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Ring Fragmentation Reactions on the Photooxidations of Toluene and *o*-Xylene

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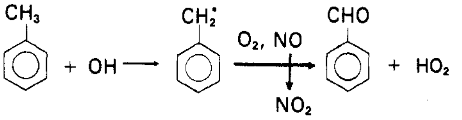
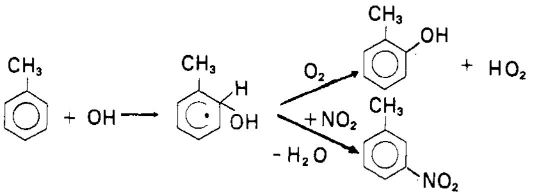
Irradiations of toluene and *o*-xylene in the CH_3ONO/NO/air system (used to generate OH radicals) have been found to produce significant yields of various C_4 and C_5 dicarbonyl compounds, aldehydes, and substituted furans. The mechanistic implications, that is, product formation via intramolecular reactions of the initially formed RO and RO_2 radicals leading to ring cleavage, are discussed in detail.

Introduction

As aromatic compounds represent a significant fraction of the reactive hydrocarbon concentration in urban atmospheres,[1] a complete understanding of the reaction rates and mechanisms associated with their photochemical conversion is necessary for the purposes of tropospheric modeling. Until recently, it was believed[2] that the dominant pathways for the reaction of OH with aromatics (their principal removal mechanism) were abstraction from the substituent methyl groups (reaction 1), yielding primarily aromatic aldehydes, and OH addition to the ring to produce phenolic compounds (reaction 2a) or nitroaromatics (reaction 2b).



(1)

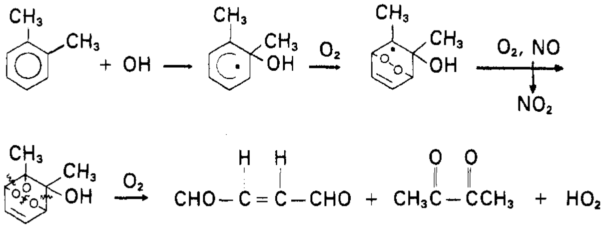


(2a)

(2b)

The sum of the yields of all aromatic products, however, was reported to be only about 20–40%.[3] Recently, several workers reported the rapid formation of significant quantities of biacetyl in *o*-xylene/NO_x/air irradiations.[4–6] In addition, 3-hexene-2,5-dione has been observed in 1,2,4-trimethylbenzene and *p*-xylene/NO_x/air irradiations.[7] These observations would seem to indicate that ring fragmentation is an important process for these aromatic compounds. Atkinson et al.[4] suggested Scheme I to account for biacetyl formation. This scheme, then, predicts significant yields of butenedial, which has not been reported for *o*-xylene. Butenedial has been tentatively indentified in a toluene/NO_x irradiation performed by A. C. Besemer,[8] although the yield was less than would be expected on the basis of production via Scheme I. In addition, the sum of the reported product yields obtained in toluene/NO_x and *o*-xylene/NO_x irradiations has accounted for far less than 100% of the reacted carbon. In order to clarify this situation and to gain a more complete understanding of the reactions of OH with aromatics, irradiations of toluene or *o*-xylene in a CH_3ONO/NO_x/air mixture were conducted in Teflon bags.

Scheme I



Experimental Section

The irradiations were carried out in 75-L FEP Teflon bags, which were contained within a cylindrical wooden enclosure. The light ($\lambda > 300$ nm) was supplied with five General Electric black lights.

The photolysis of methyl nitrite in the presence of O_2 and NO generates OH radicals via reactions 3–5. Approximately 7 ppm

$$CH_3ONO + h\nu \longrightarrow CH_3O + NO \quad (3)$$

$$CH_3O + O_2 \longrightarrow H_2CO + HO_2 \quad (4)$$

$$HO_2 + NO \longrightarrow HO + NO_2 \quad (5)$$

of the aromatics was prepared by injection of a small quantity of pure liquid into a dry air stream used to fill the bags. NO concentrations of ~5 ppm were prepared by slowly injecting small volumes of the pure gas (Matheson) into the air stream. Methyl nitrite (CH_3ONO), which was prepared according to the procedure of Taylor et al.,[9] was added by injection of a sample from a 1-L Pyrex bulb at a known CH_3ONO concentration in air into the air stream.

