Ring-cleavage Reactions of Aromatic Hydrocarbons Studied by FT-IR Spectroscopy. I. Photooxidation of Toluene and Benzene in the NO_x-Air System

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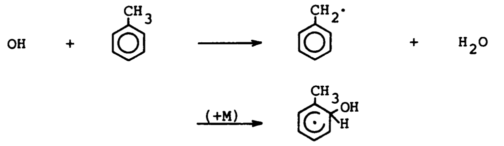
The products of the atmospheric photooxidation reactions of toluene and benzene were analyzed quantitatively using long-path FT-IR spectroscopy. Methylglyoxal (only in the case of toluene), glyoxal and maleic anhydride were observed as aromatic ring-cleavage products. In the toluene photooxidation, yields of methylglyoxal, glyoxal, and maleic anhydride were 14±4, 15±4, and 4.0±0.4% (mole/mole), respectively. The formation of small molecules, formaldehyde and formic acid, was observed. It is suggested that the precursor of the ring-cleavage reaction is OH-aromatics-O_2 adducts, and that the α-dicarbonyls and unsaturated γ-dicarbonyls are produced by ring cleavage after cyclization of the OH-aromatics-O_2 adduct. The observation of maleic anhydride is considered as an evidence of the aromatic ring cleavage into C_2 and C_4 fragments. The fraction of the ring cleavage process in the total reaction is 29 and 15—20% in the cases of toluene and benzene, respectively.

Oxidation processes of aromatic hydrocarbons initiated by the reaction of hydroxyl radicals are of fundamental interest in physical chemistry of organic compounds as well as in the development of chemical models of photochemical air pollution.[1-3] For the reactions of OH radicals with an aromatic hydrocarbon such as toluene, the initial reaction can be either abstraction (Reaction 1a) or addition to the aromatic ring (Reaction 1b).

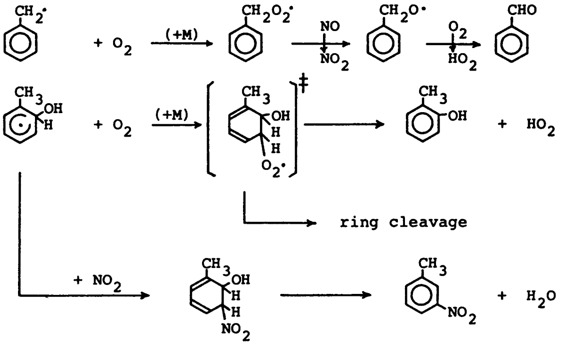


(1a)

(1b)

Studies both by measurements of the rate constant[4-12] and by analysis of reaction products[13-19] indicate that electrophilic addition of the OH radical to the aromatic ring is the dominant reactive pathway (80—93% in the case of toluene) at room temperature over the pressure range from several hundred Pa to 101 kPa (1 atm) total pressure, that side-chain hydrogen abstraction channel is small but significant (7—20% in the case of toluene), and that ring-hydrogen abstraction is a negligible channel. In the presence of O_2 and NO, aromatic aldehydes are produced from radicals obtained by side-chain hydrogen abstraction.[3,13-15,17-19] Under these conditions some of the OH-aromatics adducts yield stable products retaining the aromatic ring[3,14,15,17-19] (including phenols and aromatic nitro compounds) competing with the ring cleavage.[3,17,19-25]

The formation of α-dicarbonyls[17,19,23,24] (glyoxal, methylglyoxal, and biacetyl) in addition to small fragment molecules[3,20-22] (CO, CO_2, formaldehyde, and formic acid) has been reported. These dicarbonyls are typical reaction products caused by the ring cleavage of cyclic organic compounds as suggested in the oxidation of cycloalkanes.[26,27] Although the importance of ring-cleavage processes in the oxidation of aromatic hydrocarbons has been suggested,[3,17,24] yields and the formation mechanism of dicarbonyls are not clear.



(2)

(3)

(4)

(5)

It is well known that aromatic hydrocarbons are important constitutents in polluted atmospheres.[28] The concentration of the total aromatic hydrocarbons is often close to and sometimes higher than that of the total olefins. Recent measurements on the rate constants[4-12,29] for the reaction of hydroxyl radicals with aromatic hydrocarbons indicate that most of aromatic hydrocarbons react with OH faster than paraffins and that highly-alkyl-substituted benzenes are comparable to olefins. Therefore, the elucidation of photooxidation processes of the aromatic hydrocarbons is important to the development of chemical models of photochemical air pollution.[3,30]

In the present study, observations of the reaction products in the photooxidation of aromatic hydrocarbons in the NO_x-air system were carried out using long-path Fourier transform infrared absorption spectroscopy (LP FT-IR), in which products are observed directly without the sampling and preconcentration needed in the GC (gas chromatography) and GC/MS (gas chromatography/mass spectroscopy) analysis. The major goal of this study is the quantitative analysis of the α-dicarbonyls and unsaturated γ-dicarbonyls to elucidate the mechanism of the ring-cleavage reactions.

In this paper, the reactions of toluene and benzene are reported. Toluene is important as a prototype of the oxidation process of alkylbenzenes.

Experimental

Toluene or benzene, NO, and NO_2 diluted in 1 atm air were irradiated in a reaction chamber and reaction products were measured by LP FT-IR directly. A schematic diagram of the reaction chamber and the LP FT-IR system is shown in Fig. 1. The chamber is a stainless-steel cylinder, 0.5 m inner diameter and 3.55 m long with a volume of 0.79 m^3. Its inner wall is coated by FEP-teflon to minimize wall effects. The chamber is bakable up to 80 °C by circulating hot water through the wall, and evacuable below 1×10^{-6} Torr by an oil-diffusion pump (1500 l s^{-1}) and an oil-rotary pump (950 l min^{-1}). Fourteen black light lamps (40W, Toshiba FL40S BLB) on the inner wall of the chamber were used as a light source. The wavelength distribution of the lamp ranges from 300 to 430 nm with an intensity maximum at about 350 nm. The effective light intensity as measured by the primary photodecomposition rate of NO_2[31] was 0.22 min^{-1}.

