CONDITIONS FOR THE PHOTOCHEMICAL NITRATION OF BENZENE

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ABSTRACT

The reaction of benzene and nitrogen dioxide to produce nitrobenzene has been studied in the liquid and gas phases, in the dark, and with irradiation by light of 439 mμ and of 366 mμ. The concentration of NO_2 in the liquid was varied from 0.08 to 1.6 moles/l and in the gas from 0.0035 to 0.053 moles/l. No nitrobenzene was produced under any conditions in the liquid phase. Nitrobenzene is produced in the gas phase at high NO_2 concentrations with irradiation by 366 mμ light. The quantum yield is 0.2. At 439 mμ the quantum yield is not more than 0.02. There is a very small dark reaction. As the concentration of NO_2 in the gas is reduced the yield of nitrobenzene falls off very rapidly and is zero at the lowest concentration used, both in dark and light.

INTRODUCTION

It is known that light of wavelength 365 mμ causes decomposition of nitrogen dioxide (1) and that of 436 mμ causes activation (2). It appeared to be interesting, then, to study the different types of reaction which might occur between benzene and NO_2 on using these two wavelengths to initiate the reaction, especially in view of the reported enhancement of the yield of nitrobenzene on irradiating mixtures of benzene and nitrogen dioxide with light (6, 9). The reactions of nitrogen dioxide with organic compounds have been reviewed by Riebsomer (3*a*), Gray and Yoffe (3*b*), Topchiev (3*c*), and Titov (3*d*). Table I summarizes the experimental results of the earlier workers who used conditions comparable to those used in this work.

EXPERIMENTAL

The nitrogen dioxide was obtained from the Matheson Company and purified further by fractional distillation, the middle third being kept. It was stored at dry-ice temperatures in a covered bulb and in all cases was pure white when frozen. It was measured either as a gas at room temperature or as a liquid at 0 °C using calibrated volumes. All calculations for obtaining NO_2 concentration from measured temperature and pressure and for NO_2/N_2O_4 ratios were based on the paper of Verhoek and Daniels (11). The benzene was Fisher certified grade and further purified by freezing. It was gas chromatographically pure on use and measured by pipette or Hamilton microsyringe. The benzene and nitrogen dioxide were handled on a conventional high vacuum system and were dried with P_2O_5 just before use, except where noted. The cells for the liquid phase runs had flat windows and were made of Pyrex glass (greater than 90% transmission in the regions of interest). In run 1 a cell of 30 ml was used, in the other liquid phase runs a cell of 10 ml was used. The gas phase runs were performed in either a liter flask or a 165 ml flask. Both had a small test tube attached with ground joint for freezing the reaction mixtures into the bulb and for removal after reaction. All cells were closed with a ground glass joint and stopcock, and samples degassed prior to use.

The light source was an HBO-109 high pressure mercury vapor lamp with fused quartz envelope, from George W. Gates and Co., Inc. This lamp has an arc of 0.3 mm × 0.3 mm. This arc was placed in the focal plane of a Pyrex lens. The 439 mμ line was isolated using a Farrand Interference Filter, half band width 13 mμ, while the 366 mμ line (actually 350–386) was isolated using a 7-83 filter from Corning Glass Works. Light intensity was measured using the potassium ferrioxalate actinometer of Hatchard and Parker (12). Complete absorption occurred in the liquid phase runs and practically complete absorption in the gas phase runs. After a run samples were usually washed with 10% $KHCO_3$ and then water, dried with Drierite, and analyzed on a Burrell K-1 Kromotog using either Ap-L or silicone columns and usually a thermal conductivity cell as dectector. In runs 23–29 where very small amounts of benzene were used (0.01–0.05 ml) 0.25 ml of benzene was added after the addition of $KHCO_3$. Following each injection of a sample a standard nitrobenzene solution was injected for comparison of retention times and of areas. Identification of the nitrobenzene product was made by trapping it at the exit of the column and comparing its infrared spectrum with that of an authentic sample. Amounts were calculated by the ratio of areas of the unknown and that

