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QUANTITATIVE ANALYSIS OF MALEIC AND CITRACONIC ANHYDRIDES BY GAS CHROMATOGRAPHY

ALDO DI LORENZO

Laboratorio di Ricerche sulla Combustione, C.N.R., Istituto di Chimica Industriale e Impianti Chimici dell'Università di Napoli, Naples (Italy)

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SUMMARY

A gas chromatographic technique has been developed for quantitative analysis of the maleic and citraconic anhydrides produced by catalytic vapor-phase oxidation of methylcyclopentane with air. The main difficulty in analysing samples as obtained from the catalytic reactor is that the above anhydrides are partially hydrated to acids in the presence of the condensed water. Maleic and citraconic acids cannot, as their anhydrides, be detected quantitatively by gas chromatography nor are they completely dehydrated using the usual temperature of the injection block and flow rate of the carrier gas. Gas chromatographic analysis of methyl esters derived from maleic and citraconic acids correctly gives the amount of anhydrides and acids initially present in the sample from the reactor. The di-2-ethylhexyl sebacate/sebacic acid column separates anhydrides, esters and their isomers, allowing the control of the completeness of esterification.

INTRODUCTION

During work on the vapor-phase oxidation of methylcyclopentane over vanadium–molybdenum catalyst[1] the problem of analysing mixtures consisting of methylcyclopentane, acetic acid, water, maleic and citraconic anhydrides in dioxane solution arose. The principal difficulty in measuring such mixtures arose from the coexistence of two anhydrides and water. Many methods for analysing anhydrides, utilizing various techniques such as conventional chemical, polarographic and GC analyses, have been described in the literature[2–16]. Several authors[2–4] estimated the maleic anhydride as barium maleate monohydrate by precipitation with $BaCl_2 \cdot 2H_2O$ in alcohol solution. Others[5,6] determined maleic anhydride, in the products arising from catalytic vapor-phase oxidation of benzene, by the bromine consumption. The polarographic analysis of anhydrides, described by various authors[7–10] has recently been optimized[11]. GC has been utilized in the catalytic vapor-phase oxidation processes of alkylaromatic hydrocarbons for quantitative determination of condensed products including maleic and citraconic anhydrides[12–15]. Finally, CUCARELLA AND CRESPO[16] have developed a GC method which allows a measurement of the impurities, normally present in phthalic anhydride, which include maleic and citraconic anhydrides, after esterification with a sulfuric acid–methanol mixture.

EXPERIMENTAL

Preliminary experiments on methylcyclopentane oxidation have been made to study the composition of reaction products. The presence, in all the tests, of both maleic and citraconic anhydrides in the reaction products excluded the use of the Ba method, the Br method and polarographic analysis because these methods determine the total anhydrides but do not distinguish between them. Therefore, for quantitative determination, the previously known GC methods[12–16] have been tested.

Chemicals

Chromosorb P AW 60–80 mesh (John Manville Products Co.); di-2-ethylhexyl sebacate, didecyl phthalate, sebacic acid, phosphoric acid, methylcyclopentane, dioxane, acetic acid, *m*-xylene, maleic anhydride (Carlo Erba S.p.A.); citraconic anhydride, maleic, fumaric, citraconic, mesaconic and itaconic acids, maleic and itaconic acid dimethyl esters (Fluka AG Chemische Fabrik); fumaric, citraconic and mesaconic acid dimethyl esters were synthesized in this Laboratory by esterification of their corresponding acids with a sulfuric acid–methanol mixture and were subsequently purified.

Apparatus

All analyses were carried out with a Perkin-Elmer F 6 gas chromatograph equipped with a flame ionization detector (flow rates: hydrogen, 30 ml/min; air, 350 ml/min). The chromatograms were recorded with a Leeds & Northrup Speedomax 5 mV recorder at a chart speed of ½ in./min. Helium was used as the carrier gas. Samples were injected with a 10-μl Hamilton syringe (Model No. 701 N).

