CHROM. 5645

DETERMINATION OF PRODUCTS FROM THE OXIDATIVE DEHYDROGENATION OF ISOBUTENE BY GAS–LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

A mixture of products from the oxidative dehydrogenation of isobutene to methacrolein has been separated into two parts. The first, the absorbate, consists mainly of aldehydes, and the second, the condensate, consists mainly of acids.

The main purpose of the present work was the application of gas–liquid chromatography (GLC) or its combination with mass spectrometry (MS) to the identification of the reaction products.

Using PEG 400 plus PEG 3000 as a stationary phase, twelve components were identified in the absorbate by means of GLC–MS. Quantitative determination using the method of internal standards showed that the absorbate consists mainly of acetaldehyde, acetone and methacrolein in addition to an excess of water.

In the condensate, using Reoplex 400 plus orthophosphoric acid on Chromosorb W, twenty-four compounds were identified. The main part of the condensate is water, and of the other compounds the main ones are acetic acid, methacrylic acid and methacrolein.

INTRODUCTION

The increasing consumption of methyl methacrylate for the production of plastics (*e.g.*, methacrylic rubber and organic glass) cannot at present be covered by production from acetone and hydrogen cyanide because of the shortage of hydrogen cyanide, and other methods are therefore under serious consideration. One of the prospective processes which leads to the esters of methacrylic acid is the oxidation of isobutene (or a C_4 fraction that contains up to 50% of isobutene) to methacrolein followed by oxidation to methacrylic acid. The first step has been tested on a laboratory scale. The oxidative dehydrogenation has been carried out in a heterogenous system in the gaseous phase with the mixed oxides of molybdenum, bismuth and phosphorus as catalyst. The reaction mixture from the oxidation is passed through a water condenser where part of the condensate condenses. The volatile

products which do not condense are absorbed in a glass spiral with a counter-current flow of water (the absorbate), and the non-absorbed part is removed as a gas.

The development of a suitable analytical method for qualitative and quantitative analyses of the condensate and the absorbate was the main purpose of this work.

The direct analysis of the products of the oxidative dehydrogenation of hydrocarbons has been described in several papers and alcohols, aldehydes, acids and ethers together with carbon dioxide and monoxide, etc., have been found as products. MALINOVSKI[1] studied the direct analysis of the products of the oxidation of isobutene. The determination of carbon dioxide and oxygen was carried out on an Orsat apparatus, and the other gases were analysed by GC using firebrick plus ethylene glycol and a silver nitrate column. For the separation of aldehydes, a Teflon column with 10% of PEG 1500 was used. The total acids content was determined by potentiometric titration. Quantitative analysis of the products from the oxidation of propane by GC was described by DARDIN[2]. He used a combination of columns with 15% of silicone oil DC-550 plus stearic acid on Fluoropak 80 and 15% Convachlor-12 or 15% β,β-oxydipropionitrile on the same support and silica gel. KYRYACOS et al.[3] used GLC (40% of PEG 400 on firebrick) for the analysis of the products of the oxidation of n-hexane.

More attention has been paid to the chromatographic separation of mixtures of compounds that are qualitatively related to the products of our reaction, i.e., oxidative dehydrogenation of isobutene. Polyethylene glycols are most frequently used[4-6] as the stationary phase, e.g., for the separation and identification of impurities in methacrolein and ethylacrolein[7,8]; Porapak Q has also been recommended[9,10]. The chromatographic separation of C_2-C_4 acids was described by NIKELLY[11] and SMITH[12]. A mixture of isophthalic acid and Carbowax on acid-washed glass beads[11] or 5% Tween or Carbowax on Celite 545 was used. SEMBAEV et al.[13] determined quantitatively acrylic acid in aqueous solution in a mixture with acetic and propionic acids and lower aldehydes by GLC by using a column containing 14% of polyethylene adipate on firebrick. For the separation of organic acids, stationary phases based on polyesters[14-17] or combinations with long-chain fatty acids[18-20], Carbowax[12], PEG[17,22], and polyesters[17] mixed with orthophosphoric acid have often been used.

