NOTES

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Hot-Atom Chemistry of Bromine. II.[1] Application of the Szilard-Chalmers Process to Organic Molecular Compound-Pyrenebromanil and Related Compounds[2]

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In spite of a number of investigations of the application of the Szilard-Chalmers process[3] to organic halogen compounds, no organic molecular compounds have been tested. Two of the present authors (C. S. and T. K.) have previously reported[4] the formation of organic radiobromides activated by the ^{82m}Br-isomeric transition in a solid mixture of a bromine-benzene-molecular compound and benzene. The present note will deal with the chemcial effects of the recoil bromine atoms in pyrenebromanil (1 : 1).[5] It has a sandwich-type structure composed of pyrene and bromanil (tetrabromo-*p*-benzoquinone) molecules. The result will be compared with those on its related compounds—bromanil, bromopyrene, a pyrene-bromanil mixture, and others.

Experimental[6]

Materials. The 1 : 1 molecular compound-pyrenebromanil (P−B) was prepared by mixing equimolar solutions of pyrene (P) and bromanil (B), both in toluene. The 1 : 1 mixture of P and B (P+B) was prepared by pestling the components on an agate mortar. Bromo derivatives[7] of P (PBr_n) were prepared and purified according to Lock[8] and Hock[9] respectively. 2-Bromohydroquinone (HQBr) was prepared according to Sarauw.[10]

Neutron Irradiation. Irradiation was carried out at the reactor temperature (*ca.* 40°C) in a pneumatic tube of KUR[11] with a thermal neutron flux of 5×10^{12} n/cm^2/sec and with an accompanying γ-dose rate of 2.7×10^7 R/hr.

Extraction and Measurement of Radioactivity. After having been cooled for more than two hours[12] at room temperature, the sample was transferred into a separatory funnel containing a carbon disulfide solution of bromine. Then the inorganic species were separated by means of extraction into an aqueous mixture of bromide and bromate (I). The bromine (II) was back-extracted from the carbon disulfide layer (III). A carbon disulfide-insoluble residue which was filtered out was extracted, first with ethyl ether[13] (IV),

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[1] Part I: C. Shinomiya, A. Oyoshi and T. Kishikawa, This Bulletin, **42**, 1437 (1969).

[2] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1967.

[3] L. Szilard and T. A. Chalmers, *Nature,* **134**, 462 (1934).

[4] C. Shinomiya and T. Kishikawa, This Bulletin, **41**, 3026 (1968).

[5] B. Turcsanyi and F. Tudos, *Magy. Chem. Folysirat,* **71**, 39 (1965).

[6] All the melting points of the synthesized materials are uncorrected.

[7] 3-Bromo, 3,8- and 3,10-dibromo derivatives were obtained.

[8] G. Lock, *Ber.,* **70B**, 926 (1937).

[9] H. Hock, *Chem. Ber.,* **92**, 2735 (1959).

[10] M. Sarauw, *Ann.,* **209**, 105 (1881).

[11] Kyoto University Reactor.

[12] The ^{82m}Br(I. T.)^{82}Br reaction was completed during the time; O. U. Anders, *Phys. Rev.,* **138**, B1 (1965); J. F. Emery, *J. Inorg. Nucl. Chem.,* **27**, 903 (1965).

[13] 2-Bromo-, 2,5- and 2,6-dibromo-*p*-benzoquinones are soluble in ethyl ether.

and then with benzene[14] (V).

The ^{82}Br activities in each layer were then measured. The total organic yield, defined as the percentage of activities remaining in the organic layers, is given by;

$$OY\ (\%) = \frac{\text{Activities in (III, IV and V)} \times 100}{\text{Activities in (I, II, III, IV and V)}}$$

Paper Chromatography and Paper Electrophoresis. In order to evaluate the distribution of the activities distributed in the layer (III), paper chromatography was carried out (on Toyoroshi No. 50 filter-paper by the ascending method, with *i*-AmOH-Py-H_2O 3 : 2 : 1.5 in V/V as developer). The distribution of the activities on the paper strips was examined by autoradiography. Readioactive bands on them corresponding to the autoradiograph patterns were cut in pieces, and the activities were counted.