Irradiations were conducted for as short a time as possible to minimize secondary reactions (10.0 min for the toluene irradiations and 5.0 min for the *o*-xylene irradiations). Hydrocarbon and NO concentrations were measured before and after the irradiations. NO concentrations were determined with a Bendix NO_x chemiluminescence monitor. Formaldehyde and several other carbonyl compounds were measured by using a DNPH technique,[10] in which 3-L bag samples were pumped through 2 mL of DNPH reagent in acetonitrile contained in glass impinger bottles. The reacted hydrazones were separated and detected with a Varian 5000 HPLC. Calibrations were performed by preparation of

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[1] J. P. Heicklen, "Atmospheric Chemistry", Academic Press, New York, 1976.

[2] D. G. Hendry, *NBS Spec. Publ.* (*U.S.*), **No. 557**, 85 (1979).

[3] W. P. L. Carter, A. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.*, **12**, 779 (1980).

[4] R. Atkinson, W. P. L. Carter, and A. M. Winer, *J. Phys. Chem.*, **87**, 1605 (1983).

[5] H. Takagi, N. Washida, H. Akimoto, K. Nagasawa, Y. Usui, and M. Okuda, *J. Phys. Chem.*, **84**, 488 (1980).

[6] K. R. Darnall, R. Atkinson, and J. N. Pitts, Jr., *J. Phys. Chem.*, **83**, 1943 (1979).

[7] H. Takagi, N. Washida, H. Akimoto, and M. Okuda, *Spectrosc. Lett.*, **15**, 145 (1982).

[8] A. C. Besemer, *Atmos. Environ.*, **16**, 1599 (1982).

[9] W. D. Taylor, D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski, and G. A. Takacs, *Int. J. Chem. Kinet.*, **12**, 231 (1980).

[10] R. Kuntz, W. Lonneman, G. Namie, and L. A. Hull, *Anal. Lett.* **13**, 1409 (1980).

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TABLE I: Reactant Concentrations

species	initial concn, ppm	final concn, ppm	Δ(concn), ppm	$t_{h\nu}$, min
	Toluene Irradiations			
HC	7.0	6.0	1.0	
NO	4.7	1.9	2.8	
CH_3ONO	10.1	5.1	5.0	
				10.0
	o-Xylene Irradiations			
HC	7.0	5.8	1.2	
NO	4.8	2.2	2.6	
CH_3ONO	9.3	7.5	1.8	
				5.0

standard solutions of twice-recrystallized pure hydrazones in acetonitrile. Calibration curves were constructed for methylglyoxal, glyoxal, benzaldehyde, *o*-tolualdehyde, and biacetyl. The absolute uncertainties for those species identified and quantified by this technique were ±15%.

Hydrocarbon and aldehyde analyses were performed using a HP5985 GC/MS system. Samples of 1–5 L were pumped through an open (5-mm i.d., ~20-mL volume) Pyrex U-tube, which was fitted with 0–5-mm-high vacuum stopcocks and cooled to liquid-oxygen temperature (90 K). The Pyrex tube was then connected into the carrier gas line of the GC/MS. The sample trapped in the U-tube was then desorbed with heat and transferred to a second smaller (~2 mL) Pyrex trap (at 90 K) in the carrier gas line situated just above the column head. Injection was carried out by rapidly heating this secondary trap. Separation was achieved on a 6 ft × 2 mm (i.d.) glass column packed with 0.1% SP-1000 on 80/100 Carbopack C at a He flow rate of ~20 cm^3/min. The column was held at 40 °C for 2 min, followed by heating in 225 °C at 30 °C/min. The GC/MS (EI at 70 eV) was operated in the spectrum acquisition mode, scanning with an Analog Technology Corp. electron-capture detector after separation on a column packed with 10% Carbowax 400 on 80/100 Supelcoport at 25 °C. The reactant hydrocarbon and CH_3ONO concentrations were monitored during the irradiations with a Tenax GC column at 150 °C contained within a Varian 1200 chromatograph. CO was measured with an FID by conversion to methane with H_2 flowing over a Ni catalyst, following separation on molecular sieve 13X.

