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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, selectivity and reaction pathways, the products have been investigated by GC/MS. An Rxi-5ms 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.

1 *Keywords:*

2 Isobutane oxidation, t-butyl hydroperoxide, di-t-butyl-peroxide, multiphase process, GC/MS,

3 **1 Introduction**

4 The detection or determination of peroxides and hydroperoxides is important in very different fields like in the investigation
5 of oxidation reactions of hydrocarbons by molecular oxygen in the lab or corresponding industrial oxidation processes [1],
6 atmospheric processes [e.g. 2 – 6], chemical studies of food or fragrances [7 – 9], defense against terrorism [10 – 12] etc. In
7 all non-catalytic hydrocarbon oxidation processes, especially hydroperoxides are the first reactive intermediates. Compared
8 to methyl hydroperoxide or dimethyl peroxide which are very explosive [13] especially tertiary hydroperoxides, like t-butyl
9 hydroperoxide (TBHP), are still very reactive but relatively stable. Therefore, TBHP is commercially available as an aqueous
10 solution with 70 % hydroperoxide. It is used for industrial processes as the oxirane process [1] as well as for an increasing
11 number of reactions in the research field of organic synthesis [14]. TBHP is obtained by the non-catalyzed oxidation of iso-
12 butane at low temperatures (130 to 145 °C). However, the process also produces several other by-products like propanone
13 and t-butanol and still needs to be optimized concerning the conversion of isobutane and the selectivity of TBHP. Therefore,
14 the partial oxidation of isobutane has been investigated for the first time in a micro reactor at multiphase flow conditions and
15 a method has been developed to analyze the reaction mixture. As the development of a kinetic model was targeted, a high
16 precision and knowledge of the analytical error were desired.

17 Due to their thermal sensitivity, hydroperoxides like cumene hydroperoxide (CHP), TBHP etc. have been mostly analyzed in
18 the past by iodometric methods [15-20], and by colorimetric [21], polarographic [22] or spectroscopic methods [23]. In the
19 frame of the investigation of the isobutane oxidation [18-20], the corresponding authors also used GC, but only to determine
20 indirectly the content of t-butanol (TBA) - after reduction of the reaction mixture by triphenyl phosphine (TPP) - deducting
21 the content of TBHP determined iodometrically. This method is still applied for the determination of non-volatile hydroper-
22 oxides [9]. The main products separated in the foregoing works [24-31] were propanone, TBA, TBHP and DTBP, but exclu-
23 sively, TCD [27-29] and flame ionization detectors (FID) [25, 26, 30] have been used, which did not permit an identification
24 of all products. Also, due to the use of very short columns, often not all products were properly separated. The earliest and
25 most representative publication concerning the separation of peroxides and hydroperoxides by GC is that of Abraham et al.
26 [32] who found that a short packed column (~2 m, id = 5 mm) of 20 mesh diatomaceous earth coated with 30 % di-nonyl
27 phthalate at a maximum temperature of 78 °C (carrier gas: nitrogen, flow rate 26.33 mL/min, thermal conductivity detector
28 (TCD)) is suitable to separate TBHP, TBA and di-t-butyl peroxide (DTBP) without decomposition. GC methods using simi-
29 lar 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 Stovčík 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-5ms (30 m, id 0.2 mm, 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 °C to 100 °C) 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-5ms 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 Section

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-5ms 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.

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 (SILCOTE[®]). 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-5ms 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-5ms 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 (see Table 1 - Table 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%), isobutanal (> 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 con-

89 ducted into a stop solution, placed in the sampling unit. The reaction mixture has been collected in the sampling unit for a
90 defined period of time to obtain a suitable quantity of the reaction mixture. The quantity has been calculated based on the
91 volume of the sampling unit, the sensitivity of the analytical method and a safety buffer volume to prevent losses of the reac-
92 tion mixture. On the basis of the isobutane flow used, the collection time has been established such that 400 mg sample are
93 obtained. To prevent liquid vapors escaping by the top of the sampling unit, the reaction mixture has been introduced via a
94 glass immersion tube. During the collection, all reaction products have been absorbed in a cooled solvent (e.g. water or hep-
95 tane, toluene) as stop solution.

96 Water is well appropriated as stop solution because it dissolves nearly all products (except DTBP), does not give any disturb-
97 ing reaction with the products, prevents any reaction – compared to organic solvents - between the polar compounds formed
98 (e.g. acids and alcohols), can be frozen to get long-term stable samples and modifies very little the gas phase, because it
99 dissolves less isobutane. Nevertheless, it has the disadvantages that it is part of the reaction products, it does not dissolve
100 DTBP and it could not be directly used for injection in the GC/MS without the risk of destroying the column¹. Furthermore,
101 methanol could not be analyzed because it could not be extracted from water quantitatively by any organic solvent. Using
102 sodium sulfate to profit of the salting effect, methanol could not be found in the extraction solvent. This may be explained by
103 data found in literature according to which methanol (in contrast to higher alcohols, acetone etc.) cannot be extracted com-
104 pletely [40] from water by organic solvents.

