

TABLE II
 THE MASS SPECTRUM OF ISOBUTYLENE^a

$m/e =$	56	55	54	53	52	51	50	49	48	
$V_{ion} =$	$C_4H_8^+$	$C_4H_7^+$	$C_4H_6^+$	$C_4H_5^+$	$C_4H_4^+$	$C_4H_3^+$	$C_4H_2^+$	C_4H^+	C_4^+	
30	100	33.3	3.9	
50	103	40.8	4.9	11.0	2.5	8.6	8.4	1.6	0.22	
70	108	43.6	4.8	10.8	2.3	8.5	9.7	2.6	.38	
100	107	45.1	5.2	11.2	2.2	8.3	10.3	3.2	.54	
$m/e =$	42	41	40	39	38	37	36			
$V_{ion} =$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$	$C_3H_2^+$	C_3H^+	C_3^+			
30	16.1	175	16.9	50.1			
50	18.2	218	21.4	83.8	11.3	5.1	0.25			
70	18.7	231	22.4	87.4	12.7	7.5	.88			
100	17.2	243	22.6	87.0	12.7	8.1	1.33			
$m/e =$	29	28	27	26.5	26	25.5	25	24	15	14
$V_{ion} =$	$C_2H_5^+$	$C_2H_4^+$	$C_2H_3^+$	$C_2H_2^+$	C_2H^+	$C_2H_3^{2+}$	C_2H^+	C_2^+	CH_3^+	CH_2^+
30	18.8	42.2	21.4	1.4	0.09
50	28.1	59.5	55.1	..	11.0	0.5	5.5	1.9
70	29.1	63.3	56.6	..	13.9	6.5	..
90	29.9	64.8	55.7	0.22	14.3	2.8	2.3	0.25	6.7	..

^a No correction for C^{13} in its natural abundance, 1.1%.

shows its generic relationship to isobutane. The manner in which the spectrum changes with electron energy is illustrated in Fig. 2.

Summary

The results of a mass-spectroscopic investigation of the ionization and dissociation of propylene, propane and isobutylene by electron impact

are reported. The vertical ionization potentials of these three molecules were found to be $I_v(C_3H_6) = 9.8 \pm 0.1$ e. v., $I_v(C_3H_8) = 11.2 \pm 0.1$ e. v., and $I_v(i-C_4H_8) = 8.9 \pm 0.1$ e. v. The significance of some of the observed appearance potentials of ions in the isobutylene spectrum is discussed. The mass spectrum of isobutylene is given in detail.

EAST PITTSBURGH, PA.

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Reactions of Cobalt(III), Cobalt(II), and Iron(II) Oxides in Liquid Ammonia

BY THOMAS E. MOORE AND GEORGE W. WATT

With the single exception of the reduction studies described by Watt and Fernelius,¹ the only available information relative to reactions of metal oxides in liquid ammonia consists of a number of incidental qualitative observations² together with certain partially erroneous³ results on reactions of the acidic oxides of chromium, molybdenum and tungsten published by Rosenheim and Jacobssohn.⁴ The experiments described in this paper represent the first of a series of studies initiated for the purpose of providing information on the behavior of metal oxides toward liquid ammonia and liquid ammonia solutions of ammonium salts (acids), alkali amides (bases) and strong reducing agents.

(1) Watt and Fernelius, *THIS JOURNAL*, **61**, 2502 (1939).

(2) For primary references see Fernelius and Watt, *Chem. Rev.*, **20**, 213 (1937).

(3) Davies and Watt, forthcoming publication.

(4) Rosenheim and Jacobssohn, *Z. anorg. allgem. Chem.*, **50**, 297 (1906).

Experimental

Methods.—Unless otherwise indicated, the experimental techniques were those employed by Watt and Fernelius.¹ All analytical data were obtained using standard methods of analysis.

Materials.—All materials were carefully dried before use. All chemicals other than the oxides were either reagent grade materials or consisted of commercial products which were subjected to careful purification.

Cobalt(III) Oxide.—Baker "reagent grade" oxide was dried for ten hours at 100° and used without further treatment.

Anal. Calcd. for Co_2O_3 : Co, 71.06. Found: Co, 70.75.

Cobalt(II) Oxide.—The most satisfactory method for the preparation of this material was found to be that of Le Blanc and Möbius.⁵ However, the use of this method in the original or in modified form, as well as other known methods,⁶ failed to yield a product of the desired composition.

(5) Le Blanc and Möbius, *Z. physik. Chem.*, **A142**, 151 (1929).

