Reaction Mechanism of the Photooxidation of the Toluene–NO_2–O_2–N_2 System in the Gas Phase

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Photooxidation of the toluene (34 ppm)–NO_2(8—207 ppm)–N_2 and/or O_2(1 atm) system has been studied in a 67 dm^3 reaction chamber. The reaction was initiated by $O(^3P)$ atoms formed in the photolysis of NO_2. The main products were benzaldehyde, cresols, benzyl nitrate, *m*-nitrotoluene, 6-nitro-*o*-cresol, and 2-nitro-*p*-cresol. Their relative yields were studied as functions of reactant concentrations. The formation mechanisms of the products were proposed on the basis of the reactions of $O(^3P)$ and OH radicals with toluene in the presence of NO_2 and O_2.

Studies have been made on the photochemical oxidation of alkylbenzenes in the presence of nitrogen oxides (NO_x) and air in relation to photochemical air pollution. However, they deal mostly[1)] with ozone formation and the so-called "photochemical reactivity."[2)] A few reports[3–6)] have been given on the reaction products and mechanisms of the gas phase photooxidation of alkylbenzenes–NO_x–air system.

Kopczynski[3)] studied the photooxidation of alkylbenzenes–NO_2–air systems using a long-path infrared spectrometer and identified aldehydes, CO, CO_2, formic acid, and peroxyacetyl nitrate as reaction products. Nojima *et al.*[4a)] studied the photooxidation of the benzene–NO_2–air system and identified nitrobenzene, nitrophenols, and dinitrophenols. They also reported[4b)] the formation of glyoxal, methylglyoxal, and biacetyl which would have been produced by the cleaving of benzene rings in the photooxidation of benzene, toluene, and xylene. Ando *et al.*[5)] studied the formation yield of nitrobenzenes in the benzene–NO_2–O_2–N_2 system as functions of O_2 and NO_2 concentrations.

Photooxidation of alkylbenzenes in the atmosphere is thought to be initiated by OH or O atoms. The photooxidation of alkylbenzene–HNO_2–air systems, in which OH radicals initiated the oxidation of benzene, toluene, and ethylbenzene, was studied and the reaction mechanisms were discussed in our previous study.[6)] In this work,[7)] photooxidation of the reaction systems of toluene (34 ppm), NO_2(8—207 ppm) in N_2 and/or O_2 at 1 atm was studied for the case in which O atoms from NO_2 initiate the oxidation, giving most of the oxidized products. The final reaction products and their relative yields as functions of reactant concentrations are reported and a discussion of the reaction mechanisms is presented.

Experimental

Figure 1 shows a schematic diagram of the apparatus. The reaction chamber is a Pyrex cylinder, 225 mm i.d., 1660 mm in length, 67 dm^3 in volume: evacuated to less than 1×10^{-6} Torr. Metal parts containing gas inlets and outlets are attached to both ends of the Pyrex cylinder with Viton O-rings, the inside walls of the metal parts being lined with Teflon in order to avoid any catalytic reactions on the metal surfaces. Each end of the reaction chamber is sealed with a Pyrex window 20 mm thick, through which a photolyzing light beam can be transmitted into the gas sample.

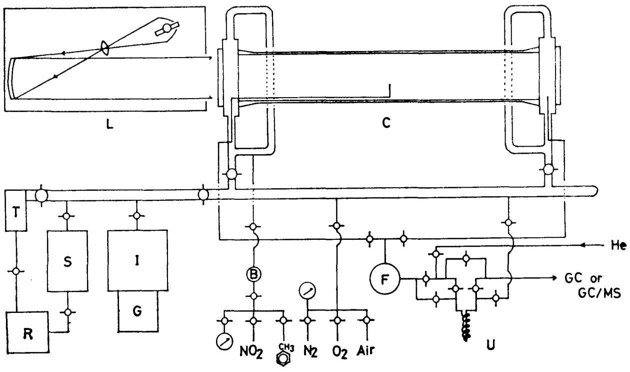


Fig. 1. Schematic diagram of the experimental apparatus. C: Reaction chamber; L: xenon arc lamp house; I: sputter ion pump; G: titanium getter pump; S: sorption pump; T: foreline trap; R: rotary pump; B: gas burette; F: sampling flask; U: low temperature spiral trap.

The light source was a 500 W xenon short arc lamp. A parallel light beam of *ca.* 200 mmϕ was obtained by using an elliptical mirror, lens, and an off-axis parabolic mirror. The effective light intensity as measured by the primary photodecomposition rate of NO_2 was 0.08 min^{-1}. The wavelengths of the irradiated light were greater than 320 nm. An oil free pumping system consisting of a sputter ion pump, titanium getter pump, cryo-sorption pump, and a rotary pump with a liquid nitrogen cooled foreline trap was used.

