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

Vaporization of Iron(II) Chloride in Bromine

BY LAURENCE E. WILSON[1] AND N. W. GREGORY

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The reaction of bromine with iron(II) chloride has been studied at 261 and 350° by the gas saturation flow method. Results indicate mixed halide molecules to be of major importance in the vapor phase, particularly after small amounts of iron(II) bromide become dissolved in the solid phase.

When iron(II) chloride is maintained at 250–300° in an atmosphere of bromine, transport of the solid to cooler regions of the system is observed, whereas appreciable sublimation of this material in high vacuum does not occur until the temperature is well above 400°.[2] To obtain further information concerning the volatile species responsible for this transport, gas saturation flow studies have been conducted, by passing bromine over solid iron(II) chloride and over mixtures of iron(II) chloride and bromide. From recent studies of the iron(II) chloride–iron(II) bromide system,[3] the iron(II) bromide–bromine system,[4] and the iron(II) chloride–chlorine system,[5] prediction of partial pressures of chlorine, Fe_2Cl_6 (and $FeCl_3$)[6] and of Fe_2Br_6 (and $FeBr_3$) in the equilibrium vapor phase can be made for a given partial pressure of bromine and given activities of the iron(II) halides. From the total amount of iron halide transported in flow experiments the relative importance of mixed halide molecules can now be ascertained.

Experimental Part

Eight flow experiments were conducted in which bromine at a measured pressure was permitted to flow over a solid solution of composition $N_{FeCl_2} = 0.808$ and $N_{FeBr_2} = 0.192$. The total quantity of iron halide removed during these experiments was not sufficient to change this composition appreciably. Four additional experiments were conducted in which bromine passed over a solid sample which, in the initial run, was pure $FeCl_2$. The apparatus, procedure and analytical techniques were essentially the same as have been described in earlier papers.[4,5,7] The measured quantities are shown in Table I. The material (other than bromine) condensed from the gas mixture leaving the reactor was a mixture of iron(III) and iron(II) halides, distinguished by color and place of condensation. The iron(II) phase deposited close to the reactor and, in most cases, was fairly well separated from the iron(III) deposit; the latter was farther along the collector tube and less in quantity. When possible the collector was separated between the two deposits and independent analyses made. The iron(II) deposit was found to contain appreciable quantities of both chlorine and bromine; from total iron and total halogen determinations, the composition was calculated and reported as a mixture of $FeCl_2$ and $FeBr_2$. The iron(III) deposit appeared to be essentially the chloride; amounts were too small to make an accurate determination of any bromide present.

The mixture of $FeCl_2$ and $FeBr_2$ used in the reactor was prepared by subliming $FeCl_2$ onto the walls and permitting equilibration with a precalculated amount of hydrogen bromide prior to initiating the flow experiments. The exchange reaction

$$FeCl_2(s) + 2HBr \rightleftarrows FeBr_2(s) + 2HCl \qquad (1)$$

has been studied in some detail at 400°.[3] Results of this work show that $FeCl_2$ and $FeBr_2$ form a complete series of solid solutions and enable prediction of the composition of the solid mixture from the measured composition of the HCl–HBr equilibrium mixture. This composition was later confirmed by direct analysis.

Discussion

Reaction of bromine with iron(II) chloride might be considered in terms of the simple equation

$$2FeCl_2(s) + Br_2(g) \rightleftarrows Fe_2Br_2Cl_4(g) \qquad (2)$$

by analogy with the behavior of $FeBr_2$ and bromine and of $FeCl_2$ and chlorine. However, because $FeCl_2$ and $FeBr_2$ form solid solutions the exchange reaction

$$FeCl_2(s) + Br_2(g) \rightleftarrows FeBr_2(s) + Cl_2(g) \qquad (3)$$

will be important until the activity of iron(II) bromide becomes significant even though ΔF^0 for (3) is a rather large positive number. Hence it is possible that the vaporization of iron(II) chloride in bromine may be caused largely by the reactions

$$2FeCl_2(s) + Cl_2(g) \rightleftarrows Fe_2Cl_6(g) \qquad (4)$$

and

$$2FeBr_2(s) + Br_2(g) \rightleftarrows Fe_2Br_6(g) \qquad (5)$$

(and the concomitant monomers) with the importance of mixed halide species such as shown in (2) questionable.