Thus GLC has been shown to be a suitable method[23].

EXPERIMENTAL

The optimal conditions for the GC separation of components from the absorbate and condensate were studied using CHROM-2 and Fractovap GV chromatographs with flame-ionization detectors. For the separation of the absorbate, the following columns were tested: Porapak Q (60–80 mesh); and 15% of PEG 400 plus PEG 3000 (ratio 30:70) on silanized Chromosorb W.

For the condensate, the following columns were tested:

Porapak Q (60–80 mesh); 16% of butanediol succinate plus 2% of orthophosphoric acid on Chromosorb W; 10% of Tween-80 on Chromosorb W; 10% of Reoplex-400 plus 1% of orthophosphoric acid on Chromosorb W; and 0.25% of Carbowax 20M plus 0.25% of terephthalic acid on glass beads.

The best separation of the absorbate was achieved on a 4-m column with I.D.

5 mm containing 15% of PEG 400 plus PEG 3000 on Chromosorb W. The column temperature was 90°, the flow-rate of nitrogen carrier gas, 40 ml/min (hydrogen, 56 ml/min; air, 220 ml/min).

Of the stationary phases tested, the highest selectivity for the separation of the condensate was achieved on a column packed with 10% of Reoplex 400 plus 1% of orthophosphoric acid on Chromosorb W. The column length was 2 m, I.D. 5 mm, with temperature-programming from 102° to 155° at 3°/min. The flow-rate of carrier gas (nitrogen) was 50 ml/min (hydrogen, 25 ml/min; air, 220 ml/min).

The same columns and the same temperature conditions as above were used in the analysis of the absorbate and condensate on an LKB 9000 Gas Chromatograph-Mass Spectrometer. The only differences were the inner diameter of the column (2.5 mm) and the use of helium as carrier gas with a flow-rate of *ca.* 15 ml/min. The detector was the ion source of the mass spectrometer (the energy of the bombarding electrons was 20 eV) together with the total ion current (TIC) monitor.

The mass spectrometer was the single-focusing type with magnetic recording to the mass scale. The ion source was the Nier type heated at 290°, and during the scanning of the mass spectra the energy of the ionizing electrons was 70 eV. The collector of ionic currents was the first dynode of the open electron multiplier.

RESULTS AND DISCUSSION

The order and the shape of the chromatographic peaks on the chromatograms of both the condensate and the absorbate were almost identical from both analytical chromatographs as well as from the LKB 9000 instrument. The differences in the relative responses were insignificant except in the case of the value for water.

Mass spectra were always recorded directly from before the sharp rise of a chromatographic peak (the spectrum of the background) up to the top of the peak. Subtraction of these two spectra gave the spectrum corresponding to the compound or compounds leaving the column in that particular peak. The quality of such a spectrum depends on the actual concentration of the compound present. The most
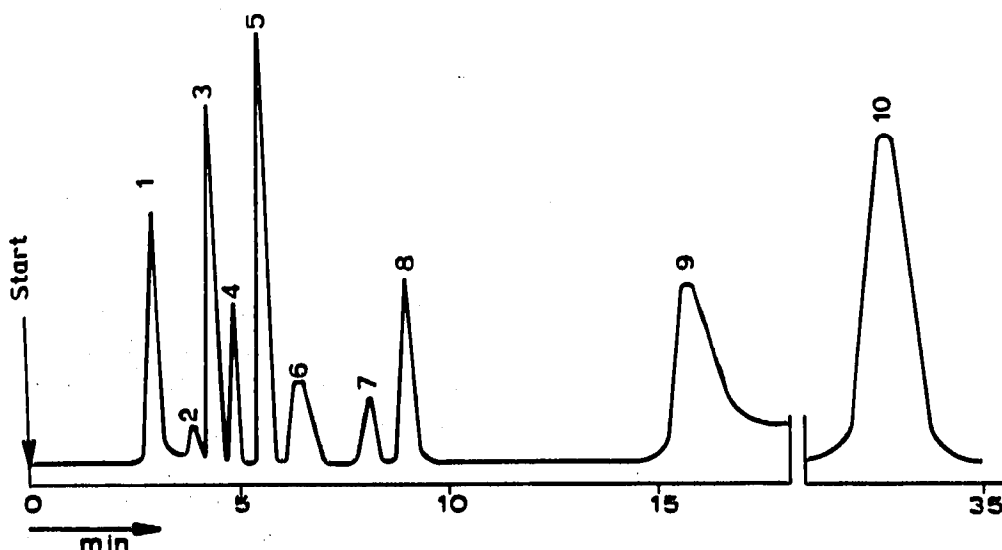

