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Investigating the potential for transisomerisation of trycresyl phosphate with a palladium catalyst and its implications for aircraft cabin air quality

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Abstract

The quality of aircraft cabin air has been an area of concern for several decades. Many investigations have linked the presence of organophosphates in air to Aerotoxic Syndrome with adverse symptoms reported by thousands of aircraft crew across the globe. Currently the source of organophosphates has been under debate, with studies pointing towards tricresylphosphates (TCP) in aircraft oil as the main source due to leaks in engine seals resulting in fumes entering the cabin. However, comparisons of oil and cabin samples have shown that the cabin samples contain a much higher proportion of ortho-substituted TCP than is commonly detected in oil. The aim of this experiment was to investigate the potential for palladium catalysts (present in aircraft air conditioning systems) to convert meta- and para- substituted TCP to produce ortho-substituted TCP through transisomerisation. This experiment was performed in a controlled laboratory setting aimed to represent the conditions likely to be experienced in aircraft. Samples were introduced to a stainless steel micro reactor tube containing the pelletized palladium catalyst using a HPLC pump with a 0.2ml/min feed flow rate. The temperature maintained at 400˚C over a period of 1 hour and samples collected using a condensing vesicle. These were then diluted and transferred to a 2 mL vial for analysis by gas chromatography mass spectrometry. No evidence supporting the transisomerisation of tricresylphosphate was obtained. This indicates that more emphasis should be placed on identifying other potential sources of ortho substituted TCP.

Keywords

Aerotoxic syndrome, air quality, aircraft, organophosphate, catalysis

1 Introduction

The term Aerotoxic Syndrome was first used to describe the symptoms and exposure conditions reported by aircraft crew across the globe. Whilst aerotoxic syndrome has not been fully accepted as a medical syndrome (Wolkoff et al., 2016) it is commonly used to refer to the symptoms resulting from long term and repeated acute exposure of crew and passengers to toxic compounds in aircraft air (Winder and Balouet, 2002). A growing number of studies have shown that aircraft crew develop symptoms consistent with exposure to organophosphates (Abou-Donia et al., 2013, Harrison and Mackenzie Ross, 2016, Liyasova et al., 2011, Payne, 2015).

In recent decades, a specific focus has been placed on aircraft oil as a potential source of these organophosphates. The oils are generally comprised of approximately 95% synthetic esters with 3% tri-cresyl phosphates (TCP) (Winder and Balouet, 2002). There are 10 structural isomers of TCP with the ortho substituted congeners considered the most toxic. The focus of many investigations in aircraft air quality and aerotoxic syndrome has been solely on tri-ortho-cresyl phosphate (ooo-TCP or ToCP), although the mono-ortho and di-ortho isomers are also highly toxic (de Boer et al., 2015, Denola et al., 2011, Henschler, 1958). Air crew and passengers can be exposed to aircraft oil and the TCP it contains through leaks in engine seals which can then contaminate bleed air which passes into the cabin air (de Boer et al., 2015).

To assess the risks from aircraft oil Megson et al. (2016) analysed samples of fresh and used oil. The results showed that only four non-ortho substituted TCP isomers were identified at detectable levels in the fresh and used oil (mmm-TCP, mmp-TCP, ppm-TCP and ppp-TCP). The lack of ToCP is consistent with a reduction in the concentrations of these compounds during oil manufacture in recent decades (Craig and Barth, 1999). Despite the removal of ToCP from oil several studies have detected ToCP in aircraft cabins (Crump et al., 2011, Rosenberger et al., 2013, Ramsden, 2013). The studies undertaken on aircraft oil show a slight variability between the proportions of TCP isomer present in different samples, brands and depending on if the oil is used or fresh (Hecker et al., 2014, Megson et al., 2016).

