, the extents of reaction were not reported, nor is it clear whether or not the cited product yields were corrected for secondary reactions).

As obvious from Figure 3 and Table 2, the 3-hexene-2,5-dione formation yield measured here decreases with increasing NO_2 concentration. Our 3-hexene-2,5-dione formation yield is 30−40% higher than that reported by Smith et al.[41] but reasonably similar to the reported glyoxal [HC(O)CHO] yields.[25,27,41] Glyoxal and 3-hexene-2,5-dione are potential coproducts from one path of the reaction of the OH-*p*-xylene adduct with O_2 (path B in Scheme 1)[8,16,49−51] and/or from further reaction of the ring-opened product $CH_3C(O)CH{=}CHC(CH_3){=}CHCHO$ (formed as shown in path C of Scheme 1) with OH radicals.[52] Much less information is available concerning the mechanism of the reactions of OH−aromatic adducts with NO_2,[51] and the reaction pathways occurring are not presently understood in any detail.[51] Calculations carried out by Andino et al.[51] indicate that the pathways involving intermediate formation of hydroxynitrocyclohexadiene(s) (path D in Scheme 2) and leading (for *p*-xylene) to formation of 2,5-dimethylphenol, nitro-*p*-xylenes, and (not shown in Scheme 2) hydroxynitro-*p*-xylenes are exothermic, while formation of an alkoxy radical plus NO (path E in Scheme 2) was calculated to be endothermic.[51] However, our present and previous[12,30,31] studies suggest that ring-retaining products do not account for more than a small fraction of the products formed from reactions of OH−aromatic adducts with NO_2, and hence that ring cleavage must also occur.

Klotz et al.[52,53] have measured OH radical reaction rate constants of (7.4−7.6) × 10^{-11} cm^3 molecule^{-1} s^{-1} for *trans,cis*- and *trans,trans*-2,4-hexadienedial[53] and 1.18 × 10^{-10} cm^3 molecule^{-1} s^{-1} for *trans,trans*-2-methyl-2,4-hexadienedial.[52] If one assumes that 3-hexene-2,5-dione is formed by reaction of the first-generation product $CH_3C(O)CH{=}CHC(CH_3){=}CHCHO$ (formed in path C of Scheme 1) with OH radicals [and estimating[48] a rate constant for this reaction of 1.2 × 10^{-10} cm^3 molecule^{-1} s^{-1} (i.e., similar to that for $HC(O)C(CH_3){=}CHCH{=}CHCHO$)], then model calculations using the reactions

$$\mathrm{OH} + p\text{-xylene} \rightarrow \alpha\, \mathrm{CH_3C(O)CH{=}CHC(CH_3){=}CHCHO} \quad (5)$$

$$\mathrm{OH} + \mathrm{CH_3C(O)CH{=}CHC(CH_3){=}CHCHO} \rightarrow \beta\,(\text{3-hexene-2,5-dione} + \text{glyoxal}) \quad (6)$$

$$\mathrm{OH} + \text{3-hexene-2,5-dione} \rightarrow \text{products} \quad (7)$$

with rate constants (in cm^3 molecule^{-1} s^{-1}) of $k_5 = 1.43 \times 10^{-11}$, $k_6 = 1.2 \times 10^{-10}$, and $k_7 = 6.0 \times 10^{-11}$, can be compared with our measured 3-hexene-2,5-dione concentrations. Figure 4 clearly shows that our measured 3-hexene-2,5-dione concentrations agree very well with predictions based on 3-hexene-2,5-dione being a first-generation product, but differ significantly from predictions based on 3-hexene-2,5-dione being a second-generation product (i.e., with reactions 5, 6, and 7). Furthermore, based on the similarity of the literature yields for glyoxal[25,27,41] to that we measure here for 3-hexene-2,5-dione and the fact that glyoxal is anticipated to be formed along with 3-hexene-2,5-dione (path B of Scheme 1), we conclude that glyoxal is also a first-generation product and the coproduct to 3-hexene-2,5-dione. Formation of 3-hexene-2,5-dione has also been reported by Becker and Klein[29] in the presence of NO_x and by Becker et al.[32] and Bierbach et al.[33] in the absence of NO_x, but (as noted above) few experimental details were reported.

