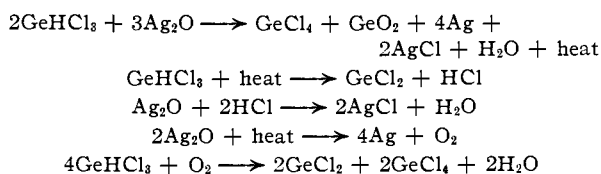by way of the sulfide, after a further oxidation with 3% H_2O_2. These two determinations indicated that the product had a divalent germanium-to-total germanium ratio of 1.04:1.00. The other sample was analyzed for chlorine as AgCl and germanium by way of the sulfide, and indicated a chlorine-to-germanium atomic ratio of 2.15:1.00.

These two ratios show clearly that the product of this reaction contains only divalent germanium and that sufficient chloride is present to satisfy all of the valence requirements of this germanium. The accuracy of the results is as good as can be expected since such small quantities were available for analysis. The evidence seems to indicate that the material is a new form of germanium dichloride, but whether this is a super-cooled liquid or a new structure has not been determined. The "decomposition" reported by Schwarz and Heinrich is apparently a transformation into the commonly observed form of $GeCl_2$, and this is borne out by the fact that no evolution of chlorine could be detected during the transformation, as would occur if it were $GeOCl_2$ decomposing into GeO and Cl_2.

The reaction of $GeHCl_3$ and oxygen also was studied. This reaction has been previously reported by Dennis, and the products were described as $GeCl_4$ and an unidentified clear, viscous oil which was present as a separate phase.[5] The reaction has been repeated by mixing trichlorogermane vapor, carried in a stream of dry helium, with dry oxygen in a reaction tube. The product consisted of two phases, as previously described, but only small quantities of the viscous oil were obtained. It was found to be insoluble in benzene and was separated from the $GeCl_4$ by an extraction with this solvent. An examination by the determination of the two ratios used above gave a divalent-to-total germanium ratio of 0.97:1.00 and a chlorine-to-germanium atomic ratio of 2.25:1.00. This is in close agreement with the results of the $GeHCl_3$–Ag_2O reaction and once again the product is most closely fitted by the formula $GeCl_2$.

The differences in the two reactions involving silver oxide and oxygen are few. The reaction of $GeHCl_3$ with oxygen was much slower and less vigorous as carried out here, but when pure oxygen reacts with liquid $GeHCl_3$ enough heat is liberated to cause the liquid to boil.[5] Since the reaction with silver oxide was highly exothermic, it is probable that the Ag_2O was decomposed to silver and oxygen rather rapidly. One very important function of the silver oxide is undoubtedly that of an acceptor for HCl. This reaction would give additional heat and aid in decomposing the $GeHCl_3$ to $GeCl_2$ and HCl by removing the HCl as it was formed.

Typical reactions which might occur in the two reactions studied are

$2GeHCl_3 + 3Ag_2O \longrightarrow GeCl_4 + GeO_2 + 4Ag + 2AgCl + H_2O + heat$

$GeHCl_3 + heat \longrightarrow GeCl_2 + HCl$

$Ag_2O + 2HCl \longrightarrow 2AgCl + H_2O$

$2Ag_2O + heat \longrightarrow 4Ag + O_2$

$4GeHCl_3 + O_2 \longrightarrow 2GeCl_2 + 2GeCl_4 + 2H_2O$

The second and fifth equations are the only ones of

(5) L. M. Dennis, W. R. Orndorff and D. L. Tabern, J. Phys. Chem., 30, 1049 (1926).

these which could occur during the reaction with oxygen gas and the last was used by Dennis to explain his results.[5] Dennis creates something of a paradox when he states that no HCl could be detected as a product of the oxygen reaction. It is not clear just how any reaction could occur without ultimately liberating HCl. It would appear that Dennis may have missed the HCl due to its extreme solubility in the germanium compounds.

The evidence presented here is in direct conflict with the previous claim for the preparation of $GeOCl_2$. The parallel nature of the reactions of trichlorogermane with silver oxide and with oxygen has been clearly exhibited, and it appears that the clear, viscous product of both reactions is a liquid modification of $GeCl_2$.