105 Shah et al. [28] used hexane as stop-solution to dissolve the non-reacted isobutane and all reaction products and to analyze
106 the reaction products by GC. Therefore, organic solvents also were tested as stop solutions. No differences concerning the
107 products have been found using heptane or toluene instead of water. Therefore, heptane has been tested as stop solution in
108 the sampling unit. Details on the use of these solvents are given below. After the collection time, the sampling unit has been
109 depressurized by the maximum constant gas flow (9500 mg/h) using a mass flow controller. Experiments have been per-
110 formed to verify that the losses of TBHP during this part of the sampling are negligible. A part of the liquefied isobutane has
111 been vaporized into a 1 L TEDLAR bag for further gas analysis.

112 In case of water, the reaction compounds needed to be extracted afterwards several times or by a big volume of an organic
113 solvent (e.g. hexane, heptane, and toluene). Otherwise, the organic stop solution, containing the dissolved liquid products,
114 was directly subjected to GC/MS analysis. Gas phase samples were obtained by collecting the gas phase for a given period of
115 time in a 1 L TEDLAR bag.

116 2.3 Methods

117 2.3.1 Separation of the liquid reaction products

118 According to literature data, a maximum column temperature of 80 °C has been suggested in relevant publications for the gas
119 chromatographic analysis of hydroperoxides and peroxides [41][42][43]. As a peroxide, DTBP is thermally more stable and
120 also less reactive than hydroperoxides [41]. TBHP, like all hydroperoxides, is sensitive to metals and high temperatures.
121 Therefore, metals have to be avoided in all parts of the chromatographic line or reaction apparatus. Polzer and Bachmann
122 [35] used a SILCOSTEEL[®] coating for the connection tubes between the reaction vessel and GC/MS. Correspondingly, in
123 the present work the syringe needles were coated by SILCOSTEEL[®] and deactivated liners were used to improve the peak
124 form and prevent decomposition of TBHP. Decomposition at the inlet of the MS has been prevented by introducing the col-
125 umn deeply into the ion source so that the products did not come into contact with any steel before fragmentation. However,
126 decomposition may even be increased by a higher glass surface, if the temperature is high enough [18]. Therefore, the tem-
127 perature has been kept as low as possible.

128 Capillary columns, which are more suitable for the use with GC/MS, allow realizing low residence times, the use of lower
129 carrier gas pressures, an improved separation of the reaction products compared to packed columns, have been applied only
130 rarely. For peroxidic compounds the lower surface area is also favorable. The first study using capillary columns was the
131 thesis of Witzgall [30] in 1988, which was focused on the catalytic oxidation of isobutane to t-butanol. He combined an HP-1
132 column (12.5 m, id = 0.2 mm, layer = 0.33 µm) with an HP-17 (25 m, id = 0.2 mm, layer = 0.17 µm). An ULTRA I column
133 (50 m, id = 0.2 mm, 0.5 µm) was also used in his thesis, but only for the separation of the products of the catalyzed high
134 temperature reaction (acetic acid, acrylic acid, propene) and not for the separation of peroxides. Analytical details were not
135 given by Witzgall [30], only in the diploma theses of his co-workers Weber [44] and Mrzena [45]. The column temperature
136 program consisted of an isothermal part at 32 °C for 3 min with a temperature slope of 29.5 K/min to 150 °C, keeping this
137 temperature for 4 min. The injector temperature was set to a constant temperature of 140 °C which is much higher than the
138 recommended temperature [41] for the analysis of hydroperoxides. However, TBHP was not the target product of the exper-
139 iments of Witzgall [30] which might explain these rather unsuitable conditions for the determination of hydroperoxides.
140 Brejc [31] applied the method of Witzgall [30] using methyl t-butyl ether as internal standard without giving further analyti-
141 cal details². Concerning the initial column temperature, the method of Witzgall [30] is similar to that of Shah [29] who used a
142 short packed column (0.2 m, id = 3 mm) of Chromosorb W (80/100 mesh). The temperature program of the column included
143 an isothermal period of 30 °C for 14 min, a heating period at 13 K/min up to 80 °C, keeping this temperature for 10 min. For
144 the analysis of samples of plug flow reactor experiments with oxygen saturated liquid isobutane, Shah et al. [28] used a ca-
145 pillary column (HP-1: 25 m, id = 0.32 mm, layer = 0.25 µm), an injector temperature of 75 °C, a sample size of only 0.02 µl

¹ Private message from M. Hannaum, SHIMADZU.

