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Note

Selective detection of dichloroacetylene and its decomposition product phosgene with the electrolytic conductivity detector combined with a special gas-sampling system

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Many chlorinated aliphatic hydrocarbons have been shown to be contaminated by dichloroacetylene (DCA); for this reason, DCA has become the object of increasing toxicological interest. The severe nephrotoxic properties of DCA have been established in several animal species^{1,2}, and a carcinogenic effect has been discussed². DCA is chemically highly reactive, and in the presence of air, it decomposes into different (mostly perchlorinated) hydrocarbons, which have been identified³; however, the major product of DCA decomposition is phosgene.

Because of the high chemical reactivity of DCA, animal experiments with this compound require special procedures in order to ensure that DCA-air to which animals are exposed can support the mixture of compounds, containing, for example, a π -bond, such as found in chlorinated ethylenes and acetylene³. In addition, on account of the rapid decomposition of DCA, preparation of stock solutions is not possible.

In the course of our investigations on the inhalation toxicity of DCA, it has been necessary to develop a method for the detection of this compound in the range *ca.* 0.1–10 ppm. The measurement must be rapid, reproducible and quantitative, and should guarantee continuous control for up to several hours. Additionally, the possible decomposition of DCA must be immediately recognizable by the detection of phosgene. A modified electrolytic conductivity detector of the Hall type⁴ allows a high degree of compliance with these conditions. The detector is specific for halogens, and the applicability of this detector and the analytical data derived from it are described in this paper.

MATERIALS AND METHODS

Chemicals

Trichloroethylene and vinylidene chloride were purchased from Merck (Darmstadt, G.F.R.). DCA was freshly synthesized from trichloroethylene as described previously¹, *i.e.*, nitrogen carried trichloroethylene vapour over anhydrous potassium hydroxide. Acetylene was obtained from Messer Griesheim (Düsseldorf, G.F.R.).

Apparatus and conditions

A Tracor gas chromatograph (Model 550), equipped with a Hall electrolytic-conductivity detector (Model 310) was used in the reductive mode. The glass column (6 ft. \times 2 mm I.D.) was packed with 30% of squalane on Chromosorb W AW (100–120 mesh) (WGA, Darmstadt, G.F.R.) and was operated at 80°; the carrier gas was helium (30 ml/min), the reactant gas was hydrogen (30 ml/min), the cell liquid (20% isopropanol) had a flow-rate of 1 ml/min, and the pyrolysis-furnace temperature was 800°. The conductivity cell was operated at ambient temperature.

Gas samples were injected by means of a tantalum gas-sampling valve with a 1-ml loop (Carle 2818). Seven bulkhead unions connected to different positions in the all-glass reaction tube and exposure chamber allowed continuous control of the concentrations of synthesized DCA vapour. One union was connected to a source of stock gas (vinylidene chloride) prepared by the injection of a known volume of liquid vinylidene chloride into a mixing jar, which was then allowed to stand for 20 min in a thermostat at 40° before measurement.

RESULTS AND DISCUSSION

This method allows convenient and rapid analytical control of the exposure mixture. Under our synthesis conditions, the conversion of trichloroethylene into

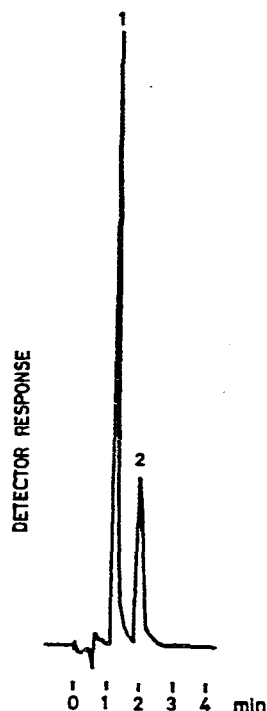
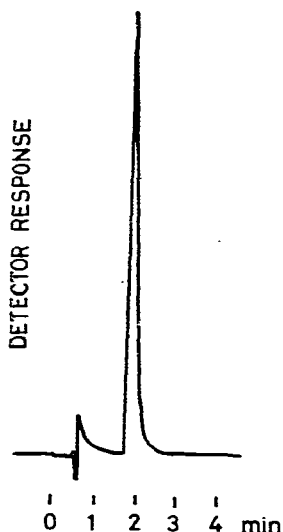


Fig. 1. Gas chromatogram of 10 ppm of DCA on a squalane column. The DCA was prepared from trichloroethylene in a nitrogen atmosphere and was mixed with acetylene (20 ppm) and air.

Fig. 2. Gas chromatogram of DCA (peak 2) and its decomposition product phosgene (peak 1) on a squalane column. Pure DCA was prepared from trichloroethylene in a nitrogen atmosphere; when air was admixed DCA decomposed immediately.

DCA is quantitative. This is shown by Fig. 1, in which only one detector-response peak (for DCA) is visible. As well as DCA, the synthesis mixture contains nitrogen and, as stabilizer, acetylene; neither substance is registered by the electrolytic-conductivity detector. The advantage of selective analysis is clear: control of the exposure mixture becomes considerably easier, and the decomposition of DCA is immediately apparent from the appearance of additional peaks. Seven different measurement positions are possible; this facilitates localization of those sites of the synthesis apparatus or the exposure unit where uncontrolled air enters.

Without the addition of a stabilizer, DCA decomposes immediately in a strong exothermic reaction. The stabilizer must always be added in excess. The rapid recognition of DCA decomposition is of great importance in any toxicological approach, as phosgene (the major decomposition product) causes lung oedema, which would rapidly kill the experimental animals. In Fig. 2, the stabilizer acetylene has been omitted; consequently, as well as that for DCA, another peak (for phosgene) is evident.

A substantial advantage of this method lies in the fact that the detector responds to chlorine analogues. Thus, DCA can be quantitatively recorded. Vinylidene chloride has proved to be useful as calibration gas; this compound also contains two chlorine atoms and has approximately the same boiling-point as DCA.

To summarize, in this paper, a sensitive and selective method for detecting DCA in air mixtures is described for the first time. The detection is quantitative. The presence of the highly toxic phosgene in addition to DCA indicates that DCA has decomposed under the influence of oxygen.

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