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

Reactions between Alkali Superoxides and Some Alkaline Earth Nitrates in Liquid Ammonia

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In the course of an attempt to prepare alkaline earth superoxides by treatment of nitrates of these metals with alkali metal superoxides in liquid ammonia, a novel reaction was encountered. Reaction between barium nitrate and potassium superoxide in formula weight ratios up to 1:4 results in the formation of a chocolate-brown substance, which, upon removal of the liquid ammonia, changes in color to a light tan. Analysis shows this material to contain barium, potassium, superoxide and peroxide ions in ratios corresponding to the composition ($2K^+$, Ba^{++}, $2O_2^-$, $O_2^=$). The stoichiometry of the reaction may be represented by the equation $Ba(NO_3)_2 + 4KO_2 \rightarrow K_2Ba(O_2)_2O_2 + 2KNO_3 + O_2$. Excessive washing of the mixed oxide with liquid ammonia removes both barium and peroxide ions. Heating at 110° in the absence of both carbon dioxide and moisture results in the rapid decomposition of both peroxide and superoxide ions, and yields a mixture rather than a definite compound. It is of interest that, of all the various combinations tested, only barium nitrate and potassium superoxide give a mixed superoxide–peroxide. Barium nitrate and sodium superoxide in formula weight ratio of 1:2 react to give chiefly barium peroxide. Similarly, from combinations of strontium nitrate and potassium superoxide, and of the former and sodium superoxide, strontium peroxide is obtained. It is noteworthy that in the one case of mixed oxide formation the cations have practically identical ionic radii: K^+, 1.33 Å.; Ba^{++}, 1.35 Å.

Sodium superoxide has been prepared in this Laboratory by reaction between sodium peroxide and oxygen at elevated temperatures and pressures.[1] Inasmuch as attempts to prepare superoxides of alkaline earth metals in a similar manner proved unsuccessful, attention was directed toward their possible production by metathesis in liquid ammonia. Reactions between some anhydrous alkaline earth metal nitrates and potassium and sodium superoxides were accordingly investigated, and although the original purpose of the study was not attained, a novel reaction was discovered. The nature of this reaction is the subject of the present report.

Experimental

Materials.—The liquid ammonia was du Pont "refrigeration grade," used without further purification. Anhydrous barium and strontium nitrates were Baker Analyzed grade. Potassium superoxide which upon analysis proved to be of 99% purity was supplied by the Naval Research Laboratory.[2] Sodium superoxide, prepared as previously described,[1] was of 96% purity.

Standardized Experimental Procedure.—The experimental system employed (Fig. 1) consisted of a reaction cell C-D of about 200 cc. capacity, surrounded by a Dry Ice bath E and connected to a source of anhydrous ammonia or dry oxygen and to the safety manometer F. The reaction cell was made up of the cell-head C connected to the cell-body D by means of a ground-glass joint. Fitted into the bottom of the cell-body were a sintered glass filter disk and a stopcock, to permit removal by filtration of any solid products formed. A sampling capsule B, for the introduction of solid reactants, could be joined to the cell-head by means of a ground-glass joint. During the process of drying the apparatus, however, the opening into which the stem of this capsule could be inserted was sealed with a ground-glass plug.

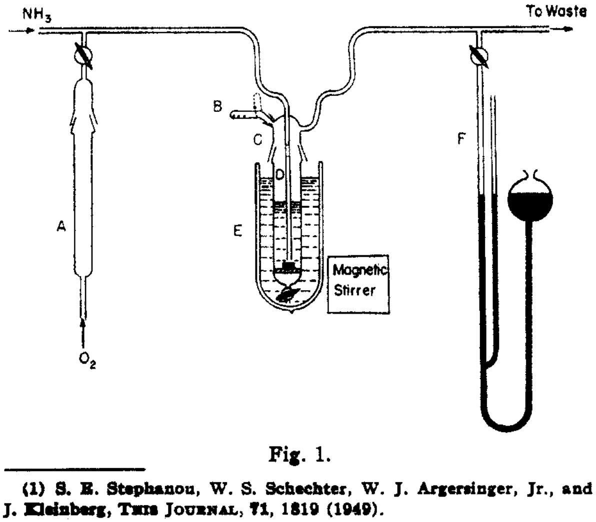

Fig. 1.

