Summary

The adiabatic (London) theory of reaction rates has been applied, for the first time, to reactions involving four atoms. It shows, unambiguously, that the thermal reaction of hydrogen with iodine will involve only iodine molecules, while the other halogens will react with hydrogen by way of the atoms. It shows further that the conversion of para to ortho hydrogen will involve an atom and a molecule rather than two molecules. It explains the well-known greater reactivity of the heavy halogen compounds over the lighter ones. These checks with experiment are independent of the ratio of coulombic to total binding except in the case of bromine. If the known theoretical ratio of coulombic to total binding for hydrogen is assumed to hold for the other atoms, approximate agreement with experiment is obtained. To obtain exact agreement in the reaction $H_2 + I_2 = 2HI$ the coulombic binding must be assumed to be only three and a half per cent. of the total binding. The theoretical evaluation of the coulombic binding is possible, but difficult, using the approximate eigenfunctions of Zener and Slater.

BERKELEY, CALIFORNIA

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THE VAPOR DENSITY OF SELENIUM TETRABROMIDE AND THE EXISTENCE OF SELENIUM DIBROMIDE

BY DON M. YOST AND JOHN B. HATCHER

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Introduction

The results of the few qualitative observations that have been made on selenium tetrabromide[1] show definitely that it decomposes to some extent at room temperature and much more so at higher temperatures, the products of the decomposition being bromine and a lower bromide or bromides of selenium. Since no information of a quantitative nature seems to exist on the chemistry involved in the decomposition, the experiments described in this paper were undertaken.

Experimental Procedure and Preparation of the Materials.—The experiments consisted essentially in determining by the Dumas method the vapor densities of mixtures of selenium and bromine over the temperature range from 250 to 500°. Carefully weighed portions of bromine and elementary selenium were introduced into a cylindrical Pyrex tube

[1] *Cf.* Abegg, Auerbach and Koppel, "Handbuch der anorganischen Chemie," Leipzig, **1927,** IV Band, 1 abt., 1 hälfte, p. 724; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green, London, **1930,** V. X, p. 899; J. Meyer and V. Wurm, *Z. anorg. Chem.*, **190,** 90 (1930).

of known volume, the bromine being contained in a small glass capsule with an easily breakable tip. The end of the tube was provided with a heavy-walled capillary whose end was drawn down to a thin tip and sealed off. After filling the tube, it was carefully evacuated, and then sealed off. A vigorous shake sufficed to break the tip of the bromine capsule, permitting the bromine to react with the selenium. The tube with the capillary was weighed and then placed in an electric furnace. After temperature equilibrium had been attained, the tip of the capillary was heated until the pressure inside the tube forced an opening through the softened glass and allowed the excess of gas to escape. The tip was not resealed until it was judged that the contents of the tube had again reached the temperature of the furnace, some cooling having resulted from the adiabatic expansion of the gas. The tube was then removed from the furnace, cooled and again weighed. The difference in the weights was the amount of material that had escaped; and this amount, subtracted from the original amount present, yielded the quantity remaining in the tube. The same tube was used for a series of experiments at increasingly higher temperatures.

The method of purifying the selenium was the same as that used in a former investigation.[2] The bromine was prepared by heating C. P. cupric bromide in a vacuum and subsequently drying and redistilling the bromine from pure potassium bromide.

Results of the Experiments

In Table I are presented results of representative vapor density measurements, of which thirty were made in all. It was assumed in making the calculations that the vapor obeyed the perfect gas law, and in the table are given the values of the apparent molecular weight M of the vapors as calculated directly from the equation, $M = 82.07(t + 273.1)m/pv$, p being expressed in atmospheres and v in cubic centimeters. The initial amount of bromine used varied from 0.37 g. to 0.53 g.

In order to determine qualitatively whether or not bromine was present in the hot vapors, their absorption spectra were observed and compared with that of an equal thickness of pure bromine at 200 mm. pressure, a visual spectrometer being used. When the atomic ratio Br:Se was four, the absorption bands of bromine were present with an intensity comparable to that observed in the comparison tube. In experiments where the composition of the mixture corresponded to selenium monobromide, no bromine bands could be seen, indicating that little or none of it was present. With a Br:Se ratio of two the bromine bands were very faint when the tube was hot and increased in intensity when, on cooling, condensation took place. This showed qualitatively that little or no bromine was

[2] Yost and Kircher, THIS JOURNAL, **52**, 4680 (1930).

TABLE I

RESULTS OF THE VAPOR DENSITY EXPERIMENTS

Formula weights: $SeBr_4$ = 398.86; Se_2Br_2 = 318.23; $SeBr_2$ = 239.03

Initial atomic ratio of Br:Se	Temp. (t), °C.	Bar., mm.	Vol. (v), cc.	Material (m) left in tube, g.	Molal weight M (calcd.)
4	250	743.9	41.4	0.1932	204.7
4	300	739.0	41.7	.1714	198.7
4	300	739.0	40.7	.1663	197.6
4	326	747.5	41.4	.1660	200.7
4	326	747.5	41.4	.1655	199.9
4	350	739.0	40.7	.1529	197.6
4	351	739.0	41.7	.1578	199.2
4	399	739.0	41.1	.1433	197.7
4	400	739.0	40.7	.1420	198.2
4	450	739.0	41.7	.1359	198.8
4	500	739.0	41.7	.1265	197.8
2	355	742.8	40.8	.1843	238.2
2	422	742.8	40.8	.1666	238.3
2	470	742.8	40.8	.1556	238.0
1	310	739.0	41.4	.4463	[a]
1	440	739.0	41.2	.3683	[a]
1	470	742.8	41.4	.2981	[a]

[a] Considerable black unvaporized liquid residue was present in these experiments, so that the values for the molecular weight would have no significance.

present until the vapor in the tube began to alter its composition as a result of condensation.

