

APPLICATION OF SOME REAGENTS USED
IN ORGANIC FUNCTIONAL GROUP ANALYSIS FOR IDENTIFICATION
OF AMINES, ALCOHOLS, ALDEHYDES AND KETONES
TO ELIMINATION OF THESE SUBSTANCES
FROM ORGANIC MIXTURES IN REACTION GAS CHROMATOGRAPHY

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Dedicated to Professor Dr J. Klikorka on the occasion of his 60th birthday.

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A number of reagents have been tested for elimination of lower aliphatic amines and alcohols from mixtures of organic compounds, *viz.* 4-toluenesulphonyl chloride, 3,5-dinitrobenzoyl chloride, N,N-dimethyl-4'-aminoazobenzene-4-carboxylic acid chloride, 3-nitrophthalic anhydride, phthalic anhydride, N,N-dimethyl-4-aminobenzaldehyde and 1-naphthyl isocyanate. Aldehydes and ketones have been eliminated with 2,4-dinitrophenylhydrazine or 4-nitrophenylhydrazine in the presence of phosphoric acid. The reaction column was placed in the thermostat along with the chromatographic column. The reagents were introduced on Celite 545 or Chromaton N.

A number of various reagents were described¹⁻³ for elimination of amines, alcohols, aldehydes and ketones: phosphoric^{4,5} and phosphorous acid⁶ for amines and organic bases, boric acid⁷⁻¹⁴ for alcohols and phenols, calcium hydride¹⁵, metal hydrides LiAlH₄, LiBH₄ (ref.¹⁰), lithium hydroxide¹⁶, 3-nitrophthalic anhydride¹⁷, trichloroacetyl isocyanate¹⁸ and potassium carbonate¹⁹. Benzidine^{7-9,17}, *o*-dianisidine^{7-9,61}, sodium hydrogen sulphite^{8,9}, the hydrides LiAlH₄, LiBH₄, NaBH₄, NaBH(OCH₃)₃ (ref.^{10,11}), hydroxylamine hydrochloride^{12,15}, semicarbazide¹⁷ and FFAP (Free Fatty Acid Phase)^{7,17,20,21} were used for aldehydes and ketones. A number of other amines⁷ and 2,4-dinitrophenylhydrazine^{7,22} were tested as elimination reagents.

The aim of our work was to use further reagents used in organic functional group analysis^{23,24} for elimination in reaction gas chromatography.

EXPERIMENTAL

Apparatus

The analyses of model mixtures and practical samples were carried out with gas chromatographs Fractovap mod. GC 200 and Fractovap mod. GD ACI (Carlo Erba, Milano) with flame ionisation detector and four-way valve for carrier gas and attached integrator mod. 75, a Kienzle printer and a Speedomax G or Speedomax W recorder. The mentioned valve for carrier gas

makes it possible to use two columns (1 and 2) in four arrangements, *viz.* the column 1 or 2 alone or series 1 plus 2 or 2 plus 1. The column 1 was represented by the reaction column, *i.e.* an aluminium tube of 0.33 or 0.50 m length and 4 mm inner diameter packed with reaction packing. The column 2 was the proper chromatographic column, *i.e.* an aluminium tube of 1.50 m length and 4 mm inner diameter with separation packing Chromosorb W silanized 80–100 mesh (Carlo Erba) + 20% Celanese Ester (Applied Science Laboratories, Inc.). The connection is schematically represented in Fig. 1. Temperature of the both columns was 393 K. Nitrogen flow rate was 0.66 to 0.675 ml/s at $1.013 \cdot 10^{-1}$ MPa at 20°C in the system chromatographic column + 0.33 m or 0.50 m reaction column. In the case of the chromatograph Fractovap mod. GV 200, one inlet was connected with the chromatographic column, and the other inlet was connected with the reaction column the other end of which was connected with the beginning of the chromatographic column by means of a T-shape connection. The arrangement is represented in Fig. 2. As the chromatographic column served a stainless steel tube of 1.90 m length and 4 mm inner diameter packed with Celite 545, 50–80 mesh (LPC Chemicals Dyes Ltd., London) + 3% KOH + 15% Apiezon L (AEI Ltd., Manchester). The reaction column was an aluminium tube of 0.20 to 0.33 m length with reaction packing. Besides the mentioned arrangement, which only enabled to connect the reaction column before the chromatographic column, we also carried out the elimination after the chromatographic column by applying two identical chromatographic columns one of which contained packing with elimination reagent, instead of the separation packing of 0.20 to 0.33 m length. Temperature of the both columns was 383 K. Nitrogen flow rate was 0.333 to 0.583 ml/s at $1.013 \cdot 10^{-1}$ MPa at 20°C in the system chromatographic column + reaction column.