Toluene and NO_2 were first put into a 105-ml glass flask and then expanded into the reaction chamber. Air, O_2, or N_2 was then introduced through four gas inlets shown in Fig. 1. The pressure was measured with Capsulon gauges (Edward High Vacuum Co.), 50 and 760 Torr full scale which were calibrated by a mercury manometer. In order to confirm that the sample gases were mixed homogeneously, four sampling ports were attached to the chamber (only two of them are shown in Fig. 1), at the center, at one-fourth of the chamber length distance from one end, and at both ends. One hour after the gases had been introduced the concentration of the toluene taken from the four different ports was found to be the same, and irradiation was thus started. Sampling was repeatedly carried out through the center port at suitable time intervals. "Pure Air" (dew point lower than −70 °C), O_2 (>99.9%, graded as "Pure gas B") and N_2 (>99.995%, graded as "Pure gas B") were supplied from Nippon Sanso Co. NO_2 was obtained by mixing NO (research grade, Matheson) with excess O_2. Toluene (research grade, Wako Pure Chemical Ind.) was used without further pruification except degassing. It contains *ca.* 0.01% xylenes, as impurity, which is negligible in the present study.

The reaction mixture was first introduced into a 700-ml constant volume glass flask and then concentrated in a GC sampling tube. The sampling tube, a Pyrex spiral of 2 mm i. d., about 4 m in extended length, was cooled to −60 °C. After the concentration, the sampling tube was heated with hot water and the sample was fed directly into a gas chromatograph. This procedure was found to minimize the yields of the products of thermal reactions of NO_2 with toluene and cresols in the smapling tube. Sampling for the GC analysis was made periodically every 45—60 min. GC analysis was carried out using a 3-m column of 5% SE-30 on Shimalite W. The GC oven temperature was raised from 80 to 200 °C at a rate of 4 °C/min. The concentration of NO_2 was monitored for several runs by the method of single beam photometry at a wavelength of 450 nm using the irradiation light as a light source. Identification of product was carried out by comparing the reference mass pattern and GC retention time using a GC-MS (JEOL, JMS-100) and a GC. In order to obtain the reference mass patterns and GC retention times, standard samples of benzaldehyde, *o*-, *m*-, *p*-cresols, benzyl nitrate, *o*-, *m*-, *p*-nitrotoluenes, *o*-nitrophenol, and 2- nitro-*p*-cresol were used. All chemicals except for benzyl nitrate were commercial products (Wako Pure Chemical Co.). Benzyl nitrate was prepared by fractional distillation of the reaction mixture of benzyl chloride and $AgNO_3$ in a dried acetonitrile solution. Identification of 6-nitro-*o*-cresol was performed by comparing the GC retention time with the reference sample obtained by the thermal reaction between *o*-cresol and NO_2. The mass pattern of 6-nitro-*o*-cresol was found to be nearly identical with that of 2-nitro-*p*-cresol.

For several experimental runs on the photooxidation of the HNO_2–NO_x–toluene–air system, known amounts of toluene and NO_2 were first introduced into the reaction chamber and then HNO_2–air mixture was introduced under a total pressure of 1 atm. The HNO_2–air mixture was produced by using 10 ml of 0.05 M $NaNO_2$ and 10 ml of 5% H_2SO_4.[6] The concentrations of HNO_2 and nitrogen oxides in the HNO_2–air mixture were determined[6] by the method of Cox[8] using a commercial chemiluminescence NO_x analyzer (Monitor Labs, Model 8440). The HNO_2–air mixture produced by the above method was found to contain *ca.* 12 ppm of HNO_2 and 2 ppm each of NO_2 and NO.

Results

The reaction products observed in the photooxidation of the toluene (34 ppm)–NO_2(8—207 ppm)–air(1 atm) system were benzaldehyde, cresols, benzyl nitrate, *m*-nitrotoluene, 6-nitro-*o*-cresol, and 2-nitro-*p*-cresol. Smaller amounts of *o*-nitrophenol and *o*- and *p*-nitrotoluene were also detected. The relative yield of *o*-cresol was about 80% of the total amout of cresols, the sum of *m*- and *p*-cresol being about 20% of the total. By means of the gas chromatograph column used in this work, *m*- and *p*-cresols could not be seperated. Figure 2 shows the relative product yields as functions of irradiation time for a typical run of toluene (34 ppm), NO_2 (7.7 ppm) and 1 atm air. In the present study product analysis was carried out at a low reactant conversion (<1%). Under these conditions amounts of all the products increased linearly with irradiation time and ratios of products could be calculated from the slope ratio of the linear plots.