Results

Irradiations of the two aromatics were performed under the conditions indicated in Table I.

The reaction products that were identified are listed in Table II along with their yields. They were identified either by their GC or HPLC retention times, from their mass spectra, or from both. For the products identified by GC/MS, the yields were calculated by assuming total ion sensitivities equal to those of the parent hydrocarbon and assuming identical sampling efficiencies for the products and the parent hydrocarbon. Our experience with the GC/MS total ion sensitivities of a variety of volatile organic compounds (e.g., toluene, benzaldehyde, xylenes, cresols, acrolein, and biacetyl) indicates that on the average they do not vary by more than ~50%. This appears reasonable on the basis of the expected similar ionization cross sections of simple hydrocarbons of similar size. In addition, we have found that the sampling efficiency of our cryotrapping technique is at least 90% for several compouns with volatilities greater than or equal to that of *o*-cresol (e.g., biacetyl). One product, biacetyl, was measured by GC, HPLC, and GC/MS. The yields determined by these three techniques all agree to within 20%. Although this finding may be fortuitous for the GC/MS biacetyl measurement, it indicates that the GC/MS semiquantitative yields should be good to within a factor of 2.

Considering the values for the product yields and the nature of the products, it seems likely that a significant degree of secondary reaction has occurred although it is possible that the relative instrument response and/or sampling efficiency may be low for some products. In addition, given the fairly high concentrations of NOx present, it is likely that significant amounts of nitrites and nitrates (which were not detected) were formed. The GC/MS total ion chromatogram for the *o*-xylene/CH_3ONO/NO irradiation is shown in Figure 1. Aside from the $C_8H_{10}O$ component, it is clear that C_4 and C_5 dicarbonyls are relatively important products (by "relatively", we mean relative to the amount of biacetyl observed). Because of their tendency to fragment adjacent to the carbonyl functionality, the spectra for these compounds are relatively simple to interpret. The mass

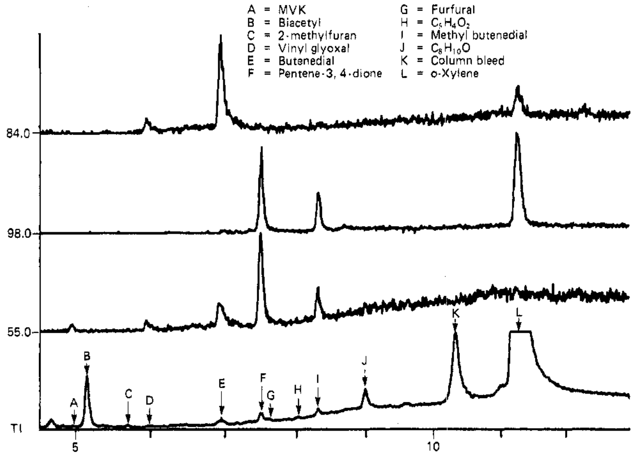


Figure 1. GC/MS selected ion and total ion chromatograms for the *o*-xylene irradiation.

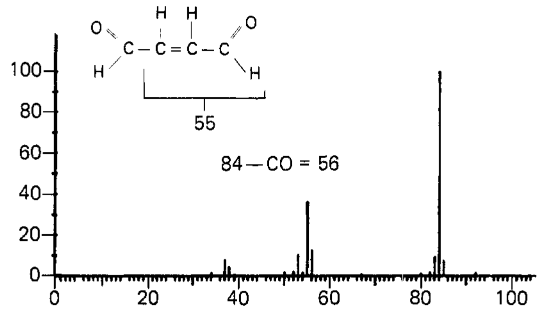


Figure 2. Butenedial mass spectrum (*m/e* 34–100).