Fig. 1. Chromatogram of the absorbate. Peaks are identified in Table I.

advantageous spectra for interpretation are those in which the intensity of all the important ions (*i.e.*, more than 5% of the most abundant fragments) is at least half an order of magnitude greater than the intensity of the ions from the background. If the spectrum of a compound is comparable with that of the background, with the exception of one or two significant fragments, the reliable identification of the structure is usually difficult.

The mass spectra of most significant components of the absorbate and condensate have been published. The proposed structures of these compounds are therefore confirmed. If the interpretation of the spectra for a particular compound is based on analogy only, the most probable alternative structure is presented. The quality of the spectra of compounds which are present in only trace amounts usually does not allow the determination of more than the type of compound present (aldehydes, ketones, ethers, etc.) and the molecular weight. In such cases where the spectra could not be compared with literature data (as a "fingerprint") the names of compounds in Tables I and III are followed by a question mark (?).

TABLE I

IDENTIFICATION OF PEAKS IN THE CHROMATOGRAM OF THE ABSORBATE

The numbers of the peaks correspond to numbers in Fig. 1. (?) = spectrum not published.

No. of peak	Compound	Molecular weight	Relative retention time	Reference/spectrum no.
1	Ethanal + methyl methanoate	44 60	0.516	24/373 24/383
2	Propanal	58	0.703	24/294
3	2-Propanone	58	0.782	24/297
4	Propenal	56	0.872	24/86
5	2-Methylpropenal	70	1.000	25/131 AG
6	Methanol	32	1.214	24/282
7	3-Buten-1-al (?) + ethanol	70 46	1.409	26/- 24/75
8	2,3-Butandione	86	1.558	24/74
9	Water	18	2.750	27/232
10	2-Methylpropenol	72	5.820	27/3363

The absorbate

The chromatogram of the absorbate consisted of ten separate peaks for which the mass spectra had been recorded at each peak maximum. It has been established in all cases except two that at least 90% of the chromatographic peak is represented by one compound. Only peaks Nos. 1 and 7 (Fig. 1, Table I) are each a mixture of two compounds in approximately equal proportions. The results of the identification of compounds from the absorbate and the relative retention times are given in Table I. The order of the compounds in Table I follows the numbering of the peaks in the chromatogram (Fig. 1).

The main component of the absorbate is water (*ca.* 98%). The amounts of the other components were determined by the method of internal standardization using *n*-propanol as the most convenient internal standard. Five standard solutions of
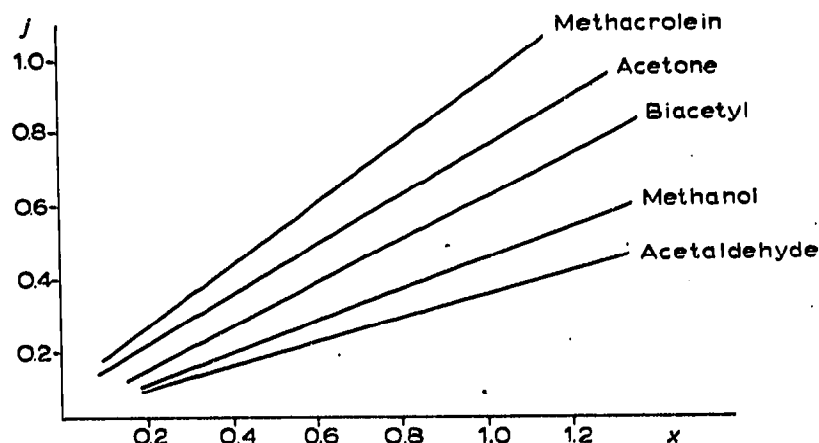
Fig. 2. Calibration graph for determination of compounds from the absorbate.

