

CHROM. 7225

PROCESS CONTROL OF ISOBUTYLENE OXIDATION BY AUTOMATIC CHROMATOGRAPHIC ANALYSIS OF THE GASEOUS PHASE COMPOSITION

A. VANKO and I. REPÁŠOVÁ

Research Institute for Petrochemistry, Nováky (Czechoslovakia)

SUMMARY

The analytical control of the continuous oxidation of isobutylene by nitrogen dioxide in dilute nitric acid by measuring the liquid reaction mixture composition is very difficult and impractical. The possibility of achieving the oxidation reaction control by analysis of the nitrogenous gaseous phase mixture was investigated. Laboratory and process gas chromatography were used to establish the correlation between the liquid and gaseous phase compositions.

INTRODUCTION

The production of methacrylic acid by the oxidation of isobutylene with nitric acid or nitrogen dioxide is based on three technological steps. In the first step, α -nitroisobutyric acid is formed from isobutylene, the second step comprises hydrolysis of the α -nitroisobutyric acid to α -hydroxyisobutyric acid, and the third step involves the dehydration of α -hydroxyisobutyric acid to methacrylic acid¹.

The reaction mechanism, especially of the first step, is very complicated and produces a series of by-products. The character of the oxidizing medium also has nitration effects and different nitro and nitroso compounds with different stabilities are formed. The reaction products also contain the excess of the oxidants and water as a diluent. A very complicated heterogeneous mixture with a strongly acidic and corrosive character is formed².

For the mass balance, one must know the composition of the gases leaving the reaction medium. These gases consist of nitrous and nitric oxides and nitrogen dioxide, carbon monoxide and dioxide and nitrogen. The oxygen from the oxidizing air oxidizes nitric oxide very rapidly to nitrogen dioxide and the former is not present in the effluent gases³.

The analytical control of the liquid reaction mixture requires the chemical modification of the compounds present. Organic acids formed in the reaction react with diazomethane to the methyl esters, water to methanol, methanol to dimethyl ether and nitric acid to methyl nitrate. These compounds can be determined with high precision and reproducibility by gas-liquid chromatography⁴.

The time required for the methylation of the liquid reaction mixture and the chromatographic analysis are equal to or longer than the reaction time. It is therefore impossible to use the analysis of the liquid phase for operating purposes, while the rapid oxidation, on the other hand, requires reliable analytical control. We solved this problem by analyzing the gaseous phase. This procedure can be carried out when a correlation exists between the compositions of the liquid and gaseous phases.

EXPERIMENTAL

Semi-continuous oxidation apparatus

The first semi-continuous measurements of oxidation were made so that calculated and weighed amounts of isobutylene flowed into the oxidizing mixture at a constant temperature (Fig. 1).

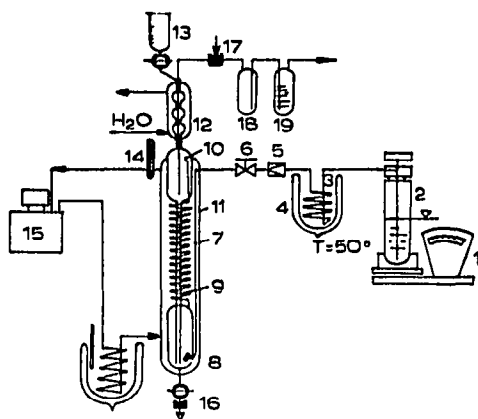


Fig. 1. Experimental discontinuous oxidation apparatus. 1 = Automatic balance; 2 = bottle containing isobutylene; 3 = copper spiral; 4 = Dewar vessel; 5 = pressure regulator; 6 = needle valve; 7 = tube; 8 = reaction chamber of reactor; 9 = reaction spiral; 10 = separator; 11 = heating mantle; 12 = cooler; 13 = calibrated reservoir of oxidation mixture; 14 = thermometer; 15 = thermostat; 16 = liquid sampling; 17 = gas sampling; 18 = empty scrubber; 19 = water scrubber.

