

## A Method for the Detection of Oxygen in Organic Compounds

BENGT SMITH and RAGNAR OHLSON

*Institutionen för Organisk kemi, Chalmers  
Tekniska Högskola, Göteborg, Sweden*

For the qualitative determination of elements in organic compounds the sodium fusion method of Lassaing has since long been the most important one. It permits the detection of most common elements occurring in organic compounds. However, neither this nor any other method permits a reliable detection of oxygen, a fact which has been a considerable drawback in qualitative organic analysis. When studying methods for the detection of elements in organic compounds by gas chromatography we found that oxygen could be identified in a simple and reasonably reliable way by cracking the substance over a glowing platinum wire in an atmosphere of helium and analyzing the pyrolysis products for carbon oxide. The new method has been applied to a substantial number of organic compounds of various types including alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids, esters, acetals, amides, anhydrides, carbohydrates, proteins, lignin, nitro compounds, sulphonic acids, oxygen-containing organosilicon compounds and oxygen-containing heterocyclic compounds.

The test was positive in every case. In the pyrolysis of oxygen-containing organosilicon compounds and nitro compounds, a large part of the oxygen was bound up in silicon dioxide and nitrogen oxides, respectively. However, enough carbon oxide was formed, if an adequate amount of substance was used. We have also investigated a number of oxygen-free organic compounds but have not obtained a positive test in any case.

The carbon oxide formed was identified using gel tubes, containing silica gel impregnated with a mixture of palladium sulphate and ammonium molybdate<sup>1</sup>. The yellow silico molybdate complex turns to green or blue in the presence of carbon oxide. Other reducing substances may give a similar test, but the silica gel layer (*cf.* below) placed before the indicating layer is stated to absorb interfering substances<sup>1</sup>.

It is also possible to identify the carbon oxide by means of gas chromatography, *e.g.* using columns containing silica gel<sup>2</sup>

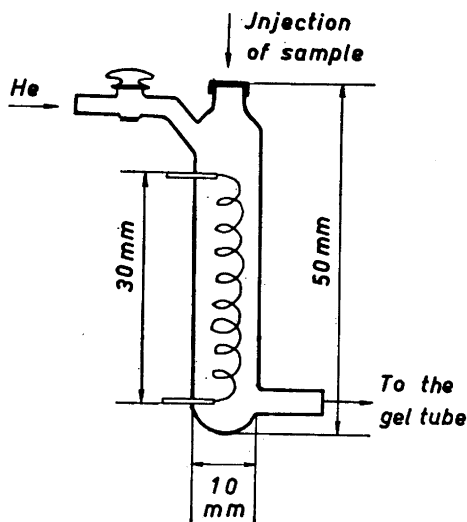


Fig. 1. Pyrolysis apparatus used for the detection of oxygen.

or molecular sieves<sup>3</sup>. These methods will be discussed in a forthcoming paper, describing the detection of oxygen and other elements in organic compounds by means of gas chromatography.

The apparatus used for the pyrolysis is shown in Fig. 1. It consisted of a pyrex glass tube containing a platinum glowing wire. The thin glowing wire (0.35 mm diam.) was welded to two thicker contact wires. The reactor was equipped with inlet and outlet tubes for helium and a tube covered by a serum cap for injecting liquid samples.

An experiment was performed in the following way. The gel tube was connected to the reactor and a stream of helium passed through for some minutes to sweep the air from the reactor. This done, the flow of helium through the reactor was interrupted by turning the three-way stopcock, and a voltage of 3–4 V was applied to the platinum wire causing it to glow. The liquid sample (1–5  $\mu$ l) was injected through the serum cap and pyrolysed by the glowing wire. After 10 sec the flow of helium was resumed and the pyrolysis products swept through the gel tube. For solid substances the same procedure was followed except that the reactor was used in a horizontal position with the sample in the middle of the reactor at the start.

Instead of helium, oxygen-free nitrogen might be used.

The gel tube \* was 100 mm long and had an outer diam. of 4 mm. It was packed to a length of 10 mm with the carbon oxide indicating gel (silica gel impregnated with a mixture of palladium sulphate and ammonium molybdate, *cf.* Ref.<sup>1</sup>). On the inlet side of the indicating layer was placed a 40 mm length and on the outlet side a 10 mm length of silica gel.

