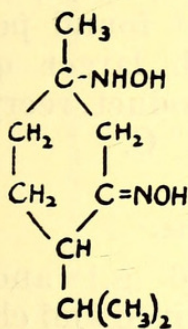


1-NITROSOMENTHONE OXIME AND ITS  
DECOMPOSITION.

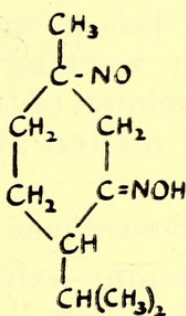
By PROFESSOR J. C. EARL, D.Sc., Ph.D.,  
D. JOHNSON, B.Sc.,  
and J. G. MCKEAN.

(Manuscript received, July 20, 1938. Read, August 3, 1938.)

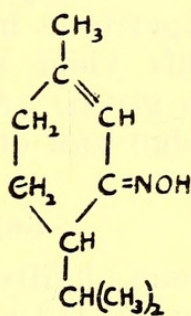
The hydroxylamino-oxime of piperitone (I) yields a nitroso-compound on oxidation (Baker and Smith, "Research on the Eucalypts", 2nd Edition, p. 392). This nitroso-compound (II) has now been isolated and studied. When first prepared it melts at 124°-125° C., but the melting point soon falls on keeping. After ten months under ordinary laboratory conditions a preparation was found to have lost the properties of a nitroso-compound and to consist mainly of piperitone oxime (III) together with some resinous material.



I



II



III

The reaction which had taken place seemed therefore to amount to the splitting off of hyponitrous acid,  $\text{HNO}$ , from the nitroso-oxime. Hyponitrous acid is unstable and breaks down easily to nitrous oxide and water, so that nitrous oxide might be expected as one of the products when the nitroso-oxime decomposes (cf. Anderson and Hammick, *J. Chem. Soc.*, 1935, 1679). The decomposition was found to be accelerated by the influence of heat. Working under carefully controlled conditions nitrous



oxide was collected and identified. The amount obtained was 34.2 per cent. of that which would be produced by a quantitative decomposition into oxime, nitrous oxide and water. The solid residue remaining after the decomposition consisted principally of piperitone oxime which was recovered readily on recrystallisation.

## EXPERIMENTAL.

### Piperitone hydroxylamino-oxime.

This was prepared by a modification of the method described by Read and Smith (*J. Chem. Soc.*, 1921, 119, 783). Redistilled piperitone (6 g.) was dissolved in methylated spirit (18 ml.) and a solution containing caustic potash (6 g.) in water (3 ml.) added. The mixture, which became brown, was heated to 75° C. on a water bath and a solution of hydroxylamine hydrochloride (6 g.) in water (6 ml.) added slowly. After heating to boiling under a reflux condenser for 15 minutes the whole reaction mixture was evaporated to dryness on the water bath. The residue was treated with water to remove potassium chloride and was then washed several times with several small quantities of alcohol. The product so obtained melted at 171° C. and was sufficiently pure for the preparation of the nitroso-compound. The yield was about 40 per cent., calculated on the piperitone used, but it was not found possible to obtain this yield when working with larger quantities than those given. A specimen of the product, recrystallised from alcohol and ether, melted at 174° C.

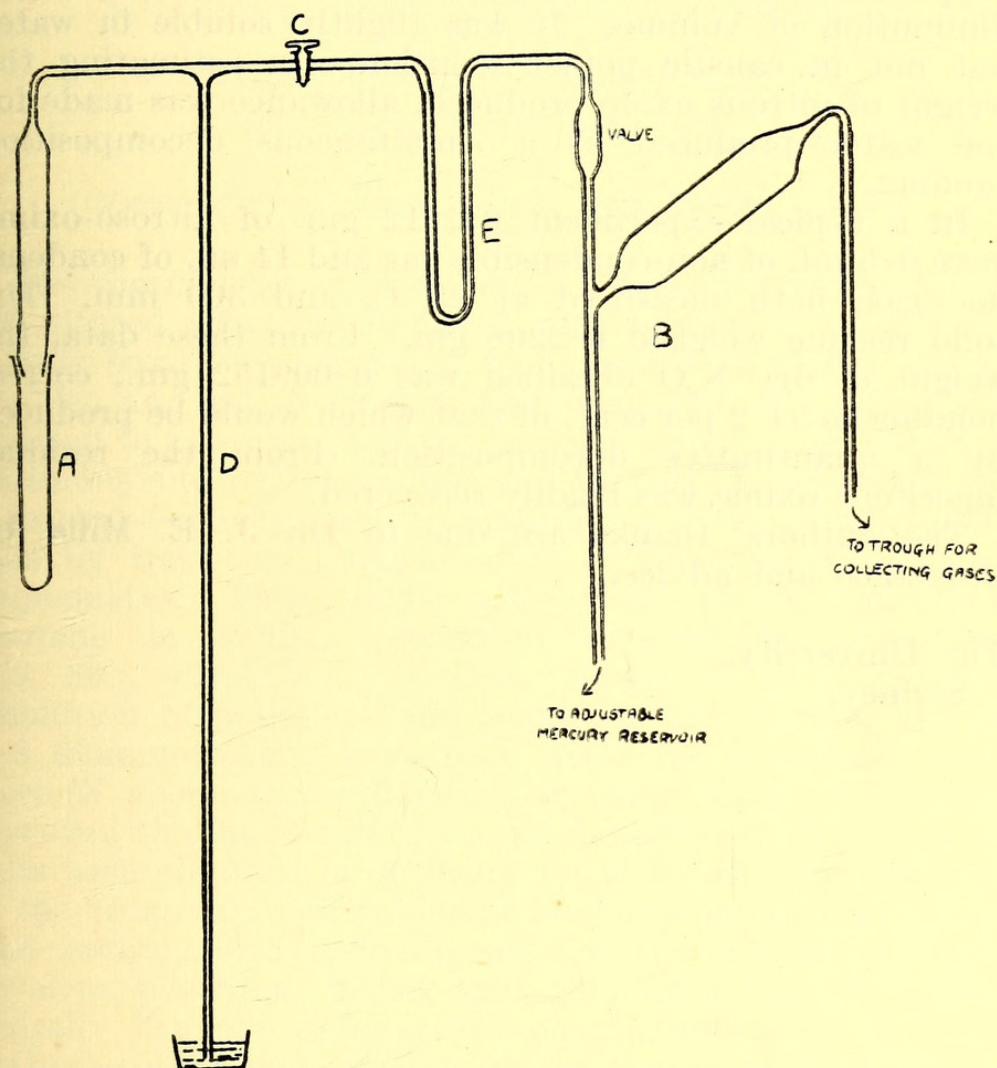
### 1-nitroso-menthone oxime.

