Photochemical Oxidation of Benzene, Toluene, and Ethylbenzene Initiated by OH Radicals in the Gas Phase

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Photochemical oxidation of benzene, toluene, and ethylbenzene initiated by OH radicals in the presence of NO and NO_2 was studied in the air by using a 67 dm^3 reaction chamber made of Pyrex glass. OH radicals were produced by photochemical decomposition of nitrous acid, the products being phenol and nitrobenzene for benzene; cresols, benzaldehyde, *m*- and *p*-nitrotoluenes, and benzyl nitrate for toluene; ethylphenols, benzaldehyde, acetophenone, and *m*- and *p*-nitroethylbenzene for ethylbenzene. The reaction mechanisms are proposed based on the addition of OH radicals to aromatic rings and the hydrogen abstraction of OH radicals from alkyl groups.

Photochemical oxidation of hydrocarbons related to air pollution has been discussed since Haagen-Smit proposed1) a mechanism for photochemical smog formation in Los Angeles whereby harmful oxidants were produced by nitrogen oxides and hydrocarbons under sunlight. Recent studies2—5) have shown that OH radicals play the most important role in the photooxidation of hydrocarbons.

From the standpoint of air pollution, the major concerns are information on the rate constants and that on the final products of the reactions of OH radicals with hydrocarbons. The former is useful for modeling the urban atmosphere, and the latter for taking precaution against injury to both plants and humans. As far as aromatic hydrocarbons are concerned the rate constants and their Arrehenius parameters of the reactions of OH radicals have been thoroughly studied by flash-resonance fluorescence6,7) and smog chamber experimental techniques,8,9) but no report was given on the final products.

The present work deals with the photo-oxidation products of aromatic molecules initiated by OH radicals produced by the photolysis of nitrous acid (HNO_2). The final products observed for benzene, toluene, and ethylbenzene in the presence of NO and NO_2 are reported and the reaction mechanisms are discussed.

Experimental

The reaction cell used was a 67 dm^3 Pyrex glass chamber (diam. 22.5 cm, length 170 cm) which can be evacuated to 10^{-7} Torr by a rotary, sorption, and titanium getter and spatter ion pumps. Aromatic hydrocarbons in a 105 cm^3 glass bulb at a known pressure were first introduced into the reaction chamber. Nitrous acid was produced from sodium nitrite and sulfuric acid according to the method of Cox.10) A round-bottomed flask (500 cm^3) containing 5% sulfuric acid was filled with pure air after evacuation. Aqueous sodium nitrite (5×10^{-2} mol/dm^3 or 5×10^{-3} mol/dm^3) was added drop by drop under a stream of pure air carrying the gaseous nitrous acid produced into the reaction chamber. To avoid excess moisture, pure air was introduced into the reaction chamber, by-passing the flask after the sodium nitrite solution had been consumed. Two Capsulon pressure gauges (Edward High Vacuum Co.) calibrated by means of a mercury manometer were used for measuring pressures.

The light source was a 500W xenon lamp. A parallel light beam of *ca.* 200 mmϕ was obtained by using an elliptic mirror, a lens, and an off-axis parabolic mirror. The reaction mixtures were irradiated through a Pyrex window. The wavelengths of the irradiated light were longer than 320 nm.

Product identification and quantitative analysis were performed using a gas chromatograph (Shimadzu 6A) and G. C. mass spectrometer (JOEL, JMS-D100). Glass columns (3 m) with 5% SE-30 on Shimalite W were used. The oven temperature was elevated from 80 to 200 °C at a programmed rate of 4 °C/min.

It should be noted that the conversion of aromatic molecules was limited to below 1% in order to avoid reactions of primary products. Dark reactions were found to be negligible. Because of the low conversion of reactants, the sampled gas had to be concentrated before introduction into the gas chromatograph or G. C. mass spectrometer. The reaction mixtures were first sampled from the reaction chamber into a 700 cm^3 glass bulb which had been evacuated before use. The sampled gas in the bulb was exhausted out slowly through a cooled spiral glass tube in order to collect products. The temperature of the spiral tube had to be kept between −80 and −60 °C, since the relatively volatile products escape above −60 °C. Nitrogen dioxide which causes thermal reaction with the reactants and products in the tube was captured below −80 °C. After the concentration the tube was warmed with hot water, and the products trapped in the tube were introduced directly into the gas chromatograph.