The fact that no ortho substituted TCP isomers were detected in oil in these previous studies poses an interesting point, as investigations in cabin air calculated that ooo-TCP represented between 10 and 60% of all TCP isomers (Rosenberger et al., 2013). The results would therefore indicate that the oil is not the source of ooo-TCP in cabin air. One potential explanation for the absence of ooo-TCP in the oil but its presence in air samples is the catalysis of meta and para isomers (by a palladium catalyst) to generate ortho-isomers. This has been proven for cresols under controlled conditions by Imbert et al. (1997) but has not been established for tricresyl phosphates. To improve air quality on aircraft a palladium based catalyst is often located after the engine and upstream of the air conditioning pack and used to decompose ozone. Air leaving the engine would be in the range of 200 to 400˚C representing similar conditions that induce the isomerisation of cresols (Imbert et al., 1997).

The aim of this investigation is to perform a laboratory based study to establish whether a palladium based catalyst can transform tricresylphosphate (TCP) isomers in similar conditions that are likely to be experienced in aircraft. This will help to establish if aircraft oil is a potential source of ToCP through transisomerisation of meta and para isomers in aircraft bleed air.

2 Methodology

2.1 Catalyst generation

A micro scale catalyst was created using palladium coated zeolite nanoparticles using a Pd/HY catalyst synthesis method. Briefly, this involved dissolving 1 g of palladium nitrate ($Pd(NO_3)_2.2H_2O$) in a beaker containing 7 ml of deionised (DI) water. In another beaker, 5 g of HY zeolite was mixed with 25 ml DI water. Ammonium solution was added drop-wise to the palladium salt solution until the pH reached 10. The same procedure was carried out to produce a HY zeolite suspension. Subsequently, palladium salt solution was added drop-wise to zeolite solution while it was stirring with a magnetic stirrer. The mixture was stirred for another 1 hour, following by 15 minutes of sonication. After impregnation of HY zeolite with Pd, the sample was filtered and washed several times with DI water to remove excess metal ions. The remaining solid catalyst was dried at room temperature for 24h following by calcination at 500 ˚C for 4 hours. The activity of synthesised Pd/HY catalyst was confirmed through oxidation of methane and results were compared with other catalysts (e.g. Pt/HY and Pd-Ni/HY). The Pd/HY catalyst generated showed a high activity in conversion of methane confirming its activity (Supplementary Information 1).

2.2 Experimental procedure

A fresh synthesised catalyst was prepared for each experiment, pelletized and placed in a stainless steel micro reactor tube. Pellets were secured in place using quartz wool. The reactor was placed in a tabular furnace with temperature program controller. Samples were introduced to the reactor using a HPLC pump (0.2ml/min feed flow rate) where they were vaporised and the temperature maintained at 400˚C over a period of 1 hour. Samples were collected in a condensing vesicle and transferred to a dedicated 20 mL vial which was stored in a fridge.

A feed mixture containing a mixture of 4 TCP isomers (mmm, mmp, mpp and ppp) was created by dissolving 1g of 99% tritolyl phosphate, (Fisher Scientific) in 100 mL of dodecane. This solution was passed through the catalyst in two separate experiments to produce a duplicate sample, a solution of dodecane was also passed through the catalyst to produce an experimental blank. An aliquot of the original TCP solution was collected to compare the composition of the TCP isomer mix before and after interaction with the catalyst. The three TCP samples were diluted by a factor of 1:10,000, and all solutions were transferred to 2 mL GC vials ready for analysis.

2.3 Sample analysis

Analysis was performed on an Agilent A5390 GC-EI-MS. A 1 µL sample was injected (1:10 split) at 280 ˚C onto a DB5 column (5% dimethylpolysiloxane, 30m x 0.25mm x0.25 µm). The oven was held at 70 ˚C for 2 minutes then ramped at 10 ˚C a minute to 300 ˚C and held for 5 minutes. The mass spectrometer was operated in full scan mode with a range of 50 to 500 Da.