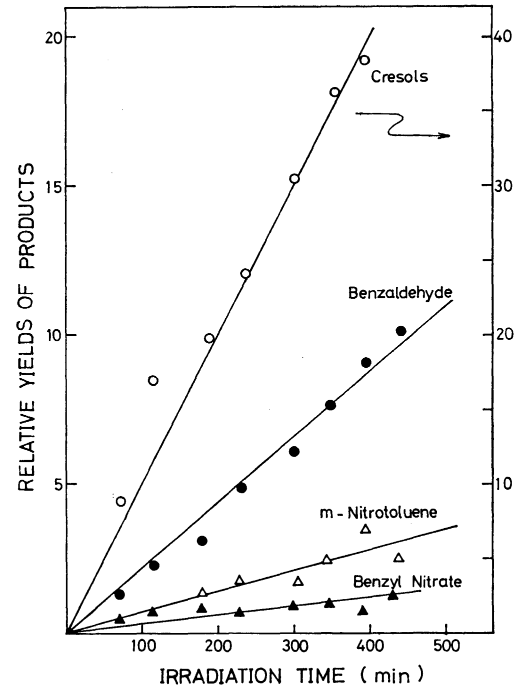


Fig. 2. Relative yields of the products *vs.* irradiation time in the photooxidation of NO_2 (7.7 ppm)–toluene (34 ppm)–air (1 atm) system. ○ Cresols; ● benzaldehyde; △ *m*-nitrotoluene and ▲ benzyl nitrate.

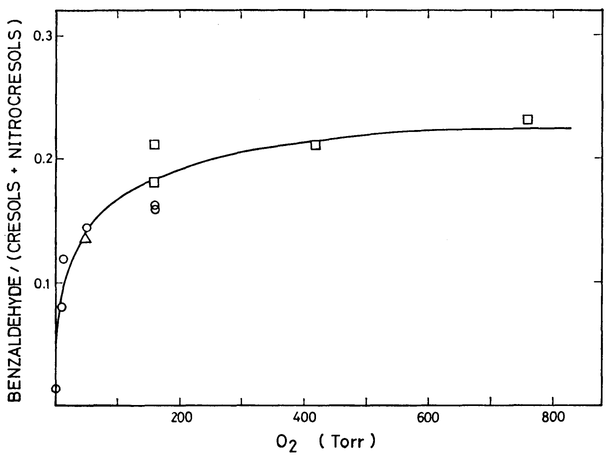


Fig. 3. The formation ratio of benzaldehyde to the sum of cresols and nitrocresols *vs.* partial pressure of O_2 in the photooxidation of NO_2–toluene (34 ppm)–O_2–N_2 (1 atm) system. Initial concentration of NO_2 are △ 6.4, ○ 24, and □ 30 ppm.

In order to clarify the formation mechanism of the products, experiments were carried out by varying the initial concentrations of O_2 and NO_2. Figure 3 shows the ratio of benzaldehyde to cresol as a function of O_2 partial pressure for several initial concentrations of NO_2. In these experiments, total pressure was kept at 760 Torr using N_2 as a buffer gas. It shoud be noted that in the absence of O_2 (NO_2–toluene–N_2 system) no benzaldehyde was formed, cresol being the major condensable product with trace amounts of nitrocresols. The yields of nitrocresols were found to be much smaller than those in the NO_2–toluene–air system for the same initial concentration of NO_2. As shown in Fig. 3, the ratio of benzaldehyde to cresols increases with increase in the concentration of O_2, reaching a saturated value at an O_2 partial pressure higher than a few hundred Torr.

The ratio of nitrocresols (the sum of 6-nitro-*o*-cresol and 2-nitro-*p*-cresol) to cresols increases linearly with the concentration of NO_2 (Fig. 4), NO_2 being measured by UV absorption at 450 nm. Figure 5 shows the ratio of benzaldehyde to the sum of cresols and nitrocresols as a function of the photo-equilibrium concentration of NO_2. In the reaction system of air at 1 atm, the concentration of NO_2 reached the photoequilibrium level within 20 min after irradiation was started, remaining nearly constant during the course of irradiation time. The photo-equilibrium concentration of NO_2 was about 50% of the initial concentration of NO_2. As shown in Fig. 5 the yield ratio of benzaldehyde to the sum of cresols and nitrocresols is independent of the concentration of NO_2. Thus, the yield of other products could be normalized by the sum of cresols and nitrocresols. Typical data for the product yields are given in Table 1.