(6) For details see Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1937, Vol. XIV, pp. 558-563.

TABLE I
 REACTIONS WITH AMMONIUM SALTS AT 100°

Oxide		Salt		NH ₃ , ml.	Time, hr.	Oxide dissolved	
Formula	Wt., g.	Formula	Wt., g.			Wt., g.	%
Co ₂ O ₃	0.4186	NH ₄ Cl	11.00	20	36	0.0000 ^a	0.00
Co ₂ O ₃	.4979	NH ₄ NO ₃	36.80	30	36	.0000 ^a	.00
CoO	.1960	NH ₄ Cl	12.90	20	20	.0163	8.32
CoO	.1896	NH ₄ NO ₃	25.80	25	20	.0083	4.38
FeO	.4596	NH ₄ Cl	11.50	20	24	.0082	1.80
FeO	.3878	NH ₄ NO ₃	20.00	25	24	.0049	1.26

^a The aqueous extracts failed to give positive tests for cobalt with α -nitroso- β -naphthol reagent which, according to Atack [*J. Soc. Chem. Ind.*, **34**, 641 (1915)] will detect one part of cobalt in one million parts of solution.

tion. The best product obtained contained 75.0% cobalt as compared with a calculated cobalt content of 78.7% for CoO.

Iron(II) Oxide.—Kahlbaum iron(II) oxide was used. The chief impurity in this material was found to be elemental carbon. *Anal.* Calcd. for FeO: Fe, 77.71. Found: Fe, 73.64. The method of Chaudron⁷ and other known methods⁸ failed to provide a product of purity greater than that of the Kahlbaum product.

Reactions with Liquid Ammonia.—Weighed quantities of the oxides were allowed to remain in contact with a large excess of liquid ammonia in sealed tubes at 25° over a period of twenty-four hours. After removal of the ammonia, the oxides were shown by analysis to have undergone no change in composition. For example, a sample of iron(II) oxide (0.5388 g.) contained 73.81% iron before treatment and was found to contain 73.84% iron after treatment with ammonia.

Reactions with Ammonium Salts.—Weighed samples of the oxides were treated with liquid ammonia solutions containing large excesses of ammonium salts in sealed "Pyrex" tubes which were heated to 100° in an autoclave of the type described by Bergstrom.⁹ After removal of the solvent, unchanged oxides of cobalt were separated by extraction with water. Both the soluble and insoluble portions were thereafter analyzed for cobalt. Unchanged iron(II) oxide was separated on the basis of its insolubility (as shown by preliminary experiments) in 1.2 *N* hydrochloric acid solution. In each case the identity of the unchanged oxide was established by analysis. Results of these experiments are given in Table I.

Reactions with Potassium Amide.—The methods used were those employed by Watt and Fernelius¹⁰ with the exception that the stopcocks were removed from the Faraday tubes prior to mixing the reactants. This procedure was found necessary in order to avoid loss of solvent due to leakage over the long periods of time and under the pressures developed due both to solvent vapor pressure and that of gases evolved during the reactions. This practice, however, suffers a disadvantage in that it does not permit of the ready collection and identification of insoluble gaseous reaction products.

Cobalt(III) Oxide.—When treated with a liquid ammonia solution of potassium amide (from 1.3110 g. of potassium) at room temperature for ten days, cobalt(III) oxide (0.5847 g.) reacted slowly to form an apparently

complex mixture of insoluble products. The only product identified was elemental cobalt which was deposited on the walls of the tube in the form of a thin bright metallic mirror. This deposit was dissolved by hydrochloric acid with evolution of hydrogen. In any case, the quantity of elemental cobalt isolated was small; for example, in a typical case 0.0085 g. of cobalt was separated from the heterogeneous insoluble products.

Cobalt(II) Oxide.—Treatment of 0.2984 g. of cobalt(II) oxide with an ammonia solution of the potassium amide from 1.1847 g. of potassium over a period of ten days at room temperature resulted in a three-fold increase in the bulk of the insoluble solid phase, the liberation of small quantities of an insoluble gas, and the production of an intensely green colored ammonia solution. Following separation of the ammonia solution from the insoluble material, the former was cooled to -70°, whereupon deep blue crystals separated together with crystals of potassium amide. Attempts to separate the blue crystalline product by fractional crystallization from ammonia were unsuccessful. The heterogeneous insoluble material reacted with hydrochloric acid with liberation of hydrogen. A representative sample of this material (0.3231 g.) was found to contain: N, 5.76; K, 17.49; Co, 58.94.

