

Gas chromatography of certain oximes

Aldoximes and ketoximes have been reported to dehydrate thermally at elevated temperatures over aluminum oxide to yield nitriles¹.

Certain aromatic aldoximes when gas chromatographed are also converted to corresponding nitriles. The degree of conversion is dependent upon the substrate and the temperature at which the chromatography is carried out. There may be other factors upon which the degree of conversion may depend such as the space velocity and the solid support on which the substrate is placed.

Acetaldoxime and acetoxime have been gas chromatographed under the same conditions without decomposition.

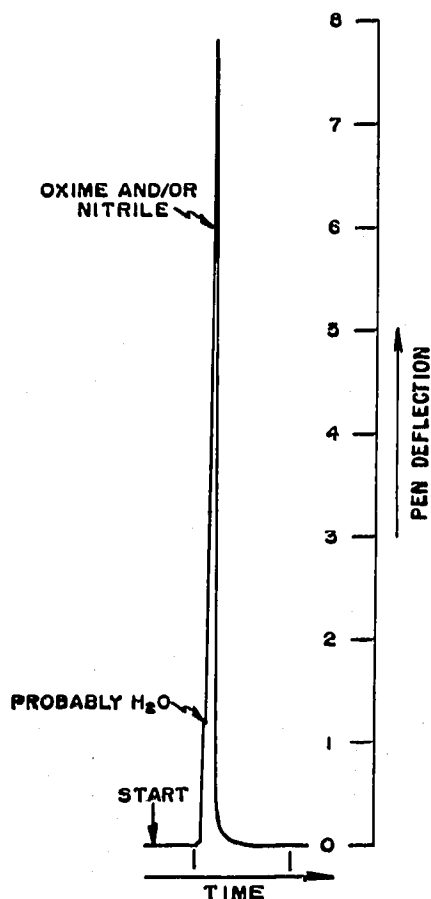


Fig. 1. Gas chromatogram of pure benzaldoxime over 2 ft. of silicone rubber on "Celite" at 200°.

Benzaldoxime (I) or salicylaldoxime (II) give normal-shaped peaks when chromatographed over two feet of silicone rubber on "Celite" at 200° (Fig. 1). Under the same chromatographic conditions, normal-shaped, well separated peaks are obtained when a mixture of these two oximes is chromatographed (Fig. 2). Although the peaks

appear normal, the infrared spectra of the components eluted from the column show that during chromatography some of each oxime is converted to a corresponding nitrile. More nitrile is formed during chromatography at 250° than during chromatography at 200°.

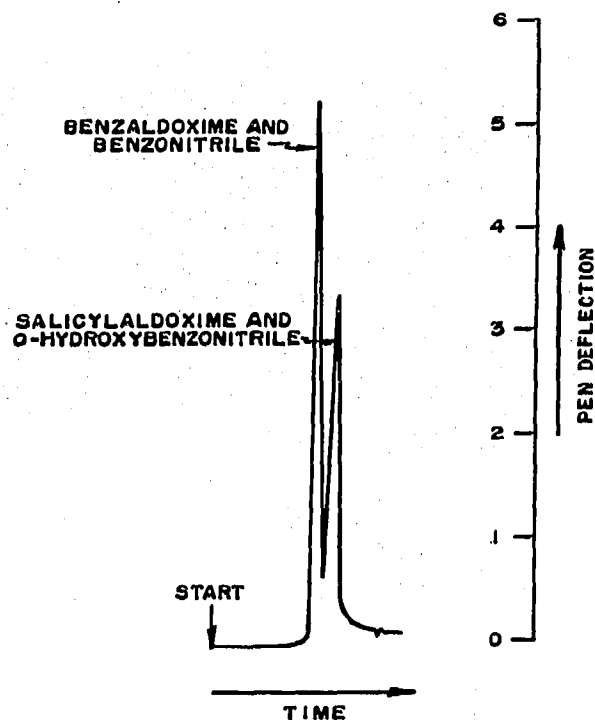


Fig. 2. Gas chromatogram of a mixture of benzaldoxime and salicylaldoxime over 2 ft. of silicone rubber on "Celite" at 200°.

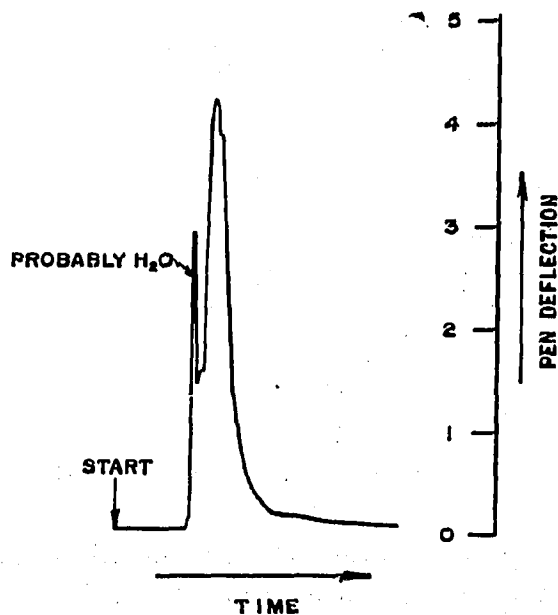


Fig. 3. Gas chromatogram of a mixture of benzaldoxime and salicylaldoxime over 2 ft. of silicone grease on "Celite" at 200°.

When benzaldoxime is chromatographed at either 200° or 250° over 2 feet of high vacuum-silicone grease on "Celite", the chromatogram obtained is similar to the chromatogram obtained over silicone rubber (Fig. 1), but the product eluted from the column is pure benzonitrile. Chromatography of salicylaldoxime at 200° over the same silicone grease column partially converts it to *o*-hydroxybenzonitrile and at 250°, the conversion is complete. At 200°, the chromatography of a mixture of (I) and (II) over the same silicone grease column gives a complicated nonreproducible chromatogram (Fig. 3). The infrared spectrum of the sum of the eluted compounds shows the presence of both unconverted oximes and the corresponding nitriles.

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A simple microtechnique for the preparation of biological samples for paper chromatographic analysis

In the course of our work on the biochemical analysis of insect tissues and body fluids, it was necessary to develop chromatographic microtechniques applicable to individual insects weighing as little as 2 mg and body fluid samples as small as 10 μ l. Although the method described relates particularly to the analysis of amino acids in biological samples, the same method, with slight modifications, has been satisfactorily used in our laboratory for analyses of carbohydrates, organic acids, and nucleic acid components as well as to follow chromatographically such enzyme reactions as transamination.

The chemical procedures used for the extraction of amino acids are those of AWAPARA¹. All steps in the extraction procedure are carried out inside a U-tube shown in Fig. 1(a). A small filter paper disc (0.5 cm diameter) is punched from Whatman No. 3 MM filter paper and is fitted snugly at the junction between the capillary and the wide tube inside arm A so that it covers the capillary and rests flatly on it. The mouth of arm B is fitted with a cork stopper which can be manipulated within limits without breaking the air seal. A known volume of any biological fluid to be analyzed is deposited on the paper disc by means of a micropipette. Eighty percent ethanol (0.3 to 0.5 ml) is then slowly added to the disc. The liquid is made to pass up and down through the disc a few times by manipulating the cork stopper

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