TABLE I

Summary of earlier work

	Conditions								Products			
Ref.	Temp. (°C)	Time	Hydrocarbons	ArH (moles)	ArH/NO$_2$ (moles)	Phase	Light used	Effect on yield of ArNO$_2$	ArNO$_2$ (%)	Poly-nitric	Phenolic (g)	Acidic
4	Low	Several days	C_6H_6	—	N_2O_3	Liquid	—	—	Some		Picric	Oxalic
5	80	6 h	C_6H_6(dry)	—	1 (N_2O_4)	Liquid	—	—	Low	Trinitro	Picric	Oxalic
5	Rm. temp.	—	C_6H_6	—		Liquid	—	—	No reaction	—	—	—
6	Rm. temp.	3 mo	C_6H_6(dry)	0.154	2.36(N_2O_4)	Liquid	—	—	3.8	—	—	—
6	Rm. temp.	3 mo	C_6H_6(dry)	0.128	2.36(NO_2)	Liquid	Sunlight	Increase	31.4	Dinitro	—	—
6	Rm. temp.	3 mo	$C_6H_5CH_3$	0.13	2.4(NO_2)	Liquid	—	—	—	—	—	Benzoic
6	55	4 h	$C_6H_5CH_3$(dry)	0.543	(NO_2)	Liquid	Hg quartz	None	—	—	—	—
6	Rm. temp.	6 h	$C_6H_5CH_3$(dry)	0.543	(NO_2)	Liquid	Hg quartz	None	—	—	—	Benzoic
7	Rm. temp.	35 days	C_6H_6	—	1.5	Liquid	—	—	30.	—	—	—
8	14–15	2 h	$C_6H_5CH_3$	0.435	0.02(NO_2)	Flow gas + CO_2	—	—	31.9	—	$C_6H_5CH_2NO_2$	—
8	14–15	2 h	$C_6H_5CH_3$	0.435	0.02(NO_2)	"	Hg quartz	Increase	45.3	—	$C_6H_5CH_2NO_2$	—
8	25–30	2 h	C_6H_6	0.513	0.024(NO_2)	"	—	—	27	—	—	—
8	25–30	2 h	C_6H_6	0.513	0.024(NO_2)	"	Hg quartz	Marginal	28.5	—	—	—
8	25–30	2 h	C_6H_6	0.513	0.05	"	—	—	27	—	—	—
8	25–30	2 h	C_6H_6	0.513	0.10		—	—	6	—	—	—
9	20	Several h	C_6H_6	—	0.82	Gas	—	—	2.18	—	—	—
9	20	Several h	C_6H_6	—	0.82	Gas	Visible	None	2.29	Some	—	—
9	20	Several h	C_6H_6	—	0.35	Gas	—	—	3.03	—	—	—
9	20	Several h	C_6H_6	—	0.35	Gas	Visible	None	3.03	—	—	—
9	Rm. temp.	5 h	C_6H_6	—	Sat. NO_2	Liquid	—	—	2.27	0.13	—	—
9	Rm. temp.	5 h	C_6H_6	—	Sat. NO_2	Liquid	7 000 – 2 000 Å	Decrease	1.49	1.56	—	—
9	Rm. temp.	5 h	C_6H_6	—	Sat. NO_2	Liquid	7 000 – 4 000 Å	Increase	3.43	1.21	—	—
9	Rm. temp.	5 h	C_6H_6	—	Sat. NO_2	Liquid	4 000 – 2 800 Å	Decrease	2.17	.72	—	—
10	20	4 mo	C_6H_6	2.25	1.08	Liquid	—	—	Combined 0.26 g	—	0.31	Oxalic
10	20	4 mo	C_6H_6	2.25	2.71	Liquid	—	—	0.87g	—	0.60	Oxalic
10	20	4 mo	C_6H_6	2.25	10.8	Liquid	—	—	2.6g	—	0.95	Oxalic

produced by the standard solution. To test the possibility of reaction of the nitrobenzene with the base or of adsorption on the drying agent, a 3.45×10^{-4} mole fraction solution of nitrobenzene was washed with 10% NaOH three times and then with water and allowed to stand over Drierite. There was no difference in the size of the nitrobenzene peak given by the washed and unwashed material. Runs 14, 15, 16, 17, and 19 were directly injected onto the column without any treatment.

The basic extract of runs 7 and 8 was acidified with HCl and extracted with 30 ml of benzene, and the benzene evaporated to dryness in a small container. The residue was ground together with a minimum amount of powdered KCl and an infrared spectrum taken of the disc. The only thing found was a small amount of some carboxylic acid which turned out to be in the reagent benzene itself.