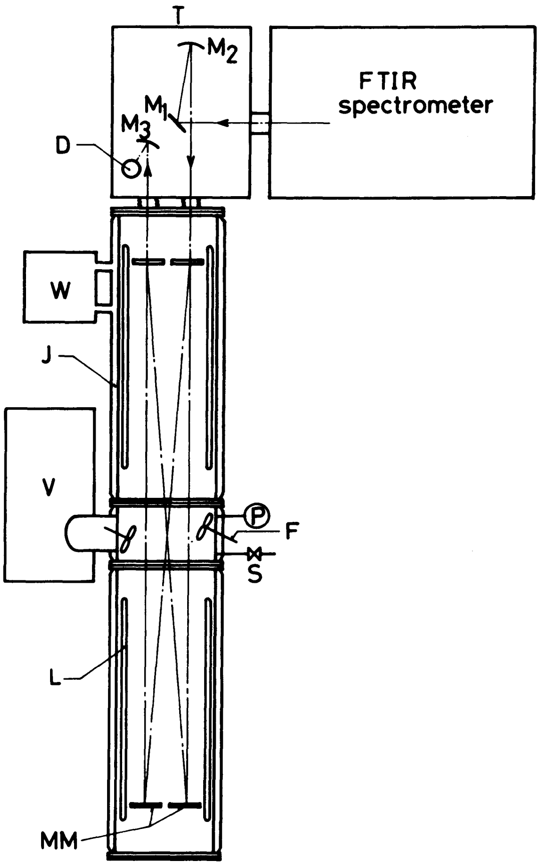


Fig. 1. Schematic diagram of reaction chamber and FT-IR optics.
M_{1-3}: Mirrors, MM: Multi-reflection mirrors, D: Liquid nitrogen cooled MCT detector, L: Black-light lamps, P: Pressure gauge, F: Mixing fans, S: Stopcock for gas inlet, V: Vacuum pumping unit, W: Water bath, J: Water jacket.

An eight-mirror multireflection system (a White cell) is set in the chamber and connected to a Nicolet 7199 FT-IR spectrometer as shown in Fig. 1. The base path between multireflection mirrors is 3.0 m and the number of reflections is 69, giving a total path length of 210.8 m. A liquid nitrogen cooled MCT (Hg-Cd-Te semiconductor) detector was used as an IR detector. The spectral resolution used in the present study was 1 cm^{-1}. IR spectra were recorded by accumulating 128 scans with 3.8 min scanning time.

The air used was supplied by an air purifier (Standard Technology Inc., model SGPU-21), in which hydrocarbons and NO in source air are converted to CO_2, H_2O, and NO_2 by a Pt/Al_2O_3 catalyst at 450 °C and CO_2, H_2O, and NO_2 are removed by a molecular sieves adsorbent. Impurities in the purified air were typically NO_x ($\approx$2 ppb), hydrocarbons (<100 ppbC), CO_2 (<1 ppm), CO (<10 ppb), and H_2O (<10 ppm). Research grade benzene and toluene were used without further purification except degassing. NO and NO_2 (both Research grade, Matheson) were used also without further purification. Standard samples of formaldehyde, formic acid, dimethylglyoxal (biacetyl), and maleic anhydride were prepared by freeze-pump-thaw cycles. Methylglyoxal and glyoxal were desiccated by molecular sieves and P_2O_5, respectively.[32,33] The chemicals used were all from Wako Pure Chemical Ind. except NO and NO_2.

The reaction mixtures were prepared as follows: The amounts of reactant gases were measured by an MKS Baratron capacitance manometer in a known volume in a gas-handling line and the gases were flushed separately by pressurized nitrogen gas into the chamber which was first filled with the matrix air. The total pressure of the reaction mixture thus obtained was 101 kPa (1 atm). The air was stirred by two mixing fans in the chamber during the irradiation.

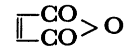
All runs were made at the temperature 22.5±1 °C controlled by the water circulation system.

Results

A. Photooxidation of Toluene. Formation of formaldehyde, formic acid, glyoxal, methylglyoxal, peroxyacetyl nitrate (PAN), maleic anhydride, and benzaldehyde was observed in the photooxidation of the toluene (4 ppm)-NO (0.17—1.50 ppm)-NO_2 (0.50—1.51 ppm)-air (1 atm) system. These products were identified by using the standard IR absorption spectra of authentic samples as listed in Table 1.

Figure 2 shows an example of the subtraction of spectra in the frequency region of 3000—2700 cm^{-1}. Figure 2a shows the absorption spectrum of products produced in the toluene (4 ppm)-NO (0.17 ppm)-NO_2 (0.50 ppm)-air (1 atm) mixture after 217 min

Table 1. The characteristic band of each product used to determine the concentration

Product		Absorption band	Wavenumber cm^{-1}
Formaldehyde	HCHO	ν_{C-H}	2781.0, 2778.5
Formic acid	HCOOH	ν_{C-O}	1105.2
Peroxyacetyl nitrate (PAN)	$CH_3C(O)OONO_2$	ν_{C-O}	1160[a]
Glyoxal	$(CHO)_2$	ν_{C-H}	2900—2750
Methylglyoxal	CH_3COCHO	ν_{C-H} in -CHO	2860—2800
Maleic anhydride (MAH)	 $\left\| \begin{matrix} -CO \\ -CO \end{matrix} \right> O$	$\nu_{C=O}$	1805.3, 840.6
Benzaldehyde	C_6H_5CHO	ν_{C-H} in -CHO	2750—2710

a) The standard spectrum of PAN was obtained by the reaction of $CH_3CHO+N_2O_5(NO_3)$ in 101 kPa (1 atm) air.[34] The absolute concentration of PAN was determined by using the reported absorption coefficient.[35]

