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Bi-Production of Labelled Diphenyl in the Hg-Photosensitization of Benzene with Tritium

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BATES and TAYLOR⁽¹⁾ noticed a strong odour of diphenyl in the photosensitized irradiation of benzene. The mechanism postulated was that of splitting of a hydrogen atom:

$$Hg(^{3}P_{1}) + C_{6}H_{6} \rightarrow Hg + C_{6}H_{5} + H.$$

followed by mutual combination of the phenyl radicals. FORBES and $CLINE^{(2)}$ produced evidence that ${}^{1}P_{1}$ rather than ${}^{3}P_{1}$ Hg-atoms were responsible for the reaction, and that photosensitization by 2537 Å produced only small conversion at room temperature but appreciable reaction at high temperature. Later on, SCOTT and STEACIE⁽³⁾ reported that no reaction occurred in the Hg-photosensitized decomposition of benzene at low temperature, asserting that benzene is an unusually efficient third body for phenyl radical and hydrogen atom recombination:

$$\begin{split} \mathbf{H} &+ \mathbf{C_6H_6} \rightarrow \mathbf{C_6H_7} \\ \mathbf{C_6H_7} &+ \mathbf{C_6H_5} \rightarrow \mathbf{2C_6H_6} \end{split}$$

while at 400°C, although the main product was diphenyl, its quantum yield at 10 mm pressure did not exceed 0.1. The main reaction steps were given as follows:

$$\begin{array}{l} \mathrm{Hg}(^{3}\mathrm{P}_{1}) \,+\, \mathrm{C_{6}H_{6}} \rightarrow \mathrm{Hg}(^{1}\mathrm{S}_{0}) \,+\, \mathrm{C_{6}H_{6}}^{\ast} \\ \mathrm{C_{6}H_{6}}^{\ast} \rightarrow \mathrm{C_{6}H_{5}}^{\cdot} \,+\, \mathrm{H} \\ \mathrm{2C_{6}H_{5}}^{\cdot} \rightarrow \mathrm{C_{6}H_{5}}^{\cdot} \mathrm{C_{6}H_{5}} \end{array}$$

where $C_6H_6^*$ is an activated molecule.

In a previous investigation on the labelling of benzene by tritium-substitution under Hg-photosensitization,⁽⁴⁾ the authors have also marked the odour of diphenyl and it was assumed that a redissociated tritiated benzene would produce labelled diphenyl by combination with a phenyl radical.

In this communication, a series of runs was performed to confirm this assumption and to gain knowledge of the amount of labelled diphenyl formed at various reaction times.

Materials and experimental techniques are essentially the same as already given.⁽⁴⁾ Benzene and tritium were irradiated in presence of a tiny drop of Hg using a high pressure Hanovia SH 616A lamp generating a high u.v. over a broad spectral range. Thus, other lines than the 2537 Å and other Hg energy levels than the ${}^{3}P_{1}$ are operative, e.g., the 2482 Å line (quantum energy 115.2 kcal.). The reactions were performed at room temperature. The purification of diphenyl for counting after irradiation was performed by distilling benzene and volatile decomposition products on the vacuum line at room temperature into a liquid-air-cooled receiver. Diphenyl was not removed with the distillates under these conditions as confirmed in a special experiment using an accurately weighed amount of diphenyl in an excess of benzene, thoroughly evaporating the latter and reweighing diphenyl. It was mixed with 1 g of pure unlabelled diphenyl to act as a carrier, using ethyl alcohols as solvent. The material was repeatedly crystallized out of ethyl alcohol until a constant count was reached. The number of recrystallizations required to attain a constant count ranged from five to eight. The starting conditions for labelling are listed in Table 1. The amount of tritium was calculated in mc using the net volume of the reaction tube, the figure 2.580 c as the activity of 1 cm³ tritium at NTP and a standard pressure chart.(4)

The results of counting labelled diphenyl produced in above runs are summarized in Table 2. Counting was performed on the ECKO universal β -liquid scintillation counter type N664B using 0.4 mg of the purified diphenyl, toluene as solvent and P.P.O. as phosphor. The counting efficiency of 40 per cent at -20° C claimed by the producers was used in the conversion to specific activity of diphenyl. The last column in Table 2 gives the specific activities assumed to be obtained had the initial amount of tritium been 100 mc.

Figure 1 shows the effect of reaction time on the formation of labelled diphenyl. The amount of labelled diphenyl before dilution was considered too small compared with the diluent diphenyl (1 g)

TABLE 1. Starting conditions of labelling								
Run No.	1	2	3	4	5	6	7	
Tritium pressure (mm Hg)	1.6	1.2	0.78	0.98	1.2	1.2	0.7	
mc tritium	102.26	76.69	49.85	62.63	76 .69	76.69	44.74	
TA7 1 1 4 C1	950 V.			20 55				

TABLE 1. Starting conditions of labelling

Weight of benzene = 350 mg. Volume of reaction tube = 20.55 cm^3 .



