



Applications of Oxone in chemical kinetics, synthetic chemistry and environmental chemistry: A review

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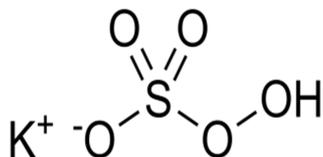
Abstract

Potassium monopersulphate (Oxone) is being widely used these days in various fields due to its unique properties which tend to make it an extremely viable option to be exercised. The oxidative nature of this compound is under study to extract the maximum benefits from this compound amongst which chemical, synthetic and environmental studies are prominent fields in which a steady research is underway. The objective of this review is to provide valuable information on various applications of oxone which are coming into light due to the diverse research work being carried out on it.

Keywords:

Introduction

Mono persulfate is a potassium salt of Caro's acid H_2SO_5 . Its IUPAC name is potassium mono persulfate, while commercially it is known as Carcoat and Oxone. It is having chemical formula $KHSO_5$ with molar mass 152.2gm/mole. It gets decomposed in water. It is an oxidant of corrosive nature.



The use of oxone has increased rapidly due to (a) its versatility of the reagent (b) stability (c) simple handling and ofcourse (d) the non-toxic nature in addition to its low cost. It oxidises aldehydes to carboxylic acids or esters (in presence of alcoholic solvent), alkenes may be oxidised to carboxylic acids (in case of internal alkenes) or epoxides (in case of terminal alkenes), thioethers gives sulfones, phosphines give phosphine oxides while tertiary amines provide us with amine oxides. This potassium salt is a component of a triple salt with the formula $2KHSO_5.KHSO_4.K_2SO_4$. OXONE® is a double potassium salt being the active ingredient the peroxymonosulfate, commonly known as monopersulfate. It derives from the peroxymonosulfuric acid H_2SO_5 (also known as

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Caro's acid, $pK_1 = \infty$, $pK_2 = 9.4$) whose structure is a tetrahedron with S atom in the centre surrounded by a perhydroxyl group and two oxygen atoms F.Javier *et al.*, (2017).

Oxone as an oxidant in kinetic studies

Kinetic studies have been undertaken to investigate the catalytic behaviours of oxone-MnOx/silica system towards aqueous Ibuprofen degradation in terms of system effects, reaction kinetics mechanisms. Kinetic studies implied that Ibuprofen removal by oxone-MnOx/silica systems using two first order kinetic models was closely related to the extents of the interferences of synthetic conditions and water chemistry components Jia-Cheng E. Yang *et al.*, (2017). The highly reactive modified IBX, i.e., I (v) species, generated in situ from DTB-IA in the presence of Oxone under mechanochemical ball milling conditions, permits unprecedented oxidation of alcohols to carbonyl compounds, vicinal diols to oxidative cleavage products and non-vicinal diols to lactones in the solid state Moorthy *et al.*, (2017). Direct oxidative cascade cyclisation of 2-aminobenzoic acids and arylaldehydes to aryl 4H-3,1-benzoxazin-4-ones with oxone using I_2 as a catalyst has also been undertaken and found to be an environmentally friendly procedure as the oxidant is not posing any danger to the ecological conditions Iyer *et al.*, (2017). A simple and efficient method for removing NO from flue gas using sulfate and hydroxyl free



radicals from activation of Oxone with cobalt and high temperature has been developed. A comparison of NO removal efficiencies and the yields of sulfate and hydroxyl free radicals in several reaction systems were carried out Simeonov *et al.*, (2017). Oxyhalogenation reactions of a variety of alkynyl silanes were studied using oxone as mild oxidant and KCl, KBr, and KI as halogen sources. In this study, reaction of an alkynylsilane with oxone-KX (X = Cl or Br) produced trichloromethyl/tribromomethyl ketones in high yields. Under similar conditions, however, reactions of alkynylsilanes with oxone-KI were found to give exclusively 1,2,2-triiodovinyl derivatives in high yields. In this study, new methods were developed for efficient one-pot transformation of alkynylsilanes into amides and esters by reaction with amines and alcohols respectively via tri halomethyl ketone Sriramoju *et al.*, (2017). Another study shows the degradation of ibuprofen in aqueous solution using oxone process mediated by Fe²⁺ with UV irradiation (FOU). Fe²⁺/Oxone (FO), Fe²⁺/UV (FU), Oxone/UV (OU) processes were investigated separately to elucidate the role of different conditions in the processes.