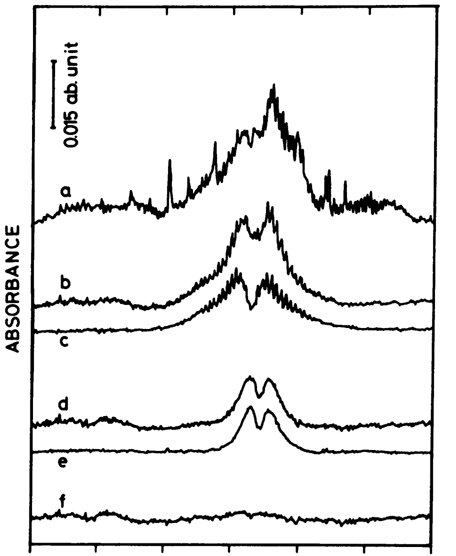


Fig. 2. Typical IR absorption spectrum of the products and spectral subtractions in the frequency region of 2700—3000 cm^{-1} (the region of the C–H stretching). a: Product spectrum from the photooxidation of the toluene (4.00 ppm)-NO(0.17 ppm)-NO_2(0.50 ppm)-air(101 kPa=1 atm) system, after 217 min irradiation. b: Spectrum after subtraction of HCHO, HCOOH, PAN, and benzaldehyde from spectrum (a). C: Spectrum of $(CHO)_2$. d: Difference spectrum, (b)−(c). e: Spectrum of CH_3COCHO. f: Difference spectrum, (d)−(e).

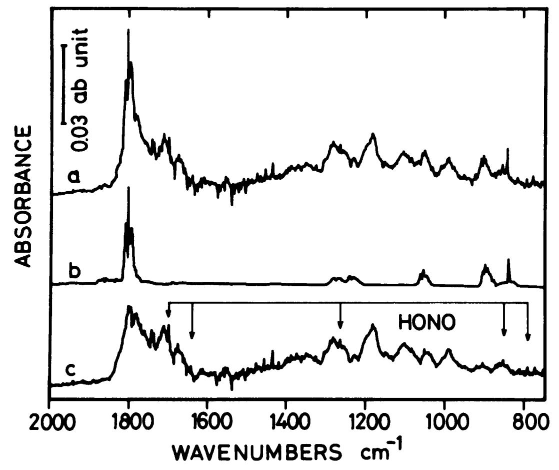


Fig. 3. Absorption spectrum of the products in the frequency region of 800—2000 cm^{-1}. a: Product spectrum under the same condition as in Fig. 2f. b: Spectrum of maleic anhydride. c: Difference spectrum, (a)—(b).

irradiation. In this case, absorption spectra of reactants and H_2O are subtracted. Rotational structure of formaldehyde (2950—2730 cm^{-1}) and broad absorption of benzaldehyde (around 2730 cm^{-1}) are apparent. Subtracting the spectra of formaldehyde, formic acid, benzaldehyde, and PAN from the spectrum (a), the spectrum (b) was obtained. The fine structure in the spectrum (b) corresponds to the absorption of glyoxal whose standard spectrum is shown in spectrum (c). Subtraction of the spectrum of glyoxal from the spectrum (b) gives the spectrum (d) which coincides with the standard spectrum of methylglyoxal, spectrum (e). Spectrum (f) shows the difference spectrum of (d)—(e). No significant absorption remained in the region from 3000 to 2700 cm^{-1} (the frequency region of the C-H stretching mode).

After these spectral manipulations, some absorption bands remained in the frequency region of 2000—800 cm^{-1} as shown in spectrum (a) in Fig. 3. Characteristic bands at 1800 and 900 cm^{-1} and sharp absorption at 840 cm^{-1} are in agreement with the standard spectrum of maleic anhydride (spectrum (b)). Subtraction of spectrum (b) from spectrum (a) gives spectrum (c) shown in Fig. 3. Several bands

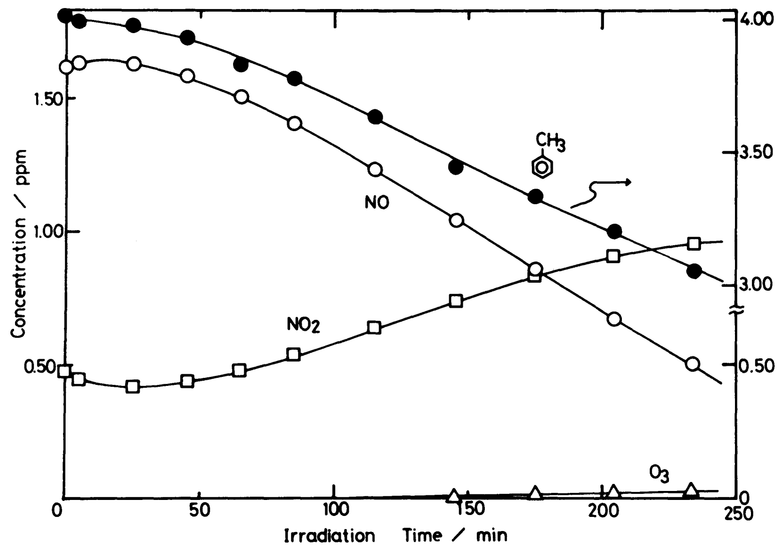


Fig. 4. Concentrations of toluene, NO, NO_2, and O_3 are plotted against the irradiation time. Initial conditions; toluene = 4.01 ppm, NO = 1.50 ppm, NO_2 = 0.50 ppm, and air = 101 kPa (= 1 atm).