RESULTS AND DISCUSSION

The results are summarized in Table II.

The lower limit for the detection of nitrobenzene was 3×10^{-5} mole fraction both for thermal conductivity and hydrogen flame detection. Much smaller samples had to be used with the hydrogen flame detector so the lower limit was no less than that with the thermal conductivity detector.

Reactions in the liquid phase at room temperature will be first considered. Yields in the dark reaction were: the present author 0.00% in 19 days; Wieland 0.00% (5); Gorislavetz 2.27% in 5 h (9); Bass and Johnson 3.8% in 3 months (6); Titov 0.69–6.9% in 4 months (10); and Schaarschmidt and Smolla > 30% in 35 days (7). Longer times with the last authors resulted in a decrease in the yield of nitro products. Ratios of reactants are not the same in any of these cases nor are reaction times, but in several pairs of experiments they are of the same order of magnitude (see Table I). Titov's solution with C_6H_6/NO_2 ratio of 10.8 (most comparable to the results here reported) had 0.0088 mole fraction nitrobenzene after 4 months. Assuming linearity of nitrobenzene production, after 19 days run 4 should have been 0.0014 mole fraction of nitrobenzene. This, however, is 40 to 50 times greater than the lower limit of detection. Also, according to Titov's results the yield of nitrobenzene should go up with an increase in the C_6H_6/NO_2 ratio; therefore, the yield in run 4, if anything, should have been higher. Titov varied the ratio by increasing the benzene, and the fact that the yield increased in almost direct proportion to the amount of benzene even though it was in an excess suggests that it was an impurity which was reacting. In the course of a study of molecular addition compounds of N_2O_4 and aromatic hydrocarbons, Addison and Sheldon (13) found no detectable reaction between benzene and dinitrogen tetroxide during a period of several hours at room temperature. In view of the negative results, the low yields when reaction did occur, and the fact that reaction with even a small amount of impurity would produce some nitric acid, the most probable conclusion is that there is no reaction between pure benzene and NO_2–N_2O_4 at room temperature.

For irradiated mixtures in the liquid phase the present author found no reaction after 3 h with unfiltered mercury light, light of 439 mμ, and light of 366 mμ. After 5 h Gorislavetz (9) found a decrease in yield from 2.27 to 1.49 with unfiltered light and increase to 3.43 (about double) with light of 700–400 mμ, and a small decrease to 2.17 with light of 400–280 mμ. Bass and Johnson (6) found an eightfold increase to 31.4% after irradiation with sunlight for 3 months. The amount of light absorbed in the last two examples is not stated. Under the conditions of the present work the quantum yield for nitrobenzene production is less than 0.01 at 439 mμ and less than 0.011 at 366 mμ. The calculation was based on the lower limit of detection of nitrobenzene and the volume of the sample.

Three runs were made on toluene with amounts and conditions approximately the same as runs 7, 8, and 9. No nitrotoluenes were found. Interestingly, Bass and Johnson (6) found no nitrotoluenes both in the dark and on irradiation with a mercury lamp.

TABLE II

Results of nitration runs

	Conditions								Products	
Run	Temp. (°C)	Time (h)	C_6H_6 (moles)	C_6H_6/NO_2 (molar ratio)	Concn. of NO_2* (moles/l × 10^2)	Phase	Light used (einsteins × 10^6)	Wavelength (mμ)	Nitrobenzene (moles × 10^6)	Other
1†	23	2	0.338	147	7.74	Liquid	—	Dark	None	—
4	25	19 days	0.1125	32.5	34.6	Liquid	—	Dark	None	—
5	27	2	0.1125	32.5	34.6	Liquid	—	Unfiltered Hg	None	—
7	25	3	0.1125	7.04	159.8	Liquid	370	439	None	—
8	25	3	0.1125	6.80	165.4	Liquid	300	366	None	None
9	25	3	0.1125	8.95	125.6	Liquid	—	Dark	None	None
13‡	25	2.58	0.1125	6.96	161.6	Liquid	314	439	None	—
14	25	3	0.00405	1.17	0.351	Gas	300	439	None	—
15	25	2.95	0.0045	1.3	0.351	Gas	200	366	None	—
19	25	1.5	0.0045	1.3	0.351	Gas	—	Dark	None	—
20	25	3	0.0045	1.3	0.351	Gas	200	366	None	—
21	100	1.6	0.00225	1.65	0.083	Gas	160	439	None	—
22	25	1.8	0.00225	Unknown§	Unknown	Liquid	180	439	None	—
23	26	2	112.5 × 10^6	0.016	4.32	Gas	—	Unfiltered Hg	85.8	—
24	21	2	506.4 × 10^6	0.070	4.28	Gas	—	Unfiltered Hg	141.9	—
25	21	2	112.5 × 10^6	0.075	0.886	Gas	—	Unfiltered Hg	14.3	—
26	23	17.5	112.5 × 10^6	0.0125	5.30	Gas	—	Dark	0.12	—
27	23	2	112.5 × 10^6	0.0136	4.87	Gas	200	439	2.78	—
28	25	2	112.5 × 10^6	0.0139	4.59	Gas	160	366	30.6	—
29	24	2	506.4 × 10^6	0.0786	0.62	Gas	—	Unfiltered Hg	0.37	—

