V. Photochemistry of Benzene in the First Absorption Band-G. Gomes

MASTER

A. Introduction

The sum (ϕ_{Σ}) of the benzene fluorescence quantum yield and the quantum yield for intersystem crossing has been demonstrated to decrease with increasing energy of excitation when in the first absorption band.¹ At 10 torr benzene this sum is close to 1.0 at 2580Å⁰ and decreases to 0.85 at 2530Å⁰ and to 0.032 at 2420Å⁰. At higher pressure of benzene (or inert gas) the falloff is somewhat less severe.

There appears to be little evidence for extensive photochemistry at 2537 or 2480Å⁰,^{2,3} which is consistent with the relatively large values for ϕ_{Σ} in this region. No photochemical studies have been reported for shorter wavelengths with the first absorption band, although it is in the wavelength region below 2480Å⁰ that extensive photochemistry is expected.

Having completed studies at 1849Å⁰⁴ and 2062Å⁰⁵ which were also prompted by observations on the absence of fluorescence for excitation into the two upper absorption systems, it was decided to extend the studies to the spectral region around 2440Å⁰. Our primary objective was to measure the disappearance quantum yield $\phi(-B)$ to determine its pressure dependence. The quantity $1-\phi_{\Sigma}-\phi(-B)$ is a direct measure of the probability for nonradiative transition to the ground electronic state, and there exists considerable interest in this process.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:
 A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe upon privately owned rights; or
 B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.
 As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

fla

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The study of pressure dependence is prompted by the observation that the benzene fluorescence quantum yield extrapolated to 'infinite pressure' continues to fall off strongly with decreasing wavelength.¹ The implication is there may be two nonradiative processes that deplete the first singlet state (other than conversion to the triplet), one of these proceeding much more rapidly than the other. If this is true, then it should be similarly evident in extrapolation of $\phi(-B)$ into the high pressure region.

B. Experimental

In the construction of a light source in the region of 2400Å⁰ for the purposes of photochemistry, it is required to have both high intensity ($\sim 10^{17}$ q/min.) and high purity. Purity is especially important in the benzene problem since the absorption is very discrete and also from the emission results it appears likely that there will be a severe wavelength dependence of $\phi(-B)$.

After a number of unsuccessful attempts to obtain suitable intensity in this wavelength region from resonance lamps, it was decided to attempt development of a filter that could be used in conjunction with an AHG high pressure Hg arc.

The emission spectrum of an AH6 lamp as obtained with an 0.3 meter model 218 McPherson monochromator + RQA1P28 photomultiplier is shown in Fig. 1. Interference filters available to us had band passes too large and

inadequate long wavelength blocking characteristics to be used effectively for our purpose. Much more suitable for isolation of the $2400\text{\AA}$ region was a filter train composed of 10 cm. Cl_2 (1 atm.) + 1 cm. NiSO_4 (500 gm/l) + 1 cm. pentamethylbenzene in cyclohexane (3 gm/l.) (see Fig. 2). The absorption characteristics of each of these individual filters is given in Figs. 3-5. The output of the AH6 which has passed through the combined filter is shown in Fig. 6. Peak intensity occurs at $2440\text{\AA}$ with sharp blocking above $2500\text{\AA}$. Although there is no benzene absorption above $2650\text{\AA}$, the actinometer employed absorbs below $4000\text{\AA}$ so that some correction is required for the filter transmission in the range $2800\text{-}3000\text{\AA}$. This was accomplished by performing actinometry with and without a pyrex filter which has a UV cut off at $278\text{\AA}$ (O.D. = 1 at $2780\text{\AA}$). The difference was generally about 4×10^{16} quanta/min.

For measurements at $2537\text{\AA}$ an electrodeless mercury resonance lamp was constructed as previously described.⁴ The output of the lamp which has passed through a Corning 7-54 filter is shown in Fig. 7. The Corning filter acts to block below $2350\text{\AA}$ and above $4000\text{\AA}$. The intensity of the $2537\text{\AA}$ resonance line was found to be in most experiments about 7×10^{17} q/min.

The actinometer employed was the ferrioxalate system as described by Hatchard and Parker.⁶ Their quantum yield of 1.25 was used at both $2537\text{\AA}$ and in the band centered

around 2440Å. The procedure for preparation and analysis of the actinometer is described below.

