TABLE II

Compound		Peimine (P)	Hydrochloride	Hydrobromide	Acid sulfate	Platinchloride	Aurichloride
M. p., °C.		224	295, dec.	293.5–294	278–280	233–235, dec.	164–165
Formula		$C_{26}H_{43}O_3N$	$P \cdot HCl$	$P \cdot HBr$	$P \cdot H_2SO_4$	$P_2 \cdot H_2PtCl_6$	$P \cdot HAuCl_4$
Carbon, %	Calcd.	74.75	68.74	62.61	60.53		
	Found[a,b]	74.65[c]	69.07, 68.77	62.92, 62.88, 63.13[a]	60.28, 60.27		
Hydrogen, %	Calcd.	10.38	9.77	8.90	8.80		
	Found[a,b]	10.42[d]	9.84, 9.85	9.04, 8.86, 8.77[a]	8.81, 8.64		
Nitrogen, %	Calcd.	3.35		2.81			
	Found[a,b]	3.56[e]		2.72[a]			
%	Calcd.			Br 16.04		Pt 15.68	Au 26.03
	Found			Br 15.55[a]		Pt 15.45 15.36	Au 24.9 25.09

Molecular weight determination (Rast); 0.288 mg. in 3.520 mg. camphor. ΔT, 9.2°. 0.268 mg. in 3.810 mg. camphor; ΔT, 7.7°. Calcd. for $C_{26}H_{43}O_3N$, 417.3. Found: 336,[a] 365.[2]

[a] Analyses made by Dr. Ing. A. Schoeller, Toelzestrasse 19, Berlin-Schmargendorf, Germany. [b] Analyses made by Dr. Carl Tiedcke, Bismarckstrasse, Hamburg 19, Germany. [c] Average: 74.75, 74.85,[a] 74.67,[a] 74.76, 74.58,[b] 74.39,[b] 74.53.[b] [d] Average: 10.30, 10.15, 10.49,[a] 10.54,[a] 10.43,[b] 10.53,[b] 10.51.[b] [e] Average: 3.52, 3.60, 3.77, 3.38,[a] 3.36,[a] 3.72.[b]

Summary

Peimine, melting at 224°, has been obtained in a more pure condition. Its formula is $C_{26}H_{43}O_3N$, instead of $C_{19}H_{30}O_2N$, which was assigned to it by Chou. The present formula is substantiated by the results of analysis of several salts; namely, the hydrochloride, bromide, acid sulfate, platinichloride and aurichloride.

SHANGHAI, CHINA RECEIVED MAY 7, 1936

NOTES

An Apparatus for the Determination of the Absorption of Small Quantities of Gas by Solutions

BY H. E. BENT, W. F. GRESHAM AND N. B. KEEVIL

The apparatus illustrated in the figure is designed to measure the absorption of small amounts of gas by solutions contained in sealed glass capsules. The apparatus allows one to break and empty the capsule, measure the amount of oxygen absorbed and make a correction for the amount of oxygen dissolved in the solvent. The sample is contained in a capsule "G" and the oxygen to be introduced is measured in a capillary by means of the scale "B," a small slug of mercury in the capillary serving to confine the gas.

The particular problem which necessitated the construction of this apparatus was the determination of the purity of small quantities of organic free radicals by measuring the quantity of oxygen absorbed. Samples of a half gram or larger may conveniently be studied in the apparatus developed for measuring the heat of the reaction.[1] Frequently, however, it is desirable to analyze with a precision of about 1% a dilute solution of a free radical which will not absorb more than about 1 cc. of oxygen. The details of breaking the capsule and measuring the absorption of oxygen together with typical experimental results are given in the following paragraphs.