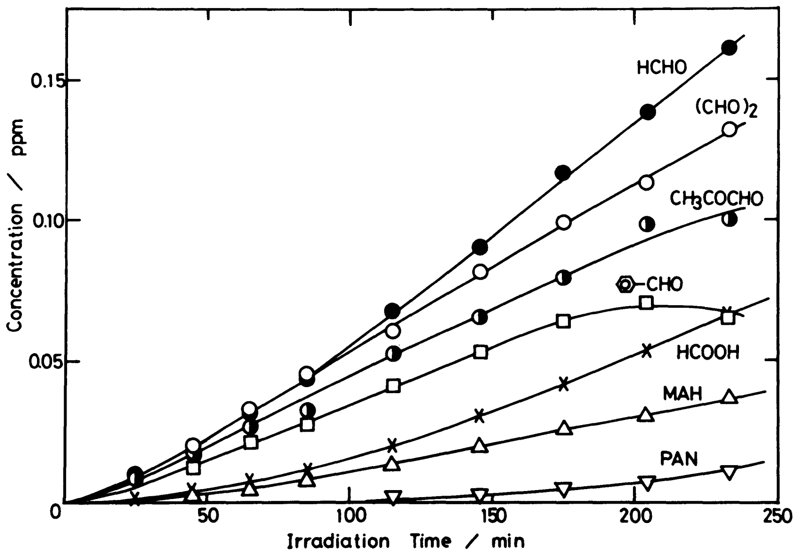


Fig. 5. Dependence of the absolute concentrations of the reaction products on irradiation time. The experimental conditions are the same as the conditions in Fig. 4. MAH: maleic anhydride. PAN: Peroxyacetyl nitrate.

in spectrum (c) can be identified to be HONO,[36] as indicated by the arrows. The remaining spectrum shows intense absorptions at 1800 and 1700 cm^{-1}, which are characteristic of the C=O stretching in carbonyl compounds. The strong absorption around 1800 cm^{-1} is attributable[37] to C=O stretching vibration in a carboxylic acid (not hydrogen-bonded), an anhydride, or a peroxyacyl nitrate. The absorption around 1700 cm^{-1} corresponds[38] to C=O stretching in aldehydes, ketones, dialdehydes, and diketones. However, the spectrum shown in Fig. 3c could not be uniquely identified in the present study.

Figure 4 shows the concentration of reactants (NO, NO_2, O_3, and toluene) plotted against the irradiation time for the photooxidation of the toluene (4.01 ppm), NO (1.50 ppm), NO_2 (0.50 ppm), and air (1 atm) mixture. Change of the concentration of products on the irradiation time is shown in Fig. 5. All these products except PAN are observed from the beginning of the irradiation.

In Fig. 6, the amounts of each product formed are plotted against the amount of toluene consumed.

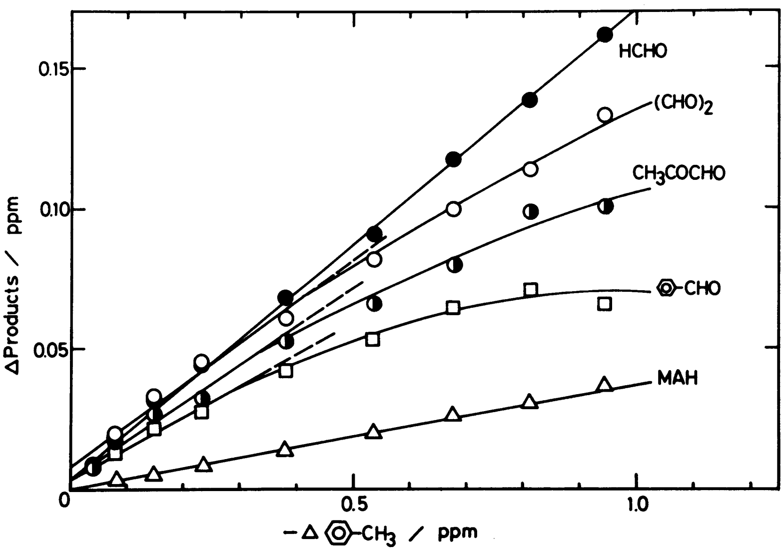


Fig. 6. Concentrations of products are plotted against the toluene consumed.

Table 2. Yields of the primary products in the photooxidation of the toluene-NO_x-air system under three different experimental conditions

	Run No. 1	2	3	average[c]
Initial concentration (ppm in 1 atm air)				
Toluene	4.00	4.01	4.00	
NO	0.17	1.50	0.51	
NO_2	0.50	0.50	1.51	
Yield of product[a]				
HCHO	0.15	0.17	0.16	0.16 ± 0.01
$(CHO)_2$	0.20	0.15	0.11	0.15 ± 0.04
CH_3COCHO	0.18	0.14	0.11	0.14 ± 0.04
MAH[b]	0.044	0.039	0.037	0.040±0.004
C_6H_5CHO	0.12	0.11	0.10	0.11 ± 0.01

a) Values were calculated by the least-square fit of four initial points of each run as shown in Fig. 6. b) MAH: maleic anhydride. c) The indicated errors are one standard deviation of three runs.

Formaldehyde and maleic anhydride increase linearly against toluene consumed, and glyoxal, methylglyoxal, and benzaldehyde show linear increase at the initial stage where toluene consumed is less than 10% of the initial concentration. The plots of formic acid and PAN (not shown) were not straight lines, indicating that both are not primary products. The initial slopes of the products shown in Fig. 6 give the formation yield of each product. Yields of products calculated under three different experimental conditions are listed in Table 2. Values shown in each run were obtained by the least-square fit of four initial points of each run as shown in Fig. 6. The indicated errors are one standard deviation of three runs.