² The intern report of the corresponding company who did the analytical works was not published.

146 and an atom emission detector (AED) because of its higher sensitivity. The method is isothermal with a column temperature
147 of 40 °C using a flow rate of 61.8 mL/min helium. Only TBHP, TBA and propanone have been identified. Furthermore, in
148 the TCD - chromatograms of Shah et al. [28] as well as of Witzgall [30], only the peaks of TBHP and DTBP are more or less
149 baseline separated.

150 The stability of TBHP also depends on the absence of other reactive organic substances which are present in the reaction
151 mixture. TBHP and DTBP cleave both to radicals by thermal decomposition. As those radicals attack any other molecules
152 and promote the decomposition of further analyte, their formation has to be prevented. Reactions of such radicals can also
153 occur with reaction products like ketones, aldehydes, acids etc. Therefore, the thermal stability of a typical reaction mixture
154 which contains such so-called oxygenates is further reduced and may conduct to an increased decomposition [18]. Another
155 difference to non-reactive analytes is the possible reaction of the analyte with the solvent. Thus, it is reasonable to determine
156 the most suitable solvent from literature to obtain reproducible results. The studies of Hiatt and Irvin [18], who investigated
157 the half-life of TBHP in several solvents (pentane, heptane, toluene, cyclohexane, cumene and benzene), show that certain
158 impurities (sulfur compounds, acids) that are generally present in organic solvents lower the half-life of TBHP in those hy-
159 drocarbons. They report that the half-life of TBHP in heptane has been increased from 3 hours to 1000 h by treatment with
160 calcium hydride. Although this has been found in 1965, this problem is still not completely eliminated for most hydrocar-
161 bons. For instance, the heptane available with analytical quality today (99 %) contains significant traces of sulfur and acids³.
162 Hence, purity of the solvent might also be important for the stability of the peroxidic reaction products in the sample and
163 their analysis.

164 Since propanone, isopropanol and methanol are part of the products they could not be used as solvents as well as many oth-
165 ers which are or too volatile or too reactive like e.g. amines, ethers, acids and halogenated alkanes like e.g. dichloromethane
166 [37]. Ethanol has been tested but samples were not stable. The formation of acetals with aldehydes and ketals with propanone
167 disturbed measurements on the long term.

168 Hexane which has been used by Shah et al. [28] had a retention time at low temperatures such that the determination of the
169 internal standard is disturbed. This and the low boiling point (68 °C) are unfavorable for a high precision of the method.
170 Furthermore, the decomposition of TBHP in hexane is slightly faster than in heptane. Therefore, it has not been investigated
171 further.

172 Heptane was an interesting solvent because according to Hiatt and Irvin [18], the half-life of 0.1 M TBHP solution in heptane
173 at 100 °C is about 1000 h and the influence of several additives has been studied. The presence of 0.28 M DTBP did not
174 affect the half-life of TBHP, although DTBP is known to lead to an induced decomposition of TBHP (Hiatt et al. [46]). Pro-
175 panone, which is also a by-product of the isobutane oxidation, has been found to give only a reaction with TBHP in heptane
176 at higher temperatures (> 170 °C). TBA is known to be unreactive with TBHP at low temperature. Thus, a reaction between
177 TBHP and DTBP in the reaction mixture or with the solvent is prevented using heptane as solvent. The decomposition of
178 tertiary peroxides like DTBP is considered to begin at temperatures above 80 °C [43]. In their investigation, Wrabetz and
179 Woog [43] found no decomposition at an injection temperature of 100 °C and a column temperature up to 80 °C using an
180 OV-1701 glass column (14 % cyanopropylphenyl methylpolysiloxane, 100 m, id = 0.3 mm). In heptane, no possible dimer of
181 heptyl radicals has been found by Hiatt and Irvin [18]. Otherwise, the decomposition depends not only on temperature but
182 also on the column, the residence time of the solvent in the heated area and on the composition of the solution. To prevent
183 any reaction in the complex reaction mixture of the isobutane oxidation, including TBHP and aldehydes, the temperature as
184 well as the residence time had been kept as low as possible. Although aldehydes, especially formaldehyde and isobutanal
185 were only present in traces, it was one of the targets to design a method which is able to analyze also mixtures including
186 other reactive substances like e.g. primary or secondary alkyl hydroperoxides and aldehydes. There is one example published
187 by Cairns et al. (1975) [47] for the separation of TBHP and an aldehyde in a reaction mixture at a temperature of 60 °C, but
188 due to the gaseous character of the reaction mixture this analytical method is not comparable. Especially, the complexity of
189 the mixture investigated in the present work was much higher. On one hand, according to literature, n-heptane [18] is espe-
190 cially suitable as solvent for the analysis of the reaction products, on the other hand, the normal analytical quality of n-
191 heptane (> 99%) contains a big number of impurities which need to be separated from the reaction products⁴. At higher tem-
192 peratures i.e. 40 °C, n-heptane and TBHP easily show co-elution. However, using an isothermal method < 35 °C, all reaction
193 products, especially n-heptane and TBHP, have been separated well. For the column, the lowest temperature that could be
194 realized during our investigations, without any cooling device and independently of temperature changes of the laboratory,
195 was 33 °C. Therefore, the column temperature was set to 33 °C for the first 38 min to prevent any reaction (Table 1). In all
196 tables concerning pressure or temperature programs, the whole length of the section is given by the time necessary to reach
197 the final value plus the length of the section at this final value, given in the last column. Except for DTBP, which has a very
198 high retention time at 33 °C, all products (propanone, TBA, heptane, TBHP, trace compounds and solvent impurities) are
199 separated during this section.

