



# The electrochemistry of tetrapropylammonium perruthenate, its role in the oxidation of primary alcohols and its potential for electrochemical recycling



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## ARTICLE INFO

### Article history:

Received 1 July 2015

Received in revised form 15 September 2015

Accepted 19 September 2015

Available online 25 September 2015

### Keywords:

tetrapropylammonium perruthenate

acetonitrile

electrochemical recycling

alcohol oxidation

electrosynthesis

## ABSTRACT

The search for strategies aiming at more sustainable (oxidation) reactions has led to the application of electrochemistry for recycling the spent catalyst. In this work, an electrochemical study of the tetrapropylammonium perruthenate catalyst (TPAP) and its activity towards a primary alcohol, *n*-butanol, has been carried out as well as a control study with *tert*-butanol. The redox chemistry of TPAP and the transition between the perruthenate anion and ruthenium tetroxide in a non-aqueous solvent have been, for the first time, investigated in depth. The oxidation reaction of *n*-butanol in the presence of TPAP has been electrochemically elucidated by performing potentiostatic experiments and registration of the corresponding oxidation current. Furthermore, it was shown that, by applying a specific potential, the reoxidized TPAP is able to oxidize/convert the primary alcohol, paving the way for practical applications using TPAP in electrochemical synthesis. The conversion of *n*-butanol into *n*-butanal was proven by the use of GC-MS.

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## 1. Introduction

The main current application of the perruthenate anion is situated in the field of organic chemistry where it is used for the selective conversion of alcohols into aldehydes. The synthesis of the tetrapropylammonium salt of the anion (tetrapropylammonium perruthenate; TPAP) by Ley and coworkers made it soluble in organic solvents and available for oxidation reactions [1]. It did become a popular reagent as it combines some desirable properties, namely air stability, commercial availability, performance at room temperature and high chemoselectivity. As ruthenium is a rather expensive transition metal and in the strive towards more sustainability, catalytic oxidation methods have been developed using catalytic amounts of TPAP in combination with *N*-methylmorpholine *N*-oxide (NMO) as a stoichiometric oxidant [2]. Commonly, dichloromethane or acetonitrile or a combination of these two solvents is used with the addition of powdered 4 Å molecular sieves to remove water formed during the

reaction. Recent advances with the TPAP/NMO method have made the oxidation of primary alcohols to carboxylic acids possible [3]. Here 10 equivalents of NMO are added, the excess of NMO stabilizes the formation of an aldehyde hydrate, which is a necessary step in the controlled oxidation of aldehydes to carboxylic acids. Within the same search for more environmentally friendly methods, it has been found that oxygen as well can be used as a stoichiometric oxidant to oxidize alcohols in combination with catalytic amounts of TPAP [4,5]. Furthermore, it has been shown that TPAP can be used as a heterogeneous catalyst with NMO or oxygen as a stoichiometric oxidant. Most of the suggested approaches consist of an ionic bond between the perruthenate anion and a heterogeneous quaternary ammonium cation, for example the polystyrene supported perruthenate [6], the mesoporous silicate MCM-41 with immobilized perruthenate [7] or the alkyl-imidazolium-based periodic mesoporous organosilica with supported perruthenate [8]. Finally, a sol-gel encapsulated TPAP [9] strategy is also reported.

Despite the fact that the perruthenate anion is an important catalyst in organic synthesis, its electrochemical behavior in organic solvents has never been studied before. A study of the catalyst in joint reaction with the oxidation of alcohols might be interesting to see if strategies can be found to make electrochemical recycling of the oxidant possible. Organic electrosynthesis [10]

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agrees well with the principles of green chemistry [11] as it is possible to regenerate the catalyst at the electrode surface at a fixed potential. Therefore, no stoichiometric co-oxidant has to be added. As a result a stream of toxic waste is avoided and a more sustainable oxidation becomes possible.