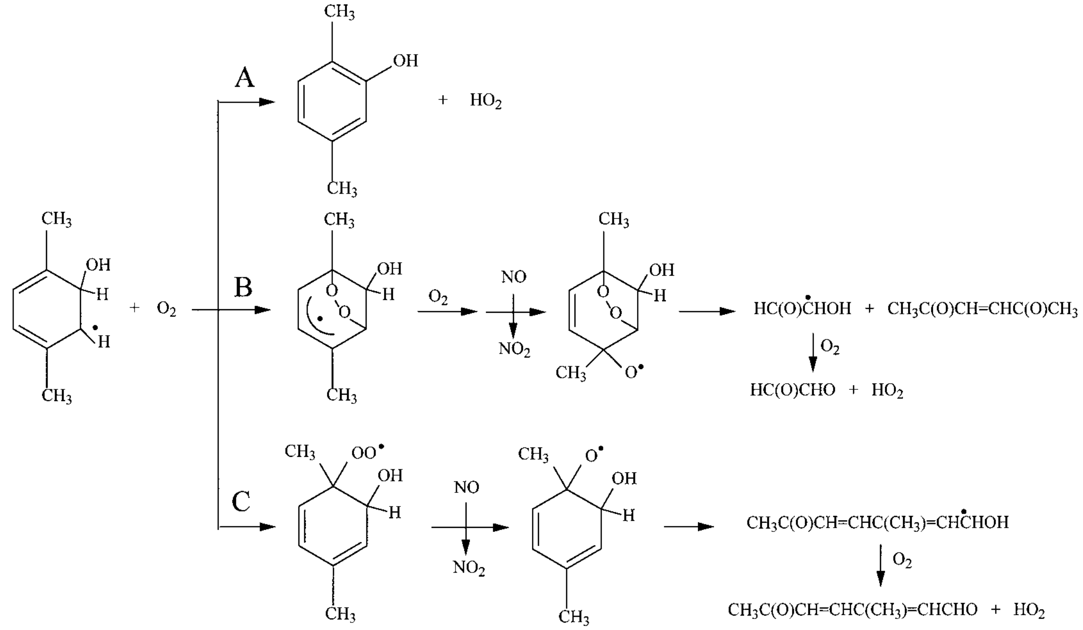
1,2,3-Trimethylbenzene. GC-MS and GC-FID analysis of irradiated CH_3ONO−NO−1,2,3-trimethylbenzene−air mixtures showed the formation of 2,3-butanedione. Plots of the amounts of 2,3-butanedione formed against the amounts of 1,2,3-trimethylbenzene reacted are shown in Figure 5. The 2,3-

TABLE 2: Comparison of the Formation Yields for *p*-Tolualdehyde, 2,5-Dimethylphenol, 3-Hexene-2,5-dione, and Glyoxal from *p*-Xylene (in the Presence of NO) Obtained in the Present Study with Literature Data

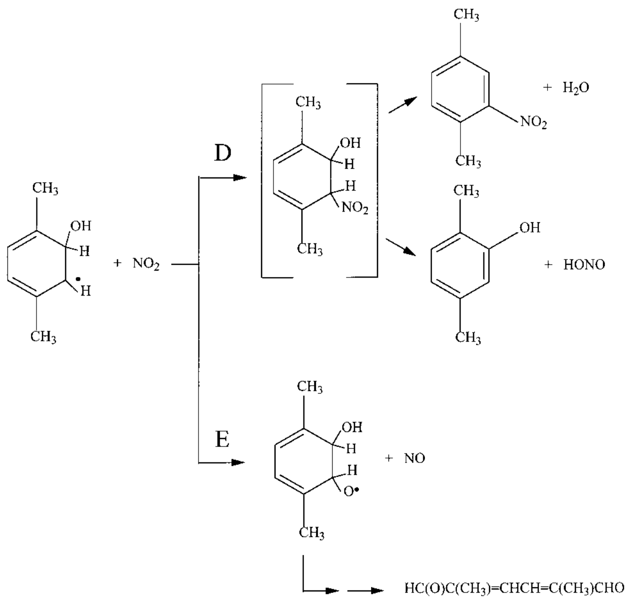
product	formation yield	$10^{-13}[NO_2]$ (molecules cm^{-3})	reference
p-tolualdehyde	0.08 ± 0.01	1.2 (initial)	Bandow and Washida[25]
	0.0701 ± 0.0103	2.6−24	Atkinson et al.[31]
	0.103 ± 0.016	0.8−1.7 (final)	Smith et al.[41]
	0.0706 ± 0.0042	2.0−8.2	this work
2,5-dimethylphenol	0.188 ± 0.038	2.6−24	Atkinson et al.[31]
	0.13 ± 0.018	0.8−1.7 (final)	Smith et al.[41]
	0.138 ± 0.016	2.0−8.2	this work
3-hexene-2,5-dione	0.221 ± 0.04	0.81−1.7 (final)	Smith et al.[41]
	0.323[a,b]	0.0	this work
	0.306[b]	0.90	
	0.193[b]	8.16	
glyoxal	0.120 ± 0.020	∼5−10 (est)	Tuazon et al.[21]
	0.24 ± 0.02	1.2 (initial)	Bandow and Washida[25]
	0.225 ± 0.039	∼5−10 (est)	Tuazon et al.[27]
	0.394 ± 0.11	0.81−1.7 (final)	Smith et al.[41]

[a] Extrapolated using the regression expression given in footnote *b*. [b] Calculated from the regression expression shown in Figure 3, of 3-hexene-2,5-dione yield = $\{0.323 - 1.92 \times 10^{-15}[NO_2] + 3.97 \times 10^{-30}\,[NO_2]^2\}$, where the NO_2 concentration is in molecules cm^{-3} units.

