BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1276—1282 (1970)

Hot-Atom Chemistry of Bromine. IV. Chemical Effects of ^{81}Br(n,γ)^{82g}Br, ^{81}Br(n,γ)^{82m}Br and ^{82m}Br(I. T.)^{82}Br Excitation in Antimony Tribromide and Benzene System[1,2]

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(Received July 19, 1969)

Antimony tribromide and a molecular compound between antimony tribromide and benzene (2 : 1) have been irradiated to provide ^{82m}Br sources. The results obtained by the dissolution of the irradiated molecular compound, by means of which technique the chemical effects of ^{81}Br(n,γ)^{82g}Br and ^{82m}Br(I.T.)^{82}Br were determined separately, had shown very low organic yields from either (n,γ) or (I.T.) excitation. The reaction of ^{82m}Br(I.T.)^{82}Br in benzene showed a growth in the organic yields. Moreover, the organic yield of ^{82}Br was lower when the system was frozen than when it was stored as a liquid. These results are explained by assuming that, in the frozen system, the antimony tribromide (^{82m}Br) forms a molecular compound with the benzene. The higher organic yields in the frozen systems than those in the molecular compound itself must be due to the formation of free bromine (^{82m}Br), which turns out to be an organic radiobromide. The hydrolytic behavior of the irradiated antimony tribromide and the molecular compound supports the idea of the presence of free bromine (^{82m}Br) at the end of the irradiation.

Since the discovery of the meta-stable-state bromine-82,[3] much work has been done on the chemical effects of the ^{82m}Br(I.T.)^{82}Br excitation in various liquid or solid organic media. The vertue of the subject transformation is that the experiment can be conducted in the absence of those transformations due to (n,γ) reactions and also of any possible influence of the accompanying gamma-radiation from a reactor. The major portion of the activity produced from the (n,γ) activation by ^{81}Br is the ^{82m}Br-activity, which undergoes the (I.T.) process (activation cross sections,[3a] $\sigma_m=3.0$ and $\sigma_g=0.3$ barns). The bromine-82m decays with a highly-converted transition[3a] of 46 keV (internal conversion coefficient, $\alpha_k=268$). This means that a large fraction of the ^{82}Br is produced with a positive charge. The ^{82m}Br source has thus far been prepared by two methods for the sake of experimental convenience: by irradiating molecular bromine,[4] and by irradiating an organic bromide.[5] A third method, to be proposed here, proceeds by irradiating an inorganic bromide.

The present work will deal with the chemical effects of radiative neutron capture by bromine-81 and of isomeric transition by bromine-82m in mixtures of antimony tribromide and benzene.

Experimental

Materials. Wako Pure Chemicals' JIS special-grade benzene was purified by the usual method. Tokyo Kasei JIS 1st-grade antimony tribromide was used after it has been purified by recrystallization (mp 96.6°C) from carbon disulfide. The other reagents used were all of a JIS special-grade, but were also further purified if necessary. The $2SbBr_3 \cdot C_6H_6$ molecular compound

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[1] Presented in parts at the 11th Symposium on Radiochemistry, Tokyo, October 1967, and at the 21st Annual Meeting of the Chemical Society of Japan, Suita, April, 1968.

[2] C. Shinomiya, A. Oyoshi and T. Kishikawa, This Bulletin, **42**, 2040 (1969).

[3] a) J. F. Emery, *J. Inorg. Nucl. Chem.*, **27**, 903 (1965). b) O. U. Anders, *Phys. Rev.*, **138**, B1 (1965).

