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

The Absorption of Oxygen by Sodium Peroxide: Preparation and Magnetic Properties of Sodium Superoxide[1]

BY S. E. STEPHANOU,[2] WILLIAM H. SCHECHTER,[3] W. J. ARGERSINGER, JR., AND JACOB KLEINBERG

According to the literature[4,5] the highest oxide of sodium that can be obtained by combustion of the metal in an excess of oxygen is the peroxide, Na_2O_2. The superoxides of potassium, rubidium and cesium may be prepared by the same method.[5,6] Although previous investigators[7] have studied the reaction between alkaline earth metal lower oxides with oxygen at elevated temperatures and pressures in attempts to prepare higher oxides, no similar experiments have been performed with sodium peroxide. Holt and Sims[5] passed oxygen at atmospheric pressure over sodium peroxide at 300–350° for sixteen hours but obtained no evidence of oxygen absorption. In a previous report[8] from this Laboratory, dealing with the rapid oxidation of sodium in liquid ammonia, evidence for the existence of sodium superoxide was described.[9] In the present investigation sodium peroxide has been subjected to treatment with oxygen at high pressures and temperatures in order to explore the possibility of preparing higher oxides by this method. Such treatment results in the formation of high yields of sodium superoxide. The preparation and magnetic properties of this substance are discussed in this paper.

Experimental

The apparatus employed (Fig. 1) consisted of a stainless steel bomb A of about 180-ml. capacity, equipped with such an arrangement of needle valves that the system could be completely evacuated or filled with oxygen under pressure. An iron–constantan thermocouple H inserted in the wall of the bomb and connected to a Brown Electronik Recorder and Regulator C allowed for temperature control. The voltage across the heating elements of the bomb jacket B was adjusted by means of the Powerstat D.

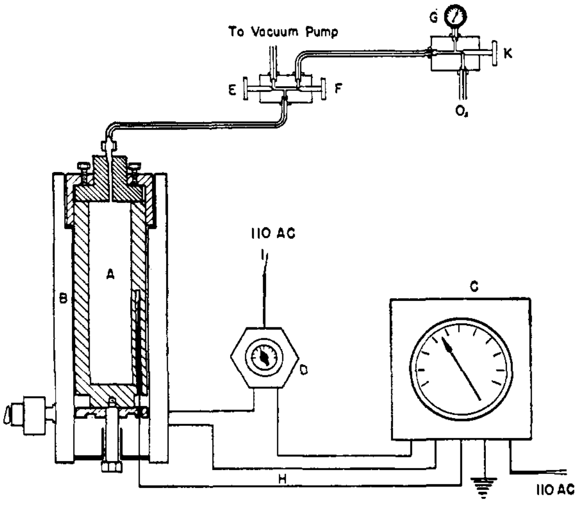

Fig. 1.

A weighed sample of sodium peroxide was placed inside a Pyrex container in the bomb and the system evacuated to 1–3 mm. for several hours; valve E was then closed and oxygen from a cylinder added slowly through valve F until the desired initial pressure was attained. Valve K was closed and the bomb heated to the desired temperature. The absorption of oxygen at a particular temperature could be followed by reading the pressure gage G at frequent intervals. When a constant pressure reading was obtained, the bomb was cooled to room temperature, the product removed and analyzed. The analysis was accomplished by decomposition of the sample with a catalyst solution which was 2 *M* with respect to hydrochloric acid and 1 *M* in ferric chloride, using the gas volumetric method described in a previous paper from this Laboratory.[8] From the corrected volume of oxygen evolved per gram of product, on the assumption that only peroxide and superoxide were present, the weight per cent. of sodium superoxide was calculated by means of the equation

$$\left[\frac{\text{cc. oxygen evolved/gram product} - 144}{162}\right] \times 100 = \%\ \text{NaO}_2$$

where the numerator of the bracketed term represents the cc. of oxygen evolved per gram beyond that required for pure sodium peroxide and the denominator the difference in cc. of oxygen evolved per gram between pure sodium superoxide and sodium peroxide. The results of the oxygen absorption studies are shown in Table I.

The starting material (du Pont Calorific Grade) analyzed as 99% sodium peroxide, calculated on the basis of the total oxygen evolved upon decom-

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(1) Abstracted from a thesis presented by S. E. Stephanou to the Graduate Faculty of the University of Kansas in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(2) Present address: Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, New Mexico.

(3) Present address: Sterling College, Sterling, Kansas.

(4) Harcourt, *J. Chem. Soc.*, **14**, 267 (1862).

(5) Holt and Sims, *ibid.*, **65**, 432 (1894).

(6) (a) Joannis, *Compt. rend.*, **116**, 1370 (1893); (b) Rengade, *Ann. chim. phys.*, [8] **11**, 348 (1907); (c) Kraus and Whyte, THIS JOURNAL, **48**, 1781 (1926).