The manipulation of the apparatus will be evident from the figure and the following description. "A" is a stopcock through which the apparatus may be evacuated after the capsule containing the solution of the free radical has been placed in the apparatus. "B" is a scale placed behind the capillary (diameter 4 mm.) in order that the volume of oxygen introduced into the absorption bulb may be accurately measured. "C" is a three-way stopcock which connects the capillary tube to the supply of oxygen and to the

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[1] Bent, Cuthbertson, Dorfman and Leary, THIS JOURNAL, **58**, 165 (1936); Bent and Cuthbertson, *ibid.*, **58**, 170 (1936).

absorption bulb. "D" leads to the oxygen supply and has a blow-off tube below it to permit better control of the pressure. By properly adjusting the pressure a small volume of mercury is introduced into the capillary through "C" before it is filled with oxygen. This slug is blown by oxygen to the top of the capillary. When the cock "C" is carefully turned to introduce oxygen into the absorption bulb which is at a slightly lower pressure the slug of mercury descends and gives a measure of the amount of gas which has been introduced. Provided the tube is clean no difficulty is encountered from the slug's dropping in the capillary. "E" is a thermometer which measures the temperature in the jacket around the absorption bulb. The absorption bulb is just above "F" and at "F" is a reference mark to which the bulb is calibrated. "G" is the capsule which is of rather peculiar design. At the top the capsule is sufficiently blunt to prevent its wedging in the constriction. At the bottom there is a little bulge which permits the glass rod "H" to hold the capsule submerged after it has been emptied. The capsule below the lower bulge is constricted for a short length before drawing down to a capillary. The reason for this is that the capsule cannot easily be emptied unless there is sufficient volume between the lower part of the capsule and the outside tube to hold all of the solution. The contents of the capsule are expelled below the surface of the mercury by warming. If the capsule had not been constricted at the bottom the solution would have come out of the capsule and surrounded the latter, thus making it difficult to expel the contents, as the solution around the outside would have warmed up first and been pushed back into the capsule. The glass rod "H" is connected by a fresh piece of gum rubber tubing. The rubber is connected to a glass tube at such an angle that it is always covered by mercury and does not come in contact with the solution. At the beginning of a run the mercury is lowered and the capsule held by the rod "H." After evacuation the mercury is raised around the capsule and the tip of capsule broken by means of this rod. After emptying the capsule the rod holds the glass down out of the way of the solution while it is absorbing oxygen. "I" is a rubber stopper which is held up by a steel washer which in turn is held securely in place by wires which are not shown. "J" is a pinchcock which permits the mercury to be held at a fixed height in the absorption bulb. "K" is a reservoir of mercury which can be evacuated for removal of mercury from the absorption bulb or may be open to the atmosphere or maintained at any desired intermediate pressure. The pressure in the absorption bulb is measured by means of the mercury column in the tube which is open at the top, a small cathetometer and steel scale, not shown.

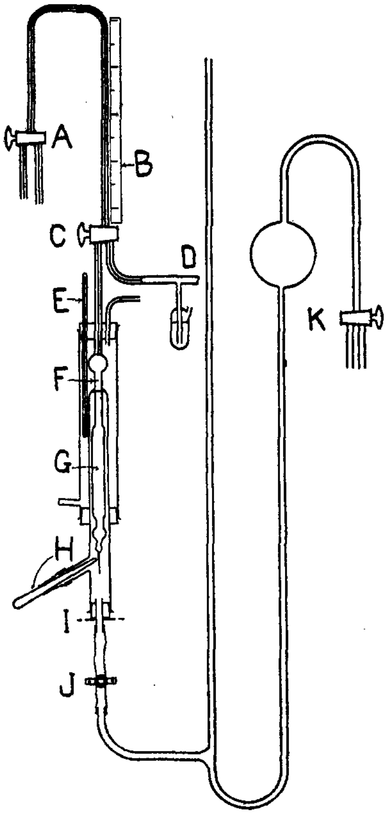

Fig. 1.

