

Partial Isobutane Oxidation to tert-Butyl Hydroperoxide in a Micro Reactor - Comparison of DTBP and Aqueous TBHP as Initiator

Willms, T.; Kryk, H.; Hampel, U.;

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INVESTIGATION OF THE PARTIAL ISOBUTANE OXIDATION TO T-BUTYL HYDROPEROXIDE IN A MICRO REACTOR.

Comparison of DTBP and aqueous TBHP as initiator.

Thomas Willms, Holger Kryk and Uwe Hampel

Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden

t.willms@hzdr.de, h.kryk@hzdr.de, u.hampel@hzdr.de

Corresponding author: Dr. Thomas Willms, t.willms@hzdr.de, Tel.: +49 351 2603180

Abstract

The oxidation of isobutane has been investigated for the first time in a micro reactor for a wide range of process conditions comparing the initiator of DTBP and TBHP as initiator on the reaction. DTBP as initiator led to nearly the double conversion, compared to the same concentration of TBHP, but the selectivity of TBHP using TBHP as initiator was higher. Using aqueous TBHP, the conversions reached up to 6 % in case of supercritical conditions but stayed below 2 % in case of two phase flow experiments. With TBHP in decane as initiator, a conversion of about 18 % was reached, but nearly no TBHP was formed. It seems that the silicon layer of the micro reactor was not stable under such experimental conditions due to the formation of high local formic acid concentrations. In the present work, for the first time, a conversion level near to that of the industrial batch process has been reached in a micro reactor for the isobutane oxidation.

Keywords: isobutane oxidation, micro reactor, two phase flow, t-butyl hydroperoxide, t-butyl peroxide

1. Introduction

Despite its hazardous properties, t-butyl hydroperoxide (TBHP) is industrially of big interest since its oxidant capacities make it suitable for the Sharpless epoxidation [1] in the frame of the oxirane process [2] for the production of propylene oxide. Furthermore, TBHP is used as initiator, e.g. for polymerizations of vinyl chloride and acrylates in petrochemical industry, and as oxidizer in organic synthesis. In industry, TBHP is produced by the non-catalyzed partial oxidation of isobutane using bubble-cap tray reactors and bubble columns at 120 - 140 °C and 25 - 35 bar where the selectivity of TBHP is about 60 mol% at conversions of 45 to 55 mol% [2]. Main by-products are t-butanol (TBA), propanone and methanol. Thus, the production process of TBHP has still a big potential of improvement. Moreover, the production of TBHP includes important safety risks. Due to the process conditions (high pressures and temperatures, pure hydrocarbons and oxygen or air), several accidents occurred in the past [3]. Related experiments are often not feasible in conventional laboratories due to

the demand of special safety equipment. Such problems are responsible for the fact that nowadays oxidation processes are still not sufficiently investigated [4].

A micro reactor is sufficiently safe to perform experiments in the explosive range of gas mixtures in the hood of a lab, if the volume of the entire lab facility is kept small and actions preventing a runaway reaction are taken. Due to the high reaction enthalpy (-100 to -250 kJ/mol) it might be favorable also to use a micro reactor to prevent hot spots. Using a regularly shaped gas liquid flow (Taylor flow) in a capillary, a defined gas-liquid interface can be achieved. To overcome mass transfer limitations across the gas-liquid interface, additional studies at supercritical conditions of the reaction mixture are useful. Thus, a modular lab facility with a micro reactor has been erected [5] to investigate the partial oxidation of hydrocarbons as a two-phase process as well as under supercritical conditions in a capillary reactor of a variable length of up to 100 m in a broad range of flow rates, temperatures (75 to 150 °C) and pressures (25 to 100 bar).

The oxidation of isobutane aiming at the production of TBHP has already been investigated in previous works using different types of reactors. Shah [6] explored the possibility to use a micro reactor realizing the process as a homogeneous liquid phase reaction by heating isobutane containing dissolved oxygen, but conversions were limited (<1 %) due to isobutane excess and short residence times. In most works [6–12] the production of TBHP has been investigated using TBHP itself as initiator for the isobutane oxidation. However, often no analytical details concerning the purity, diluents or a previous treatment have been given [6, 8, 12]. Pure di-*t*-butyl peroxide (DTBP) has been only used in a few studies [8, 12].

In the present work, for the first time, experiments on the isobutane oxidation using commercially available TBHP-70 (aqueous TBHP, 70 %) as initiator have been conducted in a micro reactor at stoichiometric oxygen ratios at two phase-flow and supercritical conditions. The results have been compared to the results obtained with pure DTBP.

