210. *Isotope Exchange between Hydrogen Bromide and Bromine.*

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When bromine containing the radioactive isotope is mixed with hydrogen bromide in carbon tetrachloride solution complete interchange takes place at room temperature in less than two minutes. Hydrogen bromide gas (from concentrated hydrobromic acid and calcium bromide) was dried by cooling to − 65°, and a saturated solution prepared in carbon tetrachloride containing a considerable amount of fresh phosphoric oxide in suspension; this was shaken at intervals for five days. Bromine, activated by a radon–beryllium source of 120 millicuries, was added to an approximately equivalent amount of the hydrogen bromide solution (concentration about 0·1*M*) and immediately afterwards the free bromine was removed by shaking with mercury. The mercurous bromide and excess mercury were filtered off, washed with carbon tetrachloride, acetone, and water, and boiled with nitric acid containing silver nitrate until all the halogen had been converted into silver bromide. The hydrogen bromide in the filtrate was converted into silver bromide. The specific activities of the two samples of silver bromide were examined by a Geiger counter, and found to be equal. This was repeated several times; in some cases the suspension of phosphoric oxide was kept in the hydrogen bromide solution during the reaction. Precautions were taken to dry the air in the flask in which the exchange occurred before introducing the solution and whilst the bromine was being added.

The rapid interchange $BrBr^* + HBr \rightleftarrows Br_2 + HBr^*$ (where the asterisk denotes the radioactive isotope) is not caused by halogen interchange between the mercurous bromide and the hydrogen bromide; in a control experiment in which active mercurous bromide was prepared separately (but in the same way) and then shaken with the hydrogen bromide solution, only a small amount of interchange occurred.

Calculation from the equilibrium concentration of bromine atoms (Gordon and Barnes, *J. Chem. Physics*, 1933, **1**, 692) shows that reaction *via* atoms, $BrBr^* \rightleftarrows Br + Br^*$ followed by $Br^* + HBr \rightleftarrows HBr^* + Br$ could not account for the rapid reaction observed, even if the activation energy of the second step were negligible. We are left with two possibilities: (*a*) a bimolecular reaction involving a collision complex or intermediate species HBr_3, or (*b*) the formation of $H_3O^{\cdot},Br'$ (ions or ion pair) which then interchanges with $BrBr^*$ and with HBr; it is possible that quite small traces of dissolved water which have escaped the action of the phosphoric oxide (say one molecule of water in 10^7 molecules of carbon tetrachloride) might suffice. The direct ionisation of hydrogen bromide seems much less probable.

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