SCHEME 1



SCHEME 2



butanedione formation yield decreased with increasing NO_2 concentration, as shown in Figure 6, and the formation yields are given in Table 3. There is no evidence for 2,3-butanedione being a second-generation product (i.e., being formed from a diunsaturated dicarbonyl such as $CH_3C(O)C(CH_3)=C(CH_3)$-$CH=CHCHO$), because the experimental data shown in Figure 5 show no evidence for a delay in the formation of 2,3-butanedione. If 2,3-butanedione was a second-generation product, the delay in its formation would probably be more pronounced than that for formation of 3-hexene-2,5-dione from *p*-xylene (shown by the calculated lines in Figure 4) because of the higher reactivity of 1,2,3-trimethylbenzene versus that of the di-unsaturated dicarbonyl precursor compared to the corresponding reactivities in the *p*-xylene reaction system.

Our yield data are compared with literature values in Table 4 and it can be seen that there is reasonable agreement between our 2,3-butanedione formation yields and those of Bandow and Washida,[26] Tuazon et al.[27] and Atkinson and Aschmann.[12]

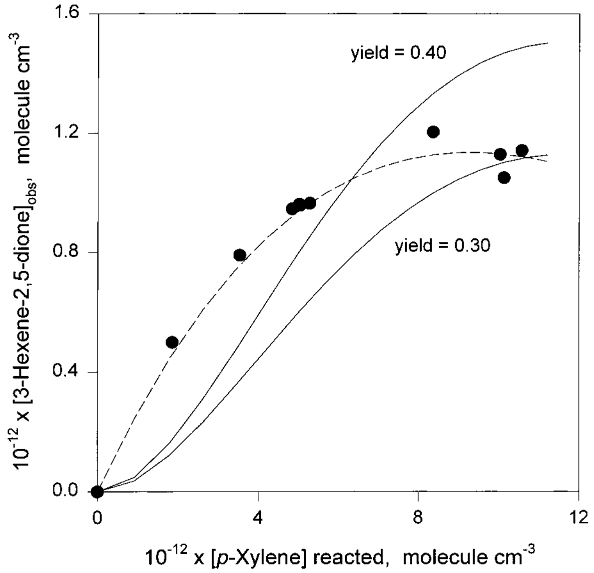


Figure 4. Plots of the amounts of 3-hexene-2,5-dione formed against the amounts of *p*-xylene reacted with the OH radical: (●) Measured 3-hexene-2,5-dione concentrations for $[NO_2]_{av} = (0.90-2.62) \times 10^{13}$ molecules cm^{-3}; (- - -) calculated concentrations of 3-hexene-2,5-dione assuming that 3-hexene-2,5-dione is a first-generation product with a molar yield of 0.29 and reacts with the OH radical with a rate constant of 6.0×10^{-11} cm^3 molecule^{-1} s^{-1}; (—) calculated concentrations of 3-hexene-2,5-dione assuming that 3-hexene-2,5-dione is a second-generation product (see text and reactions 5−7) with molar yields of 0.30 and 0.40, and reacts with the OH radical with a rate constant of 6.0×10^{-11} cm^3 molecule^{-1} s^{-1}.

1,2,4-Trimethylbenzene. GC-MS and GC-FID analysis of irradiated CH_3ONO−NO−1,2,4-trimethylbenzene−air mixtures showed the formation of 2,3-butanedione and 3-hexene-2,5-dione, with the *trans*-/*cis*-3-hexene-2,5-dione ratio increasing with the extent of reaction as observed in the *p*-xylene reaction (see above). Plots of the amounts of 2,3-butanedione and 3-hexene-2,5-dione formed, corrected for reaction with the OH radical in the case of 3-hexene-2,5-dione, against the amounts of 1,2,4-trimethylbenzene reacted are shown in Figures 7 and 8, respectively. The formation yields of both 2,3-butanedione and 3-hexene-2,5-dione decrease with increasing NO_2 concen-

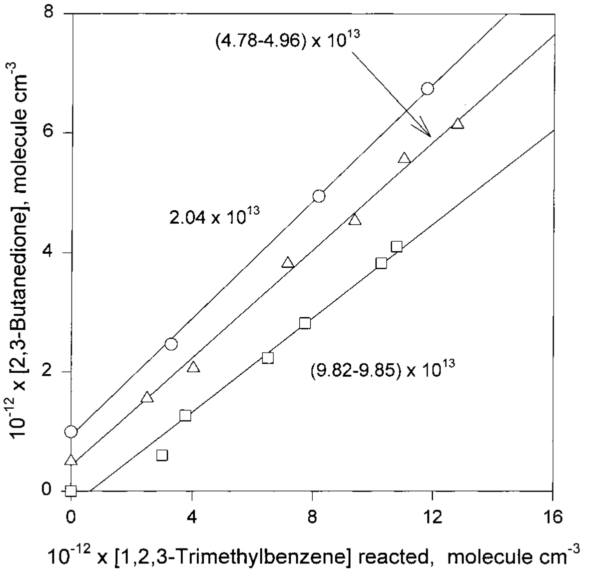


Figure 5. Plots of the amounts of 2,3-butanedione formed against the amounts of 1,2,3-trimethylbenzene reacted with the OH radical at differing average NO_2 concentrations (in molecules cm^{-3} units). The data at $[NO_2]_{av} = (4.78-4.96) \times 10^{13}$ and 2.04×10^{13} molecules cm^{-3} have been displaced vertically by 5.0×10^{11} and 1.0×10^{12} molecules cm^{-3}, respectively, for clarity.

