



Reactive chemical pathway of tributyl phosphate with nitric acid

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ABSTRACT

Tributyl phosphate and its degradation products saturated with nitric acid and exposed to elevated temperatures lead to an accidental condition known as “reactive red oil formation”. The present study aims at elucidating the chemical pathway of this reaction in an Accelerating Rate Calorimeter (ARC). The thermal characteristics obtained from ARC coupled with end product analysis using spectroscopic techniques proved that red-oil forming mechanisms varied as per the concentration of nitric acid. The chemical pathway for red oil formation was found to occur through the oxidation of butanol at lower temperatures and with dilute nitric acid, the predominant path was *via* butyl nitrite intermediate at higher temperatures. Independent ARC experiments with butanol and butyl nitrite with nitric acid validated the mechanism. This study also revealed that most of the diluents employed for TBP undergo exothermic reaction with nitric acid, even in the absence of TBP.

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1. Introduction

Tri-*n*-butyl phosphate (TBP) is employed as an extractant in nuclear fuel reprocessing industry due to its selectivity and efficiency in extracting U and Pu from spent fuel (Barney and Cooper, 1994; Geier, 1979). Despite many positive qualities as an extractant, one of the problems with the use of TBP is the formation of reactive red oil (Gordon et al., 1994; Hyder, 1994; Usachev and Markov, 2003; Gordon and O'Dell Watkin, 1994; James and Sheppard, 1991). The formation of red oil causes thermal runaway reactions resulting in an explosion of the process equipment with the release of radioactivity. In our earlier studies, the thermal behaviour of TBP (Smitha et al., 2013), its behaviour with irradiation (Samuel Vara Kumar et al., 2016), its reaction with nitric acid with different acid concentrations (Smitha et al., 2012) and the role of diluents in the red oil forming reactions (Smitha et al., 2014) were reported. The end products were analysed using various analytical spectroscopic techniques and a mechanistic pathway was suggested for red oil explosions. This study focuses on proposing a detailed mechanism and provides further evidence to present a clearer picture on the exact pathway.

In our previous studies, we had reported that formation of carboxylic acid was the reason for the formation of red oil (Smitha et al., 2012). Tributyl phosphate is an ester of phosphoric acid which on acid hydrolysis yields butanol and phosphoric acid which is also the reverse reaction for the formation of TBP (esterification). The butanol formed can react with nitric acid to yield carboxylic acid either *via* butyl nitrite intermediate or butyraldehyde (butanal) intermediate. Therefore, it is important to assess the exact mechanism which is responsible for the accidental scenario about reactive red oil involving TBP and nitric acid. This study focuses on elucidating the exact mechanism behind red oil formation and validation of the same. Therefore, it is essential to understand the reactions of butanol and butyl nitrite with nitric acid.

2. Materials and methods

2.1. Materials

Tributyl phosphate, *n*-dodecane, nitric acid, butyl nitrite and butanol used in thermal decomposition studies were of analytical grade obtained from Aldrich Chemicals.

2.2. Methods

2.2.1. Accelerating rate calorimeter

The calorimetric studies were carried out using Accelerating Rate Calorimeter. The instrumentation, principle and working are

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well described in our previous studies (Smitha et al., 2012, 2013, 2014; Samuel Vara Kumar et al., 2016). The sample mixtures were weighed and loaded in ARC (SS/Hastelloy) bomb. The samples were subjected to Heat-Wait-Search cycle from temperature ranges 50 °C to 250 °C. The heating rate was set as 5 °C/min.

2.2.2. Characterization studies

a. FT-IR

A Nicolet Impact 400 FT-IR spectrophotometer was employed to record the Infra-red spectrum. The end product obtained from the ARC experiments was spread over KBr pellets into a neat thin liquid film, and the spectra were recorded from 4000 to 400 cm^{-1} .

b. ^{13}C and ^1H NMR

^1H NMR was carried out using a Bruker 300 MHz multistate NMR Spectrometer. D_2O and CDCl_3 were used as the solvents for dissolving the aqueous and organic phase products respectively.

c. Gas chromatography – mass spectroscopy (GC–MS)

The samples collected after ARC experiments were dissolved in ethyl acetate, and subjected to GC–MS analysis using Agilent 5975 MSD Inert XL with HP 5 ms (5% phenyl methyl siloxane) capillary column (30 m x 250 μm x 0.25 μm). Helium was used as carrier gas at a flow rate of 1.5 mL/min and 35 min run time. The initial column temperature was kept at 70 °C for 3 min, and then increased linearly at 10 °C/min upto 300 °C at 9 min hold time. The injector temperature was maintained at 250 °C. The results were interpreted with the help of MS-NIST standard reference database library.

3. Conversion of butanol to butanoic acid possible pathways – an overview

The conversion of butanol to butanoic acid is dependent on two factors: temperature and strength of the nitric acid. The two probable reaction pathways of butanol with nitric acid are explained below.