The water-soluble species distributed in the layer (I) were analyzed by paper electrophoresis[1] (on Toyoroshi No. 50 filter-paper with a potential gradient of 54.5 V/cm and with 0.1 M aqueous ammonium acetate as the electrolyte solution), followed by autoradiography and measurement of the activity.

Results and Discussion

The relationship between the percentage of the ^{82}Br atoms remaining in the organic layers and the irradiation time is shown in Fig. 1. The extraction curve vary over a short period of irradiation (1—10 min), but the curves (except for P+B) seem to show no remarkable change with an increase in the irradiation time. This exception may be due to the difference in the composition of the target; *i. e.*, it is heterogeneous (mixture), where the others are all homogeneous (compounds).

TABLE 1. DISTRIBUTION OF ^{82}Br-LABELED RECOIL PRODUCTS PARTED IN CARBON DISULFIDE LAYER AT TWO IRRADIATION TIMES

Target min	Irra. time min	Yield, %, at R_f	
		0.12—0.17	1
P−B	10	43.6	56.4
	30	41.5	58.5
P+B	10	70.7	29.3
	30	64.1	35.9
B	10	71.3	28.7
	30	69.4	30.6
PBr	10	0	100
	30	0	100
PBr_2[a]	10	35.8	64.2
	30	25.8	74.2
HQBr[a]	10	71.5	28.5
	30	62.0	38.0

a) Dissolved in carbon disulfide. No extraction.

The percentages of the activity distributed on the chromatographed strips are listed in Table 1.[15] In each sample, the relative activity in the components of R_f 0.12—0.17 decreased with an increase in the irradiation time, and *vice versa*. This may indicate that the distribution of the activities distributed in the layer (III) is affected by the irradiation period in the reactor.

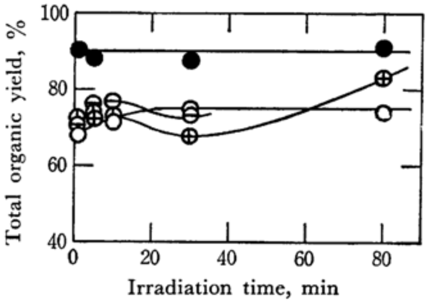

Fig. 1. Total organic yield as a function of the irradiation time.
⊖: pyrenebromanil, ⊕: pyrene-bromanil mixture, ○: bromanil, ●: bromopyrene

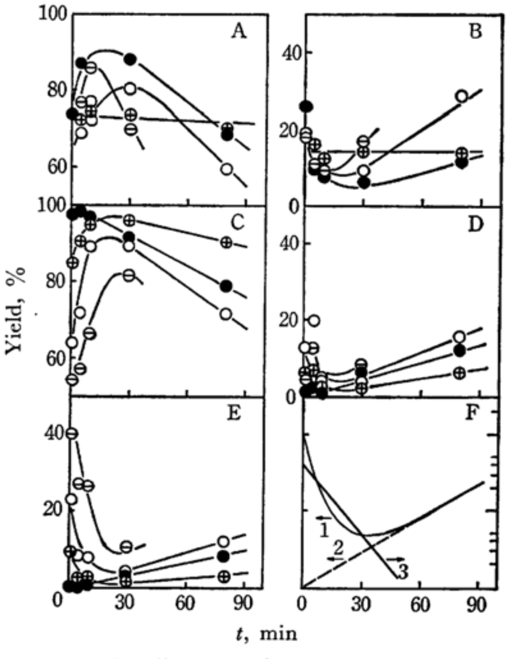

Fig. 2. Distribution of activities parted in aqueous or organic layers as a function of the irradiation time. A and B are distribution of bromide and bromine in the aqueous layers respectively. C, D and E are distribution of activities parted in the carbon disulfide, the ethyl ether and the benzene layers respectively. F is a schematic view of the analysis of a curve.
⊖: pyrenebromanil, ⊕: pyrene-bromanil mixture, ○: bromanil, ●: bromopyrene.

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[14] 1-Bromo-, 1,6- and 1,8-dibromo-, and 1,3,6-tribromopyrenes are soluble in benzene.