[4] a) R. M. Iyer and J. E. Willard, *J. Amer. Chem. Soc.*, **87**, 2494 (1965). b) N. A. Katsanos and M. I. Stamouli, *Z. Phys. Chem.*, *Neue Folge*, **47**, 306 (1965). c) J. A. Merrigan and E. P. Rack, *J. Phys. Chem.*, **69**, 2795, 2806 (1965). d) J. A. Merrigan, W. K. Ellgren, Jr., and E.P. Rack, *J. Chem. Phys.*, **44**, 174 (1966). e) J. A. Merrigan, J. B. Nicholas and E. P. Rack, *Radiochim. Acta*, **6**, 94 (1966). f) R. M. Lambrecht and E. P. Rack, COO-1617-4 (1967). g) E. P. Rack, COO-1617-6 (1967); COO-1617-10 (1968). h) R.M. Lambrecht, N. J. Parks and E. P. Rack, COO-1617-7 (1967). i) N. A. Katsanos and M. I. Stamouli, *Radiochim. Acta*, **7**, 126, 177 (1967); *ibid.*, **9**, 13 (1968). j) C. Shinomiya and T. Kishikawa, This Bulletin, **41**, 3026 (1968).

[5] a) N. A. Katsanos, "Proceedings of the Symposium on Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna (1965), p. 371; *J. Chem. Soc.*, **1965**, 4751. b) N. A. Katsanos and M. I. Stamouli, *Radiochim. Acta*, **5**, 148 (1966). c) I. L. Leontiadis and N. A. Katsanos, *Z. Phys. Chem.* (Frankfurt), **57**, 38 (1968).

($2SbBr_3Bz$) (mp 92.6°C, lit,[6] 92.5°C) was prepared[7] by adding antimony tribromide to hot benzene, followed by cooling and evaporating the excess benzene.

Neutron Irradiation. Samples sealed in a quartz ampule were irradiated in a pneumatic tube of KUR[8] at the temperature of dry ice or at the reactor temperature (*ca.* 40°C). The thermal neutron flux was 5×10^{12} n/cm^2/sec, and the accompanying gamma-radiation flux was 2.7×10^7 R/hr.

Procedure. *Dissolution Technique.* The ampule of the irradiated $2SbBr_3Bz$ molecular compound at the temperature of dry ice was immersed in a boiling-water bath immediately after it has been irradiated for 60 min; during the immersion almost all the ^{82m}Br isotopes produced by the radiative neutron capture decayed to the ^{82}Br ground state. The ampule was then cooled in a bath of dry ice and ethanol. The sample was extracted directly from the frozen state into a two-phase mixture of benzene containing a bromine carrier plus 0.5M aqueous sodium sulfite, after which hydrochloric acid (1 : 1) was added to the mixture.[9] The organic layer was then dried over calcium chloride.

Antimony Tribromide - Benzene System. The irradiated molecular compound or antimony tribromide was dissolved in benzene immediately after irradiation; it was then stored at room temperature (liquid) or at the temperature of dry ice (frozen). Aliquot portions were extracted after varying periods of time.

Counting and Analysis. A NaI(Tl) scintillation crystal and a multi-channel pulse height analyzer were used. By radiative neutron capture the activities of ^{122}Sb (half-life 2.75 day), ^{122m}Sb (4.2 min), ^{124}Sb (60 day), ^{124m}Sb (21 and 1.3 min), ^{80}Br (18.5 min), and ^{80m}Br (4.5 hr) as well as of ^{82}Br (36 hr) and ^{82m}Br (6.2 min[3]) were produced. Only the ^{82}Br activities were studied. After all, since the ^{82m}Br had dceayed to the ^{82}Br ground state, a 0.78 MeV gamma-ray photo peak was measured and used for the calculation.

Results and Discussion

Effects of the Time and Temperature of Irradiation and Those of Standing on the Organic Yields of the $2SbBr_3Bz$ Molecular Compound. To determine the effects of the accompanying gamma-ray and the temperature in the reactor, the molecular compound was irradiated for varying periods at different temperatures. Table 1 lists the overall organic yields (experimental error range, ±1%); these yields mean that it is not necessary to take the accompanying gamma dose in the reactor into consideration. Little dependency of the temperature of irradiation and standing was observed, as is shown in Fig. 1.