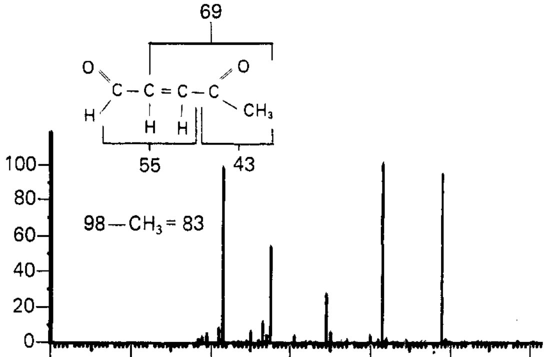


Figure 3. "Methylbutenedial" mass spectrum (*m/e* 34–120).

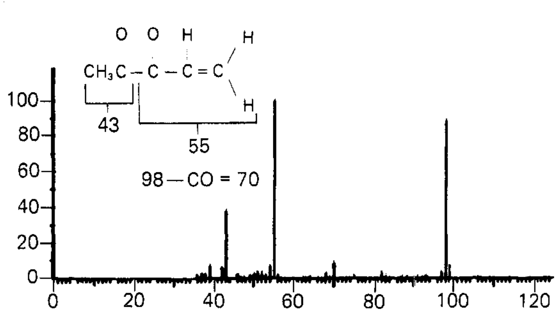


Figure 4. 1-Pentene-3,4,-dione mass spectrum (*m/e* 34–120).

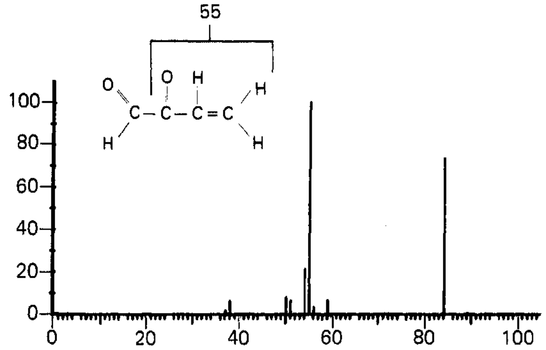


Figure 5. "Vinylglyoxal" mass spectrum (m/e 34–100).

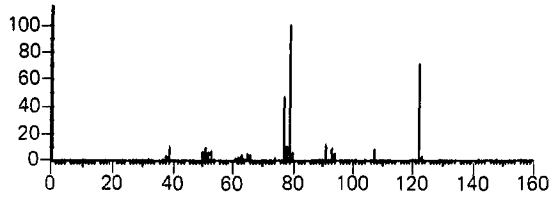
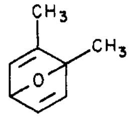


Figure 6. Unknown $C_8H_{10}O$ mass spectrum (m/e 34–160).

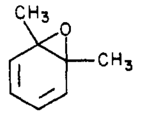
spectra, which have been interpreted as butenedial, "methylbutenedial" (we use this name for ease of reference), and 1-pentene-3,4-dione are shown in Figures 2–4, respectively. A pictorial explanation of the mass fragmentation of each molecule is also included. The production of 1-pentene-3,4-dione has not been previously speculated or reported. As with all α-diketones, the principal mass fragmentation process is scission of the C–C bond between carbonyl groups, in this case yielding large m/e 55 and 43 peaks. In all cases, the number of carbons in each product is checked from the ratio $(M + 1)/M = (\text{no. of carbons}) \times 0.011$. Although the formation of a product with a terminal vinyl group seems mechanistically awkward, methyl vinyl ketone was also observed and was identified both from its mass spectrum and GC retention time. In addition, small amounts of the analogous aldehydic dicarbonyl, $HCO\text{-}C(O)\text{-}CH{=}CH_2$ ("vinylglyoxal"), were observed, as shown in Figure 5.

Three other products observed with toluene and *o*-xylene, which should be considered as a group, in order of importance are furfural, 2-methylfuran, and furan. These species were all identified both from their GC retention times and from their mass spectra.