Pure potassium ferrioxalate crystals were prepared by mixing 3 volumes of 1.5 Molar Baker and Adamson analytical reagent potassium oxalate ($K_2C_2O_4 \cdot H_2O$) (276.36 gm/l) with 1 volume 1.5 Molar Mallinckrodt A. R. ferric chloride ($FeCl_3 \cdot 6H_2O$, 405.4 gm/l). The precipitated potassium ferrioxalate was recrystallized three times from warm water and aspirated dry. The crystals were then further dried in a current of warm air at $\sim 45^\circ C$. All operations were performed in a dark room using only Kodak (OA) safety lights for illumination. The $6 \times 10^{-3} M$ actinometer solution was prepared by dissolving 2.947 gm of the crystals in ~ 500 ml water adding 100 ml 1.0 N H_2SO_4 and diluting to one liter. The $6 \times 10^{-4} M$ actinometer solution was prepared by diluting the $6 \times 10^{-3} M$ solution and adding sufficient H_2SO_4 to bring its concentration to 0.1 N. All actinometer solutions were stored in the dark in opaque containers.

A "complexing" solution was then prepared by mixing 250 ml of phenanthroline solution with 625 ml of buffer and adding 100 ml 1N H_2SO_4 and diluting with water to 1 liter. The phenanthroline solution was made by dissolving 1 gm Aldrich 1:10 ortho phenanthroline monohydrate in 1 liter water. The buffer solution was prepared by adding 81.7 gms

B+A reagent grade sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) to 360 ml $1\text{N}\text{H}_2\text{SO}_4$ and diluting to 1 liter with water.

Three ml of actinometer solution was photolyzed, and a 2 ml aliquot of this photolyte was placed in a 10 ml volumetric flask. Four ml of the complexing solution was then added and the mixture diluted to 10 ml with water. The volumetric was shaken and then stored for 30 minutes taking care to avoid exposure to light. The optical density of this mixture in a 1 cm cell was measured on a Cary 15 recording spectrophotometer at 510 m μ . This O.D. value was corrected by subtracting the O.D. value of a blank solution prepared in the same manner but not photolyzed.

A standard calibration graph for the analysis of Fe^{2+} complex was obtained as follows. Ferrous sulfate, B+A reagent ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) 0.1M in $0.1\text{N}\text{H}_2\text{SO}_4$ was prepared. This solution was carefully diluted to $4 \times 10^{-3}\text{M}$ Fe^{2+} and from this stock, additional solutions were prepared containing Fe^{2+} concentrations varying from 2×10^{-5} to $2 \times 10^{-4}\text{M}$ plus 0.05N H_2SO_4 and further containing 50% Buffer and 10% phenanthroline solution. The calibration curve obtained from these solutions is shown in Fig. 8. The molar extinction coefficient of the ferrous complex at 510 m μ was determined to be 1.11×10^4 as compared to a value of 1.105×10^4 obtained by Hatchard and Parker⁶ and 1.11×10^4 by Smith and Diehl.⁷ The fraction of light absorbed by the ferrioxalate solution around

2400Å - 2500Å was >99%. The absorption spectrum of 6×10^{-5} M ferrioxalate and the spectrum of the ferrous complex are presented in Figs. 9 and 10.

The photolysis cells were 10 cm. cylindrical quartz cells with 22 mm suprasil quartz windows fused to the cell body. James Hinton 99.99% benzene was used without further purification. The technique for filling the photolysis cell, and the analytical procedure for determining benzene disappearance has been previously described.⁴ Actinometry was performed before and after each photolysis using 1 cm cells with 22 mm diameter windows. The photolyzing beam was made parallel over the 10 cm. length of the photolysis cell by means of suitable quartz lenses.

The number of photons absorbed by the benzene was calculated by

$$I_B = I_A \int_0^{\infty} f(\lambda) (1-T(\lambda)) d\lambda$$

where I_A is the number of photons per minute absorbed by the actinometer in the pertinent spectral region, $f(\lambda)$ is the normalized relative spectral output of the lamp and filter $\text{tain} \left(\int f(\lambda) d\lambda = 1 \right)$ and $T(\lambda)$ is the transmission of the 10 cm length of benzene at the pressure employed. Over the narrow spectral region studied no correction was required for the spectral response of the photomultiplier used in obtaining $f(\lambda)$. $T(\lambda)$ was determined with a Cary Model 15 spectrophotometer. Conversions were kept suf-

ficiently low so that variation of I_B with time could be neglected.