The ratio of benzyl nitrate to benzaldehyde increased with an increase in the concentration ratio of NO_2 to O_2 (Fig. 6). Figure 7 shows the relative yield of *m*-nitrotoluene as a function of the initial concentration

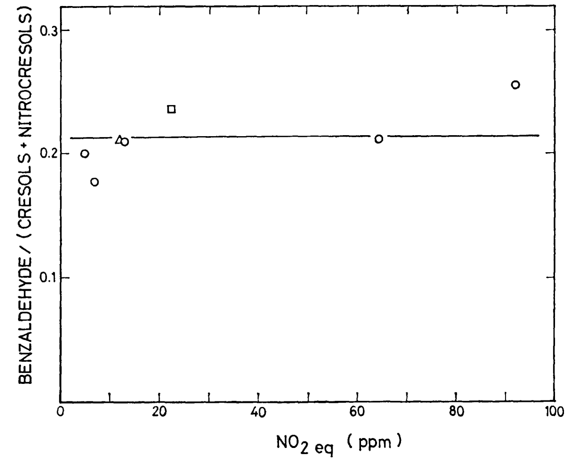


Fig. 5. The formation ratio of benzaldehyde to the sum of cresols and nitrocresols *vs.* equilibrium concentration of NO_2 for the NO_2–toluene (34 ppm)–O_2–N_2 (1 atm) system. Partial pressure of O_2 are ○ 160, △ 418, and □ 760 Torr.

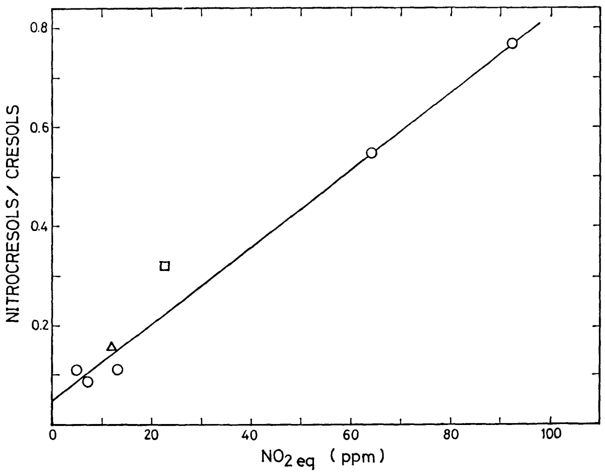


Fig. 4. The formation ratio of nitrocresols to cresols *vs.* equilibrium concentration of NO_2 for the NO_2–toluene (34 ppm)–O_2–N_2 (1 atm) system. Partial pressure of O_2 are ○ 160, △ 418, and □ 760 Torr.

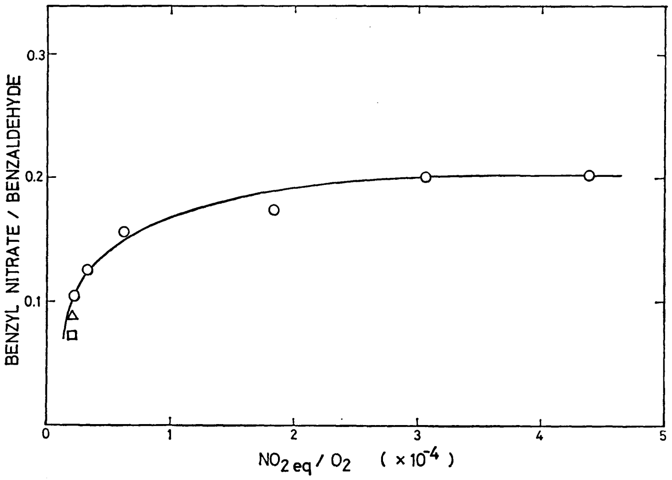


Fig. 6. The formation ratio of benzyl nitrate to benzaldehyde *vs.* the ratio of equilibrium concentration of NO_2 to O_2 for the NO_2–toluene (34 ppm)–O_2/N_2 system. Partial pressure of O_2 are △ 160, ○ 418, and □ 760 Torr.

