ments to check the adequacy of this model for use in radiation chemistry. Work is now in progress to determine its usefulness in the interpretation of experimental results. Later papers of this series will present these studies.

It is known that all particles do not have an ionization density high enough to form a continuous track. The present model breaks down when the average distance between the ions formed by the primary particle exceeds the parameter b. Possibly a second simple model can be constructed to describe these cases.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Action of Liquid Ammonia Solutions of Potassium and Potassium Amide upon Iron(II) Bromide[1]

BY GEORGE W. WATT AND W. A. JENKINS, JR.[2]

Treatment of iron(II) bromide with potassium in liquid ammonia at −33.5° yields an ammonia-insoluble product consisting of elemental iron, iron(I) nitride, and one or more products of the interaction of iron(II) bromide and potassium amide. The iron produced in these reactions is pyrophoric, does not contain adsorbed hydrogen, has a surface area of 8 m.^{2}/g., and is inactive as a catalyst for the hydrogenation of certain olefins at 30° and a hydrogen pressure of 2 atm.

The experiments described in this paper represent a continuation of studies on the reduction of salts of Group VIII elements to the corresponding metals by means of solutions of metals in liquid ammonia.[3] In these studies, emphasis is placed upon the properties of the reduction products, particularly with reference to their activity as hydrogenation catalysts.

Experimental

Materials.—With the exception noted below, all chemicals used in this work were reagent grade products used without further purification or were the same as those described previously.[3]

Iron(II) bromide was used in the form of the 6-ammonate which was prepared by a method that will be described elsewhere.[4]

Anal. Calcd. for $FeBr_2 \cdot 6NH_3$: Fe, 17.6; NH_3, 32.1. Found: Fe, 17.9; NH_3, 32.2.

Experimental Methods.—Unless otherwise specified, equipment and techniques employed were the same as those described earlier.[3] Reactions involving ammonia solutions of potassium were carried out in an apparatus of the type described by Watt and Moore[5]; those employing ammonia solutions of potassium amide were effected in equipment described by Watt and Keenan.[6] Electron photomicrographs were obtained using an RCA Type EMU-1 electron microscope; samples in Parlodion film were mounted on 200 mesh screen.[7]

The Reaction between Iron(II) Bromide and Potassium.—In a typical case, 2.932 g. of iron(II) bromide 6-ammonate suspended in 25–30 ml. of anhydrous liquid ammonia was treated with 1.209 g. of potassium ($K/FeBr_2 = 3.35$) added in one portion. All of the potassium reacted within 10 sec., hydrogen evolution was continuous throughout the total reaction time, and the bromide was converted to a black finely divided solid. The pale yellow supernatant solution was removed, the solid washed five times with 25-ml. portions of ammonia, resuspended in 25–30 ml. of ammonia, and treated with an additional 0.598 g. of potassium ($K/FeBr_2 = 1.66$). Again, hydrogen evolution was continuous, but there was no visual evidence of change in the solid phase. The ammonia-insoluble solid was washed with liquid ammonia until the washings were free of bromide ion and thereafter dried for 20 hr. at room temperature and a pressure of 0.1 mm. The resulting black solid was highly pyrophoric; qualitative tests for bromide ion were negative. Data relative to these reactions are given in Table I; variation in reaction ratios and mode of addition of potassium failed to alter appreciably the composition of the ammonia-insoluble products.

TABLE I

REDUCTION OF IRON(II) BROMIDE WITH POTASSIUM

$FeBr_2 \cdot 6NH_3$, g.	K, g.	$K/FeBr_2$	H_2, cc.	Insoluble product Fe, %	N, %
2.264	0.656[a]	2.36	83.7	76.6	6.2
2.932[b]	1.209	3.35	225.6		
	0.598	1.66	121.6	80.6	5.7
3.020	.846	2.28	106.4		
	.848	2.28	209.4	80.5	5.0
3.117[c]	.862	2.21	108.0		
	.947	2.47	211.9	82.3	7.1
2.243[d]	.875[a]	3.40	153.0	84.6	3.6

[a] One addition of potassium. [b] The insoluble product was analyzed for potassium. Found: 9.7%; total accounted for, 96.0%. [c] Potassium content of insoluble product, 6.5%; total accounted for, 95.9%. [d] Initial volume was 12–15 ml. rather than 25–30 ml.

