

Notes

CHROM. 4487

Analysis of the products of hydroammonolysis of acetone

The hydroammonolysis of acetone is the basis of the industrial production of 2-propyl amine which is an important intermediate in the pesticide industry¹. In the raw product obtained under the conditions of industrial production, several compounds are present besides the expected main components. When the reaction mixture is separated into two fractions, the first one will contain the low-boiling main constituents while the second one contains mainly the high-boiling by-products. The amount of the latter is 5–8 wt% for the given procedure. It was important for the purpose of controlling the process to determine the amount of the main product and the nature of the by-products. Gas chromatography seemed to be most suited to perform this task. Owing to the remarkable differences in the physical and chemical properties of the compounds to be separated, a combined detector and programmed-temperature technique was necessary to achieve satisfactory separation.

Experimental

Gas chromatographic measurements were carried out on a Carlo Erba Model C.ATC/t-type gas chromatograph. In the case of detection with a thermistor, the following experimental conditions were used: column, spiral of copper, length 1966 mm, I.D. 6 mm; packing, 20 wt% Carbowax 1550 on Celite 545, average particle diameter 0.315–0.400 mm; length of packing, 1952 mm (plug of nickel gauze of 7–7 mm length); carrier gas, hydrogen, inlet pressure 1.18–1.15 atm, outlet pressure 1.00 atm, flow rate at the outlet 80–100 ml/sec. Temperature of the column was 56–62°, and temperature of the evaporator was 60–90°. Measuring limit of the chart recorder was 2.5 mV; heating current of the detector, 18–20 mA; paper speed, 1.25 cm/sec; and sensitivity of the detector, 1/128–1/4.

In the case of flame ionisation detection, a Carlo Erba Model D-type gas chromatograph was used. The following experimental conditions were found to be best: column, U-shaped stainless-steel tube, length 800 mm, I.D. 6 mm; packing, 32 wt% Carbowax 1550 on Celite 545 with average particle diameter of 0.315–0.400 mm; carrier gas, nitrogen; inlet pressure, 1.15 atm; auxiliary gases, hydrogen with an inlet pressure of 1.35 atm and oxygen with an inlet pressure of 2.2 atm. Temperature of the column was 60–150°, and temperature of the evaporator, 80–170°. Measuring limit of the chart recorder was 2.5 mV; paper speed, 1.25 cm/sec; sensitivity of the detector, 1/12800–1/400. In most cases the sensitivity was adjusted to 1/6400. Samples were introduced by a 10- μ l Hamilton syringe with 0.1- μ l graduation.

The conditions of programmed-temperature gas chromatographic measurements differed from the above by the following factors: temperature of the evaporator, 190°; temperature of the column for 8 min after sample introduction, 84°, before being raised at a rate of 16°/min for 5 min. After that followed an isothermal portion at 164° until completion of the separation.

Part of the compounds were available in the pure form for the purpose of

TABLE I

RETENTION DATA OF COMPOUNDS FOUND IN TWO FRACTIONS

A = raw product of the chromatographic separation at 56°, measurement by thermistor; B = raw product of the chromatographic separation at 141°, measurement by flame ionisation detector; C = residue of the chromatographic separation at 56°, measurement by thermistor; D = residue at 131°, measurement by flame ionisation detector; E = residue at programmed temperature, measurement by flame ionisation detector.