Iron(II) Oxide.—Potassium amide (from 1.4111 g. of potassium) in liquid ammonia solution was allowed to remain in contact with iron(II) oxide (0.4286 g.) at room temperature over a period of ten days, without any visible evidence of reaction. However, the insoluble black solid phase (after thorough washing with liquid ammonia) was found to contain: N, 7.73; K, 5.40; Fe, 73.80.

Reduction Reactions.—Cobalt(III) and iron(II) oxides were reduced by liquid ammonia solutions of potassium at 0° using the same procedures as those employed by Watt and Fernelius¹ with the exception that provision was made for the collection of hydrogen resulting from the interaction of potassium and ammonia under the catalytic influence of the oxides and/or reduction products. In effecting several reactions involving the heterogeneous reduction of a given oxide, efforts were made (but none too successfully) to control (a) the concentration of the potassium solutions, (b) the rate of addition of the reducing agent, and (c) the uniformity of agitation of the reactants. After washing each insoluble product, the tube was evacuated at 80-90° at an oil pump to remove adsorbed ammonia and hydrogen.

Unchanged cobalt(III) oxide was separated from the insoluble reduction products on the basis of its insolubility (as shown by preliminary experiments) in 1 *N* hydrochloric

(7) Chaudron, *Ann. chim.*, **16**, 272 (1921).

(8) Mellor, "A Comprehensive Treatise," 1937, Vol. XIII, p. 709.

(9) Bergstrom, *J. Org. Chem.*, **2**, 424 (1937).

(10) Watt and Fernelius, *THIS JOURNAL*, **61**, 1692 (1939).

acid. It was found impossible to separate iron(II) oxide by any similar procedure even when buffered acetic acid solutions were employed. Consequently, the gross insoluble product was analyzed as such. Data relevant to reduction reactions are given in Tables II and III.

TABLE II^a

REDUCTION OF COBALT(III) OXIDE BY POTASSIUM IN LIQUID AMMONIA AT 0°

Co ₂ O ₃ , g.	Potassium G.	Equiva- lents	H ₂ , cc. at S. T. P.	Co (g.) in acid-soluble ^b product	Reduc- tion, ^c %
0.5248	0.7559	6.1	157	0.1860	50.1
.2572	0.7429	12.0	163	.1328	74.5
.2569	1.4453	23.9	341	.1700	93.6

^a Data recorded in this table represent the average results of at least three independent experiments which agreed as well as could be expected in view of the variables previously indicated. ^b In each case, the *acid-insoluble* product was shown to consist of unchanged cobalt(III) oxide. For example, *Anal. Calcd.* for Co₂O₃: Co, 70.75. Found: Co, 70.59. ^c Based on soluble cobalt.

TABLE III

REDUCTION OF IRON(II) OXIDE BY POTASSIUM IN LIQUID AMMONIA AT 0°

FeO, g.	Potassium G.	Equiva- lents	Analysis of insoluble products ^a Weight, g.	Fe, %	K, %
0.8732	0.9590	1.41	0.8914	72.01	4.42
.6112	1.3361	2.81	.6015	74.52	2.20
.4659	2.0496	5.66	.4594	74.04	2.73

^a Analysis showed that nitrogen was absent or present only in traces.

Discussion

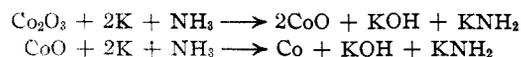
With regard to the preparation of the oxides of divalent cobalt and iron, this study has confirmed conclusions reached by earlier investigators^{6,8} to the effect that pure compounds corresponding to the formulas CoO and FeO cannot be produced by at present available methods. Apparently the most that can be accomplished is the preparation of materials in which the lower oxides predominate.

That these oxides, and cobalt(III) oxide as well, are insoluble in and unreactive toward liquid ammonia is in full accord with the earlier observations of Franklin and Kraus.¹¹ In their reactions with ammonium salts, the behavior of the oxides included in this work parallels their behavior toward the corresponding aquo acids. If it may be assumed that the ability of a liquid ammonia solution of an onium type salt to dissolve metal oxides may be looked upon as a true manifestation of acidity, then it may be concluded that the acidic solutions employed in this investigation are of considerably lesser acidic strength

than the corresponding aqueous acid solutions and that (in liquid ammonia) ammonium chloride is a stronger acid than ammonium nitrate. That cobalt(III) oxide proved to be entirely unreactive even at 100° is not surprising since this oxide is dissolved only very slowly by hot concentrated hydrochloric acid.