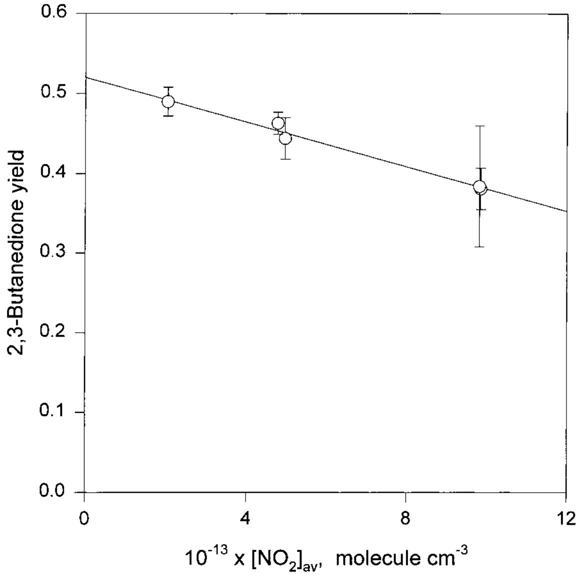


Figure 6. Plot of the 2,3-butanedione formation yields from the OH radical-initiated reaction of 1,2,3-trimethylbenzene against the average NO_2 concentration, $[NO_2]_{av}$.

TABLE 3: Products Identified and Quantified, and Their Formation Yields, from the OH Radical-Initiated Reaction of 1,2,3-Trimethylbenzene in the Presence of NO[a]

$10^{-13}[NO_2]_{av}$ (molecules cm^{-3})	2,3-butanedione	$10^{-13}[NO_2]_{av}$ (molecules cm^{-3})	2,3-butanedione
2.04	0.490 ± 0.018	9.82	0.384 ± 0.076
4.78	0.463 ± 0.012	9.85	0.381 ± 0.026
4.96	0.444 ± 0.026		

[a] Indicated errors are two least-squares standard deviations. The estimated uncertainties in the GC-FID response factors for 1,2,3-trimethylbenzene and 2,3-butanedione are ±5% each.

TABLE 4: Comparison of the Formation Yields for 2,3-Butanedione from 1,2,3-Trimethylbenzene in the Presence of NO Obtained in the Present Study with Literature Data

product	formation yield	$10^{-13}[NO_2]$ (molecules cm^{-3})	reference
2,3-butanedione	0.45 ± 0.02	1.2 (initial)	Bandow and Washida[26]
	0.316 ± 0.036	~5−10 (est)	Tuazon et al.[27]
	0.444 ± 0.053	0.58−2.4	Atkinson and Aschmann[12]
	0.520[a,b]	0.0	this work
	0.492[b]	2.04	
	0.383[b]	9.85	

[a] Extrapolated using the regression expression given in footnote *b*. [b] Calculated from the regression expression shown in Figure 6, of 2,3-butanedione yield = $\{0.520 - 1.40 \times 10^{-15}[NO_2]\}$, where the NO_2 concentration is in molecules cm^{-3} units.

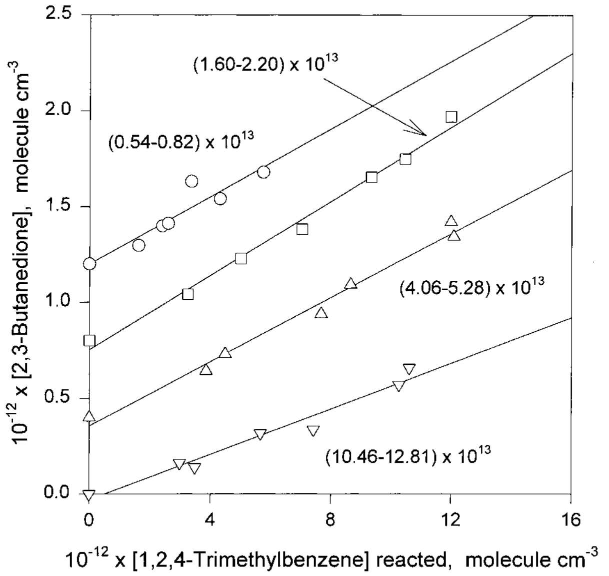


Figure 7. Plots of the amounts of 2,3-butanedione formed against the amounts of 1,2,4-trimethylbenzene reacted with the OH radical at differing average NO_2 concentrations (in molecules cm^{-3} units). The data at $[NO_2]_{av} = (4.06-5.28) \times 10^{13}$, $(1.60-2.20) \times 10^{13}$, and $(0.54-0.82) \times 10^{13}$ molecules cm^{-3} have been displaced vertically by 4.0×10^{11}, 8.0×10^{11}, and 1.2×10^{12} molecules cm^{-3}, respectively, for clarity.

