centrated and diluted with pentane to give 2.3 g. of product, m.p. ~142°.

Anal. Calcd. for $C_{42}H_{43}As_3Cl_2NRh$: C, 52.6; H, 4.5; As, 23.4; Cl, 7.4; N, 1.5; Rh, 10.7; mol. wt., 960. Found: C, 50.6; H, 4.3; As, 22.0; Cl, 9.0; N, 1.3; Rh, 12.8; mol. wt., 1360 (ebullioscopic, 0.02 *M*).

This corresponds to $L_{2.4}Rh(C_3H_4N)Cl_2$ and could not be improved by carrying out the reaction in excess diphenylmethylarsine. Attempts at chromatography resulted in even greater loss of ligand.

The infrared spectrum of this material (chloroform) showed the presence of a nitrile band at 2230 cm.$^{-1}$ and absence of hydride in the 2000 cm.$^{-1}$ region.

Treatment of Dichloro(1-cyanoethyl)tris(diphenylmethylarsine)rhodium(III) with Pyridine.—The subject complex was dissolved in excess pyridine under nitrogen and warmed to 100° for 4 hr. The cooled reaction mixture was stripped and diluted with pentane, and the resulting solid was adsorbed on a column of silicic acid. Elution with 20% ether–methylene chloride gave the pyridine compound II, m.p. ~110°. The compound was identical in infrared and n.m.r. spectra with a sample prepared by the rhodium trichloride–ethanol route.

Hydridodichlorotris(diphenylbutylphosphine)rhodium(III).—To a solution of 0.5 g. of rhodium trichloride trihydrate in 50 ml. of ethanol was added 2.0 ml. of diphenylbutylphosphine under nitrogen. After stirring for 15 min., the small amount of solid formed was filtered off, and the filtrate was allowed to stir under nitrogen for 2 days. The resulting yellow solid was filtered, washed with hexane, and dried *in vacuo* to give product (99%), m.p. *ca.* 140° dec.

The infrared spectrum (methylene chloride) exhibited a weak rhodium hydride band at 2090 cm.$^{-1}$ which disappeared on heating with carbon tetrachloride.

Anal. Calcd. for $C_{48}H_{58}Cl_2P_3Rh$: C, 63.8; H, 6.4; Rh, 11.4. Found: C, 63.4; H, 6.7; Rh, 10.8.

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The Exchange of Oxygen-18 between Water and Orthotungstate and between Water and 12-Tungstocobaltate(III)[1]

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In order to understand more completely the mechanism of electron exchange between 12-tungstocobaltate-(II) and -(III),[2] we felt that we should determine whether or not oxygen exchange occurs between water and the 12-tungstocobaltates. Hall and Alexander[4] and Spitsyn[5] have reported complete exchange of oxygen between water and orthotungstate in 1 hr. or more at 95–100°.

Before we could undertake an investigation of the exchange between water and the 12-tungstocobaltates, it seemed necessary to determine whether oxygen exchange between water and tungstate would be appreciable at 25°. This is a report of our findings on the oxygen exchange between water and orthotungstate and water and 12-tungstocobaltate(III) at 25° by means of an oxygen-18 tracer study.

Experimental Section

Materials.—Oxygen-18 enriched water (1.59 ± 0.03 atom % by our analysis) was obtained from Yeda Research and Development Co., Rehoveth, Israel. The 12-tungstocobaltate-(III), as $K_4HCoW_{12}O_{40}\cdot 16H_2O$, was prepared and purified as described previously.[3] All other reagents were of reagent grade and were used without further purification.

Measurement of ^{18}O Content.—The ^{18}O content of water, anhydrous barium and sodium tungstates, and anhydrous tetramethylammonium 12-tungstocobaltate(III) was measured by converting the oxygen to carbon dioxide by the method of Anbar and Guttman,[6] in which the oxygen-containing compound (hereafter called oxide) is heated in a sealed tube with mercury(II) chloride and cyanide. The gaseous products are purified over zinc amalgam and the ^{18}O content is determined mass spectrometrically. A Consolidated Type 21-103C mass spectrometer was employed.