The consumption of isobutylene was measured continuously by an automatic balance (1), with the decrease in the weight of the steel bottle (2) being recorded. Its effluent tube reached to the bottom. The liquid isobutylene was vapourized in the copper spiral (3), immersed in hot water (50°) in a Dewar vessel (4). The regulation of the constant flow of gaseous isobutylene was achieved by a pressure regulator (5) and needle valve (6). Isobutylene flowed through a tube (7) into the reaction mixture in the reactor (8). The liquid phase was carried simultaneously with the isobutylene after an intensive contact with it and was then separated in the separator (10). The liquid phase was returned continuously to the bottom of the reactor and the gases flowed through a condenser (12), a sampling device (17) and through a water scrubber (19). A measured amount of oxidation mixture was charged to the reactor from the calibrated reservoir (13). The reaction temperature was stabilized by circulation of water, cooled with ice in a mantle (11) equipped with a thermometer (14).

Process chromatograph and its connection to the apparatus

The heterogeneity of the gaseous phase composition required a suitable separating chromatographic system with a long service life to be found, giving information on the concentrations of oxygen, nitrogen, carbon oxides and nitrous and nitric oxides. Because the equipment had an operating function only, it was not important to know the concentration of nitrogen dioxide⁵⁻⁷. The apparatus used is illustrated in Fig. 2.

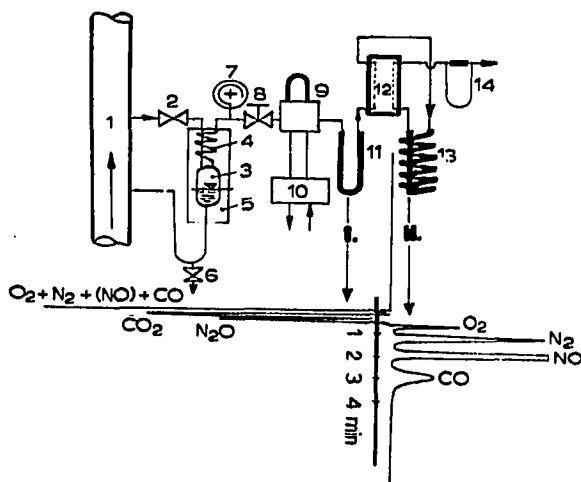


Fig. 2. Analysis system of process chromatograph and the separation of reaction gases. 1 = Effluent gases; 2 = closing valve; 3 = low-temperature condenser for nitrogen dioxide and water; 4 = cooling spiral; 5 = cooling mantle; 6 = valve; 7 = manometer; 8 = needle valve; 9 = dosing device; 10 = electropneumatic programme of dosing device; 11 = column I; 12 = katharometer; 13 = column II; 14 = flow meter.

Gases from the oxidizing reactor flow into the chromatograph. Water and nitrogen dioxide are isolated in parts (2)–(6) and the flow of gases is regulated into the dosing device (9, 10) with a needle valve (8) and manometer (7).

A constant volume of gas is transported by the carrier gas into the column I (11), which separates simultaneously oxygen, nitrogen, carbon monoxide and nitrous oxide and individually carbon dioxide and nitrous oxide. After the gases leave the measuring cell of the detector (12), this cell is replaced with a reference cell, which coincides with the time after the separation of the mixture in column II (13), and the reverse signal is recorded. The first peak from column I for oxygen, nitrogen, nitric oxide and carbon monoxide is separated in this column.

The first column is packed with Porapak Q-S, 100–120 mesh, and is 30 cm long with I.D. 3 mm. The second column is packed with molecular sieve 13X, and is 240 cm long with I.D. 3 mm. The temperature of both columns is 20°. The carrier gas is hydrogen at a flow-rate of 30 ml/min.

For measuring the correlation between the liquid and gaseous phase compositions, the need arose to oxidize isobutylene continuously in order to obtain results that would be useful for application to the process unit. We used the oxidation apparatus connected with a process chromatograph (Fig. 3).