Piperitone hydroxylamino-oxime (6 g.) and yellow mercuric oxide (12 g.) were intimately mixed and chloroform (70 ml.) added. The mixture was boiled under a reflux condenser for two hours, after which it was cooled and immediately filtered. On being allowed to stand, the filtrate deposited a pale blue crystalline material (3 to 3.5 g.). It melted, when freshly prepared, at 124°-125° C. to a blue liquid. Found: nitrogen, 13.7 per cent.; calculated for  $C_{10}H_{18}N_2O_2$ , 14.1 per cent. The substance was sparingly soluble in alcohol or ether, more so in benzene, toluene, or chloroform, the solutions being blue or green in colour. When it was heated with either alcoholic potash or alcoholic sulphuric acid, piperitone oxime was obtained.



## Thermal Decomposition of the Nitroso-oxime.

The decomposition of the nitroso-oxime was studied under conditions which allowed the gaseous products to be collected and examined. The apparatus used was as illustrated.



A weighed quantity of the nitroso-oxime was introduced into the tube A, and the whole apparatus exhausted by means of the mercury pump B. The stopcock C was then closed and the tube containing the nitroso-oxime heated at  $116^{\circ}\text{C}$ . with an oil bath for 45 minutes, by which time the mercury in the manometer D had ceased to fall. The U-tube E was then immersed in liquid air and the stopcock opened sufficiently to allow a slow stream of gas to pass through. When the manometer ceased to indicate any change in pressure, the apparatus was exhausted again by the pump and the uncondensed gas collected in a graduated



tube over mercury. It was identified as nitrogen. The liquid air bath was then removed, the condensable gases being pumped off and collected. As far as could be determined, this material consisted of nitrous oxide. It was colourless, did not go brown on mixing with air, and supported the combustion of phosphorus with a very slight diminution of volume. It was slightly soluble in water but not in caustic potash solution. In estimating the weight of nitrous oxide produced, allowance was made for the water produced as a simultaneous decomposition product.

In a typical experiment 0.2412 gm. of nitroso-oxime gave 0.5 ml. of non-condensable gas and 14 ml. of condensable gas, both measured at 25° C. and 300 mm. The solid residue weighed 0.2208 gm. From these data, the weight of dry  $N_2O$  obtained was 0.009152 gm., corresponding to 34.2 per cent. of that which would be produced by a quantitative decomposition. From the residue, piperitone oxime was readily recovered.

The authors' thanks are due to Dr. J. E. Mills for assistance and advice.

The University,  
Sydney.

---



Earl, John Campbell, Johnson, D, and Mckean, J G. 1938. "1-nitrosomethone oxime and its decomposition." *Journal and proceedings of the Royal Society of New South Wales* 72, 109–112. <https://doi.org/10.5962/p.360236>.

**View This Item Online:** <https://www.biodiversitylibrary.org/item/174130>

**DOI:** <https://doi.org/10.5962/p.360236>

**Permalink:** <https://www.biodiversitylibrary.org/partpdf/360236>

#### **Holding Institution**

Smithsonian Libraries and Archives

#### **Sponsored by**

Biodiversity Heritage Library

#### **Copyright & Reuse**

Copyright Status: In Copyright. Digitized with the permission of the rights holder

Rights Holder: Royal Society of New South Wales

License: <http://creativecommons.org/licenses/by-nc-sa/3.0/>

Rights: <https://www.biodiversitylibrary.org/permissions/>

This document was created from content at the **Biodiversity Heritage Library**, the world's largest open access digital library for biodiversity literature and archives. Visit BHL at <https://www.biodiversitylibrary.org>.