Chemical Engineering Journal 167 (2011) 504–509

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Novel Process Window for the safe and continuous synthesis of *tert.*-butyl peroxy pivalate in a micro-reactor

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ARTICLE INFO

Article history:
Received 31 March 2010
Received in revised form 20 August 2010
Accepted 24 August 2010

Keywords:
Novel Process Window
Micro-reactors
Peroxide
Organic peroxides
Continuous processing

ABSTRACT

In this paper, the two step synthesis of *tert.*-butyl peroxy pivalate using two different flow regimes is introduced, in particular the use of "segmented flow" and the concept of "dispersed flow". The use of the segmented flow process, in this case, is challenging due to the very low interfacial tension of 4 mN/m at room temperature between potassium *tert.*-butyl peroxide and pivaloyl chloride, which causes an unstable fluid interface and results in a broad segment length distribution. This low interfacial tension is further decreased by the heat of reaction (126 kJ/mol pivaloyl chloride [1]), which is partially released at the contacting point of both fluids. It is investigated to compensate the occurring instabilities by dilution of both fluids, resulting in a more regular droplet formation. The applicability of the dispersed flow concept employing a mixer-tube set-up to create a large interfacial area for the synthesis of *tert.*-butyl peroxy pivalate is discussed together with the influence of increased process temperature, as a Novel Process Window, on the reaction performance. An approximate benchmark against two processes described in a patent [2] is given to point out the benefits obtained, e.g. higher space time yield, using a pre-stage micro-reactor device.

1. Introduction

Since 1950s, organic peroxides are intensively used in the chemical industry, especially as initiators in polymer production [3]. This class of substances easily decomposes to free radicals and therefore is widely applied in free radical polymerisations, as cross-linking and bleaching agents [4]. Particularly, peroxyesters are used as initiators for the polymerisation of ethylene or vinyl chloride. The thermal instability of these substances can lead to a violent decomposition and under certain circumstances can even cause an explosion if the heat of decomposition or the heat of reaction are not removed from the system sufficiently fast [5–7].

The TBPP synthesis investigated here is a two step process and the gained information should be applicable to other perester/peroxide reactions as well [1,2,8].

The first step, namely the deprotonation of the *tert.*-butyl hydroperoxide (TBHP) is a single phase reaction performed at a reaction temperature of about 25 °C (see Scheme 1). The heat of reaction is 23 kJ/mol TBHP, resulting in an adiabatic temperature rise of 25 K for a solution of 6.78 mol/L TBHP and a solution of 4.85 mol/L KOH using a slightly excess of 1.12 eq KOH [1].

The second step, namely the formation of the peroxyester by reaction of potassium *tert.*-butyl peroxide (TBKP) with pivaloyl chloride (PIVCl) is a two phase reaction and is much more critical in terms of temperature sensitivity and corrosivity of the used reactants (see Scheme 2).

In this second reaction step, the reaction temperature is limited by the thermal stability of the formed product—TBPP ($t_{1/2}$ = 1 min at 110 °C [9]). The heat of reaction is 126 kJ/mol PIVCl, resulting in an adiabatic temperature rise of 72 K for a solution of 2.65 mol/L TBKP and a solution of 8.04 mol/L PIVCl using an excess of 1.16 eq TBKP [1]. Beside this temperature sensitivity of TBPP, the used PIVCl is a strongly corrosive reactant and its hydrolysis in the alkaline aqueous reaction mixture is an undesired side reaction that needs to be suppressed.

The conventional perester synthesis (starting from hydroperoxides and carboxylic acid halides) is carried out in a batch or in a semi-continuous process under Schotten–Baumann conditions [2,4]. The reaction temperature is predominantly controlled by step-wise dosing of the reactant and mainly limited by the thermal stability of the reactants, resulting in long reaction times (e.g. for a 1 m^3 reactor with a coefficient of heat transmission of 600 W/m^2 K (900 W/m^2 K) sufficient heat removal – at a process temperature of 20 °C – is only possible for a dosing time of 90 min (60 min) [8]). The huge hold-up and the low surface-to-volume ratio in stirred tank batch reactors are two big disadvantages of this industrial process. Due to the exothermicity of both reaction steps, it is essential to

