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Photochemical Oxidation of Toluene with Nitrogen Dioxide in Gas Phase. "Effects of Oxygen"

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Synopsis. The products and mechanism of the reaction of toluene with nitrogen dioxide have been investigated in the presence of oxygen. The volatile products observed were benzaldehyde, *o*-, *m*-, and *p*-nitrotoluene, along with 6-nitro-*o*- and 2-nitro-*p*-cresol.

Myriad descriptions of the mechanism of photochemical oxidation of aromatic hydrocarbons with nitrogen oxides have appeared over the last ten years.[1-4] These reviews have been accompanied by an even greater number of discriptions of the properties of reactive intermediates and of reaction rates. While much work has been carried out on the products and mechanism of the gas phase reaction of alkylbenzene with NO_2, mainly by Kato[5] and Akimoto *et al.*,[6] the major part of the reaction products was unfortunately a material of low volatility which could not be characterized. The present work was undertaken in the hope of obtaining additional information about the photooxidative products from the reaction of toluene with nitrogen dioxide in the presence of oxygen.

Experimental

A conventional high vacuum apparatus utilizing Teflon stopcocks was employed. A cylindrical reaction vessel made of Pyrex glass (22.5 liter), 1.5 m long and 16 cm in diameter, was connected to the storage bulbs for the reactants, to the trapping system equipped with gas-chromatographic take off bulbs, and to the high vacuum system.

Commercially available toluene was dried completely and distilled with rejection of appropriate first and last fraction until it was gas-chromatographically pure. Nitrogen dioxide dried by phosphorus pentaoxide was purified by repeated trap to tarp distillation under vacuum. The gases used were Nihon Tokushu Gas Co. extra dry grade nitrogen and oxygen, and Nihon Sanso Co. special grade air.

Known amounts of toluene and nitrogen dioxide were admitted to the reaction vessel and diluted with dry nitrogen or air to atmospheric pressure. The samples were irradiated for periods of 10 h with four Toshiba fluorescent light-bulbs, FLR40SBL-A(wavelength 300—420 nm, maximum at 360 nm, light intensity range of 4—8 $\mu W/cm^2$). The irradiated products were fractionally collected in a sample tube for gas-chromatographic analysis cooled at Dry Ice temperature. The products which were non-condensable in the Dry Ice trap were condensed in liquid nitrogen. The GLC analyses were carried out using a Hitachi 163 flame ionization detector with a 20 m long OV-101 capillary glass column. In all cases, the gas chromatographic evaluation of product yield was based on the internal standard 1-methylnaphthalene. There was an appreciable scatter in the quantitative yields of benzaldehyde and benzyl nitrate, perhaps because of some spurious loss of these highly oxidizable substances. The yields of these two compounds reported in the present work must therefore be regarded as only approximate. A maximum error of ±10% in the product yields was expected in all other cases. Non-volatile products in the reaction vessel were washed out with methanol and analyzed by GLC; they were mainly 4,6-dinitro-*o*-cresol.

Results and Discussion

Photolysis of Nitrogen Dioxide in Toluene and Nitrogen or Air System. The reaction was studied extensively at 25—30 °C at the concentration of 1000 ppm of nitrogen dioxide and toluene, respectively, for irradiation times ranging from 2—10 h. The reaction products observed were benzaldehyde(1), *o*-nitrophenol(2), *o*-nitrotoluene(3), benzylnitrate(4), α-nitrotoluene(5), *m*-nitrotoluene(6), *p*-nitrotoluene(7), 6-nitro-*o*-cresol(8), 2-nitro-*p*-cresol(9), and 4,6-dinitro-*o*-cresol(10). The yields of major products are given in Table 1.

No benzyl alcohol, *o*-, *m*-, or *p*-cresol were detected under these reaction conditions. In addition, a small amount of methane and ethane was observed for non-condensable products at 196 °C. On the other hand, there was some formation of *o*- and *p*-nitrotoluene without irradiation, but the yields are less than 1 ppm.