After the system had been dried by sweeping with anhydrous ammonia, approximately 150 cc. of liquid ammonia was condensed into the cell-body by means of the Dry Ice-cellosolve-bath E. A weighed sample of the desired alkaline earth metal nitrate (approximately 1.0–1.5 g.) was transferred in a dry-box to capsule B, which was then rapidly fitted into the cell-head. The sample was slowly introduced into the body of the cell by turning the capsule from a horizontal to a vertical position. When the alkaline metal salt had dissolved in the liquid ammonia (the process of solution being hastened by magnetic stirring), a weighed quantity of alkali metal superoxide was similarly introduced into the cell, the Dry Ice-bath was removed, and the solution was stirred for an hour by means of the magnetic stirrer. The product of reaction was filtered with the aid of suction from an aspirator pump, and washed with two portions (approximately 75 cc. each) of liquid ammonia. The system was then swept out with oxygen which had been previously dried by passage through anhydrous magnesium perchlorate in A. When all the ammonia had been removed, the cell-body was separated from the cell-head, rapidly stoppered, and placed in the dry-box, where the product was transferred to ground-glass stoppered weighing bottles.

Analytical Methods.—Inasmuch as all the reactions studied took place with the vigorous evolution of oxygen, and the product obtained from barium nitrate and potassium superoxide was paramagnetic, analyses for both superoxide and peroxide content were carried out. These analyses are described in some detail, since both of them proved to be vital to the successful identification of at least one of the products. Superoxide content of the product was calculated, as described in a previous communication[3] from the volume of oxygen (designated as superoxide oxygen) liberated per gram of material on decomposition with a glacial acetic acid–diethyl phthalate mixture. The stoichiometry of the reaction is

$$2O_2^- + 2HC_2H_3O_2 \longrightarrow H_2O_2 + 2C_2H_3O_2^- + O_2 \quad (a)$$

The volume of oxygen thus liberated, together with that obtained by complete decomposition of another portion of the product with a catalyst solution 1 *M* in hydrochloric acid and 3 *M* in iron(III) chloride, permitted determination of the peroxide content. The catalyst solution decomposes superoxide and peroxide in accordance with the equations

$$2O_2^- + aq. \longrightarrow O^{=}\cdot aq. + 3/2O_2 \quad (b)$$
$$O_2^{=} + aq. \longrightarrow O^{=}\cdot aq. + 1/2O_2 \quad (c)$$

From equations (a) and (b) it is apparent that two-thirds of the total oxygen available from superoxide is released by

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[1] S. E. Stephanou, W. S. Schechter, W. J. Argersinger, Jr., and J. Kleinberg, THIS JOURNAL, 71, 1819 (1949).

[2] We are indebted to Mr. R. R. Miller of the Naval Research Laboratory, Washington, D. C., for supplying us with this material.

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

decomposition with the acetic acid–diethyl phthalate mixture. The volume of the oxygen liberated from peroxide originally in the product may therefore be readily calculated.

The total base content of the product was determined by titration with standard hydrochloric acid to a phenolphthalein end-point. Barium and strontium were determined gravimetrically as sulfates. Since the reaction between barium nitrate and potassium superoxide yielded a solid product which consisted almost entirely of oxides, and since potassium nitrate was always present in small amounts as an impurity, the acid-titratable potassium content was calculated by difference from the observed values for total base and barium.