(7) (a) Fischer and Ploetze, *Z. anorg. Chem.*, **75**, 10 (1912); (b) Hildebrand, THIS JOURNAL, **34**, 246 (1912); (c) Holtermann, *Ann. Chim.*, **14**, 121 (1940).

(8) Schechter, Sisler and Kleinberg, THIS JOURNAL, **70**, 267 (1948).

(9) Some of the conclusions arrived at in the work then reported must be modified in the light of later experimental data. The whole problem of the oxidation of sodium in liquid ammonia is discussed by Schechter, Thompson and Kleinberg, *ibid.*, **71**, 1816 (1949).

TABLE I

THE ABSORPTION OF OXYGEN BY SODIUM PEROXIDE

Na_2O_2, g.	Temp. (°C.) for 100 hours[a]	Initial press. (atm.) at elevated temp.	Cc. O_2 (S. T. P.) evolved per g. of product	Calcd. % NaO_2[b]
9.9	32	137	140	0
11.2	150	187	147	3
11.2	200	205	161	11
10.1	250	222	181	24
11.1	300	238	215	45
12.4	350	257	274	81
10.3	400	280	286	88
9.8	450	281[c]	292	92
11.2	490	298	291	92

[a] The time allowed for reaction was one hundred hours. A study of the effect of time on the extent of reaction showed that for temperatures above 400° the quantity of oxygen absorbed after 100 hours was negligible. [b] Corrected for the 1% impurity present in the starting material. [c] A small leak developed in the system during this run.

position with the hydrochloric acid–ferric chloride solution mentioned above. The presence of carbonate was tested for by passage of the gas evolved through concentrated potassium hydroxide solution and noting any decrease in volume. The sodium peroxide used in these experiments proved to be carbonate free. To avoid decomposition due to exposure to atmospheric moisture both starting materials and products were handled in a dry-box containing phosphorus pentoxide.

Magnetic Properties

The susceptibilities of the mixtures obtained in the bomb were measured with a Gouy magnetic balance equipped with an electromagnet of the type described by Shaw.[10] The apparatus was calibrated with deaerated distilled water and air, for which the volume susceptibilities at room temperature were taken as -0.720×10^{-6} and $+0.029 \times 10^{-6}$, respectively.[11] All measurements were made at room temperature using a maximum field strength of about 6800 gausses. The cylindrical sample tube employed had a cross-sectional area of 0.495 sq. cm., and, when filled to a fixed mark 8 cm. from the bottom, contained about 5 g. of sample.

The fused product obtained from the reaction in the bomb was grounded in an agate mortar in a dry-box and the powder transferred to the sample tube. After an average of several magnetic readings was obtained, the total oxygen evolved (cc. at S.T.P.) per gram of material in the tube was determined by the gas volumetric method already described.[8] The gram susceptibilities were corrected to 20°, assuming the validity of Curie's law, and plotted against the per cent. sodium superoxide (Fig. 2) as calculated from the total oxygen evolved upon decomposition with hydrogen chloride–ferric chloride catalyst solution. It is estimated that the magnetic measurements are accurate to ±3% and the chemical analyses (from the total oxygen evolved) to ±1%. Part of the error in the susceptibility measurements is due to nonuniform packing of the powder in the sample tube.

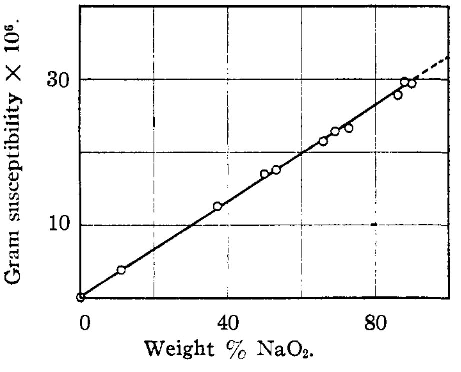

Fig. 2.—Magnetic susceptibilities of Na_2O_2–NaO_2 mixtures.

Discussion of Experimental Results

Preliminary experiments using initial oxygen pressures at room temperature ranging from 2 to 32 atmospheres showed no measurable absorption of oxygen up to temperatures of approximately 250°. Above this temperature the sodium peroxide had a tendency to react with the walls of the Pyrex container and become decomposed. As the starting pressure was increased this reaction became negligible and studies at higher temperatures and pressures were made without any appreciable decomposition taking place. It was found that, as the pressure and the temperature were increased, the final product became more yellow, and, upon analysis, evolved more oxygen than did pure sodium peroxide. In order to make a systematic study of the conditions of temperature and pressure necessary for maximum reaction of oxygen with sodium peroxide a series of runs, summarized in Table I, was made with an initial pressure of about 2000 lb. per sq. in. The selection of this pressure was dictated by the limitations of the apparatus. With increasing oxygen absorption, at increasingly higher temperatures and pressures, the color of the final product changes from a faint yellow to a bright yellow and finally, at temperatures above 350°, becomes bright orange. If the reaction temperature is higher than 300°, the final product has the appearance of a fused homogeneous mass which may readily be pulverized in a mortar. The powder thus obtained is uniformly yellow and highly hygroscopic. Upon exposure to atmospheric moisture it evolves oxygen and gradually loses its yellow color. Continued exposure to the atmosphere leaves a white residue which is a mixture of sodium peroxide and hydroxide. The yellow material reacts vigorously with water with the formation of oxygen and sodium peroxide in solution. The material appears to be stable indefinitely when stored in a desiccator over phosphorus pentoxide.

