in the usual way, it was balanced against a column of mercury in a barometer with electrical contacts to indicate, by a neon light, the attainment of the preset pressure, about 70 cm. A change of 0.01 ml. in the position of the mercury meniscus in the 25-ml. buret was easily detected with this arrangement. The apparatus would be more satisfactory, however, if the entire gas volume were thermostated.

The solvent was degassed by alternately opening to the vacuum pump for 5–15 sec. and then stirring very rapidly to produce cavitation. This was repeated 5 to 10 times. In the solubility measurement itself, gas which had been previously saturated with solvent vapor, was admitted to the saturation vessel, holding about 80 ml. of soln., and with 5 to 10 ml. remaining space, and volume–time measurements were taken and extrapolated back to the time the gas was admitted. Then the stirrer was turned on and driven very fast, producing a slightly (*ca.* 1%) supersaturated solution. The approach to equilibrium was then followed from each direction while stirring as rapidly as possible without producing cavitation and bubbles. The Ostwald solubility coefficient was calculated from the eq. $l = V_g T_s / V_s T_g$ where V_g and V_s are volumes of gas absorbed (the volume change in the buret) and volume of solution, respectively, and T_s and T_g are the absolute temperatures of the solution and of the gas in the buret.

The degree of internal consistency of the results and of agreement with the work of Lannung indicates that the measured Ostwald coefficients are accurate within 3%.

The Partition of OsO_4.—Nitromethane which had been washed with acid and Cl_2 water was equilibrated at 25° with aqueous solutions of OsO_4 containing added acid and Cl_2. The acid and Cl_2 were found to prevent the reduction of OsO_4 by trace impurities in the system. Variation of the amounts of added acid and Cl_2 up to the concentrations employed (0.05 and 0.005 M, respectively) had no effect upon the partition ratio within the accuracy of these measurements. In some cases equilibrium was approached from the opposite direction with consistent results.

Aliquots of the equilibrated phases were added to 3.0 ml. of a mixture of 50 ml. of saturated thiourea solution and 200 ml. of 6 M HCl and made up to 5.00 ml. with water. Five to ten minutes after mixing the two solutions from a single partition expt. were examined with a Beckman spectrophotometer (DU) at the absorption maximum of the pink complex[18] formed by the action of the thiourea on the OsO_4. The molar decadic extinction coefficients at the maxima were: at 481 mμ, ϵ 3850, and at 535 mμ, ϵ 2890. These were somewhat variable with the age of the reagent solution and the time of standing after the color developed, but aliquots were taken in such a way that nearly the same intensity of color developed in the analysis of each phase and, incidentally, the nitromethane concentrations were roughly the same in the resulting solutions. In this way the analytical errors partly cancel out in calculating the partition coefficients. The 481 mμ results are presented in Fig. 1. The measured partition ratio is 14.9 = molarity of $MeNO_2$ layer/molarity of H_2O layer. The measurements at the longer wave length gave the same result.

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[18] F. J. Welcher, "Organic Analytical Reagents," IV, D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 183.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Reactions of Some Metal Salts with Alkali Superoxides in Liquid Ammonia

BY DALE L. SCHECHTER AND JACOB KLEINBERG

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The reactions of a variety of anhydrous metal salts with potassium and sodium superoxides in liquid ammonia medium have been studied. Where the reactants are brought together in stoichiometric proportions required for metathesis and reaction occurs, the superoxide ion is unstable and solid superoxides cannot be isolated. Lithium, magnesium, calcium, cadmium and zinc nitrates are converted to solid products containing large proportions of the corresponding peroxides. Except for lithium and calcium peroxides, which have been previously prepared in small yield by direct oxidation of liquid ammonia solutions of the metals, this is the first time that these peroxides have been prepared in the anhydrous state. Decomposition of peroxide, followed by ammonolysis of the "normal" oxide, and oxidation of amide to nitrite and hydroxide, also occur. Aluminum chloride tetraammoniate reacts with sodium superoxide in a 1:6 mole ratio to yield a product containing sodium, aluminum and "non-reducible anion base" in the same ratio as that found in Na_3AlO_3. Copper(II) nitrate tetraammoniate reacts with either sodium or potassium superoxide to form products consisting largely of monoxide, hydroxide and copper(II) amide.

