

Short Communication

Determination of phosgene as its N,N,N',N'-tetraethylurea derivative by gas chromatography

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ABSTRACT

A gas chromatographic method with flame-ionization for the determination of free phosgene as its N,N,N',N'-tetraethylurea derivative and the application of the method to the determination of excess phosgene either in solution or in a reaction mixture is described. The detection limit is 5 ppm.

INTRODUCTION

The commercial applications of phosgene in chemical synthesis are widely known. Extensive information is available regarding the detection and determination of phosgene, mostly in air and gas mixtures, using gas chromatography (GC) [1-6], spectrophotometry [3,7-9], electrochemical methods [10,11] and aniline in bromometric titrations [12]. More recently, the determination of low concentrations of phosgene in air by GC using di-*n*-butylamine coated on a solid sorbent [13] and high-performance liquid chromatography for determining the conversion efficiency of phosgene into *sym*-diphenylurea [14] have been investigated.

Recently, we have been engaged in the synthesis of benzyl chloroformate by the reaction of phosgene with benzyl alcohol, and efforts have been directed to developing a GC method for the determination of excess phosgene in the reaction mixture. For this purpose, diethylamine has been used selectively as a derivatizing agent to convert phosgene into N,N,N',N'-tetraethylurea (TEU) as a stable product. The relative strengths of phosgene in toluene solvent at elevated temperatures have also been investigated.

The GC determination of phosgene as the TEU derivative with flame ionization detection gave good recoveries. To our knowledge, this is the first report of a gas chromatographic assay of phosgene in solution or in a reaction mixture. The method described here is simple and convenient for personal monitoring.

EXPERIMENTAL

Chemicals and reagents

Diethylamine, dichloromethane, toluene and benzyl alcohol were purchased from Aldrich. Phosgene gas and N,N,N',N'-tetraethylurea, N,N-diethyl benzyl-carbamate and diethylamine hydrochloride standards were supplied by Makhteshim Chemical Works.

Instrumentation

A Varian Model 3700 gas chromatograph with a flame-ionization detector, equipped with a 6 ft. \times 3 mm I.D. glass column filled with a 1:1 mixture of 10% QF-1 and 15% DC-200 on Gas-Chrom Q (80–100 mesh) was used. The column temperature was maintained at 150°C, the injector at 230°C and the detector at 240°C. The carrier gas was helium at a flow-rate of 35 ml/min. A 5- μ l sample was injected each time by means of a 10- μ l Hamilton syringe. Chromatograms and peak areas were recorded on a Spectra-Physics Model 4720 integrator.

Procedure for derivatization

A stock solution of 10% (v/v) diethylamine in dichloromethane was prepared and 40 ml of this solution was transferred into a 100-ml volumetric flask which was stoppered and weighed. This flask was allowed to stand in the cold (5°C) then the sample (0.5–1 g) containing phosgene was added with a disposable pipette and the flask was shaken manually. After leaving it for 20 min at room temperature, the flask was reweighed to determine the exact sample weight taken. Then the flask was filled to the mark with dichloromethane. Injections of 5 μ l each time were then made in the sequence TEU standard and derivatized sample.

Preparation of spiked samples

A stream of phosgene was passed for some time into a previously weighed 100-ml volumetric flask containing about 70 ml of toluene. The flask was reweighed to determine the weight of phosgene added before filling to the mark with toluene. Samples of 25 ml were removed in duplicate and converted into the TEU derivative as described above. Likewise, five spiked samples were treated separately. The results obtained are given in Table I.

Synthetic reaction mixture

Benzyl chloroformate was prepared by passing phosgene into benzyl alcohol at 5°C. The excess phosgene was evaporated by passing a stream of nitrogen through the reaction mixture, during which time the temperature was allowed to rise at room temperature. Six test samples were removed at intervals of 20 min and converted into the TEU derivative as described above. The results ranged from 0.02% (minimum) to 12% (maximum) of phosgene in the reaction mixture.

Relative strengths of phosgene in toluene at elevated temperatures

First, phosgene was passed into 250 ml of toluene in a 500-ml flask until it was saturated at room temperature (24–25°C). Before removing the test samples in duplicate, a steady temperature was maintained for 20 min at each stage during an increase, *e.g.*, at 30, 40, 50, 65 and 80°C. The test samples were then converted into the TEU derivative as described above. The results of the relative strengths of phosgene in solvent toluene at elevated temperatures are given in Table II.

RESULTS AND DISCUSSION

The TEU derivative of phosgene has good GC properties, as shown in Fig. 1. The linearity of the calibration graph, tested in the range 6–110 mg per 100 ml, was very good, with a correlation coefficient of 0.9998 and a relative standard deviation of 0.7% (nine measurements). To evaluate the analytical applicability of the GC method, samples of known amounts of phosgene in toluene were converted into the TEU derivative as described above and analysed as shown in Table I. The recoveries of phosgene ranged from 93 to 97%, which confirmed that the conversion of phosgene into the TEU derivative was instantaneous.