It is therefore suggested that a stepwise introduction of Fe²⁺ and oxone is an efficient approach to ensure the TOC removal and toxicity elimination in FOU Lam *et al.*, (2017). The use of zero valent metallic iron (Fe⁰) in the photo-Fenton process under the UV illumination as a promising and novel technique. Oxidants like oxone a peroxymonosulfate (PMS) and ammonium persulfate a peroxydisulfate (PDS) were used in comparison with classical hydrogen peroxide (HP). PMS was found to be a better oxidant in comparison with HP and PDS at higher pH conditions especially in the pH range of 5–7 Srinivas *et al.*, (2016). There is great interest in developing Mn water-splitting catalysts due to their low cost, abundance, and relevance to the oxygen-evolving complex (OEC). Complexes with the ligand bipy-alkH were shown to evolve O₂ when driven by Oxone. The catalytic mixture generated from the precursor complex [Mn (bipy-alkH)Cl₂] retained activity in unbuffered solution beyond 160 h Sharninghausen *et al.*, (2016). A study was undertaken in which a mechanism of Fe (II) – oxone conditioning was developed to improve sludge dewaterability Xiao *et al.*, (2017).

Oxone in synthesis of various compounds

The synthesis of a wide variety of carbamates from amines, alcohols and carbon monoxide has been achieved by means of a Rh-catalysed oxidative carboxylation reaction that uses Oxone as a stoichiometric oxidant Iturmendi *et al.*, (2017). A straightforward synthesis of diaryliodonium salts is achieved by using Oxone as the stoichiometric oxidant Yusubov *et al.*, (2017). The indeno[1,2,3-de]chromenes class of compounds has been synthesized by using Oxone as a terminal oxidant through a Pd-catalysed cross-dehydrogenative coupling reaction at room temperature by developing a new method Reddy *et al.*, (2017). A very simple method to synthesize an efficient and stable Ni-based water-oxidizing electrode was reported from the reaction of metallic nickel foam and Oxone Moghaddam *et al.*, (2017). An efficient approach to the synthesis of 2,1-benzisoxazoles through direct construction of the N-O bond by the chemoselective oxidation of 2-aminoacylbenzenes with Oxone is developed. This alternative methodology is characterized by its simple and transition-metal-free conditions and good functional group compatibility utilizing Oxone as a green oxidant instead of hypervalent iodine compounds.

Moreover, this new procedure simplifies the number of steps compared to the previously reported procedure by circumventing the use of 2-azido-substituted aryl ketones Chiarini *et al.*, (2016). Mild and efficient method for the preparation of iodylarenes by oxidation of iodoarenes with Oxone in aqueous acetonitrile at room temperature is described. This new procedure allows the preparation of various iodylarenes with electron-donating or electron-withdrawing substituents in the aromatic ring including the previously unknown 1,2-diiodylbenzene Yoshimura *et al.*, (2016). An efficient and convenient method for the synthesis of 3-aryl[1,2,4]triazolo[4,3-a]pyridines has been developed involving RuCl₃/Oxone oxidative cyclization of 2-(2-arylidenehydrazinyl)pyridines, which occurs chemoselectively at the pyridine nitrogen. RuCl₃ can be used as an efficient homogeneous catalyst for the synthesis of triazolopyridines through a direct intramolecular cyclization involving C[sbnd]N bond formation Raviteja *et al.*, (2016).



Use of Oxone for diluting the ill effects of various pollutants in water and soil

Landfill leachates of the city of Badajoz (located in south-west Spain) have been treated by wet air oxidation at high temperature (180-270°C) and pressure (40-70 atm.). Typical operating variables such as temperature and oxygen partial pressure have been investigated with no effect of any being found and moderate to low chemical oxygen demand conversions (20-30% depending on initial concentration). Initial pH shows a positive influence when acidic conditions are used. Addition of hydrogen peroxide (0.01 M) as a hydroxyl radical promoter is able to provide an additional 15% increase in the final COD removal achieved. If a sulfate radical promoter is used (i.e., Oxone) the process is significantly improved, with COD conversions in the range 60-80%, also depending on the initial COD of the leachates. A first attempt to comprehend the chemistry of this oxidizing system suggests an instantaneous decomposition of Oxone that initiates the radical chain also involving hydroxyl and organic radicals Rivas *et al.*, (2005). Hexachlorocyclohexane isomers (HCHs) are one of the most ubiquitous and most easily detected organochlorine pesticides in environmental samples. HCH tends to bioaccumulate in human and animal adipose tissue. Since certain HCHs cause central nervous system, reproductive, and other endocrine damages, there is a necessity of a suitable remediation method to remove HCH from contaminated groundwater and soil. A study was conducted to evaluate the potential of peroxymonosulfate (Oxone) induced by cobalt salt ($\text{Co}(\text{NO}_3)_2$; Co(II)) to degrade HCHs. Cobalt(II) nitrate has been chosen instead of cobalt(II) chloride (which presents better activation properties for Oxone) in order to avoid an excess of chloride interference and more additional chlorination by-products.

