

*Superoxide Ions in Commercial Sodium Peroxide.*

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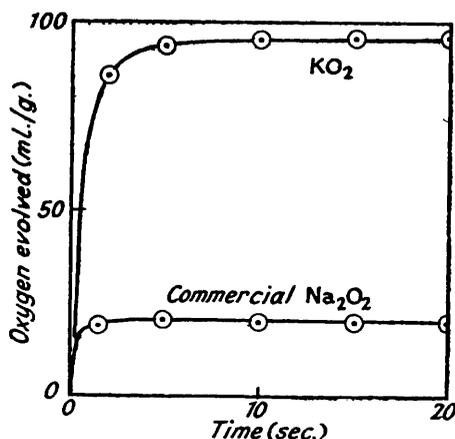
Experiments on the pale yellow sodium peroxide available commercially show it to contain about 10% of sodium superoxide, the sodium salt of the HO<sub>2</sub> free radical. In water, oxygen is evolved extremely rapidly according to the scheme  $2\text{NaO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{O}_2 + \text{H}_2\text{O}_2 + 2\text{NaOH}$ , analogous to the very rapid evolution given by the deep orange paramagnetic potassium superoxide. Two different samples of the pale yellow sodium peroxide were paramagnetic, with  $\chi = 2.7$  and  $2.2 \times 10^{-6}$  c.g.s. units. These values correspond to the presence of 9.2% and 7.7% of NaO<sub>2</sub> respectively. A determination of the sodium content of the former sample confirmed this.

ALTHOUGH potassium, rubidium, and caesium form two higher oxides, the peroxides and the superoxides containing the ions O<sub>2</sub><sup>=</sup> and O<sub>2</sub><sup>-</sup> respectively, it was long thought that sodium could form only the peroxide (Holt and Sims, *J.*, 1894, 65, 432; Rengade, *Ann. Chim. Phys.*, 1907, 11, 348; Kraus and Whyte, *J. Amer. Chem. Soc.*, 1926, 48, 1781; Neuman, *J. Chem. Phys.*, 1934, 2, 31). Joannis (*Compt. rend.*, 1893, 116, 1870) claimed that an oxide corresponding to Na<sub>2</sub>O<sub>3</sub> was formed by oxidising sodium in liquid ammonia at -50°, although Kraus and Whyte found that only the peroxide was formed at -33°.

George (*Discuss. Faraday Soc.*, 1947, 2, 203, 218) reported that pale yellow samples of commercial sodium peroxide contain about 10% of NaO<sub>2</sub>, and Schechter, Sisler, and

Kleinberg (*J. Amer. Chem. Soc.*, 1948, **70**, 267) reported that  $\text{NaO}_2$  is present in solutions of sodium treated with oxygen in liquid ammonia at  $-77^\circ$ . These investigations, the first based on paramagnetic-susceptibility determinations, measurements of oxygen evolution, and sodium analyses, and the second on oxygen-absorption measurements, first established that sodium forms the superoxide as do the heavier alkali metals. Schechter, Thomson, and Kleinberg later (*ibid.*, 1949, **71**, 1816) showed that under optimum conditions up to 85% of  $\text{NaO}_2$  can be prepared in liquid ammonia; Stephanou, Schechter, Argersinger, and Kleinberg (*ibid.*, p. 1819) obtained yields of  $\text{NaO}_2$  as high as 92% by treating  $\text{Na}_2\text{O}_2$  with oxygen at 490/298 atm.; and Seyb and Kleinberg (*Analyt. Chem.*, 1951, **23**, 115) described an oxygen-evolution method for estimating  $\text{NaO}_2$  and the amount present in synthetic  $\text{NaO}_2$ - $\text{Na}_2\text{O}_2$  mixtures.

The experiments on the commercial sodium peroxide have not hitherto been reported in detail because many of the essential features are covered by the work of Kleinberg *et al.* The present publication was decided upon for two reasons. The commercial  $\text{Na}_2\text{O}_2$  containing about 10% of  $\text{NaO}_2$  provides a useful magnetically dilute material for studying the paramagnetic resonance absorption of the  $\text{O}_2^-$  radical (Bennett, Ingram, Symons,



A comparison of the oxygen evolution when a sample of potassium superoxide containing 61% of  $\text{KO}_2$ , and sodium peroxide, react with water, showing the small but equally rapid evolution from sodium peroxide attributable to the presence of 10.3% of  $\text{NaO}_2$ .

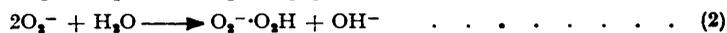
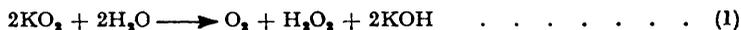
George, and Stanley Griffith, *Phil. Mag.*, 1955, **46**, 443), and it is therefore desirable to substantiate fully the presence of  $\text{O}_2^-$  by physical and chemical means. Secondly, it is desirable to draw attention to the fact that such a readily available material contains the  $\text{O}_2^-$  ion, and that for many experiments on  $\text{O}_2^-$  the commercial sodium peroxide may be used in place of  $\text{NaO}_2$ ,  $\text{KO}_2$ , etc., which are somewhat difficult to prepare.