A major product (second only to biacetyl) in the *o*-xylene irradiations is of empirical formula $C_8H_{10}O$ (see Figure 1). Although some isomer of dimethylphenol might be expected, this compound can be ruled out from comparison with published dimethylphenol spectra.[11] These compounds all exhibit strong M − 1 peaks, in contrast to the spectrum shown in Figure 6. *o*-Methylbenzyl alcohol and *o*-methylanisole are similarly ruled out. On the basis of mechanistic considerations (see Discussion) and from interpretation of the spectrum shown in Figure 6, possible candidate structures are compounds A and B. Compound A,



A



B

which can be envisioned as a substituted 2,5-dihydrofuran (commercially available) and compound B, an epoxide, are probably stable in the gas phase. However, without actual standards it would be difficult to know if compound A, a fairly strained ether, and compound B are stable at the GC temperature at elution (225 °C).

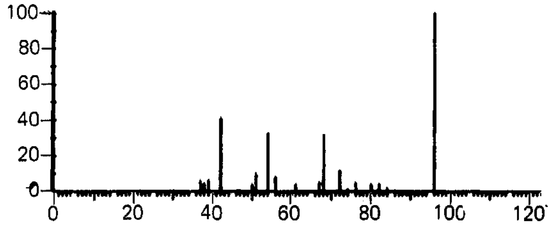
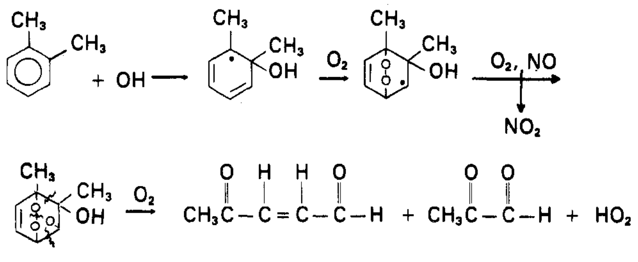
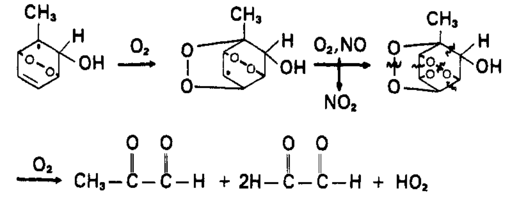


Figure 7. Unknown $C_5H_4O_2$ mass spectrum (m/e 34–120).

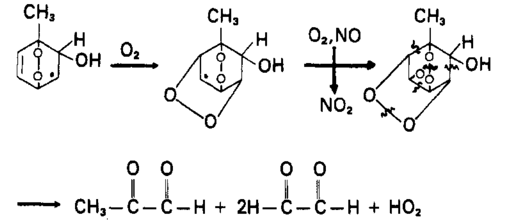
Scheme II



Scheme III



Scheme IV



With both toluene and *o*-xylene, an unknown product of empirical formula $C_5H_4O_2$ is present. Its mass spectrum is shown in Figure 7. Also found in relatively significant quantities, in agreement with other researchers,[3] were benzaldehyde and *o*-cresol in the toluene irradiation and *o*-tolualdehyde in the *o*-xylene irradiation. In addition, significant quantities of glyoxal and methylglyoxal as well as copious amounts of CO and formaldehyde were found. The significance of the latter two, however, is questionable, since formaldehyde is produced with each CH_3ONO photolysis and CO is produced from secondary reactions of formaldehyde.

The most disturbing aspect of the results in Table II is that on the basis of current literature evidence for the yields of aromatic products we would expect the sum of the ring cleavage product yields to be on the order of ~60%.[4] We found considerably smaller yields of these ring fragmentation products (the total carbon yield for *o*-xylene was 22%). However, as we have indicated, there are a number of possible contributing factors, including the assumed calibration factors and the strong possibility of secondary decay of the products, most of which can photolyze or react rapidly with OH radicals. It is, however, most likely that there are major reaction pathways that have not been observed. In any event, these results present interesting implications with regard to possible mechanistic routes, which are discussed below.