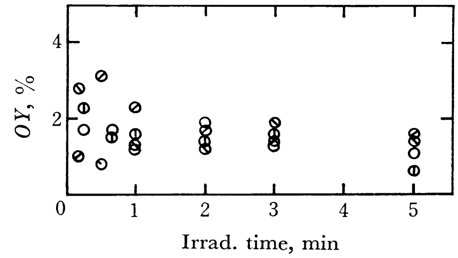

Fig. 1. Organic yields induced by $^{81}\mathrm{Br}(n,\gamma)^{82}\mathrm{Br}$, $^{81}\mathrm{Br}(n,\gamma)^{82m}\mathrm{Br}$ and $^{82m}\mathrm{Br}(\mathrm{I.T.})^{82}\mathrm{Br}$ processes at the molecular-compound $2SBr_3Bz$. Effects of temperature at time of these nuclear events.

Experimental error range is ±1%.

	Temp.	
	Irrad.	Standing
○	Dry ice	Dry ice
⦶	Dry ice	Room
⊘	Reactor	Dry ice
⦸	Reactor	Room

TABLE 1. THE EFFECTS OF THE ACCOMPANYING GAMMA-RADIATION AND TEMPERATURE IN THE REACTOR,[a] AND THE EFFECTS OF TEMPFRATURE AT TIME OF STANDING ON OVERALL ORGANIC YIELDS AT THE IRRADIATED MOLECULAR-COMPOUND $2SbBr_3Bz$

Temp.		Overall organic yield,[b] %, at the irrad. period (sec) of							
Irrad.	Standing [c]	11	15	30	40	60	120	180	300
Dry ice	Dry ice		1.7	0.8	1.7	1.2	1.9	1.3	1.1
Dry ice	Room		2.3		1.5	1.6	1.4	1.6	0.6
Reactor [d]	Dry ice	1.0		3.1		2.3	1.7	1.9	1.6
Reactor	Room	2.8		0.8		1.3	1.2	1.4	1.4

a) Thermal neutron flux of 5×10^{12} n/cm^2/sec and caccompanying gamma-dose rate of 2.7×10^7 R/hr.
b) Experimental error range of ±1%.
c) During the time of standing (for 60 min) almost all the ^{82m}Br decayed to the ^{82}Br ground state.
d) *ca.* 40°C.

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6) "International Critical Tables of Numerical Data," Vol. IV, ed. by E. W. Washburn, McGraw-Hill, New York (1933), p. 195; B. N. Menshutkin, *J. Phys. Chem. Soc. (Chem. Part)*, **43**, 393, 401, 425 (1911).

7) Procedure for the preparation of antimony trichloride-benzene (2 : 1) was applied; C. Shinomiya and T. Asahina, *Nippon Kwagaku Kwaishi*, **59**, 1165 (1939).

8) Kyoto University Reactor.

9) In dilute hydrochloric acid or in water a hydrolyzed product (white precipitate) of antimony tribromide can be produced, which interupts to separate the phases.

TABLE 2. THE EFFECTS OF DISSOLUTION ON OVERALL ORGANIC YIELDS INDUCED BY ^{81}Br(n,γ)^{82}Br, ^{81}Br(n,γ)^{82m}Br and ^{82m}Br(I.T.)^{82}Br PROCESSES AT THE MOLECULAR-COMPOUND 2SbBr$_3$Bz [a)]

Major nucl. reaction	Standing		Overall organic yield, %, at the irrad. period (sec) of			
	Time min	Temp.	15	30	60	300
(n,γ)	60	100°C	0.7		0.4	0.5
(n,γ)+(I.T.)	6	Dry ice [b)]	1.3	1.0	1.2	0.5
(n,γ)+(I.T.)	60	Dry ice	1.7	0.8	1.2	1.1
(I.T.)	60	Dry ice	1.0		0.8	0.6

a) Irradiation was carried out at the temperature of dry ice.
b) Temperature of dry ice/ethanol.

