TABLE I

EXCHANGE BETWEEN IODINE AND MONOPYRIDINE IODINE(I) *p*-CHLOROBENZOATE IN PYRIDINE; CONCENTRATION OF COMPLEX, 5.53 × 10^{-2} *M*

Concn. of elementary iodine (mole/l.)	Concn. of unipositive iodine (mole/l.)	Specific activity of unipositive iodine immediately after mixing	Specific activity of total iodine in reaction mixture	Exchange, %
1.04×10^{-1}	2.76×10^{-2}	1411	1422	99.2
5.20×10^{-2}	2.76×10^{-2}	1137	1175	96.8
2.72×10^{-2}	2.76×10^{-2}	2201	2272	96.9
2.74×10^{-3}	2.76×10^{-2}	1021	1001	101.9
2.68×10^{-5}	2.76×10^{-2}	1272	1303	97.6
3.44×10^{-7}	2.76×10^{-2}	84	78	107.7

TABLE II

EXCHANGE BETWEEN IODINE AND PYRIDINE-COÖRDINATED UNIPOSITIVE IODINE COMPLEXES IN PYRIDINE

Monopyridine iodine(I) compound	Concn. of unipositive iodine (mole/l.)	Concn. of elementary iodine (mole/l.)	Specific activity of unipositive iodine immediately after mixing	Specific activity of total iodine in reaction mixture	Exchange, %
β-Naphthoate	2.66×10^{-2}	2.77×10^{-2}	1370	1342	102.0
p-Chlorobenzoate	2.76×10^{-2}	2.72×10^{-2}	2201	2272	96.9
m-Nitrobenzoate	2.69×10^{-2}	2.77×10^{-2}	1347	1334	100.9

Procedure and Calculation of Results.—A weighed sample of irradiated iodine was made up to volume in pyridine to give a solution of the concentration desired. One-ml. aliquots of this solution were introduced into ground-glass stoppered erlenmeyer flasks, each of which contained 100 mg. of a unipositive iodine complex dissolved in 4 ml. of pyridine. After thorough mixing, some of the flasks were placed in a thermostat at 26.3°, and from others the complex was immediately thrown out of solution by treatment with petroleum ether. The complex was filtered through a Hirsch funnel and washed with petroleum ether until the washings showed no activity. It was then air-dried, weighed, mounted in the center of a 6.4 × 8.3 cm. card, and counted in a conventional glass-walled Geiger tube of approximately 30 mg. per sq. cm. wall thickness. The thermostated flasks were withdrawn at appropriate time intervals and the contents were treated in the manner just described.

One-ml. aliquots of the original radioactive iodine solution were withdrawn and converted to silver iodide standards. For the more concentrated iodine solutions this was accomplished by reduction with 0.1 *M* sodium bisulfite solution, acidification with dilute nitric acid, and precipitation of the silver iodide with 0.1 *M* silver nitrate solution. The silver iodide precipitates were washed first with nitric acid and then with alcohol, dried at 110°, weighed, and counted. For iodine concentrations of 2.74×10^{-3} and 2.68×10^{-5} *M*, 1 ml. of a standard sodium iodide carrier was also added. For the most dilute iodine solution, 3.44×10^{-7} *M*, the aliquot of radioactive iodine solution was added to 1 ml. of a standard inactive iodine–pyridine solution, after which the iodine was converted to silver iodide as described above.

The counts per minute obtained on the complexes and the standards were corrected for background and chemical yield, and were all calculated (for any particular experiment) to a specific time. Since the geometry was the same throughout, no correction for geometry was necessary. Also, no correction was made for absorption by the window of the counter, since the same tube was used in all the experiments. The percentage of exchange was calculated by means of the formula

$$\frac{\text{specific activity of iodine in complex at end of reacn.}}{\text{specific activity of total iodine in reacn. mixture}} \times 100$$

where the specific activity is defined as counts per min. per mg. of substance.

Data for the exchange, as determined immediately after mixing the radioactive iodine and unipositive iodine complex solutions, are shown in Tables I and II. The values obtained for longer periods of time check those which are tabulated. The values in the column headed "Concn. of unipositive iodine" were obtained by calculating the quantity of iodine in the weight of complex used and dividing by 253.84.