200 Table 1: Column temperature program for liquid separation

Section	Temperature rate [K/min.]	Final tem- perature [°C]	Length of section [min.]
---------	---------------------------	--------------------------	--------------------------

³ 10 mg/kg acids (as acetic acid) and 10 ppm sulfur are given in the analytical certificate of 99% pure heptane.

⁴ Better qualities of 99.5 or 99.8 % are quite expensive (Sigma Aldrich: 75 Euro/5 ml and Merck: 120 Euro/ 5 ml).

1	0	33	38
2	10	40	6
3	250	290	0.63

201 Table 2: Pressure program for separation of liquid reaction products

Section	Pressure rate [kPa/min.]	Final Pressure [kPa]	Length of section [min.]
1	0	100	12
2	10	200	16
3	20	300	3.33

202

203 DTBP has been separated at 40 °C to reduce the length of the method after separating all other compounds to prevent de-
 204 composition of the reaction mixture. To decrease further the method to a length of about 46 min, a pressure program was
 205 applied (Table 2). For quantitative analysis, MTBE has been added as internal standard (IS).

206

207 To obtain a very mild method, a low injector temperature was desirable, but the boiling point of heptane (99 °C) [48] sug-
 208 gested an auto injector temperature above 100 °C. However, we found that, beginning with an injector temperature of 36 °C,
 209 a long isothermal period of 40 °C works as good as a period of 100 °C using an adequate pressure program. Despite the high
 210 boiling points of TBHP and DTBP (about 111 °C) the low injector temperature is not a problem. It has already been re-
 211 marked by Cullis and Fersht (1963) [42] that most peroxides and hydroperoxides have a high vapor pressure so that despite
 212 their high boiling points a high injector temperature is not necessary. The program of the injector temperature is given in
 Table 3.

213

Table 3: Auto injector temperature program

Section	Temperature rate [K/min.]	Final tempe- rature [°C]	Length of section [min.]
1	0	36	0.5
2	40	40	5
3	20	70	29.15
4	50	250	6.4

214

215 For the injection the normal mode was used. A temperature of 40 °C in the injector should have prevented any reaction of the
 216 reaction components.

217

218 The lower vapor pressure at room temperature of heptane (4.74 kPa at 20 °C [48]) compared to that of hexane (16.2 kPa at
 219 20 °C [48]) reduces vaporization losses and improves the reproducibility. From the solvents investigated by Hiatt and Irvin
 220 [18], toluene had not been tested further, despite its lower vapor pressure (2.91 kPa at 20 °C [48]), because our investigations
 221 of the sample stability has shown that benzaldehyde is formed quickly even at low temperatures by reaction of TBHP with
 222 toluene. The formation of benzyl radicals and their corresponding products like bibenzyl and benzaldehyde or benzyl alcohol
 223 by oxidation at higher temperatures is well-known [18]. The content of benzaldehyde⁵ increased linearly with time (at 23 °C
 224 about 0.8 mmole/ day), even if the sample was cooled down to 16 °C (about 0.2 mmole/ day) using the cooling option of the
 225 auto sampler. The formation of benzaldehyde and other products by reaction of toluene with peroxides is a considerable
 226 inconvenience. Benzaldehyde like all aldehydes is quite reactive towards hydroperoxides and the formation of bibenzyl oc-
 227 curred sometimes and its high boiling point (284 °C [49]) was unfavorable for a low temperature method.