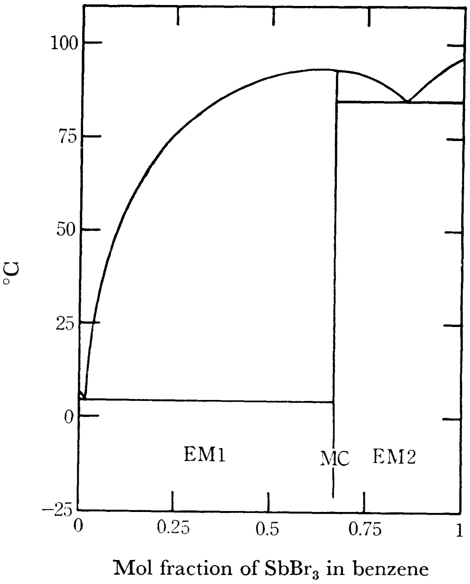

Fig. 2. Phase diagram of SbBr$_3$-C$_6$H$_6$.
EM1: Eutectic mixture (C$_6$H$_6$+2SbBr$_3$·C$_6$H$_6$)
EM2: Eutectic mixture (2SbBr$_3$·C$_6$H$_6$+SbBr$_3$)
MC: Molecular compound (2SbBr$_3$·C$_6$H$_6$)

Dissolution of the Irradiated 2SbBr$_3$Bz Molecular Compound. The following experiments were performed in order to obtain information on the effects of the isomeric transition-induced process. Immediately after the irradiation, quartz ampules containing 2SbBr$_3$Bz were immersed in the boiling-water bath; the molecular compound in the ampule were thus decomposed into a two-phase mixture of its components - benzene (gas, bp 80.1°C) and antimony tribromide (liquid, mp 92.6°C), as may be seen in the phase diagram of the SbBr$_3$-C$_6$H$_6$ system⁶⁾ in Fig. 2.

After the completion of the (I.T.) process, the sample was resolidified in the bath of dry ice and ethanol and then extracted. The observed overall organic yields at the various irradiation periods are listed in Table 2. The results of standing at the temperature of dry ice are also listed in the table. If there were an organic radiobromide-(^{82m}Br) which had been produced by the (n,γ) activation and subsequent recoil bond-forming processes, the following (I.T.) process might cause the organic radiobromide to dissociate the ^{82}Br atom resulting from Coulombic repulsion. The overall organic yield value on the first line in each irradiation-time column in Table 2 may then be attributed, for the most part, to the organic radiobromides-(^{82g}Br) produced directly by the (n,γ) activation.

A slight increase in the organic yield with an increase in the standing time was observed (the values on the second and the third lines). The values on the last line, which are attributed to the fraction of the (I.T.)-excited reaction, are obtained by subtracting the value on the first line from that on the third line in each column.

Reaction of Bromine-82m Prepared by Irradiating Antimony Tribromide or the 2SbBr$_3$-Bz Molecular Compound in Liquid and Solid Benzene. To ascertain whether or not the increase in the organic yield is affected by the (I.T.) depending process, the following rate determinations in liquid and solid benzene were carried out. As soon as the end of the irradiation of SbBr$_3$ or

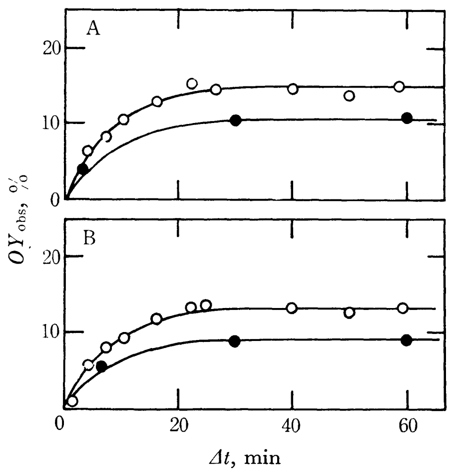

Fig. 3. Growths of ^{82}Br organic yields in benzene.
A) Irrad. SbBr$_3$. B) Irrad. 2SbBr$_3$Bz.
○: Liquid, ●: Frozen

$2SbBr_3Bz$, the sample-benzene system (1.64×10^{-4} mol fraction of $SbBr_3$) was produced as is described in the Experimental section. The inorganic radiobromine in a portion of the system was separated by extraction at different time intervals. Figure 3 shows plots of the activities of the overall organic yield obtained from systems left to stand for various length of time, Δt, after the preparation of the systems. The curves increase with an increase in the standing time.