Table 1. Relative product yield (cresols+nitrocresols = 1.0) in the photooxidation of the NO_2-toluene-O_2/N_2 system (total pressure = 760 Torr)

Initial NO_2 (ppm)	NO_{2eq} (ppm)	O_2 (Torr)	Benzaldehyde	Cresols	Benzylnitrate	*m*-Nitrotoluene	Nitrocresols
174	92	160	0.26	0.23	0.052	0.021	0.77
145	64	160	0.21	0.45	0.040	0.015	0.55
38	13	160	0.21	0.89	0.033	0.062	0.11
20	7	160	0.18	0.91	0.023	0.060	0.09
11	5	160	0.20	0.89	0.021	0.071	0.11
24	6	47	0.15	0.93	0.016	0.030	0.07
30	12	418	0.21	0.84	0.018	0.043	0.16
30	23	760	0.24	0.68	0.017	0.045	0.32

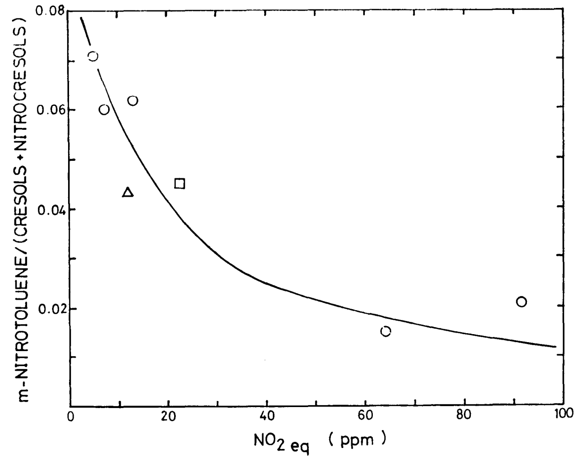


Fig. 7. The formation ratio of m-nitrotoluene to the sum of cresols and nitrocresols *vs.* equilibrium concentration of NO_2 for the NO_2–toluene (34 ppm)–O_2/N_2 system. Partial pressure of O_2 are ○ 160, △ 418, and □ 760 Torr.

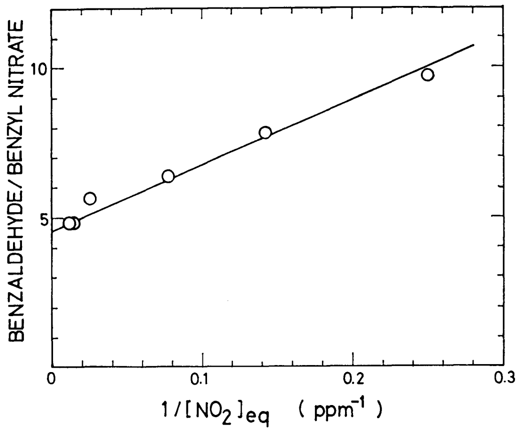


Fig. 8. The formation ratio of benzaldehyde to benzyl nitrate *vs.* the reciprocal of the equilibrium concentration of NO_2 for the NO_2–toluene (34 ppm)–air (1 atm) system.

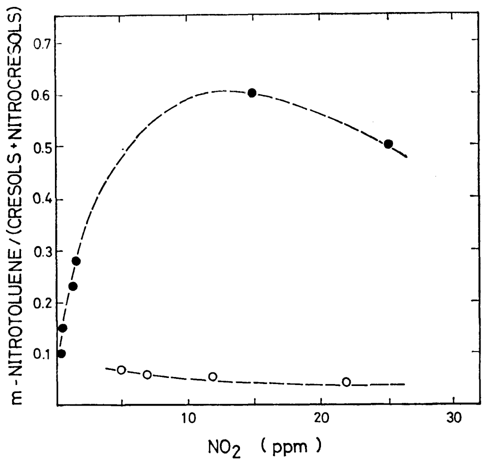


Fig. 9. The formation ratio of *m*-nitrotoluene to the sum of cresols and nitrocresols *vs.* initial concentration of NO_2 for the HNO_2–NO_2–toluene (34 ppm)–air (1 atm) system (●) and the NO_2–toluene (34 ppm)–air (1 atm) system (○).

