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THE THIN-LAYER CHROMATOGRAPHY OF ALKYL AND HALOGEN SUBSTITUTED BENZALDEHYDE 2,4-DINITROPHENYLHYDRAZONES

WALTER C. EISENBERG
Department of Chemistry, State University College of Arts and Science, Geneseo, N. Y. 14454 (U.S.A.)
AND
ROBERT E. GILMAN AND K. THOMAS FINLEY*
Department of Chemistry, Rochester Institute of Technology, One Lomb Memorial Drive, Rochester, N. Y. 14623 (U.S.A.)
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SUMMARY

The thin-layer chromatographic separation of alkyl and halogen substituted benzaldehyde 2,4-dinitrophenylhydrazones has been studied using a zinc carbonate adsorbant on glass plates and a 90% carbon disulfide–10% chloroform solvent mixture as the eluant. The halogen substituted benzaldehyde 2,4-dinitrophenylhydrazones were separated from the standard compound, benzaldehyde 2,4-dinitrophenylhydrazone. Of the alkyl derivatives examined only 4-isopropylbenzaldehyde 2,4-dinitrophenylhydrazone separated.

The adsorptive properties of thin layers of zinc carbonate were investigated and an eluotropic series was established.

INTRODUCTION

In an earlier paper[1] we reported the results of our thin-layer chromatographic study of several monosubstituted benzaldehyde 2,4-dinitrophenylhydrazones (2,4-DNPH). Nine of the nineteen compounds reported in that study could not be separated from binary mixtures with benzaldehyde 2,4-DNPH. All of these inseparable compounds contained alkyl or halogen substituents. In recent related studies, JART AND BIGLER[2] reported that the 4-chloro-, 4-bromo-, and 4-methylbenzaldehyde 2,4-DNPHs were not separable from benzaldehyde 2,4-DNPH ($R_{benzaldehyde}$ values of 0.99, 0.99 and 1.03, respectively). FREYTAG AND NEY[3], however, reported the separation of 3-methyl- and 4-methylbenzaldehyde 2,4-DNPHs from benzaldehyde 2,4-DNPH on chromatoplates of Kieselgel G.

We now wish to report the separation of seven of the nine alkyl and halogen substituted compounds from binary mixtures with benzaldehyde 2,4-DNPH.

* Present address: Eastman Kodak Company, Research Laboratories Rochester, N. Y. 14650, U.S.A.

EXPERIMENTAL

Materials

The 2,4-DNPH derivatives of the benzaldehydes reported in this study were all prepared by the procedure of SHRINER *et al.*[4] and were recrystallized from 95% ethanol until the melting points agreed with the literature values.

The developing solvents and the zinc carbonate (B4312) adsorbant were "Baker Analyzed" Reagent Grade.

Preparation of the chromatographic plates

A 250 μ layer of zinc carbonate adsorbant was spread on glass plates (200 × 200 mm) with a Desaga adjustable applicator (Model 3-11-S). The slurry consisted of 70 ml of distilled water and 25 g of zinc carbonate that contained 5% of a soluble starch binder. The plates were air dried for 24 h, activated in a drying oven at 110° for 1 h, and stored in a desiccating cabinet until used.

Development of the chromatographic plates

Standard Desaga developing tanks were used. Each was lined with Whatman No. 1 filter paper and presaturated with solvent for 1 h. All plates were developed over a distance of 150 mm.

RESULTS AND DISCUSSION

A report on the thin-layer chromatographic separation of mixtures of 2,4-DNPH derivatives of aliphatic aldehydes with zinc carbonate chromatoplates[5] prompted us to investigate this novel adsorbant with our alkyl and halogen substituted compounds.

