one-half mole of quinone afforded the optically active quinine salt of  $\alpha$ -apopodophyllic acid with a melting point of 213-214° and a rotation  $[\alpha]^{27}$ D Anal. Calcd. for C<sub>42</sub>H<sub>46</sub>N<sub>2</sub>O<sub>10</sub>: C, 68.28;  $-232^{\circ}$ . H, 6.28; N, 3.79. Found: C, 68.1; H, 6.2; N, 3.9. A mixture of this salt with the quinine salt of authentic  $\alpha$ -apopodophyllic acid (m.p. 214–215°;  $[\alpha]^{27}D$  – 235°) melted at 213–214°. The synthetic [a] D = 255 ) merted at 215-214 . The synthetic  $\alpha$ -apopodophyllic acid  $[\alpha]^{26}D = -158^{\circ}$ ) regenerated from the salt melted at 168-169° and did not depress the melting point of an authentic sample  $[\alpha]^{24.5}$ D -158°). Determination and comparison of the infrared and ultraviolet absorption curves confirmed the identity of the synthetic and authentic acids. Lactonization of  $\alpha$ -apopodophyllic acid to  $\alpha$ -apopicropodophyllin (with its double bond in the 1,2-position<sup>6</sup>) was effected by heating as described in the literature<sup>5</sup> or preferably by boiling the acid with 10% sulfuric acid. The  $\alpha$ -apopicropodophyllin melted alone or admixed with authentic  $\alpha$ -apopicropodophyllin (m.p. 235–237°) at 233-235°. The action of dry hydrogen chloride in glacial acetic acid followed by hot aqueous acetone containing calcium carbonate transformed a-apopicropodophyllin to picropodophyllin, m.p.  $216-217^{\circ}$ . Anal. Calcd. for  $C_{22}H_{22}O_8$ : C, 63.75; H, 5.35. Found: C, 63.5; H, 5.4. The melting point of a mixture of this material with authentic picropodophyllin (m.p. 214-215°) was 214-215°. To clinch the identity, the acetate of the picropodophyllin from  $\alpha$ -apopicropodophyllin was prepared<sup>7</sup> and compared with an authentic sample. The melting points and the rotations of the two acetates were, respectively, 209-211° and 210-211°, and  $[\alpha]^{26}D + 26.5$  and  $[\alpha]^{28}D + 28.8^{\circ}$ ; the melting point of a mixture of the two acetates was not depressed.

(7) E. Späth, F. Wessely and L. Kornfeld, *Ber.*, **65**, 1536 (1932); W. Borsche and J. Niemann, *Ann.*, **494**, 126 (1932).

Boston University Walter J. Gensler Boston, Massachusetts Shih Yi Wang Received October 7, 1954

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# ON THE NON-EXISTENCE OF DISCRETE O<sub>3</sub>-IONS IN $K_2O_3$

Sir:

The existence of definite oxides of the alkali metals (except lithium) having the formula  $M_2O_3$ , and variously called trioxides or sesquioxides, has been generally accepted since the early investigations of Joannis<sup>1</sup> and Rengade.<sup>2</sup> These compounds are obtained in the rapid oxidation of the alkali metals dissolved in liquid ammonia or as intermediates in the thermal dissociation of the superoxides  $MO_2$ . They can be identified by the sharp color change and their chemical analysis corresponds closely to the stoichiometric formula  $M_2O_3$ . In some cases their density and melting point have been determined. Furthermore, de Forcrand<sup>3</sup> has measured the dissociation pressure and the heat of formation of the potassium compound  $K_2O_3$ .

However, no actual determination of their

(1) M. A. Joannis, Compt. rend., 116, 1370 (1893).

(2) E. Rengade, ibid., 140, 1536 (1905); 144, 920 (1907).