3 Results & discussion

A total of 4 samples were analysed, these included a dodecane blank, the TCP mixture (prior to interaction with the catalyst), and 2x TCP mixtures (post interaction with the catalyst). The TCP mixture used in this experiment contained the four main TCP isomers present in jet oil (mmm, mmp, mpp and ppp) (Megson et al., 2016). The results showed no generation of any ortho substituted isomers and no signs of transisomerisation for any of the other cresyl phosphates (present at <0.0003%). (Figure 1). Several two and three ring PAHs along with their alkylated homologues were detected in the samples. However, they were also detected in the blank solvent samples indicating that their formation was not due to the presence of TCP.

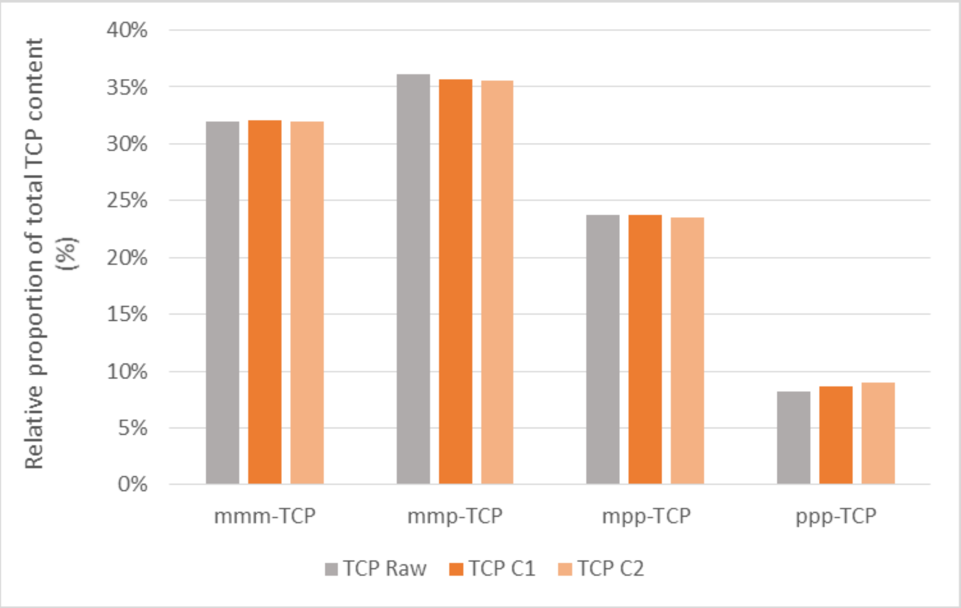

Figure 1. Percent abundance of each of the 4 TCP isomers recorded in the original TCP mixture (TCP Raw) and the two replicates passed through the catalysts (TCP C1 and TCP C2).

These results represent an important development to understanding the cause of aerotoxic syndrome. Much debate on the potential cause of aerotoxic syndrome has focused on ToCP. This was believed to originate from aircraft oil, however Megson et al. (2016) analysed samples of fresh and used oil and identified that only four non-ortho substituted TCP isomers were present. Despite the removal of ToCP from oil several studies have continued to detect ToCP in aircraft cabins (Crump et al., 2011, Rosenberger et al., 2013, Ramsden, 2013). Historically, US patent 4,605,790 dated August 12 1986, described the transisomerisation of phenol isomers using catalysis, with the possibility of increasing the proportion of ortho isomers. Such perspective led to the question whether the ozone catalytic systems fitted on commercial aircraft could also modify the tricresyl phosphates entering the aircraft bleed air system in a similar way. The results of this research indicate that this is not the case.

4 Conclusion

Transisomerisation of products in aircraft oil is currently a very understudied area and so the authors were unable to find any suitable data for comparison. To the best of our knowledge the results of this research present the first published data on the potential for the production of *ortho* substituted tricresylphosphates from aircraft oil.

The results indicate that although transisomerisation can occur for cresols when passed through a palladium catalyst, it does not occur for tricresyl phosphates. It should be noted that this study was performed in a scaled down laboratory environment. Whilst operation temperatures were controlled and matched to those likely to be experience in aircraft, other factors such as pressure and altitude could not be replicated. If, as this study suggests, transisomerisation of TCP does not occur then the source of ortho substituted TCP in aircraft cabins needs to be further investigated.

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