2. Experimental

The process has been performed using a micro reactor, consisting of silicon coated capillary (ID 1 mm, length 100 m)[5]. Since hydroperoxides are known to be sensitive to metal ions, the capillary and other wetted parts were coated by amorphous silicon [5, 13]. A silicon coated high pressure syringe pump has been used to inject the initiator at a defined small volume flow into the micro reactor during the entire reaction time. More details on the experimental facility are published elsewhere [5]. The parameters used in the present work are largely identical with those used in case of the experiments with DTBP [14, 15]. However, compared to the initiator concentration used in case of DTBP, higher minimum (0.25 mol%) and maximum concentrations (2.5 mol%) of TBHP have been used.

The reaction product has been analyzed by GC/ MS using a non-polar Rxi5ms column and helium as carrier gas. More Details have been published elsewhere [16]. However, due to formation of methyl *t*-butyl ether (MTBE), benzene has been used as internal standard instead of MTBE. In literature, the

conversion has been mostly calculated directly on the basis of the consumed isobutane [11]. In the present work, the converted isobutane has been calculated from the formed reaction products.

3. Results and discussion

Comparison of TBHP and DTBP as initiators

The general influence of the experimental parameters using DTBP as initiator has been investigated previously [14, 15]. In the present work, the presence of an initiator is crucial for the reaction since the silicon layer prevents any catalysis of the isobutane oxidation by steel which might otherwise catalyze the reaction. Therefore, the initiator and its concentration play an important role. A comparison of the results obtained with aqueous TBHP and pure DTBP at two phase flow conditions is given in Figure 1.

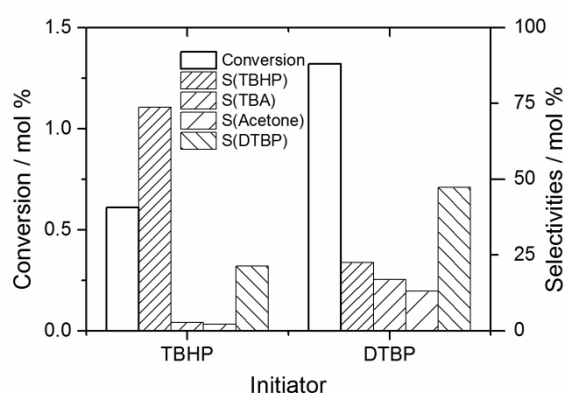


Figure 1: Conversions and selectivities with different initiators (130 °C, 42.5 bar, 1:1 O₂: IB, 0.25 mol% initiator, residence time r.t. 4 h) at two phase flow conditions.

On one hand, DTBP was a more efficient initiator, since at two phase flow conditions, the conversion (1.3 mol%) of isobutane with DTBP as initiator was higher than that (0.5 mol%) obtained with aqueous TBHP. On the other hand however, using DTBP as initiator, the selectivity of TBHP (10 mol%) was smaller than that observed with TBHP as initiator (50 mol%). Both observations obtained with the micro reactor confirm the findings of Winkler and Hearne [12]. This can be explained by the fact that DTBP as well as acetone, the decomposition product of DTBP [17], favors the decomposition of TBHP [18]. It is therefore remarkable that, using TBHP as initiator, the highest TBHP selectivity is accompanied by the lowest acetone selectivity.

At supercritical conditions the conversion levels of the isobutane oxidation obtained at the same initiator concentrations of TBHP and DTBP were much higher and practically identical (Figure 2). However, in view of the negative effect of higher temperatures on the selectivity of TBHP, a lower residence time has been applied at supercritical conditions. Therefore, the result cannot be compared with Figure 1.

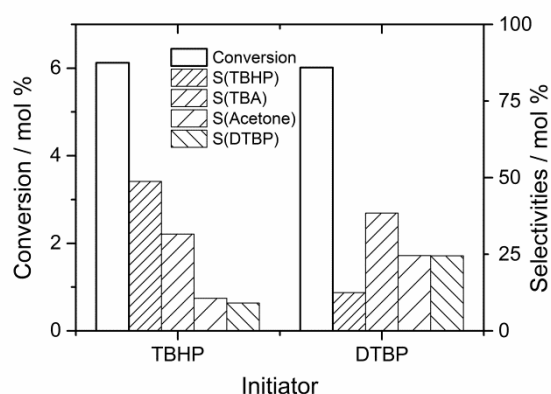


Figure 2: Conversions and selectivities with different initiators (145 °C, 55.0 bar, 1:1 O₂: IB, 1.00 mol% initiator, r.t. 2 h) at supercritical conditions.

Despite the lower residence time, the conversion increased considerably as a consequence of the higher temperature and pressure and/or of lacking mass transfer resistances across the phase boundaries at supercritical conditions. In this case, the conversion degrees obtained with both initiators were nearly equal. This might show that at two “phase-flow conditions” the component water of the aqueous TBHP has an influence on the reaction but not at supercritical conditions. Using TBHP as initiator, the selectivity of TBHP in all experiments was generally much higher than that obtained in experiments with DTBP. With the initiator DTBP, much more TBHP is decomposed and generally a much higher selectivity of DTBP than of TBHP has been observed. However, in both cases the selectivities of DTBP and acetone are comparable, although they are much smaller for TBHP as initiator. The selectivities of TBA are of a comparable value. So in this case also, at a higher conversion, the findings of Winkler and Hearne [12] could be clearly confirmed.