The concentrations of nitrogen oxides were measured with a commerical chemiluminescence NO_x analyzer (Monitor Labs, Model 8440). The analyzer is capable of measuring simultaneously the concentrations of NO and NO_x, where NO_x here is the sum of HNO_2, NO and NO_2.

$$[NO_x] = [HNO_2] + [NO] + [NO_2] \tag{i}$$

The concentrations of HNO_2, NO, and NO_2 were determined by the method of Cox10) as follows. When the mixture of HNO_2, NO_2, and NO is bubbled through an aqueous alkaline solution (0.1 M NaOH), HNO_2 and a certain amount of NO_2 and NO are removed. Thus the concentrations of HNO_2, NO, and NO_2 are determined, from Eq. i and the following relation.

$$[NO_x]_{\mathrm{alkaline}} = (1-a)[NO] + (1-b)[NO_2] \tag{ii}$$

Factors *a* and *b* were obtained by independent measurement of the loss of NO and NO_2 after bubbling through alkaline solution. The values of *a* and *b* were determined to be 0.1 and 0.2, respectively.

Benzene, toluene and ethylbenzene were supplied by Wako Pure Chem. Ind. Co. Pure air and nitrogen gases (Takachiho Chem. Ind. Co.) were used without purification. As an authentic sample, benzyl nitrate was prepared by fractional distillation of the reaction mixture of benzyl chloride and silver nitrate in a dried acetonitrile solution.

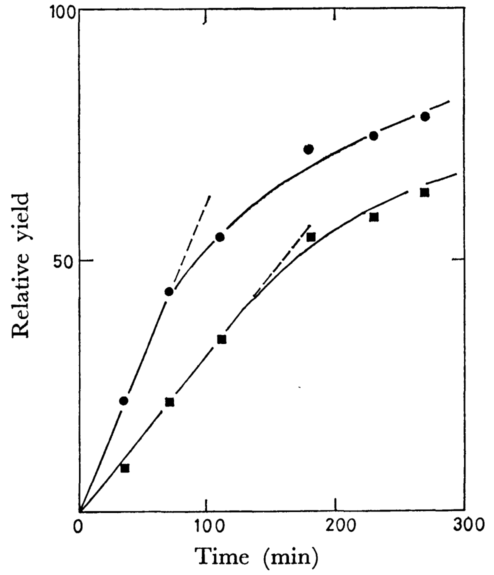


Fig. 1. Relative yields of phenol (●) and nitrobenzene (■) *vs.* irradiation time in the photo-oxidation of benzene-HNO_2-air system.

Results

Phenol and nitrobenzene were the major products when the mixture of benzene and HNO_2 in the air was irradiated. A small amount of nitrophenols was detected as well.

Figure 1 shows typical formation curves of the products as a function of irradiation time when the initial concentrations of benzene and HNO_2 were 31 and 3.2 ppm, respectively. NO_2 at 1.4 ppm and NO at 1.2 ppm were present in the initial reaction mixture, since HNO_2 partially decomposes into NO and NO_2.

As shown in Fig. 1, the amounts of phenol and nitrobenzene first increase linearly with time, then show convex curvatures, which would be due to the decrease of the concentration of HNO_2 by photochemical decomposition. The ratio of nitrobenzene to phenol was found to increase as the reaction proceeds, the increase of NO_2 concentration during irradiation being responsible for this. The ratios of nitrobenzene to phenol determined from the initial inclinations of their formation curves are shown in Table 1. The ratio changes with the initial concentration of NO_2. Nitophenols were minor products and a relative yield less than 1% of phenol was dependent on the temperature of the spiral trap. They might be produced by a thermal reaction of phenol and NO_2 in the spiral trap, although photochemical formation is not excluded.

Table 1. Relative product yields in the photo-oxidation of the benzene-HNO_2-NO_x-air system

Initial concentration			Relative yield	
HNO_2 ppm	NO_2 ppm	NO ppm	Phenol	Nitro-Benzene
0.52	0.02	0.06	1.0	0.08
3.2	1.4	1.2	1.0	0.50