Attempts in this Laboratory to prepare barium and strontium superoxides in liquid ammonia by metathetic reactions involving alkali metal superoxides, although unsuccessful, have led to the isolation of a mixed superoxide–peroxide of the composition $(2K^+, Ba^{++}, 2O_2^-, O_2^=)$, and also to the formation of anhydrous barium and strontium peroxides of relatively high purity.[1] The present communication describes the results of reactions in liquid ammonia between a variety of anhydrous salts [$LiNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2 \cdot 6NH_3$, $Zn(NO_3)_2 \cdot 4NH_3$, $Cd(NO_3)_2 \cdot 6NH_3$, $AlCl_3 \cdot 4NH_3$ and $Cu(NO_3)_2 \cdot 4NH_3$] and sodium and potassium superoxides. In every case where the reactants are mixed in the stoichiometric proportions necessary for metathesis and reaction occurs, the superoxide ion is unstable and decomposes with the liberation of oxygen. Although no new superoxides or mixed superoxides–peroxides have been obtained, solid products containing large proportions of the anhydrous peroxides of lithium, magnesium, calcium, cadmium and zinc have been isolated.

Experimental

Materials.—"Refrigeration grade" Spencer ammonia was dried before use by condensation into a stainless steel tank containing metallic sodium. The head of this tank, which had an ordinary needle valve as outlet, was removable, permitting the addition of the drying agent. The potassium and sodium superoxides employed (98 and 94% purity, respectively) were supplied by the Callery Chemical Co., Callery, Pa. Baker Analyzed grade anhydrous lithium nitrate was used without further purification. Anhydrous calcium nitrate was obtained by dehydration of the tetrahydrate at 130–140° for 4 hr., followed by heating in a vacuum oven at 70° and 0.3 mm. pressure for 19 hr. Aluminum chloride tetraammoniate was prepared by passage of a slow stream of mixture of gaseous ammonia and dry nitrogen (roughly one volume to five) through an erlenmeyer flask containing a few grams of Baker Analyzed anhydrous chloride. The flask was immersed in a Dry Ice–cellosolve-bath in order to dissipate the heat evolved in the ammoniation process and thereby inhibit the ammonolytic reaction.

The ammoniates of magnesium, zinc, cadmium and copper nitrates were all prepared from Baker Analyzed grade or the equivalent commercially available hydrated com-

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[1] E. Seyb, Jr., and J. Kleinberg, THIS JOURNAL, **73**, 2308 (1951).

pounds. In each case, except with the hydrated copper salt which was ammoniated directly as described below, the commercial hydrate was first placed in a vacuum oven at room temperature and 0.3 mm. pressure for about a week. The material remaining was then placed in a long horizontal Pyrex tube and subjected to a fairly rapidly flowing stream of gaseous ammonia. At first the material became extremely wet, and in some cases passed completely into solution. However, crystals soon began to separate, and eventually the entire sample was converted to a crystalline mass. When the solid had regained a reasonably dry appearance, it was removed, crushed and replaced in the ammonia stream; this procedure (*i.e.*, removal and crushing) was repeated every two days (every few hours in the preparation of the copper compound) until the material no longer changed in composition, as shown by analysis. After 36 hours, all the water in the copper salt had been replaced by ammonia and carried out of the system by the gas stream. The time required for essentially complete conversion to ammoniate for each of the other salts ranged from two to three weeks, depending on the rate of the flow of gaseous ammonia through the tube.

TYPICAL ANALYTICAL DATA FOR THE SALTS PREPARED

Salt	Metal content wt., % Calcd.	Metal content wt., % Found	Ammonia content wt., % Calcd.	Ammonia content wt., % Found
$Ca(NO_3)_2$	24.44	24.50		
$Cu(NO_3)_2 \cdot 4NH_3$	24.85	24.75	26.64	26.05
$Mg(NO_3)_2 \cdot 6NH_3$	9.71	9.78	40.79	39.15
$AlCl_3 \cdot 4NH_3$	13.38	12.76	33.81	36.35
$Cd(NO_3)_2 \cdot 6NH_3$	33.20	33.25	30.18	28.80
$Zn(NO_3)_2 \cdot 4NH_3$	25.39	25.50	26.46	26.20

