

THIN-LAYER CHROMATOGRAPHY OF ISOMERIC OXIMES. I.

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(Received January 31st, 1963)

Theoretically two isomeric forms of each aldoxime and unsymmetrical ketoxime are possible. A review of the literature indicates that in the reaction of carbonyl compounds with hydroxylamine very often only one product is obtained. It is, however, doubtful whether the isolated products, although having constant melting points, always represent samples of pure isomers.

The only successful separation of isomeric oximes was achieved in the case of benzoin oximes and anisoin oximes by adsorption chromatography applying the brush method¹. The authors, however, claim that the application of this method is somewhat limited by the catalytic action of the adsorbent on the isomerization. To our knowledge, no separation by paper chromatography has up to now been achieved. Infrared spectroscopic data² indicate the possibility of distinguishing the isomeric oximes on the basis of the position of the OH stretching frequency. None of these methods, however, can guarantee the presence of one single isomer in the isolated product.

In view of the lack of a method for the analytical separation and rapid determination of isomeric oximes, we have studied the thin-layer chromatography of the following oximes: α - and β -benzaloximes, α - and β -benzoin oximes, and, α - and β -anisoin oximes.

Following the directions given in the literature³ α - and β -benzaloximes were obtained in the pure state. The preparation of α - and β -benzoin oximes was carried out according to WERNER AND DETSCHEFF⁴. α -Benzoin oxime was easily obtained in the pure state by crystallization from dilute alcohol, whereas the β -form showed two spots on the chromatogram. The preparation of the β -form was attempted without any heating of the reaction mixture, but the resulting product, purified as given in the literature, was shown by thin-layer chromatography to be, in spite of its correct melting point, a mixture of both isomeric forms. A chromatographically pure sample of the β -form was obtained only after recrystallization from an ether-petroleum ether mixture. The oximation of anisoin, prepared according to BÖSLER⁵, was carried out as described by ZECHMEISTER¹. A pure sample of the α -form was isolated from the reaction mixture by recrystallization from an ether-petroleum ether mixture. The pure β -form was obtained as follows: the reaction product (oximation performed without heating) was dissolved in hot benzene and the solution was frozen; when the mixture was left at room temperature crystals separated which were sparingly soluble in benzene. Successive treatment with benzene and centrifuging of the suspension gave a sample of the pure β -anisoin oxime.

Good separation with very different R_F values of isomeric oximes (Table I) was

achieved on thin layers of silica gel G (according to STAHL) using benzene-ethyl acetate and benzene-absolute methanol, respectively.

TABLE I
 R_F VALUES OF OXIMES

Compound	$R_F \times 100$	
	α -Form	β -Form
Benzaldoxime	50	32
Benzoin oxime	14	37
Anisoin oxime	5	23

Fig. 1 shows the separation of α - and β -benzaldoximes, α - and β -benzoin oximes, and α - and β -anisoin oximes, using benzene-ethyl acetate (50:10 v/v).

The spots were detected by spraying the plate with aqueous 0.5% cupric chloride solution, when the oximes appeared as coloured spots of oxime-metal complexes. In the case of isomeric benzoin oximes and anisoin oximes, each isomer gave a different colour. The complex of the α -isomer was green and that of the β -form brown; the latter turned to green within a short period indicating possible isomerization of the complex. The pure isomeric oximes, however, are stable on silica gel, since brown and green spots appeared on spraying plates which had been left to stand for several days after development.



Fig. 1. Thin layer chromatogram of isomeric oximes. The oximes were dissolved in tetrahydrofuran and 10 μ l of a 0.5% (w/v) solution of each oxime was applied to the plate. Adsorbent: silica gel G (according to STAHL). Solvent system: benzene-ethyl acetate (50:10 v/v). Solvent front 14 cm. Spraying reagent: saturated alcoholic solution of cupric acetate monohydrate. (1) α -Benzaldoxime; (2) β -Benzaldoxime; (3) Mixture of isomeric benzaldoximes; (4) α -Benzoin oxime; (5) β -Benzoin oxime; (6) Mixture of isomeric benzoin oximes; (7) α -Anisoin oxime; (8) β -Anisoin oxime; (9) Mixture of isomeric anisoin oximes.

α -Benzaldoxime failed to give a colour reaction with the above reagent, but when the plate was sprayed with a saturated alcoholic solution of cupric acetate monohydrate and kept at 100° for 10 min, the green colour of the complex was easily obtained.

It has been observed that the isomeric oximes, when kept in solutions of tetrahydrofuran or alcohol for a period of two to three days exhibited a marked tendency to isomerization.

The separation of isomeric oximes was also performed on a micro preparative scale.

Thin-layer chromatography has proved a convenient and rapid method for analytical separation and determination of isomeric oximes.

EXPERIMENTAL

Materials

α -Benzaldoxime, m.p. 35°; β -benzaldoxime, m.p. 130°; α -benzoin oxime, m.p. 151°; β -benzoin oxime, m.p. 99°; α -anisoin oxime, m.p. 123°; β -anisoin oxime, m.p. 125.5°. Melting points are not corrected.

Solvent systems

Benzene-ethyl acetate (50:10 v/v); benzene-absolute methanol (50:10 v/v).

Spraying reagents

Aqueous 0.5 % cupric chloride solution; saturated alcoholic cupric acetate monohydrate solution; alcoholic ferric chloride solution.

Method

Smooth glass plates (20 × 13 × 0.5 cm) were coated with a 0.2 mm thick layer of standardized silica gel G (according to STAHL) by means of a home-made applicator. The plates were then dried in an oven at 110° for 10 min, allowed to cool and kept in a moisture-free chamber. Spots of 0.5 % solutions of oximes in tetrahydrofuran (w/v) were applied from a capillary pipette in a line 2.5 cm from one edge of the plate, at intervals of 2 cm. The development was carried out by the ascending method in closed rectangular tanks (24 × 16 × 8 cm), saturated for 1 h with the appropriate solvent system. The tanks were lined with filter paper for good equilibration. The time required for the development (the solvent front moved 14 cm) was approximately 45 min. The developed chromatograms were then removed from the tanks, dried and sprayed with the detecting reagent.

For micro preparations the solutions were applied as bands of continuous spots, and the plates were developed twice. A narrow strip of the adsorbent was then sprayed and used as a guide for scraping the bands from the glass surface. The silica gel portions containing single isomers were extracted, the extracts evaporated at room temperature and the solids obtained applied separately on a new plate. Each extract gave only one spot.

SUMMARY

α - and β -Benzaldoximes, α - and β -benzoin oximes, and α - and β -anisoin oximes have been separated by thin-layer chromatography. In view of the highly different R_F values and the simple procedure, this method can be used for analytical separation, rapid determination and semimicro preparation of isomeric oximes.

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J. Chromatog., 12 (1963) 70-73