It is apparent from the data of Table I that, over a wide range of ratios of elementary iodine to unipositive iodine concentrations, the former exchanges completely with the latter immediately after mixing. The data of Table II demonstrate that this exchange is independent of the nature of the organic anion in the complex.

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Some Reactions of Elemental Bromine, Hydrogen Bromide and Szilard–Chalmers Bromine with Ethylene Bromide[1]

BY GERRIT LEVEY AND JOHN E. WILLARD

When the bromine of liquid ethylene bromide undergoes neutron capture ($Br^{79}(n,\gamma)Br^{80}$) or isomeric transition (Br^{80}(4.4 hr.) → Br^{80}(18 min.)) approximately half of the radioactive product can be extracted into aqueous sulfite solution and therefore must be present as hydrogen bromide or bromine.[2] It is not known which of these products predominates. We have tested the possibility of distinguishing between them by: (a) separating bromine from hydrogen bromide by reaction with freshly reduced copper; (b) separating hydrogen bromide from bromine with dry sodium hydroxide; (c) determining the apparent activation energy for reaction of the extractable bromine with ethylene bromide to re-enter organic combination, and comparing it with the apparent activation energy for the reactions of bromine and of hydrogen bromide with ethylene bromide. The investigations have indicated that the proposed methods as applied are not satisfactory for determining the nature of the extractable bromine. Other significant information obtained is reported below. All of the experiments have been done with vacuum techniques and repurified, degassed reagents.

Reaction of Hydrogen Bromide and of Bromine with Copper and with Sodium Hydroxide.—Bromine can be removed quantitatively from a gas stream by a short train of copper which has been oxidized in air and freshly reduced with hot hydrogen but cannot be distinguished from hydrogen bromide in mixtures of the two by this method because the latter also reacts with the copper, although less efficiently.

Hydrogen bromide can be removed quantitatively from a

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[1] From the Ph.D. thesis of Gerrit Levey, Univ. of Wis., 1949.

[2] Bromine atoms may be expected to react with ethylene bromide sufficiently rapidly compared to the time required for the experiment so that they probably need not be considered.

gas stream by a train of dry sodium hydroxide but cannot be distinguished from bromine by this method because the latter also reacts, although less efficiently.

Reaction of Bromine with Ethylene Bromide.—Table I gives the results of experiments on the rate at which elemental radiobromine enters organic combination when dissolved in liquid ethylene bromide in the dark. The apparent activation energy obtained from the log k *vs.* $1/T$ plot of the data is 31.7 kcal./mole. Fractionation of the organic products with carriers indicated that $\geqq 75\%$ of the organically bound radiobromine was in the form of 1,1,2-$C_2H_3Br_3$. Radiobromine dissolved in ethylene bromide entered organic combination at room temperature when illuminated.

TABLE I

REACTION OF BROMINE WITH ETHYLENE BROMIDE

INITIAL BROMINE CONCN. 1×10^{-3} M./L. IN ALL CASES

Temp., °C.	Time, hr.	Br_2 reacted, %[a] (1)[c]	(2)[c]	k, $(m./l.)^{1/2}$ min.$^{-1}$ $\times 10^4$ [b] (1)	(2)
25	..	4.8[d]	4.2[d]	..	..
115	4.5	31.0	31.2	0.33	0.35
120	3.5	46.0	52.9	0.73	0.87
125	2.0	43.1	37.1	1.16	0.97
133	1.0	46.2	43.3	2.5	2.4
140	0.75	59.1	55.3	4.7	4.4

[a] Assuming that the products are $C_2H_3Br_3$ and HBr and that the % reacted is therefore equal to twice the % of the radiobromine found in organic combination. [b] Assuming that $d[Br_2]/dt = -k[Br_2]^{1/2}$. [c] Columns (1) and (2) give the results of two separate series of experiments. [d] Presumably due to photochemical reaction during preparation of the reaction mixtures. This % was deducted from the total % observed at the higher temperatures in obtaining the figures recorded.

Reaction of Hydrogen Bromide with Ethylene Bromide.—Thirty determinations indicate that from 115 to 180° radiobromine present as hydrogen bromide in liquid ethylene bromide enters organic combination with a half-life in the range from 20 hours to 15 minutes. The results were too erratic to allow calculation of a temperature coefficient. Fractionation experiments indicated that the reaction products were about 70% 1,2-$C_2H_4Br_2$ and 30% higher boiling materials.