| No. | Compound ^a | A (56°) | B (141°) | C (56°) | D (131°) | E |
|-----|---|------------|-------------|------------|-------------|------|
| 1 | <i>n</i> -Hexane | 0.12 | 0.10 | — | — | — |
| 2 | Cyclohexane | 0.12 | 0.10 | — | — | — |
| 3 | Ammonia | 0.12 | — | — | — | — |
| 4 | Isopropylamine | 0.15 | 0.37 | — | — | 0.36 |
| 5 | Di-isopropylamine | 0.23 | 0.39 | 0.23 | 0.38 | 0.38 |
| 6 | Acetone | 0.34 | 0.54 | — | 0.54 | 0.54 |
| 7 | Isopropanol | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 8 | Water | 3.01 | — | 3.01 | — | — |
| 9 | Isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) | 1.65 | 1.19 | 1.67 | 1.20 | 1.21 |
| 10 | — | — | 1.37 | — | 1.35 | 1.38 |
| 11 | Methyl isobutyl ketone | — | 1.50 | — | 1.55 | 1.60 |
| 12 | <i>n</i> -Propanol | — | 1.50 | — | 1.55 | 1.97 |
| 13 | Triacetone | — | 0.78 | — | 0.79 | 0.80 |
| 14 | 2-Methyl-4-pentanol | — | 0.84 | — | 0.85 | 0.85 |
| 15 | Mesityl oxide | — | 0.84 | — | 0.85 | 0.87 |
| 16 | — | — | 0.89 | — | 0.89 | 0.89 |
| 17 | Di-isobutyl ketone | — | 0.89 | — | 0.89 | 0.92 |
| 18 | 2,6-Dimethyl-4-heptanol | — | 0.89 | — | 0.89 | 0.93 |
| 19 | — | — | 0.96 | — | 0.96 | 0.97 |
| 20 | Triacetone diamine | — | 1.00 | — | 1.00 | 1.00 |
| 21 | Diacetone amine | — | 1.03 | — | 1.04 | 1.04 |
| 22 | Acetone isomers | — | 1.06 | — | 1.06 | 1.07 |
| 23 | — | — | — | — | 1.09 | 1.09 |
| 24 | — | — | — | — | 1.09 | 1.12 |
| 25 | 2,4-Diamino-2-methyl pentane | — | — | — | 1.18 | 1.19 |
| 26 | Diacetone alcohol | — | — | — | — | 1.31 |
| 27 | Diacetone-alkamine | — | — | — | — | 1.31 |
| 28 | — | — | — | — | — | 1.48 |
| 29 | Triacetone amine | — | — | — | — | 1.83 |

^a Compounds 10, 16, 19, 23, 24 and 28 have not been identified.

identifying the separated compounds. A number of compounds were prepared in the course of the present work in the pure form according to methods taken from the literature²⁻⁴. Very often the mixtures obtained in the reactions were used.

Results and discussion

The results of the evaluation of the chromatograms obtained at various temperatures and on programmed-temperature column by a standard addition method are summarized in Table I.

In Table I are given the compounds found in the two fractions by means of different detectors. Retention data are related to substance 7 for substances 1-12 and to substance 20 for compounds 13-29. In Table II the amounts of the main constituents of the sample are given in %.

TABLE II

MAIN CONSTITUENTS OF THE SAMPLE

| <i>Constituent</i> | <i>Amount (in %)</i> |
|--------------------|--------------------------|
| Ammonia | 5.3 |
| 2-Propylamine | 44.3 |
| Di-isopropylamine | 11.2 |
| Acetone | 1.8 |
| 2-Propanol | 4.1 |
| Water | 28.8 |
| By-products | 4.5 |

The formation of the great number of compounds is due to simultaneous and consecutive reactions. Compounds 3–8 are starting materials or main products. Tri-isopropylamine was also expected as a product⁵, but it could not be identified in the mixture. This is in accordance with the experience of KUFFNER *et al.*^{6–9} who have proved that this compound can be produced under special conditions only and is not formed during hydroammonolysis.

Most of the by-products are formed during the reaction of acetone with ammonia, condensation of acetone, and reduction reactions brought about by hydrogen. Previous work indicates the formation of normal and cyclohexane¹⁰. According to the same source also the formation of *n*-hexylamine can be expected, although this could not be found in the mixture by a standard addition method. Propyl alcohol may be produced from isopropyl alcohol by isomerisation.

The method described seemed to be best for the gas chromatographic analysis of the given complicated system.

On the basis of the method elaborated for the quantitative analysis of the product, the optimum conditions of the hydroammonolysis reaction of acetone could be determined.

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