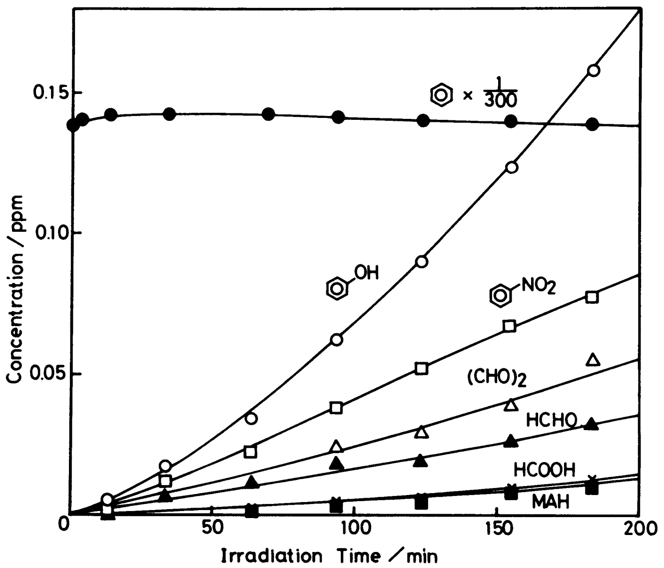


Fig. 7. Concentrations of benzene and reaction products are plotted against the irradiation time. Initial conditions; benzene=42.65 ppm, NO_2=1.50 ppm, and air=101 kPa (=1 atm).

B. Photooxidation of Benzene. In the case of benzene, formation of formaldehyde, formic acid, glyoxal, maleic anhydride, phenol, and nitrobenzene was observed. Since the rate constant for the reaction of OH+benzene is about one-fifth[5,8,11] of that for OH+toluene, this experiment was carried out with a high concentration of benzene. The concentrations of reaction products as a function of irradiation time are shown in Fig. 7. In this case the mixture of 42.7 ppm of benzene, 1.5 ppm of NO_2 in 1 atm air was photolyzed. Since the amount of benzene consumed was too small to measure, yields of each product could not be determined exactly.

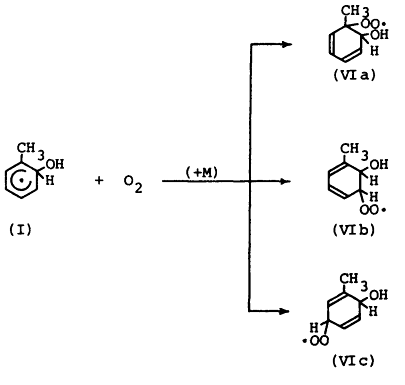
Discussion

A. Photooxidation of Toluene. In the NO–NO_2–air system, the reaction of aromatic hydrocarbon is initiated mainly by OH radicals formed by the photodecomposition of HONO[39] produced in both homogeneous[36] and heterogeneous[40] reactions among NO, NO_2, and H_2O. Further, OH radicals can be produced in a long chain mechanism[41] involving the reaction of HO_2+NO. The effect of the reaction of toluene with oxygen atoms must be considered. O(^{3}P) is produced in the photodecomposition of NO_2 with the photolysis rate constant of 0.22 min^{-1} in the present chamber, and is readily removed by O_2 under 1 atmospheric air with the rate of 7.4×10^4 s^{-1}.[42a] Using steady state approximation for oxygen atoms, we can roughly estimate the oxygen atom concentration to be at most 2.5×10^6 molecule cm^{-3} under the present experimental conditions. OH radical concentration is in the range of $(1-5)\times10^6$ molecule cm^{-3} under the similar conditions of smog chamber experiments.[40b] Since the rate constant of toluene with OH radicals under 1 atmospheric air is about 6×10^{-12} molecule^{-1} cm^3 s^{-1} [4–12] which is 10^2 times larger than that with O(^{3}P),[42b–d] the contribution of the reaction of toluene with oxygen atoms can be neglected in the present study.

OH radicals react with toluene by both abstraction (Reaction 1a) and addition (Reaction 1b) reactions. O_2 adds to the benzyl radical produced in Reaction 1a and the peroxyl radical product reacts with NO, and benzaldehyde and benzyl nitrate are eventually produced. The OH–toluene adduct produced in Reaction 1b yields cresols and *m*-nitrotoluene by subsequent reactions. Details of yields and reaction mechanisms for the formation of these high-boiling-point products were reported and discussed previously.[3,14,15,18,19] The addition of OH radicals to toluene is predominantly at the 2-position since *o*-cresol was produced predominantly.[14,15,18]

The low-boiling-point products measured previously are CO, CO_2, formaldehyde, formic acid,[3,20–22] glyoxal, and methylglyoxal.[23,24] Recently C_4 and C_5 compounds and substituted furans were detected in the toluene photooxidation products.[24c,d] In the present study, the formation of maleic anhydride was observed and analyzed quantitatively in addition to these products. Systematic analysis of these low-boiling-point products from various methylbenzenes is crucial to elucidate the mechanisms of ring-cleavage reaction.

Atkinson *et al.*[3] suggested that the OH-toluene adduct produced in Reaction 1b is the precursor of the ring-cleavage reaction. In air, addition of O_2 to the adduct can occur at the 1-, 3-, or 5-position[3] as shown in Reaction 6. According to Atkinson *et al.*,



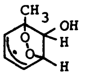
(6a)

(6b)

(6c)

O_2 addition at the 5 position should be the least thermochemically favored, since the double bonds are unconjugated.