Results and Discussion

The reaction between barium nitrate and potassium superoxide is worthy of special emphasis. When potassium superoxide is added to a solution of barium nitrate in liquid ammonia, an immediate and vigorous evolution of oxygen and the formation of a chocolate-brown solid are observed. On removal of ammonia, the latter changes in color to a light tan. With formula weight ratios of barium nitrate to potassium superoxide up to 1:4, a product is obtained which consistently contains barium, potassium, superoxide and peroxide ions in ratios corresponding to the composition ($2K^+$, Ba^{++}, $2O_2^-$, $O_2^=$). Some typical data are shown in Table I. With formula weight ratios less than 1:4 the tan product is noticeably contaminated with yellow superoxide, and on analysis the superoxide to peroxide ratio in the product is found to be appreciably greater than two. The reaction yielding the mixed superoxide-peroxide may therefore be formulated

$$Ba(NO_3)_2 + 4KO_2 \longrightarrow K_2Ba(O_2)_2O_2 + 2KNO_3 + O_2$$

The mixed superoxide-peroxide is analogous to the so-called "sesquioxides" Rb_4O_6 and Cs_4O_6 which have been shown to contain both the superoxide and the peroxide ions.[4] The analogy is all the more striking in view of the fact that potassium and barium, the cations in the mixed oxide, possess practically identical ionic radii, 1.33 and 1.35 Å., respectively.[5]

TABLE I

ANALYSIS OF PRODUCT FORMED BY REACTION BETWEEN $Ba(NO_3)_2$ AND KO_2 IN LIQUID AMMONIA

The first 4 rows are data for a formula weight ratio of $Ba(NO_3)_2$ to KO_2 of 1:2; the last 2 rows of data are for a formula weight ratio of 1:4

Ba, milli-eq./g.	Total base, millieq./g.	Cc. (S.T.P.) superoxide oxygen/g.	Cc. (S.T.P.) oxygen/g. liberated on complete decomposition	Ion ratios Ba^{++}	K^+	O_2^-	$O_2^=$	Product accounted for, %
6.10	12.00	66.5	134	1	1.93	1.95	1.00	94
6.26	12.76	67.0	135	1	2.08	1.92	0.99	97
6.08	11.90	69.3	139	1	1.92	2.03	1.02	95
5.84	11.96	68.0	135	1	2.09	2.08	1.02	93
5.74	11.10	64.0	127	1	1.88	1.99	0.97	88
5.70	11.28	64.3	127	1	1.96	2.02	1.01	89

At room temperature in the absence of moisture, the mixed oxide appears to be stable indefinitely. Heating at 110° in the absence of both carbon dioxide and moisture results in the rapid decomposition of both peroxide and superoxide ions, and yields a mixture of no definite composition. Excessive washing of the mixed oxide with liquid ammonia removes both barium and peroxide ions.

Substitution of sodium superoxide for the potassium compound results in a marked difference in the reaction with barium nitrate. When these substances are brought together in the formula weight ratio calculated for complete metathesis ($1Ba(NO_3)_2$ to $2NaO_2$), oxygen is immediately liberated, the yellow color of the superoxide slowly disappears, and a heavy white precipitate is formed. Analysis of this material showed it to consist primarily of barium peroxide (Table II).

TABLE II

ANALYSIS OF PRODUCT OF REACTION BETWEEN $Ba(NO_3)_2$ AND NaO_2 IN LIQUID AMMONIA

Formula weight ratio of $Ba(NO_3)_2$ to NaO_2, 1:2

Ba, millieq./g.	Total base, millieq./g.	$O_2^=$, millieq./g.	Product accounted for, %
10.88	10.83	10.66	91
11.28	11.25	11.48	95
10.88	10.90	10.00	90

In the case of strontium nitrate, reaction with either potassium or sodium superoxide yields chiefly the alkaline earth metal peroxide (Table III). No evidence, other than the appearance of a transitory light brown color in the liquid ammonia medium when potassium superoxide is used as reactant, is obtained for mixed oxide formation.

TABLE III

ANALYSIS OF PRODUCTS OF REACTION BETWEEN $Sr(NO_3)_2$ AND ALKALI METAL SUPEROXIDES IN LIQUID AMMONIA

Formula weight ratios, 1:2; the first two rows of data are for KO_2, the last row for NaO_2

Sr, millieq./g.	Total base, millieq./g.	$O_2^=$, millieq./g.	Product accounted for, %
15.40	15.35	14.92	91
15.46	15.50	15.20	92
16.26	16.30	14.56	95

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[4] A. Helms and W. Klemm, *Z. anorg. allgem. Chem.*, **241**, 97 (1939); **242**, 33, 201 (1939).

[5] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd Ed., 1940, p. 346.