Separation of binary mixtures

The thin-layer chromatographic separation of alkyl and halogen substituted benzaldehyde 2,4-DNPHs relative to the standard compound, benzaldehyde 2,4-DNPH, is reported in Table I. The values presented are defined relative to the standard compound in the following manner:

$$R_{\text{benzaldehyde}} = \frac{R_F \text{ substituted benzaldehyde 2,4-DNPH}}{R_F \text{ benzaldehyde 2,4-DNPH}}$$

Seven of the nine substituted benzaldehyde 2,4-DNPHs that were chromatographed as binary mixtures were separable from the standard compound, benzaldehyde 2,4-DNPH. This may be attributed to the polar nature of the substituent in the case of the halogen substituted compounds, all of which were found to migrate slower than the standard.

The methyl substituted derivatives gave R_F values close to that of benzaldehyde 2,4-DNPH and when chromatographed as mixtures were inseparable from the standard.

4-Isopropylbenzaldehyde 2,4-DNPH was found to be separable, migrating faster than benzaldehyde 2,4-DNPH. This can be attributed to the greater aliphatic

TABLE I

$R_{benzaldehyde}$ VALUES OF SUBSTITUTED BENZALDEHYDE 2,4-DNPHs

Apparatus and conditions: tank, 90 % carbon disulfide–10 % chloroform, glass plate, zinc carbonate.

Substituent	$R_{benzaldehyde}$
4-F	0.74
4-Br	0.78
4-Cl	0.79
3-Cl	0.84
3-Br	0.86
3-F	0.87
$3\text{-}CH_3$	1.00
$4\text{-}CH_3$	1.00
$4\text{-}CH(CH_3)_2$	1.10

TABLE II

PRECISION OF $R_{benzaldehyde}$ VALUES OF SUBSTITUTED BENZALDEHYDE 2,4-DNPHs

Substituent	*S.D.*
4-F	± 0.019
4-Br	± 0.020
4-Cl	± 0.020
3-Cl	± 0.012
3-Br	± 0.015
3-F	± 0.015
$3\text{-}CH_3$	± 0.009
$4\text{-}CH_3$	± 0.008
$4\text{-}CH(CH_3)_2$	± 0.022

TABLE III

ELUOTROPIC SERIES OF SOLVENTS FOR ZINC CARBONATE

Apparatus and conditions: tank, glass plate, zinc carbonate.

Eluant	*R_F benzaldehyde 2,4-DNPH*
Carbon disulfide–acetone (85 : 15)	0.92
Acetone–cyclohexane (50 : 50)	0.87
Tetrahydrofuran	0.87
Acetone	0.84
Dioxane	0.82
Benzene–ethyl acetate (80 : 20)	0.77
Benzene	0.76
Carbon disulfide– chloroform (90 : 10)	0.66
Toluene–cyclohexane (75 : 25)	0.56
Benzene–cyclohexane (60 : 40)	0.48
Carbon tetrachloride	0.24
Carbon disulfide–benzene (95 : 5)	0.15
Cyclohexane	0.05
Carbon disulfide	0.00

nature of the substituent which increases the solubility of the derivative in the eluant and decreases the adsorbant–derivative interaction.

Precision of experimental work

The precision of this experimental work is expressed in terms of the standard deviation of 9–12 $R_{benzaldehyde}$ values for each of the compounds studied. These are presented in Table II. These standard deviations lie within the limits of $\pm$ 0.05 which is generally considered acceptable. The precision of a larger number of determinations was obtained by taking the standard deviation of some 50 R_F values of benzaldehyde 2,4-DNPH. It was found to be $\pm$ 0.033, which although less precise, lies within the limits normally found satisfactory.

Eluotropic series of solvents (ref. 6)

An eluotropic series, a series of solvents in order of increasing eluting power, was established for the zinc carbonate adsorbant. This information was obtained from the data collected in the selection of the optimum solvent system and is shown in Table III. The eluting power of the solvent is reported in terms of the R_F value of the standard compound, benzaldehyde 2,4-DNPH—the larger the R_F value, the greater the eluting power of the solvent.

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