

GAS-CHROMATOGRAPHIC ANALYSIS IN THE HETEROGENEOUS CATALYTIC OXIDATION OF PROPENE AND 1-BUTENE

J. ŠRÁMEK

*Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2*

Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

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Chromatographic columns filled with dimethylsulpholane on Chromosorb P, polyethylene glycol 500 on Celite and molecular sieve 13X were used in determining all compounds of heterogeneous catalytic oxidation of propene and 1-butene. Construction of apparatus made it possible to dose the same volume of sample before and after the reactor, even if the pulse technique was used. Thus, we could directly measure the dependence of conversion on the time factor W/F .

In the petrochemical processing of unsaturated hydrocarbons propene is oxidized mainly to acrolein, and 1-butene is oxidized to butadiene or maleic anhydride. Other oxidation products, whose proportion depends on the catalyst, temperature, feed and some other factors, are carbon dioxide, carbon monoxide, water, acetaldehyde, acetone, propionaldehyde and propylene oxide. In a detailed kinetic study it is necessary to distinguish 1-butene and *cis*- and *trans*-2-butenes (in the reactions followed 2-methylpropene has never been found). The usual analytical methods are gas chromatography¹ and mass spectroscopy^{2,3}. The gas chromatography is usually carried out at room temperature to prevent some compounds (*e.g.* acrolein) from polymerization in the columns, and not all compounds are generally determined.

The present paper describes the optimum conditions for a complete gas-chromatographic determination of these compounds in quantities of 0.1 μmol or higher (at 0.1 to 3 μmol the relative accuracy is 5 to 7%, at greater concentrations 3 to 5%) by combination of three chromatographic columns. In the use of an integral reactor with continuous feeding in of the mixture only maleic anhydride formed in the oxidation of 1-butene was determined by titration after absorption in water. In pulse measurements its amount was calculated from the ratios in the continual feeding on the individual catalysts.

EXPERIMENTAL

The gas chromatograph was manufactured at our Institute. The temperature of the heat-conductance detector was kept at 30°C. The flow rate of helium as carrier in each column was 65 ml

(NTP)/min, the column temperature was 25°C, the inner diameter of the tubes 4.5 mm. Column A: 20 g of 25% dimethylsulpholan on Chromosorb P, mesh 30/60 (Carlo Erba), length 4.5 m. Column B: 3.5 g of 22% polyethylene glycol, m.w. 500 on Celite, 80—100 mesh (B.D.H.), length 1 m. Column C: 3 g of molecular sieve 13 X, mesh 100/120 (Carlo Erba), length 0.45 m. The four- and six-way stopcocks with teflon seals were also made in the Institute.

The dosing volumes K_2 and K_6 (Fig. 1) were calibrated by being filled with mercury, which was then distilled off and weighed. Calibration for the gases was made with the aid of these stopcocks by analysis of gaseous mixtures of known compositions (prepared by mixing the pure gases in closed vessels); the pressures were read on a mercury manometer. In the case of liquids we employed the equilibrium vapour tension. At the usual conversions and selectivities the compounds are gaseous even at room temperature.

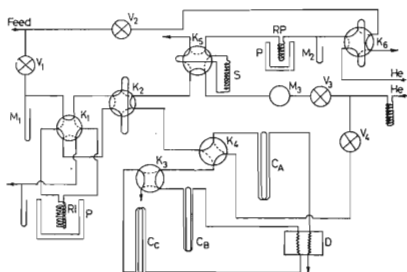


FIG. 1

Scheme of the Apparatus

K_{1-6} stopcocks, $C_{A,B,C}$ columns, Rl reactor for continual feeding, Rp reactor for operation, M_{1-3} mercury manometers, D heat-conductance detector, S spiral, V_{1-4} needle valves, P oven.

TABLE I

Corrected Relative Elution Times of the Individual Compounds on Columns A, B, C

The times of the elution maxima of butadiene, acroleine and oxygen are 8.5, 8.4 and 1.2 min, respectively.