When sealed 300-ml. Pyrex flasks containing 150 mm. of hydrogen bromide (tagged with Br^{82}) and 200 mm. of ethylene bromide (pressures measured at room temp.) were heated no reaction occurred in thirty minutes at 225° but significant organic combination of the activity took place at 270° and above. Prolonged heating at the higher temperatures gave an equilibrium distribution of the activity. After 105 min. at 308°, 150 min. at 317°, 90 min. at 320°, 120 min. at 338° the activity found in the organic products was 46.5, 45.3, 44.1 and 42.9%, respectively. A total of 73% organically bound activity would be expected in the equilibrium mixtures if they contained the original pressures of hydrogen bromide and ethylene bromide. Fractionation experiments on the organic products of the 308 and 317° reactions indicated that about 61% of the activity was in a form lower boiling than ethyl bromide (probably C_2H_3Br), 4% was 1,1-$C_2H_4Br_2$ and 35% was 1,2-$C_2H_4Br_2$. It is probable that the bromine originally in hydrogen bromide entered organic combination through the equilibrium $C_2H_4Br_2 \rightleftarrows C_2H_3Br + HBr$. Decomposition of ethylene bromide at 340–370° has been reported previously.[3]

Reaction of Ethylene Bromide with Bromine which has Undergone Radiative Neutron Capture.—When tubes of purified, degassed ethylene bromide were bombarded with neutrons from a 100 mg. Ra–Be source it was regularly observed that about 50% of the bromine which underwent radiative neutron capture could be extracted by an aqueous solution of sulfite ion and bromide ion.

When similar tubes were heated to 119° and above following irradiation the inorganic bromine which had been produced by radiative neutron capture re-entered organic combination at a measurable rate. For example, after 90 min. at 119° only 24% rather than 50% was extractable. When the organic products from the combined hot atom and thermal reactions which had occurred in such a sample were fractionated with carriers about half the activity was found as 1,2-$C_2H_4Br_2$, about a third as 1,1-$C_2H_4Br_2$, about 10% as 1,1,2-$C_2H_3Br_3$ and a few per cent. as ethyl bromide.

Reaction of Ethylene Bromide with Br^{80} (18 min.) Produced by the Isomeric Transition.—When purified degassed ethylene bromide which had been synthesized from bromine containing Br^{80} (4.4 hr.) was allowed to stand at room temperature and then extracted with aqueous sulfite–bromide solution, approximately 50% of the Br^{80} (18 min.) daughter of the Br^{80} isomeric transition was always found in inorganic form. At higher temperatures, up to 220°, the results were somewhat variable but did not show any definite trend away from 50% extractable. Since the system was maintained at the reaction temperature for nearly four half lives of the Br^{80} (18 min.) just prior to extraction, essentially all of the daughter activity measured at the time of extraction had been formed at the reaction temperature.

When molecular bromine containing Br^{80} (4.4 hr.) was allowed to stand in liquid 1,2-$C_2H_4Br_2$ at room temperature the fraction of the isomeric transitions which resulted in organic combination of the Br^{80} (18 min.) was about 20% and essentially all of this organically bound activity appeared as 1,2-$C_2H_4Br_2$. At liquid air temperatures the total organic yield was somewhat higher but approximately two-thirds of the organically bound Br^{80} (18 min.) was in the form of 1,1,2-$C_2H_3Br_3$ and only one-third as $C_2H_4Br_2$. This effect of change in phase and temperature is qualitatively similar to that reported for the radiative neutron capture reaction on the propyl bromides.[4] It shows an increase in proportion of polybromination products not observed in the isomeric transition reaction in bromotrichloromethane.[5]

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The Uranyl Nitrate–Water System Above 60°[1]

BY W. L. MARSHALL, JR., J. S. GILL AND C. H. SECOY

Although there are some data in the literature[2–5] for the solubility of uranyl nitrate in water, the discrepancy of these data indicated the necessity for a check on the measurements. We have measured the solubility from the incongruent melting point of the hexahydrate at about 60° to the melting point of the dihydrate at 184°. Our results show a lower solubility than that given in most of the earlier data and also indicate an incongruent melting point for the trihydrate rather than the congruent point inferred in some of the previous work. The system is thermally stable up to the revised melting point of the dihydrate. Above this point decomposition of the nitrate ion occurs.

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