In the cases of barium and sodium tungstates and the tetramethylammonium 12-tungstocobaltate(III), satisfactory conversion of the oxides to CO_2 could not be effected unless large excesses by weight (4:1:1 or 5:1:1) of the oxide, compared to $HgCl_2$ and $Hg(CN)_2$, were used. With water, nearly equal proportions by weight or excess mercury salts gave good conversion. The reason for the need to use excess oxide is not understood, but has been observed by others.[7] Samples of Na_2WO_4 of 200 mg.; $BaWO_4$, 200–250 mg.; $[(CH_3)_4N]_5[CoW_{12}O_{40}]$, 250 mg.; and H_2O, 5–10 mg. were used.

In order to obtain anhydrous tungstates and 12-tungstocobaltate for conversion to CO_2, it was necessary to heat the hydrated $BaWO_4\cdot {}^1/_2H_2O$, $Na_2WO_4\cdot 2H_4O$, and the unknown hydrate of $[(CH_3)_4N]_5[CoW_{12}O_{40}]$ under a stream of "prepurified" nitrogen to avoid exchange of oxygen with the atmosphere. Sodium and barium tungstates were heated at 550° and the 12-tungstocobaltate at 200° to constant weight and no residual water.

In order to verify the necessity of heating in nitrogen, several series of experiments were run in which labeled $BaWO_4$ samples were heated in the air at 550° and then were converted to CO_2 and checked mass spectrometrically (see Table I).

TABLE I

LOSS OF ^{18}O FROM $BaWO_4$ BY EXCHANGE WITH OXYGEN OF THE AIR AT 550 ± 10°[a,b]

Length of time heated, min.	Sample 1	2	3	4
	^{18}O content (atom %) of $BaWO_4$			
0	1.41	1.41	1.41	1.41
30	0.81	0.89	0.85	0.99
60	0.61	0.64	0.60	0.73
90	0.42	0.57	0.54	0.53
120	0.30	...	0.46	0.50

[a] $BaWO_4\cdot {}^1/_2H_2O$ heated to remove water. Samples 1 and 2, $BaWO_4$ was precipitated from freshly prepared Na_2WO_4 solutions; samples 3 and 4, from solutions 23–24 hr. old. [b] ^{18}O content at zero time calculated from content of Na_2WO_4 and $BaCl_2$ solutions and the assumption of rapid, complete exchange.

Exchange Reaction Procedures.—Weighed samples of $Na_2WO_4\cdot 2H_2O$ (natural abundance of ^{18}O) were dissolved in ^{18}O-labeled water containing 1 *M* NaCl and a small amount of NaOH (10^{-2} *M* or less) to make a 0.1 *M* WO_4^{2-} solution. Solution was complete in 30 sec. or less.

Two methods of separating tungstate from water were em-

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[1] Support by the U. S. Atomic Energy Commission under grant AT(11-1)-1001 is gratefully acknowledged.

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ployed. In the first method, $BaCl_2$ in either natural or ^{18}O-enriched water was added within a few seconds of mixing the sodium tungstate and water, and barium tungstate was precipitated within 10–15 sec. The barium tungstate was filtered off and dried *in vacuo* at room temperature to give $BaWO_4 \cdot {}^1/_2H_2O$.

In the second method, sodium tungstate solutions were allowed to sit for 1 hr. or more and then were evaporated by vacuum distillation (until crystallization began) at 25° or at 30–50°. The $Na_2WO_4 \cdot 2H_2O$ was crystallized out either at room temperature or at 0°.

For the 12-tungstocobaltate(III), 1.72-g. samples of $K_4HCoW_{12}O_{40} \cdot 16H_2O$ were dissolved in 5.0 ml. of enriched water. The pH of the final solutions was 1–2 and the 12-tungstocobaltate was 0.1 *M*. Precipitation of the tetramethylammonium salt was carried out immediately by addition of excess tetramethylammonium bromide[3] in enriched water. The precipitate was dried *in vacuo* for 3 hr. at room temperature before being dried in a nitrogen stream at 200°.

Results and Discussion

The data on the experiments carried out by means of precipitation of $BaWO_4$ are summarized in Table II. All of the results for sodium tungstate in enriched water show complete exchange of oxygen between water and orthotungstate ion in the time required for mixing and separating the reagents. The one experiment in which the ^{18}O was introduced only in the $BaCl_2$ reagent suggests slightly less than complete exchange. It seems possible that the exchange might be studied by flow or other techniques for investigating moderately fast reactions.