(3) R. de Forcrand, ibid., 158, 991 (1914).

structure has been reported so far. Originally they were assumed to contain the  $O_3^-$  ion for which the electronic structure may be written<sup>4</sup>

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but, of late years, the tendency has been to consider them as lattice compounds of the peroxides and superoxides with general formula  $M_2O_2 \cdot 2MO_2$ . Recently, in connection with a spectroscopic investigation of the  $HO_2$  radical now under way in this laboratory, we have examined the infrared spectrum of the presumed K<sub>2</sub>O<sub>3</sub> made by heating KO<sub>2</sub> in an open crucible until the characteristic brick-red solid was obtained. Because of the extreme hygroscopic nature of these compounds great care was necessary in preparing the samples for spectroscopic studies. A mull in Nujol was found to be the most appropriate technique. Repeated recordings of the spectrum of this material over the whole rock-salt region failed to produce any absorption band attributable to O<sub>3</sub><sup>=</sup> ions. Similarly, no specific band was observed in the case of the superoxide KO2, either mulled in Nujol or as a "dust" film on a rock-salt plate, at least as long as the powder was protected from the atmosphere. Short exposure to damp air immediately brought out nearly a dozen bands belonging to the carbonate, hydroperoxide and, possibly, other ions. In particular the characteristic frequency of the peroxide group at 880 cm.-1 was prominent under such conditions.

These observations are consistent with the fact that both the peroxide and the superoxide ions,  $O_2^-$  and  $O_2^-$ , are homopolar, hence their vibrations are infrared inactive. Therefore, we consider the absence of characteristic infrared bands as sufficient evidence to rule out any  $O_3^-$  ions in the alkaline sesquioxides. These must be molecular compounds of normal peroxides and superoxides as commonly presumed. This question could best be confirmed by X-ray diffraction or by a study of phase equilibria in the systems: alkali metals-oxygen.

We are grateful to the Callery Chemical Co., Callery, Penn., for a generous sample of potassium superoxide. This work was done while one of us (K.B.H.) held a research fellowship from the Consolidated Mining and Smelting, Trail, B.C.

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

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**Received September 7, 1954** 

## **PARAMAGNETIC RESONANCE IN LIQUID SULFUR\*** Sir:

We have examined liquid sulfur in the range from  $190^{\circ}$  to  $375^{\circ}$  by means of paramagnetic resonance absorption spectroscopy and have found that in this temperature range the intensity of the paramagnetism of the melt increases with temperature. These results support the hypothesis, used in

\* Supported in part by the Squier Signal Laboratory, U. S. Army Signal Corps.

Sir:

theoretical studies by Powell and Eyring<sup>1</sup> and Gee,<sup>2</sup> that liquid sulfur contains chain-type polymers. The point of view adopted by Krebs<sup>3</sup> that large rings are the primary type of polymeric material is probably incorrect.

The sulfur was purified by the method of Bacon and Fanelli,<sup>4</sup> but after being subjected to repeated cycles of heating and cooling until the elapsed time of heating approached about 30 hours, a few black particles were observed in the sample, and the width of the resonance line had increased by about a factor of two. In addition, the sample showed a very weak paramagnetic absorption at room temperature whereas no absorption had been detected at room temperature before the extended period of heating. It is evident that greater care must be taken to insure a high degree of purity, and therefore our present results cannot be relied on for quantitative validity.

Our measurements<sup>5</sup> were made on sulfur which had been degassed by 15 cycles of melting and freezing under vacuum (about 10<sup>-3</sup> mm.). The concentration of radicals was found to increase by a factor of from 100 to 200 in the range from 190 to 375°; the absolute value of the intensity corresponds to a radical concentration of the order of  $10^{-5}$  mole/1. at 200°. The value of  $\Delta H$  for breaking a S-S bond in a long chain that is derived from these data is consistent with the value obtained by Gee<sup>2</sup> from the viscosity data of Bacon and Fanelli,<sup>5</sup> and the observed radical concentration at 200° corresponds in order of magnitude to that estimated by Gee. The width of the resonance line is about  $15^{\circ}$  gauss at 190° and appears to increase to about 35 gauss at 375°. The spectroscopic splitting factor (g-value) is 2.02.

Bacon and Fanelli<sup>6</sup> reported that several varieties of C.P. sulfur were blackened after they were subjected to boiling for 2–3 minutes over a free-flame. We have found that N. F. sublimed sulfur flowers supplied by the Amend Drug Co. yields black particles after even less severe heat treatment. These black particles are paramagnetic at room temperature; the line width is about 20 gauss and the g-value is 2.01. It should be emphasized that in the absence of black particles the observed intensity of paramagnetic absorption was reversible with temperature and paramagnetism was not detected below about 190°.