tration, as shown in Figure 9, and the formation yields are given in Table 5. Again there is no evidence for 2,3-butanedione or 3-hexene-2,5-dione being a second-generation product (i.e., being formed from diunsaturated dicarbonyls such as $CH_3C(O)C(CH_3)=CHC(CH_3)=CHCHO$ and $CH_3C(O)CH=CHC(CH_3)=CHC(O)CH_3$, respectively). Once again, owing to the increased reactivity of 1,2,4-trimethylbenzene the delay in second-generation product formation would probably be more pronounced for the 1,2,4-trimethylbenzene reaction than for formation of 3-hexene-2,5-dione from *p*-xylene (calculated lines in Figure 4).

Our formation yields are compared with the available literature data in Table 6. Our present formation yields for 2,3-butanedione are in reasonable agreement with those of Bandow and Washida,[26] Tuazon et al.,[27] and Smith et al.,[41] and suggest that the differences between the literature formation yields[26,27,41] are at least in part due to the different NO_2 concentrations present in those studies.[26,27,41] While our 3-hexene-2,5-dione formation yields are higher by a factor of ~2 than those reported by Smith et al.,[41] our yields are slightly lower than the yield of methylglyoxal,[26,27,41] the expected coproduct to 3-hexene-2,5-dione and which can also be a coproduct to other C_6-1,4-unsaturated dicarbonyls. 3-Hexene-2,5-dione was also observed in low yield by Tagaki et al.[18] in an irradiated NO−air−1,2,4-trimethylbenzene mixture (the low yield being almost

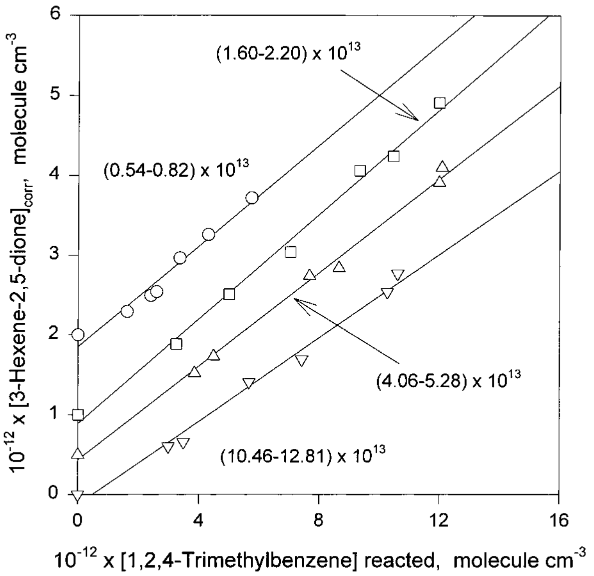


Figure 8. Plots of the amounts of 3-hexene-2,5-dione formed, corrected for reaction with the OH radical (see text), against the amounts of 1,2,4-trimethylbenzene reacted with the OH radical at differing average NO_2 concentrations (in molecules cm^{-3} units). The data at $[NO_2]_{av}$ = (4.06−5.28) × 10^{13}, (1.60−2.20) × 10^{13}, and (0.54−0.82) × 10^{13} molecules cm^{-3} have been displaced vertically by 5.0 × 10^{11}, 1.0 × 10^{12}, and 2.0 × 10^{12} molecules cm^{-3}, respectively, for clarity.

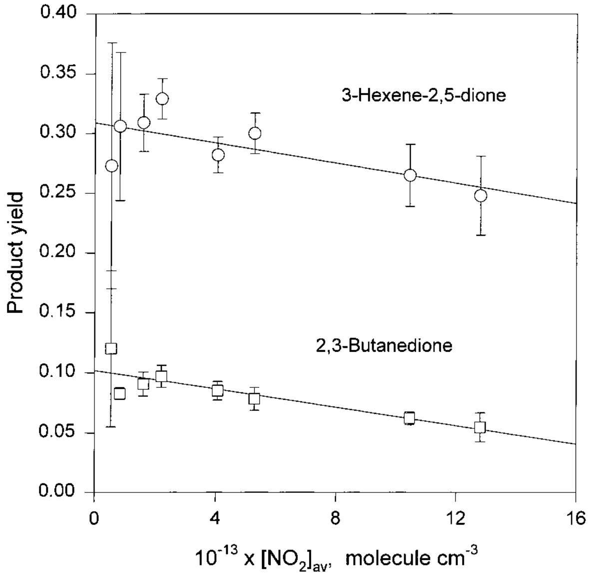


Figure 9. Plots of the 2,3-butanedione and 3-hexene-2,5-dione formation yields from the OH radical-initiated reaction of 1,2,4-trimethylbenzene against the average NO_2 concentration, $[NO_2]_{av}$.

certainly due to secondary reactions and photolysis of 3-hexene-2,5-dione).