Packing of the Reaction Column

Chromaton N 0.25–0.31 mm (Lachema, Brno) + 20% 4-toluenesulphonyl chloride; Chromaton N + 20% 3,5-dinitrobenzoyl chloride; Chromaton N + 4% KOH + 20% 3,5-dinitrobenzoyl

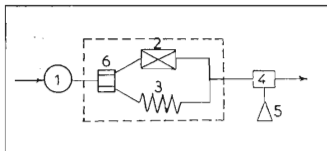


FIG. 1

Schematic representation of the arrangement of reaction column in the gas chromatograph Fractovap mod. GD ACI. Meaning of the symbols: → flow direction of the carrier gas, 1 the dosing block, 2 the reaction column, 3 the chromatographic column, 4 detector, 5 the recorder with attached integrator, 6 the four-way valve for the carrier gas

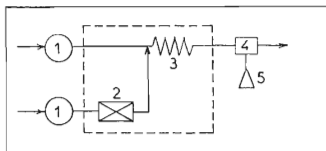


FIG. 2

Schematic representation of the arrangement of reaction column in the gas chromatograph Fractovap mod. GV 200. For explanation of the symbols see Fig. 1

chloride; Celite 545 + 20% N,N-dimethyl-4'-aminoazobenzene-4-carboxylic acid chloride; Chromaton N + 4% KOH + 20% 6,6-dimethyl-4'-aminoazobenzene-4-carboxylic acid chloride; Chromaton N + 20% 3-nitrophthalic anhydride; Celite 545 + 20% phthalic anhydride; Chromaton N + 20% N,N-dimethyl-4-aminobenzaldehyde; Celite 545 + 20% 1-naphthyl isocyanate; Celite 545 + 5% H_3PO_4 + 15% 2,4-dinitrophenylhydrazine; Celite 545 + 5% H_3PO_4 + 15% 4-nitrophenylhydrazine. Introduction of the elimination reagents on the support was carried out in the same way as that used for impregnation of stationary phases for packing chromatographic columns.

Test Substances

Aliphatic amines: methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, sec-butylamine, tert-butylamine, cyclohexylamine, allylamine, diethylamine, di-n-propylamine, di-isopropylamine, triethylamine.

Aliphatic alcohols: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutyl alcohol, tert-butyl alcohol, n-pentyl alcohol, isopentyl alcohol.

Aldehydes and ketones: acetaldehyde, isobutyraldehyde, crotonaldehyde, heptanal, benzaldehyde, acetone, methylethyl ketone, methylisopropyl ketone, methylpropyl ketone, methylisobutyl ketone, methylpentyl ketone, methylhexyl ketone, diethyl ketone, ethylbutyl ketone, dipropyl ketone, cyclopentanone, cyclohexanone, acetylacetone, mesityloxide.

Aliphatic and aromatic hydrocarbons: pentane, heptane, octane, benzene, toluene, cyclohexane.

Esters: ethyl acetate, isopropyl acetate, isopentyl acetate, propyl propanoate, butyl propanoate, ethyl butanoate.

Test of Elimination Efficiency of the Reagents

The elimination efficiency of the reagents was tested first by injection of the chosen individual compounds in the reaction column alone^{22,25}, next by gradual injection of model mixtures of the compounds in the chromatographic column and in the system of the reaction plus the chromatographic column. In each of the model mixtures toluene was present as a standard for better orientation in the chromatogram and for better quantitative evaluation of the achieved elimination. The model mixtures were composed in such a way that they always contained some representatives of other groups besides the group of compounds tested. The elimination of aliphatic amines and alcohols was followed on the gas chromatograph Fractovap mod. GV 200, that of carbonyl compounds and alcohols was followed on Fractovap mod. GD ACI. For testing the elimination efficiency of 1-naphthyl isocyanate the temperature of the reaction and chromatographic columns was 363 K.

Thermostability of the elimination reagents on supports was followed by measuring ionisation current in dependence on linearly increasing temperature.

RESULTS AND DISCUSSION

Applicability of the investigated reagents to elimination of lower amines, alcohols and carbonyl compounds is demonstrated by the following results.

4-Toluenesulphonyl Chloride

The reagent eliminates completely lower aliphatic primary, secondary and tertiary amines and some alcohols within the temperature range 373–423 K up to the carrier gas flow rate 0.75 ml/s. It proved suitable to attach a 0.01 to 0.02 m column of the carrier impregnated with potassium hydroxide solution at the end of the reaction column. Besides the expected elimination of primary and secondary amines, there also takes place elimination of tertiary amines due probably to formation of stable salts with either hydrochloric or 4-toluenesulphonic acid (set free by hydrolysis of the reagent) or with the sulphonamides containing acidic N–H bond. n-Alcohols $C_1 - C_4$ and isoalcohols C_4 and C_5 are also eliminated from the mixtures.

3,5-Dinitrobenzoyl Chloride (alone or with potassium hydroxide)

The reagent without or with KOH eliminates completely not only primary and secondary but also tertiary amines from the mixtures within temperature range 373–423 K up to the carrier gas flow rate 0.75 ml/s. Aliphatic n-alcohols $C_1 - C_4$ and isoalcohols C_4 and C_5 are eliminated from the mixtures within the temperature range 413–423 K below the carrier gas flow rate 0.333 ml/s the elimination being only partial at higher flow rates. If potassium hydroxide is present with the reagent, elimination of alcohols does not take place even at those lower flow rates.