corresponding compounds in the following concentration ranges were used for preparing the calibration graphs: ethanal 0.02–1.2, propanone 0.02–1.5, 2-methyl-propenal 0.05–2.0, 2,3-butandione 0.03–1.2, methanol 0.05–1.0% w/w.

The calibration graph is presented in Fig. 2. Peak area ratios of the compound and n-propanol (y-axis) are plotted against their weight-% ratios (x-axis).

Component No. 1, a mixture of methyl formate and acetaldehyde (Table I), has been interpreted only by calibration with acetaldehyde; for components Nos. 2,3 and 4, where acetone is the major compound, calibration with acetone was used. Components Nos. 7 and 10 were not calibrated. The presence of these compounds was determined only in a few samples and in very low concentrations. The concentration range of the compounds determined in the absorbate and the relative errors of the analyses in the given concentration range are shown in Table II.

TABLE II

COMPOUNDS DETERMINED IN THE ABSORBATE

Compound	Concentration range (% w/w)	Maximum relative error (%)
Ethanal	0.02–0.5	11
Propanone	0.02–0.5	8
2-Methylpropenal	0.02–1.2	8
Methanol	0.05–0.5	12
2,3-Butandione	0.02–0.5	11

The condensate

The condensate as well as the absorbate is a mixture of compounds dissolved in water. The chromatogram of the condensate from an analytical chromatograph shows 29 peaks (Fig. 3). In the TIC record from the LKB 9000 instrument, a large asymmetrical wave from water is detected at the position of peaks Nos. 4 and 5, the remaining separation being unchanged.

In most cases, the chromatographic peak represents only one individual compound (Table III). Two compounds of about equal concentration are eluted in peak No. 15, *viz.* acrylic and methoxyacetic acids. In peak No. 17, methacrylic acid

TABLE III

IDENTIFICATION OF COMPOUNDS IN THE CHROMATOGRAM OF THE CONDENSATE

The numbers of the peaks correspond to numbers in Fig. 3. a = not identified because of low concentration of compound. (?) = spectrum not published.

No. of peak	Compound	Molecular weight	Relative retention time	Reference/ spectrum no.
1	Methanal	30	—	24/84
2	Methanol	32	—	24/282
3	2-Methylpropenal	70	0.067	25/131 AG
4	Water	18	0.081	27/232
5	a		0.124	
6	2-Methylpropenol	72	0.143	27/3363
7	Unsaturated alcohol	86	0.179	28
8	a	88	0.215	
9	Hydroxypropanone	74	0.267	25/167 AG
10	Ethanoic acid	60	0.363	24/640
11	a		0.425	
12	Unsaturated aldehyde	96	0.525	26
13	Polyoxymethylene		—	29
14	2,5-Hexandiol	114	0.714	27/1063
15	Propenoic acid +	72	0.783	25/1 AA
	methoxyethanoic acid	90		27/1963
16	a		0.876	
17	2-Methylpropenoic acid	86	1.000	25/189 AG
	Cyclopentene carboxaldehyde (?)	96		30
18	a		1.12	
19	Methylbenzaldehyde	120	1.24	25/23 H
20	a		1.33	
21	Maleic acid +	116		25/20 C
	furanoic acid	112	1.54	25/1 BD
22	1-Cyclohexene carboxylic acid	126	1.69	27/4679
23	a		1.93	
24	a		2.11	
25	Methyl ester of higher fatty acid		2.50	31
26	Phenol	94	4.59	25/39 D
27	p-Cresol	108	6.60	25/7 AD
28	Phthalide	134	7.76	27/5152
29	Dimer of 2-methylpropenal	140	8.96	32

is the major component, cyclopentene carboxaldehyde being the minor one. Similarly, maleic acid prevails considerably over furanoic acid in peak No. 21.