**Results.**—There is both qualitative and quantitative evidence for the existence of superoxide ions in certain commercial samples of sodium peroxide.\* The qualitative observation that many samples are pale yellow is clearly at variance with a composition  $[\text{2Na}^+, \text{O}_2^-]$ . The colour has occasionally been attributed to traces of iron, but the samples examined contained only 0.017%, which makes this explanation extremely unlikely. Superoxides are deep orange at room temperature, so the presence of some 10% of superoxide ions in the samples of sodium peroxide is in accord with their pale yellow colour. The quantitative evidence is based on measurements of oxygen evolution, paramagnetic susceptibility, and sodium content.

**Oxygen evolution.** It is well known that superoxides evolve oxygen extremely rapidly in water according to reaction (1). George (*loc. cit.*) suggested that the most probable mechanism is proton transfer (2), followed by rapid electron transfer (3). Samples of sodium peroxide (20–30 mg.) also evolve a small amount of oxygen extremely rapidly,

\* A sample of sodium peroxide used in America was quite white and presumably contained no  $\text{O}_2^-$ , whereas most samples available in this country are pale yellow like those used in these experiments. Apparently the conditions used in the industrial preparation are sufficiently dissimilar to favour a different equilibrium mixture in the reaction  $\text{O}_2 + \text{O}_2 \rightleftharpoons 2\text{O}_2^-$ .

as shown by the comparison with  $\text{KO}_2$  in the Figure : in both cases the evolution is complete in less than 3 sec. The results are given in terms of oxygen evolved per g. at N.T.P., and the figure for sodium peroxide, 21 ml./g., corresponds to 10.3% of  $\text{NaO}_2$  present.



Oxygen is evolved from the hydrogen peroxide liberated by the solution of the  $\text{Na}_2\text{O}_2$  and the decomposition of the  $\text{NaO}_2$  far more slowly, at least an hour being required for complete reaction. The rate of the initial rapid evolution is greater than 20 ml.  $\text{g}^{-1} \text{sec}^{-1}$ , compared with 0.03 in the subsequent peroxide decomposition, so the rates thus differ by a factor of at least 600. However, if a catalyst is present, then a large proportion of the peroxide is also decomposed in 3—5 sec. With 1.0M- $\text{Fe}^{3+}$ , 74% and 46% of decomposition was obtained in water and in 5.0N-sulphuric acid respectively : and with 1.0M- $\text{Fe}^{2+}$ , 63% and 44%. Acidic saturated solutions of sodium persulphate gave 16%, but with 0.1M- $\text{Ag}^+$  ions present, and in alkaline solution, 87% and 80% decomposition was observed. These results are very similar to those obtained with  $\text{KO}_2$  (George, *loc. cit.*), and confirm that this rapid catalytic decomposition, like the reaction of the  $\text{O}_2^-$  ions, occurs predominantly within the environment of the solid peroxide or superoxide particles as they dissolve, with however, some of the hydrogen peroxide diffusing away, for otherwise 100% decomposition would be obtained.

**Paramagnetic susceptibility.** Superoxides are paramagnetic, for they contain the ionic radical  $\text{O}_2^-$ , an oxygen molecule with an additional electron (Neuman, *J. Chem. Phys.*, 1934, 2, 31). The susceptibility of two samples of sodium peroxide has been measured, and in both cases they were paramagnetic with mass susceptibilities of  $\chi = 2.7$  and  $2.2 \times 10^{-6}$  c.g.s. units. By extrapolation from the value for 92%  $\text{NaO}_2$ , Stephanou, Schechter, Argersinger, and Kleinberg (*loc. cit.*) obtained  $\chi = 33.0 \times 10^{-6}$  c.g.s. units for the pure compound. This value is uncorrected for the diamagnetic contribution, which, although affecting the value for the pure compound only slightly, will be increasingly important as the percentage of  $\text{NaO}_2$  in a mixture decreases. Savithri and Rao (*Proc. Indian Acad. Sci.*, 1942, 16, A, 221) determined the molar susceptibility of  $\text{Na}_2\text{O}_2$  as  $\chi_M = -28.1 \times 10^{-6}$  c.g.s. units, from which the susceptibility per g. can be calculated as  $\chi = -0.36 \times 10^{-6}$  c.g.s. unit. The susceptibilities of the two commercial sodium peroxide samples thus correspond to mixtures containing 9.2 and 7.7% of  $\text{NaO}_2$  respectively.

The paramagnetism is a feature of the solid peroxide, because the syrupy liquid, obtained by cautiously adding the minimum amount of water dropwise to get the solid into solution, was found to be diamagnetic, with  $k = -0.5 \times 10^{-6}$  c.g.s. unit, and furthermore completely colourless. These observations show that the colour and the paramagnetism cannot be due to heavy-metal impurities, for, whilst solution might diminish the colour, the paramagnetism would remain.