TABLE 5: Products Identified and Quantified, and Their Formation Yields, from the OH Radical-Initiated Reaction of 1,2,4-Trimethylbenzene in the Presence of NO[a]

$10^{-13}[NO_2]_{av}$ (molecules cm^{-3})	3-hexene-2,5-dione	2,3-butanedione
0.54	0.273 ± 0.104	0.120 ± 0.065
0.82	0.306 ± 0.062	0.0825 ± 0.0049
1.60	0.309 ± 0.024	0.0906 ± 0.0099
2.20	0.329 ± 0.017	0.0969 ± 0.0092
4.06	0.282 ± 0.015	0.0849 ± 0.0077
5.28	0.300 ± 0.017	0.0782 ± 0.0095
10.46	0.265 ± 0.026	0.0622 ± 0.0054
12.81	0.248 ± 0.033	0.0545 ± 0.0121

[a] Indicated errors are two least-squares standard deviations. The estimated uncertainties in the GC-FID response factors for 1,2,4-trimethylbenzene, 2,3-butanedione, and 3-hexene-2,5-dione are ±5% each.

TABLE 6: Comparison of the Formation Yields for 2,3-Butanedione and 3-Hexene-2,5-dione from 1,2,4-Trimethylbenzene in the Presence of NO Obtained in the Present Study with Literature Data

product	formation yield	$10^{-13}[NO_2]$ (molecules cm^{-3})	reference
2,3-butanedione	0.11 ± 0.01	1.2 (initial)	Bandow and Washida[26]
	0.048 ± 0.009	~5−10 (est)	Tuazon et al.[27]
	0.114 ± 0.024	0.9−1.6 (final)	Smith et al.[41]
	0.102[a,b]	0.0	this work
	0.100[b]	0.54	
	0.053[b]	12.8	
3-hexene-2,5-dione	0.161 ± 0.012	0.9−1.6 (final)	Smith et al.[41]
	0.309[a,b]	0.0	this work
	0.307[b]	0.54	
	0.255[b]	12.8	
methylglyoxal	0.37 ± 0.01	1.2 (initial)	Bandow and Washida[26]
	0.357 ± 0.017	~5−10 (est)	Tuazon et al.[27]
	0.44 ± 0.074	0.9−1.6 (final)	Smith et al.[41]

[a] Extrapolated using the regression expression given in footnote *b*.
[b] Calculated from the regression expressions shown in Figure 9, of 2,3-butanedione yield = {0.102 − 3.83 × $10^{-16}[NO_2]$} and 3-hexene-2,5-dione yield = {0.309 − 4.20 × $10^{-16}[NO_2]$}, where the NO_2 concentration is in molecules cm^{-3} units.

Atmospheric Implications. Our product analyses show that the ring-cleavage products 2,3-butanedione and 3-hexene-2,5-dione exhibit a dependence of their formation yields on the NO_2 concentration, as previously observed for the formation of 2,3-butanedione from the OH radical-initiated reaction of *o*-xylene.[12] Our present observations indicate that 2,3-butanedione and 3-hexene-2,5-dione are formed as primary products from the reactions of the OH−aromatic adducts studied here with O_2 and with NO_2, and in higher yield from the O_2 reactions than from the NO_2 reactions. Our yields extrapolated to zero NO_2 concentration should be applicable to ambient atmospheric conditions (provided that there is sufficient NO that peroxy radicals react dominantly with NO). Our formation yields of 3-hexene-2,5-dione from *p*-xylene and 1,2,4-trimethylbenzene are similar to those reported for glyoxal from *p*-xylene and of methylglyoxal from 1,2,4-trimethylbenzene, respectively, and therefore suggest that these are coproducts as expected from, for example, path B in Scheme 1.

The formation yields of 2,3-butanedione and 3-hexene-2,5-dione from the reactions studied here do not change as dramatically as does that of 2,3-butanedione from *o*-xylene,[12] and yields from the reactions of the OH−aromatic adducts with NO_2 (Y_{NO_2}) and the rate constant ratios k_{NO_2}/k_{O_2} for the reactions of the OH−aromatic adducts with NO_2 (k_{NO_2}) and O_2 (k_{O_2}) cannot be unambiguously obtained. However, extrapolation of our yield data to $1/[NO_2] = 0$ suggests that the yields are as follows: formation of 3-hexene-2,5-dione from *p*-xylene, Y_{O_2} = 0.32 (Table 2) and Y_{NO_2} ~ 0.15; formation of 2,3-butanedione from 1,2,3-trimethylbenzene, Y_{O_2} = 0.52 (Table 4) and Y_{NO_2} ~ 0.30; formation of 2,3-butanedione from 1,2,4-trimethylbenzene, Y_{O_2} = 0.10 (Table 6) and Y_{NO_2} ~ 0.05; and formation of 3-hexene-2,5-dione from 1,2,4-trimethylbenzene, Y_{O_2} = 0.31 (Table 6) and Y_{NO_2} ~ 0.25.