The Reaction between Iron(II) Bromide and Potassium Amide.—In the course of efforts to identify products formed in the reduction of iron(II) bromide with potassium, the reaction between this salt and potassium amide was studied. A suspension of 2.702 g. of iron(II) bromide 6-ammonate in 50 ml. of ammonia was treated with 10 ml. of ammonia solution containing the potassium amide equivalent to 0.719 g. of potassium. The bromide was immediately and completely converted to a black insoluble solid which was washed and dried as described above. This product also was markedly pyrophoric.

Anal. Found: Fe, 61.0; N, 15.9; K, 8.7.

Preparation of Potassium Amide.—In order to obtain samples for X-ray diffraction patterns, potassium amide was prepared by the iron-catalyzed interaction of potassium and liquid ammonia.

Anal. Calcd. for KNH_2: K, 70.5. Found: K, 69.9.

X-Ray Diffraction Patterns.—As a means of identifying the products of the reduction of iron(II) bromide, X-ray

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[1] This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

[2] Radiation Laboratory, The University of California, Berkeley, California.

[3] G. W. Watt, W. F. Roper and S. G. Parker, THIS JOURNAL, forthcoming publication.

[4] G. W. Watt and W. A. Jenkins, Jr., "Inorganic Syntheses," Vol. IV.

[5] G. W. Watt and T. E. Moore, THIS JOURNAL, **70**, 1197 (1948).

[6] G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

[7] The assistance of Mr. L. L. Antes is gratefully acknowledged.

diffraction patterns were obtained for these products, the product of the interaction of iron(II) bromide and potassium amide, and potassium amide. Except for the latter, unsatisfactory patterns resulted from the use of Cu $K\alpha$ radiation, but satisfactory patterns were obtained using Mo $K\alpha$ radiation (Zr filter; 80 kv. and 20 ma.; exposure time, 22–24 hr.; samples mounted in thin-walled Pyrex capillaries and rotated at 2 r.p.m.). Typical data are given in Tables II and III.

TABLE II

X-RAY DIFFRACTION DATA

Prod. from FeBr$_2$ + K	Fe[a]		Fe$_3$N[a]		Prod. from FeBr$_2$ + KNH$_2$
d	*d*	I/I_1	*d*	I/I_1	*d*
2.97					2.88
2.54					2.43
2.33			2.38	0.20	
2.19			2.19	0.25	
2.04	2.05	1.00	2.09	1.00	
1.77					1.76
					1.83
1.59			1.61	0.25	
1.47	1.43	0.46			
1.34					
1.29					
1.23			1.24	0.25	1.22
1.16	1.16	0.54	1.16	.20	
			1.14	.10	
1.09			1.09	.03	
			1.04	.05	

[a] Data from A.S.T.M. Index of X-ray diffraction patterns.

TABLE III

X-RAY DIFFRACTION DATA FOR POTASSIUM AMIDE

d	I/I_1	*d*	I/I_1
3.86	0.09	1.94	0.10
3.53	0.16	1.85	.16
3.01	1.00	1.75	.06
2.71	0.44	1.65	.10
2.43	.13	1.41	.09
2.23	.14	1.34	.05
2.07	.19	1.10	.05

Thermal Decomposition of Reduction Products.—In a typical experiment involving methods described previously,[8] 0.236 g. of a product from the reduction of iron(II) bromide with potassium was heated slowly to 550° and maintained at this temperature for 3 hr. The total volume of gas liberated amounted to 12.4 cc. and was found to consist of 9.9 cc. of nitrogen (4.06×10^{-4} mole), 2.5 cc. of ammonia (1.02×10^{-4} mole), and only traces if any hydrogen. The total nitrogen content of the solid sample calculated on the basis of these data is 5.4%, as compared with the value (Table I) of 5.0% found by direct analysis. In similar experiments equally good or better correlations were obtained in terms of total gases liberated in relation to iron content determinations made before and after thermal decomposition.