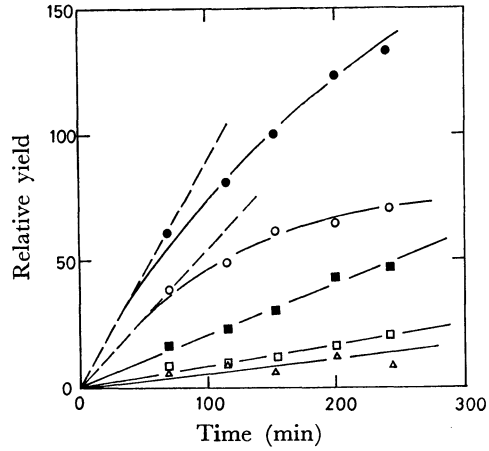


Fig. 2. Relative yields of cresols (●), benzaldehyde (○), *m*-nitrotoluene (■), *p*-nitrotoluene (□), and benzyl nitrate (△) *vs.* irradiation time in the photo-oxidation of toluene-HNO_2-air system.

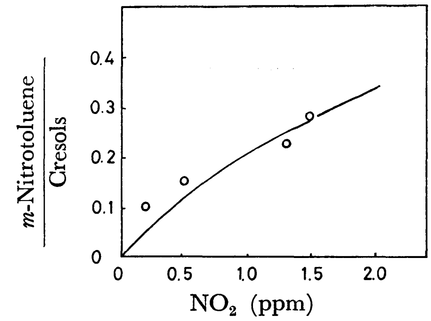


Fig. 3. Yields of *m*-nitrotoluene relative to cresols as a function of initial concentration of NO_2 in the photo-oxidation of toluene-HNO_2-air system.

The major products in the toluene–HNO_2–air system were cresols, benzaldehyde, and *m*-nitrotoluene. Small amounts of *p*-nitrotoluene, benzyl nitrate, and nitrocresols were observed. A trace amount of an unidentified substance giving mass peaks at *m/e*: 124(39), 123(18), 122(100), 94(93), 82(54), 66(48), and 54(69) was also observed. The relative yield of *o*-cresol was found to be *ca.* 80% of the total amount of cresols and that of *m*- and *p*-cresol *ca.* 20%. *m*- and *p*-cresols could not be separated by gas chromatograph column. The yield of nitrocresols was less than 5% that of cresols. Since most nitrocresols are considered to be produced thermally from cresol and NO_2 in the trap as in the case of nitrophenol, the yield of nitrocresols was added to that of cresols (Table 2 and Figs. 2 and 3).

The plots of [cresol+nitrocresol] and benzaldehyde *vs.* irradiation time are convex upwards. This would be due to the consumption of HNO_2 (Fig. 2). 6 ppm of HNO_2 were reduced to 2.3 ppm after 4 h irradiation. On the other hand, *m*-nitrotoluene seems to increase linearly with time. Both HNO_2 and NO_2 contribute to the formation of *m*-nitrotoluene. Thus an increase of NO_2 during the course of irradiation would compensate a decrease of HNO_2, resulting in an apparent linear increase of *m*-nitrotoluene. 1.3 ppm of NO_2 observed before irradiation was increased to 2.1 ppm after 4 h irradiation.

Table 2. Relative product yields (cresol = 1.0) in the photo-oxidation of the toluene-HNO_2-O_2/N_2 system

Initial concentration				Relative yield			
HNO_2 ppm	NO_2 ppm	NO ppm	Atmosphere	Benzaldehyde	Benzyl-nitrate	*m*-Nitro-toluene	*p*-Nitro-toluene
4	0.2	0.4	air	0.45	0.06	0.10	0.10
7	0.5	1.0	air	0.42	0.06	0.15	0.10
6	1.3	2.1	air	0.61	0.06	0.23	0.09
12	1.5	1.5	air	0.48	0.05	0.28	0.11
3	0.3	0.4	N_2	—	—	0.43	0.17
12	2.0	3.6	N_2	—	—	0.97	0.14

Table 3. Relative product yields (ethylphenol = 1.0) in the photo-oxidation of the ethylbenzene(EB)-HNO_2-NO_x-air system

Initial concentration			Relative yield			
HNO_2 ppm	NO_2 ppm	NO ppm	Benzaldehyde	Acetophenone	*m*-Nitro-EB	*p*-Nitro-EB
1.7	0.5	0.2	0.60	1.73	0.11	0.08
7.9	1.2	3.0	0.65	2.02	0.37	0.16

The ratios of products determined from the initial slopes on the formation curves of the products are shown in Table 2. It is evident that the ratio of benzaldehyde to cresols is constant irrespective of the concentration of NO_2. On the other hand, the ratio of *m*-nitrotoluene to cresols increases with increasing initial concentration of NO_2 as shown in Fig. 3.