C. Results and Discussion

At $2537\text{\AA}^0$ no disappearance was found at benzene pressures of 5 and 10 torr within the limits of detection of our technique. From this an upper bound of 0.02 can be placed on $\Phi(-B)$. Measurements at lower pressures are currently in progress.

At $2440\text{\AA}^0$ benzene was found to disappear linearly with absorbed quanta to 3% conversion. The time dependence of the benzene optical density is presented in Fig. 11 for a pressure of 10 torr. Similar results were obtained at 5 torr and 0.1 torr and also in the presence of N_2 .

Polymer was formed in all cases at $2440\text{\AA}^0$. The absorption spectrum of the polymer is identical to that observed for photolysis at $1849\text{\AA}^{0.4}$ and $2062\text{\AA}^{0.5}$. The polymer could be removed by heating above 600°C in the presence of C_2 .

Unlike the case of shorter wavelengths photolysis, no fulvene was produced at $2440\text{\AA}^0$. If fulvene is photolyzed at $2440\text{\AA}^0$, this result is expected since the fraction of light absorbed by fulvene is much larger at $2440\text{\AA}^0$ than at the shorter wavelengths. At $2440\text{\AA}^0$ the ratio of benzene to fulvene extinction coefficients is ca 250. Therefore even at low conversions substantial light absorption is expected.

The quantum yield for fulvene disappearance at $2440\text{\AA}$ was determined by preparing ca. 0.1 torr fulvene by photolysis of benzene at $1849\text{\AA}$ to 75% conversion. This was then irradiated at $2440\text{\AA}$ and a disappearance quantum yield of 0.04 obtained. Benzene did not appear, nor could any product other than polymer be identified. Similarly, photolysis of fulvene at $2537\text{\AA}$ did not produce benzene confirming an earlier report on this by Shindo.⁴

From the benzene-fulvene extinction coefficient ratio and the fulvene disappearance quantum yield and the fulvene disappearance quantum yield it is clear that even if benzene converted to fulvene with unit quantum yield--no fulvene would be found at our conversions.

The disappearance quantum yield has so far been only determined at 5 and 10 torr benzene to be 0.18 and 0.145 respectively. These values are surprisingly large when compared to results at shorter wavelengths. At comparable pressures these quantum yields would be 0.02 and 0.01 at $2062\text{\AA}$ and 0.06 and 0.03 at $1849\text{\AA}$.

The relatively ^{SLIGHT} ~~small~~ pressure dependence of the quantum yield at ^{$2440\text{\AA}$} ~~$2062\text{\AA}$~~ is qualitatively consistent with the fall off of fluorescence at high pressures. The implication is that the fast non-radiative process, depleting the excited benzene population, is a photochemical disappearance. However, measurements over a wider range

of pressures are necessary to confirm this view, and such measurements are currently in progress. However, it is already clear from the measurements at 5 and 10 torr that there exists another non-radiative process other than photochemistry and intersystem crossing that depletes excited benzene since $1 - \phi(-B) - \phi_{\Sigma}^{\circ}$ remains substantially greater than zero at 2440Å.

REFERENCES

1. Chen, Teh-Suan, Effect of Exciting Wavelength and Foreign Gases on Fluorescence and Intersystem Crossing in Benzene Vapor. Ph.D. Thesis, University of Minnesota, 1967.
2. J.K. Foote, M.H. Mallon, and J.N. Pitts, Jr., J.A.C.S. 88, 3709 (1966).
3. L. Kaplan, K.E. Wilzbach, J.A.C.S. 89, 1030 (1967).
4. K. Shindo and S. Lipsky, J.Chem.Phys., 45 2292 (1966).
5. G. Gomes, Paper IV, this progress report.
6. C.G. Hatchard and C.A. Parker, Proc.Roy.Soc. (London) A235, 518 (1956).
7. G.F. Smith and H. Diehl, Quantitative Analysis. John Wiley and Sons, New York, 1952.

FIG. 1

FIG 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11