VI. Reaction of Benzene with Bromobenzene and
4-Bromobiphenyl--Possible Application as a High
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A. Introduction

We have previously reported that a photochemical reaction occurs on 2537Å excitation of benzene in deaerated solutions containing 0.01M bromobenzene.¹ Only three products were detected, quaterphenyl (93%), biphenyl (6.5%), and traces of terphenyl (0.3%). The quaterphenyl is easily excited and has high fluorescence quantum yield permitting the reaction to be studied at very low conversions. Additionally, the high sensitivity of fluorescence detection suggested the possibility of using the reaction for low intensity actinometry and low dose high energy dosimetry. For the latter purpose preliminary experiments were performed using Co⁶⁰ gamma excitation and again generation of biphenyl and quaterphenyl observed.

Studies on the effect of O₂ and cyclohexane indicated that the yield of quaterphenyl might be dose rate dependent thereby rendering the reaction unsuitable for most actinometric or dosimetry applications. Additionally, the yield of quaterphenyl was found to be strongly inhibited by traces of oxygen so that careful degassing techniques were required for reproducible results.

For the purposes of developing a more useful dosimeter we have also recently begun to study a similar photochemical reaction between benzene and 4-bromobiphenyl. This

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reaction has also been studied by Kharasch, Sharma and Lewis.² They report that on photolysis with an unfiltered Hg resonance lamp up to ca 80% conversion, p-terphenyl and biphenyl were the major products and formed in the ratio of 1:1. Oxygen was found not to have appreciable inhibiting effect either on the yields or product distribution. They suggest a free radical mechanism, the important processes being

Additional reactions suggested are reactions of the 4-biphenylyl radical with HBr to produce biphenyl, addition of Br· to benzene and then reaction of this adduct with 4-biphenylyl radical to produce biphenyl and bromobenzene. Additionally Br· can dimerize to Br₂ or add to the bromine-benzene adduct.

We present in this report preliminary results of some measurements we have made on this system using both ultra-violet light and Co⁶⁰ gamma rays as excitation source.

B. Experimental

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Matheson, Coleman and Bell spectroquality benzene was used without further purification. Bromobenzene (Eastman) was purified by distillation in N_2 atmosphere retaining only the middle fraction. Bromobenzene- d_5 (Stohler Isotope Chemicals), 99.5% D , was used without purification. p-terphenyl (Pilot scintillation grade) was used without purification. 4-bromobiphenyl (Eastman) was purified by repeated vacuum sublimations until the intensity of fluorescence of a 0.01M solution in deaerated benzene was at the level of the benzene Raman emission for excitation at $3140\overset{\circ}{\text{\AA}}$ and right angle observation (see description of fluorimeter).

Photolysis studies were performed with an AH6 1000 watt Hg arc filtered for $2550\overset{\circ}{\text{\AA}}$ emission with 1 cm $NiSO_4$ (500 g/l), 2 cm of Cl_2 gas (1 atm) and 1 cm KI_3 (0.11 g/l I_2 + 0.16 g/l KI) and for $3140\overset{\circ}{\text{\AA}}$ emission with 1 cm $NiSO_4$ and a second order interference filter. Conversions were always kept below 0.01%. No actinometry of the source has yet been performed.

High energy irradiations were performed at the University of Minnesota Gamma Facility employing a configuration containing ca 10^4 curie of Cs^{137} . Energy absorbed was determined with the Fricke dosimeter.

The fluorimeter employed for determining the production of terphenyl and quaterphenyl was constructed as follows.

Quartz lenses focused the output of a medium pressure 100 watt Hanovia SH Hg arc on the entrance slit of a f/3.4 Jarrell-Ash grating monochromator. A 1 cm cylindrical quartz cell with 22 mm suprasil I quartz windows attached via Pt/AgCl was placed ca 2 cm from the exit slit of the exciting monochromator. Another Jarrell-Ash f/3.4 monochromator was placed with the plane of its entrance slit parallel to the exciting beam. The entrance slit of this monochromator viewed the emission from immediately behind the front window of the fluorescence cell which was placed within a few millimeters of the slit. The light passing the analyzing monochromator was detected by an EMI 9558Q photomultiplier operated at 700 volts. The d.c. signal from the multiplier was measured by a Keithley 601 electrometer used in conjunction with a Hewlett Packard Model 7001AM x-y recorder. The fluorimeter was sufficiently sensitive that an emission spectrum of 2×10^{-9} M p-terphenyl could be determined without difficulty. Grating ghosts and Raman scattering provided the background above which all emissions had to be detected.