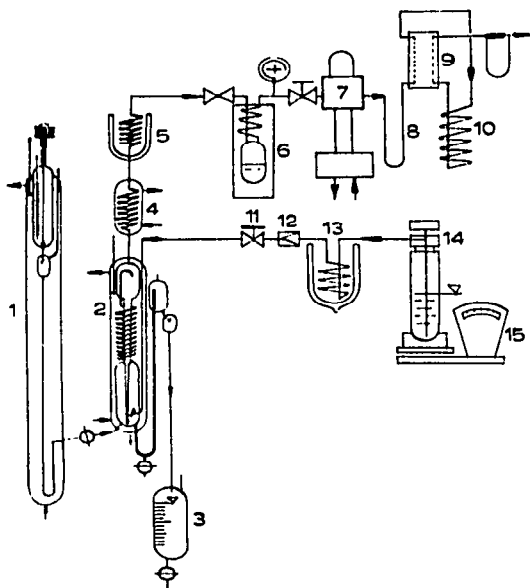


Fig. 3. Continuous oxidation apparatus with chromatographic control of effluent composition. 1 = Pulse dosing device for oxidants; 2 = reactor; 3 = product reservoir; 4 = water cooler; 5 = low-temperature condenser (-78°); 6 = low-temperature condenser; 7 = chromatograph dosing device; 8 = column I; 9 = katharometer; 10 = column II; 11 = needle valve; 12 = pressure regulator; 13 = vapourising device; 14 = isobutylene flask; 15 = automatic balance.

The original circulating semi-continuous oxidation apparatus was modified by utilizing a continuous flow of oxidation mixture by means of a pulse dosing device (1) with a calibrated volume of the reservoir. The effluent gases were cooled with a water cooler (4) and a low-temperature condenser (-78°) (5). The connected analyzing system was as in Fig. 2.

RESULTS AND DISCUSSION

We examined the two apparatuses for the above purposes. The results from the semi-continuous model were sufficient for a preliminary assumption to be made about the reaction character according to Fig. 4.

There is a relationship between the compositions of the liquid and gaseous phases. Large amounts of nitrous and nitric oxides are formed at a sufficient rate of oxidation, with a higher level of carbon oxides, formed by the destruction of the carbon skeleton. There is a decrease in the amounts of organic substances. The amount of nitrogen dioxide is a function of its partial pressure in the system, which means that the amount of oxidizing material decreases. This factor can be simply eliminated by cooling the effluent gases.

The rates of formation of α -nitroisobutyric acid and its simultaneous hydrolysis to α -hydroxyisobutyric acid are proportional to the concentration of nitrous oxide and nitric oxide, respectively.