When the reaction was carried out in a nitrogen atmosphere, the products obtained were cresols and *m*- and *p*-nitrotoluene. It should be noted that the ratio of *m*-nitrotoluene to cresols is four times greater than that observed in the air with the same concentration of NO_2. The ratio of *o*-cresol to *m*- and/or *p*-cresol was the same as that for the air system.

In the photochemical oxidation of ethylbenzene, the products identified were ethylphenols, acetophenone, benzaldehyde, *m*-nitroethylbenzene, and *p*-nitroethylbenzene. Nitroethylphenols were also observed as minor products. Phenyl acetaldehyde was not obtained. The formation curves of the products were essentially the same as in the cases of benzene and toluene.

The ratios of the products to ethylphenols are shown in Table 3. With increase in the initial concentration of NO_2 the yield of *m*-nitroethylbenzene increases markedly. The ratios of acetophenone and benzaldehyde to ethylphenols are independent of the concentrations of NO_2. The main product was acetophenone, the yield of which was approximately twice that of ethylphenols.

Discussion

In an aromatic hydrocarbon–HNO_2–air system, photochemical oxidation is initiated by OH radicals formed in the photolysis of HNO_2.[10,11]

$$HNO_2 + h\nu(330\text{—}390\,\text{nm}) \longrightarrow OH + NO. \tag{1}$$

The reaction of the OH radicals with aromatic hydrocarbons competes with the reactions,

$$OH + NO \xrightarrow{M} HNO_2, \tag{2}$$

$$OH + NO_2 \xrightarrow{M} HNO_3, \tag{3}$$

$$OH + HNO_2 \xrightarrow{M} H_2O + NO_2, \tag{4}$$

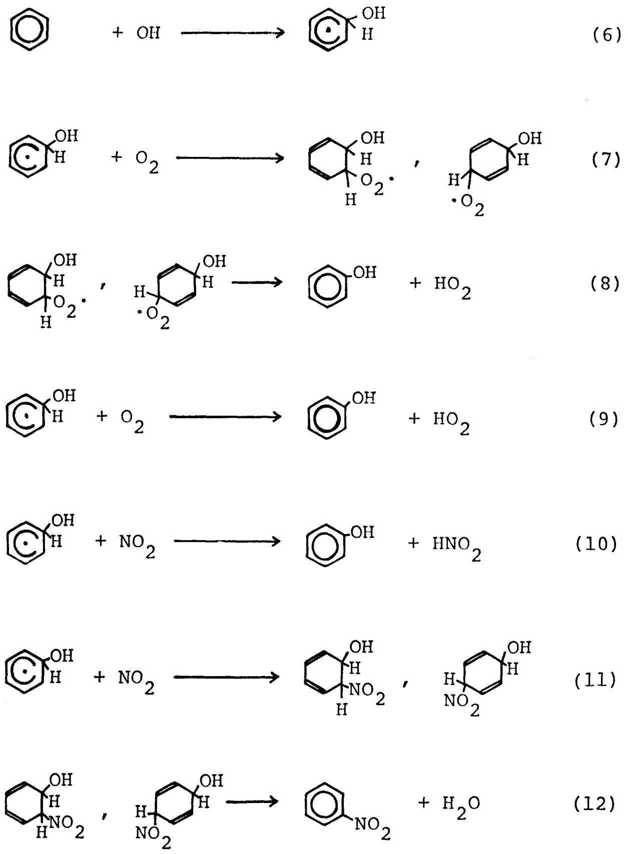
where NO and NO_2 are unavoidably present in the initial reaction mixture and also formed in the photolysis of HNO_2. In such a reaction system, a part of the OH radicals would be reproduced by the reaction

$$HO_2 + NO \longrightarrow OH + NO_2, \tag{5}$$

since HO_2 radicals are expected to be produced in the reaction of OH radicals with aromatic hydrocarbons. Thus, the photochemical oxidation in the present system is a chain process in which an OH radical acts as a chain carrier.

Benzene–HNO_2 System. In the photochemical reaction of the benzene–HNO_2–air system, the initial step should be the OH radical addition to the benzene ring followed by the reactions with O_2 and NO_2 (Scheme 1).

