BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (4), 1253—1254 (1978)

Gas Phase Photochemical Reactions of Nitrogen Dioxide. Effect of Oxygen on the Conversion of Benzene into Nitrobenzene

Kazuo WATANABE, Hiroshi ISHIKAWA, and Wataru ANDO
Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki 300-31

(Received September 3, 1977)

Synopsis. Gas phase photochemical nitration of benzene with nitrogen dioxide in the presence of oxygen was studied. Conversion of benzene into nitrobenzene was drastically accelerated by oxygen.

Vapor phase nitration of benzene with nitrogen dioxide to produce nitrobenzene has been studied to some extent under thermal and photochemical conditions in oxygen free systems,[1] but no examination has been reported on the effect of oxygen. From the viewpoint that the role of oxygen is significant in photoreaction, studies were carried out in the gas phase photochemical reaction of hydrocarbons with nitrogen dioxide in the presence and absence of oxygen. We would like to report that addition of oxygen remarkably causes a high conversion of benzene into nitrobenzene in gas phase nitration.

A cylindrical reaction vessel made of Pyrex glass (350 ml) and equipped with Teflon stopcocks and silicon rubber septum was used. Commercial benzene was dried completely and distilled, first and last fractions being rejected until it became gas chromatographically pure. Nitrogen dioxide dried over phosphorus pentaoxide was purified by repeated trap to trap distillation in a vacuum. Extra pure dry nitrogen and oxygen (Nihon Tokusyu Gas Co.) were used. Known amounts of benzene and nitrogen dioxide were admitted to the reaction vessel under reduced pressure, and diluted with either dry nitrogen or oxygen. Samples were irradiated externally for period of 2 h with a 400 W high-pressure mercury lamp at the temperature of running water. The irradiated products were extracted with dry dichloromethane and analyzed with a Hitachi 163 flame ionization detector with a 20 m OV-101 capillary glass column. Gas chromatographic peaks were identified by comparison of their retention times and of mass spectra with those of authentic samples.

Results and Discussion

A solution of 5.48×10^{-4} mol of benzene and 22.3×10^{-4} mol of nitrogen dioxide was introduced into the reaction vessel with a syringe and irradiated for 2 h. The irradiated mixture was extracted with dry dichloromethane and analyzed by GLC. Nitrobenzene was obtained in 28% yield on the basis of starting benzene. Neither phenol nor nitrophenol was obtained in a detectable yield.[2]

The same reaction was carried out in the presence of oxygen. Irradiation of a mixture of 5.48×10^{-4} mol of benzene and 22.3×10^{-4} mol of nitrogen dioxide and 22.3×10^{-4} mol of oxygen afforded nitrobenzene in 55% yield. The presence of oxygen increases the yield of nitrobenzene. The yield of nitrobenzene on the photolysis of nitrogen dioxide and benzene with a variable concentration of oxygen was examined. The results are given in Table 1. We see a remarkable increase in the yield of nitrobenzene in the presence of oxygen. Although we did not measure the absolute rate of reaction, results show that oxygen accelerates the conversion rate into nitrobenzene in the vapor phase photochemical reactions.

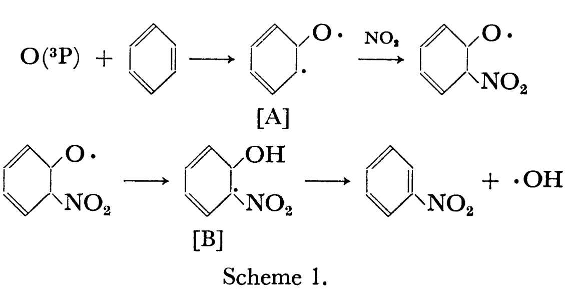
TABLE 1. YIELDS OF NITROBENZENE IN C_6H_6-NO_2-O_2 SYSTEM[a)]

Run	Reaction conditions			Yields of nitrobenzene (%)
	NO_2 (mol)	O_2 (mol)	N_2 (mol)	
1	4.1×10^{-4}	0	0	trace
2	4.1×10^{-4}	22.3×10^{-4}	0	3
3	4.1×10^{-4}	0	22.3×10^{-4}	trace
4	4.1×10^{-4}	44.6×10^{-4}	0	21
5	4.1×10^{-4}	0	44.6×10^{-4}	1
6	22.3×10^{-4}	0	0	28
7	22.3×10^{-4}	11.2×10^{-4}	0	50
8	22.3×10^{-4}	22.3×10^{-4}	0	55
9	22.3×10^{-4}	33.5×10^{-4}	0	71
10	22.3×10^{-4}	44.6×10^{-4}	0	82
11	22.3×10^{-4}	66.9×10^{-4}	0	85
12	22.3×10^{-4}	0	44.6×10^{-4}	11

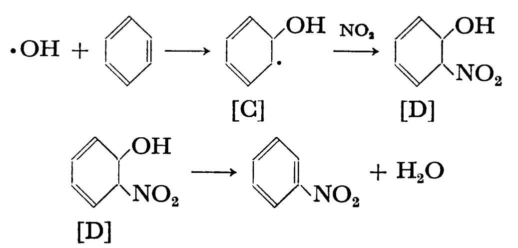
a) 5.48×10^{-4} mol of benzene was used in each run.

The following scheme might account for the formation of nitrobenzene. Oxygen atom, generated by photodissociation of nitrogen dioxide, adds benzene ring to produce biradical [A], which reacts with nitrogen

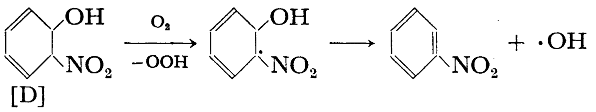
$$NO_2 \xrightarrow{h\nu} NO_2^* \longrightarrow NO + O(^3P)$$



Scheme 1.



Scheme 2.



$$\cdot OOH + NO \longrightarrow \cdot OH + NO_2$$

$$2NO + O_2 + M \text{ (surface of wall)} \longrightarrow 2NO_2 + M$$

Scheme 3.

dioxide to produce adduct [B] with concomitant migration of hydrogen atom (intramolecular hydrogen abstraction by oxyl radical). Here, monoradical species [B] should smoothly eliminate hydroxy radical to produce nitrobenzene (Scheme 1). Hydroxy radical generated herein effectively undergoes addition to benzene ring to produce [C], which reacts with nitrogen dioxide to produce 6-nitro-2,4-cyclohexadiene-1-ol [D]. The formation of nitrobenzene by direct dehydration from [D] might be expected (Scheme 2). The mechanisms indicate that nitrobenzene formation is significantly affected by oxygen. In the presence of oxygen, there are two additional routes for the efficient formation of nitrobenzene. The first mechanism assumes the effective conversion of nitric oxide into nitrogen dioxide by oxygen, keeping the high concentration of nitrogen dioxide in the system. An alternative route on the participation of oxygen involves the formation of hydroperoxy radical from [D] which will oxidize nitric oxide to form nitrogen dioxide and hydroxy radical. These ideas are summarized in Scheme 3. Reproduction of nitrogen dioxide would be important for increasing the yield of nitrobenzene.

References

1) D. L. Bunbury, *Can. J. Chem.*, **43**, 1714 (1965), and references cited therein.

2) In low concentration (0.1—1 ppm) of nitrogen dioxide, phenol and *o*-nitrophenol were obtained as main products.