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Potassium Superoxide and the Three-Electron Bond*

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The highest oxide of potassium is shown to be paramagnetic, with a susceptibility corresponding to the formula KO_2 , the crystals being supposed to contain O_2 ions in a $^2\Pi$ state. The electronic structure $:\ddot{\text{O}}::\ddot{\text{O}}:-$ is

proposed for the superoxide ion. It is suggested that the substance be called potassium superoxide rather than tetroxide.

IN stating his rule that the number of valence electrons present in a molecule is a multiple of two, Lewis¹ pointed out that a number of substances, namely, NO , NO_2 , ClO_2 , the so-called free radicals of Gomberg, and the divalent nitrogen compounds of Wieland, are exceptions to the rule, inasmuch as the molecules of these substances contain an odd number of valence electrons. He termed such molecules "odd molecules." He noted that they are paramagnetic, and that most of them absorb very strongly in the visible region of the spectrum, that is, are highly colored.

In order to account for the stability of NO , NO_2 , etc., Pauling,² in a discussion of the nature of the chemical bond, argued that no single electronic structure with the odd electron on a given atom can satisfactorily represent the structure of the molecule. He then introduced the idea that the molecule resonates among several electronic structures, the accompanying extra resonance energy tending to stabilize the molecule. Thus in the case of NO he postulated two structures which were represented by $:\ddot{\text{N}}::\ddot{\text{O}}:$ and $:\ddot{\text{N}}::\ddot{\text{O}}:$. He found these two structures to have nearly the same energy, in which case resonance between them would lead to a more stable combined structure having a double bond and a three-electron bond, which he represented by $:\text{N}::\text{O}:$. A similar treatment was accorded NO_2 which he represented by

$(:\ddot{\text{O}}::\text{N}::\ddot{\text{O}}:, :\ddot{\text{O}}::\text{N}::\ddot{\text{O}}:)$, the double bond changing places regularly with the single and the three-electron bond. He also discussed the normal state ($^3\Sigma$) of the oxygen molecule, containing one electron-pair bond and two three-electron bonds, corresponding to the structure $:\ddot{\text{O}}::\ddot{\text{O}}:$.

Recently Brockway³ has examined ClO_2 by electron diffraction methods, and has found that the observed chlorine-oxygen distance in this compound is compatible with the presence of a three-electron bond and an electron-pair bond between the chlorine and one oxygen, and an electron-pair bond between the chlorine and the other oxygen. He represented this electronic structure by $(:\ddot{\text{O}}::\text{Cl}:\ddot{\text{O}}:, :\ddot{\text{O}}:\text{Cl}::\ddot{\text{O}}:)$.

The highest oxide of potassium is commonly known as the tetroxide, K_2O_4 . A reasonable electronic structure for the $\text{O}_4^{=}$ ion is $:\ddot{\text{O}}:\ddot{\text{O}}:\ddot{\text{O}}:\ddot{\text{O}}:=$. Such a structure corresponds to a colorless and diamagnetic substance. If, however, the formula of the substance were KO_2 , it would contain O_2^- ions, for which we could write the structures $:\ddot{\text{O}}:\ddot{\text{O}}:-$ and $:\ddot{\text{O}}:\ddot{\text{O}}:-$. These two have the same energy; resonance between them would give a $^2\Pi$ state, $:\ddot{\text{O}}::\ddot{\text{O}}:-$, with a three-electron bond between the oxygen atoms. An ion such as this, containing an odd number of electrons, would cause the substance to be paramagnetic, and probably colored.

The substance actually has a deep orange color at ordinary temperatures, suggesting the

* Contribution No. 387, Gates Chemical Laboratory.

¹ G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, p. 80. Chemical Catalog Co., 1923.

² Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); **53**, 3225 (1931).

³ L. O. Brockway, Proc. Nat. Acad. Sci. **19**, 303, 868 (1933).

formula KO_2 . In order to decide definitely between the two formulas, I undertook, at the suggestion of Professor Linus Pauling, the determination of the magnetic susceptibility. The substance was found to be paramagnetic, with a susceptibility corresponding to a Bohr magneton number of 2.04 at room temperature. This is close to the value 1.73 for the spin moment of one unpaired electron, and to the value 1.84 for a $^2\Pi$ molecule with doublet separation as in NO , as calculated by Van Vleck, the disagreement being explicable as resulting from experimental error or possibly from mutual interaction of the magnetic dipoles in the condensed phase. Hence we may say with confidence that the highest oxide of potassium has the formula KO_2 . In view of this, the usual name potassium tetroxide seems unsatisfactory; at the suggestion of Professors W. C. Bray and E. D. Eastman of the University of California we propose that the substance be called potassium superoxide. The superoxide ion, $:\ddot{\text{O}}:\ddot{\text{O}}:^-$, occupies an intermediate position between the peroxide ion, $:\ddot{\text{O}}:\ddot{\text{O}}:^-$, and the normal oxygen molecule, $:\ddot{\text{O}}:\ddot{\text{O}}:$.