218 2.3.2 Separation of the gas reaction mixture

219

220 The second line (see Fig. 1) allows separating the reaction gases. The gas samples – obtained on one hand from the vaporized
 221 isobutane and on the other hand from the gas phase – could not be separated by the Rxi-5ms column used for the analysis of
 222 the liquids. Although it separates easily propene, isobutene, isobutane and traces of other hydrocarbons (such as impurities of
 223 isobutane like n-butane etc.), carbon dioxide is not base line separated from the air/CO/methane peak. Thus, a GASPRO
 224 column is used for separating the air/CO-Peak from carbon dioxide and higher hydrocarbons of the gas phase (C₂ – C₄). The
 225 separation of permanent gases cannot be accomplished by a GASPRO column at temperatures higher than 25 °C, only at low
 226 temperatures [50]. Therefore, permanent gases are separated from the sample using a DEANS switch. Turning the DEANS
 227 switch on, the gases are conducted over a mole sieve column and analyzed by TCD. For the gas separation method, the pres-
 228 sure had been set to 163 kPa, the switch pressure to 50 kPa and the SPL liner temperature to 70 °C. The temperature program
 229 is given in Table 4. After 5.7 min, the switching unit is turned off and gases are analyzed by MS.

239

Table 4: Column temperature program for gas separation

Section	Temperature-rate	Final temperature	Length of section
---------	------------------	-------------------	-------------------

⁵ In some charges of pure toluene (> 99.8 %) significant quantities of benzaldehyde were found but it could not be eliminated by treatment with calcium hydride. Partly, also MTBE was already present as an impurity and disturbing the calibration.

	[K/min.]	[°C]	[min.]
1	0	40	8 241
2	10	150	7 242
3	50	250	0.5 243

244

245

246 3 Results and discussion

247 3.1 Liquid products

248 The main reaction products of the homogenous low temperature oxidation of liquid isobutane (below 150 °C) which have
 249 been separated were TBHP, TBA, propanone, DTBP, methanol and water ([19], [20], [24], Aguilar and Blasquez [27], Shah
 250 et al. [28], Shah [29], Witzgall [30], Brejc [31]). The application of the method in the present work (Table 1 to Table 3) al-
 251 lowed the separation of all liquid organic reaction products (Fig. 2, Fig. 3).

252 A split of 10 has been used for all measurements of liquid samples in heptane to obtain a higher sensitivity for trace products.
 253 Table 5 contains a list of all identified products and the corresponding chromatographic data of the separation in heptane. It
 254 has been verified that TBHP in heptane gave no additional decomposition products (e.g. TBA, acetone) at the corresponding
 255 retention times.

256

257

258 TBHP, DTBP, TBA and propanone were the main reaction products. The chromatogram shows that, besides these com-
 259 pounds, a lot of other products were present in minor quantities during the partial oxidation of liquid isobutane. Methanol has
 260 been only found in traces and was very near to the isobutane peak.

261

262 In addition to the main products, also 2-propanol, isobutanol, as well as some trace compounds, e.g. isobutene, isobutanal
 263 and methanal have been separated which have been reported in studies concerning the combustion of isobutane in the gas
 264 [51-61] or in the liquid phase [62] at temperatures above 170 °C. Among the impurities of heptane, especially the peak of
 265 n-pentane disturbed the measurement of isopropanol. The peak of pentane was very near to the peak of isopropanol (R = 0.7)
 266 and could not be separated significantly better by any pressure change up to 10 kPa or reduction of the column temperature
 267 down to 20 °C.

268 Furthermore, methyl, isopropyl and t-butyl esters of formic acid have been separated. The formation of formic acid has al-
 269 ready been reported for the low temperature oxidation of isobutane [24] [28] but due to the low solubility in heptane it would
 270 not have been possible to measure it, even if it was present.

271

272 Table 5: Compounds, peak numbers and retention times for the separation of the liquid reaction mixture

273 (* impurities of the solvent and of the reactants).

Name	No.	t _R [min.]
nitrogen gas/oxygen gas	1	4.27
Carbon dioxide	2	4.35
Formaldehyde	3	4.70
Isobutane	4	5.29
Methanol	5	5.48
Isobutylene	6	5.65
n-Butane*	7	5.78
Methyl formate	8	6.29
Isopentane	9	7.52
Propanone	10	8.18
2-Propanol	11	8.35
Pentane*	12	8.50
Methylal	13	9.52
TBA	14	9.71
Isobutanal	15	12.00
MTBE	16	12.90
Hexane*	17	15.60
Unknown	18	17.30
Isobutanol	19	18.60
tert-Butyl formate	20	18.90
2-Methyl hexane*	21	23.30
2.3-Dimethyl Pentane*	22	23.60
3-Methyl hexane*	23	24.50
1.3 -Dimethyl cyclopentane *	24	25.90

4-Methyl 1-heptene*	25	26.30
1,2-Dimethyl cyclopentane*	26	26.90
Heptane (solvent)	27	28.60
TBHP	28	31.40
Methyl cyclohexane*	29	33.70
Ethyl cyclopentane*	30	36.60
Di-tert-butyl peroxide	31	41.20
Toluene*	32	43.70
Octane*	33	46.00