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On the Reaction of Europium Dichloride with Solutions of Hydrochloric Acid

BY C. T. STUBBLEFIELD AND L. EYRING

Observations have been made for many years on the reactions of the rare earth dichlorides in acid solutions [1-4] In general, the previous investigations led to development of methods of separation of europium from the other rare earths and to determinations of oxidation potentials.

The purpose of the present study is to investigate the path of reaction of europium dichloride with various concentrations of hydrochloric acid saturated with hydrogen, oxygen or air.

Experimental Methods

Materials and Analysis.—The europium was obtained as 99.8% pure Eu_2O_3 from Research Chemicals. The dichloride was analyzed by a gravimetric chloride determination and was found to be pure $EuCl_2$.

Preparation of Dichloride.—Samarium and ytterbium trichlorides are prepared by the interaction of thionyl chloride vapor and the oxides at 400° for 24 hours in a simple and effective cycling system.[5] The same apparatus was used to prepare europium trichloride, but carbon tetrachloride replaced thionyl chloride as the chlorinator since the latter reactant produced some europium sulfide. The bright yellow trichloride thus prepared is rapidly and completely soluble in water without a trace of turbidity.

Europium dichloride was produced by hydrogen reduction of the trichloride in a quartz boat at 300° within six hours. The white $EuCl_2$ dissolves in dilute hydrochloric acid to give a slowly decomposing yellow solution.

Although a copious evolution of gas accompanies the solution of samarium or ytterbium dichloride in dilute hydrochloric acid, the volume of gas evolved when europium dichloride is dissolved depends upon the availability of dissolved oxygen gas and hydrogen ions.

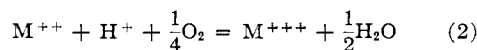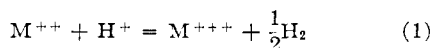**Experimental Results.**—The divalent europium ions may react by one of the paths

(1) H. N. McCoy, THIS JOURNAL, 58, 1577 (1936).
(2) L. F. Yntema, ibid., 52, 2782 (1930).
(3) P. W. Selwood, ibid., 57, 1145 (1935).
(4) D. W. Pearce, Chem. Revs., 16, 121 (1935).
(5) G. Machlan, C. T. Stubblefield and L. Eyring, THIS JOURNAL, 77, 2975 (1955).

$$M^{++} + H^+ = M^{+++} + \frac{1}{2}H_2 \qquad (1)$$

$$M^{++} + H^+ + \frac{1}{4}O_2 = M^{+++} + \frac{1}{2}H_2O \qquad (2)$$

Obviously, only path (1) is possible if oxygen is excluded. A small gas buret was used to measure the extent of gas evolution or absorption accompanying these reactions in different atmospheres.

The buret was so designed that a fragile glass bulb containing the crystalline dichloride sample could be mounted in the hydrochloric acid solution of desired concentration and the solution saturated with H_2, air or O_2, or in fact any desired gas. The stopcocks were closed and the solution and the atmosphere above it allowed to attain the temperature and pressure of the constant temperature room. The bulb was then broken and the change in volume of the atmosphere observed as gas was evolved or absorbed in the reaction. The results of these determinations are shown in Tables I, II and III for the reactions of $EuCl_2$ with various HCl solutions.

TABLE I

GAS ABSORPTION UPON REACTION OF $EuCl_2$ WITH OXYGEN
SATURATED 0.015 M HCl SOLUTION AT 25°

Sample size, moles × 10^5	3.02	2.99
Mole of gas absorbed/mole of $EuCl_2$	0.30	0.27

TABLE II

GAS ABSORPTION UPON REACTION OF $EuCl_2$ WITH AIR
SATURATED HCl SOLUTIONS AT 25°

HCl concn. (moles/l.)	Sample size (moles × 10^5)	Moles gas absorbed/ mole of $EuCl_2$	HCl concn. (moles/l.)	Sample size (moles × 10^5)	Moles gas absorbed/ mole of $EuCl_2$
0.015	2.49	0.27	1.50	3.33	−0.03
.015	2.58	.15	1.50	2.04	.07
.015	2.48	.06	6.00	2.25	.08
.015	2.82	.04			

