TABLE I

Ketone	Selenazole	Formula	M.p., °C. Found[a]	M.p., °C. Reported	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found
Acetoacetic ester	2-Amino-4-methyl-5-carbethoxy	$C_7H_{10}N_2O_2Se$	180–181	181–182[h,i]	15[m]	12.02	12.25
	2-Acetamido-4-methyl-5-carbethoxy	$C_9H_{12}N_2O_3Se$	216–218	[l]		10.18	10.25
Acetophenone	2-Amino-4-phenyl	$C_9H_8N_2Se$	132–133	132–133[c,d,e,f,g,h]	65	12.56	12.45
	2-Acetamido-4-phenyl	$C_{11}H_{10}N_2OSe$	197–199	196.5–197.5[g]		10.57	10.62
Propiophenone	2-Amino-4-phenyl-5-methyl	$C_{10}H_{10}N_2Se$	141–142	[l]	84	11.81	11.81
	2-Acetamido-4-phenyl-5-methyl	$C_{12}H_{12}N_2OSe$	206–207	[l]		10.03	10.20
p-Chloroacetophenone	2-Amino-4-(*p*-chlorophenyl)-	$C_9H_7N_2ClSe$	160–162	160–160.5[g]	51	10.88	10.97
	2-Acetamido-4-(*p*-chlorophenyl)-	$C_{11}H_9N_2ClOSe$	269–270	263–264[g]		9.35	9.63
m-Nitroacetophenone	2-Amino-4-(*m*-nitrophenyl)-	$C_9H_7N_3O_2Se$	194–195	[l]	116[j]	15.67	15.18
	2-Acetamido-4-(*m*-nitrophenyl)-[b]	$C_{11}H_9N_3O_3Se$	306–307	[l]		13.55	12.85
Desoxybenzoin	2-Amino-4,5-diphenyl	$C_{15}H_{12}N_2Se$	189–190	[l]	15	9.36	9.42
	2-Acetamido-4,5-diphenyl	$C_{17}H_{14}N_2OSe$	204–205	[l]		8.21	8.46
Cyclohexanone	2-Amino-4,5,6,7-tetrahydrobenzo	$C_7H_{10}N_2Se$	126–127	125.5–126[g]	20[n]	13.93	13.20[k]
	2-Acetamido-4,5,6,7-tetrahydrobenzo	$C_9H_{12}N_2OSe$	142–143	140[g]		11.52	11.23
α-Tetralone	2-Amino-4,5-dihydronaphtho(1.2)-	$C_{11}H_{10}N_2Se$	149–150	[l]	44	11.24	11.06
	2-Acetamido-4,5-dihydronaphtho(1.2)-	$C_{13}H_{12}N_2OSe$	241–242	[l]		9.62	9.58

[a] All melting points observed on a Fisher–Johns melting point apparatus. [b] Low solubility of this compound required acetone–water as a solvent while alcohol–water was adequate for all other compounds reported. [c] G. Hofmann, *Ann.*, **250**, 304 (1888). [d] Backer and de Jonge, *Rec. trav. chim.*, **60**, 495–501 (1941). [e] Jensen and Schmith, *Dansk. Tids. Farm.*, **15**, 197–199 (1941). [f] Guha and Roy, *Current Sci.*, 12, 150 (1943). [g] Backer and Bos, *Rec. trav. chim.*, **62**, 580 (1943). [h] Roy and Guha, *J. Indian Chem. Soc.*, **22**, 82 (1945). [i] Mistakenly reported as 2-amino-4-methyl-5-carboxyselenazole by Roy and Guha (ref. *h*). [j] See discussion in text. [k] Calcd.: C, 41.71; H, 5.01. Found: C, 41.81; H, 4.93. [l] Not previously reported. [m] Average of three runs. [n] Average of two runs.

0°. The yield of pure selenourea, m.p. 200–205°, varied from 20–30%.