Influence of the initiator concentration

Initiators are generally used for experiments in laboratories to prevent long induction times of the reaction [19]. Our findings confirmed the observation of other authors [7, 11, 12] that higher concentrations of the initiator, DTBP as well as TBHP, lead to higher conversions using the same residence time (Figure 3). Using aqueous TBHP as initiator, especially the selectivity of TBA increased with the initiator concentration at the expense of TBHP.

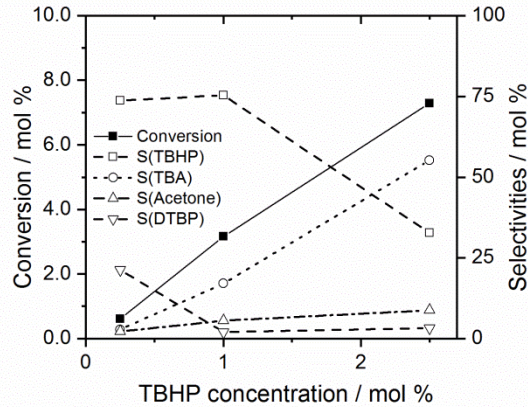


Figure 3: Effect of the concentration of TBHP as initiator on the conversion and the product selectivities of the isobutane concentration ($T=130\text{ }^{\circ}\text{C}$, $p=42.5\text{ bar}$, $r.t.=4\text{ h}$, O_2 : IB =1:1; pure oxygen).

Using DTBP as initiator (Figure 4), the yield of TBHP increased at first but then stayed practically constant leading to a decreased selectivity of TBHP at higher initiator concentrations due to the higher conversion. Initiator concentrations of DTBP higher than 0.5 mol% gave increased selectivities of the by-products (TBA, acetone, DTBP).

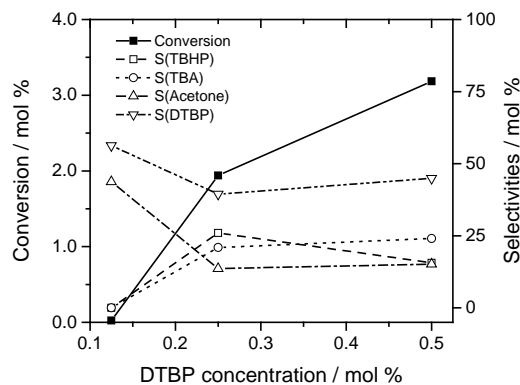


Figure 4: Effect of the concentration of DTBP as initiator on the conversion and the product selectivities of the isobutane concentration ($T=130\text{ }^{\circ}\text{C}$, $p=42.5\text{ bar}$, $r.t. 4\text{ h}$, O_2 : IB =1:1; 25 % O_2 , 75 % N_2).

Effect of Oxygen Concentration in the gas phase

In the following, the influence of the ratio of oxygen to isobutane on the conversion and the selectivity of TBHP is represented (Figure 5 a).

At the higher oxygen to isobutane ratio, the conversion increased, but due to the lower selectivity the yield of TBHP stayed practically constant. Furthermore, the selectivities of TBA and acetone also stayed nearly constant, the selectivity of DTBP increased considerably. Thus, an excess of oxygen is apparently not beneficial for a high TBHP selectivity.

