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)

Procedure for isolating diacetyl peroxide

Relatively large samples (50–500 μl) of commercial diacetyl peroxide were injected into the GC column. The peroxide fractions (retention times 20–35 min depending on sample size) were collected in conventional U-tube glass fraction collection devices maintained at dry ice temperature. In order to minimize thermal decomposition of diacetyl peroxide, the filament current is turned OFF for this operation. As the dimethyl phthalate is not eluted under the GC conditions used, the column packing at the head of the column gets an additional loading of a phthalate ester which acts as a liquid phase; consequently, the retention time for diacetyl peroxide gradually increases after a number of samples have been injected. (For convenience, it is recommended that a short replaceable pre-column be positioned in front of the analytical column.)

The diacetyl peroxide thus isolated analyzed 99 wt. % by iodometric procedures[24] and had a melting point of 25.5° compared to 26.5°, 27° and 30° reported elsewhere[25–27]. The measured refractive index just above the melting point (n_D^{26}) was 1.4006. This property has not, to the authors' knowledge, been previously reported—probably because of the highly hazardous nature of the peroxide.

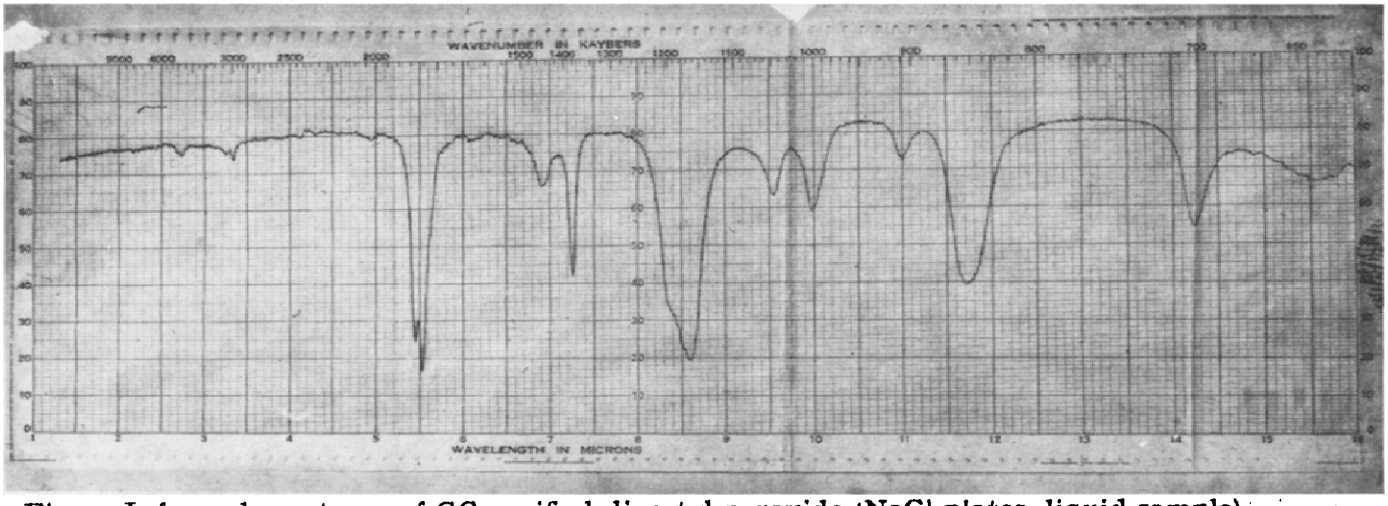

Fig. 1. Infra-red spectrum of GC purified diacetyl peroxide (NaCl plates, liquid sample).

The infra-red spectrum of the purified diacetyl peroxide is shown in Fig. 1. It is similar to, but simpler than that reported by MINKOFF[28]—possibly indicating that the material purified by gas chromatography was of higher purity. A pair of strong carbonyl absorptions observed in the 5.5 μ region corresponded to those reported by DAVISON[20]. No decomposition of diacetyl peroxide was observed when the peroxide was allowed to remain in contact with the I.R. salt plates at room temperature for a period of 1 h.

Quantitative determination of diacetyl peroxide

The GC method has been successfully used for quantitative determinations of diacetyl peroxide in laboratory and plant investigations. Linear relationships between peak area and peroxide concentration prevail. Minimum detectable limits for diacetyl peroxide using a filament current of 225 mA and a 50 μl sample size are in the order of 300 p.p.m. by wt.

Detection of diacetyl peroxide in GC effluent

Diacetyl peroxide (or any easily reduced peroxide) can be detected in the GC effluent very simply by bubbling the effluent gas through about 0.5 c.c. of an acidified KI–starch solution. The bubbler solution turns dark (brown black) as soon as the peroxide begins to elute. Limits of detection of diacetyl peroxide using this technique were of the order of 15 μg.

Preparation of solutions of diacetyl peroxide

Solutions of diacetyl peroxide in solvents, other than dimethyl phthalate, could be obtained by bubbling the GC effluent (during elution of peroxide) through a fritted glass disc immersed in the desired solution. Almost complete absorption of diacetyl peroxide could be obtained, for example, in an acidified isopropanol solution.

Explosion hazard

Suitable safety precautions were enforced at all times during the course of this work—even when working with small (0.005–0.100 c.c.) quantities of diacetyl peroxide. Protective glass shielding was used during handling and storage of liquid or solid samples. Over a period of two months, when dozens of samples were handled, only one small (5 μl) liquid sample of purified diacetyl peroxide exploded.

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Received May 20th, 1966