Preparation of Selenazoles.—To a mixture of 0.02 mole of selenourea and 0.02 mole of ketone (100% excess) was added 0.01 mole of iodine. After thorough mixing, the reaction mixture was heated on a steam-bath for about 36 hours. The mixture was then extracted three times with ether to remove excess ketone or unreacted iodine.

The ether-moist salt was treated with concentrated ammonia to decompose the salt. The ammoniacal suspension was cooled in an ice-bath and the precipitate, red to purplish-black in color, separated and thoroughly extracted with boiling alcohol. The alcoholic extracts were combined, diluted with water and the precipitated selenazole filtered and dried. The selenazole was recrystallized to constant melting point from alcohol–water.

The acetyl derivatives were prepared by heating the selenazole with acetic anhydride. The derivatives were recrystallized from alcohol–water.

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Exchange between Radioactive Iodine and Derivatives of Monopyridine Iodine(I) in Pyridine[1,2]

BY JACOB KLEINBERG[3] AND JAMES SATTIZAHN

It is generally accepted that in violet solutions iodine exists primarily as I_2 molecules, whereas in brown solutions the iodine is bound chemically in some manner to the solvent.[4] The exact nature of the binding between iodine and the solvent molecules in brown solutions has not, in general, been determined.

Solutions of iodine in pyridine are brown. Conductivity studies on iodine–pyridine solutions[5] have been interpreted in large measure on the basis of the assumption of the dissociation of dissolved iodine into positive IPy^+ and negative I_3^- ions. A recent investigation[6] of the absorption spectra of pyridine solutions of iodine and positive iodine salts of the type IPyX (where X = NO_3 or OOCR) has given considerable support to this assumption. These spectrophotometric studies also give added significance to the data now to be presented, based on earlier work on the exchange in pyridine solution between radioactive iodine and pyridine-coördinated unipositive iodine complexes of the general formula IPyOOCR. In all the cases studied, complete exchange was found to have taken place immediately after the iodine and the positive iodine compound were brought into contact. The rapidity of the exchange is in complete harmony with the ionization mechanism postulated for iodine in pyridine solution.

Experimental

Materials.—The radioactive iodine, I^{128}, was prepared in a nuclear pile by neutron irradiation of and capture by iodine of Mallinckrodt reagent grade. The time of irradiation depended on the ultimate concentration of iodine desired; for the more dilute solutions the sample was irradiated to saturation. Monopyridine iodine(I) β-naphthoate,[7] *p*-chlorobenzoate and *m*-nitrobenzoate[8] were prepared by the reaction of inactive iodine with the silver salts of the appropriate acids in the presence of pyridine. Pyridine (Eastman Kodak Co. white label quality) was dried for at least two weeks over sodium hydroxide pellets and then distilled directly before use, an intermediate fraction of b.p. 104–106° at approximately 590 mm. pressure being collected. The petroleum ether, Mallinckrodt analytical reagent grade, b.p. 30–60°, was used without further purification.

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] The unipositive iodine–pyridine complex ion of the formula IPy^+ will be designated as monopyridine iodine(I).

[3] Department of Chemistry, University of Kansas, Lawrence, Kansas. The work herein described was performed during the summer of 1948, when the senior author was an employee of the Los Alamos Scientific Laboratory.

[4] For discussions of the nature of iodine solutions, see J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948); H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949); **72**, 2273 (1950).

[5] L. F. Audrieth and E. J. Birr, THIS JOURNAL, **55**, 668 (1933).

[6] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **73**, 88 (1951).

[7] H. Carlsohn, "Über eine neue Klasse von Verbindungen des positiv einwertigen Iods," Verlag von S. Hirzel, Leipzig, 1932.

[8] R. A. Zingaro, Master's Thesis, University of Kansas, 1948. We are indebted to Mr. Zingaro for our supply of these positive iodine complexes.

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 ($Br^{80}(4.4 \text{ hr.}) \rightarrow Br^{80}(18 \text{ min.})$) 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.