3.1. Mechanism 1: via butanal intermediate

Nitric acid oxidations are very complex and involve a large number of intermediates (Ogata, 1978). In many nitration reactions, undesirable oxidation takes place as a side reaction (Camera et al., 1983). A primary alcohol undergoes oxidation through an aldehyde to form carboxylic acid with same number of carbon atoms (Gandarias et al., 2016). This aldehyde formed is highly unstable. This reaction is highly exothermic. Woezik studied the oxidation of alcohol in order to understand the thermal runaway reactions and to carry out safe operation procedures of nitric acid oxidation in a semi-batch reactor (Van Woezik, 2000). Svetlakov et al. (2007) studied the oxidation of aliphatic alcohols and diols to carboxylic acids with nitric acid. The authors interpreted that the primary aliphatic alcohols with a normal backbone of any length were readily oxidised with nitric acid into the corresponding carboxylic acids in 75–90% yield with the same number of carbon atoms. This reaction is self-heating thermal runaway reaction with the evolution of reddish brown NO_x gases and found to happen in the presence of concentrated nitric acid at temperatures around 60–75 °C. According to the TOMSK – 7 accident reports (Usachev and Markov, 2003), the explosion had occurred when concentrated nitric acid was added accidentally to the extraction vessel and left without stirring by the operators for several hours which led to the release of large volume of NO_x gases which led to the rise in pressure. Tomsk-7 accident was the only accident reported in the extraction vessel, where no heating was carried out. In our ARC experiments employing 30% TBP with higher concentrations of nitric acid, an exotherm was observed even at low temperatures than the reported value (Smitha et al., 2012). The above evidence suggests TBP in the pres-

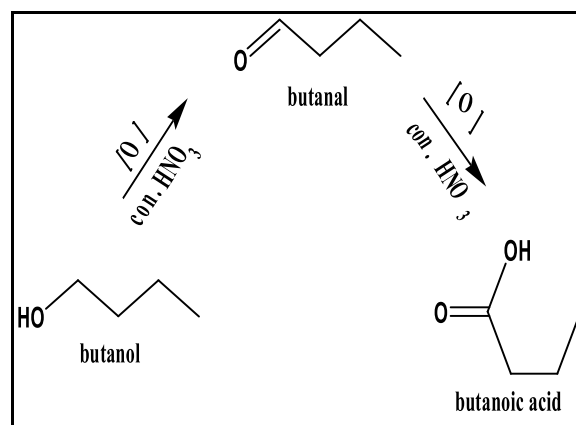


Fig. 1. Schematic pathway of oxidation of butanol via butanal.

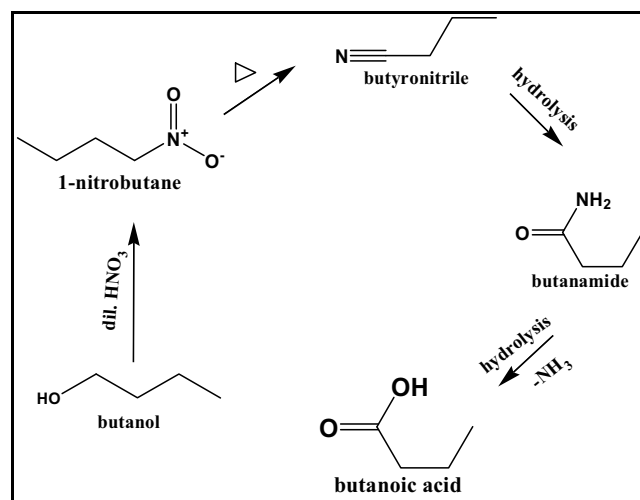


Fig. 2. Schematic pathway for the formation of butanoic acid via butyl nitrite.

ence of concentrated nitric acid undergo oxidation to form butanoic acid via butanal intermediate (Fig. 1).

3.2. Mechanism 2: via formation of butyl nitrite

Iyer and Klein conducted detailed studies on the reactions of 1-nitrobutane (Iyer and Klein, 1997) and butyronitrile (Iyer et al., 1996) in pure high-temperature water. It was reported that butyl nitrite on heating formed an ester of nitric that was highly unstable. It lost nitrous acid to form butyronitrile which in turn was hydrolyzed to butanamide, which further hydrolyzed and lost ammonia to form butyric acid. This reaction occurred with dilute nitric acid at temperatures around 110–120 °C (Smitha et al., 2012, 2014). Similar conditions were found in evaporators and denitrators, wherein red oil explosions were reported. In partition cycles of the Purex process, dilute nitric acid is used for back stripping and heated to very high temperatures in evaporators for volume reduction, in order to get higher DF (decontamination factor) for subsequent extraction cycles. Thus, this evidence suggest under dilute nitric acid conditions the conversion of butanol to butanoic acid occurs via butyl nitrite intermediate as shown in Fig. 2 (Phillip Savage, 1999) at elevated temperatures.

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