IV. Photochemistry of Benzene Vapor at 2062Å-G. Gomes

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A. Introduction

Excitation of benzene vapor in its third absorption system at 1849Å leads to disappearance of the benzene with a quantum yield which extrapolates to unity at zero pressure.^{1,2} The pressure dependence of the disappearance quantum yield is found to be unusually severe, implying that a long-lived metastable state of benzene is involved. From comparison of various gases in efficiency of deactivating this metastable state, it was concluded that the state had high vibrational energy content. In order to directly investigate the effect of vibrational energy content on the disappearance quantum yield and the sensitivity of this yield to pressure of foreign gases, the current study at 2062Å was undertaken. The absorption at 2062Å is in the second absorption system of benzene. Here, too, as in the case of third band excitation, the vapor exhibits no fluorescence. Thus, high disappearance quantum yields were again anticipated.

B. Experimental

The light source for the photolysis was an iodine lamp which was first developed by Harteck.³ The emission is concentrated predominantly in the 2062Å resonance line. In attempting to develop an electrodeless version of the lamp, considerable difficulty was experienced. These early attempts gave lamps which were either unstable or did not

fly

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possess sufficient intensity. In large part, much of this difficulty was due to the presence of traces of water vapor.

A successful lamp was finally constructed using the following procedure. The lamp consisted of a cylindrical quartz body 15 cm long and 26 mm in diameter with a side arm. The lamp was baked out and pumped down overnight to a pressure of 10^{-6} torr. Iodine, in the presence of sodium metal, was sublimed through a teflon stopcock into the side arm of the lamp where a dry ice-acetone trap had been placed. After 5 to 10 minutes a brown color appeared in the cold finger. This brown color disappeared when the trap was removed, indicating that the iodine present in the lamp was less than its vapor pressure at room temperature. The iodine in the lamp was degassed several times and pumped down to a pressure of 10^{-6} torr using a liquid nitrogen trap. The lamp was then filled with Xenon at a pressure of ca. 1 torr.⁴ The new lamp was powered by a 100 watt 2450 megacycle microwave source operated at 80% full power. A spectrum of the lamp is shown in Fig. 1.

The $2062\text{\AA}$ line from this lamp had an intensity of ca. 5×10^{17} quanta/min. Usually a discharge from a tesla coil was used to start the lamp, but occasionally the lamp would start without a tesla coil immediately on application of the microwave power.

Ammonia was chosen as actinometer. The photolysis of NH_3 has been studied at $2040\text{\AA}$ and at $2100\text{\AA}$.⁵ Since little or no change in quantum yield has been reported at these

wavelengths, it is assumed that the quantum yield for the disappearance of NH_3 at $2062\text{\AA}$ will be the same.

The decadic extinction coefficients of benzene and ammonia were determined at $2062\text{\AA}$ with a Cary Model 15 spectrophotometer to be $\epsilon(\text{Benzene}) = 0.016 \text{ torr}^{-1} \text{ cm}^{-1}$ and $\epsilon(\text{NH}_3) = 0.008 \text{ torr}^{-1} \text{ cm}^{-1}$. To match optical densities it is, therefore, required to perform actinometry at an NH_3 pressure of 2x the benzene pressure. The benzene photolysis was studied over a pressure range from 0.5 to 5 torr. The disappearance quantum yield of benzene has been studied in the range 10 torr to 800 torr.⁶ For benzene pressures less than 4 torr it was, therefore, necessary to use 100 torr of NH_3 for which the quantum yield is known to be 0.25, and then make corrections for the absorption of benzene.

The photolyzed NH_3 was analyzed for total moles of H_2 and N_2 with a Saunders-Taylor apparatus and then the ratio of H_2/N_2 determined using an Hitachi RMU-6D mass spectrometer. In all experiments reported here, this ratio was 3.0, indicating absence of hydrazine.

The actinometry cells were cylindrical quartz 10 cm long and 22 mm in diameter with graded seal and break seal. Actinometry was performed before and after every experiment. Agreement was always within 5%.