Precise measurements will require not only more highly purified sulfur than has been used, but also a reliable standard of paramagnetic intensity usable over the entire temperature range. In addition to the value of  $\Delta H$  for a S-S bond, such measurements can be used with data like that of Hammick, *et al.*,<sup>7</sup> for the weight fraction of polymer to obtain

(1) R. E. Powell and H. Eyring, THIS JOURNAL, 65, 648 (1943).

- (2) G. Gee, Trans. Faraday Soc., 48, 515 (1952).
  (3) H. Krebs, Angew. Chem., 65, 293 (1953).
- (4) R. F. Bacon and R. Fanelli, THIS JOURNAL, 65, 639 (1943).

(5) A preliminary account of our instrument, which employs a type 2K25 Klystron at a wave length of 3.2 cm., has been published: J. M. Hirshon, R. L. White and G. K. Fraenkel, *Rev. Sci. Instr.*, 23, 772 (1952). A detailed account has been submitted for publication by J. M. Hirshon and G. K. Fraenkel to *Rev. Sci. Instr.* 

(6) R. F. Bacon and R. Fanelli, Ind. Eng. Chem., 34, 1043 (1942).

(7) D. L. Hammick, W. Cousins and E. Langford, J. Chem. Soc., 797 (1928).

the degree of polymerization as a function of temperature. Present limitations on sensitivity preclude measurements at temperatures much lower than 190°.

DEPARTMENT OF CHEMISTRY COLUMBIA UNIVERSITY NEW YORK 27, N. Y. Donald M. Gardner

N. Y. George K. Fraenkel Received October 20, 1954

### NEW SODIUM PHOSPHATES

A new series of sodium hydrogen phosphates has been discovered and two new compounds have been isolated. At 300° and above, monosodium orthophosphate reacts with orthophosphoric acid to yield sodium acid metaphosphate melts and when the melts are slowly cooled crystalline acid metaphosphates are formed. The crystallization is hastened if the melt is stirred for two or three minutes after the sample reaches the required composition.

A tetrametaphosphate results from the reaction:  $2NaH_2PO_4 + 2H_3PO_4 \xrightarrow{400 \text{ °C.}} Na_2H_2(PO_3)_4 + 4H_2O$ 

The crystalline acid metaphosphate has a unique X-ray pattern, it melts near 400° and has one of two alternate structures

A second reaction

$$2\mathrm{NaH}_{2}\mathrm{PO}_{4} + \mathrm{H}_{3}\mathrm{PO}_{4} \xrightarrow{300^{\circ}\mathrm{C.}} \mathrm{[Na}_{2}\mathrm{H}(\mathrm{PO}_{3})_{3}]_{n} + 3\mathrm{H}_{2}\mathrm{O}$$

yields a compound, the crystals of which are fibrous. The disodium monohydrogen acid metaphosphate also has a unique X-ray pattern and melts near 420°. The structure of this compound is not yet known but indications are that it is a long chain compound (polyphosphate). The reactions involving other ratios of monosodium orthophosphate to orthophosphoric acid also yield acid metaphosphates but are more difficult to isolate in a pure condition than those mentioned above.

The author gratefully acknowledges the assistance of Dr. William Edwards and Mr. R. Ferguson.

INORGANIC CHEMICALS DIVISION MONSANTO CHEMICAL COMPANY DAYTON, OHIO Edward J. Griffith

RECEIVED OCTOBER 2, 1954

### THE LINKAGE OF GLUCOSE IN COLIPHAGE NUCLEIC ACIDS<sup>1</sup>

Sir:

Independent reports<sup>2,3</sup> of two unusual properties of the deoxyribonucleic acids (DNA) of the related T6 and T4 coliphages led to the present investigation. The inability of pancreatic deoxyribonuclease (DNase) and intestinal phosphatase to hydrolyze T6 DNA to a reasonable quantity of hydroxy-

(1) Work performed under Contract No. W-7405-eng-26 for the Atomic Energy Commission,

(2) S. S. Cohen, Symp. Quant. Biol., 18, 221 (1953).

(3) M. Jesaitis and W. F. Goebel, ibid., 18, 205 (1953).