The equilibrium constant of reaction 3 can be calculated from known thermodynamic properties of $FeCl_2$ and $FeBr_2$. Thus from the measured bromine pressure the chlorine pressure (small) may be calculated provided the ratio of the activities of the two solid components is known. The activity ratio can be calculated from the hydrogen halide exchange equilibrium data at 400°; however the individual activities are needed for calculation of pressures of Fe_2Cl_6 and Fe_2Br_6. Since the solid solutions showed a fair approximation to ideal behavior in the study of (1), activities have been taken as mole fractions for the purpose of estimating the partial pressures of the simple halides given in Table I. On this basis iron(III) chloride and iron(III) bromide together account for only 10% of the total amount of iron halide transported from the reaction zone in the first eight experiments (this figure is remarkably constant, not changing with bromine pressure or with temperature); the remainder must be attributed to mixed halide molecules.

The collection of large amounts of $FeCl_2$ provides further evidence that the mixed halide species

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(1) National Science Foundation Fellow, 1954–1957.

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(7) A more detailed account of experiments and calculations may be found in the Doctoral Thesis of Laurence E. Wilson, University of Washington, 1957.

TABLE I

GAS SATURATION FLOW DATA. BROMINE OVER SAMPLES OF $FeCl_2$

Expt. no.	°K.	Br_2, press., mm.	Flow rate, cc./min.	Moles Br_2 $\times 10^3$	Material collected during run, Moles Fe coll. $\times 10^5$, Light cond. $FeCl_2$	Light cond. $FeBr_2$	Dark cond.	Total	$\frac{n_t(Fe)}{n_t(Br_2)}$ $\times 10^2$	n(calcd.) $\times 10^5$ Fe_2Cl_6 ($FeCl_3$) c	Fe_2Br_6 ($FeBr_3$) b	$\frac{n_t(Fe)(calcd.)}{n_t(Fe)(obsd.)}\frac{c+b}{c+b+m}$	a ($FeBr_2$) calcd.
Flow experiments over mixture of $FeCl_2$ (N = 0.808) and $FeBr_2$ (N = 0.192)													
1	623.9	214.6	18.6	12.53	21.6	4.95	1.09	27.6	2.20	0.364 (.212)	0.791 (.288)	0.102	
2	621.7	205.3	27.9	11.24	16.06	6.64	...	22.7	2.02	.308 (.181)	.680 (.248)	.106	
3	624.4	208.7	28.2	15.60	24.36	8.77	...	33.1	2.12	.457 (.270)	.991 (.368)	.107	
4	623.2	205.0	26.6	18.24	31.34	8.66	1.84	41.8	2.29	.519 (.307)	1.137 (0.344)	.095	
5	624.5	211.0	2.3	3.39	6.63	1.15	0.75	8.52	2.51	.100 (.059)	.217 (.0804)	.091	
6	621.4	64.2	11.9	3.90	7.53	1.14	0.43	9.10	2.33	.106 (.125)	.234 (.152)	.105	
7	534.7	214.1	11.7	8.24	Not sep. tot. 1.52		0.07	1.59	0.193	.0124 (.0038)	.0574 (.0067)	.094	
8	533.7	193.5	11.5	29.59	4.05	1.20	0.39	5.64	0.190	.0427 (.0135)	.200 (.0242)	.093	
Flow experiments with initial sample (no. 9) pure $FeCl_2$													
9	623.8	213.7	13.9	9.60	40.6	2.81	40.0	83.3	8.68	19.3 (1.4)	0.000439 (.00592)	0.480	0.0052
10	623.8	200.9	13.6	8.86	29.0	3.36	14.3	46.7	5.27	6.75 (0.80)	.00268 (.0169)	.306	.0137
11	621.9	195.4	13.3	9.57	20.0	9.23	7.91	37.1	3.88	3.66 (0.59)	.0104 (.0289)	.214	.0258
12	622.1	208.7	12.7	13.42	Not sep. tot. 37.1		7.70	44.8	3.34	3.52 (0.660)	.0310 (.0570)	.174	.0377

are of major importance in the vaporization process. In gas saturation flow experiments with chlorine over $FeCl_2$,[5] only iron(III) chloride was deposited; hence in the present experiments $FeCl_2$ must be formed by the decomposition of mixed halide molecules. In the bromine–iron(II) bromide case[4] essentially all of the iron(III) bromide, the only important species in the vapor phase, decomposed to $FeBr_2$ and bromine on condensation.