Although the replacement of water in a salt hydrate by ammonia is a difficult matter, the analytical data show that the compounds employed as reactants were of satisfactory purity. For aluminum chloride tetraammoniate, the ammonia content is high and the aluminum content is low, facts which indicate the occurrence of some ammonolysis during the ammoniation process. Metal content of the magnesium and cadmium salts is very close to the theoretical value in each case, yet the ammonia content is low. This suggests the presence of some water of hydration. On the assumption that the deviation of ammonia content from theoretical is attributable to the presence of hydrate water, calculation for the cadmium nitrate case shows that there is one molecule of water present for about every four cadmium ions. Both cadmium nitrate and zinc nitrate ammoniates gave essentially the same reaction with sodium superoxide. Since the analysis of zinc nitrate ammoniate showed that little or no hydrate water could be present in the compound, it is assumed that the presence of a small amount of water in the cadmium compound had little effect on the general nature of reaction with superoxide.

With the exception of aluminum chloride ammoniate, the salts used as reactants are readily soluble in liquid ammonia.

Standardized Experimental Procedure.—The apparatus and technique employed for effecting reaction between salts and alkali metal superoxide were essentially those described in a previous communication.[1] The reactants were permitted to remain in contact with each other for about 1 hr. at the boiling point of the salt solution, about −30°. After reaction, soluble material was filtered off and the product was washed twice by stirring with 30 to 40-cc. portions of liquid ammonia, each washing being followed by filtration. The solid product was dried by means of anhydrous nitrogen and transferred to a weighing bottle in a dry-box.

Analytical Methods.—Calcium was determined by precipitation as the oxalate, followed by titration of this substance with standardized potassium permanganate solution. Aluminum and magnesium were determined gravimetrically as the 8-hydroxyquinolate and pyrophosphate, respectively. Copper and cadmium were determined electrolytically. Zinc was precipitated and weighed as zinc tetrathiocyanatomercurate(II), $Zn[Hg(SCN)_4]$. Lithium, potassium and sodium analyses were all performed by means of a model 52-C Perkin–Elmer flame photometer.[2] The Volhard method was employed for chloride analysis. Superoxide and peroxide determinations were performed by a technique described in previous communications.[1,3]

For the determination of total base content[4] of the products, a weighed sample was dissolved in a sufficient excess of standardized hydrochloric acid (*ca.* 0.1 *N*) and the excess acid was then back-titrated with standardized sodium hydroxide solution to a brom thymol blue end-point. Indicators such as methyl orange, phenolphthalein and phenol red were destroyed by the acidic peroxide solutions.

The quantity of available ammonia present in the products as ammoniate and/or as amide was determined by placing a weighed sample in a strong aqueous sodium hydroxide solution, distilling the liberated ammonia into an excess of standardized hydrochloric acid and titrating unused acid with a base of known normality. Any ammonia present as such in the sample is merely liberated, but amide in aqueous solution is hydrolyzed as

$$NH_2^- + H_2O \longrightarrow OH^- + NH_3$$

Thus, one equivalent of amide liberates on equivalent of ammonia in the determination of available ammonia, but gives rise to two equivalents of base in the analysis for total base.

There is no way of distinguishing between hydroxide and "normal" oxide or between bound ammonia and amide. However, since one mole of bound ammonia and one mole of amide each liberates one mole of ammonia when treated with strong base, and since one mole of amide is converted to one of hydroxyl and one of ammonia on contact with water, the number of equivalents of available ammonia liberated per gram of sample subtracted from the total equivalent base content per gram as determined by titration gives the sum of superoxide, peroxide, "normal" oxide, hydroxide and amide per gram of material. It follows that the "non-reducible anion base"[5] content can be obtained by the subtraction of the sum of superoxide, peroxide, and available ammonia from the total base content.

Qualitative tests for nitrite ion[6] were made on all solid products and on the evaporated filtrates resulting from the reactions.

Results and Discussion

General Observations.—Whenever reaction occurs between salt and superoxide, molecular oxygen is copiously evolved. Analysis of solid products (Tables I–III) brings out two interesting facts: (a) In case of reaction between the stoichiometric quantities of materials required for metathesis (*e. g.*, $1LiNO_3:1NaO_2$), very little superoxide is ordinarily present in the product; (b) the presence of "non-reducible anion base" ($O^= + OH^- + NH_2^-$) is common.

