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Note

Direct gas chromatographic determination of the products of catalytic air oxidation of *n*-butene-1 to maleic anhydride in the gaseous reaction mixture

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Catalytic gas phase oxidation of *n*-butene-1 with air yields a large number of oxidation products in addition to maleic anhydride (MA), butene isomers and butadiene resulting from oxidative dehydrogenation. These are mainly furan, crotonaldehyde, acetic acid, propionic acid, acrylic acid, α-methylacrylaldehyde, ethyl methyl ketone, butanedione, isobutyraldehyde, water, carbon monoxide and carbon dioxide. Up to now, the analysis of these reaction products has been mostly carried out in such a way that higher boiling products are condensed and/or are subjected to absorption from the reaction gas by suitable solvents before gas chromatographic analysis of the remaining gaseous components. This procedure is mainly used because of the high boiling and melting point of MA, as severe problems arise when the gaseous reaction mixture is introduced into the gas chromatograph.

However, this procedure is disadvantageous when separating MA and water by condensation from the gas because at least part of MA will be hydrolysed to maleic acid. The problem is even more severe when water is used as an absorbent. However, under the usual conditions the resulting maleic acid is not amenable to subsequent direct gas chromatographic analysis. Hence, the determination of MA is performed following complete hydration to maleic acid, mainly by potentiometric titration, whereas the other products are determined by gas chromatography. It is known, however, that MA can be determined directly by gas chromatography on various columns with stationary phases consisting of phthalic acid ester[1,2], silicone oil[2], cyanosilicone oil[3] or Porapak Q[4,5]. Columns with polyesters[6] and di(2-ethylhexyl) sebacate + sebacic acid[7] as stationary phases are also applicable to the gas chromatographic determination of MA.

A method is described below that allows the direct quantitative gas chromatographic analysis of the products of the gas-phase oxidation of *n*-butene-1 ("direct method"), without the need to analyse any condensate or absorbent for these products ("indirect method").

GAS CHROMATOGRAPHIC ANALYSIS

In the oxidation of *n*-butene-1 the resulting gaseous products are divided into two fractions. One fraction is passed through two cold traps filled with ice, in which

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TABLE I

CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSIS OF GASEOUS PRODUCTS FROM OXIDATION OF *n*-BUTENE-1

Separation column	*Conditions for analysis*	*Detector*	*Substances*	*Retention time (sec)*
Molecular sieve 13X (100–200 mesh), 1 m × 3 mm I.D.	He, 25 ml/min, room temperature, isothermal, 2-ml sample loop	Thermal conductivity	CO	190
Dimethylsulpholane on Chromosorb (30–60 mesh), 5 m × 3 mm I.D.	He, 25 ml/min, room temperature, isothermal, 2-ml sample loop	Thermal conductivity	CO_2	150
			n-Butene-1	300
			trans-Butene-2	360
			cis-Butene-2	402
			Butadiene	540
Di(2-ethylhexyl) sebacate + sebacic acid on Chromosorb W AW, 2 m × 2 mm I.D.	N_2, 25 ml/min, 120°C, isothermal, detector 200°C, injector 200°C, inlet 150°C, 1-ml sample loop	Flame ionization	C_4 hydrocarbons	44
			Furan	69
			Isobutyraldehyde	90
			α-Methylacrylaldehyde	97
			Butanone	109
			Crotonaldehyde	172
			Acetic acid	251
			Propionic acid	480
			Acrylic acid	618
			MA	1050

the higher boiling products are condensed. The remaining gaseous products (butenes, butadiene, carbon monoxide and carbon dioxide) are analysed on a dimethylsulpholane–chromosorb column and on a molecular sieve column. The second fraction is cooled only to 150°C and passed via a heated tube directly to a heated gas sample loop of the gas chromatograph; the remaining products are analysed on a di(2-ethylhexyl) sebacate + sebacic acid–Chromosorb column. Equilibrium calculations for the hydration of MA have shown that even in the presence of water vapour under the above conditions virtually no maleic acid is formed. Table I gives the analytical conditions together with retention times of the different components. Fig. 1 illustrates a typical chromatogram for the oxygenated derivatives of *n*-butene-1 together with the total C_4 hydrocarbons.

For the quantitative evaluation of the chromatogram, the necessary response factors for the liquid products under ambient conditions or at higher temperatures were determined in such a way that a carrier gas stream was loaded with pure substance and introduced into the gas chromatograph for calibration. In each instance the