When the atomic ratio was unity, corresponding to Se_2Br_2, complete vaporization of the material was never attained even at 500°. The unvaporized residue was a black liquid, whose appearance was that of molten selenium, but which might have contained some dissolved monobromide. With a Br:Se ratio of two or four the material vaporized completely without difficulty and in the former case gave rise to a molecular weight whose significance will appear later. Clear solutions containing no free bromine always resulted when the tetrabromide tubes were opened under water after the vapor density experiments had been made.

Discussion of Results

Since Table I shows that the molecular weight calculated from the measurements with mixtures having the composition of selenium tetrabromide is almost exactly one-half the formula weight of this substance, it follows that the tetrabromide does not exist as such under the conditions of the experiments, but decomposes completely in such a way that two molecules result from one of the tetrabromide. That this dissociation is complete is shown by the fact that the molal weight remains the same throughout the whole range of temperatures investigated (250–500°).

Such a decomposition might occur in the following ways

$$SeBr_4 = Se(s) \text{ or } (l) + 2Br_2(g) \quad (1)$$
$$2SeBr_4 = Se_2Br_2(g) + 3Br_2(g) \quad (2)$$
$$SeBr_4 = SeBr_2(g) + Br_2(g) \quad (3)$$

The decomposition according to equation (1) is, however, excluded since no solid or liquid selenium (whose vapor pressure[3] is 4 mm. at 400°) was ever present in the tubes having a Br:Se ratio of four.

If the decomposition of the tetrabromide took place according to reaction (2), normal values for the molecular weight of the monobromide[4] would have resulted in the experiments with it alone, and no unvaporizable residue should have remained, providing it were not decomposed. Yet, as may be seen from the last three results in the table, the monobromide experiments do not yield a normal molecular weight and considerable unvaporizable residue remained even at the highest temperature.

The possibility of the monobromide decomposing into the tetrabromide and selenium according to the reaction

$$2Se_2Br_2 = SeBr_4(g) + 3Se(l) \quad (4)$$

is excluded by the fact that the tetrabromide as such does not exist even in the presence of bromine, as already shown. That decomposition of the monobromide into bromine and selenium did not occur is shown by the fact that no absorption bands of bromine were found when the Br:Se ratio was unity and that the escaping vapor showed itself, on testing, to be rich in selenium. Moreover, no residue of selenium was ever found in the tetrabromide experiments even at 220° where the vapor pressure of liquid selenium is only 0.005 mm.[5] It appears then that the decomposition of the tetrabromide does not take place according to reaction (2).

There remains therefore only the possibility that the decomposition of the tetrabromide takes place in accordance with reaction (3). If this be the case, complete vaporization of the mixtures used should occur when the Br:Se ratio is two, and this was in fact found to be true. Moreover, if the existence of selenium dibromide is assumed, the results of the experiments on the selenium monobromide are easily explained by assuming that the monobromide decomposes according to the reaction

$$Se_2Br_2 = Se(l) + SeBr_2(g) \quad (5)$$

One must conclude, therefore, that selenium monobromide does not exist to any appreciable extent in the vapor phase at the temperatures of 250–500°; but that the hitherto unknown compound selenium dibromide does so exist. The dibromide vapor, however, seems not to condense as

[3] Preuner and Brockmöller, *Z. physik. Chem.*, **81**, 129 (1913).

[4] The vapor pressure of the monobromide, if it existed as such, would have exceeded one atmosphere since at the lowest temperatures the total initial pressures in tubes containing the tetrabromide were about four atmospheres, and one-half of this would be due to the monobromide.

[5] L. E. Dodd, THIS JOURNAL, **42**, 1579 (1920).

such to a solid or liquid phase, but to break up into the familiar liquid monobromide and solid tetrabromide.

It is of interest to point out that the equilibrium relations of a system composed of selenium and bromine are very similar to those of one composed of selenium and chlorine.[2,6]

Solid Selenium Tetrabromide.—The appearance, on cooling, of the substance in the tubes containing selenium tetrabromide was observed. The vapor itself has a dark red color (as does also selenium dibromide). The first solid material that appears is black in color and forms small hexagonal plates. As the temperature becomes lower still, the crystals that form possess a red color but are not, under a pocket lens, hexagonal in shape. If the temperature is suddenly lowered from about 50° to room temperature by holding the tube under the water tap, the clear portions of the tube are covered with very small lemon-yellow crystals. These differently colored substances may all be different modifications of solid selenium tetrabromide; no attempt was made to study them further.

Summary

The vapor density of mixtures corresponding in composition to selenium tetrabromide has been determined over the temperature range from 250 to 500°. The results show that it is completely decomposed at these temperatures into bromine and the previously unknown selenium dibromide.

Experiments with selenium monobromide showed that it decomposes, to a considerable extent at least, into selenium and selenium dibromide on vaporization. Mixtures of the composition of selenium dibromide vaporize completely, and in the vapor phase consist principally of selenium dibromide itself.

PASADENA, CALIFORNIA

[6] Simons, THIS JOURNAL, **52**, 3483 (1930)