



The gas chromatographic analysis of the reaction products of the partial isobutane oxidation as a two phase process



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ABSTRACT

The partial oxidation of isobutane to *t*-butyl hydroperoxide (TBHP) has been studied analytically for the first time as a two-phase process in a capillary micro reactor. In order to obtain detailed information on products, yields, selectivities and reaction pathways, the products have been investigated by GC/MS. An Rxi-5 ms column and a PTV-injector have been used to analyze the liquid products. TBHP, di-*t*-butyl peroxide (DTBP), *t*-butanol (TBA), and propanone as main products as well as further by-products e.g. methanal, isopropanol, isobutanol and isobutanal in minor quantities have been identified by MS. The liquid products have been obtained by quenching the reaction and vaporizing the isobutane afterwards by pressure reduction using a mass flow controller allowing a constant mass flow. For all liquid reaction products calibrations, a validation of the method including limits of quantification and detection as well as calculation of uncertainties has been performed. The results have been applied successfully for the investigation of the selectivities of the main products (TBHP, DTBP, TBA, propanone) of the isobutane oxidation. In the frame of the analytical investigation of this reaction a correlation coefficient of $r^2 > 0.999$ for TBHP and DTBP, which is necessary to perform a validation, has been obtained for the first time. The gaseous phase has been analyzed using a GASPRO column, a DEANS switch, a mole sieve column and a TCD detector. Apart from the gaseous reactants, isobutene has been found.

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1. Introduction

The detection or determination of peroxides and hydroperoxides is important in very different fields like in the investigation of oxidation reactions of hydrocarbons by molecular oxygen in the lab or corresponding industrial oxidation processes [1], atmospheric processes [2–6], chemical studies of food or fragrances [7–9], defense against terrorism [10–12] etc. In all non-catalytic hydrocarbon oxidation processes, especially hydroperoxides are the first reactive intermediates. Compared to methyl hydroperoxide or dimethyl peroxide which is very explosive [13] especially tertiary hydroperoxides, like *t*-butyl hydroperoxide (TBHP), are still very reactive but relatively stable. Therefore, TBHP is commercially available as an aqueous solution with 70% hydroperoxide. It is used for industrial processes as the oxirane process [1] as well as for an increasing number of reactions in the research field of organic synthesis [14]. TBHP is obtained by the non-catalyzed oxidation of isobutane at low temperatures (130–145 °C). However, the process also produces several other by-products like propanone and

t-butanol and still needs to be optimized concerning the conversion of isobutane and the selectivity of TBHP. Therefore, the partial oxidation of isobutane has been investigated for the first time in a micro reactor at multiphase flow conditions and a method has been developed to analyze the reaction mixture. As the development of a kinetic model was targeted, a high precision and knowledge of the analytical error were desired.

Due to their thermal sensitivity, hydroperoxides like cumene hydroperoxide (CHP), TBHP etc. have been mostly analyzed in the past by iodometric methods [15–20], and by colorimetric [21], polarographic [22] or spectroscopic methods [23]. In the frame of the investigation of the isobutane oxidation [18–20], the corresponding authors also used GC, but only to determine indirectly the content of *t*-butanol (TBA) – after reduction of the reaction mixture by triphenyl phosphine (TPP) – deducting the content of TBHP determined iodometrically. This method is still applied for the determination of non-volatile hydroperoxides [9]. The main products separated in the foregoing works [24–31] were propanone, TBA, TBHP and DTBP, but exclusively, TCD [27–29] and flame ionization detectors (FID) [25,26,30] have been used, which did not permit an identification of all products. Also, due to the use of very short columns, often not all products were properly separated. The earliest and most representative publication concerning the

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separation of peroxides and hydroperoxides by GC is that of Abraham et al. [32] who found that a short packed column (~2 m, id = 5 mm) of 20 mesh diatomaceous earth coated with 30% dinonyl phthalate at a maximum temperature of 78 °C (carrier gas: nitrogen, flow rate 26.33 mL/min, thermal conductivity detector (TCD)) is suitable to separate TBHP, TBA and di-*t*-butyl peroxide (DTBP) without decomposition. GC methods using similar packed columns with inert phases (di-dodecyl phthalate, silicone etc.) were applied by Bell and McDowell [21], Bukata et al. [33] and Cervený et al. [34]. Correspondingly, similar conditions using packed columns were mostly utilized to analyze the reaction products of the low temperature oxidation of isobutane in the past, e.g. by Mistrik and Kostal [24] (citing Stovcik and Mistrik [25,26]), Aguilar and Blasquez [27] and finally, in 2000, by Shah et al. [28] (citing [29]). Analytical methods applying capillary columns to the isobutane oxidation have been applied only in a few cases [28,30,31], often resulting in a limited separation of the products and limited precision of their calibrations. The results will be compared in detail later with those of the present work.

In other works on the separation of hydroperoxides and peroxides in different reaction mixtures an HP-101 is used to analyze compounds in the gas phase (Polzer and Bachmann [35]) or an Ultra I to analyze reaction mixtures of the hydrogen peroxide alkylation (Foglia and Silbert [36]). Hong [37] analyzed some hydroperoxides (TBHP, CHP, DTBP and two others) in the gas phase using a split/split less injector and an HP-5 ms (30 m, id = 0.2 mm, layer = 0.33 μm). He stated that the temperature for the separation of hydroperoxides should be kept as low as possible, used a starting temperature of 30 °C (7 min), flat temperature ramps (4 K/min) afterwards as well as a pressure program. Although, on one hand his method had very low limits of detection, which is adequate for his analytical problem, the reproducibility of his measurements (about 10%) and the insufficient separation of TBHP by his method were not suitable for the analysis of the kinetics of the isobutane oxidation.