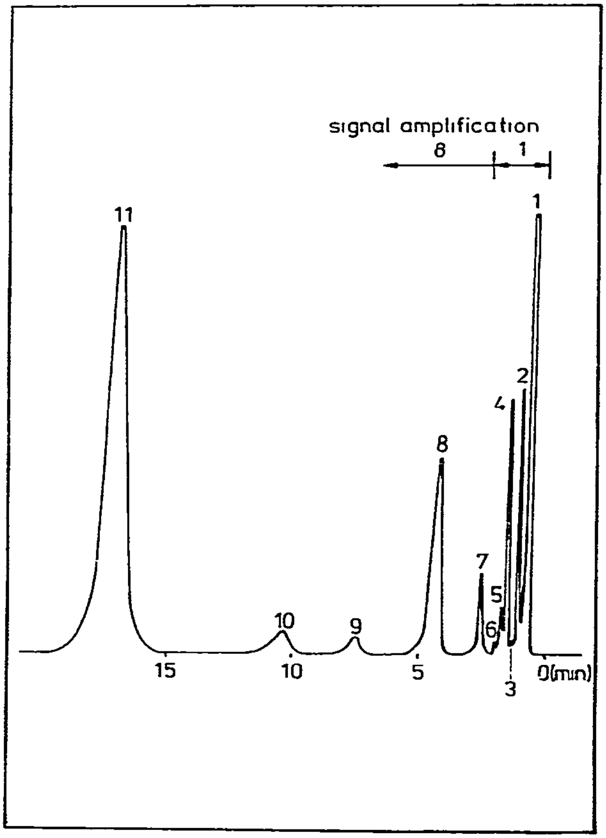

Fig. 1. Chromatogram of a characteristic gaseous reaction mixture produced by air oxidation of *n*-butene-1 to MA. Concentration of *n*-butene-1 at reactor inlet: 1.5 mole-%. Identities of peaks, with yields in wt.-% in parentheses: 1 = C_4 hydrocarbons (65.8); 2 = furan (3.1); 3 = isobutyraldehyde (0.1); 4 = α-methylacrylaldehyde (4.1); 5 = ethyl methyl ketone (0.9); 6 = butanedione (0.3); 7 = crotonaldehyde (0.5); 8 = acetic acid (2.5); 9 = propionic acid (0.1); 10 = acrylic acid (0.3); 11 = MA (13.1).

prevailing concentrations in the gas stream were determined with the help of the vapour pressure according to ref. 8. Saturation was achieved by first bubbling the carrier gas through the liquid and subsequently passing it through a reflux condenser having a temperature of 10–15°C below that of the liquid so that part of the evaporated liquid is re-condensed. The saturation pressure corresponds to the condenser temperature, which could be accurately measured. The response factors, f, obtained in this way on the basis of propionic acid are compared in Table II for four important *n*-butene-1 oxidation products (MA, acrylic acid, propionic acid and acetic acid), with values being determined by the gas chromatographic analysis of acetone solution or by calculation according to ref. 9 by $f = M_i/(n_C \cdot 12)$, where M_i is the molecular mass of i and n_C is the number of "available" carbon atoms of i).

For the remaining components of a typical product gas no response factors were experimentally determined, as they were present either in only minute concentrations below the limit of determination (ethyl methyl ketone, butanedione and isobutyraldehyde) or could not be analysed quantitatively owing to polymer formation (α-methylacrylaldehyde, crotonaldehyde and furan) under the conditions of gas chromatography used. For these reaction products the response factors are actually estimated according to ref. 9 in order to obtain at least some indication of the magnitude of their concentrations.

The response factors measured for MA and propionic acid, as is evident from Table II, agree well with the calculated values[9]. On the other hand, large deviations for acetic acid and especially for acrylic acid may possibly be caused by polymerization, which can occur at elevated temperatures. Direct determination of the MA content in a product gas by gas chromatography corresponds, within the limits of experimental accuracy, with the value obtained when MA was first absorbed in acetone and water and then the MA content was determined by potentiometric titration of maleic acid in water and gas chromatographic determination of MA dissolved in acetone. It should be mentioned, however, that the response factor for MA in acetone solution derives from the gas phase.

The linearity of the response factors with respect to concentration was examined over the range 0.05–0.8 mole-% for each substance; the result for MA is shown in Fig. 2. After about 100 analyses of the product gas, the estimated response

TABLE II

RESPONSE FACTORS OF MONOCARBOXYLIC ACIDS AND MA BASED ON PROPIONIC ACID

For separating column and conditions for analysis, see Table I.

Reaction product	*Response factor*		
	Direct (gas phase)	*Indirect (acetone solution)*	*Calculated*[9]
Acetic acid	1.50 ± 0.03	1.75 ± 0.05	1.62
Propionic acid	1.0	1.0	1.0
Acrylic acid	1.26 ± 0.03	1.40 ± 0.05	0.97
MA	1.26 ± 0.02	1.30 ± 0.10	1.32

factors were re-checked to establish whether the separating properties of the gas chromatographic columns had changed. The measured deviations were within the standard deviation of the response factors.

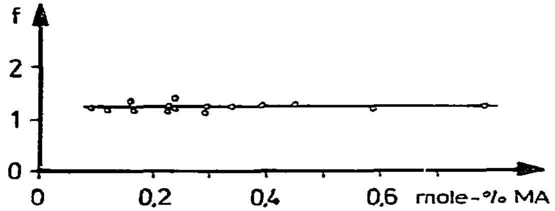

Fig. 2. Response factor of MA based on propionic acid as a function of gas loading with MA.

CONCLUSION

The direct gas chromatographic determination of the products in the gaseous mixture obtained by air oxidation of *n*-butene-1 needs less time than the "indirect method" involving titration of maleic acid and gas chromatographic determination of the other products. The accuracies of the two methods are comparable. The direct method is suitable for establishing quickly and simply the resulting intermediates in the gas phase, *i.e.*, butadiene, furan and crotonaldehyde, which occur at higher concentrations on incomplete conversion of *n*-butene-1, and impurities in MA, especially monocarboxylic acids, which occur on complete conversion of *n*-butene-1.

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