Addition of OH radicals to benzene has been shown to occur in the radiolysis[12,13] and photolysis[14] studies of aqueous solutions of benzene. In pulse radiolysis[12] of the aqueous solution of benzene, a transient absorption spectrum assigned to hydroxycyclohexadienyl radical has been detected. The final products in the aerated solution were phenol, peroxide, and hydroperoxide, whose yields were dependent on the pulse intensity. At low pulse intensities where the formation of peroxide and hydroperoxide due to radical-radical reactions was unfavorable, phenol was the main product and could account for 80% of the yield of OH radicals. On the other hand, photolysis[14] of benzene–H_2O_2 and γ-radiolysis[13] of benzene, both in aqueous solutions in the presence of oxygen, are known to give phenol and hydroxy-2,4-hexadienedial (CHO–C(OH)=CH–CH=CH–CHO and CHO–CH=C(OH)–CH=CH–CHO) as final products.



Scheme 1.

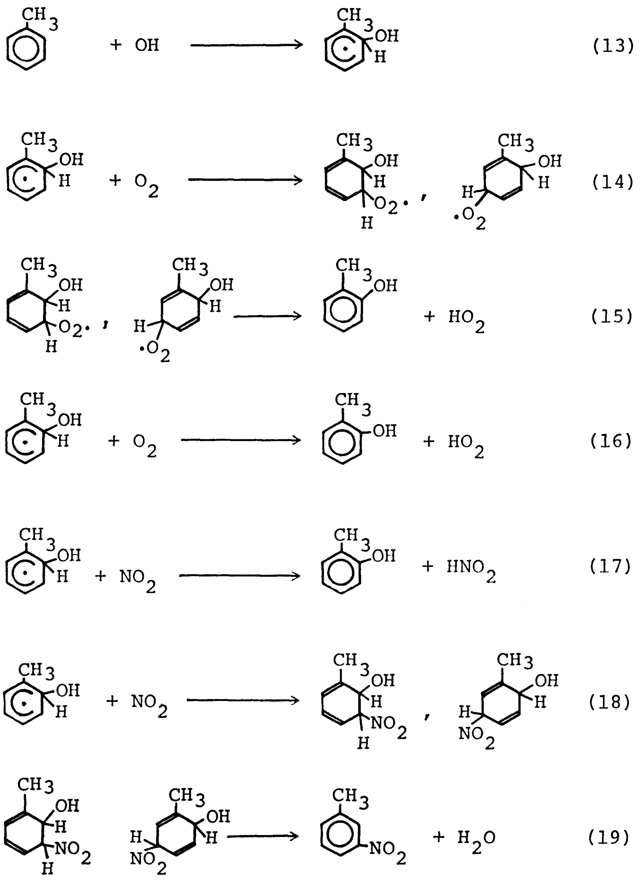
In the present reaction system, the final products were phenol and nitrobenzene and the formation mechanism can be visualized as in Scheme 1. The reaction sequence (7)—(8) is the same as the one suggested[12–14] for the formation of phenol in aqueous solutions. In the gas phase, however, Reactions 9 and 10, direct abstraction of the hydrogen atom by O_2 and NO_2, might also occur.

No formation of hydroxy-2,4-hexadienedial was observed. The compound is thought[13,14] to be formed *via* bimolecular reaction of 4-hydroxy-2,5-cyclohexadienylperoxyl radicals in aqueous systems. Since the concentration of benzene is two orders of magnitude lower than that in the aqueous studies, absence of the product due to the bimolecular radical-radical reaction is reasonable.

When NO_2 is present, it will add to the 4-hydroxy-2,5-cyclohexadienyl radicals to give nitrocyclohexadienols as a reaction intermediate and the elimination of H_2O from the intermediate will give nitrobenzene as a final product. Formation of nitrobenzene has been reported[15] in the radiolysis of aqueous $NaNO_3$ solution containing benzene, and the reaction mechanism based on the addition of NO_2 to the 4-hydroxy-2,5-cyclohexadienyl radicals followed by the elimination of H_2O has been postulated. The fact that the relative yield of nitrobenzene to phenol increases with increase in the initial concentrations of NO_2 can be explained by the mechanism shown in Scheme 1.

Nitrophenol was obtained as a very minor product. This is in line with the study of the radiolysis of aqueous $NaNO_3$–benzene system,[15] but differs from the one in the gas phase photo-oxidation systems[16,17] containing much higher concentrations (≈1000 ppm of each reactant) of benzene and NO or NO_2 in the air. Formation of nitrophenol instead of phenol was probably due to the secondary nitration of phenol either in the gas phase or during the analytical procedure.