To assure that the detected amounts of the aldehydes have not been modified or formed by decomposition of TBHP or its column reactions with the other reaction products, further tests with the method of the present work were performed. Due to the complex reaction mixture, the gas chromatographic method has been applied to a solution containing TBHP and methanol. This did not result in the formation of any detectable formaldehyde and formic acid, which are possible oxidation products of methanol. Furthermore, a solution of 0.01 vol% isobutanol and 0.06 vol% TBHP was also analyzed applying the developed method to assure that isobutanol has not reacted during the separation. No trace of isobutanic acid – the oxidation product of isobutanol – was found. A comparison of the chromatograms with that of a solution of TBHP and isobutanol of the same concentration in heptane as in the mixture shows that neither propanone nor TBA is formed nor any compound of the solution is consumed by a reaction. Thus, isobutanol in the reaction mixture did not react with TBHP during the GC measurement and could be determined by the gas chromatographic method. Methylal, methyl formate and t-butyl formate have been separated and identified too. However, they might have been originated from the reaction mixture or from a reaction which has taken place during sampling or during the separation on the column. To decide between these possibilities, water was used as stop solution. Using water as solvent, methanol, methylal, t-butyl formate and methyl formate have been found as well. Methanol has also been found with water as stop solution. Its oxidation product, formic acid, has been already been found by Shah et al. [28] and Mistrik and Kostal [24] in concentrations of about 0.1 N traces in the liquid products at high temperatures and conversions. As an esterification of the alcohols in the presence of an excess of water would not occur, methyl formate and t-butyl formate must have been formed during the reaction. Besides the liquid reaction products, many impurities (solvent, educts) and some gases were separated. Isobutane, traces of n-butane and isobutene were present in the liquid after depressurizing and extraction with solvent due to the solubility of those gases. The peaks of all substances were symmetric in heptane.

Calibrations and statistical treatment

In the foregoing studies of Witzgall [30] and Shah et al. [28], data has been only evaluated statistically in a rudimentary way. Witzgall [30] gave calibration parameters but neither correlation coefficients nor calibration plots, nor any further statistical evaluation of the calibration results to validate his results. Furthermore, no internal standard was used. Shah et al. [28] only separated and quantified TBHP, TBA and propanone. No correlation coefficients, uncertainties etc. for the calibration plots and the corresponding calibration factors were given⁶. Since the kinetic model of Witzgall can be considered as failed [31], extensive studies and error calculations have been performed due to the high reactivity of the reaction products to assure a good data quality for a kinetic evaluation.

For the main compounds methanol, TBA, propanone, TBHP, DTBP and MTBE, the reproducibility of measurements varying the glass inlet, the syringe needle, the internal standard concentration and the compound mixture has been studied. Using a SKY Liner[®] of RESTEK did not result in any significant improvement of the reproducibility compared to a SHIMADZU PTV inlet neither did a coating of the injection needle by silicon (SILCOTEC GmbH). Coating may be more important for higher injector temperatures. To assure a good reproducibility, the optimum concentration of the internal standard for the calibration and the optimum ratio of the analyte to the IS concentrations had to be determined. The ratio of the concentrations of IS and the analyte has been set to unity due to own studies and the studies of Freitag [63].

The calibrations have been performed with a mixture of methanol, TBA, propanone, TBHP, DTBP and MTBE. However, the methanol peak in the product chromatogram interfered with that of isobutane and was so small that the determination of methanol was difficult.

As the calibration has been done by using an internal standard, the x axis is the ratio of the analyte concentration and the concentration of the IS (named x), and the y axis is the ratio (named y) of the MS peak area of the analyte and that of the IS. A summary of the statistical data for all investigated substances is given in Tab. 6. Calculations of the accuracy to obtain the error bars (absolute error) of the calibrations have been done on the basis of the EURACHEM/ CITAC Guide [64]. Data has been tested for linearity [65][66] (Mandel's test), runaways (Huber's test [67]), normal distribution (David's test [68]), variance homogeneity (Bartlett's test[69]) and trends (Neumann's test [70]). The analyte solution has been prepared using a micro

⁶ After digitalisation of the data points of Shah [29], except for acetone ($R^2 = 0.9925$), correlation coefficients below $R^2 = 0.99$ have been determined for the working range of concentrations.

321 balance. The limits of detection (LOD) and quantification (LOQ) have been obtained according to the DIN 32645 [69, 70,
322 71] at small concentrations by further calibrations which are not given here.