Further experiments were made on the recovery of phosgene from the benzyl chloroformate reaction mixture. Samples were removed at intervals and treated with diethylamine. In these samples there was the possibility of not only free phosgene but

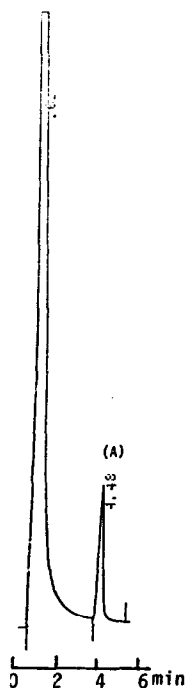


Fig. 1. Chromatogram of the N,N,N',N' -tetraethylurea (TEU) derivative of phosgene. Attenuation, $16 \cdot 10^{-10}$; other conditions as given under Experimental.

TABLE I
RECOVERY OF PHOSGENE FROM SPIKED SAMPLES

| Sample No. | Amount added (g per 100 ml) | Average recovery (g per 100 ml) ($n = 2$) | Recovery (%) ^a |
|------------|-----------------------------|---|---------------------------|
| 1 | 2.731 | 2.541 | 93 |
| 2 | 4.144 | 3.928 | 94.8 |
| 3 | 3.342 | 3.175 | 95 |
| 4 | 5.179 | 4.956 | 95.7 |
| 5 | 9.892 | 9.595 | 97 |

^a R.S.D. (all results) = 1.53%.

also benzyl chloroformate reacting with diethylamine to form *N,N*-diethyl benzylcarbamate and diethylamine hydrochloride as impurities. The TEU derivative of the test samples was then subjected to GC and no interference from the above impurities was observed. A chromatogram for the separation is shown in Fig. 2. The minimum and maximum recoveries of phosgene from the benzyl chloroformate reaction mixture were in the range 0.02–12%.

The relative strengths of phosgene in toluene solvent were studied at elevated temperatures. It was observed that the stability of phosgene in toluene decreased with

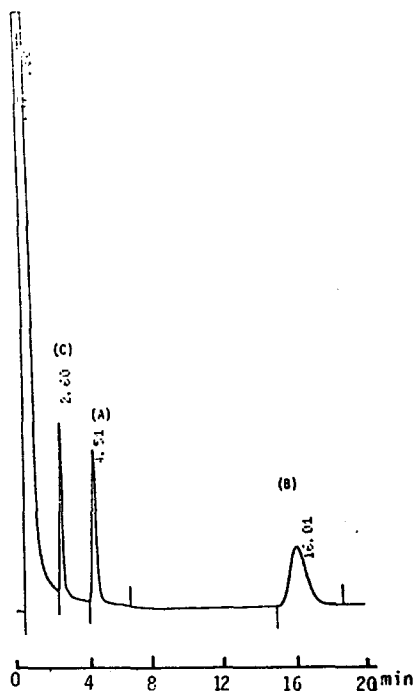


Fig. 2. Chromatogram showing the separation of impurities such as *N,N*-diethyl benzylcarbamate (B) and diethylamine hydrochloride (C) from the main peak of the TEU derivative (A) of phosgene. GC conditions as in Fig. 1.

TABLE II

RELATIVE STRENGTHS OF PHOSGENE IN TOLUENE SOLVENT AT ELEVATED TEMPERATURES

| Temperature (°C) | Average phosgene content (g/100 ml) \pm S.D. (n = 2) |
|-------------------|--|
| 24-25 (saturated) | 77.8 \pm 1.8 |
| 30 | 72.1 \pm 0.9 |
| 40 | 48.6 \pm 1.1 |
| 50 | 35.8 \pm 1.2 |
| 65 | 22.2 \pm 1.5 |
| 80 | 13.3 \pm 1.2 |

increase in temperature; the results obtained are given in Table II. Such studies of the solubility of phosgene in toluene are important for practical application in organic synthesis.

Determination of phosgene at the ppm level was achieved using a flame ionization detector sensitivity of 10^{-11} . At this sensitivity, it was possible to detect the TEU derivative of phosgene at a level of 5 ppm ($2.5 \cdot 10^{-5}$ mg), as shown in Fig. 3.

In conclusion, the GC method described here is simple and convenient and is proposed as an alternative procedure for the determination of the extremely corrosive and toxic phosgene.

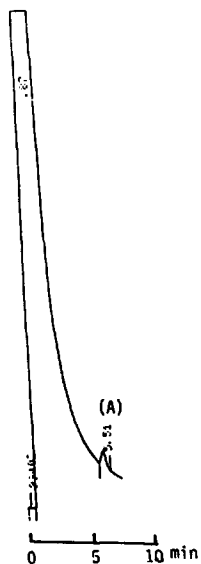


Fig. 3. Chromatogram of TEU derivative at a minimum level of 5 ppm (2.5×10^{-5} mg). Attenuation, $8 \cdot 10^{-11}$; helium flow-rate, 30 ml/min; other conditions as in Figs. 1 and 2.

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