Surface Area Measurements.—By a modification[3,8] of the method of Brunauer, Emmett and Teller, the surface area of the product from the reduction of iron(II) bromide with potassium was found to be 8.3 sq. m./g. Electron photomicrographs showed reasonably uniform particle size with an estimated average diameter of 0.1 micron. On the assumption of spherical particles, the calculated surface area is 7.6 sq. m./g.

Catalytic Activity.—As evaluated under conditions described in detail elsewhere,[3] products of the reduction of iron(II) bromide with potassium were found to be entirely inactive as catalysts for the hydrogenation of hexene-1, allyl alcohol and propargyl alcohol. On the other hand, it was observed qualitatively that these products are exceptionally active catalysts for the reaction between potassium and liquid ammonia.[9]

Discussion

The data in Table I show that reduction of iron(II) bromide with potassium yields products in addition to elemental iron and that the gross composition of the ammonia-insoluble reduction products varies over only a fairly narrow range despite considerable variation in the reaction conditions employed.[10] Absence of bromide ion in the insoluble products shows that the conversion of the iron(II) bromide is complete. The most probable interference with complete reduction to elemental iron is the competing interaction of iron(II) bromide and potassium amide resulting from the reaction between potassium and the solvent under the pronounced catalytic influence of iron formed in the primary reduction reaction.

The anticipated initial product of the reaction between iron(II) bromide and potassium amide is iron(II) amide, but if the gross ammonia-insoluble product consisted of elemental iron and iron(II) amide, complete thermal decomposition should yield at least 4 moles of ammonia per mole of nitrogen, providing hydrogen is not formed during the decomposition. The fact that the present experiments showed that thermal decomposition of the reduction products gave 4 moles of nitrogen per mole of ammonia strongly suggested the presence of a nitride, and the presence of Fe$_3$N was confirmed by the X-ray diffraction data given in Table II. These data show also the presence of elemental iron, one or more products arising from the interaction of iron(II) bromide and potassium amide, and (together with the data of Table III) the absence of potassium amide. The only two diffraction maxima ($d = 1.34$ and 1.29) not accounted for by the above products do not correspond to any of the lines for possible contaminants such as potassium bromide or potassium hydroxide.

On the basis of information presently available, it has not been found possible to deduce a reasonable mechanism for the formation of Fe$_3$N. Postulation of a mechanism to account for this product[11] is rendered especially difficult because this substance is not formed in the reaction between the bromide and potassium amide (see Table II). Bergstrom[12] has studied the reaction between iron(II) salts and potassium amide at 25° and his results, although not conclusive, suggested the formation of Fe$_3$N$_2$ and an unspecified potassium compound. We were unable to obtain any evidence for the presence of this particular nitride and it appears that the presence of potassium is more likely attributable to the presence of one or more salts of amphoteric bases comparable to those postulated as products of reactions between nickel(II) amide and potassium amide.[3]

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[8] H. E. Ries, Jr., R. A. Van Nordstrand and W. E. Kreger, THIS JOURNAL, **69**, 35 (1947).

[9] *Cf.* W. M. Burgess and H. L. Kahler, Jr., THIS JOURNAL, **60**, 189 (1938).

[10] In numerous additional experiments for which data are not included here, the iron content of the ammonia-insoluble products was found to range from 79 to 81%.

[11] This nitride has been reported previously as a product of the interaction of an equilibrium mixture of ammonia and hydrogen with iron at 400–440° [S. Brunauer, M. E. Jefferson, P. H. Emmett and S. B. Hendricks, THIS JOURNAL, **53**, 1778 (1931)].

[12] F. W. Bergstrom, *ibid.*, **46**, 2631 (1924).