The production of p-terphenyl from bromobiphenyl is sufficiently efficient that the development of p-terphenyl emission could be seen immediately upon exposure of the solution to the 3140⁰Å light from the exciting monochromator. By oxygen saturating the solution prior to the emission

measurement, it was found that production of p-terphenyl was sufficiently inhibited to prevent detectable build up during the time necessary for the spectral scan (about 3-4 minutes).

The calibration curve for p-terphenyl was determined using known concentrations of p-terphenyl in oxygen saturated benzene solutions containing 0.01M bromobiphenyl.

The analysis of the products of the benzene + bromobenzene-d₅ experiments was performed with an Hitachi RMU-6D mass spectrometer.

C. Results and Discussion

Exposure of a 0.01^m solution of bromobenzene-d₅ in benzene to 8×10^4 r of Cs¹³⁷ gamma rays at a dose rate of 8×10^3 r/min gave the following product distribution.

$\psi-\psi'$	$0.071 \pm 0.002\%$
$\psi-\psi-\psi$	$0.503 \pm 0.014\%$
$\psi-\psi-\psi'$	$0.484 \pm 0.014\%$
$\psi-\psi-\psi-\psi$	$8.23 \pm 1.27\%$
$\psi-\psi-\psi-\psi'$	$36.7 \pm 4.1\%$
$\psi'-\psi-\psi-\psi'$	$54.1 \pm 5.6\%$

These results are qualitatively consistent with the results previously obtained,¹ if one additionally

postulates the exchange reaction

The primary process appears to be production of a phenyl radical which rapidly reacts with benzene to produce {phenylcyclo-hexadienyl} radical. This then dimerizes with high efficiency to form a reduced precursor of quaterphenyl. Apparently, reaction of {phenylcyclo-hexadienyl} with benzene cannot compete with the dimerization reaction, since only a trace of terphenyl is produced. The discrepancy in ratio of terphenyl to biphenyl for gamma and 2537Å^o irradiation is not understood. However, in both cases quaterphenyl is overwhelmingly the major product.

In order to determine the dose-rate dependence of quaterphenyl production (from bromobenzene-benzene (0.01M)), samples were irradiated at a dose rate of 4.55×10^{17} ev/hr/cc and 2.43×10^{16} ev/hr/cc for 10 hours. The ratio of quaterphenyl produced at high to low dose was 300 to 1 thereby confirming the expected dose rate dependence. In the photolysis of 0.01M solutions of 4-bromobiphenyl in benzene, the only product we have seen in emission is p-terphenyl. In the case of γ -radio-lysis we find in addition to p-terphenyl, traces of quaterphenyl. For both cases, biphenyl may be present but we are unable to determine it by emission since the large

excess of bromobiphenyl obscures light absorption by the biphenyl.

Upon air saturation of the 4-bromobiphenyl solutions, quaterphenyl production (for gamma excitation) is completely inhibited as has been found for the bromobenzene system. The yield of p-terphenyl is also reduced, but to an extent dependent upon the nature of excitation. At 2550⁰Å (80-90% absorption by benzene and 10-20% absorption by bromobiphenyl) the terphenyl yield is reduced by a factor of 3.1 whereas at 3130⁰Å (absorption mostly by bromobiphenyl) reduction is by a factor of 4.6.