The reactions with potassium amide proved to be slow, very complex, and probably incomplete. The presence of elemental cobalt among the reaction products provides new evidence of the reducing action of the amide ion. The insoluble heterogeneous products also may have contained unchanged oxides, lower oxides, potassium hydroxide, and possibly salts of amphoteric bases resulting from the interaction of the reduced metals and potassium amide.¹² That mixtures were produced is shown by the fact that in every one of a considerable number of cases, the analytical data failed to conform to the composition of any known or probable compound.

The reduction of cobalt(III) oxide is believed to occur in two stages



This view is supported by the physical appearance of the products obtained when six, twelve and twenty-four equivalents of potassium are used, and by the fact that the insoluble product obtained using six equivalents of potassium is dissolved by hydrochloric acid without appreciable liberation of hydrogen whereas hydrogen is evolved extensively when the products obtained using twelve or twenty-four equivalents of potassium are treated similarly. Furthermore, the weights of potassium amide found by analysis¹³ of the ammonia-soluble products were found to agree only with the theoretically possible weights of amide corresponding to the assumption that cobalt(II) oxide is the principal product of reactions involving six equivalents of potassium. Similarly, the weights of potassium amide found in reactions involving twenty-four equivalents of potassium agree only with values calculated on the assumption of essentially complete reduction to elemental cobalt. Of the possible bases for the determination of extent of reduction, analysis for soluble cobalt is believed to be the most reliable. Reproducible values for hydrogen evolved by the catalyzed reaction between potassium and

(12) Cf. Bergstrom and Fernelius, *Chem. Rev.*, **12**, 43 (1933).

(13) Data available but not included in this paper.

(11) Franklin and Kraus, *Am. Chem. J.*, **20**, 827 (1898).

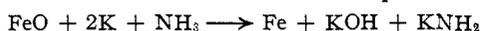
TABLE IV
THE EXTENT OF REDUCTION OF IRON(II) OXIDE BY POTASSIUM

K (equivalents)	Insol. prod., g.	KOH, ^a g.	Cor. wt. of insol. prod., ^b g.	Fe, g.	FeO, g.	Reduction, %	FeO accounted for, %
1.41	0.8914	0.0565	0.8349	0.1050	0.7299	16.4	99.9
2.81	.6015	.0190	.5825	.0742	.5083	16.5	99.5
5.66	.4594	.0180	.4414	.0582	.3832	17.1	99.2

^a Calculated on the basis of potassium found by analysis of the insoluble products. ^b Corrected by subtraction of the weight of KOH—column 3.

ammonia could not be obtained due probably to leakage around the stopcocks and to the absorption of hydrogen by the reduction products.¹⁴ Calculations based on analyses of ammonia-soluble products also led to divergent results probably as a result of difficulty encountered in complete removal of the solvent ammonia.

Iron(II) oxide is incompletely reduced to elemental iron in accordance with the equation



If it is assumed that the insoluble product consists of iron, iron(II) oxide, and potassium hydroxide, the values given in Table IV may be calculated from the data of Table III. The validity of this interpretation is supported by the excellent agreement between the weights of iron(II) oxide used initially and that accounted for in terms of the analytical data.

The fact that the extent of reduction of iron(II) oxide does not increase appreciably [as in the case of cobalt(III) oxide] with increase in the quantity of potassium used provides evidence that iron(II) oxide (or its reduction products) is a much more active catalyst for the conversion of potassium to potassium amide than is cobalt(III) oxide (or its reduction products). Although no rate measurements were made, it was observed

that evolution of hydrogen is, in either case, relatively slow until some of the oxide has been reduced. Hence, it seems likely that the observed catalytic activity is to be attributed more to the reduction products than to the parent oxides.

Summary

1. Cobalt(III), cobalt(II) and iron(II) oxides are insoluble in and unreactive toward liquid ammonia at room temperature.

2. Cobalt(III) oxide is unreactive toward liquid ammonia solutions of ammonium chloride or nitrate at 100° while, under the same conditions, cobalt(II) and iron(II) oxides are partially dissolved.

3. Cobalt(III), cobalt(II) and iron(II) oxides react slowly with liquid ammonia solutions of potassium amide at room temperature to form complex mixtures of soluble and/or insoluble products.

4. Cobalt(III) oxide is reduced to cobalt(II) oxide and finally to elemental cobalt by liquid ammonia solutions of potassium at 0° to an extent dependent upon the Co₂O₃/K ratio. Under the same conditions, iron(II) oxide is reduced to elemental iron only to a very limited extent.

(14) Cf. Burgess and Eastes, *THIS JOURNAL*, **63**, 2674 (1941).