It can be seen that there is a general agreement in the product yields under the reaction conditions.

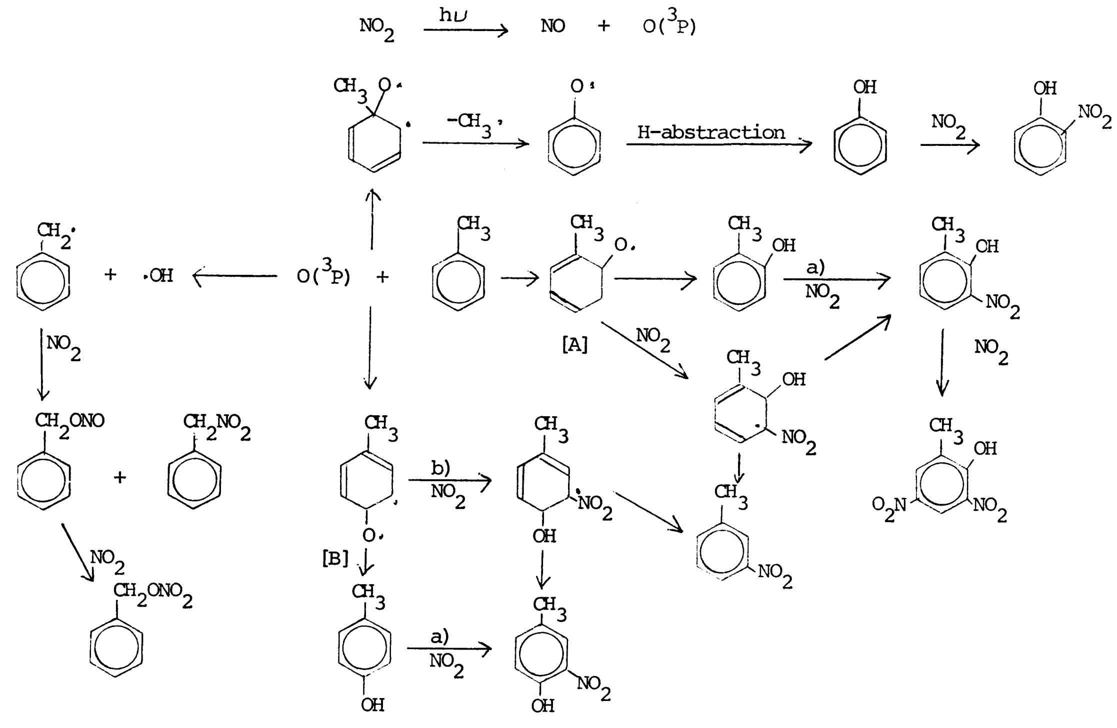
The available evidence suggests that in the photolysis of toluene with nitrogen dioxide in nitrogen atmosphere, nitrogen dioxide is the major light absorbing species in the region of less than 398 nm, forming nitric oxide and ground state oxygen atoms. Thus it seems likely that atomic oxygen is the predominant agent involved in the initial attack on the aromatic ring to form biradical [A], followed by isomerization of phenolic compounds, which then react with nitrogen dioxide to form nitrocresol. On the other hand, the intermediate biradical [A] and [B] may react with nitrogen dioxide, followed by dehydration to give *o*-, *m*-, and *p*-nitrotoluene. A possible reaction sequence is shown in Scheme 1.

The formation of *o*-nitrophenol could be explained by the ipso-attack of oxygen atom at the position of methyl group to form phenol, which then reacts with nitrogen dioxide to give nitrophenol. By analogy with the formation of nitrocresol, the formation of 4,6-

TABLE 1. YIELDS (ppm) OF THE REACTION PRODUCTS IN THE REACTION OF TOLUENE AND NITROGEN DIOXIDE IN ATOMOSPHERE OF NITROGEN[a)]

Product	1	2	3	4	5	6	7	8	9	10
Run 1	trace	0.8	0.3	0.3	4.2	9.5	2.2	27	14.4	5.2
Run 2	trace	0.6	0.3	0.2	3.2	10.5	2.3	26	13.2	5.2

a) 10 h irradiation for 1000 ppm toluene and 1000 ppm No_2.