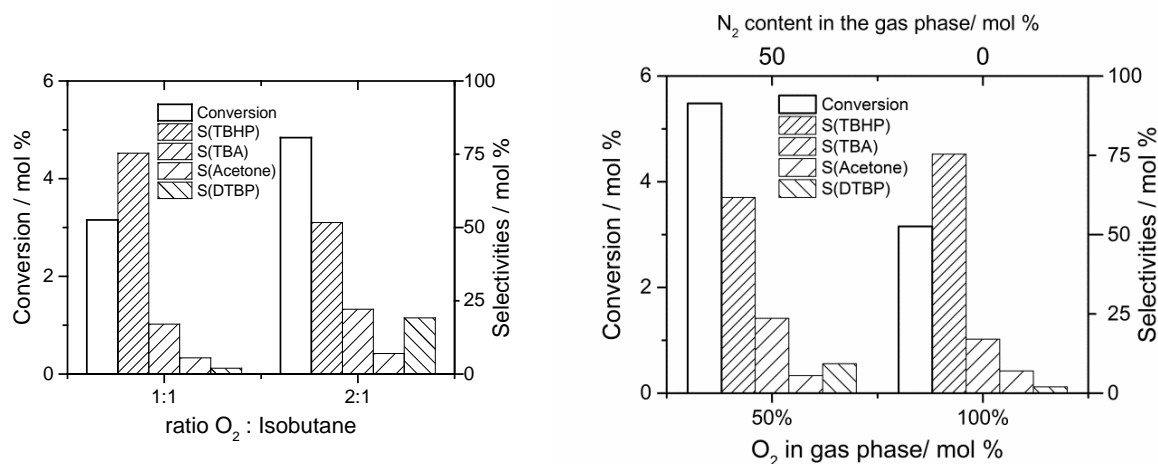


Figure 5: Conversions and yields of the isobutane oxidation (130 °C, 42.5 bar, 1.00 mol% TBHP, r.t. 4 h) a) at different ratios of oxygen to isobutane b) at oxygen/ nitrogen mixtures.

Dependence of conversion and selectivity on the content of oxygen in the gas phase

Despite the same ratio of oxygen to isobutane (1:1), the dilution of oxygen in the gas phase by nitrogen resulted in an increased conversion combined with a slightly lower selectivity of TBHP at the lower oxygen concentration (Figure 5 b). Similar effects have been observed with DTBP as initiator at lower initiator concentrations of 0.25 mol%. It seems that nitrogen prevents side-reactions or degenerating branching reactions, which occur at higher oxygen concentrations. Such side reactions, leading to formic acid and carbon oxides, may become more important. Thus, the TBHP yield might be optimized using a lower oxygen concentration in the gas phase.

Dependence on the solvent of the initiator

The highest conversion, near to industrial process conditions of 18 mol%, has been obtained using a solution of TBHP (60 mol%) in decane instead of water (Figure 6). Thus, the lower conversions resulting with aqueous TBHP might be due to the water content. In later experiments, only selectivities close to zero have been obtained. Therefore, it seems that the silicon layer has been destroyed during that experiment and that the selectivity of this experiment had been also influenced already by steel from the reactor capillary. The selectivity of isobutene, carbon dioxide, methanol, t-butanol and acetone increased considerably. Contrary to previous experiments, also acetic acid esters have been found. The destruction of the silicon layer of the reactor has been explained by the formation of formic acid which was found to destroy also the silicon layer of differential scanning crucibles (DSC) at high temperatures.

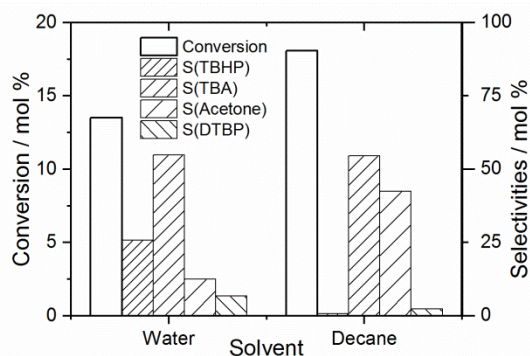


Figure 6: Conversions and selectivities of the isobutane oxidation using water and decane as solvents for the initiator (145 °C, 55 bar, 2.50 mol% TBHP, r.t. 4 h 1:1 O₂: IB, no N₂)

4. Summary and conclusions

The oxidation of isobutane has been performed in a micro reactor reaching for the first time conversions of isobutane comparable to the industrial process. The selectivities were much better with TBHP as initiator than with DTBP but decreased rapidly with conversion.

Obviously, the solvent has an important influence on the reaction. With TBHP in decane at super-critical conditions, the highest conversion of 18 mol% could be reached. However, the no TBHP has been obtained in the experiment with TBHP in decane. The silicon coating was not stable under such experimental conditions anymore, so this selectivity might be influenced by the wall material (steel). For further experiments at high conversions, a stable and inert reactor material will be necessary.

5. Acknowledgements

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6. Symbols used

IB: Isobutane

TBHP: t-butyl hydroperoxide

DTBP: di-t-butyl peroxide

TBA: t-butanol

ID: inner diameter

GC/ MS: Gas chromatography coupled with mass spectrometry

MTBE: methyl t-butyl ether

r.t.: residence time

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Figure Legends

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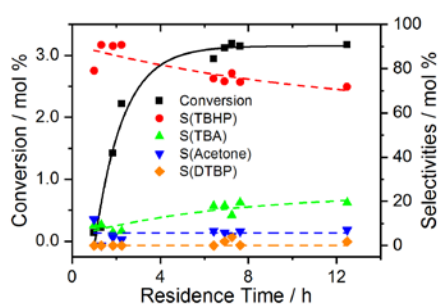
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First experiments for the oxidation of isobutane at high oxygen concentrations using aqueous TBHP as initiator in a micro reactor are presented. Comparing t-butyl hydroperoxide and t-butyl peroxide as initiators, in this work the highest conversion of isobutane obtained ever for the isobutane oxidation in a micro reactor is reported.