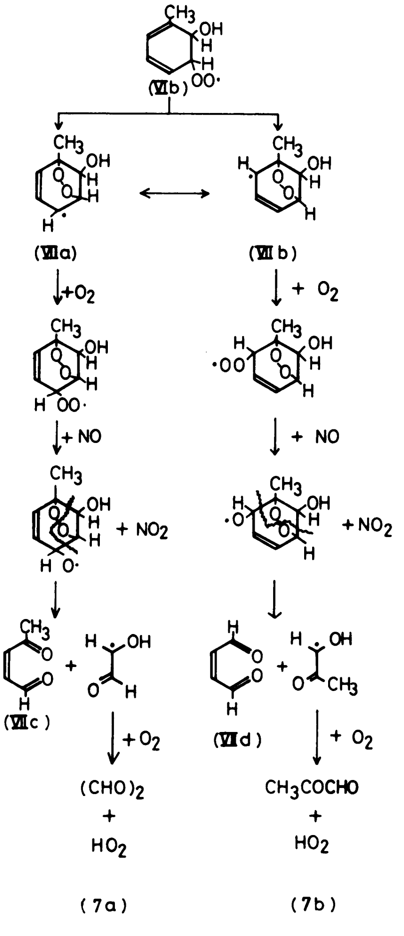
Two types of ring-cleavage mechanisms are considered for the OH–toluene–O_2 adduct. The first is a cyclization type of reaction suggested by Atkinson *et al.*[3] For example, in the case of the compound **VIb**, bicyclo[3.2.1] cyclization gives allyl-type radicals, 6,7-dioxabicyclo[3.2.1]octane compounds (DBO[3.2.1]), and both glyoxal and methyl-



DBO[3.2.1]

glyoxal can be produced from DBO[3.2.1]. Scheme 1 depicts the reactions which lead to formation of both glyoxals from **VIb** (DBO[3.2.1] is represented formally as **VIIa**↔**VIIb** by its resonance structures). In this scheme glyoxal and methylglyoxal are produced exclusively in Reactions 7a and 7b, respectively. As for the compound **VIa**, the other possible OH-toulene-O_2 adduct, bicyclo[3.2.1] cyclization gives the same allyl radical compound, DBO[3.2.1], as from **VIb**. Therefore, in the bicyclo[3.2.1] cyclization mechanism, the formation ratio of glyoxal to methylglyoxal is governed by the ratio of Reaction 7a to 7b, in other words, the relative probability of oxygen-molecule addition to the alternate radical points (shown as **VIIa** and **VIIb**) in DBO[3.2.1]. When the OH–aromatics–O_2 adducts undergo bicyclo[2.2.2] cyclization process, glyoxal and methylglyoxal can be produced from compounds **VIa** and **VIb**, respectively, as suggested by Atkinson *et al.*[19] In this case, the ratio of glyoxal and methylglyoxal is governed by the ratio of compound **VIa** and **VIb**; *i.e.* position of the O_2 addition in Reaction 6. The bicyclo[2.2.2] intermediate, 2,3-dioxabicyclo[2.2.2]octane compounds (DBO[2.2.2]), might have a lower ring strain energy than the DBO[3.2.1] intermediate, but a radical point and a double bond are isolated. These are conjugated to make an allyl-type radical in the DBO[3.2.1] intermediate. Thus, so far, it is not evident that either of the DBO[2.2.2] or the DBO[3.2.1] intermediate is more stable.

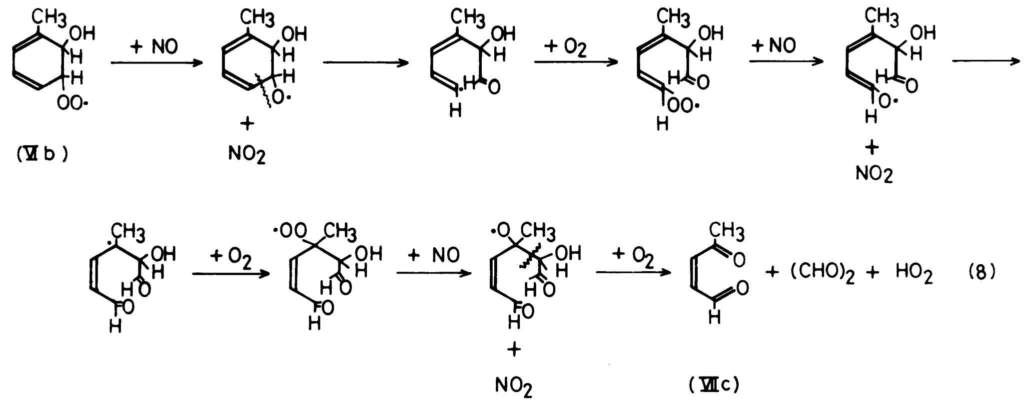
Another possible ring-cleavage mechanism is a ring opening type of reaction shown in Scheme 2, Reaction 8. For example, glyoxal and compound **VIIc** are produced from compound **VIb** by the mechanism shown in Scheme 2. When the reaction starts from compound **VIa**, methylglyoxal and compound **VIId** are produced. In this case, the ratio of glyoxal and methylglyoxal is governed by the ratio of compounds **VIb** and **VIa**.



Scheme 1.

As shown in Table 2, the formation ratio of glyoxal to methylglyoxal seems one to one. Recently two groups have reported the yield of these compounds in the toluene photooxidation. Shepson *et al.*[24c)] have reported 8.0 and 7.5% yield for glyoxal and methylglyoxal, respectively. The values reported by Tuazon *et al.*[24b)] are 0.111±0.013 and 0.146±0.014 for glyoxal and methylglyoxal, respectively. The present result and these recent data clearly show that the formation ratio of glyoxal and methylglyoxal in the toluene photooxidation is almost one to one, although the yield obtained by Shepson *et al.* are little bit smaller than the others. The formation ratio of glyoxal to methylglyoxal, 1:1, can be explained from both the cyclization, Scheme 1, and the ring opening, Scheme 2, mechanisms. In the case of Scheme 1, the probability of O_2 addition to the resonance structures **VIIa** and **VIIb** should be the same in order to explain the formation ratio. While in the case of Scheme 2, the formation ratio of **VIb** to **VIa** in Reaction 6 is to be 1:1.