If the observed increase in the ^{82}Br organic yield is a result of chemical excitation by the (I.T.) alone, the rate of growth should be dependent only on the decay of the ^{82}Br and should be related to the half-life of the ^{82m}Br. Therefore, when OY_{obs}^{∞} represents the overall organic yield attained after all the ^{82m}Br has decayed to the ^{82}Br ground state, when OY_{obs}^{0} represents the organic yield present at the time the system is prepared (*viz*., for the irradiated $SbBr_3$, $OY_{obs}^{0}=0$; for the irradiated $2SbBr_3Bz$, $OY_{obs}^{0}=$[the values listed on the first line of the irradiation-time column in Table 2 which are due to $^{81}Br(n,\gamma)^{82g}Br$]), and when $OY_{obs}^{\Delta t}$ represents the organic yield at any time before the ^{82m}Br has completely decayed, the growth of the ^{82}Br organic yield will be given[4d,4j] by:

$$(OY_{obs}^{\Delta t}-OY_{obs}^{0})=(OY_{obs}^{\infty}-OY_{obs}^{0})(1-e^{-\lambda\Delta t}),$$

where λ is the decay constant of ^{82m}Br. By rearranging the equation, $\log(OY_{obs}^{\infty}-OY_{obs}^{0})-(OY_{obs}^{\Delta t}-OY_{obs}^{0})/(OY_{obs}^{\infty}-OY_{obs}^{0})$ *versus* Δt should yield a straight line (Fig. 4) with a slope of $-0.693/2.303T_{1/2}$. The half-life of ^{82m}Br was determined to be 6.00 and 5.87 min from the yields of the liquid systems of the irradiated-$SbBr_3$ - C_6H_6 and of the irradiated-$2SbBr_3Bz$ - C_6H_6 respectively. The close relative rates of increase in the overall organic yields[10] in the different systems can be attributed to the ^{82m}Br(I.T.)-excited reaction. Similar phenomena have been reported in liquid and solid systems of irradiated-Br_2 - C_6H_6 by two of the present authors (C.S. and T.K.) in a previous paper.[4j]

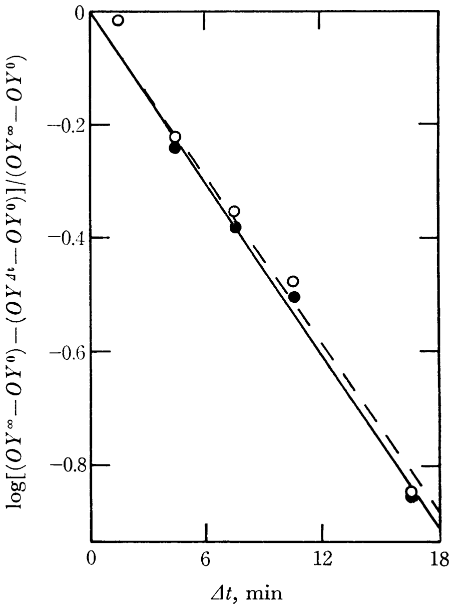

Fig. 4. Bromine-82 organic yields as a result of isomeric transition in benzene.
○: Irrad. $SbBr_3$, ●: Irrad. $2SbBr_3Bz$

Behavior of the ^{82}Br Produced by (n,γ)- and (I.T.)-activation at $SbBr_3$ and $2SbBr_3Bz$. If water is added to antimony tribromide, various antimony oxybromides are formed. An appropriate amount of water hydrolyzes it to form $Sb_4O_5Br_2$, the solubility of which in water is very low.[12]

$$4SbBr_3+5H_2O\longrightarrow Sb_4O_5Br_2+10HBr$$

Stoichiometrically speaking, five-sixths of all the bromine atoms are present in the aqueous solution, and the rest in the precipitate. The hydrolysis of the compound provides a means to study the Szilard-Chalmers reaction,[13] in which a portion of the radiobromides produced by the (n,γ) reaction is found in an un-recombined form and thus can be extracted with water. The results of the hydrolysis are listed in Table 3. The higher bromide yield which was obtained by hydrolysis a short time after the irradiation can be attributed to the presence of the ^{82m}Br activities. When the irradiated sample was left standing for 90 min at the temperature of dry ice, the hydrolyzed yield of bromide was reduced nearly to the calculated value. The results of the hydrolysis coincide with those of dissolution.