These Y_{O_2} yields suggest that in the atmosphere, the OH radical-initiated reaction of *p*-xylene leads to the formation of (with percentage yields) *p*-tolualdehyde, 7%; *p*-methylbenzyl nitrate, 0.8%;[31] 2,5-dimethylphenol, 13%; 3-hexene-2,5-dione + glyoxal, 32%; and 2-methyl-1,4-butenedial + methylglyoxal, 12%,[21,25,27,41] thus accounting for ~65% of the products and reaction pathways. Formation of C_8-di-unsaturated dicarbonyls (as shown in Scheme 1) and unsaturated epoxydicarbonyls[8] such as

must then account for some or all of the remaining products.

Similarly, under atmospheric conditions 1,2,3-trimethylbenzene is anticipated to form: 2,3-butanedione + $CH_3C(O)CH{=}CHCHO$, 52%; methylglyoxal + $CH_3C(O)C(CH_3){=}CHCHO$, 18%;[26,27] and glyoxal + $CH_3C(O)C(CH_3){=}C(CH_3)CHO$, 7%,[26,27] thus accounting for ~77% of the products and with ring-retaining products (trimethylphenols, dimethylbenzaldehydes and dimethylbenzyl nitrates) plus C_9-di-unsaturated dicarbonyls and unsaturated epoxydicarbonyls[8] accounting for some or all of the remaining products. 1,2,4-Trimethylbenzene is anticipated to form dimethylbenzaldehyes, 3.6%;[41] trimethylphenols, 2.2%;[41] 2,3-butanedione + $HC(O)C(CH_3){=}CHCHO$, 10%; methylglyoxal + $CH_3C(O)CH{=}C(CH_3)CHO$ and/or $CH_3C(O)C(CH_3){=}CHCHO$, ~10%; methylglyoxal + 3-hexene-2,5-dione, 31%; and glyoxal + $CH_3C(O)C(CH_3){=}CHC(O)CH_3$, 8%,[26,27,41] thus accounting for ~65% of the products and with other ring-cleavage products (for example, C_9- di-unsaturated dicarbonyls and unsaturated epoxydicarbonyls[8]) accounting for the remaining products.

Acknowledgment. The authors gratefully thank the U.S. Environmental Protection Agency for support of this research through Grant No. R826371-01-0 (“Ozone and Fine Particle Formation in California and in the Northeastern United States”) to the California Institute of Technology, and Grant No. R825252-01-0 (from the U.S. Environmental Protection Agency–National Center for Environmental Research and Quality Assurance). While this research has been funded by Federal funds from the U.S. Environmental Protection Agency, the results and content of this publication do not necessarily reflect the views and opinions of the Agency or the U.S. Government. The authors also gratefully thank Drs. Harvey E. Jeffries and Kenneth G. Sexton (University of North Carolina at Chapel Hill) for the gift of a sample of *cis*-3-hexene-2,5-dione synthesized by Dr. Ramiah Sangaiah.

References and Notes

(1) Hoekman, S. K. *Environ. Sci. Technol.* **1992**, *26*, 1206.

(2) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Traverse, M. *Environ. Sci. Technol.* **1999**, *33*, 318.

(3) National Research Council, *Ozone-Forming Potential of Reformulated Gasoline*; National Academy Press: Washington, DC, 1999.

(4) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Hesson, J. M. *Environ. Sci. Technol.* **1999**, *33*, 329.

(5) Lurmann, F. W.; Main, H. H. “Analysis of the Ambient VOC Data Collected in the Southern California Air Quality Study”, Final Report to California Air Resources Board Contract No. A832-130, Sacramento, CA, February 1992.

(6) Atkinson, R. *J. Phys. Chem. Ref. Data*, **1989**, *Monograph 1*, 1.

(7) Atkinson, R. *J. Phys. Chem. Ref. Data*, **1994**, *Monograph 2*, 1.

(8) Atkinson, R. *Atmos. Environ.* **2000**, *34*, 2063.

(9) Knispel, R.; Koch, R.; Siese, M.; Zetzsch, C. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1375.

(10) Zetzsch, C.; Koch, R. Annual Report to the CEC on CYTROXA, 1994.

(11) Koch, R.; Knispel, R.; Siese, M.; Zetzsch, C. Absolute Rate Constants and Products of Secondary Steps in the Atmospheric Degradation of Aromatics. In *Proceedings of the 6th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants*; Angeletti, G., Restelli, G., Eds.; European Commission, 1994; pp 143–149.

(12) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1994**, *26*, 929.

(13) Hoshino, M.; Akimoto, H.; Okuda, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 718.

(14) Darnall, K. R.; Atkinson, R.; Pitts, J. N., Jr. *J. Phys. Chem.* **1979**, *83*, 1943.

(15) Tagaki, H.; Washida, N.; Akimoto, H.; Nagasawa, K.; Usui, Y.; Okuda, M. *J. Phys. Chem.* **1980**, *84*, 478.

(16) Atkinson, R.; Carter, W. P. L.; Darnall, K. R.; Winer, A. M.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1980**, *12*, 779.