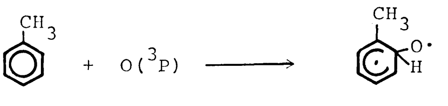
of NO_2. It is remarkable that the relative yield of *m*-nitrotoluene, one of the nitrated products decreases with increase in NO_2 concentration. In order to compare the yield of *m*-nitrotoluene in the NO_2–toluene–air system with that in the HNO_2–NO_x–toluene–air system at a comparable initial concentrations of NO_2, two runs for the HNO_2 (12 ppm)–NO_2 (15 ppm and 25 ppm)–toluene(34 ppm)–air(1 atm) system were carried out. The result is shown in Fig. 9, where four data points for HNO_2 runs of lower NO_2 concentrations (less than 2 ppm) are taken from the work of Hoshino *et al.*[6)]

Discussion

Formation Mechanisms of Cresol and Nitrocresol. Since in the present study the wavelength of the irradiated light is greater than 320 nm and toluene absorbs no light in this spectral region, the photooxidation is initiated by $O(^3P)$ atoms formed in the photolysis of NO_2:

$$NO_2 + h\nu(320\text{—}400\,\text{nm}) \longrightarrow NO + O(^3P). \qquad (1)$$

The reaction of $O(^3P)$ atoms with toluene has been studied[9)–11)] in some detail by mercury photosensitization of the N_2O–toluene system. The main volatile products were cresols and CO. Small amounts of phenol, methane, and ethane, and predominant polymer formation were observed. There are differences in the relative yields of cresol isomers in these studies. The ratios of *o*-cresol to total cresols were reported to be 64% (Jones and Cvetanović[9)]), 78% (Grovenstein and Mosher[10)]), and 94% (Gaffney *et al.*[11)]). Formation of *p*-cresol was noted only by Jones and Cvetanović.[9)] In the present reaction system of NO_2–toluene–O_2–N_2, the cresols are the major condensable products in the absence of O_2, and also main products in the presence of O_2 (see Table 1). In both cases, more than 80% of total cresols was *o*-cresol. This is closer to the results of Gaffney *et al.*[11)] From these data, the formation of *o*-cresols in the present reaction system is considered to be mainly due to the reaction of the $O(^3P)$ atom with toluene. This reaction would proceed *via* oxygen atom addition to the benzene ring followed by the intramolecular hydrogen atom transfer reaction.[9)]

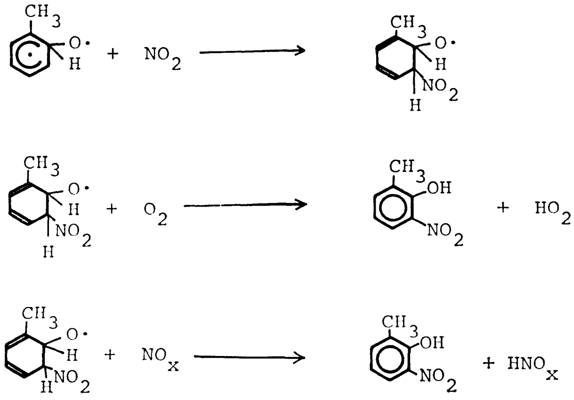


(2)

(3)

The existence of the long-lived biradical formed in Reaction 2 has been suggested in the work of Mani and Sauer.[12)] However, it should be noted that the reaction of OH radicals with toluene also gives *o*-cresol.[6)]

The ratio of nitrocresols to cresols increases linearly with the photo-equilibrium concentration of NO_2, while the ratio of the sum of cresols and nitrocresols to benzaldehyde remains constant (Figs. 4 and 5). The results suggest that nitrocresols should be formed in the competitive reaction of NO_2 with the same precursor as that giving cresols. The following reaction mechanism is proposed:



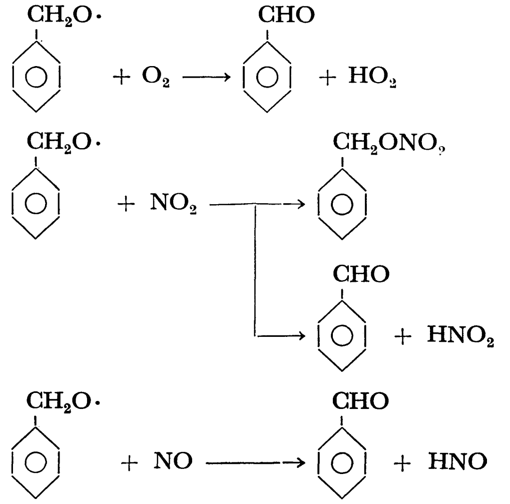
(4)

(5)

(6)

where NO_x denotes NO or NO_2. The result showing that the formation of nitrocresol is suppressed in the absence of O_2 can be explained by the absence of Reaction 5. According to Reactions 2—6, 6-nitro-*o*-cresol should be the major product among nitrocresol isomers if we assume that NO_2 combines with the biradical almost entirely at the carbon atom adjacent to the one to which the oxygen atom is attached (Reaction 4).