In order to interpret these results, we have also measured the quenching of the benzene emission by air in the presence of 0.01 M bromobiphenyl and find reduction by a factor of 1.3. This is essentially what Kharasch and coworkers suggest. Apparently, therefore, there exists another intermediate (i.e. other than excited benzene) in the production of terphenyl that is sensitive to oxygen. According to the free radical mechanism, this intermediate could be either biphenyl or $C_6H_5-C_6H_4-C_6H_5$ (i.e. A). Since the terphenyl production involves disproportion^{ation} of A with biphenyl, one might expect then a dependence of quenching efficiency on the rate of energy absorption--the higher the rate the less effective the quencher. The difference between 2550 and 3130⁰Å excitation may be explained

in this way. Similarly in gamma radiolysis we have found that on addition of air, the terphenyl yield is reduced by 2.7, 2.2, 1.8, 1.6 and 1.3 at dose rates of 3×10^{14} , 7×10^{14} , 14×10^{14} , 38×10^{14} and 79×10^{14} ev/gmin.

All of our gamma ray results are summarized in Table I. The yield of terphenyl (c/OD) in all solutions clearly declines with increasing dose and more strongly in the absence of air. The results do not indicate any pronounced effect of dose rate.

As mentioned earlier, traces of quaterphenyl are detected in the gamma irradiated system. No yields have yet been determined but the concentration definitely increases with increasing dose.

Since terphenyl concentrations were determined from emission measurements, it is possible that in the presence of quaterphenyl there is some quenching by energy transfer to the quaterphenyl. In order to confirm this the OD=2.60 solution was diluted by factors of 10 and 100 with .01M bromobiphenyl + benzene solution. The terphenyl concentration decreased by such dilution by a factor of 6.7 and 67 respectively which is consistent with the quenching explanation. On this basis the "true" terphenyl concentration in the OD=2.60 solution is $39 \times 10^{-6}M$ which raises $C(N_2)/OD$ to a value of 1.5×10^{-5} . This, however,

is still significantly below the lowest dose value for this ratio of 2.7×10^{-5} .

In the presence of air, no quaterphenyl is detected and yet $c(\text{air})/\text{OD}$ also declines, although to much less extent. There appears, therefore, to remain a dose dependence, independent of the presence of quaterphenyl. The origin of this effect is not yet known.

At low doses, the G value for production of p-terphenyl is calculated to be 0.92. If this G value persists to lower doses, the reaction can be used to determine doses as low as 6.5×10^{13} ev/g (i.e. ca 1 rad). This assumes our lower limit of detection of p-terphenyl to be 1×10^{-9} M. With a stable lamp, it should be possible to ^{buck}~~block~~ out the Raman and grating ghost contributions to the background. We estimate that ultimate sensitivity for p-terphenyl emission will be ca 3×10^{-10} M thereby permitting use of the reaction to estimate doses down to 0.3 rad. However, further studies of the dose and dose-rate dependence are clearly required and this work is currently in progress.

TABLE I. Gamma Radiolysis of .01M Bromobiphenyl
+ Benzene Solutions

OD (1/m) ^a	dose rate ^b	c(N ₂)x10 ⁶ (m/l) ^c	c(air)x10 ⁶ (m/l) ^d	c(N ₂)/ODx10 ⁵	c(air)/ODx10 ⁵
0.020	1.00	0.54	0.20	2.70	1.00
0.045	2.25	1.00	0.45	2.22	1.00
0.096	4.80	1.50	0.83	1.57	0.87
0.139	1.39	2.25	----	1.61	----
0.245	2.45	2.75	----	1.12	----
0.255	12.8	3.30	2.10	1.29	0.82
0.570	5.70	7.30	----	1.28	----
2.605	26.1	26.0	20.0	1.00	0.77

- a) OD refers to optical density of Fricke dosimeter in one cm cell at 305 mμ. To obtain dose (ev/g H₂O) multiply OD by 1.75x10¹⁸.
- b) To obtain dose (ev/g H₂O-min) multiply by 2.91x10¹⁴.
- c) Concentration of p-terphenyl in nitrogenated solutions.
- d) Concentration of p-terphenyl in aerated solutions.

REFERENCES

1. F. Hirayama, AEC Report No. COO-913-13, 1967.
2. N. Kharasch, R. K. Sharma, H.B. Lewis, Chemical Communications 418 (1966).