tion of dibutyl phthalate in benzene for several weeks were weighed and then decomposed by heating to 110°. The weight losses corresponded to 1.00–1.02 moles of benzene per mole of salt.

Cooling and heating curves on mixtures of benzene and tetrabutylammonium perchlorate of 70, 75, and 82% salt content showed a common thermal arrest at 62°. Above this temperature a rather viscous liquid phase remained at equilibrium with a white solid.

Decomposition pressures of the complex at 20.0, 25.0, and 31.0° were observed to be 16.2, 24.2, and 39.0 mm. with an uncertainty in the pressure measurements estimated to be ±2%. These measurements were made with a mercury manometer connected to a high vacuum pump and, through a ground glass joint, to a small bulb in a constant temperature bath, which contained the compound. With a known weight of salt and benzene initially present, the composition of the system was determined from time to time by detaching and weighing the bulb. When the mole ratio of benzene to salt fell below 1.00 the equilibrium pressure remained constant while further benzene was pumped off.

The solubility of tetrabutylammonium perchlorate at 25° in water was found to be 0.0101 ± 2% *m* in the absence of benzene while in the three-phase system (benzene solution, water solution, crystalline complex) the concentration of salt in the aqueous phase was 0.0052 *m*.

Discussion

The 0.0168 *M* concentration of tetrabutylammonium perchlorate at 25° in the upper layer of the unstable two liquid phase system is consistent with the solubility of 0.014 *M* in benzene at the freezing point of benzene as reported by Rothrock and Kraus.[2] In the earlier investigation crystallization of the complex had apparently never been initiated.

The weight loss experiments, and the observation that a constant equilibrium pressure was reached only when the benzene to salt mole ratio was below one, indicate a 1:1 mole ratio in the complex. As the complex is not very stable, losing benzene readily when exposed to the atmosphere at room temperature and melting incongruently at 72°, it presumably exists only in the crystalline state.

Standard state free energy increases accompanying the formation of the crystal complex from crystalline tetrabutylammonium perchlorate and liquid benzene have been calculated from the dissociation pressures at 20, 25, and 31° and benzene vapor pressures of 75.9, 95.2, and 124.8 mm. at these temperatures. Numerical values for ΔF° are -0.90, -0.81, and -0.70 kcal. mole^{-1}. From the variation of ΔF° with temperature, $\Delta H^\circ = -6.1$ kcal. mole^{-1} and $\Delta S^\circ = -17.8$ cal. mole^{-1} deg.$^{-1}$, independent of temperature within the limits of experimental precision.

The free energy of formation of the complex from liquid benzene and the solid salt may also be calculated from the solubility measurements. If the uncomplexed solid dissolves in the aqueous solution at 0.0101 *m*, is then transferred to the aqueous phase saturated with benzene having 0.0052 *m* salt concentration, and the complex is crystallized from this solution, the free energy change is

$$\Delta F^\circ = RT \ln \frac{(0.0052)^2}{(0.0101)^2} = -0.78 \text{ kcal.}$$

Any difference in the activity coefficient of the salt in the two solutions has been neglected here and the benzene vapor pressure of the aqueous phase when saturated with benzene assumed to be essentially that of pure benzene.

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[2] D. A. Rothrock and C. A. Kraus, *J. Am. Chem. Soc.*, **59**, 1699 (1937).

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Vapor Deposition of Pure Ruthenium Metal from Ruthenocene

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Received February 6, 1964

Biscyclopentadienyl metal compounds (metallocenes), because of their relatively high vapor pressure, may offer an attractive route to vapor deposition of metals, if used under the correct conditions. In previously reported studies, ferrocene decomposed to give hydrogen and diferrocenyl,[1] and other transition metal cyclopentadiene compounds gave deposits of metal carbide along with the metal.[2] However, a pure ruthenium metal film (99.99%) was deposited from bis(cyclopentadienyl)ruthenium at 595° in a hydrogen gas stream in the present work.

Experimental

Ruthenocene was prepared by the reaction of ruthenium trichloride with cyclopentadienylsodium in 1,2-dimethoxyethane.[3] The crude product when sublimed *in vacuo* yielded a yellow crystalline solid with a sharp melting point of 199–200°.[4]

A small porcelain boat containing 1 g. of ruthenocene was placed in a 25 × 300 mm. Vycor tube fitted with an inlet and exit port (note Fig. 1). A cylindrical graphite susceptor (21 × 126 mm.), grooved to accommodate a sheathed thermocouple, was inserted in the Vycor tube approximately 3 in. from the porcelain boat. A small resistance furnace was positioned to heat the porcelain boat and contents. A radiofrequency induction heater coil outside the Vycor tube surrounded the graphite susceptor at a distance approximately 1 in. from the resistance heater. A flow of dry hydrogen (100 cc./min.) was passed through the Vycor tube *via* the inlet port. The ruthenocene was heated to 94° by the furnace while the induction heater was controlled so that the graphite susceptor temperature was maintained at 590–600° for approximately 2 hr. This arrangement was used to provide more accurate temperature measurement, but a separately controlled resistance furnace outside the tube could be used just as well. About 100 mg. of ruthenocene was consumed in the course of the run.