TABLE III

HYDROGEN EVOLUTION UPON REACTION OF $EuCl_2$ WITH H_2
SATURATED 6 M HCl AT 25°

Sample size (moles × 10^5)	H_2 evolved (moles × 10^5)	Moles of H_2 evolved/mole of $EuCl_2$
2.14	0.93	0.43
2.62	1.14	.43

The enthalpy change upon reaction of the dichlorides in acid solution is a very sensitive test of the path by which the reaction proceeds because of the formation of water when oxygen is involved. Table IV shows the results when the dichlorides are reacting with hydrochloric acid solutions in the calorimeter in the presence or absence of oxygen. It should be noticed that the $EuCl_2$ runs were made in dilute acid when oxygen was deliberately added to the reaction mixture, hence in this case the difference between the calculated enthalpy changes in the presence and absence of oxygen is not simply the heat of formation of one-half mole of water. The calculated values in the case of $EuCl_2$ are based on an estimated heat of solution of $EuCl_2$ of −10 kcal. mole^{-1}. The estimates

for the reactions of $SmCl_2$ and $YbCl_2$ are from previous work.[5]

TABLE IV

ENTHALPY CHANGES ON REACTION OF RARE EARTH DI-
CHLORIDES WITH HCl SOLUTIONS AT 25°

Chloride	Reaction time (min.)	No. of runs	HCl concn. (mols/l.)	Condition	Calculated[a] ΔH, (kcal./mole)	Observed ΔH (kcal./mole)
$SmCl_2$	5	3	6.00	H_2 satd.	−42	−42.2 ± 0.2
		2	6.00	Air satd.	−76	−42.2 ± .2
$YbCl_2$	10	5	6.00	H_2 satd.	−42	−41.2 ± .2
$EuCl_2$	60–110	9	6.00	H_2 satd.	−20	−27 to −36
	25–110	4	0.015	O_2 satd.	−61	−51 to −60

[a] For the condition of hydrogen saturation, the calculated ΔH refers to the reaction proceeding by path (1), while for the condition of air or oxygen saturation, it refers to the reaction proceeding by path (2).

It was observed[5] that the heat of reaction of $SmCl_2$ is the same within the limit of error whether oxygen is present or not. The consistency of the results for ytterbium dichloride indicates that the reaction proceeds only by path (1). The term "H_2 saturated" means that the hydrochloric acid solution was hydrogen saturated before assembly of the calorimeter. The space above the solution in the calorimeter was filled with air. The term "O_2 saturated" means that the hydrochloric acid solution was oxygen saturated prior to assembly and the air above the calorimeter solution was replaced with oxygen as completely as possible.

The wide variation of results on the heat of reaction of $EuCl_2$, even when conditions were duplicated, shows the extreme sensitivity of the reaction to small variations in the concentration of oxygen.

Discussion and Conclusions

The data presented in Tables III and IV indicate that the reaction of $EuCl_2$ with hydrochloric acid in the absence of oxygen goes according to equation 1. Whereas $EuCl_2$ reacts slowly under these conditions (many hours are required for completion), $SmCl_2$ and $YbCl_2$ react completely in ten minutes. It is apparent, however, that presence of any oxygen whatever will lead to side reactions.

The result of experiments when the oxygen and HCl concentrations were varied (Tables II and IV) indicate that both reactions (1) and (2) are important. It is very difficult to get reproducible results under these conditions.

When oxygen was plentiful (Tables I and IV), the reaction went essentially exclusively by reaction (2). The data of Table I show an oxygen absorption somewhat greater than would be expected on the basis of equation (2). This difference also was observed in other experiments which were only semi-quantitative. Tests for Cl_2 or H_2O_2 were negative in all cases; hence, no interpretation can be placed on these unexpected results at present. The general problem will be pursued further in an effort to gain a complete understanding of these interesting reactions.

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