Based on the assumed activity of $FeCl_2$ and the chlorine pressure calculated from the equilibrium constant for (3), predicted amounts of iron(III) chloride vapor are seen (Table I) to be somewhat less than the total amount of iron(III) halide deposit measured. This suggests that a small amount of iron(III) mixed halide condenses with the chloride, although the discrepancy may be due in large part to the difficulty of making a complete separation of the iron(II) and iron(III) deposits.

The amount of iron(III) bromide calculated to be in the vapor phase is only about 25% of the observed iron(II) bromide deposit; the rest is attributed to decomposition products of mixed halide molecules.

In experiment nine the mean activity of $FeCl_2$ may be assumed very near unity. The activity of $FeBr_2$ is initially zero but increases simultaneously with the production of chlorine *via* reaction 2. As expected iron(III) chloride is of increased importance in this experiment, constituting about one-half the total iron halide vaporized from the reactor. A mean value of the activity of $FeBr_2$ in these runs (9–12) was calculated from (3) by assuming all of the iron(III) deposit to be the chloride which then fixes the chlorine pressure; the amount of iron(III) bromide predicted from this estimate is a very small part of the total bromide collected. In runs 10, 11 and 12 the partial pressures of Fe_2Cl_6 and $FeCl_3$ drop markedly; the ratio of the total number of moles of iron to moles of bromine in the vapor phase appears to be approaching that observed in the first eight experiments.

It seems most unlikely that any error introduced by the assumption that the solid solutions are ideal could be so great as to preclude the conclusion that mixed halide species are of major importance in the vaporization process. Even in experiment nine iron chloride only accounts for 50% of the material transported from the reactor.

The composition of the mixed halide species in the vapor phase appears complex. If reaction 2 were the only one to be considered (in addition to (4) and (5)), the iron(II) deposit in the condensation zone should be largely $FeCl_2$ in experiments 9–12 and, relative to the quantity of bromine in the gas mixture, should only be *ca.* 20% larger than in experiments 1–6. Probably all possible species from Fe_2Br_5Cl to Fe_2Br_5Cl, as well as monomeric forms, are of some importance. It may be noted that, under the conditions of these experiments, dimers of iron(III) chloride and of iron(III) bromide are extensively dissociated to monomers. Anticipating a similar behavior for mixed halide species, redistribution of halogens would be facilitated by dissociation–recombination reactions

For molecules to have a significant number of bromine atoms the ratio of Br/Cl pressure must be large. The ratio in experiments 1–5 was approximately 6×10^4.

The decrease of moles of iron halide in the vapor with temperature is more pronounced than in the chloride system. The heats of reactions 4 and 5 are *ca.* 6.44 and 16.3 kcal., respectively; $-2.3R \cdot [\Delta \log n(\text{Fe})/n(\text{Br}_2)/(\Delta 1/T)]$ in the present system is 18.1 kcal. These values are not strictly comparable, however; the latter must be considered as a composite of a number of possible reactions and also does not allow for the difference in degree of dissociation of dimers to monomers at the two temperatures.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Fluoride Complexes of Zinc, Copper and Lead Ions in Aqueous Solution

BY ROBERT E. CONNICK AND ARMINE D. PAUL

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The equilibrium quotient for the reaction $Zn^{++} + HF = ZnF^{+} + H^{+}$ at 25° and an ionic strength of 0.50 has been determined to be $(6.6 \pm 1) \times 10^{-3}$. The corresponding value for cupric ion is $(6.2 \pm 1) \times 10^{-3}$. The reactions written as $M^{+2} + F^{-} = MF^{+}$ have equilibrium quotients of 5.4 ± 1 and 5.0 ± 1 for zinc and copper, respectively, under the same experimental conditions. Extrapolation of the latter values to zero ionic strength gives estimated values of 18 ± 4 and 17 ± 4, respectively, for the equilibrium constants. From measurements at 15 and 35° approximate values for ΔH and ΔS of the above reactions were obtained. The fluoride complex of Pb^{++} was too unstable to be detected unambiguously. An upper limit was set to its stability.