323 For TBA and propanone the peak areas of the highest concentrations gave runaways according to the test of Huber [67].
324 Therefore, only 5 points were used for the calibration. For DTBP and TBHP, the norm requires only 5 equally spaced points;
325 therefore the data pair of the smallest concentration was omitted. Correlation coefficients R^2 for isobutanal, TBHP and DTBP
326 were higher than 0.999. The relative standard deviation of the procedure [68] (RSDP), which is an indicator for the quality of
327 the calibration, was better than the maximal value of 4.1 % (for 5 points, working range $x_{\max} = 5 \cdot x_1$ with $x_1 \sim 0.2$ mg/g) for
328 isobutanal, isobutanol, TBHP and DTBP but not for isopropanol, methanol, TBA and propanone. After eliminating the run-
329 aways, propanone and TBA yielded slightly lower correlation coefficients than those of DTBP and TBHP ($R^2 > 0.996$) (Fig.
330 4 – Fig. 7).

331 Table 6: Overview on the parameters a and b of the linear regressions $y = a \cdot x + b$ with their uncertainties (Δ), concentration
332 range (Range), correlation coefficient (R^2), relative standard deviations of the procedure (RSDP), LOQ and LOD of all inves-
333 tigated substances with heptane as solvent.

compound	a [1000* $\mu\text{g/g}$]	Δa [1000* $\mu\text{g/g}$]	b	Δb	Range [mg/g]	RPSD [%]	R^2	LOD [$\mu\text{g/g}$]	LOQ [$\mu\text{g/g}$]
Methanol	0.1234	0.1339	0.0690	0.2646	0.0546-0.2829	9.78	0.9850	48.1	129.8
2-Propanol	0.5281	0.1287	0.0591	1.0611	0.2425-1.2366	13.1	0.9573	83.3	218.8
Isobutanol	0.9971	0.0606	-0.2777	0.4583	0.2237-1.1338	3.33	0.9980	13.3	045.1
Isobutanal	0.7865	0.0088	0.0576	0.0412	0.2237-1.1138	0.59	0.9999	10.4	36.7
Propanone	0.5111	0.0843	-0.2181	0.6512	0.2461-1.2723	8.82	0.9976	70.5	220.2
TBA	0.8539	0.0672	-0.2780	0.4804	0.2268-1.1727	4.23	0.9989	42.0	114.6
TBHP	0.5658	0.0193	-0.1396	0.1133	0.1862-0.9629	1.83	0.9991	15.0	51.0
DTBP	1.0514	0.0170	-0.0882	0.1193	0.2223-1.1492	0.87	0.9998	25.5	77.6

334 Despite the lower vapor pressure compared to hexane and the internal standard, a precision of the calibration plots of more
335 than $r^2 = 0.999$ could only be reached for Isobutanal, DTBP and TBHP. Also, methanol could not be calibrated together with
336 the other compounds, the linear correlation coefficient was only about $r^2 = 0.7$. By separate calibration $r^2 = 0.9850$ was ob-
337 tained. Since the calibration of methanol without other products gave reasonable results, this was not due to problems with
338 the gaschromatographic method. Furthermore, no reaction products of methanol and TBHP could be found.
339 The observation, that the quantity of water - present in form of drops in the calibration solutions and stemming from the
340 TBHP solution - was varying in the final calibration solution permitted to suppose that the calibration problem is related to
341 the water present in the calibration solutions. So this problem should be related to the high tendency of methanol to dissolve
342 in water [40] but it was not possible to prove this without pure TBHP.
343
344

345 3.2 Gaseous products

346 According to Shah et al. [28] and Mistrik and Kostal [24], the gas phase may comprise - besides isobutane and oxygen -
347 carbon monoxide, carbon dioxide, isobutene, ethane and methane depending on the reaction conditions. Carbon monoxide
348 and carbon dioxide were also found by McCormic et al. [51] and Zeelenberg and Bickel [52].
349 Witzgall [30] separated hydrocarbon gases by a 1.8 m POROPAK Q column 80/100 mesh connected to a TCD. Air and CO
350 were isolated from the gas mixture by a valve and separated by a 1.8 m mole sieve column after separation of the other com-
351 pounds. Aguilar and Blasquez [27] used a packed column (2 m, id = 3 mm) coated with di-isododecyl phthalate for the sepa-
352 ration of liquid products and coupled it to a mole sieve column (5Å) to separate permanent gases. Fan et al. [62] separated
353 permanent gases by a mole sieve column and hydrocarbons, like isobutane and isobutene, by an active alumina column using
354 a TCD. In our method, all gaseous components of the gas mixture were separated by a GASPRO column connected to a
355 mole sieve column by a DEANS switch. To demonstrate the successful separation of the possible reaction products, the test
356 gas was used. Oxygen, nitrogen, methane and carbon monoxide were separated and analyzed by TCD (Fig. 8). Owing to the
357 twin-Line configuration, carbon dioxide as well as the hydrocarbons propene, isobutane and isobutene could be analyzed by
358 GC/MS (Fig. 9).
359