I am indebted to Professor Pauling for suggesting the investigation.

EXPERIMENTAL PART

Preparation of the oxide

Potassium superoxide was prepared by slow burning of potassium metal in incompletely dried oxygen at 300° . The apparatus used is shown diagrammatically in Fig. 1. About 15 g of potassium was first washed in ether to remove the oil from the surface. The apparatus was swept out with dry nitrogen after which the metal was placed in chamber *A*. The metal was then melted and filtered through the glass wool pad at the base of *A* into the vessel *C*, the volume of which was 50 cc. A slight pressure of nitrogen was found necessary to force the molten metal through the filter pad. The apparatus was next sealed at *B* and the metal slowly distilled into *E*. The distillation was carried out under reduced pressure and took place at about 200° . A portion of the distillate was retained in the tubes *F* for tests on the purity of the metal by means of magnetic measurements. When cool, the appa-

ratus was placed under a slight pressure of nitrogen at *G*, the tubes *F* were then sealed off and the apparatus broken at *D*. The vessel *E* was then placed in a metal bath (m.p. 65°) and raised slowly to a temperature of 300° . At the same time a stream of nitrogen was passed through the apparatus, through *D*. Pure oxygen which was washed in concentrated sulfuric acid and passed through soda lime and calcium chloride in tubes 30 cm long was then gradually substituted for the nitrogen. The gas was passed slowly into the apparatus with constant heating for 50 hours. At the end of this time the potas-

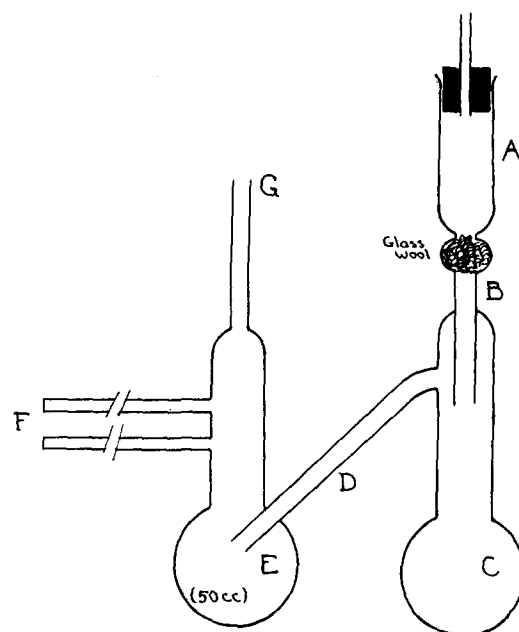


FIG. 1. Apparatus for distilling potassium and preparing potassium superoxide.

sium had been completely converted into the superoxide in the form of an orange powder. The product was allowed to cool in a stream of oxygen and the apparatus was finally sealed at *G* and *D*. Because of the great reactivity of the oxide with moisture and carbon dioxide in the atmosphere all subsequent manipulations of the compound were carried on in a "dry chamber." Even here the substance absorbed some moisture on standing more than an hour. The oxide was analyzed for alkali by titrating its aqueous solution with standard acid. The percent potassium was 1.8 percent higher than required by

the formula K₂O₄ or KO₂; this discrepancy may be due to water absorbed during manipulations attendant on grinding and weighing the samples.

The behavior of the potassium during oxidation was the same as reported by Holt and Simms.⁴ The oxygen used was dried as described above on the recommendation of these authors. They found that more thorough drying is undesirable since it becomes extremely difficult to burn potassium in extremely dry oxygen.

Magnetic measurements

The magnetic susceptibilities of the oxide, a sample of the metal from which it was prepared, and of an aqueous solution of the oxide were measured in the usual manner. A Sartorius micro-balance was used for the weighings. Acknowledgment is here made to Dr. Alfred Faessler of the Norman Bridge Laboratory of Physics for the kind loan of his apparatus.

The substances measured were enclosed in glass tubes 0.17 cm in diameter and with ends

sealed off square. These tubes were sections from the same piece of glass tubing.

Potassium was found to be slightly paramagnetic, with a volume susceptibility of 0.40×10^{-6} at 21.5° in a field strength of 13,290 gauss. This is slightly lower than the value of 0.52×10^{-6} reported in the *International Critical Tables* and shows that the metal used was free from paramagnetic and ferromagnetic impurities.

Potassium superoxide was found to be paramagnetic. The volume susceptibility was 30.44×10^{-6} at 25.6° in a field strength of 8740 gauss. The effective Bohr magneton number was calculated from this to be 2.04 for the formula KO₂.

The aqueous solution of the oxide was slightly diamagnetic as would be expected of a pure solution of potassium hydroxide. This indicates that the paramagnetism exhibited by the oxide was inherent to the oxide and not to impurities. All of the values reported above have been corrected for the magnetic effects of the enclosing tubes.

⁴ Holt and Simms, J. Chem. Soc. T. 432 (1894).