In recent years there has been interest in the stability of complexes formed between metal ions and fluoride ions in aqueous solution. In addition to the importance arising from the relatively high stability of many of these complexes, they should provide a simple series for the testing of any theory of ionic complexing.

The stability constants of the fluoride complexes of only three cations of charge +2 have previously been determined. Therefore it was desirable to extend the measurements to other cations and in particular to some of the elements of the first long series. Zinc, copper and lead were selected for study. Complexing constants previously had been measured for Be^{++},[1,2] Mg^{++} [3] and Sn^{++}.[4]

A potentiometric method[5] was used in which the concentration of the complexed fluoride was determined by measuring the change in fluoride complexing of ferric ion in the same solution. The latter was detected by the ferrous–ferric potential.

Experimental

The apparatus and procedure have been described in detail elsewhere.[3,6,7] Briefly, three half-cells A, B and C were prepared for each experiment with the same initial concentrations of $Fe(ClO_4)_3$, $Fe(ClO_4)_2$ and $HClO_4$. Half-cell A contained in addition a known concentration of zinc, copper or lead perchlorate. The ionic strengths of all were adjusted to 0.500 *M* with sodium perchlorate and the volumes were equal. To half-cells A and B were added measured volumes of 0.500 *M* sodium fluoride and the potentials of A–C and B–C were measured after each addition. Correction was made for the small initial potentials with no added fluoride which averaged 0.20 millivolt for the experiments.

Stock solutions of zinc perchlorate, cupric perchlorate and plumbous perchlorate were prepared by solution of the corresponding oxide in perchloric acid. The preparation of the other solutions has been given previously.[7] All concentrations are expressed in moles per liter, *M*, at room temperature.

The data for a typical experiment are shown in Table I. The potentials in the second and third columns are in millivolts, mv. In Table II are given the initial concentrations and highest stoichiometric fluoride concentrations, (ΣF^{-}), for all of the experiments. The complete data for the experiments may be found elsewhere.[8]

TABLE I

COMPLEXING OF ZINC ION BY FLUORIDE ION AT 25°

Initial concentrations: $HClO_4 = 0.005338$ *M*; $Zn(ClO_4)_2 = 0.08676$ *M*; $Fe(ClO_4)_2 = 0.0002221$ *M*; $Fe(ClO_4)_3 = 0.0006838$ *M*; $NaClO_4 = 0.2296$ *M*. Ionic strength = 0.5000 *M*; initial vol. = 110.06 ml.; NaF = 0.5000 *M*.

NaF added to cells A and B (ml.)	E_{B-C} (mv.)	E_{A-C} (mv.)	$\bar{n}$	(HF)/(H⁺)
0.0489	8.65	8.26	0.00012	0.00272
.0978	19.51	18.91	.00014	.00888
.1467	32.43	31.57	.00017	.01532
.1956	46.32	45.15	.00021	.02740
.2445	59.07	58.02	.00022	.04312
.2934	71.97	70.23	.00030	.0628
.3423	83.42	81.05	.00056	.0849
.3912	93.98	90.70	.00082	.1088
.4648	108.12	105.41	.00109	.1545
.5384	120.84	116.46	.00118	.1974
.6120	132.14	127.71	.00154	.2500
.6856	142.13	136.12	.00250	.2961
.7592	151.28	142.19	.00370	.3333

Analysis of Results

The interpretation of the data follows that of references 3 and 7. The difference between the total fluoride concentrations in the sample half-cell A and the reference half-cell B at the same potential equals the concentration of fluoride com-

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