360 A summary is given in Table 7. In contrast to the foregoing methods, the configuration used allowed identifying of any high-
361 er hydrocarbon gas ($> C_1$) present in the reaction gases by MS. However, applying this method to gaseous reaction mixtures
362 of oxidation experiments, only isobutane, nitrogen and oxygen were found. The reason for this is probably the low conver-
363 sion of isobutane, which has been obtained until now in the micro reactor, combined with the dilution of the reaction gases
364 with nitrogen and the resulting low concentrations of the reaction gases.

365 Table 7: GC retention times during the analysis of gaseous compounds.

No.	compound	t_R [min.]	Calibration-factor a [mole^{-1}]	detector
1	Oxygen	5.45	4.4100184E+10	TCD
2	Nitrogen	6.43	5.9678561E+10	

3	Methane	7.37	2.1607693E+10	MS
4	Carbon monoxide	11.08	2.5309620E+10	
5	Carbon dioxide	5.90	4.3296316E+14	
6	Propene	16.39	1.0564951E+15	
7	Isobutane	17.99	1.7165036E+15	
8	Isobutene	22.71	1.7620513E+15	

366
367
368

Since calibrations for gases have been made with only one data point, obtained by three manual measurements of 150 μ l probe gas, no statistic treatment has been performed.

369 4 Summary and outlook

370 A new gas chromatographic method was developed using modern techniques like a PTV-injector, a pressure program, deac-
371 tivated equipment (liners etc.) allowing optimized substantially improved quantitative analysis of reactants, products and a
372 wide range of by-products of the low temperature oxidation of isobutane compared to earlier works. It has been shown by a
373 thoroughly conducted validation of the analytical method that modern gas chromatographic techniques permit to obtain an
374 improved quality of the calibration data and a better separation of the main isobutane oxidation products especially TBHP,
375 TBA, methanol, propanone and DTBP. Furthermore, methanal, isobutanol, isobutanal, t-butyl formate, isopropanol and methyl
376 formate as well as methylal have been separated and identified in low concentrations using mass spectrometry. Among
377 those products e.g. isopropanol and isobutanol have been separated properly and identified for the first time in the reaction
378 mixture of the low temperature isobutane oxidation. The analytical method was submitted to a complete statistical treatment
379 including uncertainty calculations and several mathematical tests (homogeneity of variance, linearity, runaways etc.). Fur-
380 thermore, gas chromatographic tests were performed concerning the most reactive reaction products (TBHP, methanol, iso-
381 butanal) to assure that the sample composition is not distorted due to the gas chromatography itself. The results have been
382 applied successfully for the investigation of the selectivities of the main products (TBHP, DTBP, TBA, propanone) as well
383 as several minor products of the isobutane oxidation. In total, the method is a good basis for a later and more detailed kinetic
384 investigation of the isobutane oxidation. In the frame of the analytical investigation of this reaction a correlation coefficient
385 of $r^2 > 0.999$ for TBHP and DTBP, which is necessary to perform a validation, has been obtained for the first time.
386 Still, the determination of some reaction products, being interesting for a kinetic investigation, should be improved. Metha-
387 nol and isobutylene are not main products of the reaction but might be necessary too for such an investigation. They are not
388 baseline separated and could not be determined exactly in the present work. It is intended to investigate if the usage of a
389 cooling device for the column permits to improve the separation of such products at low retention times and if other
390 measures, e.g. using another solvent, could improve the precision of the method.

391 Author Information

392 Notes

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544

- 545 **Figure captions**
- 546 Fig. 1: Dual MS-twin line configuration of the GC/MS-TCD.
- 547 Fig. 2: Chromatogram of the liquid reaction mixture in heptane (filament off during solvent peak 27 (heptane); peaks of
548 solvent impurities 21 – 26, 29, 30 and 32; peak numbers assigned in table 5; TIC: Total ion count).
- 549 Fig. 3: First part of the chromatogram Fig. 2 (peak numbers assigned in table 5).
- 550 Fig. 4: Diagram of the Calibration of TBHP.
- 551 Fig. 5: Diagram of the calibration of propanone.
- 552 Fig. 6: Diagram of the Calibration of TBA.
- 553 Fig. 7: Diagram of the calibration of DTBP.
- 554 Fig. 8: Separation of permanent gases by TCD (split = 5). The peak at 19.75 min could not be identified (peak assignment
555 in Table 7)
- 556 Fig. 9: Separation of carbon dioxide and the hydrocarbons of the probe gas by GC/MS (split = 5).