TABLE 3. HYDROLYTIC BEHAVIOR OF ^{82}Br IN IRRADITATED $SbBr_3$ OR $2SbBr_3Bz$

Irrad. sample	Standing[a] min	Yield, %	
		$Sb_4O_5Br_2$	Br^-
$SbBr_3$	2	3.9	96.1
$SbBr_3$	90	14.9	85.1
$2SbBr_3Bz$	90	15.8±1.2	84.2±1.2
$SbBr_3(^{82}Br)$[b]		18.4±1.6	81.6±1.6
Calculated		16.7	83.3

a) Time between the end of irradiation and hydrolysis.
b) Synthesized by using ^{82}Br as a tracer.[12]

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[10] Major products (see Ref. 11) was bromobenzene-(^{82}Br). The detailed report will be published in another paper.

[11] Presented at the 13th Symposium on Radiochemistry, Nagoya, October 1969, Preprint, p. 98.

[12] Detailed data will be submitted in another paper.

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

Table 4. Overall organic yields by ^{82m}Br(I.T.)^{82}Br process

Irrad.		Standing[a]		OY^{∞}_{net}
Sample	Time min	Solvent	Phase	%
$2SbBr_3Bz$	0.25	No	Solid	1.0
$2SbBr_3Bz$	1	No	Solid	0.8
$2SbBr_3Bz$	5	No	Solid	0.6
$2SbBr_3Bz$	0.25	Benzene[b]	Liquid	17.2±2.2
$2SbBr_3Bz$	5	Benzene	Liquid	18.8±0.6
$2SbBr_3Bz$	1	Benzene	Frozen	12.9±0.6
$SbBr_3$	0.25	Benzene	Liquid	15.4±1.9
$SbBr_3$	5	Benzene	Liquid	20.1±1.4
$SrbB_3$	1	Benzene	Frozen	13.8±0.9

a) During the time of standing all the ^{82m}Br decayed to the ^{82}Br ground state.

b) $SbBr_3$ concentration was 1.64×10^{-4} mol fraction.

Determination of the ^{82}Br Organic Yield Resulting from the ^{82m}Br(I.T.)^{82}Br Process in the Liquid and Solid Systems. Correcting for the contributions of the activities of the ground-state ^{82}Br produced directly from the (n,γ) reaction and for those of the activities decayed from the ^{82m}Br before preparing the reaction systems, one can obtain the net organic yield values (OY^{∞}_{net}); these values are presented in Table 4.

As has been pointed out in the introduction, the decay of the ^{82m}Br goes through a 46 keV highly-converted transition; this suggests that a large fraction of the ^{82}Br is produced with a positive charge. It would appear that the chemical stabilization of the daughter ^{82}Br in the present liquid systems is due either to ion-molecule reactions of these charged atoms with the surrounding organic medium or to reaction of the neutralized hot atoms with the medium.

It is well known that molecular bromine is stable in benzene, forming a charge-transfer complex[14] (the charge-transfer energy is 4.25 eV[15]), and that aromatic bromination with molecular bromine proceeds quite gently in a non-polar organic medium such as benzene.[16] The electron acceptability of bromine in the charge-transfer complex depends on the state of bromine in the following order: $Br^+ > Br^0 > Br_2$. Also, the positively-charged ^{82}Br ion produced by the (I.T.) and the accompanying internal conversion processes is a much better electron-acceptor; the chance of its staying alive to form a charge-transfer complex with benzene may be small, since its electron affinity is high (the ionization potential of benzene is 9.25 eV,[17] lower than that of bromine by 2.59 eV). The fact that not all the bromines formed *via* the (I.T.) are found in the organic combination suggests that the ion-molecule reaction is less significant in the present systems. The ^{82}Br may, therefore, react by means of the energetic reaction. Some recent data[11] on the ^{82m}Br(I.T.)-induced reaction in alkyl benzenes indicate that the values of the overall organic yield follow the same order as the ionization potential of the benzenes. The charge-transfer complex may, then, act as a reaction intermediate. The small growth in the observed organic yield after 25 min (plateaus in Fig. 3) indicates that the simple free-radical reactions of the bromine atoms after complete thermalization are negligible.

On the other hand, in the resolidified systems, which are composed of polycrystalline mixtures[18] (eutectic mixture) of benzene plus the $2SbBr_3Bz$ molecular compound, the free bromine produced by the (n,γ) or (I.T.) reaction and remaining before resolidification may also be composed of a molecular compound ($^{82m}Br\cdot C_6H_6$ or $Br_2(^{82m}Br)\cdot C_6H_6$[4j,19]). Lambrecht and Rack,[4h] after a consideration[4d,20,21] of the clustering of bromine in an organic medium, put forward a scheme attempting to provide a better understanding of solid-state organic yields in polycrystalline systems. Their scheme can be rather satisfactorily applied to the present systems by replacing $(Br_2)_n$ by $(2SbBr_3Bz)_n$, because a very low organic yield has been observed in the irradiated molecular compound (the benzene in the molecular compound may be comparatively inert, since the ionization potential of antimony is 8.46 eV,[17] lower than that of benzene by 0.79 eV): That is, the ^{82}Br atoms formed by the (I.T.) process in the molecular-compound clusters mostly remained inorganically in the clusters, while those formed in the polycrystalline benzene reacted within the benzene, and while those formed on the surface of the molecular-compound clusters remained either organically or inorganically.

Distribution of Organic Radiobromides in the Irradiated Molecular Compound. The fractional distillation of the benzene layer of the

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[14] L. J. Andrews and R. M. Keefer, "Molecular Complex in Organic Chemistry," Holden-Day, San Francisco (1964).

[15] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **72**, 4677 (1950).

[16] For aromatic bromination with molecular bromine two theories have been proposed: a) R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **78**, 255, 4549 (1956); b) P. B. D. de la Mare and J. T. Harvay, *J. Chem. Soc.*, **1956**, 36; *ibid.*, **1957**, 131, 923.

[17] "Kagaku Binran, Kiso-hen. II," ed by S. Nagai, Maruzene, Tokyo (1966), p. 1124.

[18] Examined concentration of antimony tribromide was below the eutectic point (mol fraction to give the eutectic point is 1.9×10^{-2}; see Fig. 2).

[19] O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, **12**, 1146 (1958).

[20] R. M. H. Hahne and J. E. Willard, *J. Phys. Chem.*, **68**, 2582 (1964).

[21] M. Milman, *J. Amer. Chem. Soc.*, **80**, 5592 (1958).

