Reaction of Bromine Activated by Bromine-82m Isomeric Transition in Liquid and Solid Benzene*1

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The discovery of the ^{82m}Br(I.T.)^{82}Br nuclear reaction[1,2] has made it possible to study isomeric transition-induced reactions free from any possible influence of the gamma-radiation from a reactor. The chemical effects of the subjecting transformation in liquid organic media have been investigated by Iyer and Willard[3] and by Stamouli and Katsanos.[4] To determine whether a similar chemical effect occurs (1) in the solid state, we mixed neutron-irradiated molecular bromine with benzene, and allowed it to stand at the temperature of dry ice for 60 min, by which time almost all the ^{82m}Br had decayed to ^{82}Br. The inorganic radiobromine was then separated by means of extraction.

A separate run was performed (2) in the liquid state. After mixing irradiated bromine with benzene at room temperature, the inorganic radiobromine in a portion of the mixture was separated by extraction at different time intervals. To analyze the rate of growth of the organic yield in the run (2), $OY^{\infty}_{\mathrm{obs}}-OY^{\Delta t}_{\mathrm{obs}}$ were plotted against Δt, where $OY^{\infty}_{\mathrm{obs}}$ represents the ^{82}Br organic yield reached in the system (1) or system (2) after all the ^{82m}Br had decayed to the ^{82}Br ground state, and where $OY^{\Delta t}_{\mathrm{obs}}$ represents it at any time before the ^{82m}Br has completely decayed. The plot gave a straight line. The half-time of the reaction so obtained was 6.27 min.

Correcting for the contributions of the activities of the ground-state ^{82}Br produced directly from radiative neutron capture and for those of the activities decayed from ^{82m}Br before mixing, one can obtain the net organic yields ($OY^{\infty}_{\mathrm{net}}$).

TABLE 1. ORGANIC YIELD OF ^{82}Br PRODUCED IN SOLID AND LIQUID BENZENE AS A RESULT OF THE DECAY OF ^{82m}Br(Br$_2$) BY ISOMERIC TRANSITION

Phase	Mole fraction of $Br_2 \cdot 10^3$	Total organic yield, $OY^{\infty}_{\mathrm{net}}$ %	Ref.
Solid	4.23	113.1±15.6	
Liquid	4.23	34.0± 3.1	
Liquid	8.11	26.1± 0.6	4a

Bromine-82m decays by a highly converted transition[2] 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. If the observed increases in the ^{82}Br organic yield result from chemical excitation by the isomeric transition, the rate of growth should depend only on the decay of ^{82m}Br (the half-lives in Refs. 1—3 are 6.05, 6.20, and 6.20 min, respectively). The closed value of the rate data may be attributed to the ^{82m}Br-decay-depending reaction. Because it is well known that aromatic bromination with molecular bromine proceeds quite gently in a nonpolar organic medium unless an electrophilic reagent such as ferric bromide is added. Stamouli *et al.*[4a] have reported the organic yield value of 26.1% where the bromine concentration was 8.11×10^{-3} mol fraction. Though the value in the present work is a little higher, it may be considered to be reasonable[4a] if the difference in the bromine concentration is taken into consideration.

In the solid system at the temperature of dry ice, a valid amount of activities in the system was found only in the benzene layer. Bromine forms a 1 : 1 molecular compound with benzene[5] (mp −14.0°C). Though the phase diagram of the system has not yet been completed, no evidence of the bromine clumping which is formed in certain hydrocarbon systems[6,7] is found in the present system. Electron capture during partial neutralization from the immediate environment (*i. e.*, a molecular compound or molecular compound-benzene) will cause further excitation and damage within a highly-localized region. The high solid-state organic yield must be the result of recombination reactions with damaged organic fragments or benzene. A more detailed report will be published later.

The investigation was performed at the Research Reactor Institute, Kyoto University.

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