These results on the oxidation system showed the applicability of operating

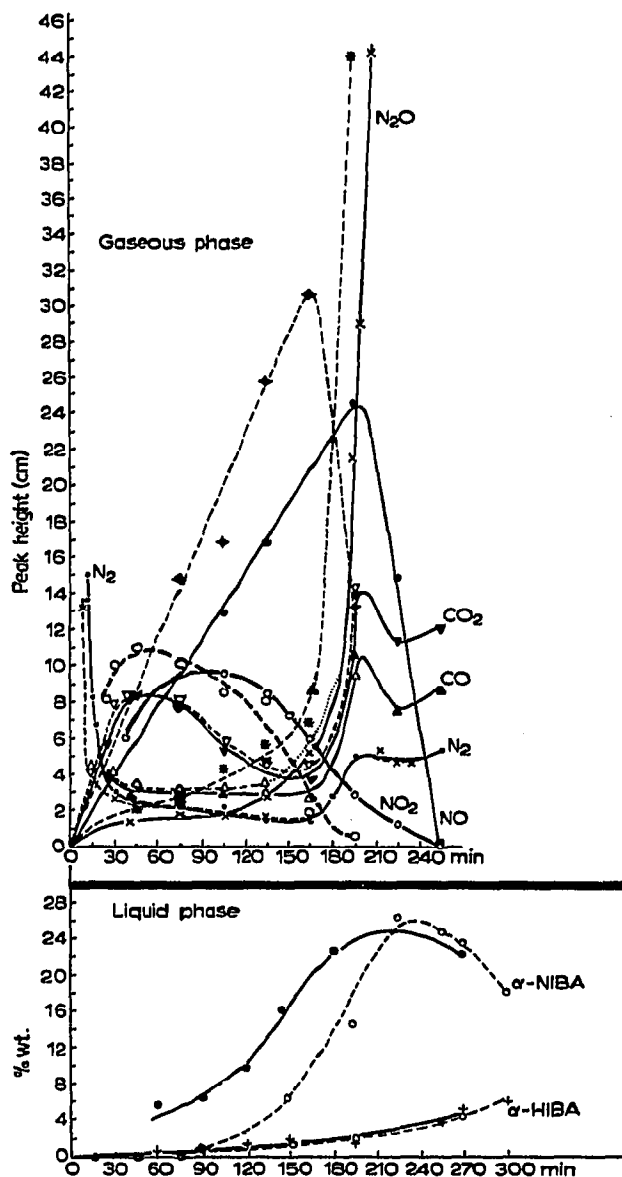


Fig. 4. Semi-continuous oxidation of isobutylene. Solid line, first run; broken line, repeat of first run. α -HIBA = α -hydroxyisobutyric acid; α -NIBA = α -nitroisobutyric acid.

isobutylene oxidation according to the composition of the gaseous phase. The continuous apparatus connected with the process chromatograph confirmed the results from the semi-continuous apparatus (Fig. 5).

We used extreme ratios of the reaction components for the oxidation model and the correlation of the compositions of the liquid and gaseous phases. In one case, the oxidation was carried out with molar ratios of nitrogen dioxide and nitric acid