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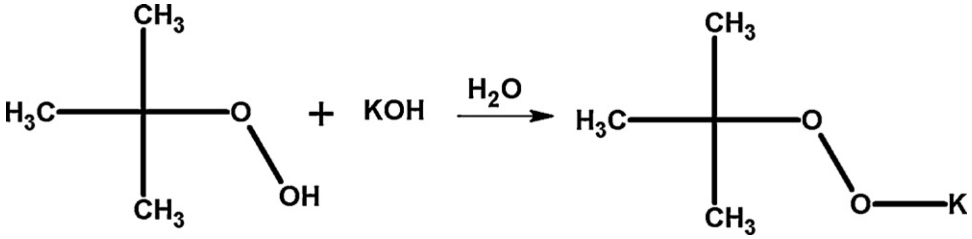
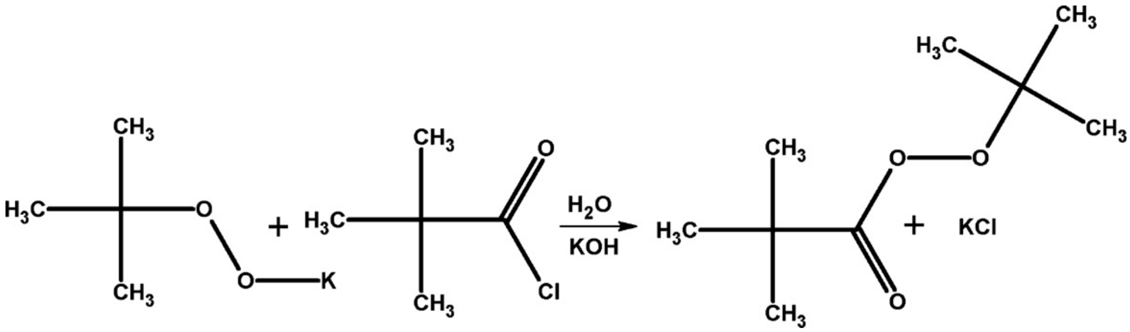
doi:10.1016/j.cej.2010.08.081



Scheme 1. Deprotonation of *tert.*-butyl hydroperoxide—1st step.



Scheme 2. Conversion to *tert.*-butyl peroxy pivalate—2nd step.

control the reaction temperature as accurately as possible to avoid heat accumulation and finally a thermal runaway. Whilst in the first reaction step a homogenous solution is obtained, an immiscible two phase liquid–liquid mixture is created in the second reaction step, by which PIVCl and TBPP form the organic phase. The diffusion/mass transfer between the two phases is a limiting parameter for the formation of TBPP and thus sufficient mixing quality has to be provided.

All, in the section above mentioned topics need to be considered for a shift from batch to continuous processing, using the benefits of micro-structured devices to achieve advantages in process safety e.g. smaller reaction volume and thus lower hold up of reactants and improved process performance by better control of reaction temperature, residence time, fast mixing, etc. [10–22]. Two concepts were followed: (i) the use of "segmented flow", and (ii) the applicability of "dispersed flow". Segmented flow is a highly ordered flow pattern with defined interfacial areas and liquid layer thicknesses [23]. This hydrodynamic environment facilitates kinetic analysis for controlled selectivity, e.g. to foster the desired perester formation versus the undesired hydrolysis of the PIVCl. The internal circulation (see Fig. 1) within the formed slugs contributes to decrease transport limitations and can also enhance reaction rates at normal reaction conditions [24–28]. Thus the resulting mass transfer between the wall flow and that along the axis is enhanced.

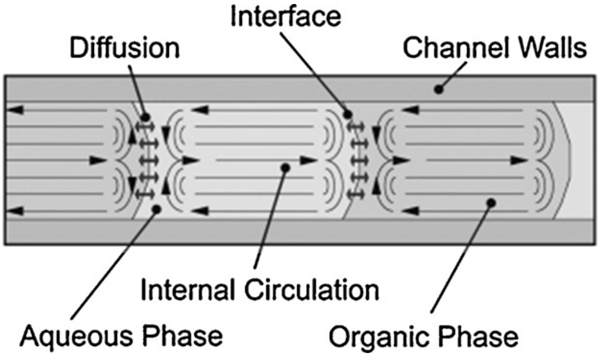


Fig. 1. Internal circulations within the immiscible slugs [23]. (Reproduced by permission of The Royal Society of Chemistry.)

Segmented flow is influenced by many parameters such as pressure fluctuations, temperature effects, wetting behavior, interfacial tension and flow rate ratio of aqueous to organic phase [29]. As a second flow regime, dispersed flow is investigated for its applicability to produce TBPP. In particular, the influence of increased process temperature on process performance is investigated. This paper gives an introduction to two concepts to produce an organic peroxide in a pre-stage micro-reactor device to gain information that is needed to develop a specially adapted micro-reactor concept.

2. Experimental

2.1. Segmented flow experiments

The experimental set-up consisted of different types of T-mixers from various manufacturers such as Little Things Factory, Upchurch Scientific, and Swagelok. The visualized droplet formation was performed in glass T-mixers (ID 0.8 and 1.6 mm) from Little Things Factory. The pictures of the segments were taken with an Olympus SZ60 microscope connected to a digital camera. The measurement of slug length was realized by setting a reference length in the pictures or via scale paper.

2.2. Dispersed flow experiments

The experimental set-up (see Fig. 2) consisted of a caterpillar micro-mixer (CPMM-V1.2-R300/12-PEEK-prefla from IMM) fed with KDScientific syringe pumps (20 mL polypropylene syringes) for providing the necessary residence time a Teflon tube (ID 0.8 mm) was connected and embedded into a water bath to maintain the reaction temperature.

For all described experiments the deprotonation reaction of TBHP with KOH was done in batch mode. The reaction mixture was then transferred into syringes or pumps. Following chemicals where used: