[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Ruthenium Chlorides

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In connection with the corrosion of iridosmine,[1] the authors have described the qualitative effect of high-temperature, dry chlorination on pure ruthenium metal. During a subsequent investigation of the reaction, ruthenium chlorides thus prepared were identified by reduction and X-ray analyses, and their chemical properties were observed.

Published researches on the direct chlorination of ruthenium, though numerous, are frequently controversial in their conclusions about the extent of the reaction and the nature of the products. Claus[2] and, later, Howe, Howe and Ogburn[3] described conditions for the dry synthesis of $RuCl_2$ which were disputed by Joly,[4] Gutbier and Trenkner[5] and Kraus and Kukenthal,[6] who all found these methods led to partially chlorinated mixtures containing $RuCl_3$. Wohler and Balz[7] reported that $RuCl_3$ was the final product, but that its preparation was limited to temperatures below 845°, due to the high dissociation pressure of the trichloride. By the direct, high-temperature chlorination of ruthenium, Remy[8] and Morgan and Burstall[9] succeeded in preparing highly insoluble forms of $RuCl_3$. Wohler and Balz[7] obtained chlorination at a lower temperature by mixing the metal with sodium chloride, which contaminated the product. Several investigators[7,8,9,10] have reported a variety of products, including carbonyl compounds, from chlorination in the presence of carbon monoxide.

The authors' investigation was limited to the dry corrosion of pure ruthenium sponge by gaseous chlorine. Temperatures were chosen to combine a reasonable rate of reaction with low dissociation pressure for ruthenium chloride. The conversion of the volatile trichloride could be made complete yielding a pure product. Two distinct crystalline modifications were recovered.

Experimental

The apparatus, more fully described elsewhere,[1] consisted of a pre-heated silica chlorination chamber into which a porcelain boat containing the metallic sample was introduced. A continuous current of chlorine gas throughout the ignition period served to expel traces of air and sweep out volatile products. Spectrographically pure ruthenium sponge was used, and the chlorine was previously dried by passing it through concentrated sulfuric acid and over phosphorus pentoxide. Special precautions against the formation of highly volatile ruthenium tetroxide included flushing the reaction tube with chlorine just before inserting the sample, and recommencing the passage of chlorine immediately afterward. On completion of each experiment, the reaction tube was disconnected and sealed, allowing the contents to cool in an atmosphere of chlorine.

Chlorinated products were recovered as non-volatile boat residues and as sublimate, which deposited on cooler sections of the apparatus and was occasionally carried over into dilute hydrochloric acid, contained in a train of bubbling towers. Colorimetric and spectrographic tests[1] indicated that only a small proportion of the ruthenium reached the receiving solutions. The relative amounts of residue and sublimate depended upon the extent of chlorination; prolonged treatment at about 700° invariably caused complete conversion to the more volatile product, most of which crystallized on the walls of the reaction tube, at room temperature.

Composition of the Residue.—The black residues from two incomplete chlorinations (2–3 hours at about 600°) were analyzed for ruthenium, by reduction in hydrogen. A variation in the chlorine content suggested incomplete chlorination to ruthenium trichloride rather than the presence of lower chlorides.

Composition of the Sublimate.—Two distinctly different types of tube deposit were obtained, often simultaneously. One was a dark brown, greasy layer, and the other consisted of shiny black leaflets. The two were separated mechanically under a hand lens, and the results of their analyses are given in Table I. The brown material was slightly hygroscopic but, on drying, both brown and black modifications showed a ruthenium content within 0.2% of the theoretical value for ruthenium trichloride.

TABLE I

COMPOSITION OF RUTHENIUM CHLORIDE FROM TUBE DEPOSITS

Color	Drying method	Sample, mg.	Recovered Ru, mg.	Ru,[a] %	Av.
Brown	None	8.92	4.28	48.0	
Brown	None	9.32	4.37	46.9	47.4
Brown	None	11.66	5.52	47.4	
Brown	Kept over	2.087	1.009	48.4	
Brown	P_2O_5	1.196	0.576	48.2	48.4
Brown	Kept over	1.547	0.750	48.5	
Brown	P_2O_5	1.847	0.894	48.4	
Brown	103°,	2.595	1.266	48.9	
Brown	20 hr.	3.150	1.538	48.8	48.9
Brown	103°,	3.974	1.930	48.9	
Brown	20 hr.	2.769	1.357	49.0	
Black	None	14.85	7.29	49.1	
Black	Kept over	2.373	1.163	49.1	
Black	P_2O_5	2.325	1.139	49.0	

[a] Theoretical composition of $RuCl_3$, 48.88% Ru.

The two substances differed greatly in chemical properties. Whereas the black crystals were negligibly soluble in water, hydrochloric acid and ethanol, these were solvents for the brown chloride. Aqua regia, which readily attacked the latter, had much less effect on the former. The brown trichloride in water formed a brown solution. The hydrochloric acid solution was reddish brown, and was

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[1] Martha A. Hill and F. E. Beamish, *Anal. Chem.*, **22**, 590 (1950).

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[3] J. L. Howe, J. L. Howe, Jr., and S. C. Ogburn, Jr., THIS JOURNAL, **46**, 335 (1924).

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[6] F. Kraus and H. Kukenthal, *ibid.*, **137**, 32 (1924).

