Notes

Dimethylsulfoxide as a suitable solvent for trimethylsilylation of catecholamines

In the gas chromatographic separation of biological amines, one of the most important problems is the preparation of suitable derivatives for the unstable and polyfunctional catecholamines such as epinephrine, norepinephrine and dopamine. This communication reports on the effect of solvents for trimethylsilylation of the catecholamines. Previously we reported[1] that a satisfactory separation of the catecholamines and related compounds was achieved by trimethylsilylation with hexamethyldisilazane using pyridine as a solvent followed by the condensation with methyl propyl ketone. In the later studies, however, pyridine was found to be unsuitable for quantitative determination of such extremely unstable catecholamines as those mentioned above, since it required a long reaction time at a high temperature for the completion of the trimethylsilylation. Recently CAPELLA AND HORNING[2] used dimethylformamide as a reaction medium. By comparison with pyridine, dimethylformamide accelerated the trimethylsilylation 10 to 20 times, but it had the disadvantage that it had a tendency to condense with the primary amines.

We found dimethylsulfoxide to be an excellent solvent for trimethylsilylation of catecholamines, namely, it accelerated the trimethylsilylation to the same extent as dimethylformamide while not forming any by-product, even when heated at 80°. The trimethylsilylated primary amines condensed readily with various aliphatic ketones at room temperature to form the Schiff's bases.

The determination of catecholamines extracted from a bovine adrenal medulla was carried out by the following procedure and the values obtained were similar to those obtained by fluorometric determination.

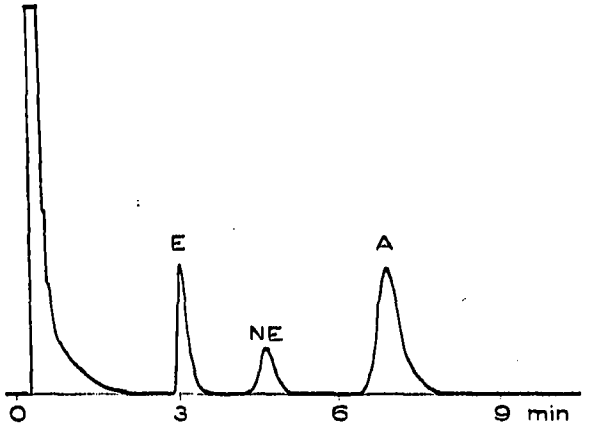

Fig. 1. Gas chromatogram of catecholamines from a bovine adrenal medulla. Trimethylsilyl derivative of epinephrine (E) and Schiff's base-trimethylsilyl derivative of norepinephrine (NE). Internal standard: Allethrin (A). Conditions: 7% DC-1107 on 80–100 mesh Gas-Chrom P, 1.5 m × 4 mm, 170° and 80 ml of nitrogen per min.

One ml of sample solution in 0.2 *N* acetic acid containing less than 500 μg of catecholamines extracted from an adrenal medulla was evaporated to dryness in a 40° water bath under a reduced pressure. The residue was treated with 0.2 ml of dimethylsulfoxide, 0.2 ml of dioxane and 0.5 ml of hexamethyldisilazane for 10 min. at 80°. After cooling, a known amount of a chloroform solution of allethrin (internal standard), 2 ml of chloroform and 2 ml of cold water were added, shaken and centrifuged. After separation and drying, the chloroform phase was evaporated to a small volume. Then, 0.5 ml of acetone was added, the mixture allowed to stand for 15 min at room temperature and applied to a gas chromatograph (Fig. 1).

A complete report will be published in the near future.

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Received May 9th, 1966

J. Chromatog., 25 (1966) 471–472

A gas chromatographic method for isolation and determination of diacetyl peroxide

Isolation of diacetyl peroxide is extremely hazardous because of the highly explosive nature of the dry crystals[1,2]. SHANLEY[3] has described a safe method for the isolation of small quantities of diacetyl peroxide (80 % purity). This paper is concerned in part with a gas chromatographic (GC) procedure for isolating small quantities of relatively pure diacetyl peroxide from a commercially available 25 % solution in dimethyl phthalate. Some measured physical properties of the purified peroxide are included.

A number of papers have recently been published in connection with GC analysis of organic peroxides. A list of these papers is appended[4–23]. This paper also describes a GC procedure for the quantitative analysis of diacetyl peroxide.

Equipment and materials

Gas chromatograph—Perkin Elmer, Model 154D, thermal conductivity detector
I.R. spectrophotometer—Beckman Model IR-4
Abbe refractometer—Carl Zeiss, Jena
GC column—11 ft. × $^1/_4$ in O.D., pyrex glass tubing, 10 % diisodecyl phthalate on Fluoropak 80
Diacetyl peroxide—25 % solution in dimethyl phthalate obtained from Lucidol Division of Wallace and Tiernan, Inc., Buffalo, New York

Gas chromatographic conditions used were as follows:

Temperature—injection block 100°; column 75°; detector 75°
Carrier gas—helium (200–250 c.c./min)