

The decomposition of tert.-butyl hydroperoxide studied by differential scanning calorimetry.

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Abstract:

In the frame of a the investigation of the oxidation of isobutane to t-butyl hydroperoxide (TBHP), which has been investigated for the first time as a two-phase process in a capillary reactor at high temperatures and pressures, the prevention of decomposition of TBHP was an important subject. The observed products di-*tert.*butyl peroxide, *tert.*butanol, acetone, and methanol are due to the thermal decomposition of TBHP, which is also influenced by wall effects. Therefore, the decomposition of TBHP has been studied by Differential Scanning calorimetry (DSC) at higher temperatures using for the first time different DSC conditions (several crucible types and pressure conditions, heating rate, substance mass etc.). An aluminium crucible, a medium pressure and different high pressure stainless steel crucibles (steel, gilded, silicon coated) have been used to show the influence of the crucible on the DSC curve. The influence of a protection of the sample against the gilded copper blowout disk by aluminium foil on the DSC has been investigated. It has been found that the blowout-disk has an important influence on the DSC curve. The reaction mechanism of the decomposition of TBHP and its kinetics at different conditions has been discussed. It has been shown mathematically for the first time that, despite the complex mechanism, a first order kinetics can actually describe the reaction at low temperature conditions. Kinetics has been investigated by evaluation of the DSC curves using an nth order approach and a model free kinetics approach.

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