The perruthenate anion ( $\text{RuO}_4^-$ ) is the active part of TPAP and the formal oxidation state of ruthenium in the perruthenate anion is +7 ( $\text{Ru}^{\text{VII}}$ ). This anion has already been studied electrochemically in water but without taking into account the presence of alcohols [12]. In this study, different ruthenium-oxy species were observed: ruthenium tetroxide ( $\text{RuO}_4$ ), the ruthenate anion ( $\text{RuO}_4^{2-}$ ) and ruthenium oxide ( $\text{RuO}_2$ ), with an oxidation state of respectively +8 ( $\text{Ru}^{\text{VIII}}$ ), +6 ( $\text{Ru}^{\text{VI}}$ ) and +4 ( $\text{Ru}^{\text{IV}}$ ). A few methods have already been developed, making use of the electrochemical recycling of ruthenium-oxy species for the catalytic oxidation of alcohols, but all focusing on  $\text{RuO}_2$ . Therefore water has to be added as a solvent or co-solvent. For example,  $\text{RuO}_4$  can function as the oxidant in a two phase system of tetrachloromethane and water [13]. In this case, active chloride species ( $\text{Cl}_2$  or  $\text{Cl}^+$ ) are generated at the electrode surface in the sodium chloride solution (water phase) and oxidize  $\text{RuO}_2$  to  $\text{RuO}_4$ , which is responsible for the subsequent oxidation of the alcohol in the organic phase. As this approach still uses another reagent (chloride) as secondary oxidant, this method cannot be regarded as a pure electrochemical oxidation of the ruthenium catalyst. Moreover it is performed in a toxic solvent, which is considered as an ozone depleting agent [14]. The same author reports on a method in which  $\text{RuO}_2$  is directly oxidized at the electrode surface to a  $\text{Ru}^{7+}$  species in an alkaline acetonitrile/water mixture, followed by the  $\text{Ru}^{7+}$  promoted oxidation of alcohols [15]. This method is presented without any electrochemical investigation. An improved method making use of the neutral conditions of the Ley oxidation would be beneficial. Another strategy that has been used is to make use of  $\text{RuO}_2$  as an electrode material. In basic media the  $\text{RuO}_2$  can be electrochemically oxidized to  $\text{RuO}_4^{2-}$  and  $\text{RuO}_4^-$  which can react with alcohols [16]. Studies have been performed on the oxidation of glucose [17,18] and benzylalcohol [19]. Also, the use of  $\text{RuO}_2$  as a material for pseudocapacitance is currently under examination and it is possible that the formation of the perruthenate anion has an influence on the mechanism explaining the high capacitance of hydrous ruthenium oxide [16].

In this article, the results of an in-depth investigation of the electrochemical behavior of the perruthenate anion in a non-aqueous neutral solvent are presented. Additionally, the oxidation reaction of *n*-butanol in the presence of TPAP has been electrochemically elucidated by performing potentiostatic experiments and by recycling of the spent catalyst under mild conditions.

## 2. Experimental

Anhydrous acetonitrile was purchased from VWR and kept dry over activated molecular sieves under argon atmosphere. Tetrapropylammonium perruthenate (97%) and tetrabutylammonium tetrafluoroborate (for electrochemical analysis, >99.0%) were purchased from Sigma-Aldrich and used as received. *n*-Butanol was purchased from Merck and used as received.

All electrochemical measurements were performed by using a Potentiostat/Galvanostat PGSTAT 101 from Metrohm, connected with a PC provided with NOVA 1.10 software. A three-electrode cell was used with a platinum working electrode of 2 mm diameter (Metrohm, the Netherlands) or a glassy carbon working electrode of 3 mm diameter, a platinum sheet counter electrode and a bridged Ag/AgCl reference electrode with 2 M LiCl ethanol solution as inner solution and acetonitrile as bridge solution. All potentials mentioned are relative to this reference electrode unless stated otherwise. This reference electrode has a voltage difference of

+150 mV versus a standard hydrogen electrode (SHE) and the voltage difference versus the ferrocene redox couple ( $\text{Fc}^+/\text{Fc}$ ) is –500 mV. The working electrode was pretreated by mechanical polishing. It was subjected to sequential polishing with a cloth covered with alumina powder of 1 and 0.05  $\mu\text{m}$  particle size (SPI supplies, USA) for 10 minutes to remove any adherent  $\text{Al}_2\text{O}_3$  particles. The electrode surface was rinsed thoroughly with deionized water and cleaned in an ultrasonic bath containing deionized water for 2 minutes. Next the electrode was rinsed with acetone and dried. Solutions of 0.1 M  $\text{Bu}_4\text{NBF}_4$  in acetonitrile were freshly made and purged with nitrogen gas for 10 minutes to remove oxygen before each measurement. Rotating disk measurements were measured with a controlled speed rotator (Metrohm, the Netherlands). A typical potentiostatic experiment was done as follows, a cell was filled with a freshly prepared solution of 0.1 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_3\text{CN}$  (20 mL), electrodes were added and nitrogen gas was purged for 10 minutes. Then, a constant potential was applied and after 200 seconds TPAP (14 mg, 0.04 mmol) was added, after 300 seconds the rotation was initiated (2000 rpm) and finally after 350 seconds *n*-butanol (37  $\mu\text{L}$ , 0.4 mmol) was added. Electrolysis experiments were performed in a homemade airtight electrolysis cell. The working electrode used is a reticulated vitreous carbon (RVC) electrode with a surface area of 10.5  $\text{cm}^2/\text{cm}^3$ . A typical electrolysis experiment was done as follows, the cell was filled with a freshly prepared solution of 0.1 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_3\text{CN}$  (30 mL), electrodes were added and nitrogen gas was purged for 10 minutes. Next TPAP (21 mg, 0.06 mmol) and *n*-butanol (55  $\mu\text{L}$ , 0.6 mmol) were added and a constant potential (or no potential) was applied under stirring for 5 hours at room temperature. The resulting mixture was distilled and samples were taken from the distillate for analysis with gas chromatography-mass spectrometry (GC-MS).

GC-MS samples were analyzed on an Agilent 7890A gas chromatograph connected via a splitter to both a quadrupole MS and a FID detector. The instrument was equipped with a fused silica capillary column (OPTIMA 5MS Accent – 0.25  $\mu\text{m}$ , 30 m, 0.25 mm ID – manufactured by Machery-Nagel). The column had a silarylene stationary phase with ultra-low bleeding and a polarity similar to 5% diphenyl/95% dimethylpolysiloxane (i.e. non-polar) and a maximum temperature of 340 °C (isothermal).

## 3. Results and discussion

### 3.1. Electrochemical screening of TPAP

An electrochemical study of TPAP in a non-aqueous solvent has been performed by using cyclic voltammetry. The use of both dichloromethane and acetonitrile were tested because these are the solvents used for a classical TPAP/NMO oxidation. Dichloromethane was found not to be useful to perform cyclic voltammetry on TPAP as no reproducible redox reactions could be obtained. The redox processes observed are not stable as a function of scan number as can be seen in the supporting information (Fig. S1). On the other hand, the use of acetonitrile was successful and reproducible peaks could be obtained. The metal coordinating properties of acetonitrile could probably account for this different behavior [20]. Other advantages of acetonitrile are its higher conductivity and higher boiling point, so less evaporation occurs under a nitrogen flow. Fig. 1 represents the current-potential behavior of 1 mM TPAP in acetonitrile with 0.1 M  $\text{Bu}_4\text{NBF}_4$  as electrolyte and with a scan rate of 100  $\text{mVs}^{-1}$ . A scan of the platinum electrode in a solution of acetonitrile without TPAP is also shown and in this case no redox processes are observed. In the presence of TPAP four different redox processes can be distinguished. At ca. 0.9 V a first anodic peak  $I_a$  can be observed, upon reversal of the scan direction a cathodic peak  $I_c$  appears around

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