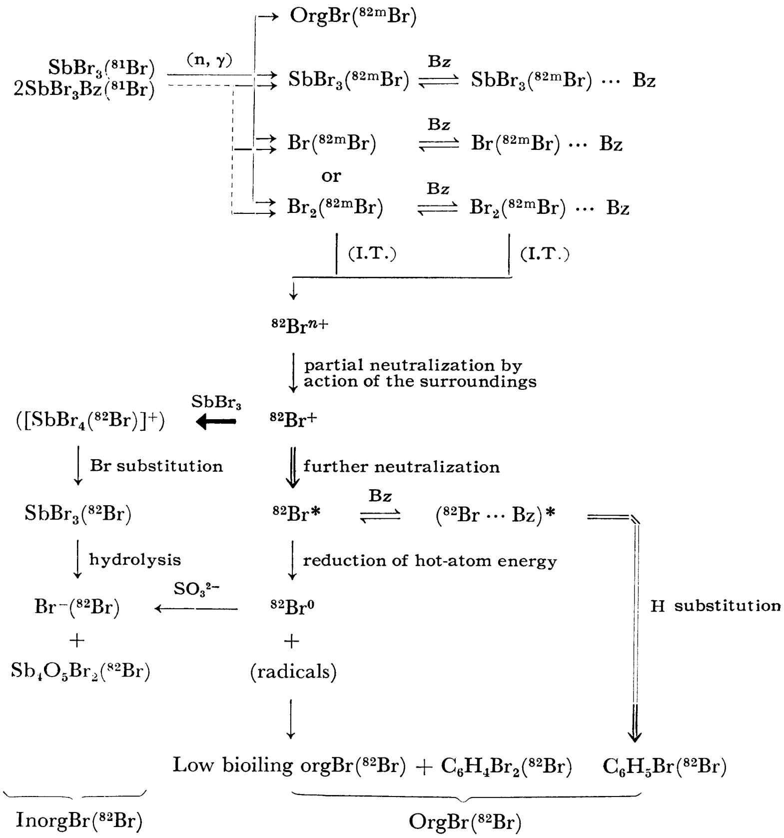

Fig. 5. Deactivation and organic-radiobromide formation process of the ^{82}Br atoms produced by the ^{82m}Br(I.T.) process in liquid or frozen systems of the irrad.-$SbBr_3$ - C_6H_6 and irrad.-$2SbBr_3Bz$ - C_6H_6.

⟹ Predominant path in the liquid system, or in or on the surface of the BrBz or Br_2Bz in the forzen system

➞ Predominant path in the $(2SbBr_3Bz)_n$ clusters in the frozen system

$^{82}Br^*$ Energetically hot bromine atom

irradiated $2SbBr_3Bz$ after all the ^{82m}Br has decayed indicates the formation of low- and high-boiling products as well as of bromobenzene. Recrystallization with the addition of inactive *p*-dibromobenzene indicated its formation. The distributions (%) of (low bp fraction, bromobenzene and dibromobenzenes) in the benzene layers at the irradiation times of 1, 3, and 20 min were (24, 64, and 34), (21, 37, and 42) and (15, 46, and 39) respectively.

Contribution of Thermal Exchange and Substitution Reactions. To determine whether the organic yield built up after 60 min is due only to the (I.T.) process or whether a part of it is due to the thermal exchange and/or thermal substitution reactions of antimony tribromide(^{82}Br) with bromobenzene or with benzene, the following experiment was performed by synthesizing antimony tribromide(^{82}Br).[12] It was dissolved in an organic medium (12.5×10^{-3} g-atom/*l* of $SbBr_3(^{82}Br)$ and 3.54×10^{-3} g-atom/*l* of C_6H_5Br in benzene, or 20.0×10^{-3} g-atom/*l* of $SbBr_3(^{82}Br)$ in bromobenzene). The reaction mixture was then stored at 25 or 19.5°C (±0.5°C reguration) and portions were extracted at regular intervals in the manner described above. The activities of both the organic and aqueous layers were then measured. After the conventional treatment of the isotopic exchange,[22] the apparent half-time values and the fractional exchange values at 60 min, after the preparation of the reaction mixture in all cases, were found to be 10^4 hr and 0.001 respectively; these value indicate no prominent role of either isotopic exchange or substitution reactions.

From these findings, the probable paths of the organic-radiobromide formation in the irradiated-$SbBr_3$ - benzene or the irradiated-$S2bBr_3Bz$ - benzene systems due to the (I.T.) process by the ^{82m}Br may be assumed to be as is illustrated schemati-

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22) O. E. Meyers and R. J. Prestwood, "Radioactivity Applied to Chemistry," ed. by A. C. Wahl and N. A. Bonner, 2nd Ed., John Wiley & Sons, New York (1958), p. 7.

cally in Fig. 5.

The authors are grateful to Dr. Akira Oyoshi of this University for his encouragement; to Drs. Shiro Iwata and Yoshiyuki Kiso, Mr. Kazuhisa Sasajima, and the personnel of the Research Reactor Institute, Kyoto University, for their assistance in the irradiation, and to the Institute for giving, under Contracts 42147 and 42211, the co-operative facilities which made this research possible.