Scheme 1.

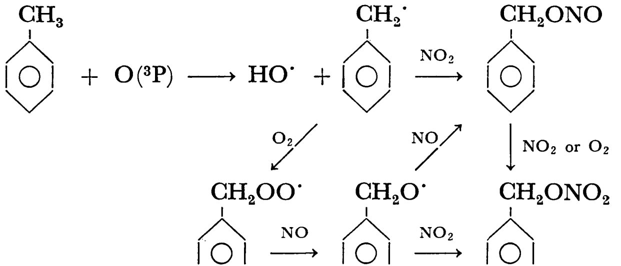
dinitro-*o*-cresol presumably proceeds by addition of nitrogen dioxide to 6-nitro-*o*-cresol to give an encounter pair, followed by intramolecular nitro group attack on the paraposition and subsequent aromatization to produce the 4,6-dinitro-*o*-cresol.

Although the activation energy of hydrogen abstraction is generally much higher than that for addition, and there is no report of the hydrogen abstraction of toluene with oxygen atom, one anticipates that in the reaction of nitrogen dioxide with toluene hydrogen abstraction may occur in view of the formation of α-nitrotoluene and benzyl nitrate. The presence of methane and ethane suggests the formation of methyl and phenyl radicals which can abstract a hydrogen atom to form methane and benzene, or recombine to form ethane.

The Role of Oxygen in the Photochemical Reaction of Toluene and Nitrogen Dioxide. In the presence of air, the products distribution for the photolysis of nitrogen dioxide and toluene was studied; the results are given in Table 2. There is a drastic increase in the yield of the products, in comparison to the oxygen free system. This is readily understandable in terms of the conversion of nitric oxide to nitrogen dioxide by oxygen. Oxygen must play an especially important role in the formation of benzyl nitrate. Benzyl nitrate may be formed from the strong interaction of the intermediate of the benzyl radical with oxygen, followed by a reaction most likely with nitric oxide or nitrogen dioxide.

Table 2. Effects of oxygen on product yields (ppm) (NO_2 1000 ppm, toluene 1000 ppm, irradiation time 10 h, temperature 25—30 °C.)

Product	1	2	3	4	5	6	7	8	9	10
Run 1	2.5	2.9	0.5	9.9	0.6	2.7	2.0	49.4	16.3	38.0
Run 2	2.8	2.9	0.6	7.1	0.7	2.6	1.1	46.4	18.4	55.1
Run 3	2.3	3.0	0.9	6.0	0.9	2.3	1.3	44.6	16.3	60.8



From this and previous work, the reaction of the aromatic hydrocarbons with nitrogen dioxide can be satisfactory explained in terms of the general reaction mechanism of an oxygen atom with an aromatic ring. The difference in the yield of products between nitrogen and air systems arises because of the recyclization of nitric oxide to nitrogen dioxide.

References

1) S. L. Kopczynski, *Int. J. Air Wat. Poll.*, **8**, 107 (1964).
2) D. L. Dunburg, *Can. J. Chem.*, **43**, 1714 (1965).
3) A. P. Altshuller, C. R. Cohen, S. F. Sleva, and S. L. Kopczynski, *Science*, **138**, 442 (1962).
4) A. P. Altshuller, S. L. Kopczynski, W. A. Lonneman, F. D. Sulterfield, and D. L. Wilson, *Env. Soc. Tech.*, **4**, 44 (1970).
5) T. Kato and Y. Hanai, *Env. Soc. Rep. Yokohama Univ.*, **3**, 1 (1976).
6) (a) M. Hoshino, N. Washida, H. Akimoto, G. Inoue, and M. Okuda, Symp. Photochemistry Kyushu, 1976.
(b) H. Akimoto, G. Inoue, M. Okuda, M. Hoshino, and N. Washida, Symp. Photochemistry Tokyo 1975.