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(10) Shaw, *Rev. Sci. Instruments*, **2**, 611 (1931).

(11) All magnetic susceptibilities in this paper are given in c. g. s. units.

The addition to the yellow material of a 20% (by volume) solution of glacial acetic acid in carbon tetrachloride[12] causes the oxygen absorbed by the peroxide in the bomb to be released almost quantitatively. Treatment of the residue with an excess of potassium iodide solution and titration of the iodine liberated with standard sodium thiosulfate solution showed the presence of about 95% of the original peroxide used. The reaction with water described above and the behavior toward glacial acetic acid is exactly that to be expected of a superoxide. Kraus and Parmenter[13] have shown that potassium superoxide decomposes in water in accordance with the equation

$$2KO_2 \xrightarrow{H_2O} K_2O_2 + O_2$$

Acidification of a superoxide would be expected to give the unstable acid HO_2 which would decompose to hydrogen peroxide and oxygen. The chemical composition, physical appearance and reactions of the yellow material formed by reaction between sodium peroxide and oxygen leave no doubt that it contains large percentages of sodium superoxide, NaO_2.

The magnetic properties of the material give additional proof of the presence of sodium superoxide. It is evident from the values of the gram susceptibilities shown in Fig. 2 that the product obtained from the bomb is highly paramagnetic. Furthermore, the gram susceptibility of this product increases linearly with the quantity of oxygen absorbed (indicated in the plot by an increasing calculated weight % of sodium superoxide). Extrapolation of the straight line in Fig. 2 to a quantity of oxygen absorbed corresponding to 100% conversion to sodium superoxide gives for the gram susceptibility of this substance a value of $+33.0 \times 10^{-6}$. The "effective magnetic moment," μ, for pure sodium superoxide was calculated from the well-known relation, $\mu = 2.83 \sqrt{X_M T}$, where T is the absolute temperature and X_M the molar susceptibility. The value obtained, 2.07 molar Bohr magnetons is an excellent agreement with the moments of other superoxides reported in the literature.[14,15,16]

The fact that the plot of gram susceptibility *vs.* weight per cent. sodium superoxide is linear indicates that Wiedemann's mixture law[17] is being followed. In this case, the law assumes the familiar form, $\chi = \chi_1 P_1 + \chi_2 P_2$, where χ is the susceptibility of the mixture, χ_1 and χ_2 the susceptibilities of sodium peroxide[18] and sodium superoxide, respectively, and P_1 and P_2 the respective weight fractions of the two compounds. The linearity is of significance in two respects: (1) It indicates that when sodium peroxide reacts with oxygen at high temperatures and pressures, the formation of an oxide intermediate between the peroxide and superoxide is quite unlikely; and (2) since the contribution of diagmagnetic substances is small compared to that of the superoxide, it permits the use of magnetic measurements for the rapid determination of sodium superoxide in the presence of diamagnetic impurities. Use of the magnetic method gave values for superoxide content in mixtures of sodium superoxide and peroxide which agreed within ±3% with values obtained by chemical analysis.

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Summary

1. The reaction between sodium peroxide and oxygen at elevated temperatures and pressures has been shown to result in the formation of sodium superoxide.

2. Yields as high as 92% sodium superoxide have been obtained.

3. Magnetic measurements on the products of reaction between sodium peroxide and oxygen show a linear relationship when gram susceptibility is plotted against weight per cent. of sodium superoxide. Extrapolation to 100% sodium superoxide gives an effective moment of 2.07 Bohr magnetons for this compound.

4. The determination of sodium superoxide in the presence of diamagnetic impurities may be effected with reasonable accuracy by means of the magnetic method.

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[12] Anhydrous carbon tetrachloride was used as an inert diluent for the acetic acid.

[13] Kraus and Parmenter, THIS JOURNAL, **56**, 2385 (1934).

[14] Neuman, *J. Chem. Phys.*, **2**, 31 (1934).

[15] Klemm and Sodomann, *Z. anorg. allgem. Chem.*, **225**, 273 (1935).

[16] Helms and Klemm, *ibid.*, **241**, 97 (1935).

[17] Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 231.

[18] The sodium peroxide used in these experiments was found to be diamagnetic, having a gram susceptibility of -0.23×10^{-6}.