Summary

The photochemical chlorination of tetrachloroethylene in carbon tetrachloride solution has been studied in monochromatic light of wave length 4358 Å., and the specific rates have been expressed in absolute units. The rate has been found proportional to the square root of $(I_{abs.})$, at least approximately proportional to the first power of (Cl_2), and only moderately dependent on (C_2Cl_4); Equation (IX) summarizes these results. Under the conditions of the experiments, the quantum yield has varied from 300 to 2500. Two alternative mechanisms, one involving C_2Cl_5 and one involving Cl_3, have been discussed, and both found to account for the observations.

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THE DENSITY AND MOLECULAR STATE OF RHENIUM TETRACHLORIDE AND RHENIUM HEXACHLORIDE IN THE GASEOUS STATE

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Introduction.—Previous experiments on the nature of the rhenium chlorides[1] have shown that more than one compound is formed when chlorine is passed over the heated metal. Some of the substances so formed are reported to be easily volatile. Hönigschmid,[2] in an attempt to determine the atomic weight of rhenium by the analysis of a chloride, found the best preparations to be mixtures since the proportions of rhenium and chlorine were not constant and led in the more reproducible cases to the formula $ReCl_{4.3}$. He also observed that this substance decomposed on heating in an atmosphere of nitrogen with the formation of a less volatile product, whereas similar treatment in the presence of chlorine resulted in complete volatilization without apparent change.

In the present article are presented the results of vapor density measurements made on various mixtures of rhenium and chlorine in order to determine the molecular state and composition of some of the rhenium chlorides.

Experimental Method and Preparation of Materials.—The vapor density measurements were carried out in the same manner as in a previous investigation,[3] the method consisting of heating weighed amounts of rhenium and chlorine in previously evacuated tubes until the contents were completely reacted and vaporized and then allowing the excess to escape

[1] W. Noddack, Z. Elektrochem., 34, 627 (1928).

[2] Hönigschmid and Sachtleben, Z. anorg. Chem., 191, 147 (1931).

[3] Yost and Hatcher, THIS JOURNAL, 53, 2549 (1931).

until the pressure became atmospheric. By weighing the tubes before and after releasing the excess, and knowing the initial weights present and the volumes of the tubes, the vapor densities could be calculated.

As a source of rhenium the very pure potassium perrhenate now available was used. To obtain the metal the finely pulverized perrhenate was reduced with hydrogen. The hydrogen was passed slowly through a Pyrex tube heated almost to the softening point over about 30 cm. of its length. The gas then passed over the salt which, however, was not otherwise heated until reduction was well started. The reduction was then carried to completion with moderate heating of the salt. The resulting mixture, after cooling, was washed several times with hot water to remove the potassium hydroxide formed as well as the unreduced perrhenate. The black product obtained was dried, ground in a mortar, again washed several times with hot water, and dried. This material was placed in a silica tube and treated with hydrogen at bright red heat in order to reduce the last traces of rhenium oxides that are present after the first reduction.

Chlorine from a cylinder was purified by passing through water and then through a long drying tube containing anhydrous calcium chloride. It was condensed with liquid air in small capsules provided with easily breakable tips. The capsules were sealed and weighed, their weight empty having been previously determined.

Results of the Vapor Density Experiments.—The results of the vapor density measurements are presented in Table I. In the last column are given the values M of the apparent molecular weights calculated from the equation $M = [m\ 82.07(273.1 + t)]/pv$ in which m is the weight of material present in v cc. at the pressure p in atmospheres and the temperature t.

TABLE I

RESULTS OF THE VAPOR DENSITY MEASUREMENTS

Expt.	Atomic ratio Cl:Re	Weight of material, m, g.	Pressure p in mm.	Temp., t, °C.	Volume v, cc.	Apparent molecular wt., M
1	4	0.2742	748	670	45.1	478
2	4	.3378	748	670	58.5	476
3	4	.2796	748	670	47.2	465
4	4	.4256	748	670	69.9	478
5	4	.2671	746	567	40.4	465
7	6	.1328	738	563	37.1	253
8	6	.1205	738	616	37.1	244
9	6	.1721	738	560	48.9	248
10	6	.1587	738	609	48.9	242
15	7.540	.1220	746	565	38.5	222
16	7.540	.1186	746	618	38.5	230
11	8	.1129	741	558	42.1	188
12	8	.1044	741	618	42.1	186
13	8	.0947	741	558	34.7	191
14	8	.0874	741	618	34.7	187

The vapors are assumed to obey the law of perfect gases. Measurements were made using various atomic ratios of Cl : Re and with varying initial amounts of rhenium and chlorine.

It was necessary to work at rather high temperatures since complete vaporization of the material did not take place below these temperatures, and at temperatures much higher than the highest used the glass reaction bulbs softened.

The reaction between metallic rhenium and chlorine is very slow at room temperature but much more rapid at 650°. In order to assure complete reaction it was necessary to heat the tubes containing the rhenium and chlorine in the ratio 1:4 for fourteen hours at 620° while tubes containing larger proportions of chlorine required somewhat less time.

The vapors at and above atmospheric pressure were in all cases dark reddish-brown in color and quite opaque in layers 2.5 cm. thick. The color of the vapors was, as far as could be determined visually, independent of the ratio of rhenium to chlorine used, thus indicating that at least one constituent was present in appreciable amounts in all of the experiments. The solid condensing out at room temperature consisted principally of small crystals which, when thin, were dark red by transmitted light, and when thick practically black. When tubes containing chlorine and rhenium in the ratio 6:1 and greater were cooled with liquid air and then allowed to come again to room temperature, a small amount of yellowish-red solid was observed which volatilized readily on warming with the hands. Free chlorine could always be seen in tubes containing chlorine in excess of that necessary to form the tetrachloride.