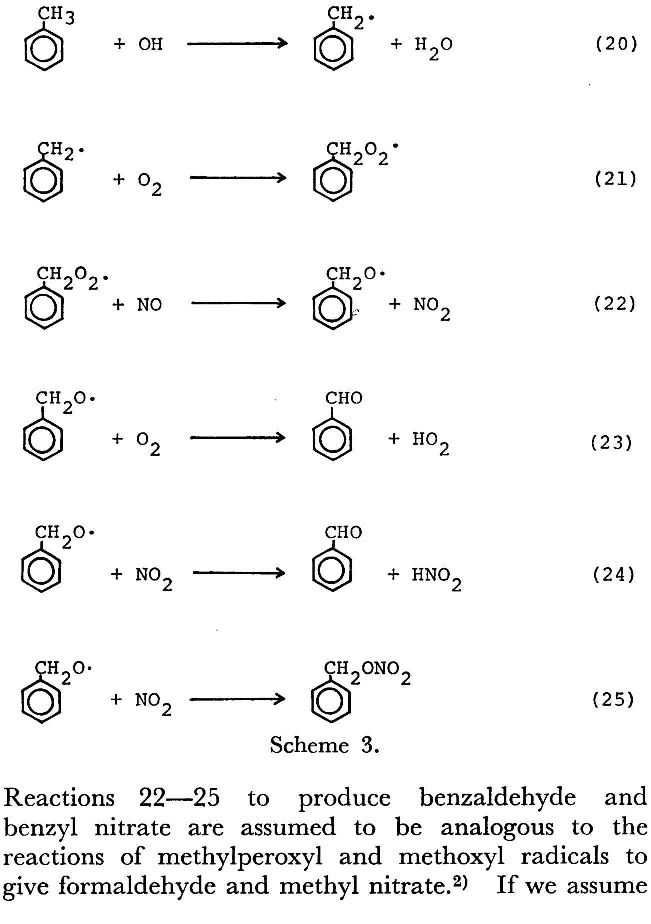
Toluene–HNO_2 System. In the reaction of the toluene–HNO_2–air system, cresols and *m*-nitrotoluene seem to be produced by the same reaction sequences as those for benzene. Approximately 80% of the total cresol formed was *o*-cresol. Predominant formation of *o*-cresol has recently been reported[18] in the reaction of toluene with oxygen atoms produced in the mercury photosensitization of N_2O. On the other hand, the formation ratio of *m*- and *p*-cresol to *o*-cresol is much higher in the radiation-induced hydroxylation[19] of toluene in aqueous solutions both in the presence and absence of metal salts. Hence it is concluded that the ortho position of toluene is regarded as the predominant reactive site both for OH radicals and oxygen atoms in the gas phase and that OH radicals discriminate the attacking site of substituted benzene more specifically in the gas phase than in aqueous solutions. The formation mechanism of cresols and *m*-nitrotoluene is proposed to be as follows.



Scheme 2.

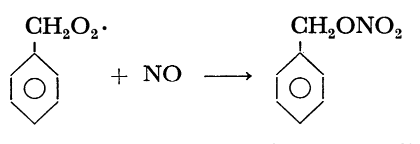
A marked increase in the yield of *m*-nitrotoluene relative to cresols with an increase of initial concentration of NO_2 (Table 2 and Fig. 3) is in line with the proposed mechanism. It should be noted that the addition of OH radicals to the para position (not shown in Scheme 2) also leads to *m*-nitrotoluene when NO_2 adds to the methyl-substituted hydroxycyclohexadienyl radicals followed by elimination of H_2O. A minor product, *p*-nitrotoluene, might be produced *via* an intermediate radical of an OH adduct at the meta position followed by elimination of H_2O. However, the increase of *p*-nitrotoluene with an increase of the initial concentration of NO_2 is much less marked (Table 2), no *o*-nitrotoluene, which is also expected from the OH adduct at the meta position, being obtained. This suggests a different reaction path for *p*-nitrotoluene although an alternate mechanism can not be specified.

