## Synthesis of Radioactive Parathion Using $S^{35}$[1,2]

BY JENS A. JENSEN AND GEORGE W. PEARCE

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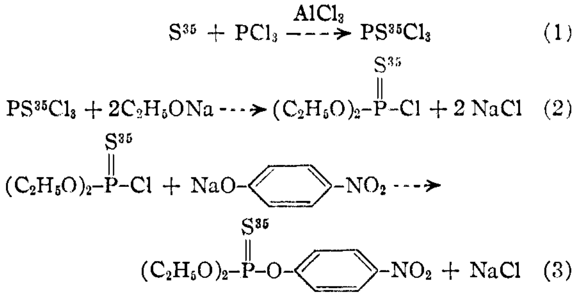
The insecticidal compound parathion, O,O-diethyl-O-*p*-nitrophenyl thiophosphate has been prepared and radioactively labeled with $S^{35}$. The following steps were used



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

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

(3)

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.

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[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).

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## The Solubility of Rubidium Iodate

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

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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 $\mu$ and *d*.

TABLE I

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

| $m_{KNO_3}$ | $c_{RbIO_3}$ | $d_{satd.soln.}$ | $\mu^{1/2}$ | $10^3x_{Rb^+}$ |
|---|---|---|---|---|
| 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 $\mu_1$ and $\mu_2$ 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

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

$f_x$ and $\gamma_c$ can be calculated from these values and the relations

$$f_x = x_0/x \text{ and } \gamma_c = \frac{C_0}{C}$$

**Aqueous $HNO_3$ Solutions.**—The existence of a maximum in the solubility of rubidium iodate in the nitric acid solutions seems surprising. Great care was taken to make sure that this is not due to an analytical error. It may be that one or both of the acid iodates[2] is part of the solid phase.

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(2) Mellor, "Comprehensive Treatise on Inorganic Chemistry," Vol. II, Longmans, London, 1927, pp. 337–338, gives the formulas $RbIO_3 \cdot HIO_3$ and $RbIO_3 \cdot 2HIO_3$.

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## Reactions of 1-Methylvinyl Acetate

BY CHARLES D. HURD AND LEON L. GERSHBEIN

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Marvel[1] reported the formation of 4-acetoxy-2,5-dimethyl-1,3-dioxane by interaction of vinyl acetate and acetaldehyde, pretreated with metallic sodium. The same cyclic acetal apparently was made by Spaeth[2] a few years later by acetylating the adduct of aldol and acetaldehyde. Marvel noted that vinyl acetate was ineffective in the reaction with other aldehydes such as propionaldehyde, *n*- and isobutyraldehyde. A comparable inertness was found in the present work with 1-methylvinyl acetate and acetaldehyde. Aldol was the only product isolated.

Methylvinyl acetate serves as an acetylating agent toward benzene in the presence of aluminum chloride. Acetophenone was the major product.

### Experimental

1-Methylvinyl acetate, b.p. 96–98°, was prepared by the reaction of ketene with acetone in the presence of sulfuric acid.[3]

**Non-reaction with Acetaldehyde.**—A total of 25 g. of methylvinyl acetate was shaken into 11 g. of acetaldehyde previously treated with a small amount of sodium.[1] Absolute ethanol (25 ml.) was then introduced. After two days at 25°, the alcohol and ester were distilled off under reduced pressure, and 6.35 g. of aldol, b.p. 80–90° (34 mm.), was obtained. On redistillation, it boiled at 94.5–95° (33 mm.), 80.5° (20 mm.), $n^{20}_D$ 1.4532, $d^{20}_{20}$ 1.090. Analytical figures (C, 55.4; H, 9.01) confirmed the identity of aldol (calcd.: C, 54.5; H, 9.09).