In carrying out a run the capsule is first introduced by removing the rubber stopper "I." The pinchcock is closed and the space surrounding the capsule evacuated. Mercury is then allowed to rise, floating the capsule above the rod "H." A correction is made for any trace of residual gas by measuring it before adding the oxygen. The quantity amounted usually to one or two tenths of a cubic centimeter. The pressure is then adjusted, the tip broken and the contents expelled by gentle warming, the broken tip being kept slightly below the surface of the mercury. The pressure is then adjusted to a little less than one atmosphere and an excess of oxygen introduced. The volume of the gas phase is increased to three times that of the calibrated bulb (9.9 cc.), an auxiliary calibration fixing this point, and the solution allowed to stand with occasional shaking in order to come to equilibrium. The ether meniscus is then raised to the graduation on the constriction at "F" and the amount of residual oxygen computed from the total pressure and the vapor pressure of the solvent. A correction is applied for the amount of oxygen dissolved in the solvent at the partial pressure of the oxygen existing at the time equilibrium is being established. The compression of the oxygen, as the solution is raised, increases its solubility. However, the surface of contact is so small at the constriction that the new equilibrium is approached very slowly. Since this is a correction to a correction it is not of importance. When ether is used as a solvent the largest error is due to the changing vapor pressure of ether with slight change in temperature. The table illustrates the accuracy which may be obtained without thermostating the water jacket. Doubtless a more accurate control of the temperature by circulating water at constant temperature through the jacket would still further improve the results. The apparatus was checked by determining the solubility of oxygen in ether using a sample of ether about three times as large as that required in the determination of the purity of a free radical. An error of 10% in determining the solubility of oxygen in ether amounts to about 0.5% in the correction to be applied to a run on a free radical. The data on diphenyl α-naphthylmethyl in the table give an idea of the accuracy of the method.

ABSORPTION OF OXYGEN BY DIPHENYL α-NAPHTHYLMETHYL

Concn. of cpd. from soly., wt. %	1.427	1.427
Ether soln., g.	3.074	3.279
O_2 (N. T. P.) added, cc.	2.535	3.065
Inert gas in capsule, cc.	0.165	0.119
Gas after run, cc.	.982	1.275
O_2 abs. by cpd. $\times 10^3$, g.	2.34	2.55
Concn. cpd. in wt. %	1.395	1.426
Purity, %	98.7	100.0

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

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The Catalytic Oxidation of Carbon

BY HANS M. CASSEL

The activating effect of sodium chloride on the combustion of soot in contact with it, described by R. K. Taylor,[1] has recently been the object of further interesting experiments by Day, Robey and Dauben,[2] using other salts as activating substances. In explaining their observations these authors refer to a theory proposed by H. S. Taylor and H. A. Neville[3] for the heterogeneous reaction of steam with carbon.

It should be taken into consideration, however, that the topochemical relations in the two cases are distinctly different: in the steam experiments the salt particles are imbedded in the carbon surface; in the combustion experiments, on the other hand, the oxygen molecules have to penetrate the soot layer before they can possibly reach the salt surface.[4] It is difficult to see how the contact of the soot with the salt is maintained and continues to be effective once the reaction has started in the interface.

On the basis of the earlier work of Eucken[5] two observations made by me may offer a more satisfactory explanation. Eucken, studying the combustion of graphite under low pressures, observed a rather low rate on smooth surfaces. But after a longer attack by oxygen the carbon surface takes on a velvet-like appearance, accompanied by an acceleration of the reaction. The condition of the surface may, however, be "ironed out" again by a process which Eucken calls "healing." Probably this is due to the reaction $2CO = C + CO_2$ which takes place in the range of not too high temperatures, the formation of CO being the first step of oxidation. According to R. K. Taylor, this process of regeneration seems to occur also in the case of burning soot, for he observed a slowing down of the reaction "presumably because of the more rapid oxidation at first of smaller particles or more active patches on the carbon surface."

I deposited a layer of soot on Pyrex glass by cracking CH_2Cl_2 at about 450°. In burning this by exposing it to a current of oxygen at about 600° the reaction once started generally spreads parallel to the surface, the soot being removed as if swept out by a piston. The fact that the reaction does not visibly proceed perpendicularly to the surface indicates that the carbon deposit is more easily attacked from the sides than from the

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[1] R. K. Taylor, THIS JOURNAL, **52**, 3025 (1930).

[2] J. E. Day, R. F. Robey and H. J. Dauben, *ibid.*, **57**, 2725 (1935).

[3] H. S. Taylor and H. A. Neville, *ibid.*, **43**, 2055 (1921).

[4] The impermeability of thin layers of soot is evident in the case where it acts as an emulsifier.

[5] A. Eucken, *Z. angew. Chem.*, **43**, 986 (1930).