Benzaldehyde and benzyl nitrate are reasonably assumed to be formed from benzyl radicals as intermediates. Hydrogen atom abstraction by OH radicals from the methyl group of toluene occurs at slightly elevated temperatures in gas phase reactions.[20] Since the C–H bond-dissociation energy[21] in the methyl group of toluene is only 83 kcal/mol as compared to 91 kcal/mol for the tertiary C–H bond of isobutane, it is reasonable to assume that the hydrogen abstraction competes with the addition to the aromatic ring even at room temperature. Kinetic studies[6,7] on the determination of rate constants for the reaction of OH radicals with toluene also suggest the competitive abstraction of hydrogen atom from the methyl group. The formation mechanism of benzaldehyde and benzyl nitrate is thus proposed as follows, in analogy with the reaction sequence postulated[2] for alkyl radicals in the presence of O_2, NO, and NO_2.



Scheme 3.

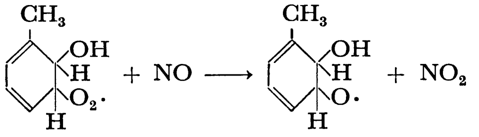
Reactions 22—25 to produce benzaldehyde and benzyl nitrate are assumed to be analogous to the reactions of methylperoxyl and methoxyl radicals to give formaldehyde and methyl nitrate.[2] If we assume the distribution of the final products given in Table 2 represents the initial step ratio of the OH addition to hydrogen atom abstraction, the percentage of the abstraction is estimated to be 25—35%. The value is in line with the suggestion by Davis *et al.*[6] that over half of the time, the reaction at room temperature proceeds *via* addition based on the pressure dependence of the rate constants. However, since no material balance has been studied, the above value should be taken as a first approximation. Formation of benzyl nitrate apparently did not increase with the increase of the initial concentration of NO_2, and an alternative path



(26)

might take place as proposed by Darnall *et al.*[22] in the case of alkylperoxyl radicals containing more than four carbon atoms.

The unidentified minor product in the photo-oxidation of toluene, giving mass peaks at *m*/*e*, 124, 123, 122, 94, 82, 66, and 54, might be 2-methyl-2,4-hexadienedial. A possible reaction mechanism to give the product is as follows.



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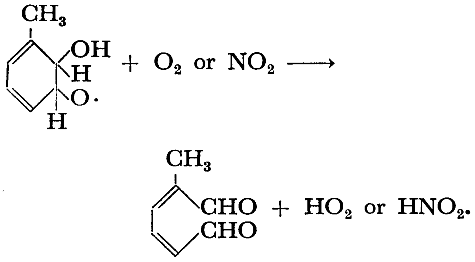
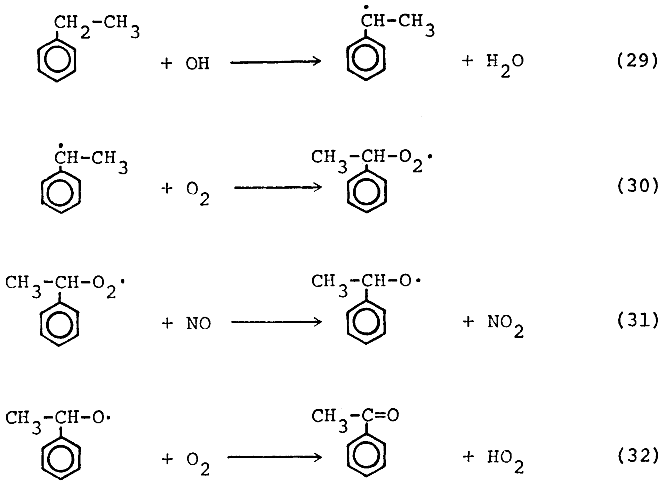


(28)

Although the mass pattern observed is what is expected for the compound, the identification is tentative since no authentic sample was available.

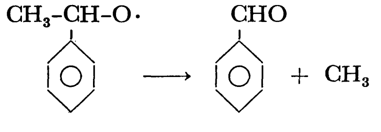
In an atmosphere of N_2 instead of air, the products obtained are cresols and *m*- and *p*-nitrotoluene. Benzaldehyde and benzyl nitrate, thought to be produced *via* benzylperoxyl radicals, were not observed. The results are in line with the proposed schemes 2 and 3. On the other hand, in the absence of O_2 bibenzyl and/or α-nitrotoluene derived from benzyl radicals can be expected as final products. Neither of them, however, was detected. Presumably, the poor yields of these products may be due to the low concentration of the radicals and NO_2. The ratio of *m*-nitrobenzene to phenol in the N_2 atmosphere was four times greater than that in the air. This observation is qualitatively explained by the fact that the hydrogen atom abstraction by O_2, Reactions 14, 15, and/or 16, does not contribute to the formation of cresols in the absence of O_2, resulting in a greater ratio of *m*-nitrotoluene to cresols as compared with that obtained in the air.

