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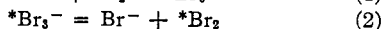
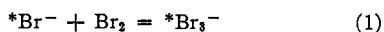
**Halogen-Halide Exchange Reactions in Aqueous Solution**

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**Introduction**

Exchange reactions between halogens and halide ions in aqueous solution have been studied extensively by the method of radioactive indicators. Long and Olson<sup>1</sup> found the exchange between chlorine and chloride ion in acidified aqueous solution to be immeasurably fast. Grosse and Agruss<sup>2</sup> concluded that the bromine-bromide exchange is fairly slow, being governed by the rate of hydrolysis of the bromine, which they proposed as the exchange mechanism. Rojinskiĭ and Gopshtein<sup>3</sup> stated that this exchange is rapid. Juliusburger, Topley and Weiss<sup>4</sup> found that iodide exchanges with iodine in aqueous solution. Hull, Shiflett, and Lind<sup>5</sup> found this exchange to be rapid, approximately complete in one to two minutes. With the exception of (2), none of the reports on bromine and iodine give actual numerical data on the degree of completeness of the exchange reactions, and none indicate the estimated precision of the measurements. Because of these facts, and especially because of the apparently conflicting reports about bromine, it seemed desirable to carry out a study of the exchanges from which quantitative results could be obtained.

A reasonable mechanism for the exchanges is the formation and dissociation of trihalide ion, according to the following scheme for bromine



where the asterisk indicates a tagged (radioactive) bromine. This being the mechanism, the exchanges would be rapid; whereas a mechanism involving the hydrolysis of the halogen might be expected to lead to a relatively slow rate of exchange, as reported by Grosse and Agruss.

**Experimental Part**

**Materials.**—Standardized solutions of sodium bromide and potassium iodide in distilled water were used as sources of halide ion. Bromine solution was made by dissolving c. p. bromine in distilled water, 0.1 *N* in sulfuric acid.

(1) Long and Olson, *THIS JOURNAL*, **58**, 2214 (1936).

(2) Grosse and Agruss, *ibid.*, **57**, 591 (1935).

(3) Rojinskiĭ and Gopshtein, *Physik Z. Sowjetunion*, **7**, 672 (1935).

(4) Juliusburger, Topley and Weiss, *J. Chem. Phys.*, **3**, 437 (1935).

(5) Hull, Shiflett and Lind, *THIS JOURNAL*, **58**, 535 (1936).

The iodine solution used was almost saturated with iodine, and was 0.01 *N* in sulfuric acid. (In preliminary runs halogen solutions were used to which no acid had been added.) The halogen solutions were found to contain halide ion in amounts about 1-2% of the amount of halogen present; this was corrected for in predicting the exchange ratios for complete exchange. The carbon tetrachloride used was redistilled, the fraction taken coming over in a 0.1° range. The radioactive halogen was produced by irradiating redistilled *n*-butyl bromide and ethyl iodide with slow neutrons. In preliminary experiments radon-beryllium sources (initial radon intensity about 200 millicuries) were used; in later experiments were used deuterium-deuteron neutrons from the deuterium-deuteron disintegration apparatus in this Laboratory (radium equivalent about 10 curies).

**Procedure.**—After irradiation the organic halide was shaken vigorously with distilled water, a procedure which was found to remove a large fraction of the total activity into the water phase, presumably as halide ion. In a few cases the activity was removed by washing with water containing added sodium bromide or potassium iodide. The aqueous phase was boiled for three minutes to remove stray droplets of organic phase, the desired amount of sodium bromide or potassium iodide added, and the solution diluted to definite volume in a volumetric flask. The solution was then standardized with 0.02 *N* silver nitrate solution. This gave a standard solution of halide, containing radioactive halide. The bromine solution was diluted to the desired concentration with distilled water (about 40 ml. diluted to 250 ml.); the iodine solution was not diluted. These halogen solutions were standardized with 0.02 *N* thiosulfate solution immediately before and after each run.