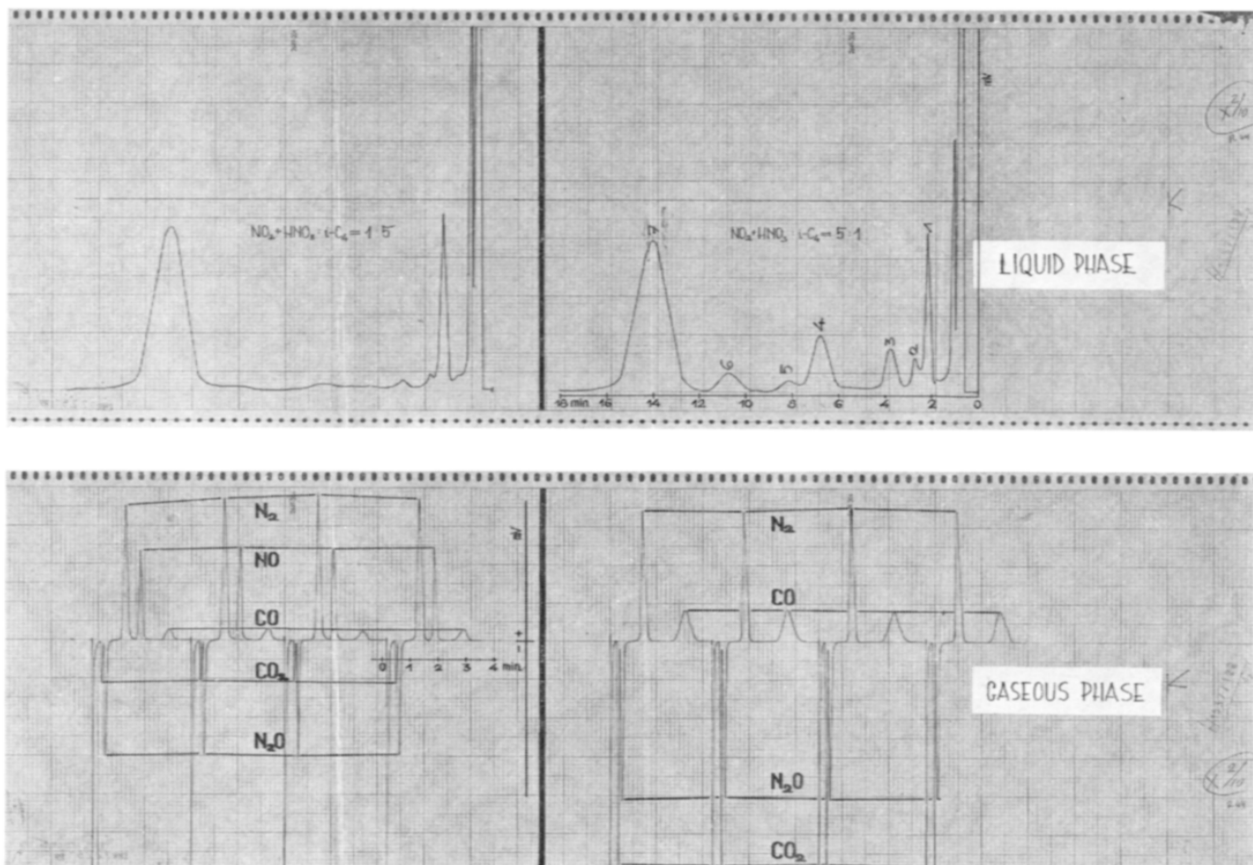


Fig. 5. Correlation between gaseous and liquid phase compositions. Chromatogram of liquid phase (methylated reaction product), acids as methyl esters: 1 = α -Hydroxyisobutyric; 2 = α -methoxyisobutyric; 3 = oxalic; 4 = α -nitroisobutyric; 5,6 = unidentified; 7 = octenoic (internal standard).

mixture* to isobutylene of 5:1. The high content of nitrous oxide and CO_2 and the substantial concentration of carbon monoxide in the effluent gas are characteristic of this ratio. The liquid phase contains oxalic acid as the main by-product. The main component in the gaseous phase is carbon dioxide. Simultaneously, the hydrolysis proceeds in the liquid phase, probably caused by circulatory mixing, mass exchange and the high flow-rate of gases.

At molar ratios of nitrogen dioxide and nitric acid to isobutylene of 1:5, the ratios of the gases were rapidly changed. The concentration levels of nitrous oxide and carbon dioxide are lower than in the first case. The level of carbon monoxide is lower and nitric oxide is present in the spectrum. The difference between the spectra is evident.

* The composition of the oxidation mixture was 52 vol. parts of 55% nitric acid and 78 vol. parts of nitrogen dioxide.

The composition of the liquid phase is simpler and hydrolysis is more intensive than with the first molar ratio. The results obtained demonstrate that the process control of the oxidation by chromatography of the gaseous phase is really possible.

By measuring the dependence of the molar ratios on different temperatures, an operating model of the process can be developed.

REFERENCES

- 1 E. F. Schoenbrunn and J. H. Gardner, *J. Amer. Chem. Soc.*, 82 (1960) 4905.
- 2 B. V. Ustavshchikov, M. P. Farberov and V. A. Podgornova, *Neftekhimiya*, 2 (1962) 592.
- 3 L. Komora and M. Polievka, Research Institute of Petrochemistry, Nováky, private communication, 1970.
- 4 L. Mikkelsen and P. S. Richmond, *Anal. Chem.*, 34 (1962) 74.
- 5 J. M. Trowell, *Anal. Chem.*, 37 (1965) 1152.
- 6 J. M. Trowell, *J. Chromatogr. Sci.*, 9 (1971) 253.
- 7 A. Vanko, L. Beriac, S. Adásek and A. Hankus, in H. P. Angelé and H.-G. Struppe (Editors), *Gas Chromatography 1963, 4th Symposium on Gas Chromatography, Leuna, May 1963*, Akademie-Verlag, Berlin, 1963, p. 214.