The reaction cells were 10 cm pyrex cells with 22 mm suprasil quartz windows. The windows were sealed with glyptal rather than platinum-silver chloride to facilitate

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disassembly for removal of the polymer. The cell was fitted with both a cold finger and a liquid N₂ trap. The latter was used for condensing out the benzene while the cell was in the spectrophotometer for measurement of polymer absorption. The procedure for filling the cell, determining the pressure of benzene and added gases, and for monitoring benzene disappearance has been previously described.

James Hinton 99.99% benzene was used without further purification. Matheson anhydrous ammonia was purified by techniques previously described.

C. Results and Discussion

The photolysis of benzene vapor at 2062Å⁰ is qualitatively very similar to the reported photolysis at 1849Å⁰.¹ After correction for absorption of light by the polymer, the disappearance of benzene is found to be linear with time to 25% conversion. (See Fig.2.) Two major products are observed: a volatile compound and a polymer. The polymer absorption spectrum is identical to that observed at 1849Å⁰ (see Fig. 3). The absorption spectrum of the volatile product (see Fig. 4) is also identical to that observed at 1849Å⁰ and has recently been characterized as fulvene.^{7,8} As pressure increases, both the disappearance yield and the initial appearance yield of fulvene decrease monotonically, in such a way as to maintain a constant ratio. At all pressures a steady state of fulvene is achieved. The steady state level increases with the addition of 0.1 atm-N₂. Further addition of N₂

has little effect on the steady state level (See Fig. 5). The polymer yield decreases monotonically with decreasing pressure. In Table I these observations are summarized.

The quantum yield for the disappearance of benzene is at all pressures lower than that observed at 1849Å. However, for both photolyses the disappearance quantum yield could be fit to an equation

$$\frac{1}{\Phi} = 1 + c(P_{N_2} + \Delta P_B) \quad (1)$$

where P_B is the pressure of benzene. In Fig. 6 $\frac{1}{\Phi}$ is shown plotted against $P_{N_2} + 115P_B$. For purposes of comparison, Fig. 7 shows Shindo's results for the 1849Å photolysis similarly plotted.

For both 1849Å and 2062Å photolysis the disappearance quantum yield at zero pressure is 1.0. However, the effectiveness of benzene with respect to Nitrogen in reducing the disappearance quantum yield is substantially lower in the 2062 photolysis. At 1849Å $\Delta=211$, whereas at 2062Å, $\Delta=150$. This difference is consistent with the mechanism previously suggested for benzene disappearance. Shindo postulated that the primary step in the disappearance process was an internal conversion to a vibrationally hot ground state molecule. The large discrepancy between nitrogen and benzene in deactivating this hot molecule was attributed to its high vibrational energy content. The reduced vibrational energy content at 2062Å is, therefore, consistent with the reduced value of Δ .

As previously discussed,¹ the constant c is interpreted to be the product of the lifetime of the vibrationally hot ground state molecule with the rate constant for deactivation by collision with N_2 . Assuming the deactivation rate constants to be the same at $1849\text{\AA}$ and $2062\text{\AA}$, the increase in c at the longer wavelength is most plausibly attributed to a longer lifetime, which is again consistent with reduced vibrational energy content.

In summary no new features are found in $2062\text{\AA}$ photolysis and all the results are consistent with the mechanism suggested to explain the $1849\text{\AA}$ photolysis.

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TABLE I.

P_B (Torr)	P_{N_2} (Atm.)	$\phi(-R)$	Fulvene Yield $\left[\frac{dO.D.}{dq} \right]_{q=0} \times 10^{18}$	Polymer Yield $[O.D./q] \times 10^{19}$	Fulvene Yield/ $\phi-B$ $\times 10^{18}$
1					
1	0	0.095		3.02	
1	0	0.090		3.0	
1	0	0.091		3.01	
1	0.1	0.065	0.225	1.47	3.47
1	0.15	0.047	0.190	0.31	4.06
1	0.2	0.037	0.140	0.228	3.83
1	0.4	0.027	0.085	0.195	3.15
1	1.0	0.012	0.060	0.098	4.95
0.5	0	0.211		11.4	
0.75	0	0.150			
2	0	0.050		2.35	
3	0	0.044		1.96	
4	0	0.023		1.70

FIG. 1

FIG. 2

FIG. 3

FIG. 4

O.D.

FIG. 5

FIG. 6

FIG. 6-A

FIG. 7