[15] The standard R_f values were not determined. The present research was made on the distinction of distribution patterns of the recoil products for the two irradiation times.

TABLE 2. DISTRIBUTION OF ^{82}Br-LABELED RECOIL PRODUCTS PARTED IN AQUEOUS LAYERS AT VARIOUS IRRADIATION TIMES

Target	Irra. time, min	Yield,a) %			
		Br_2	Br^-	Sum of unknowns	Origin b)
P−B	5	10.5	76.8	6.4	6.3
	10	9.4	85.5	4.2	0.0
	30	16.6	70.1	12.4	0.8
P+B	5	15.3	72.2	9.6	3.1
	10	13.1	74.8	8.3	1.9
	30	14.2	73.6	14.5	1.4
	80	13.9	70.0	10.5	4.7
B	5	10.7	68.2	—	6.4
	10	12.9	72.6	10.2	1.0
	30	8.5	80.0	8.8	1.2
	80	28.6	59.2	10.2	1.8
PBr	5	9.9	87.0	0	0.6
	10	8.4	83.5	0	7.4
	30	6.2	87.9	0	2.1
	80	11.9	68.4	0	19.5
PBr_2 c)	10	—	41.8	0	53.7
	30	—	55.8	0	37.4
	80	—	56.3	0	33.5
HQBr c)	5	—	39.8	27.4	20.1
	10	—	65.1	12.4	19.2
	30	—	58.3	19.7	26.5
	80	—	47.1	4.7	31.4

a) The relative yield was calculated from activities in the aqueous layers I and II. The values of Br^-, sum of unknowns and origin were calculated from activities distributed on the paper electrophoregrams. The sum of less than 100% was due to a "smear" of activity extending.16)

b) Yield on an original spot may be of bromine and/or an organic bromide which has remained in the layer I.

c) Dissolved in carbon disulfide. The paper electrophoresis was carried out without extraction.

Among the samples, PBr, PBr_2, and P−B showed higher relative activities at the component of R_f 1, while the rest, B, HQBr, and P+B, showed more at the components of R_f 0.12—0.17. As compared with B, the distribution of P+B is not definitely affected when P is mixed in. When P−B is compared with P+B, on the other hand, the contribution of P is clear. The greater values at the component of R_f 1 in the irradiated P−B suggest the presence of a pyrene-radiobromine combination.

Table 2 lists the distribution of the ^{82}Br-labeled recoil products among the irradiated samples distributed in the aqueous layers (I and II) at various irradiation periods. In each case the major portion of the activities was found in the form of bromide. Three or four components, the mobilities of which were comparatively small, were obtained on paper strips of B, P−B, P+B, and HQBr. These components were not obtained on strips of PBr and PBr_2. These facts suggest that the components may be fragments of organic radiobromides originating in bromanil.

Figure 2 shows the relationship between the percentages of the ^{82}Br activities distributed in the aqueous or the organic layers and the irradiation time. The curves of the bromide and the bromine in P+B (see Figs. 2A and B) show a less remarkable change with the irradiation time. This may be because of the different behavior of the curve of its total organic yield.

The curves decreased (or increased) with an increase in the irradiation time. The longer the irradiation period, the better the (negative) proportionality to the irradiation time the curves seemed to show. To analyze the curve (see Fig. 2F) the final proportional portion was extrapolated back to time zero; on substracting the extrapolated line (2) from the original curve (1), another straight line (3) on a semilogarithmic scale was obtained. From the analyses of the curves, the following experimental equations were established;

$$Y = Y_0 \cdot e^{-rt} + mt \qquad (m>0)$$

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16) J. Jack and G. Harbottle, *Trans. Faraday Soc.*, **54**, 520 (1958).

or; $Y = Y_0 \cdot e^{-rt} + mt + (1 - e^{-rt}) \quad (m<0)$

where Y, Y_0, m, and r are the yield at time t, the initial yield, the proportion constant, and the inclination of the semilogarithmic plot respectively. The quantitative treatment of such values as Y_0, m, and r should be discussed primarily on the basis of the theoretical derivation as functions of the reactor irradiation time and other considerable parameters. This question will be discuss in another paper.

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