1. Shepherd, M. *Anal. Chem.* **19** (1947) 77.
2. Smith, R. N., Swinehart, J. and Lesnini, D. G. *Anal. Chem.* **30** (1958) 1217.
3. Brenner, N. and Ettore, L. S. *Anal. Chem.* **31** (1959) 1815.

Received November 30, 1960.

\* We have used tubes manufactured and sold by LKB-Produkter Fabriksaktiebolag, Stockholm.

## The Crystal Structure of Pd<sub>3</sub>P

STIG RUNDQVIST and  
LARS-OTTO GULLMAN

*Institute of Chemistry, University of Uppsala,  
Uppsala, Sweden*

An X-ray investigation of the palladium-phosphorus system was recently begun at this Institute. Preliminary results show that the system is far more complex than is indicated in the equilibrium diagram given by Wiehage *et al.*<sup>1</sup> It is especially noteworthy that at least four intermediate phases seem to exist in the range 0–25 atom % phosphorus. The existence of a phase near the composition Pd<sub>3</sub>P, as observed by Wiehage *et al.*<sup>1</sup>, was confirmed by our results. A single-crystal investigation showed that Pd<sub>3</sub>P has the cementite

(*D* O<sub>11</sub>) structure. The homogeneity range, determined from alloys quenched from 740°C, was found to extend from approximately Pd<sub>3</sub>P<sub>0.75</sub> to Pd<sub>3</sub>P<sub>1.0</sub> with the following lattice parameters (accuracy ± 0.05 %): phosphorus-rich limit  $a = 5.980$  Å;  $b = 7.440$  Å;  $c = 5.164$  Å and palladium-rich limit  $a = 5.645$  Å;  $b = 7.558$  Å;  $c = 5.071$  Å.

The crystal structure was determined by examination of single-crystals selected from an alloy with the approximate composition Pd<sub>3</sub>P<sub>0.95</sub>. 62  $F(h0l)$ -values and 63  $F(0kl)$ -values were recorded with niobium-filtered MoK-radiation in a multiple-film Weissenberg camera with thin iron foils between successive films. Atomic parameters were refined from electron density projections and difference syntheses. Fourier summations and structure factor calculations were made on the electronic digital computer BESK with programs devised by Åsbrink *et al.*<sup>2</sup>

The final  $R$ -value for the recorded  $F(h0l)$ -values was 0.087, applying an isotropic temperature factor with  $B = 0.72$  Å<sup>2</sup>; the corresponding figures for the  $F(0kl)$ -values were  $R = 0.088$ ,  $B = 0.67$  Å<sup>2</sup>. (The five largest  $F(0kl)$ -values, which were obviously weakened owing to extinction, were omitted in the final stages of refinement).

The following structural data for Pd<sub>3</sub>P<sub>0.95</sub> were obtained: Space group  $Pnma - (D_{2h}^{16})$ ;  $Z = 4$ . (Table 1.)

The standard deviations quoted were calculated using Cruickshank's formula<sup>3</sup>.

Interatomic distances are listed in Table 2.

It is of interest to note that in addition to Pd<sub>3</sub>P described above, the compounds Pd<sub>3</sub>Si and Pd<sub>3</sub>B also possess the cementite structure<sup>4,5</sup>. A case of isomorphism between a boride, a silicide and a phosphide of the same metal is thus demonstrated.

Further reports of the work on palladium phosphides will be published later in this journal.

Table 1. Structural data for Pd<sub>3</sub>P<sub>0.95</sub>.

$$a = 5.947 \text{ \AA}; b = 7.451 \text{ \AA}; c = 5.170 \text{ \AA}; U = 229.1 \text{ \AA}^3$$

		$x$	$\sigma(x)$	$y$	$\sigma(y)$	$z$	$\sigma(z)$
8 Pd <sub>I</sub>	in 8( <i>d</i> )	0.1783	0.0002	0.0636	0.0003	0.3373	0.0003
4 Pd <sub>II</sub>	in 4( <i>c</i> )	0.0264	0.0004	—	—	0.8700	0.0004
4 P	in 4( <i>c</i> )	0.8834	0.0011	—	—	0.4550	0.0011