**Reaction with Benzene. Run 1.**—To a stirred mixture of 27 g. of anhydrous aluminum chloride in 120 ml. of benzene was added a total of 20 g. of 1-methylvinyl acetate in 40 ml. of benzene over a period of 15 minutes. Some heat was liberated; hence the reaction was moderated by tap cooling. After 20 minutes at 25°, the contents were refluxed for 2 hours, cooled and poured onto ice. From the benzene layer, after washing and drying, were obtained these fractions at 30 mm.: (1) boiling range 94–104°, $n^{20}_D$ 1.5335, 5.75 g.; (2) 117–137°, $n^{20}_D$ 1.5515, 0.75 g. of green oil. Redistillation of (1) yielded colorless acetophenone, b.p. 97–98° (25 mm.). It formed a semicarbazone which after two recrystallizations from aqueous ethanol melted at 203.5–204° (uncor.) and which remained unchanged on admixture with an authentic sample of acetophenone semicarbazone. The absence of ester was ascertained by the saponification test.

**Run 2.**—When 88 g. (0.66 mole) of anhydrous aluminum chloride in 80 ml. of benzene was added to 20 g. of the acetate in 40 ml. of benzene and the mixture refluxed for 15 hours on the steam-bath, the acetophenone fraction at 87–94° (17 mm.) weighed 17.7 g. A small forerun (0.45 g.) was obtained. Of the viscous residue (5.1 g.), 3.2 g. of amber-orange oil boiled at 134–167° (4 mm.).

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(1) C. S. Marvel, J. Harmon and E. H. Riddle, *J. Org. Chem.*, **4**, 252 (1939).

(2) E. Spaeth, R. Lorenz and E. Freund, *Ber.*, **76**, 57 (1943).

(3) B. H. Gwynn and E. F. Degering, THIS JOURNAL, **64**, 2216 (1942).

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## The Peroxide-catalyzed Addition of Carbon Tetrachloride to *d*-Limonene

BY SHALOM ISRAELASHVILI AND ERICH DIAMANT

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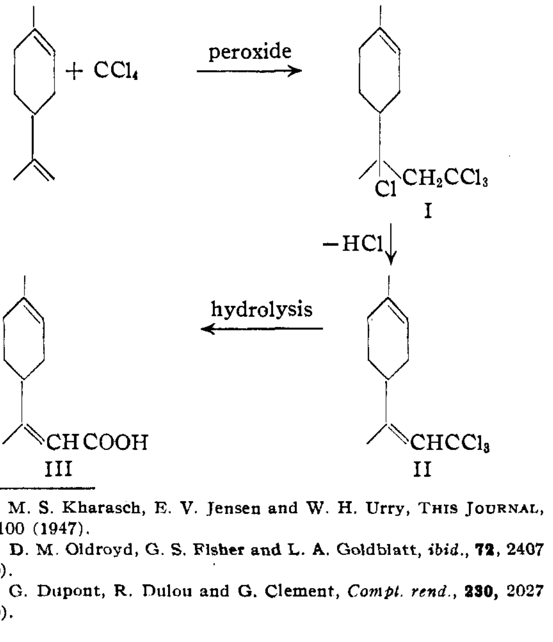
The peroxide-catalyzed addition of polyhalogenated methane to a terminal carbon–carbon double bond has been reported by Kharasch and his co-workers.[1] In the terpene series, it has been shown that the peroxide-catalyzed addition of carbon tetrachloride to *β*-pinene[2] and nopinene[3] gave good yields of a one-to-one addition product. In this paper we wish to report the applicability of these reactions to *d*-limonene.

We have studied the radical addition reaction of chloroform, bromoform and carbon tetrachloride to *d*-limonene. It was found that *d*-limonene reacts with carbon tetrachloride in the presence of four mole per cent of benzoyl peroxide to give a good yield (60–70%) of a one-to-one addition product, whereas chloroform and bromoform failed to react under the same conditions. However, the addition did not take place readily, even with the relatively large amount of peroxide used. The addition product obtained (II) is optically active $[\alpha]^{13}_D$ + 15.8°. Bromine titration reveals the presence of two double bonds and according to analysis it contains three chlorine atoms. It is believed that the initial adduct (I) is converted to product (II) by elimination of one molecule of hydrogen chloride from carbon atoms 8 and 9 as



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(1) M. S. Kharasch, E. V. Jensen and W. H. Urry, THIS JOURNAL, **69**, 1100 (1947).

(2) D. M. Oldroyd, G. S. Fisher and L. A. Goldblatt, *ibid.*, **72**, 2407 (1950).

(3) G. Dupont, R. Dulou and G. Clement, *Compt. rend.*, **230**, 2027 (1950).