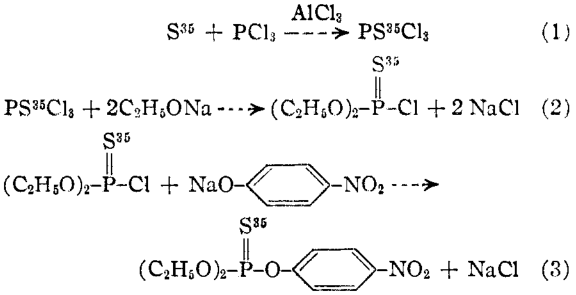
Synthesis of Radioactive Parathion Using S^{35} (1,2)

BY JENS A. JENSEN AND GEORGE W. PEARCE

RECEIVED FEBRUARY 1, 1952

The insecticidal compound parathion, O,O-diethyl-O-*p*-nitrophenyl thiophosphate has been prepared and radioactively labeled with S^{35}. The following steps were used



$$S^{35} + PCl_3 \xrightarrow{AlCl_3} PS^{35}Cl_3 \qquad (1)$$

$$PS^{35}Cl_3 + 2C_2H_5ONa \dashrightarrow (C_2H_5O)_2\text{-}\overset{S^{35}}{\overset{\|}{P}}\text{-}Cl + 2\,NaCl \qquad (2)$$

Phosphorus thiochloride was obtained by the method described by Knotz.[3] The cooled liquid was not washed but distilled directly. Reactions (2) and (3) followed those published by Fletcher, *et al.*[4-5] Seventy-five millimoles of S containing approximately 16 millicuries of activity yielded 44.4 millimoles of parathion (59%); sp. gr. 1.26 ± 0.01; $n^{25}{}_D$ 1.5380; specific activity, 220 microcuries per millimole.

---

(1) From the Communicable Disease Center, Public Health Service, Federal Security Agency, Savannah, Georgia.

(2) For detailed paper order Document 3566 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(3) Østerr F. Knotz, *Chem. Z.* **50**, 128 (1949).

(4) J. H. Fletcher, *et al.*, *ibid.*, **70**, 3943 (1949).

(5) J. H. Fletcher *et al.*, *ibid.*, **72**, 2461 (1950).

SAVANNAH, GA.

The Solubility of Rubidium Iodate

BY W. D. LARSON AND J. J. RENIER

RECEIVED JANUARY 28, 1952

No data for the solubility of rubidium iodate at 25° were found in the literature. Measurements of its solubility in water and in potassium nitrate solutions were undertaken to provide these data, and to determine the activity solubility product of the salt. The solubility of this salt in dilute nitric acid solutions was also measured.

Experimental

Rubidium iodate was prepared by the addition of an excess of iodic acid solution to rubidium carbonate solution; the precipitate was washed with cold water. The iodic acid was prepared by adding 35 g. of Mallinckrodt A.R. I_2O_5 to 25 ml. of water; the rubidium carbonate solution was prepared by adding 25 g. of the salt (from Fairmount Chemical Company) to 25 ml. of water. These two were slowly mixed with mechanical stirring which was continued for 30 minutes. The salt was washed by decantation three times, and finally collected on a coarse sintered glass filter, where it was given a final washing. It was air-dried and stored over anhydrous calcium chloride. The samples of rubidium iodate were found to contain over 99.9% of the theoretical amount of IO_3^-. Potassium nitrate and nitric acid were C.P. grade chemicals. Potassium nitrate was dried for several hours at 150° before weighing. Conventional volumetric methods were used. In the density determinations, buoyancy corrections were made. Potassium iodate, carefully recrystallized, was the primary standard.

The solubility of rubidium iodate in water was determined in glass bottles coated with paraffin wax and in uncoated glass bottles. The results were identical. This was taken to indicate that no significant amounts of Rb^+ exchanged with alkali metal ions in the glass, since the IO_3^- concentration was the same in either coated or uncoated bottles.

The temperature was constant at 25.0° (as read from a thermometer certified by the U.S. Bureau of Standards) to within less than 0.05°. The bottles were rotated end-over-end for at least 12 hours; experiments had shown that eight hours ensured saturation.

At least two independent experiments were performed for each concentration of potassium nitrate or nitric acid; two or more samples were taken for analysis from each saturated solution. The analyses agreed with each other to within about one part in eight or nine hundred.

The data are summarized in Tables I and II. In the tables, m, c and x refer to the molality, molarity and mole fraction, respectively. The ionic strength and density are represented by μ and d.

TABLE I

SOLUBILITY OF $RbIO_3$ IN AQUEOUS KNO_3 SOLUTIONS AT 25.0°

m_{KNO_3}	c_{RbIO_3}	$d_{satd. soln.}$	$\mu^{1/2}$	$10^3 x_{Rb^+}$
0	0.0919	1.0160	0.3031	1.665
0.05001	.0972	1.0196	.3830	1.747
.1004	.1018	1.0236	.4482	1.851
.1511	.1054	1.0285	.5044	1.917
.2021	.1070	1.0318	.5530	1.949
.2547	.1118	1.0370	.6017	2.037
.2940	.1143	1.0396	.6345	2.084
.4069	.1192	1.0475	.7187	2.179
.5025	.1220	1.0538	.7813	2.235

TABLE II

SOLUBILITY OF $RbIO_3$ IN AQUEOUS HNO_3 SOLUTIONS AT 25.0°

m_{HNO_3}	c_{RbIO_3}	$d_{satd. soln.}$	c_{HNO_3}
0	0.0919	1.0160	0
0.05020	.1051	1.0216	0.04977
.1006	.1175	1.0250	.09941
.1511	.1297	1.0290	.1490
.2016	.1415	1.0337	.1985
.2516	.1533	1.0385	.2473
.2933	.1626	1.0414	.2878
.4056	.1546	1.0472	.3984
.5006	.1495	1.0506	.4908

Aqueous KNO_3 Solutions.—When the Debye–Hückel equation is applied to solubility data, it is convenient to write it in the form[1]

$$\mu_1^{1/2}\mu_2^{1/2}A^2 + (\mu_1^{1/2} + \mu_2^{1/2})\,A + 1 - \frac{B(\mu_2^{1/2} - \mu_1^{1/2})}{\log\,(L_2/L_1)^{1/2}} = 0$$

$A = 0.329 \times 10^8\,a$, where a is the mean distance of closest approach; $B = 0.509$ at 25°: $L_1^{1/2}$ and $L_2^{1/2}$ are the mole fractions of Rb^+ ion in the two solutions; and μ_1 and μ_2 are the ionic strengths in these same solutions. Values of A were obtained by solving the equation with data from pairs of solutions which had quite different ionic strengths. Using fourteen pairs of data, this procedure yields a value of $A = 0.674 \pm 0.026$. This value of A leads to a value of x_0, the mole fraction of Rb^+ when the square root of the ionic strength is zero, of $1.237 \pm 0.004 \times 10^{-3}$, and a corresponding value of $c_0 = 0.06834$ mole/liter of solution. The mole fraction and molarity activity coefficients

---

(1) F. H. MacDougall, "Thermodynamics," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1939, p. 316.