Discussion

Since most of the products that we have identified are common to both aromatics, we will discuss the reaction pathways for *o*-

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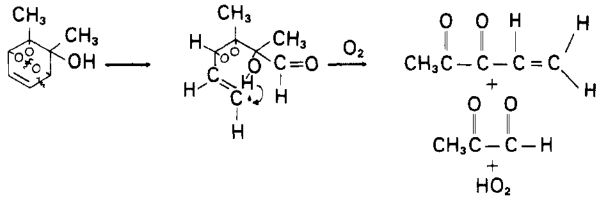
(11) E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Eds., "Registry of Mass Spectral Data", Wiley, New York, 1974.

TABLE II: Products Identified in the Photooxidations of Toluene and *o*-Xylene

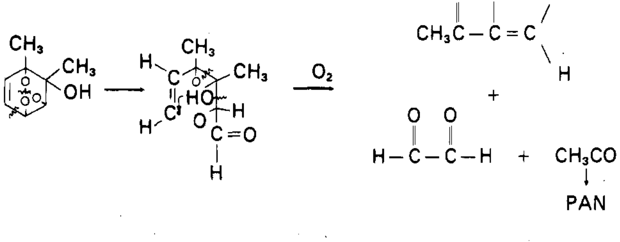
Toluene	(% yield)	o-Xylene	(% yield)
CO*		CO*	
PAN	(0.6)	PAN	(0.4)
DNPH Analysis			
H_2CO		H_2CO	
$CH_3C(O)CHO$	(7.5)	$CH_3C(O)CHO$	(11.6)
$(CHO)_2$	(8.0)	$(CHO)_2$	(3.4)
C_6H_5CHO	(5.4)	o-Tolualdehyde	(4.7)
GC/MS Analysis			
o-Cresol‡	(ND)§	$CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_3$ ‡	(8.5)
$CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH=CH_2$	(1.5)	$C_8H_{10}O$	(3.7)
$CHO-CH=CH-CHO$	(1.0)	$CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH=CH_2$	(1.7)
$CHO-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$		$CHO-CH=CH-CHO$	(1.3)
2-Methyl furan‡	(0.4)	$CHO-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$	(1.2)
Furfural‡	(0.3)	2-Methyl furan‡	(0.4)
$CH_3\overset{O}{\overset{\|}{C}}-CH=CH_2$ ‡	(0.2)	Furfural‡	(0.7)
$C_6H_4O_2$	(ND)§	$C_6H_4O_2$	(0.2)
$H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH=CH_2$	(0.1)	$CH_3\overset{O}{\overset{\|}{C}}-CH=CH_2$	(0.2)
Furan‡	(<0.1)	$H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH=CH_2$	(0.3)
		Furan‡	(<0.1)

*Secondary product.
‡Confirmed by GC retention times on GC/MS runs.
§ND = Not determined quantitatively.