"Normal" oxide undoubtedly arises from decomposition of unstable higher oxides, accompanied by oxygen evolution. Amide and hydroxide probably result from ammonolysis of "normal" oxide in accordance with the equation

$$O^= + NH_3 \longrightarrow OH^- + NH_2^-$$

The amide thus formed may appear as such in the product, or may be oxidized, at least in part, to hydroxide and nitrite by the molecular oxygen resulting from decomposition of higher oxides.

$$2NH_2^- + {}^3/_2O_2 \longrightarrow OH^- + NO_2^- + NH_3$$

It should be noted that all insoluble products and all evaporated filtrates of reaction gave positive tests for nitrite ion. Where no reaction occurred between salt and alkali metal superoxide (*e.g.*, be-

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(2) "Instruction Manual, Flame Photometer," Model 52-C, The Perkin–Elmer Corp., Norwalk, Conn., 1952.

(3) E. Seyb, Jr., and J. Kleinberg, *Anal. Chem.*, **23**, 115 (1951).

(4) Total base content includes that derived from higher oxides (superoxide and peroxide), "normal" oxide ($O^=$), hydroxide, bound ammonia and amide, all of which may be present in a product.

(5) The combination $O^= + OH^- + NH_2^-$ is henceforth designated by this term.

(6) F. Feigl, "Qualitative Analysis by Spot Tests," 3rd ed. Elsevier Press, Inc., Houston, Texas, 1949, p. 248.

TABLE I

ANALYSIS OF PRODUCTS FORMED BY REACTION BETWEEN $AlCl_3 \cdot 4NH_3$ AND NaO_2 IN LIQUID AMMONIA[a]

Mole ratio of reactants $Al^{+++}:NaO_2$	Superoxide, meq./g.	Peroxide, meq./g.	$O^{=} + OH^{-} + NH_2^{-}$, meq./g.[b]	Available NH_3, meq./g.	Al^{+++}, meq./g.	Na^{+}, meq./g.	Cl^{-}, meq./g.	Product accounted for, %[c]
1:3	0.53	0.73	30.82	0.14	27.33	8.74	3.99	86.6
1:3	.91	.21	30.85	.52	25.65	10.20	3.88	89.1
1:6	.42	.15	31.88	.04	16.03	16.72	0.30	81.1
1:6	.57	.00	31.15	.05	16.22	15.81	0.31	78.9

[a] Color of products was white. [b] Referred to in text as "non-reducible anion base." [c] Calculated on the premise that all "non-reducible anion base" is "normal" oxide.

TABLE II

ANALYSIS OF PRODUCTS FORMED BY REACTION BETWEEN $Cu(NO_3)_2 \cdot 4NH_3$ AND ALKALI METAL SUPEROXIDES IN LIQUID AMMONIA[a]

Mole ratio of reactants $Cu^{++}:MO_2$	Superoxide, meq./g.	Peroxide, meq./g.	$O^{=} + OH^{-} + NH_2^{-}$, meq./g.[b]	Available, NH_3, meq./g.	Cu^{++}, meq./g.	Na^{+} or K^{+}, meq./g.	Total base, meq./g.	Product accounted for, %[c]
			Sodium superoxide reactions					
1:2	0.31	1.89	15.99	6.25	18.57	1.03	24.44	88.8
1:2	.05	1.80	16.70	4.06	19.29	1.28	22.61	87.5
1:4	.00	0.94	20.42	0.29	13.58	7.79	21.65	79.4
1:4	.02	0.56	20.87	0.14	13.39	9.15	21.59	81.5
			Potassium superoxide reactions					
1:2	3.33	0.00	15.61	3.22	13.82	4.36	22.16	89.6
1:2	1.18	2.24	16.25	2.38	16.72	3.25	22.05	90.2
1:4	5.95	0.00	11.91	1.70	12.33	6.08	19.56	94.4
1:4	7.60	0.00	9.33	0.34	9.78	7.78	17.27	93.9

[a] Color of products ranged from dark brown to greenish-brown. [b] Referred to in text as "non-reducible anion base." [c] Calculated on the premise that all "non-reducible anion base" is "normal" oxide.