If glyoxal and methylglyoxal are produced, unsaturated γ-dicarbonyls, compound **VIIc** (*cis*-4-oxo-2-pentenal) and **VIId** (*cis*-2-butenedial), are expected to form as counterparts of ring-cleavage products against glyoxal and methylglyoxal, respectively. In their extensive study of identifying the ring fragmentation products on the photooxidation of toluene, Shepson *et al.*[24c)] were successful to detect the compounds **VIIc** and **VIId** using GC/MS, although the apparent yields of these products were quite small, one eighth or less than those of glyoxals. These products might have absorptions in the aldehydic C–H stretching frequency region (2850—2700 cm^{-1}). However, as shown in spectrum (f) in Fig. 2, no significant absorption was observed in this region. This indicates that these products are probably very unstable in the gas phase due to a wall

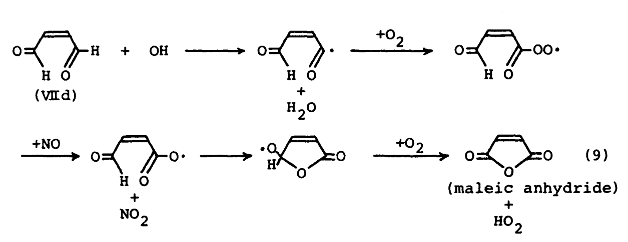


Scheme 2.

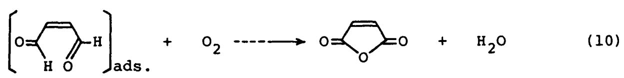
loss and also partly due to a photolysis and a reaction with OH radicals.

Maleic anhydride was observed in the present study, and seems a primary product apparently from Fig. 6. However, since the two hydrogen atoms originally attached to the carbons which become carbonyl carbons in maleic anhydride should be removed to form maleic anhydride, it seems unlikely to yield maleic anhydride as a primary product according to the mechanism generally applied to the photooxidation of hydrocarbons.

Maleic anhydride can be produced by the following reactions from *cis*-2-butenedial (compound **VIId**) which is expected to be produced as a counterpart of methylglyoxal. Rate determining step for Reaction 9 is considered to be the first step under atmospheric air. The rate constant for the step has been estimated[3] under the assumption that the aldehydic hydrogen in compound **VIId** has a similar reactivity to OH radicals as other aldehydes. The estimated value is 3×10^{-11} molecule^{-1} cm^3 s^{-1}, while the rate constant for the reaction of toluene with OH radicals which would be expected as the rate determining step to produce **VIId** has been measured to be about 6×10^{-12} molecule^{-1} cm^3 s^{-1} [4–12] under 1 atmospheric air. Therefore, only Reaction 9 can not explain the observed linear increase of maleic anhydride against toluene consumption.



Another possible route of the formation of maleic anhydride is the oxidation of *cis*-2-butenedial on the wall surface of the reaction chamber. Recently, Dumdei, and O'Brien[24d] reported the observation of 2-butenedial and 4-oxo-2-pentenal among various compounds recovered by solvent extraction from the reaction vessel walls in which the photooxidation of toluene was performed. In the present study, since the gas in the reaction chamber was stirred by fans, *cis*-2-butenedial can collide with the wall in about one minute. Although both Reactions 9 and 10 are probable, at present the mechanism to form maleic anhydride is not clear. A similar reaction mechanism can be considered for *cis*-4-oxo-2-pentenal (compound **VIIc**), with maleic anhydride production by the release of a methyl radical. However, as will be described in a subsequent paper II, maleic anhydride is not produced from *cis*-4-oxo-2-pentenal. As shown in Table 2, the yield of maleic anhydride is about one fourth of yields of both glyoxal and methylglyoxal. This implys that most of the unsaturated γ-dicarbonyls are photodecomposed or consumed by other reactions including adsorption on the reactor surface. In any case, the observation of maleic anhydride suggests the occurrence of the aromatic ring cleavage of toluene into C_2+C_4 fragments.



If the fragmentation of methyl radicals from *cis*-4-oxo-2-pentenal occurs, formaldehyde can be produced as follows:

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 \qquad (11)$$

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2 \qquad (12)$$

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \qquad (13)$$

The formation mechanism of formic acid is not clear although there might be many possible formation routes in secondary reactions involving *cis*-2-butenedial and *cis*-4-oxo-2-pentenal, particularly, in surface reactions. According to Su *et al.*,[43] formic acid can be produced by the photooxidation of formaldehyde. Formic acid might also be produced by the reaction of OH radicals with glyoxal and methylglyoxal.

$$OH + (CHO)_2 \longrightarrow HCO + HCOOH \qquad (14)$$

$$OH + CH_3COCHO \longrightarrow CH_3CO + HCOOH \qquad (15)$$

Recently, Plum *et al.*[44] reported that the rates of reactions of OH+glyoxal and methylglyoxal are very fast. PAN may be formed from the acetyl radical produced by the photodecomposition of methylglyoxal as suggested by Darnall *et al.*[24a]

In the previous studies,[13–15,18,19] high-boiling-point products formed in the photooxidation or the OH radical reaction with toluene were analyzed. The major products were benzaldehyde and *o*-cresol. The benzaldehyde yield from toluene of 0.11 obtained in the present study is in reasonable agreement with yields obtained previously by the GC analysis.[45] On the other hand, the yield of cresols reported in the previous studies was scattered from 13 to 68%.[46] In the present study, high-boiling-point products except benzaldehyde could not be identified. It is suggested that the fraction of the ring-cleavage process is 29% of toluene consumed and that 71% of total products may be high-boiling-point compounds retaining the aromatic ring[47] (benzaldehyde is 11% and other products including cresols are 60%).