Column	Compound	Rel. elution time (corrected)	Column	Compound	Rel. elution time (corrected)
A	carbon dioxide	0.32	B	acetaldehyde	0.36
	propene	0.37		acetone	0.65
	1-butene	0.57		propionaldehyde	0.84
	<i>trans</i> -2-butene	0.67		propylen oxide	0.92
	<i>cis</i> -2-butene	0.75		acroleine	1.00
	butadiene	1.00	C	oxygen	1.00
		carbon monoxide		3.56	

A scheme of the apparatus is shown in Fig. 1. In the continual feeding-in of the gases the six-way stopcock K_1 made it possible to bring the mixture of gases before and after the reactor RI in a dosing volume of $5.23 \text{ ml} \pm 0.5\%$ (25°C) in the stopcock K_2 . This volume was brought through the stopcocks K_3 and K_4 into the individual columns. At the same time the pulse measurements were carried out. Gaseous mixtures of identical compositions were introduced through the stopcock K_6 , volume $2.63 \text{ ml} \pm 0.5\%$ (25°C), into the reactor RP. The reacted mixture was brought through an approx. 3 m long spiral to the stopcock K_5 ; on opening this stopcock the mixture entered the chromatographic circuit. In this way it was possible to analyse the pulse under standard chromatographic conditions at various values of the time factor W/F (W is weight of the catalyst in g and F the total rate of the feed in mol/s). The approximate time of opening the stopcock K_5 after opening K_6 was determined from analyses of the feeding mixture brought in from K_2 and K_6 . The kinetic analyses in the pulse-operated reactor were performed only in the reactions that had proved in the continually fed reactor to be of first order, at least to one component of the feed.

RESULTS AND DISCUSSION

At the given quantities (usually 0.1 to $5 \mu\text{mol}$) of the compounds considered the calibration curves were straight lines and passed through the origin. From Table I it can be seen that the separation of the compounds was satisfactory. Qualitatively it was possible to prove as little as $0.03 \mu\text{mol}$. Figs 2 and 3 show typical chromatograms after the oxidation of propene and/or 1-butene on vanadium molybdate at 392°C .

The elution waves of propene, 1-butene, *cis*- and *trans*-2-butene, oxygen, carbon dioxide and butadiene were sufficiently symmetrical and narrow. By the use of the stopcock K_2 or K_6 it has been proved that these compounds can be determined quantitatively from the heights of the elution waves only. This fact considerably

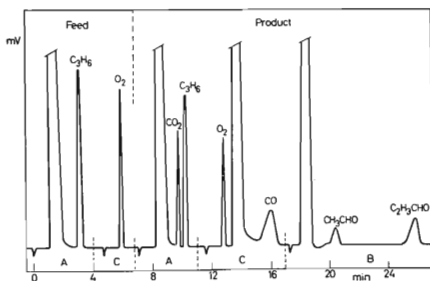


FIG. 2

A Typical Chromatogram after Oxidation of Propene on Vanadium Molybdate at 392°C

simplifies the calculation of the conversion and, thus, the determination of the activities of the individual catalysts.

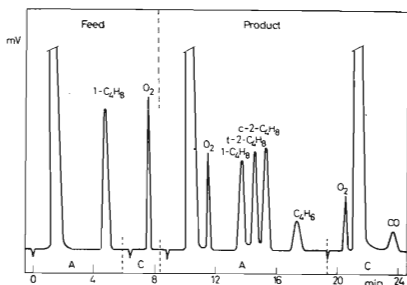


FIG. 3

A Typical Chromatogram after Oxidation of 1-Butene on Vanadium Molybdate at 392°C

The total conversion was calculated from the equation $x = 100(1 - h_B/h_A)$, where h_A and h_B are the heights of the elution waves of propene or 1-butene or oxygen before and after the reaction, respectively. The equation is a simplified one, in view of the relative error of the analysis ($\pm 2-4\%$ at 3–10%, v/v, of the hydrocarbons or oxygen in the feed). For this reason it was possible to disregard the difference in pressure before and after the reactor (about 8 mm Hg) and the change in mole number (the conversions ranged between 10 and 50%, the maximum selectivity was at 30%). The conversions into other compounds were determined by planimetry of the peaks for a given amount and composition of the feed.

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