N,N-Dimethyl-4'-aminoazobenzene-4-carboxylic Acid Chloride (alone or with potassium hydroxide)

The reagent is frequently used for identification of alcohols and amines^{26,27}. If it is used alone for elimination, then at 373–394 K and below 0.25 ml/s flow rate primary, secondary and tertiary amines are only eliminated from the mixtures. Under the same working conditions with added KOH the only components eliminated are primary and secondary amines and n-alcohols $C_1 - C_5$ and isoalcohols C_4 and C_5 . The reagent is highly thermostable.

3-Nitrophthalic Anhydride

Complete elimination of primary, secondary and tertiary amines is achieved within 423–463 K temperature range up to 0.5 ml/s flow rate of carrier gas. Increasing temperature increases the amount of eliminated alcohols from the mixtures.

Phthalic Anhydride

Lower primary, secondary and tertiary amines are eliminated completely at 383 K up to 0.75 ml/s flow rate of carrier gas. Elimination of n-alcohols $C_1 - C_5$ and isoalcohols C_4 and C_5 is only partial. Elimination of tertiary amines (in the case of the both anhydrides) is due to partial decarboxylation of the reagent.

N,N-Dimethyl-4-aminobenzaldehyde

Within temperature range 373–383 K and up to 0.75 ml/s flow rate of carrier gas complete elimination involves only primary amines with C_1 – C_4 n-alkyl groups. Primary amines with branched alkyl groups are eliminated only incompletely.

1-Naphthyl Isocyanate

Owing to its greater volatility the reagent can be used at lower temperature only. At 363 K and up to 0.66 ml/s flow rate of carrier gas the reagent eliminates completely primary aliphatic alcohols and amines. Elimination of secondary amines and alcohols is only partial, the tertiary isomers being unreactive.

4-Nitrophenylhydrazine and 2,4-Dinitrophenylhydrazine

Even at very low flow rates of carrier gas the reagents only eliminate some carbonyl compounds from the mixtures. Increasing amount of phosphoric acid in the reaction

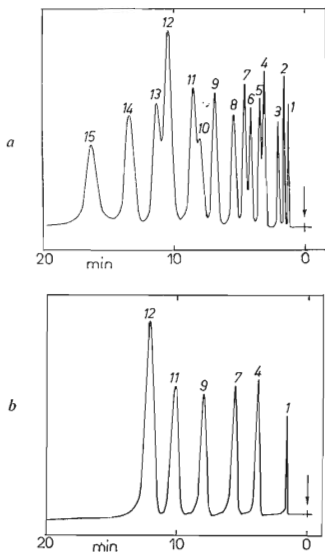


FIG. 3

Chromatograms of a model mixture without the reaction column (a) and after including the reaction column according to Fig. 1 (b). Aluminium chromatographic column of 1.5 m length and 4 mm inner diameter packed with Chromosorb W silanized + 20% Celanese Ester; aluminium reaction column of 0.33 m length and 4 mm inner diameter packed with Celite 545 + 5% H_3PO_4 + 15% 2,4-dinitrophenylhydrazine; temperature of the both columns 393 K. Order of the peaks: 1 pentane, 2 acetone, 3 isobutyraldehyde, 4 2-butanol, 5 methylisopropyl ketone, 6 diethyl ketone, 7 1-butanol, 8 methylisobutyl ketone, 9 toluene, 10 mesityloxide, 11 1-pentanol, 12 isopentyl acetate, 13 dipropyl ketone, 14 methylpentyl ketone, 15 cyclohexanone

column affects favourably completeness of the elimination²² which, at a chosen working temperature, only depends on the carrier gas flow rate. The both reagents are currently applicable within temperature range 323–493 K. In the presence of 5% phosphoric acid the former and the latter reagent eliminated completely all the tested carbonyl compounds up to the carrier gas flow rates 0.583 and 0.83 ml/s, respectively. The presence of phosphoric acid in the reaction column also caused complete elimination of amines and a slight lowering of the peaks of alcohols. Figs 3a,b show an example of elimination of some carbonyl compounds.

Capacity of the reaction column with the chosen elimination reagent, *i.e.* the amount of compound which can be eliminated from a sample under optimum working conditions, can be calculated from stoichiometry of the reaction taking place and amount of the elimination reagent in the reaction column. In this work we followed the efficiency of elimination of the reacting substances whose amounts in samples ranged between tens and hundredths of per cent. Influence of the reaction column on elimination of the component which are not eliminated but accompany the reacting main component of the sample was followed within their concentration range 1–30%. Lower concentrations were not tested.

As none of the investigated reagents fulfils all requirements proposed by Haken and coworkers⁹, they can be used for rapid orientation in analyses of unknown mixtures of volatile substances.

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