

## Note

### Quantitative gas chromatographic analysis of low-molecular-weight alkylphosphines in the presence of phosphine and hydrocarbons

A. BOSSARD\*, R. KAMGA and F. RAULIN

*Laboratoire de Physico-Chimie de l'Environnement, Université Paris XII, 94010 Creteil Cedex (France)*

(Received April 26th, 1985)

In the course of experiments on the gas phase synthesis of volatile organophosphorus compounds, in particular from methane–phosphine mixtures<sup>1,2</sup>, the need arose for a fast and convenient method for the quantitative analysis of simple alkylphosphines in the presence of C<sub>1</sub>–C<sub>4</sub> hydrocarbons and phosphine.

No information on this analytical problem, nor on the more general problem of the gas chromatographic (GC) analysis of alkylphosphines, was available in the literature. However, in previous studies on methane–ammonia mixtures, we used a Chromosorb 103 glass column for separating and quantitatively analyzing mixtures of C<sub>1</sub>–C<sub>4</sub> nitriles, amines and hydrocarbons<sup>3</sup>. We assumed that such a column could also be used for the analysis of the homologous organophosphines, in the presence of the same hydrocarbons, taking into account the analogy between organonitrogen and organophosphorus compounds.

In the present paper, we describe the conditions of separation with this GC column and the molar responses (relative to ethane) to a flame ionization detector of methylphosphine and ethylphosphine.

## EXPERIMENTAL

### *Apparatus*

The gas chromatograph was an Intersmat Model IGC 120 FL, equipped with a flame ionization detector and a linear temperature programmer. It was connected to a Shimadzu integrator recorder. By changing the flame-base assembly of the detector, the latter can easily be converted into a thermoionic detector, specific to organophosphorus compounds. However, the use of such a detector to analyse phosphine-rich mixtures and alkylphosphines appeared very difficult, giving poorly reproducible results. In addition the thermoionic detector had a very short lifetime, its platinum wire being rapidly destroyed in the presence of large amounts of phosphine. Thus, we used only the classical flame ionization detector, which is suitable down to 100 pmol of organics.

### *Chemicals for calibration*

All the hydrocarbons and phosphine were purchased from l'Air Liquide SA (Le Plessis Robinson, France). Methylphosphine was synthesized by deprotonation

of phosphine with potassium hydroxide in an anhydrous medium, followed by reaction with methyl iodide, as described by Jolly<sup>4</sup>.

Ethylphosphine was synthesized by the same method using ethyl iodide in place of methyl iodide<sup>5</sup>.

#### Chromatographic conditions

The glass chromatographic column (3.2 m × 3 mm I.D.) was packed with Chromosorb 103 (100–120 mesh) (Waters, Milford, MA, U.S.A.). The best results were obtained with the following temperature program: 40°C isothermal for 6 min, then 4°C/min to a final temperature of 175°C. The injector temperature was 190°C and that of the detector was 200°C. The flow-rate of the carrier gas (nitrogen) was 40 ml/min.

#### RESULTS AND DISCUSSION

The retention times of the C<sub>1</sub>–C<sub>4</sub> hydrocarbons, phosphine, methylphosphine and ethylphosphine, obtained under the described chromatographic conditions, are given in Fig. 1. The analysis of these two alkylphosphines, without interference from the C<sub>1</sub>–C<sub>4</sub> hydrocarbons, can be accomplished in less than 30 min.

The detector was calibrated for these organophosphorus compounds. Its response is linear in the range 1–100 nmol. The observed molar responses, relative to ethane (RMR 1) are: methylphosphine, 0.5; ethylphosphine, 1.5; propane, 2.0. Phosphine gives a very poor response: its RMR is less than 0.01.

This method has been successfully used to analyze the alkylphosphines produced during spark-discharge irradiation of methane–phosphine, ethane–phosphine and methane–methylphosphine gaseous mixtures. An example of a chromatogram

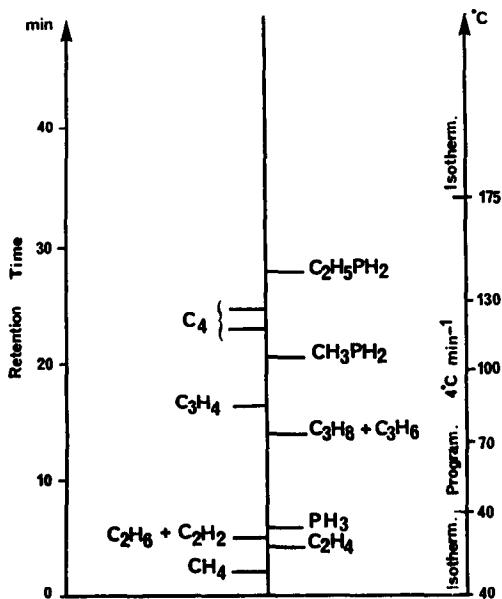


Fig. 1. Retention times of hydrocarbons, phosphine and alkylphosphines on Chromosorb 103.

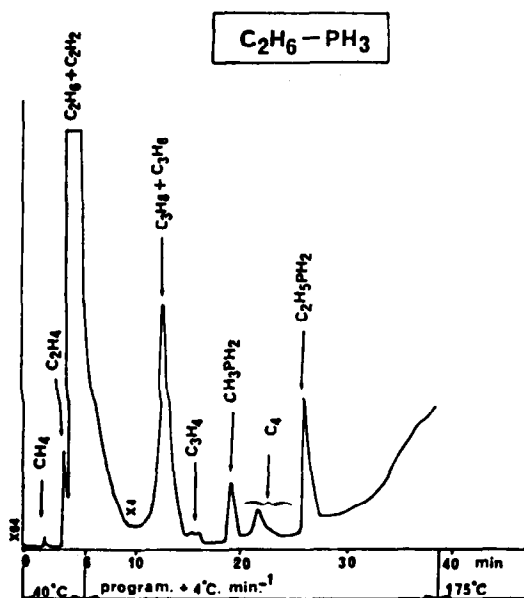


Fig. 2. Chromatogram of the analysis on Chromosorb 103 of a sample obtained by sparking (1 min) of an ethane (18.5 Torr)-phosphine (1.5 Torr) mixture.

of a sample resulting from sparking (1 min) of an ethane (18.5 Torr)-phosphine (1.5 Torr) mixture is shown in Fig. 2. Identification of the peaks was by comparison of the retention times with those of calibration samples. The identification of alkylphosphines was confirmed by comparing this chromatogram with that of a sample resulting from the sparking (1 min) of pure ethane.

#### REFERENCES

- 1 R. Kamga, *Thèse de 3ème cycle*, Chimie Physique Université Paris VI, 1984.
- 2 A. Bossard, R. Kamga and F. Raulin, *Icarus*, submitted for publication.
- 3 A. Bossard and G. Toupance, *Nature (London)*, 288 (1980) 243.
- 4 W. L. Jolly, *Inorganic Syntheses*, Vol. XI, McGraw-Hill, New York, 1968, p. 124.
- 5 R. Kamga, A. Bossard and F. Raulin, *J. Chem. Res.*, submitted for publication.