TABLE III

ANALYSIS OF PRODUCTS FORMED BY REACTION OF $Mg(NO_3)_2 \cdot 6NH_3$, $Ca(NO_3)_2$, $LiNO_3$, $Cd(NO_3)_2 \cdot 6NH_3$ AND $Zn(NO_3)_2 \cdot 4NH_3$ WITH ALKALI METAL SUPEROXIDES IN LIQUID AMMONIA[a]

Mole ratio of reactants	Superoxide, meq./g.	Peroxide, meq./g.	$O^{=} + OH^{-} + NH_2^{-}$, meq./g.[b]	Available NH_3, meq./g.	Metal ion,[c] meq./g.	Na^{+} or K^{+}, meq./g.	Total base, meq./g.	Product accounted for, %[d]
$1Li^{+}:1NaO_2$	0.77	35.37	2.56	0.64	34.92	3.61	39.34	94.7
$1Li^{+}:2NaO_3$	2.11	28.77	3.78	0.70	27.72	8.83	35.36	96.5
$1Mg^{++}:2NaO_2$	1.74	12.11	14.72	1.48	26.17	4.76	30.05	82.0
$1Mg^{++}:4NaO_2$	2.41	13.55	12.05	0.78	21.38	8.68	28.79	86.3
$1Mg^{++}:2KO_2$	7.47	9.40	3.90	.84	13.15	7.79	21.61	89.9
$1Mg^{++}:4KO_2$	10.70	5.29	0.97	.30	5.49	11.03	17.26	93.8
$1Ca^{++}:2NaO_2$	2.92	14.27	4.21	1.54	19.62	2.49	22.94	83.2
$1Ca^{++}:4NaO_2$	4.17	7.62	11.98	1.35	13.85	9.22	25.02	86.4
$1Ca^{++}:2KO_2$	0.88	17.28	1.56	3.25	21.48	0.58	22.97	82.6
$1Ca^{++}:4KO_2$	7.84	8.92	1.95	0.55	10.42	8.32	19.26	95.3
$1Cd^{++}:2NaO_3$	0.11	11.98	1.71	.86	12.98	1.02	14.66	97.7
$1Cd^{++}:4NaO_2$	.66	10.05	3.54	.76	12.31	2.05	15.01	96.2
$1Zn^{++}:2NaO_2$	.35	13.69	4.61	3.14	17.15	1.85	21.79	92.4
$1Zn^{++}:4NaO_2$	1.51	9.19	8.50	1.16	14.59	6.34	20.36	90.6
$1Zn^{++}:2KO_2$	1.18	14.68	1.95	2.72	17.08	1.40	20.53	94.8
$1Zn^{++}:4KO_2$	7.01	7.90	1.22	1.20	9.29	7.47	17.33	97.7

[a] Color of products ranged from white to yellow, depending on amount of unreacted alkali metal superoxide present. [b] Referred to in text as "non-reducible anion base." [c] Refers to metal ion other than Na^{+} or K^{+}. [d] Calculated on the premise that all "non-reducible anion base" is "normal" oxide.

tween lithium nitrate and potassium superoxide), no test for nitrite ion was observed.

In the tables of analytical data, the values listed in the column headed "Product accounted for, %" were calculated on the assumption that all the "non-reducible anion base" content is "normal" oxide, which has an equivalent weight about one-half that of hydroxide or amide. It is evident that such a calculation, particularly if the hydroxide and amide contents of the solid are large, would lead to relatively low values for the percentage of product accounted for. If the "non-reducible anion base" content of the solid product is large, it is probable that the quantities of hydroxide and amide present are not inconsequential; in these cases it would be expected, therefore, that the percentage of product accounted for would be relatively low. Examination of the data does indeed reveal a tendency in this direction.

Preliminary experiments showed that whereas potassium superoxide is relatively insoluble and altogether stable in liquid ammonia, the sodium compound is not only soluble to the extent of roughly 0.3 g. per 100 cc. of solvent but also undergoes some decomposition when stirred in this medium. It is not surprising, therefore, that when sodium superoxide in excess of the quantity required for metathesis is added to a metal salt, the equivalent superoxide content of the solid product is not only low, but even less than the sodium content (see Table III). On the other hand, in an analogous situation involving excess potassium superoxide, the superoxide content of the solid product is relatively high and essentially equal to that of the alkali metal.