In preliminary analyses, various columns, including those described in the literature for maleic and citraconic anhydride separation[12–14], were tested to select the most suitable working conditions for separating the products obtained from the reactor. Two columns were prepared from a 2-m length of ¼-in. stainless-steel tubing; the first was packed with 25% di-2-ethylhexyl sebacate and 10% sebacic acid on 60–80 mesh acid-washed Chromosorb P, and the second with 25% didecyl phthalate on 60–80 mesh acid-washed Chromosorb P, previously treated with 10% sulfuric acid as described in ref. 17. The operation was done isothermally at 120° and gave a good separation of methylcyclopentane, dioxane, acetic acid, *m*-xylene (used as internal standard in the quantitative evaluations), maleic and citraconic anhydrides. During the experiments it was noted that the didecyl phthalate–phosphoric acid column was not suitable for routine analysis, as it easily deteriorated, with drop in retention time for the various substances and consequent overlapping of the dioxane and acetic acid peaks.

A hydrogen flame ionization detection system was used because many dilute solutions (about 15 g of dioxane per g of condensed products) had to be analyzed. Water, not detectable with this system, was determined by Fischer's method.

Under the previously described experimental conditions synthetic mixtures of methylcyclopentane, acetic acid, *m*-xylene, maleic and citraconic anhydrides, prepared by weighing the individual components and then dissolving them in dioxane, were analyzed. The analyses of these mixtures were still reproducible even after several days. On the contrary the same mixtures with water did not give good results. In particular, maleic anhydride behaved irregularly. If these mixtures were analyzed directly after preparation, the maleic anhydride values were approximately those obtained for mixtures without water. However, on repeating the analyses, the values gradually decreased until they were about half and then remained almost constant. Instead, the values for citraconic anhydride, always present in the products from the reactor and the synthetic mixtures in amounts lower than the maleic anhydride, did not alter. Such irregularity of maleic anhydride in the presence of water has not been hitherto reported in the literature[13–15].

Since GC analysis of maleic acid from a solvent solution gave a peak whose retention time corresponded to the maleic anhydride, while the area of the acid was about half with respect to that of the anhydride at the same concentration, the irregularity in the quantitative determination of maleic anhydride in the synthetic mixtures with water was attributed to its hydration into the acid. Thus complete dehydration from acid to anhydride was not possible with the ordinary injection block temperature and carrier gas flow rates.

On the other hand, maleic acid was always present in the mixtures from the reactor. In fact, by adding to these mixtures, after the first analysis, a solution of acetyl chloride and acetic acid to improve the dehydration of the acid to anhydride and then repeating the analysis, higher values of maleic anhydride were obtained.

Thus, the possibility of determining the maleic acid and anhydride as maleic acid dimethyl ester was studied. The esterification was preceded by a GC quantitative determination of methylcyclopentane, acetic acid and citraconic anhydride to avoid possible errors due to loss, especially of methylcyclopentane, in the methylation procedure. Then, citraconic anhydride was added to the solution to be utilized as an internal standard for determination of the maleic acid dimethyl ester.

In principle, our method was similar to that given in ref. 16. The methylation was carried out using a sulfuric acid–methanol mixture (1:4). The esters produced were extracted with ether; the ethereal solution was washed with Na_2CO_3 and Na_2SO_4 until neutral and was concentrated. A 2-μl sample was introduced into the gas chromatograph. But with these working conditions the maleic anhydride was not satisfactorily determined. A chromatographic check of the esterification procedure showed that the methylation was partial and extraction of esters with ether incomplete. Moreover, it was not possible to concentrate the solution because a water and an ether phase were obtained.

The presence of water in the products from the reactor and their considerable dilution in dioxane were among the reasons for non-quantitative esterification. Therefore, after the analysis of products in dioxane solution and the addition of citraconic anhydride, the solution was concentrated before the esterification to eliminate most of the dioxane, water and methylcyclopentane. A mixture of methanol and sulfuric acid (8:1) was added to the concentrate and was esterified by refluxing the solution on a water bath for 2 h. After cooling, the mixture was neutralized with a 20% aqueous solution of Na_2CO_3 and a 2-μl sample was injected into the gas chromatograph. By this procedure, the analysis of an alcoholic solution of dimethyl esters derived from maleic and citraconic acids gave the correct amount of maleic anhydride

TABLE I

RELATIVE RETENTION DATA

Column temperature, 120°; carrier gas flow rate, 90 ml/min; retention time of maleic anhydride, 14 min.