A metallic film, mirror-like in appearance and easily removable, formed on the wall of the Vycor tube immediately adjacent to the graphite susceptor. A nonuniform ruthenium metal deposit formed on the graphite susceptor. In contrast to the mirror-like film of the Vycor substrate, this metallic deposit was dull and light gray in appearance. The nonuniformity in the

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[1] I. B. Johns, E. A. McElhill, and J. O. Smith, *J. Chem. Eng. Data*, **7**, 277 (1962).

[2] J. J. Bulloff, U. S. Patent 2,898,235 (Aug. 4, 1959).

[3] D. E. Bublitz, W. E. McEwen, and J. Kleinberg, *Org. Syn.*, **41**, 96 (1961).

[4] H. C. Kaufman, "Handbook of Organometallic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p. 1525.

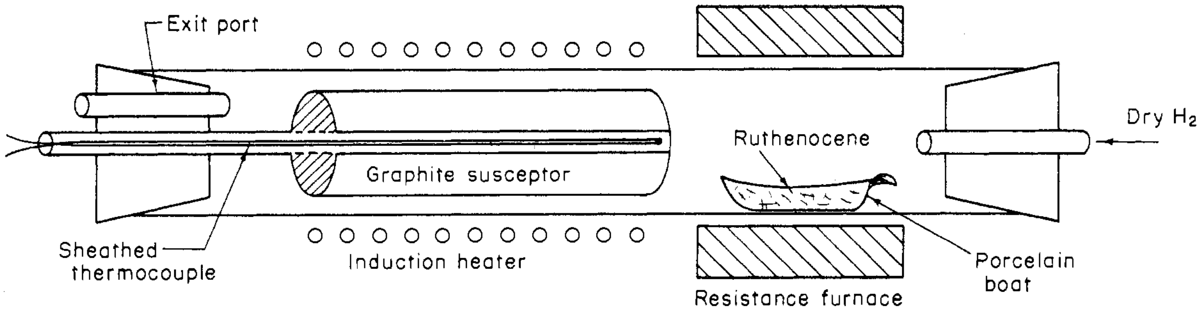

Fig. 1.—Metal vapor deposition apparatus.

film deposit may be due to temperature gradients along the graphite susceptor.

An X-ray diffraction powder diagram of the film deposit taken from the Vycor substrate indicated clean well-crystallized ruthenium metal. The X-ray parameters as shown in Table I agree exactly with standard ASTM data and no extraneous lines were found. The ruthenium metal film was compared with the $RuCl_3$ starting material by emission spectrographic analysis. A small amount of iron (about 0.01%) was found in both the metal film and the original $RuCl_3$. Palladium in the starting material (about 0.1%) was not detected in the vapor-deposited ruthenium, indicating that it is present in an amount less than 0.005%. Small amounts of silicon and boron from the Vycor substrate were also detected.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR VAPOR-DEPOSITED RUTHENIUM FILM[a]

d, Å.	*I*	*hkl*
2.343	41	100
2.142	37	002
2.056	100	101
1.5808	23	102
1.3530	25	110
1.2189	24	103
1.1715	5	200
1.1434	26	112
1.1299	20	201
1.0705	4	004
1.0278	7	202
0.9738	6	104
0.9056	15	203
0.8857	6	210
0.8673	26	211
0.8395	18	114
0.8185	10	212
0.8043	15	105

[a] Radiation source used was Cu $K\alpha$.

Discussion

Deposition of films by dissociation of covalent cyclopentadienyl metal compounds or their derivatives suggests a potential source of pure metal. Metallocenes of the transition metals can be prepared in a pure state and exhibit appreciable vapor pressure at low temperatures (~100°), thus facilitating vapor transport in a gas stream. Ferrocene, for example, has a vapor pressure of 10 mm. at 100°.[4] Metallocenes in contrast to metal carbonyls offer the advantage of easier handling and eliminate the possibility of metal film contamination by oxides.

The hydrogen atmosphere appears to be a significant factor in obtaining a pure metallic deposit from a biscyclopentadiene compound. Recent thermal stability studies of a number of organic compounds by Johns[1] have shown that ferrocene decomposes to diferrocenyl at 454° in an inert atmosphere. In this reaction a carbon–hydrogen σ-bond is broken but the π-bonding of the ferrocene remains unchanged. In the patent by Bulloff[2] examples are cited of vacuum deposition of manganese, titanium, and vanadium mixed with their metal carbides. In this case decomposition of the metallocene took place at the hot surface where the deposit formed and not all of the metal–carbon bonds were broken. In the presence of a flow of hydrogen gas, we have shown that ruthenocene decomposed to give a film of pure ruthenium metal and a product or products removed in the gas stream.

Although the dissociation products other than the metal film were not identified in this study, we suggest the following mechanism for the reaction in the presence of hydrogen.

$$Ru(C_5H_5)_2 \longrightarrow Ru + 2C_5H_5\cdot$$

$$2C_5H_5\cdot + H_2 \longrightarrow 2C_5H_6$$

Further experiments will be necessary to establish the mechanism definitely.

Acknowledgment.—The authors are grateful to the International Nickel Company, Inc., for permission to publish the finding of this investigation.

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The Reaction of Copper(II) Chloride with Lithium Borohydride[1]

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Received February 21, 1964

In this investigation the stoichiometry of the reduction of copper(II) chloride with lithium borohydride has been determined. This work provides evidence

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[1] This work was supported in part by Olin Mathieson Chemical Corporation.

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