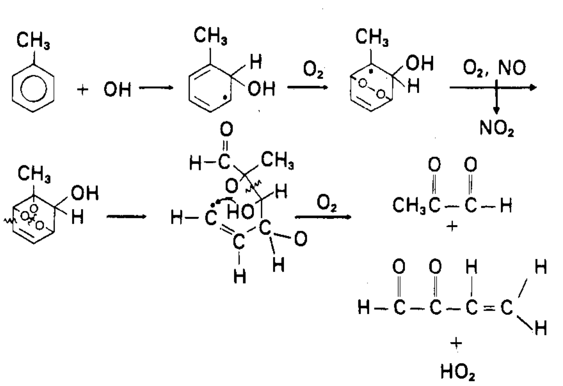
Scheme V



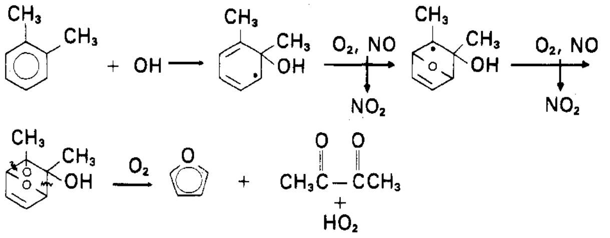
Scheme VI



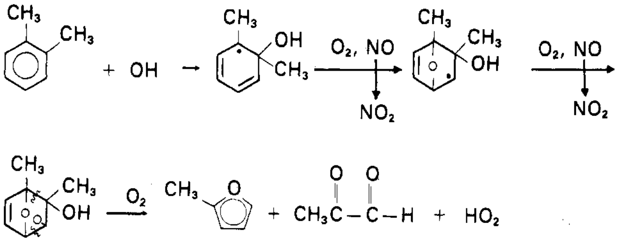
Scheme VII



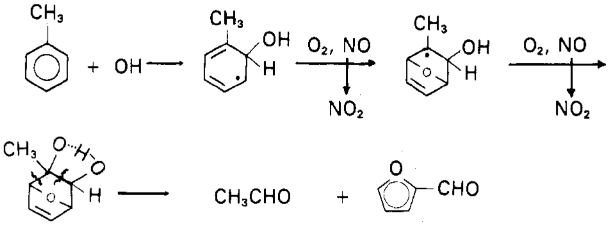
Scheme VIII



Scheme IX



Scheme X



xylene as the general case. In this discussion, OH addition occurs at a methyl-substituted carbon for *o*-xylene and at the carbon-2 position for toluene, so as to be consistent with the relative importance of biacetyl and *o*-cresol production for *o*-xylene and toluene, respectively.[4] Two important reaction pathways that may occur produce either biacetyl and butenedial (see Introduction, Scheme I) or methyl glyoxal and "methylbutenedial" (Scheme II), as discussed by Carter et al.[3]

In the case of toluene, however, Killus and Whitten[12] suggested that Schemes III and IV may be important. For *o*-xylene this mechanism would lead to production of two glyoxals and a biacetyl. Since for both mechanisms the methylbutenedial and glyoxal yields (relative to methylglyoxal and biacetyl) are lower than would be expected, it is not clear which is operative for *o*-xylene.

The presence of relatively large amounts of "pentenedione" (1-pentene-3,4-dione) indicates that intramolecular H atom transfer must occur, probably from the precursor to biacetyl formation (Scheme I), as shown in Scheme V.

The production of pentenedione is supported by the observation of methyl vinyl ketone, which may arise as shown in Scheme VI.

The explanation for the production of "vinylglyoxal" is not obvious for *o*-xylene but may be produced for toluene as shown in Scheme VII.

The observation of furan and methylfuran can be explained as shown in Schemes VIII and IX for *o*-xylene. The presence of furfural is explained for toluene in Scheme X. It is thus suggested as a possible mechanism for producing CH_3CHO as a primary product.

If Schemes I and VIII were the only source of biacetyl, they would suggest that the biacetyl yields should equal the sum of

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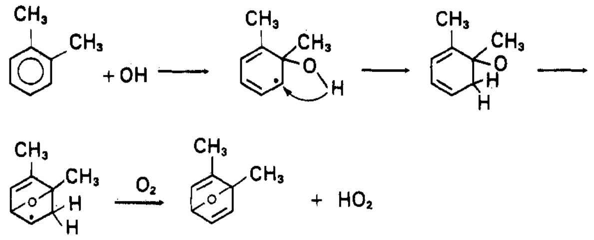
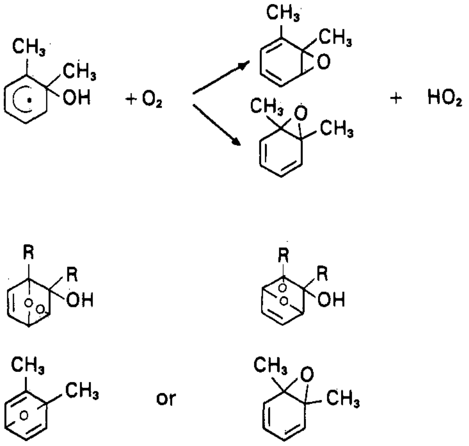
(12) J. P. Killus and G. Z. Whitten, *Atmos. Environ.*, **17**, 1597 (1983).