For the exchange, the desired amount of halide solution (25.0 or 50.0 ml.) was pipetted into a separatory funnel containing about 50 ml. of carbon tetrachloride, then the desired amount of halogen solution (25.0 or 50.0 ml.) pipetted in, the mixture shaken vigorously, and the phases separated. Three more extractions were then made with 25-ml. portions of carbon tetrachloride. The time interval from the beginning of the mixing of the solutions to the completion of the first extraction was taken to be the interval during which practically all the observed exchange took place. The combined carbon tetrachloride phases were shaken with water containing a slight excess of sodium bisulfite to reduce the halogen, giving aqueous solutions of halide. This solution of halide and also the aqueous phase remaining from the extractions were each boiled three minutes under a watch glass to remove droplets of carbon tetrachloride. The halide in the solutions was then precipitated with silver nitrate and collected on a 5.5-cm. filter paper in a Büchner funnel, care being taken to distribute the precipitate evenly on the filter paper. Where necessary, inactive halide was added before the precipitation in amounts sufficient to make the total amount of precipitate the same in all cases in any given run.

TABLE I  
EXCHANGE OF RADIOACTIVE BROMIDE WITH BROMINE AND IODIDE WITH IODINE

Run number	Bromide with bromine				Iodide with iodine	
	1	2	3	4	1	2
Halogen, millieq.	0.388	0.415	0.435	0.890	0.0533	0.111
Halide, millieq.	0.420	0.417	0.420	0.415	0.0609	0.0616
Halogen activity, cts./min.	1810	282	794	1000	2630	2115
Halide activity, cts./min.	2000	282	794	490	2880	1190
Predicted activ. ratio, halogen/halide	0.924	0.995	1.04	2.14	0.88	1.80
Activ. ratio found, halogen/halide	0.905	1.00	1.00	2.04	0.91	1.77
Deviation from predicted, %	-2.1	+0.5	-3.9	-4.7	+3.4	-1.7
Total activity in control	3750	590	1646	1492	5660	3300
Total activ. in exchange run	3810	564	1588	1490	5550	3305
Deviation from control, %	+1.6	-4.4	-3.5	-0.1	-1.9	+0.2

The precipitates were sucked dry, mounted flat under cellophane, and placed on top of the Geiger counter for measurement of the radioactivity. To check on the total activity recovered, another sample of the radio-halide solution was carried through the same procedure, starting with the second three minutes boiling.

The counter used was a point counter having a window of 0.005 inch (0.12 mm.) hardened copper, 7 cm. in diameter. The counter was operated in connection with the Neher-Pickering type of counter circuit, a resistance-capacity coupled amplifier, a thyratron scaling circuit, and a Cenco mechanical impulse register. In order to compare intensities at a given time, the counts were carried on over a period of about an hour, decay curves plotted, and extrapolated back to a common time.

### Results

For complete exchange the radioactivity should be divided between the halogen and halide in the ratio of the masses of halogen and halide present. This ratio is called hereinafter the predicted exchange ratio. The experimentally obtained exchange ratio is given by the ratio of the radioactivity in the halogen separation to that in the halide separation. The percentage difference between the ratio predicted and that obtained can be considered a measure of the apparent degree of completion of the exchange.

In Table I are given the results for the bromine-bromide exchange, and for the iodine-iodide exchange.

In preliminary experiments it was found that the apparent degree of completeness of the exchange reaction did not increase with time. For example, after one and three-tenths minutes a bromine-bromide ratio of 1.62 was obtained, after thirty minutes 1.55; for iodine-iodide, after one and one-half minutes 2.16, after nine minutes 2.16. Because of large but undetermined halide contamination of the halogen solutions, it was not attempted precisely to predict ratios for these cases.

### Discussion

From the spread of the points about the decay curves the probable error in the measurement of the activity itself is less than 1%. Other sources of error are (1) titration errors (probably not more than 1%), (2) losses in handling, (3) uneven distribution of precipitates on the filter papers, leading to uncompensated self-absorption errors.

The close agreement between the total activity recovered in the exchange runs and that in the control runs limits the probable error due to (2) and (3) to less than 5%. This corresponds to an error of the same amount or less in the ratio of the radioactivities.

It is apparent that the exchange ratios found agree with the predicted ratios for complete exchange within the estimated experimental error of 5%. This shows that the bromine-bromide and iodine-iodide exchanges are complete within this experimental error in sixty seconds. This conclusion is borne out by the preliminary experiments which showed that the exchanges were as complete in one minute as they were in nine to thirty minutes. It is probable that they are complete within a much smaller time than sixty seconds.

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### Summary

The exchange reaction between bromine and bromide ion, and that between iodine and iodide ion, in acidified aqueous solution has been shown to be rapid and complete within sixty seconds, within an experimental error of 5%.