Therefore, it was tried to apply an Rxi-5 ms with a length of 60 m and higher capacity (1 μm) to the analysis of the products of the isobutane oxidation in liquid samples. Also a PTV injector (Programmed Temperature Vaporization) had not been applied to this problem before and opens up new possibilities for the analysis of hydroperoxides and the liquid reaction products of the isobutane oxidation. So, this work is a step towards a detailed kinetic investigation and an improved model of the isobutane oxidation by GC/MS using modern techniques.

2. Experimental

2.1. Material

The isobutane oxidation has been performed using an in-house-developed micro reactor. Details are published elsewhere [38]. For the separation of the reaction products, a gas chromatograph mass spectrometer system (GC/MS QP 2010 Ultra) of SHIMADZU including an auto sampler AOC-20i/20s with cooling option for the samples, a PTV-injector, a Split/Split less injector (SSL), a DEANS switch [39] and a twin line adapter have been used. All media-bearing parts of the GC/MS, including auto injector and MS connections are inert by using deactivated steel. The two lines of the dual-MS-Twin-Line configuration are:

- PTV-Injector + Rxi-5 ms column (60 m, id = 0.25 mm, layer = 1 μm) + MS
- SSL-Injector + GASPRO column (60 m, id = 0.53 mm, layer = 4 μm) + Deans Switch + TCD/MS

A scheme of the configuration is given in Fig. 1.

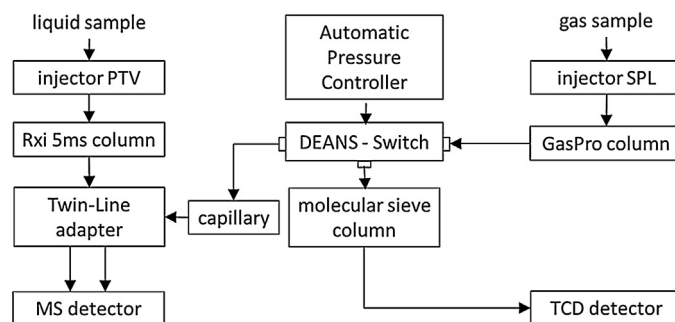


Fig. 1. Dual MS-twin line configuration of the GC/MS-TCD.

Liquid samples were stored in the SHIMADZU auto sampler and cooled down to about 16 °C. For the syringe of the Auto Sampler, a special copper-free syringe needle (ILS) was used, which was also coated by silicon (SILCOTEC®). The PTV-injector enables the analysis of thermally sensitive compounds by allowing a temperature program with a low starting temperature of the injector. The glass inlet was a deactivated PTV inlet liner of SHIMADZU.

The liquid products were separated on the first line of the dual line construction using the Rxi-5 ms column. In former works on the isobutane oxidation, mostly short packed nonpolar columns [29] or complicated constructions of nonpolar (HP-1) and relative polar (HP-17) capillary columns [30] were taken to analyze the reaction mixture of the isobutane oxidation while using high column and injector temperatures. To improve the separation and prevent overloading of the column by polar compounds, a slightly more polar column, an Rxi-5 ms column (like HP-5) with 1 μm layer, was selected in the present study using very low temperatures for the injector and the column as well as an additional pressure program Tables 1–3. Also, as short columns do not permit an adequate separation of complex mixtures, a 60 m column has been taken.

The liquid compounds TBA, isobutanol, isopropanol, methanol, methyl *t*-butyl ether (MTBE), propanone (all p.a. quality >=99.5%), *n*-heptane (p.a. quality >99%), toluene (>99.8%), isobutanol (>98%) as well as DTBP (98.5%) were used without further purification. TBHP has been available commercially only as an aqueous solution (69–70%) (LUPEROX®). All substances have been purchased from SIGMA ALDRICH.

For the separation of the gaseous products, the second line of the column construction has been utilized which includes a GASPRO column, a DEANS switch connected to a mole sieve column (Fig. 1) and a TCD. The thermal conductivity detector used (WLD GC2010, SHIMADZU) is a wide range TCD, which allows determining rather high concentrations of the relevant gases and has a high sensitivity.

For the development of the GC method, a gas mixture (“test gas”) containing the most important, possible reaction components (isobutane, nitrogen, isobutene, carbon dioxide, carbon monoxide and propene) at concentrations of 1 vol% as well as 0.5 vol% oxygen (all with an inaccuracy of 1% maximum) diluted in helium was used (LINDE GmbH).

2.2. Sampling

Details of the micro reactor and the utilized sampling unit are given elsewhere [38]. The sampling of a two phase (liquefied gas–gas) plug flow is not straight forward. As a sample taken directly out of the flow would be undefined, the liquid phase has been separated for analysis from the gas phase in a sampling unit made of silicon-coated steel. To quench the reaction mixture, it has been first cooled at the outlet of the micro reactor to 10 °C by means of a micro heat exchanger and then conducted into a stop solution, placed in the sampling unit. The reaction mixture has been

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