one-half mole of quinone afforded the optically active quinine salt of α-apopodophyllic acid with a melting point of 213–214° and a rotation $[\alpha]^{27}\mathrm{D}$ −232°. *Anal.* Calcd. for $C_{42}H_{46}N_2O_{10}$: C, 68.28; 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 α-apopodophyllic acid (m.p. 214–215°; $[\alpha]^{27}\mathrm{D}$ −235°) melted at 213–214°. The synthetic α-apopodophyllic acid $[\alpha]^{26}\mathrm{D}$ −158°) regenerated from the salt melted at 168–169° and did not depress the melting point of an authentic sample $[\alpha]^{24.5}\mathrm{D}$ −158°). Determination and comparison of the infrared and ultraviolet absorption curves confirmed the identity of the synthetic and authentic acids. Lactonization of α-apopodophyllic acid to α-apopicropodophyllin (with its double bond in the 1,2-position[6]) was effected by heating as described in the literature[5] or preferably by boiling the acid with 10% sulfuric acid. The α-apopicropodophyllin melted alone or admixed with authentic α-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 α-apopicropodophyllin to picropodophyllin, m.p. 216–217°. *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 α-apopicropodophyllin was prepared[7] and compared with an authentic sample. The melting points and the rotations of the two acetates were, respectively, 209–211° and 210–211°, and $[\alpha]^{26}\mathrm{D}$ +26.5 and $[\alpha]^{28}\mathrm{D}$ +28.8°; 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
BOSTON, MASSACHUSETTS
WALTER J. GENSLER
SHIH YI WANG

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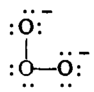
ON THE NON-EXISTENCE OF DISCRETE O_3^- IONS IN K_2O_3

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[1] and Rengade.[2] 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[3] has measured the dissociation pressure and the heat of formation of the potassium compound K_2O_3.

However, no actual determination of their structure has been reported so far. Originally they were assumed to contain the $O_3^=$ ion for which the electronic structure may be written[4]



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_2O_3 made by heating KO_2 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 $O_3^=$ ions. Similarly, no specific band was observed in the case of the superoxide KO_2, 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.

[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).

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

DEPARTMENT OF CHEMISTRY
LAVAL UNIVERSITY
QUEBEC, CANADA
PAUL A. GIGUÈRE
KENNETH B. HARVEY

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PARAMAGNETIC RESONANCE IN LIQUID SULFUR*

Sir:

We have examined liquid sulfur in the range from 190° to 375° 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

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