FIG. 1. The effect of irradiation time on the formation of labelled diphenyl.

 TABLE 2. Reaction times and specific activities of diphenyl

				Spec.
				act.
		Net		stand-
	Irradia-	count/sec.		ardized to
	tion	of total	Spec.	Init. 100
Run	time	diphenyl	act.	mc of
No.	(hr)	$(\times 10^{-3})$	(mc/g)	tritium
1	1	1848	0.125	0.122
2	2	2712	0.183	0.239
3	3	1912	0.129	0.259
4	4.5	2374	0.160	0.255
5	10	5786	0.391	0.510
6	13	7674	0.518	0.675
7	18	6190	0.418	0.934

Weight of diphenyl carrier = 1 g. Counting efficiency = 40 per cent.

and was neglected in the calculation of the final specific activity. The curve indicates a small but steady rise of specific activity with time with a hump at 2-3 hr irradiation time. This indicates that while in the early stages the reactions:

$$C_6H_5 + T \rightarrow C_6H_5T \tag{1}$$

$$C_6H_6 + T \rightarrow C_6H_6T \tag{2}$$

$$C_{6}H_{6}T + C_{6}H_{5} \rightarrow C_{6}H_{6} + C_{6}H_{5}T \qquad (3)$$

$$C_6H_5 \cdot + C_6H_5 \cdot \rightarrow C_6H_5 \cdot C_6H_5$$
(4)

are predominant; the reactions

$$C_6H_5T + Hg \rightarrow C_6H_4T + H + Hg(^1S_0)$$
(5)

$$C_6H_4T \cdot + C_6H_5 \rightarrow C_6H_4T \cdot C_6H_5$$
(6)

participate more effectively at longer irradiation periods leading to an increased yield of diphenyl. Reaction (5) is a predecessor for formation of labelled diphenyl, and depends upon previous formation of substituted benzene. As the highest yield of labelled benzene is obtained at 2 hr irradiation time,⁽⁴⁾ the hump in the curve can be understood.

It was estimated that the activity of 1 ml pure tritium at NTP is 2.58 c. Its specific activity is therefore 9627 c/g. The specific activity of diphenyl labelled with one tritium atom, as that produced in equation (6), should therefore be 185 c/g. It can hence be estimated that diphenyl produced in run 1 was diluted 1.48×10^6 times corresponding to an initial amount of labelled diphenyl equal to about 0.68×10^{-3} mg or 0.2×10^{-3} per cent of the original amount of benzene (350 mg). In run 7, these last two figures are 2.28×10^{-3} mg and 0.65×10^{-3} per cent, respectively. It must be remembered that unlabelled diphenyl is also produced by reaction (4), but its amount is too small to be isolated or determined accurately.

National Research Centre Dokki, Cario, U.A.R.

Atomic Energy Establishment A. H. ABD EL-GHANY Anshas, U.A.R.

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A Rotating Collimator with Adjustable Field Sizes for the 22.5-MeV Betatron

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THE NEED for an adjustable rotating collimator for our 22.5 MeV betatron at the University of Illinois arose when we encountered difficulties in using the old system in many of our therapeutic and research problems.

This betatron, a prototype of the one invented by Professor D. W. Kerst, previously of the University of Illinois, has been modified many times over the period of some 17 yr. Before developing the new collimating system described in this note, we used a number of heavy lead collimators of different sizes. These collimators were inserted into the X-ray port of the betatron to give definite fixed beam sizes. Attached to each of these inserts were a number of lucite cones (Fig. 1) whose lengths depended on the desired source-to-skin distance (SSD); for example, at 80 cm we used a cone that gave a field size 8×12 cm, at 100 cm SSD a field size of 10×15 cm, at 133 cm SSD, 13×20 cm, etc. We found this old system inconvenient since we had to change the whole heavy lead collimator (approximately 70–80 lb in weight) every time a need for a new field size arose.

Figure 2a shows sketches of the new collimator with dimensions to fit the X-ray port of our betatron. The shaded portions in Fig. 2a represent the inner lead insert (described below), and Fig. 2b shows the actual beam size between source and skin surface. The system is composed of two inserts (Fig. 3). The outer insert, attached permanently to the port of the betatron, serves as collimator for circular fields. The inner insert with rectangular aperture is mounted when rectangular field sizes are needed. This part, weight only 15 lb, can be rotated 360° about the axis of the beam and can give various field sizes when proper lucite cones are attached. Figure 4 shows the relative intensity of the X-ray beam (flattened by an aluminum compensator) at 80 cm from the source. The intensity is maximum along a center line perpendicular to the front of the betatron magnet. The output at maximum energy of 22.5 MeV is about 125 rad/min.

Figure 5 is a multiple-exposure photograph of the beam taken when the system was rotated in steps of 45° in the vertical plane. This picture clearly shows the flexibility of our new collimator. The only changeable parts now are the lucite cones. With a number of light weight attachments we can obtain



FIG. 2a. Horizontal and vertical sectional sketches of the new collimator. The dimensions are in cm.