Two possible mechanisms, Scheme 1 and 2, were suggested as the ring-cleavage reaction. In these reactions, the number of NO molecules which are converted to NO_2 when one toluene molecule is consumed are two and four in the cases of Scheme 1 and 2, respectively, including the reaction of $HO_2+NO \rightarrow OH+NO_2$. This number for the photooxidation of toluene obtained in the previous studies[48,49] are scattered from 1.2 to 2.3 depending upon the experimental conditions. A determination of this number was made in the present reaction chamber. Three measurements were carried out in the toluene (4 ppm) and NO (2 ppm) system.[50] The number obtained from the ratio of toluene consumed to NO consumed in the initial stage (<100 min) were 1.5, 1.5, and 1.6 in these measurements with an average value of 1.5. The number of 1.5 consists of three types of reactions: (1) Formation of benzaldehyde from benzyl radicals produced by the side-chain-hydrogen abstraction (in this case the number is two:[51] (2) Formation of cresols from OH–aromatics adducts (in this case the number is one:[51] (3) Ring cleavage as discussed in the present study. Assuming the fraction of these three types of reactions, (1), (2), and (3), are 11, 60, and 29% of total reaction, respectively, the number in the ring-cleavage reaction can be estimated[52] to be 2.4—2.6. In the ring-cleavage reaction, both α-dicarbonyls and unsaturated γ-dicarbonyls are produced when one toluene molecule is consumed. A part of the unsaturated γ-dicarbonyls is converted to maleic anhydride, and another part of them may be decomposed (including the release of methyl radicals). Therefore, some additional NO should be converted to NO_2 by reaction related to unsaturated γ-dicarbonlys (including the formation of formaldehyde *via* Reactions 11—13). In order to satisfy the estimated number of 2.4—2.6, the preferred number is two rather than four in the reaction related to α-dicarbonyls. Thus, the cyclization mechanism, Reaction 7 is preferred over Reaction 8 as the ring-cleavage mechanism.

B. Photooxidation of Benzene. In the previous work on the photooxidation of benzene, the formation of phenol and nitrobenzene[14,18] and glyoxal[23] were reported as products. In the present study, the formation of formaldehyde, formic acid, and maleic anhydride were observed in addition to the products previously identified. It has been suggested,[14,18] that both phenol and nitrobenzene are produced from the same precursor, OH–benzene adduct.

If phenol and nitrobenzene are the high-boiling-point products and glyoxal is produced by the ring cleavage reaction, the ratio of the high-boiling-point products to the ring-cleavage product can be calculated from the concentration of products shown in Fig. 7. The yields calculated are 80—85% (high-boiling-point products) and 15—20% (ring-cleavage products).

Formaldehyde was detected in the photooxidation of benzene, although the yield is smaller than in the case of toluene. One possible formation route of formaldehyde is the photodecomposition of glyoxal as suggested by Plum *et al.*[44]

$$(CHO)_2 + h\nu \longrightarrow H_2CO + CO \qquad (16)$$

The heterogeneous reaction of *cis*-2-butenedial produced as a counterpart of glyoxal might be possible to produce formaldehyde.

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45) Yields obtained in the previous studies are 0.073 (Ref. 19), 0.12 (Ref. 3), and 0.15 (Ref. 18).

46) Yields reported are 0.131 (Ref. 19), 0.21 (Ref. 3), and 0.68 (Ref. 18).

47) The ratios of the *o*-cresol/benzaldehyde yields reported previously are 1.8 (Refs. 19 and 3), 2.1 (Ref. 14), and 4.5 (Ref. 18). If these values are used to the estimation of the yield of cresols in the present study, the yields are 20, 23, and 50% of toluene consumed, respectively. The ratio of [benzaldehyde]/[total high-boiling-point products] obtained under the conditions of high NO_2 concentrations (Ref. 15) was about 0.16. Total high-boiling-point products were mostly cresols, nitrocresols, and *m*-nitrotoluene. If this value, 0.16, is used, the yield of total high-boiling-point products can be estimated to be 68% of toluene consumed. This value is in excellent agreement with the value of 71% estimated in the present study.

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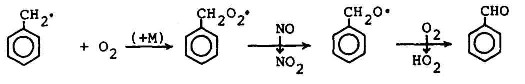
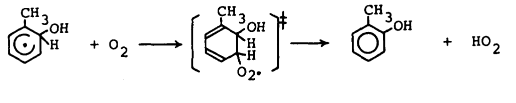
50) For the determination of this number, the conditions in the absence of NO_2 was desired, because the photodecomposition of NO_2 ($NO_2 \rightarrow NO + O$) disturbs the measurement.

51) The formation mechanisms of benzaldehyde (A) and *o*-cresol (B) suggested (Refs. 14, 15, and 48) are



(A)



(B)

52) The number, $n=2.4$ is obtained from the equation; $0.11\times2+0.60\times1+0.29n=1.5$. This number is a lower limit, because in the presence of NO_2, formation of some benzyl nitrate and *m*-nitrotoluene at the expense of benzaldehyde and cresols, observed. Therefore, effective numbers slightly less than 1 and 2 should be used in the above equation. However, even when the photooxidation was carried out in the NO_2–toluene system,[15] yields of benzyl nitrate and *m* nitrotoluene were always less than 10% of benzaldehyde and cresols, respectively. Therefore, the value can be estimated to be 2.4—2.6.