Aluminum Chloride Tetrammoniate–Sodium Superoxide Reactions.—These substances react in the molar ratio ($1AlCl_3\cdot4NH_3:3NaO_2$) required for metathesis, and also, surprisingly, in the ratio 1:6. Examination of the data of Table I reveals that practically the total content of the solid product from reaction in the 1:6 ratio consists of sodium, aluminum and "non-reducible anion base." Moreover, the molar ratios Na:Al: "non-reducible anion base" are very close to 3:1:3, which, on the assumption that all "non-reducible anion base" arises from "normal" oxide, strongly suggests the formation of the compound Na_3AlO_3 during the course of reaction. It is not inconceivable that aluminum chloride and sodium superoxide first react to form a mixed superoxide–peroxide

$$2AlCl_3\cdot4NH_3 + 12NaO_2 \longrightarrow Al_2(O_2)_3\cdot6NaO_2 + 6NaCl + 3O_2 + 4NH_3$$

and that this mixed oxide then loses oxygen to give Na_3AlO_3

$$Al_2(O_2)_3\cdot6NaO_2 \longrightarrow 2Na_3AlO_3 + 6O_2$$

It is to be expected that Na_3AlO_3 (which may be regarded as a combination of "normal" oxides) would be ammonolyzed to some extent, and that ammonolysis would be followed by oxidation to give hydroxide and nitrite.

The product of the $1AlCl_3\cdot4NH_3:3NaO_2$ reaction, which is contaminated with sodium chloride, contains practically no higher oxide. The absence of higher oxide is believed to be attributable, not to catalytic decomposition, but rather to the instability of the product (aluminum superoxide) resulting from a metathetic reaction.

Copper(II) Nitrate Tetrammoniate–Alkali Metal Superoxide Reactions.—Solid products resulting from reaction of copper(II) nitrate with sodium superoxide (Table II) contain little higher oxides, even when sodium superoxide is added in excess of that amount required for metathesis, whereas products from reaction with potassium superoxide sometimes contain considerable quantities of higher oxide. This is not entirely unexpected, merely from consideration of the comparative solubility and stability characteristics of sodium and potassium superoxides previously described. The high proportion of "non-reducible anion base" in all the products demonstrates the instability of higher oxides in the presence of copper(II) ion in liquid ammonia. In view of the well-known ability of copper(II) to catalyze the decomposition of peroxide in aqueous medium, it is entirely conceivable that the absence of higher oxides in the products is in large measure the result of catalytic action. However, since in the products there is a considerable quantity of copper ion tied up with "non-reducible anion base," this cation must also take part in some metathetic reaction.

Reactions of the Nitrates of Lithium, Magnesium, Calcium, Cadmium and Zinc.—Except for the failure of lithium and cadmium nitrates to undergo reaction with potassium superoxide, each of the salts noted in the heading reacts with sodium superoxide and also with potassium superoxide in the stoichiometric proportions required for metathesis to give a product rich in the corresponding peroxide (Table III). When potassium superoxide in amount twice that required for metathesis (*e.g.*, $1Zn(NO_3)_2:4KO_2$) is employed as reactant, the excess apparently is found unchanged in the product. This fact demonstrates that the peroxide found in the product does not arise from catalytic decomposition of superoxide, and is, therefore, strongly indicative that the initial reaction between salt and superoxide is a metathetic one, peroxide being produced from dissociation of an unstable superoxide intermediate, *e.g.*

$$Zn(NO_3)_2 + 2KO_2 \longrightarrow Zn(O_2)_2 + 2KNO_3$$
$$Zn(O_2)_2 \longrightarrow ZnO_2 + O_2$$

The analytical data show that some decomposition of peroxide also occurs in each case to give "normal" oxide, which in turn is converted, at least in part, to hydroxide and amide by ammonolysis. Of the peroxides formed, the magnesium compound appears to be the least stable in liquid ammonia; solid products contain only about 25% by weight of this oxide. The extent of decomposition of the peroxides of lithium, calcium, cadmium and zinc into "normal" oxides is relatively small. In the products formed from reactants brought together in the stoichiometric quantities required for metathesis, calculations, based on the premise that any alkali metal is present as a combination of superoxide and peroxide, show that these peroxides are present in the appropriate solid products in amounts as large as 75, 62, 84 and 70%, respectively. A search of the literature reveals that, except for the preparation of lithium and calcium peroxides in small yield by direct oxidation of liquid ammonia solutions of the metals,[7] this is apparently the first time these peroxides have been prepared directly in the anhydrous state.

Finally, it should be pointed out that although sodium and cadmium ions have practically the same ionic radii (Na^+, 0.95 Å.; Cd, 0.97 Å.), no mixed superoxide–peroxide product similar to that obtained[1] from reaction between barium nitrate and potassium superoxide is isolated.

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LAWRENCE, KANSAS

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[7] J. K. Thompson and J. Kleinberg, THIS JOURNAL, **73**, 1243 (1951).