Formation Mechanisms of Benzaldehyde and Benzyl Nitrate. Benzaldehyde and benzyl nitrate were formed only in the presence of O_2. Formation of these products strongly suggests the presence of the benzyloxyl radical as their precursor in the reaction system. Competitive reactions



(7)

(8a)

(8b)

(9)

yield the relation

$$\frac{[\mathrm{B.A.}]}{[\mathrm{B.N.}]}=\frac{k_7}{k_{8a}}\frac{[O_2]}{[NO_2]_{eq}}+\frac{1}{k_{8a}}\left(k_{8b}+k_9\frac{[NO]_{eq}}{[NO_2]_{eq}}\right) \quad (10)$$

where B.A. and B.N. stand for benzaldehyde and benzyl nitrate, respectively, and $[NO]_{eq}$ and $[NO_2]_{eq}$ are the concentrations of NO and NO_2 under photoequilibrium. Under the conditions of 1 atm air, $[NO]_{eq}/[NO_2]_{eq}$ was nearly constant (≈ 1.0) irrespective of the initial NO_2 concentration. Thus, the plot of [B.A.]/[B.N.] *vs.* $[O_2]/[NO_2]_{eq}$ should give a straight line according to Eq. 10. The points (circular) in Fig. 6 are plotted again in Fig. 8 on the scale of [B.A.]/[B.N.] *vs.* $1/[NO_2]_{eq}$. From the slope of Fig. 8, the value of k_7/k_{8a} was deduced to be 1.4×10^{-4}. For similar reactions of methoxyl radicals

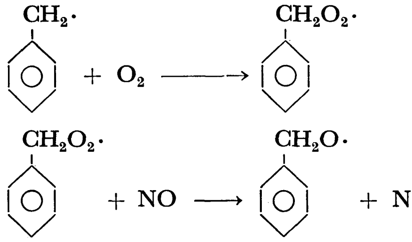
$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \quad (11)$$

$$CH_3O + NO_2 \longrightarrow CH_2ONO_2 \quad (12a)$$

$$ \longrightarrow CH_2O + HNO_2 \quad (12b)$$

the value of $k_{11}/k_{12}=5.6\times10^{-5}$ was given by Wiebe *et al.*[13] Glasson[14] reported the value of $k_{11}/k_{12a}<(7.4\pm0.7)\times10^{-5}$. Our value for the benzyloxyl radical is nearly of the same order of magnitude, but slightly higher than the above values for the methoxyl radical.

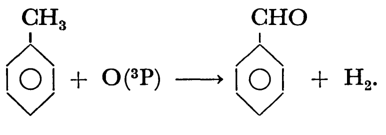
Benzyloxyl radicals are thought to be formed *via* reactions



(13)

(14)

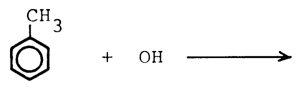
Analogous reactions for alkyl radicals have been proposed by Heicklen *et al.*[15] According to the above reaction scheme, no benzaldehyde and benzyl nitrate would be formed in the absence of O_2. Their yields would increase with the increase of the concentration of O_2 to the extent where all benzyl radicals are trapped by O_2. Our experimental result (Fig. 3) confirmed that this is the case for benzaldehyde. Our results that no benzaldehyde and benzyl nitrate could be detected in the O_2 free system also suggests the above reaction mechanism. Recently, Sloane[16] observed the product with an *m/e* of 106 in the reaction of $O(^3P)$ and toluene under molecular beam conditions and proposed a reaction



(15)

If this reaction had occurred in the present reaction system, benzaldehyde would have been formed even in the O_2 free system. Thus, Reaction 15 is not important under our experimental conditions.

Formation Mechanism of m-*Nitrotoluene.* The yield of *m*-nitrotoluene decreases with increase of NO_2. This unexpected behavior of *m*-nitrotoluene can be explained if we assume that it is formed by the reaction which is initiated by OH radicals rather than by $O(^3P)$ atoms. In our study of the photooxidation of toluene in the HNO_2–NO_x–toluene–air system, where the OH radical reaction predominates, the relative yield of *m*-nitrotoluene to cresols is much higher than that in the present system. The yield of *m*-nitrotoluene in the HNO_2–NO_x–toluene–air system is compared with that in the NO_2–toluene–air system in Fig. 9. In the HNO_2 system, the relative yield of *m*-nitrotoluene to cresols+nitrocresols increases when the concentration of NO_2 increases in the region less than 10 ppm of NO_2. An opposite tendency is observed in the NO_2 system. The formation mechanism of *m*-nitrotoluene and cresols in the HNO_2–NO_x–toluene–air system, was proposed⁶⁾ to be as follows.