*Recorded as if the NO_2–N_2O_4 mixture was all NO_2.

†Omitted runs were: runs with a lower light intensity under conditions where no reaction occurs, procedural checks, or involved toluene.

‡Benzene was half saturated with water.

§A mixture of nitrogen oxides was used.

Reaction to produce nitrobenzene does occur in the gas phase. The production of nitrobenzene is very dependent on irradiation, contrary to Schorigin and Toptschiew (8) and to Gorislavetz (9). The production of nitrobenzene is very dependent on the concentration of nitrogen dioxide, in agreement with the authors just mentioned. Comparing runs 23, 24, 25, and 29 and runs 20 and 28 (Table II) it is seen that as the concentration of nitrogen dioxide is reduced, the amount of nitrobenzene falls precipitously even though the nitrogen dioxide is in a large excess except in run 20. Comparing runs 23 and 24 it is seen that increasing the benzene/NO_2 ratio does not decrease the production of nitrobenzene. The fact that it increases is not surprising as about 76% of the benzene was nitrated in run 23. Light of wavelength 366 mμ with a quantum yield of 0.2 is more than 10 times as effective as that of 439 mμ. It may well be that the reaction apparent at 439 mμ is due to a few percent of 404.7 mμ (which can also dissociate NO_2, (14)) getting through the filter.

In a recent paper on the photolysis of NO_2, Pitts, Sharp, and Chan (14) propose a mechanism in which three reactive species are produced by the action of light, activated NO_2, O atoms, and NO_3. Since absorption is practically total at all concentrations here studied the amount of these reactive species produced should at least be of the same order of magnitude at all nitrogen oxide concentrations. Since light of 439 mμ is relatively ineffective, activated NO_2 is most probably not the species involved. Since the concentration of N_2O_4 falls more rapidly than the total oxide concentration (Table III), although not as rapidly as the production of nitrobenzene, it would appear that both N_2O_4 and O atoms or NO_3 are needed for the photochemical nitration of benzene at room temperature. Possibly the oxygen atoms combine with the N_2O_4 to make N_2O_5 which is quoted (3*d*) as being many times more effective than N_2O_4 as a nitrating agent. Titov, however, goes on to suggest that N_2O_5 is so effective because it dissociates to form NO_3 which of course would be present in the photolysis of NO_2 alone.

TABLE III

Actual concentrations of N_2O_4 and NO_2 as total oxide concentration changes calculated at 25°

Total oxide as NO_2 (moles/l × 10^2)	Fraction N_2O_4 dissociated	N_2O_4 (moles/l × 10^2)	NO_2 (moles/l × 10^2)
4.28	0.216	1.68	0.924
0.886	0.421	0.256	0.392
0.62	0.487	0.159	0.302
0.35	0.584	0.073	0.205

No explanation can be offered for the lack of effect of light observed by the other workers. Schorigin and Toptschiew (8) do observe a substantial increase in yield of nitrotoluenes on irridation of toluene and NO_2 (Table I). With benzene and NO_2 they observe a variation in yield with temperature. At 10–12° it is 12.7%, at 25–30° it is 28.5%, at 55–60° it is 31.6%, and at 80–85° it is again 12.7%. Since at 1 atm N_2O_4 is 20% dissociated at 27°, 53% at 60°, and 90% at 100° (15), the variation that they observe might be explained by the requirement that both NO_2 and N_2O_4 be present for nitrobenzene to be formed.

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