**Analysis.** The sodium content of sodium peroxide provides a sensitive check on its composition. As well as  $\text{Na}_2\text{O}_2$  (Na, 59.0%) and  $\text{NaO}_2$  (Na, 41.8%), it may contain  $\text{Na}_2\text{O}$  (Na, 74.3%) produced by prolonged heating during the combustion, and also sodium carbonate (Na, 43.4%) resulting from reaction with carbon dioxide. The presence of  $\text{Na}_2\text{O}$  thus leads to a high value for the sodium content, and the presence of  $\text{NaO}_2$  or  $\text{Na}_2\text{CO}_3$  to low values. Both samples of commercial sodium peroxide examined were fine, freely running powders, so the absorption of water vapour which would give hydrogen peroxide and sodium hydroxide, and hence a sticky solid, may be ignored.

The carbonate content of one of the samples was determined by the difference between the gas evolved from 0.1N-sulphuric acid and from 0.1N-sodium hydroxide, an independent check, involving absorption with potassium hydroxide, having shown that carbon dioxide as well as oxygen was evolved in acid solution. The mean of duplicate measurements gave a carbonate content of  $9.0 \pm 1.3\%$ . Estimation of the sodium as anhydrous sulphate gave values of 55.6% and 55.8% in duplicate determinations. The mean sodium content of 55.7% is significantly below that for  $\text{Na}_2\text{O}_2$  containing  $9.0 \pm 1.3\%$  of  $\text{Na}_2\text{CO}_3$  (*i.e.*

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57.5—57.8% Na), and, if it is assumed that the discrepancy is entirely due to the presence of  $\text{NaO}_2$ , calculation shows that 55.7% of Na corresponds to an  $\text{NaO}_2$  content of 11%. This value is to be compared with those of 10.3% and 9.2% obtained from the oxygen evolution and the paramagnetic-susceptibility measurements on the same sample. The presence of  $\text{Na}_2\text{O}$  and the absorption of water vapour, which would also affect the sodium content, could not be estimated, but the very close agreement between the three determinations of superoxide ion content, which is well within experimental error, strongly suggests that these factors are negligible.

Although it seemed very unlikely, the possibility that the superoxide content of the commercial sodium peroxide was due to the presence of potassium needed checking. Tests with sodium cobaltinitrite showed that there was less than 1 part of potassium in 600 parts, far too little to account for a superoxide content of about 10%.

The main reason why the presence of the higher oxide has been overlooked for so long is probably that the purity of sodium peroxide is usually determined by estimating the hydrogen peroxide liberated on the addition of water. However, hydrogen peroxide is also formed from  $\text{NaO}_2$ , and so the  $\text{Na}_2\text{O}_2$  content does not appear so low as it otherwise would. In fact, if estimated by peroxide titration, samples containing 10, 20, 30% of  $\text{NaO}_2$  would still appear to be 97.2, 94.5, and 91.5% of  $\text{Na}_2\text{O}_2$ .

### EXPERIMENTAL

*Analysis for Iron.*—Sodium peroxide (0.100 g.) was dissolved in water, neutralised with sulphuric acid, and evaporated to dryness to remove hydrogen peroxide. The residue was taken up in acetate buffer of pH 5.0, a little ascorbic acid added to reduce ferric to ferrous iron, and this was then estimated colorimetrically with 2:2'-dipyridyl. The 0.100 g. sample thus treated and made up to 100 ml.; the solution was found to contain  $3 \times 10^{-6}\text{M-Fe}^{2+}$ , corresponding to an initial content of 0.017% by weight.

*Analysis for Sodium and Potassium.*—This was carried out by treating a known weight of the peroxide with water, evaporating to dryness, adding an excess of concentrated sulphuric acid, again evaporating, heating to red heat, cooling, and weighing the anhydrous sodium sulphate formed: 0.4846 g. and 0.5255 g. of peroxide gave 0.7970 g. and 0.9047 g. of sulphate respectively. The sodium content of the peroxide is thus 55.6 and 55.8%; mean, 55.7%. Tests with sodium cobaltinitrite solution and a very dilute potassium chloride solution as a standard showed the potassium content of the peroxide to be less than 4 parts in 2500.

*Oxygen Evolution.*—The apparatus and method of operation were as described before (George, *loc. cit.*).

*Magnetic Susceptibility.*—This was measured at 19° by using a simple Gouy balance with a permanent magnet of field strength 4900 gauss and a cylindrical specimen tube of cross-sectional area 0.183 sq. cm. holding 1.4 ml. The solid peroxide samples showed a net increase in weight in the magnetic field of 6.1 and 7.4 mg., indicating paramagnetism, whereas their very concentrated solutions showed a decrease of about 1.1 mg., indicating diamagnetism. The balance was calibrated with a standard nickel chloride solution: 1 mg.  $\equiv 0.445 \times 10^{-6}$  unit of  $k$ , the volume susceptibility. The density of the packed samples was 1.25; hence the two samples had volume susceptibilities  $k = 3.3$  and  $2.7 \times 10^{-6}$ , and mass susceptibilities  $\chi = 2.7$  and  $2.2 \times 10^{-6}$ .