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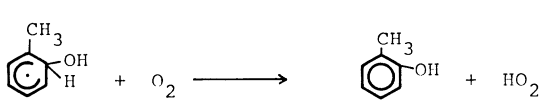

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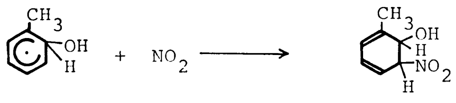

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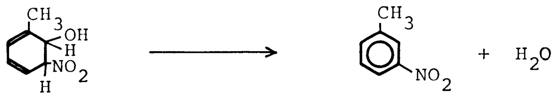


(19)

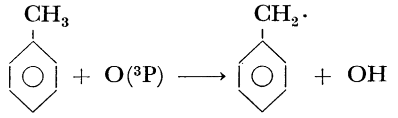
The increase in the ratio of *m*-nitrotoluene to cresols with increase in the concentration of NO_2 can be explained by the competition between Reactions 17 and 18. On the other hand, in the present reaction system of NO_2–toluene–air, most of the cresols are formed in the reaction of $O(^3P)$ with toluene, *m*-nitrotoluene being assumed to be formed in Reactions 16, 18, and 19. In this case, the competition between Reaction 16 and the following Reactions 20 and 21 would result in a decrease in the relative yield of *m*-nitrotoluene at higher NO_2 concentrations because of the quenching of OH radicals by NO_2 and NO.

$$OH + NO_2 \xrightarrow{M} HNO_3 \tag{20}$$

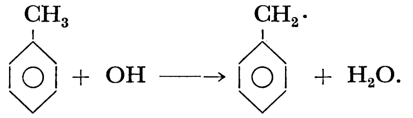
$$OH + NO \xrightarrow{M} HNO_2 \tag{21}$$

Although second order rate constants at 760 Torr for Reactions 20 and 21 are comparable,¹⁷,¹⁸⁾ Reaction 20 would be more effective sink of OH radicals since the photolysis of HNO_2 regenerates them.

Formation of Benzyl Radicals. According to the proposed reaction mechanism, side chain oxidation products, benzaldehyde and benzyl nitrate are formed *via* benzyloxyl radicals, which should be formed from benzyl radicals *via* Reactions 13 and 14. Benzyl radicals could be formed in the present reaction by the reaction of toluene with either $O(^3P)$ or OH radicals, *i.e.*,



(22)



(23)

OH radicals are produced mainly by the reaction

$$HO_2 + NO \longrightarrow OH + NO_2 \tag{24}$$

where HO_2 radicals are formed in Reactions 5, 7, and 17. Reaction 22 and the photolysis of HNO_2 formed in Reactions 6, 8b, and 21 would also contribute to the production of OH radicals.

OH radicals abstract hydrogen atoms from the methyl group of toluene(Reaction 23) and also add to benzene ring (Reaction 16) at room temperature. From the pressure dependence of the rate constant of the reaction of OH radicals with toluene, Davis *et al.*¹⁹⁾ deduced that over half of the total reaction proceeds *via* addition reaction. Perry *et al.*²⁰⁾ estimated the room temperature rate constant of the hydrogen abstraction reaction by extrapolation of the data above 380 K, where the reaction is assumed to proceed solely *via* abstraction, and obtained the fraction of the abstraction reaction of $16\pm^{0.07}_{0.05}\%$ at room temperature. In our product analysis study of OH radicals with toluene,⁶⁾ the fraction of abstraction reaction was estimated to be 25—35%.

The reaction of toluene with $O(^3P)$ has been thought to proceed only *via* ring addition since no dibenzyl formation takes place in the mercury photosensitization of the N_2O and toluene system. However, the NO_2 dependency on the formation of *m*-nitrotoluene (Fig. 9) shows that the contribution of OH radicals in the NO_2 system is not remarkable. Thus, the formation of benzaldehyde in the present study would be explained by Reaction 22. About 20% of the reaction of $O(^3P)$ with toluene should proceed *via* hydrogen abstraction from the methyl group of toluene.

The discrepancy might be caused by either of the following: (1) the contribution of OH radicals cannot be neglected in the present NO_2 system; the NO_2 dependency on the formation of *m*-nitrotoluene is a result of other unknown reactions or, (2) although benzyl radicals are formed in the mercury photosensitization of the N_2O and toluene system, they are quenched by the excess of oxygen atoms, turning polymers.

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