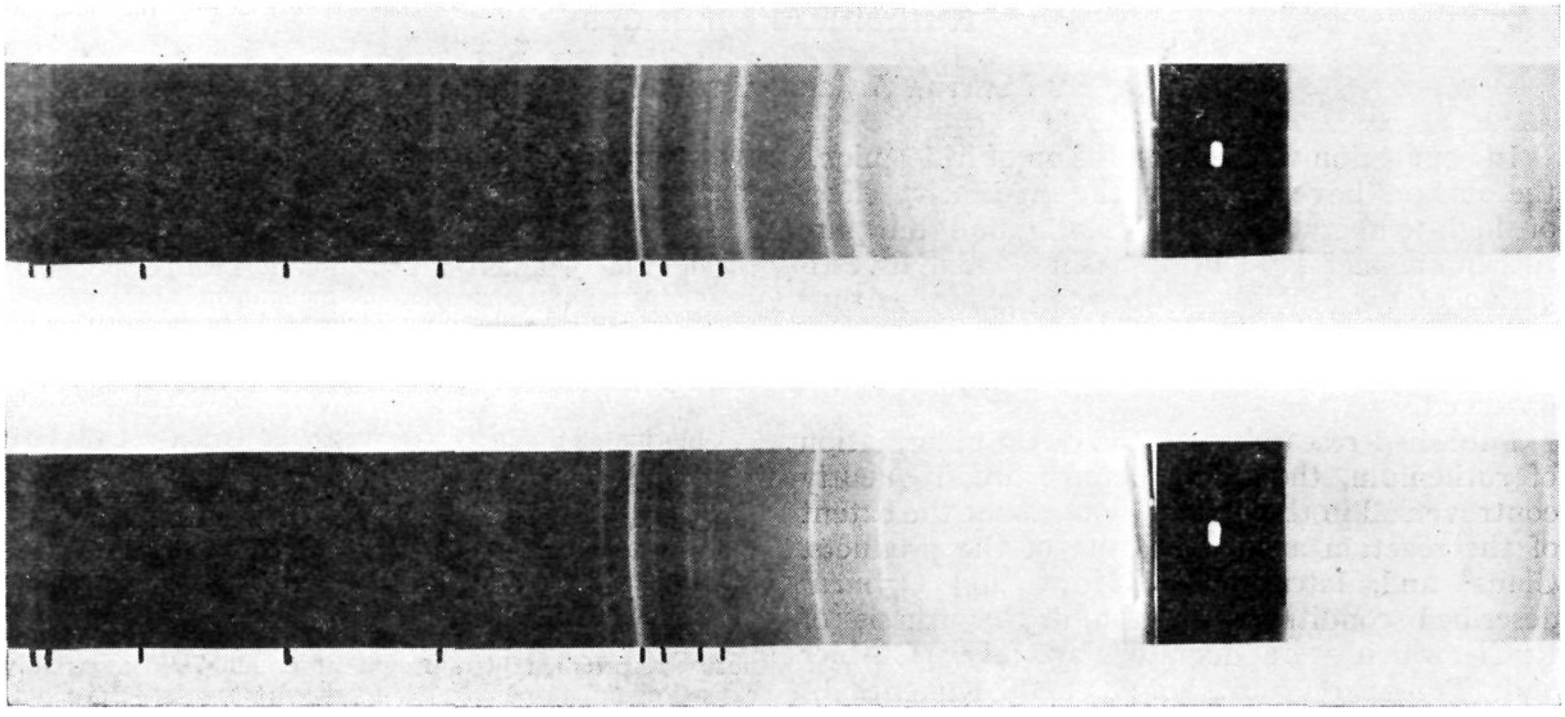
[7] L. Wohler and P. Balz, *ibid.*, **139**, 411 (1924).

[8] H. Remy and T. Wagner, *ibid.*, **168**, 1 (1928).

[9] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1936, 41.

[10] H. Remy, *Z. anorg. Chem.*, **137**, 365 (1924).

Brown ruthenium trichloride.



Black ruthenium trichloride.

Fig. 1.

reduced to a blue solution by addition of powdered zinc. Absolute ethyl alcohol added to the brown chloride produced a brown liquid which, upon addition of zinc, became green and finally yellow.

Complete conversion of metallic ruthenium to sublimed ruthenium trichloride usually required at least forty-eight hours for a 50-mg. sample, at 700°. Some of the brown trichloride was always obtained, while formation of the black crystals seemed to be favored by conditions which retarded the reaction. Semi-quantitative recovery of ruthenium as sublimate was possible, and the degree of solubility of the product depended on the relative amounts of the two forms of chloride.

Crystal Structure.—Specimens of both brown and black varieties of sublimed ruthenium trichloride were examined by X-ray analysis in the Central Research Laboratory of Canadian Industries, Limited. Figure 1 shows definite and distinctive crystal structures for both materials. The samples were irradiated in the presence of beryllium, the lines of which are indicated.

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Summary

Ruthenium is completely converted to the trichloride by dry chlorination at 700°. The trichloride sublimed to two different allotropic modifications with widely different properties. The shiny, black form was the more inert, while the brown product was hygroscopic.

Evidence for the presence of the di- or monochloride in incompletely chlorinated residues was inconclusive.

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The Raman and Infrared Spectra of Perfluoropropane[1]

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Octafluoropropane is a compound which has a number of possible industrial applications, among them being refrigeration. Consequently, its thermodynamic properties are of interest. One common method of obtaining this information for the gas phase is to calculate it statistically from a knowledge of the fundamental frequencies of vibration. To these values are added the corrections for the deviation from ideal gas behavior. With the addition of vapor pressure and heat of vaporization data, the basic Mollier diagram can be constructed. In order to provide the basic information for such a calculation for perfluoropropane, its Raman and infrared spectrum has been studied.

Experimental

The octafluoropropane used in this research was prepared electrochemically by the 3M-Simons process.[3] The sample was distilled through a 50-plate stainless steel helix

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(1) Presented before the Symposium on Fluorine Chemistry of the 116th Meeting of the American Chemical Society.

(2) Chemistry Department, Purdue University, Lafayette, Ind.

(3) J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).