Ethylbenzene–HNO_2 System. Of the products obtained in the ethylbenzene–HNO_2–air system, ethyl phenol and *m*- and *p*-nitroethylbenzene will be derived from the addition of OH radicals to an aromatic ring as in the case of toluene. The reaction mechanism is analogous to Scheme 2 for toluene. Acetophenone is considered to be produced *via* 1-phenylethyl radicals formed by the abstraction of an α-hydrogen atom by OH radicals. The proposed mechanism is as follows.



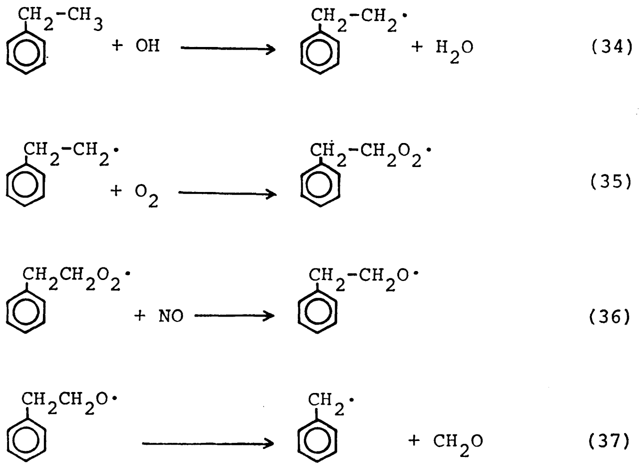
Scheme 4.

Another major product, benzaldehyde, is thought to be produced by the decomposition of 1-phenylethoxyl radicals as follows.



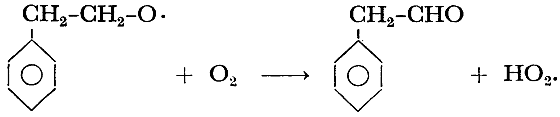
(33)

Bond cleavage in alkoxyl radicals to give a carbonyl compound and methyl radical has been assumed[23] in the photochemical oxidation of isobutane in the presence of NO and NO_2. Another possibility for the formation of benzaldehyde is the one initiated by the abstraction of a β-hydrogen atom in ethyl group of ethylbenzene. The reaction scheme is shown as Scheme 5.



Scheme 5.

According to Eqs. 21 and 22, benzyl radicals produced may be oxidized to give benzaldehyde. However, if this reaction mechanism holds, phenylacetaldehyde should also be expected as



(38)

Benzyl nitrate is also expected as in the case for toluene. Since neither of these products was obtained, we conclude that the β-hydrogen abstraction does not occur in the reaction of OH radicals with ethylbenzene, and Scheme 4 should be adopted to interpret the formation of benzaldehyde.

The ratio of yield of products formed *via* hydrogen atom abstraction to those *via* OH radical addition increases markedly for ethylbenzene as compared with the case of toluene. Thus, from the product distribution (Table 3) the percentage of the hydrogen abstraction may be deduced to be 60—70%. The apparent increase in percentage of the hydrogen abstraction reaction would be due to the weaker bond energy of α-hydrogen-carbon bond in the ethyl group of ethylbenzene than that in the methyl group of toluene.

Atmospheric Importance. It is well-known that aromatic hydrocarbons (alkylbenzenes) constitute a substantial fraction of hydrocarbons in the polluted urban atmosphere. For example, the average percentage of aromatic hydrocarbons in the Los Angeles Basin was reported[24] to be roughly 20%. In Japan, the presence of a higher percentage of aromatic hydrocarbons has been noted,[25,26] amounting to 30—35% in average. Thus it is expected that the reaction products observed in the present study should also be formed in such an ambient air. Phenols, aromatic carbonyl compounds and nitrobenzenes, and nitrates should be of concern since they are found to be formed even at atmospheric concentrations of NO and NO_2. Recently, nitrocresols were observed[16] in rain drops collected in Yokohama. This suggests that the nitration of phenols occurs easily in both gas phase secondary reactions and in aerosol droplets, since the nitrocresols are only a minor products in the primary reaction of OH radicals in the presence of atmospheric concentration of NO and NO_2.

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