Only semi-quantitative analysis has been carried out in the case of the condensate (an aqueous solution of acetic, acrylic and methacrylic acids was used for calibration). Even on the basis of such a simplified determination, it is possible to say that apart from water, which is the major component of the condensate, only methacrolein, acetic acid and methacrylic acid are present in significant amounts (up to 1%). The concentrations of the remaining compounds are substantially lower.

CONCLUSION

Methacrolein, methacrylic acid and acetic acid are the main products from the catalytic oxidative dehydrogenation of isobutene. Other compounds are probably produced by the competitive homolytic reactions, condensation, oxidative dehydrogen-
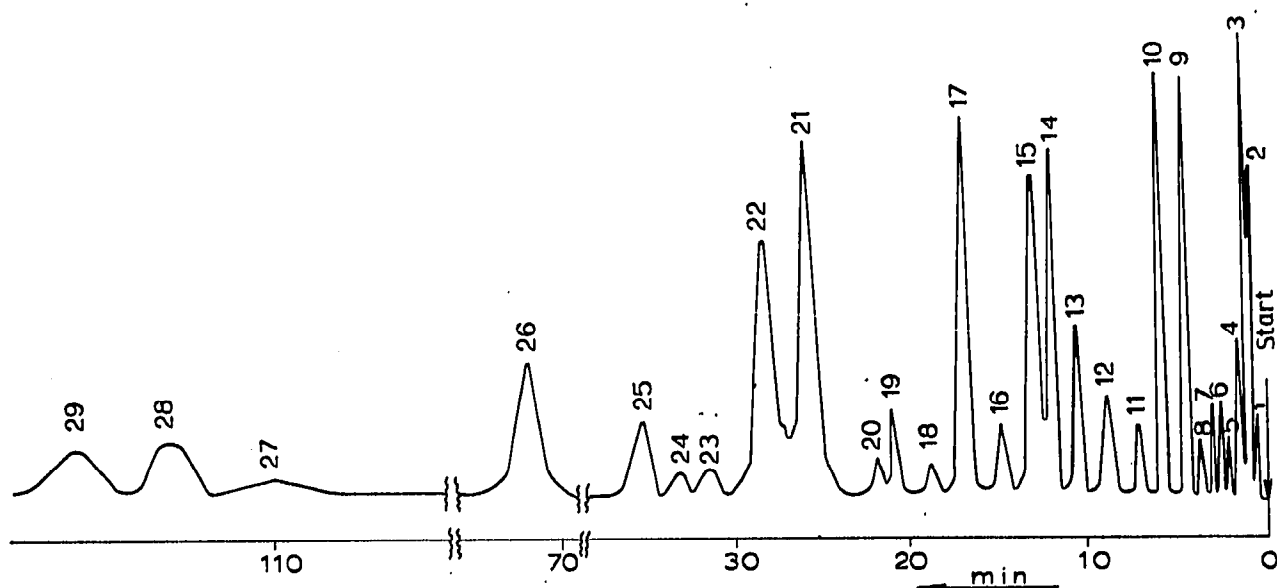
Fig. 3. Chromatogram of the condensate. Peaks are identified in Table III.

ation and cyclization processes. It is worth mentioning that together with lower aldehydes, alcohols and acids, some oxygen-containing derivatives of benzene are also present in the products.

Apparently the combination GLC–MS is a very powerful technique for the identification of the components of very complicated reaction mixtures. The chromatographic data (retention volumes) and the mass spectrum are obtained simultaneously for each compound and this combination may often be sufficient for structural identification. When it is not possible to interpret the mass spectrum reliably because a compound is present only in trace amounts, at least a tentative structure may be postulated. To obtain comparable results by using only analytical chromatography, a large stock of standards and long experimental times would be needed.

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