Sample	*Relative retention time*
Maleic anhydride	1.00
Fumaric acid dimethyl ester	1.38
Maleic acid dimethyl ester	1.47
Citraconic anhydride	1.61
Itaconic acid dimethyl ester	2.00
Citraconic acid dimethyl ester	2.11
Mesaconic acid dimethyl ester	2.21

and acid initially present in the sample from the reactor. The di-2-ethylhexyl sebacate–sebacic acid column separated anhydrides, esters and their isomers (Table I) and this enables control of the completeness of the esterification.

RESULTS

Both direct analysis of the products from the reactor dissolved in dioxane and determination of maleic anhydride and acid as maleic acid dimethyl ester were carried out with the column prepared from a 2-m length of ¼-in. stainless-steel tubing packed with 25% di-2-ethylhexyl sebacate and 10% sebacic acid on 60–80 mesh acid-washed Chromosorb P. The operation was done isothermally at 120° with a helium carrier gas flow rate of 90 ml/min.

Internal standards were used for quantitative analysis. Calibration curves of methylcyclopentane, acetic acid and citraconic anhydride were obtained by plotting the concentration for each compound *vs.* the ratio of its peak area to that of *m*-xylene (20% referred to weight of the products). In the same way the calibration curve for maleic anhydride was obtained using citraconic anhydride as an internal standard, obtained in small part from the reaction and the rest being added by weight to the mixture up to 10% referred to weight of the products. Curves were linear at the concentrations used.

Some mixtures of known composition were analyzed for control purposes. Table II shows, for example, a comparison between compositions valued in weight and those measured by GC giving the relative differences and percentage errors.

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TABLE II

ANALYSIS OF METHYLCYCLOPENTANE, ACETIC ACID, MALEIC AND CITRACONIC ANHYDRIDES AND WATER IN DIOXANE SOLUTION

Column temperature, 120°; carrier gas flow rate, 90 ml/min.

Substance	*Theor. values*	*Exper. values*	*Diffe-rences*	*Errors (%)*	*Theor. values*	*Exper. values*	*Diffe-rences*	*Errors (%)*	*Theor. values*	*Exper. values*	*Diffe-rences*	*Errors (%)*
	Mixture 1				*Mixture 2*				*Mixture 3*			
Methylcyclopentane	14.60	14.85	+0.25	1.71	29.80	30.15	+0.35	1.17	44.00	43.30	−0.70	1.59
Acetic acid	3.48	3.40	−0.08	2.30	2.26	2.30	+0.04	1.72	1.85	1.83	−0.02	1.08
Maleic anhydride	24.62	24.70	+0.08	0.32	20.60	20.49	−0.11	0.53	14.90	14.60	−0.30	2.01
Citraconic anhydride	2.60	2.56	−0.04	1.54	3.24	3.27	+0.03	0.91	2.62	2.59	−0.03	1.14
Water[a]	54.70	54.60	−0.10	0.18	44.10	44.13	+0.03	0.07	36.63	36.71	+0.08	0.22
	Mixture 4				*Mixture 5*				*Mixture 6*			
Methylcyclopentane	52.50	52.20	−0.30	0.57	69.20	70.10	+0.90	1.30	80.20	80.05	−0.15	0.19
Acetic acid	1.15	1.08	−0.07	6.09	0.59	0.57	−0.02	3.39	0.35	0.36	+0.01	2.86
Maleic anhydride	10.40	10.60	+0.20	1.92	7.15	7.10	−0.05	0.70	4.05	4.10	+0.05	1.23
Citraconic anhydride	1.72	1.66	−0.06	3.48	0.84	0.83	−0.01	1.19	0.29	0.31	+0.02	6.91
Water[a]	34.23	34.19	−0.04	0.12	22.22	22.01	−0.19	0.89	15.11	15.21	+0.02	0.66

[a] Determined by Fischer's method.

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