Four experiments were carried out in which sodium tungstate was separated from the solution by distillation of solvent at reduced pressures, followed by crystallization of $Na_2WO_4 \cdot 2H_2O$. This was done to check for separation-induced exchange in the barium precipitation method. In one experiment the solution was evaporated in the 20–40° range and then was cooled in ice to hasten crystallization. The calculated equilibrium ^{18}O content was 1.41%; found, 1.50 ± 0.00%.

TABLE II

^{18}O CONTENT OF $BaWO_4$ PRECIPITATED AT 25° FROM Na_2WO_4 SOLUTION

$[Na_2WO_4] = 0.01$ *M*, $[NaCl] = 1.0$ *M*, $[BaCl_2]$ in precipitating reagent, 1.0 *M*

Soln.	Vol., ml.	pH	^{18}O content of H_2O in soln., atom %	^{18}O content of $BaWO_4$, atom % ± std. dev.
Na_2WO_4	25.25	11.0	1.57	
$BaCl_2$	3.50	7.0	0.20[a]	
Mixture	28.75		1.41[b]	1.38 ± 0.08
Na_2WO_4	25.25	11.0	1.57	
$BaCl_2$	3.50	7.0	0.20	
Mixture	28.75		1.41	1.42 ± 0.05
Na_2WO_4	25.25	11.0	1.58	
$BaCl_2$	3.50	12.0	0.20	
Mixture	28.75		1.41	1.55 ± 0.02
Na_2WO_4	25.25	11.0	0.204	
$BaCl_2$	3.50	12.0	1.46	
Mixture	28.75		0.354	0.266 ± 0.004
Na_2WO_4	12.5	12.0	1.46	
$BaCl_2$	1.75	12.0	0.20	
Mixture	14.25		1.31	1.42 ± 0.04
Na_2WO_4	25.00	12.0	1.46	
$BaCl_2$	3.50	12.0	1.46	
Mixture	28.40		1.46	1.48 ± 0.05
The sample below stood for 1.0 hr. before $BaWO_4$ precipitation				
Na_2WO_4	25.00	12.00	1.46	
$BaCl_2$	3.50	12.0	1.46	
Mixture	28.50		1.46	1.48 ± 0.006

[a] The content of our natural water and "Bone Dry grade" CO_2 was 0.206 ± 0.003%; the literature value is usually 0.204 (G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd Ed., John Wiley and Sons, New York, N. Y., 1964). [b] Calculated, assuming complete exchange.

In the other three experiments samples were maintained at room temperature for 1 hr. and also were held at 25.0° during evaporation. They were cooled in an ice bath during the crystallization. Two samples were run without added NaOH and at the pH of 11.0. In the first of these two experiments the calculated equilibrium ^{18}O content of the tungstate oxygen was 1.41%; found, 1.51 ± 0.02%. In the second the calculated was 1.40%; found, 1.43 ± 0.03%. In the final experiment, with 0.01 *M* NaOH, the calculated ^{18}O content of the tungstate at equilibrium was 1.27%; found, 1.30 ± 0.00%. Errors are standard deviations for from two to four replicate CO_2 samples. Results seem to indicate complete exchange in the time of mixing and separation, and the 3–7% enrichment of ^{18}O in the tungstate is probably real.[8]

In the experiments to check for oxygen exchange between water and 12-tungstocobaltate(III) and to determine whether or not it was rapid enough to be considered in the electron exchange between 12-tungstocobaltate(II) and -(III), the ^{18}O content calculated for no exchange was 0.206% (estimated from multiple analyses of natural water and Matheson "Bone Dry grade" CO_2). The ^{18}O content of the tetramethylammonium 12-tungstocobaltate(III) samples averaged 0.211 ± 0.002%). Complete exchange requires 1.49% ^{18}O. No appreciable oxygen exchange is indicated.

It seems safe to report that there is relatively rapid exchange (within a few minutes) of ^{18}O between water and orthotungstate at 25°, which might possibly be studied by simple stop-flow techniques. There seems to be no appreciable exchange of oxygen between water and 12-tungstocobaltate(III). The latter information tends to support our previous suggestion of an outer-sphere mechanism for the electron exchange between 12-tungstocobaltate(III) and -(II).[3]

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[8] J. Bigeleisen, private communication.

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Cyclic Heteroatomic Inorganic Compounds. A New Class of Phosphorus–Nitrogen–Boron Compounds

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A new class of cyclic compounds has been obtained which contains the elements phosphorus, nitrogen,