(17) Besemer, A. C. *Atmos. Environ.* **1982**, *16*, 1599.

(18) Tagaki, H.; Washida, N.; Akimoto, H.; Okuda, M. *Spectrosc. Lett.* **1982**, *15*, 145.

(19) Atkinson, R.; Carter, W. P. L.; Winer, A. M. *J. Phys. Chem.* **1983**, *87*, 1605.

(20) Dumdei, B. E.; O’Brien, R. J. *Nature* **1984**, *311*, 248.

(21) Tuazon, E. C.; Atkinson, R.; Mac Leod, H.; Biermann, H. W.; Winer, A. M.; Carter, W. P. L.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1984**, *18*, 981.

(22) Shepson, P. B.; Edney, E. O.; Corse, E. W. *J. Phys. Chem.* **1984**, *88*, 4122.

(23) Leone, J. A.; Flagan, R. C.; Grosjean, D.; Seinfeld, J. H. *Int. J. Chem. Kinet.* **1985**, *17*, 177.

(24) Bandow, H.; Washida, N.; Akimoto, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2531.

(25) Bandow, H.; Washida, N. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2541.

(26) Bandow, H.; Washida, N. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2549.

(27) Tuazon, E. C.; Mac Leod, H.; Atkinson, R.; Carter, W. P. L. *Environ. Sci. Technol.* **1986**, *20*, 383.

(28) Gery, M. W.; Fox, D. L.; Kamens, R. M.; Stockburger, L. *Environ. Sci. Technol.* **1987**, *21*, 339.

(29) Becker, K. H.; Klein, Th. OH–Initiated Oxidation of p-Xylene under Atmospheric Conditions. *Proceedings of the 4th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants*; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1987; pp 320–326.

(30) Atkinson, R.; Aschmann, S. M.; Arey, J.; Carter, W. P. L. *Int. J. Chem. Kinet.* **1989**, *21*, 801.

(31) Atkinson, R.; Aschmann, S. M.; Arey, J. *Int. J. Chem. Kinet.* **1991**, *23*, 77.

(32) Becker, K. H.; Barnes, I.; Bierbach, A.; Kirchner, F.; Thomas, W.; Wiesen, E.; Zabel, F. “OH Initiated Oxidation of NMVOC under Variable NO_x Conditions”; EUROTRAC Annual Report 1992, Part 8: LACTOZ, Commission of the European Communities, Garmisch-Partenkirchen, Germany, September 1993; pp 87–98.

(33) Bierbach, A.; Barnes, I.; Becker, K. H.; Klotz, B.; Wiesen, E. OH–Radical Initiated Degradation of Aromatic Hydrocarbons. In *Proceedings of the 6th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants*; Angeletti, G., Restelli, G., Eds.; European Commission, 1994; pp 129–136.

(34) Seuwen, R.; Warneck, P. *Int. J. Chem. Kinet.* **1996**, *28*, 315.

(35) Yu, J.; Jeffries, H. E.; Sexton, K. G. *Atmos. Environ.* **1997**, *31*, 2261.

(36) Yu, J.; Jeffries, H. E. *Atmos. Environ.* **1997**, *31*, 2281.

(37) Kwok, E. S. C.; Aschmann, S. M.; Atkinson, R.; Arey, J. *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 2847.

(38) Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *J. Atmos. Chem.* **1998**, *30*, 209.

(39) Klotz, B.; Sørensen, S.; Barnes, I.; Becker, K. H.; Etzkorn, T.; Volkamer, R.; Platt, U.; Wirtz, K.; Martín-Reviejo, M. *J. Phys. Chem. A* **1998**, *102*, 10289.

(40) Moschonas, N.; Danalatos, D.; Glavas, S. *Atmos. Environ.* **1999**, *33*, 111.

(41) Smith, D. F.; Kleindienst, T. E.; McIver, C. D. *J. Atmos. Chem.* **1999**, *34*, 339.

(42) Berndt, T.; Böge, O.; Herrmann, H. *Chem. Phys. Lett.* **1999**, *314*, 435.

(43) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. *Environ. Sci. Technol.* **1995**, *29*, 1674.

(44) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. *Int. J. Chem. Kinet.* **1980**, *12*, 231.

(45) Tuazon, E. C.; Atkinson, R.; Carter, W. P. L. *Environ. Sci. Technol.* **1985**, *19*, 265.

(46) Aschmann, S. M.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **2000**, *104*, 3998.

(47) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N. Jr. *J. Phys. Chem.* **1982**, *86*, 4563.

(48) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.

(49) Bartolotti, L. J.; Edney, E. O. *Chem. Phys. Lett.* **1995**, *245*, 119.

(50) Lay, T. H.; Bozzelli, J. W.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 6543.

(51) Andino, J. M.; Smith, J. N.; Flagan, R. C.; Goddard, W. A., III.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 10967.

(52) Klotz, B. G.; Bierbach, A.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **1995**, *29*, 2322.

(53) Klotz, B.; Barnes, I.; Becker, K.-H. *Int. J. Chem. Kinet.* **1999**, *31*, 689.