When the tubes were opened under water the rhenium chlorides reacted with it forming a black precipitate except when the chlorine-to-rhenium ratio was 8:1, in which case a yellow solution was formed which rapidly became colorless with the formation of perrhenic acid. When the black crystals were added to 6 N hydrochloric acid a salmon-pink colored solution resulted which gave no precipitate even after two weeks but did gradually become green in color. These results are in agreement with those found recently by Briscoe, Robinson and Stoddart[4] in their experiments on the solid tetrachloride. They also established that the dark crystals had the composition $ReCl_4$.

Discussion of the Results

As may be seen from the results of the experiments, the maximum deviation to be expected between the apparent molecular weights is less than 4%. The mean error is somewhat less than this. It is to be observed that the variation of the apparent molecular weights with temperature is small and of the order of magnitude of the errors involved.

4 Briscoe, Robinson and Stoddart, J. Chem. Soc., 134, 2263 (1931).

The formula weight of $ReCl_4$ is 328.14 while the average value obtained in experiments 1 to 5, in which the atomic ratio of rhenium to chlorine is 1:4, is much greater than this, namely, 472. This fact indicates that polymerization takes place but that it does not go to completion since the observed molecular weight is not a simple multiple of the formula weight. If the polymer is assumed to dissociate rapidly and reversibly in accordance with the reaction

$$Re_2Cl_8(g) = 2ReCl_4(g) \tag{1}$$

then agreement with the observed molecular weights would result if the degree of dissociation were 0.39. That equilibrium was attained rapidly was shown by the fact that variations in the initial pressures had no effect on the values of the vapor densities although only some ten seconds were necessary for the excess material to escape before atmospheric pressure was attained.

In the experiments in which the atomic ratio of Re:Cl was 1:6 the average observed molecular weight is 247, while the formula weight of $ReCl_6$ is 399.06. Evidently the hexachloride does not exist as such to the exclusion of other substances at the temperatures of the experiments. If it is assumed that the following reactions take place

$$ReCl_6(g) = ReCl_4(g) + Cl_2(g) \tag{2}$$
$$2ReCl_4(g) = Re_2Cl_8(g) \tag{3}$$
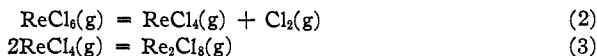
and that the reactions are rapid and reversible, then a mixture could result whose apparent molecular weight would be that observed. Moreover, it is possible to calculate the equilibrium constant for reaction (2), since that for reaction (3) is known from the experiments on the tetrachloride. The following two values are found for the temperature range of the experiments, the pressures being expressed in millimeters of mercury.

$$\frac{P_{Re_2Cl_8}}{P^2_{ReCl_4}} = 1.86 \times 10^{-3} \qquad \frac{P_{ReCl_4} P_{Cl_2}}{P_{ReCl_6}} = 708$$

The assumptions made may now be tested using the results of the experiments in which the rhenium-to-chlorine ratio was 1:8 and making the assumption that no higher chlorides are formed. This latter assumption seems a reasonable one to make since the experiments on the hexachloride showed that even it undergoes extensive decomposition. Using the equilibrium constants just given, together with the pressure shown in the table for the experiments in question, an apparent molecular weight of 183 is calculated. This is in good agreement with the observed value, 188. The evidence then, both of a qualitative and quantitative nature, supports the assumptions made above regarding the nature of the rhenium chloride vapors.

It is to be noted that the calculations have been made on the assumption that all the experiments were at the same temperature, which was not

the case.   The fact that the vapor densities are, within the limits of experimental error, independent of the temperature indicates that the equilibria involved are not undergoing any great changes in the temperature range employed.

There remains to be considered the possible existence of the compounds Re_2Cl_4, Re_2Cl_6 and $ReCl_7$ under the conditions of the experiments.   If either of the first two or both were formed without the simultaneous presence of the tetrachloride, then the apparent molecular weights in the experiments in which the ratio of $Re : Cl$ was $1:4$ would have been 328 or less, much smaller than those found experimentally.   It is necessary, therefore, that Re_2Cl_8 be present along with the Re_2Cl_4 or Re_2Cl_6.   Assuming Re_2Cl_8 to be in equilibrium with either of these two lower chlorides and chlorine, the calculated molecular weights for the case in which excess chlorine is present are found not to be in agreement with those determined experimentally.   The simultaneous existence of either of the two lower chlorides together with the tetrachloride, hexachloride and chlorine does not, from purely chemical considerations, seem very probable.

The possibility that $ReCl_7$ rather than $ReCl_6$ is present in the tubes with excess chlorine does not seem at all likely since it is hardly to be expected that rhenium would exhibit its maximum valence with chlorine under the conditions of the experiments.   Moreover, when it is assumed that a heptachloride is present in equilibrium with the tetrachlorides and chlorine the calculated molecular weight of the 1:8 mixtures is found to be much too high.   The assumption that the vapors consist of the polymerized and simple tetrachlorides and the hexachloride in addition to chlorine suffices for the explanation of the experimental results.[5]

Summary

The vapor densities of mixtures of rhenium and chlorine in various proportions have been determined in the neighborhood of $600°$.   The results show that a polymerized tetrachloride, Re_2Cl_8, exists in equilibrium with $ReCl_4$, and that in the presence of excess of chlorine the hexachloride is also formed and is present in equilibrium with the tetrachlorides and chlorine.

The reaction between metallic rhenium and chlorine was found to be slow at temperatures much below $650°$.   After completion of the reaction and cooling to room temperature black or dark red crystals are formed which consist principally of the tetrachloride.

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[5] The results of the experiments of Briscoe, Robinson and Stoddart indicate that some of the substances previously described as higher chlorides may be oxychlorides or related substances.