Scheme XI



Scheme XII



the yields of furan plus butenedial. Since the furan yield is negligible, this is obviously not the case (see Table II). It is reasonable to assume, however, that butenedial is much more reactive than biacetyl and that much of it may have undergone secondary decay.

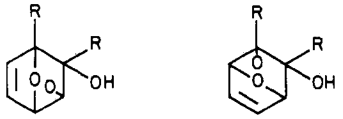
In the case of toluene, however, one would expect the methylglyoxal yields to be comparable to the butenedial yields, if Scheme II were operative. The fact that the methylglyoxal yield is much larger than that of butenedial cannot be explained as a result of secondary decay, since methylglyoxal is undoubtedly as reactive to OH as is butenedial. Since the yields of methylglyoxal and glyoxal are considerably larger than those of the butenedials, it would appear that the glyoxals are not always produced along with the butenedials. These results then seem to indicate that the mechanism suggested by Killus and Whitten is more important than Scehemes I and II for toluene and *o*-xylene.

A plausible reaction scheme for the formation of the $C_8H_{10}O$ compound is shown in Scheme XI. An additional possibility is shown in Scheme XII.

One would expect, however, that loss of CH_3 (122 − 15 = 107) would be a more important process for any of these compounds than Figure 6 suggests. In addition, one would not expect so large a peak at *m*/*e* 79 as is seen (rearrangement to $C_6H_7^+$). Although the fragment ions at *m*/*e* 39, 50–52, 63–65, 77, and 79 are all typical of substituted aromatics,[13] it is still unclear what this product might be. Another unidentified product (Figure 7) that is produced is of empirical formula $C_5H_4O_2$. From its yield (Table II), we assume it is marginally important. Although significant amounts of benzaldehyde and *o*-cresol from the toluene irradiations and *o*-tolualdehyde from the *o*-xylene irradiations were produced, their yields, as expected, were well below 20%. The yields of formaldehyde and CO are questionably significant since formaldehyde is produced in copious amounts via the CH_3ONO photolysis and CO is produced from either photolysis of or OH reaction with formaldehyde. Although PAN is produced, its yields are very low (see Table II); it probably arises through the photolyses of biacetyl or methylgyloxal, which produce acetyl radicals, or as shown in Scheme VI.

Conclusions

Although there are some uncertainties in these experiments due to the possibility of secondary product decay and unknown calibration factors, several unique and probably important reaction pathways in the photooxidations of these important hydrocarbons have been observed. The large amount of the $C_8H_{10}O$ compound (xylene irradiations) and pentenedione (xylene and toluene irradiations), which suggest the existence of intramolecular H atom transfer reactions, and the production of furan-type compounds may be significant. Formation of the latter compounds suggests that the following intermediates exist in the photooxidations of aromatic compounds.



In addition, this work represents the first positve identification of butenedial and methylbutenedial which have been previously speculated as being important products. Clearly, if the dicarbonyl compounds discussed here can be synthesized, chamber experiments with quantitative determinations under more realistic reactant conditions are warranted. Although our calculated yields of the ring fragment products seem low, observation of these species represents a step forward in eliminating the uncertainties associated with the speculated pathways for the reactions of OH with aromatics.

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Registry No. PAN, 2278-22-0; CO, 630-08-0; H_2CO, 50-00-0; $(CHO)_2$, 107-22-2; CHO–CH=CH–CHO, 2363-83-9; $CH_3C(O)CHO$, 78-98-8; C_6H_5CHO, 100-52-7; OH, 3352-57-6; *o*-xylene, 95-47-6; 4-oxo-2-pentenal, 5729-47-5; 2-methylfuran, 534-22-5; furfural, 98-01-1; 1-buten-3-one, 78-94-4; 2-oxo-3-butenal, 16979-06-9; furan, 110-00-9; *o*-cresol, 95-48-7; 4-penten-2,3-dione, 91238-45-8; *o*-tolualdehyde, 529-20-4; 2,3-butandione, 431-03-8; toluene, 108-88-3.

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(13) F. W. McLafferty, "Interpretation of Mass Spectra", W. A. Benjamin, Inc., New York, 1966.