This study revealed that Oxone induced by Co(II) shows a high degradation rate with HCH isomers, which can make it an attractive method for HCHs decontamination in the future Waclawek *et al.*, (2016). Oxone (potassium monopersulfate, MPS) has been used to oxidize the herbicide tembotrione in aqueous solution. Tembotrione elimination kinetics by MPS direct oxidation has been studied. The influence of the main operating variables affecting the process (MPS concentration,

temperature and pH) has been evaluated Solís *et al.*, (2016). This study will aid in developing new methods to reduce the concentration of herbicides in soil and water streams thereby helping to reduce water and air pollution.

The increasing application of OXONE in water remediation studies relies on the potential oxidizing capacity of the radicals generated after its decomposition. At laboratory scale some authors have investigated the potential of OXONE in the removal of phenols, HAPs, pesticides, and dyes. Although OXONE is raising some expectation as an alternative water remediation technology; the number of works focused on its decomposition kinetics is rather low. Accordingly, a study has been carried out with the aim of elucidating the influence of some operating variables in OXONE decomposition when either Co(II) is used as homogenous catalyst or a perovskite solid is utilized as heterogeneous catalyst Javier Rivas *et al.*, (2005). Sulfate radical-based advanced oxidation processes (SR-AOPs) are powerful technologies to treat various pollutants. Among these SR-AOPs, UV/persulfate (UV/PS) and UV/Oxone were chosen to degrade and mineralize Acid Blue 113 (AB113) wastewater for their strong reactivity. UV/Oxone process was observed to be more sensitive to UV intensity and pH on TOC mineralisation Shu *et al.*, (2016). Oxone can also be used to oxidize hydrogen sulfide (H_2S) in waste streams. This provides a convenient method of deodorizing a waste stream (or stack, via scrubbing) without the necessity of on-site manufacture or handling of hazardous chemicals such as Caro's acid. Other reduced sulfur compounds, such as mercaptans, sulfides, disulfides and sulfites may also be oxidized. Cyanide in waste streams from metal plating or mining operations can be oxidized rapidly using Oxone.

Other useful applications

As a denture cleaner

The formulations containing at least 25% Oxone provide excellent decolorization of food and other organic stains. In addition, formulations usually include sodium perborate monohydrate, sodium carbonate and/or bicarbonate, and may also include citric acid, EDTA or DTPA chelants, flavour/fragrance ingredients, and food colorants.



In Electronics

It is used for copper cleaning and surface preparation in printed wiring board fabrication.

Oxone is a free-flowing powder chemical micro etchant that contains an acidic per acid as its active ingredient. It provides the predictable and stable etch rate regulation that is needed to improve process control values for multi-step processing of thin foils, HDI, and SAP processes. Oxone provides the high copper solubility and ease of use needed in today's fast-paced PCB fabrication environment. Oxone bonding morphology improves adhesive and cohesive bond strength.

Hydrometallurgy and metal finishing

Oxone, is used in metal extraction, separation from ores or waste, hydrometallurgy, and surface treatment of metals or metal alloys. It may be used in both direct and indirect oxidation techniques.

Oxone chemistries can also be used in non-ferrous metal finishing applications: etching or micro etching surfaces to reduce thickness, remove oxidation, or pre-clean before bonding or plating. Additionally, Oxone finds application in vibratory finishing techniques.

Laundry bleach

Oxone is an effective low-temperature, non-chlorine bleach when formulated to provide at least 25ppm of active oxygen in wash water. Conventional anhydrous alkalis and fillers can be used to attain a pH of 9-10, and to control dose. Oxone can be used with colors when care is taken to completely dissolve Oxone before contact with damp fabrics to avoid dye damage.

Repulping

Oxone monopersulfate compound can be used as a processing aid in repulping internal broke or a secondary fiber furnish. Paper products containing polyamide epichlorohydrin (PAE) wet strength resins can be effectively repulped to make same grade paper. Oxone has been demonstrated on a variety of sanitary, food, packaging, and specialty papers containing wet strength resin and made from different furnishes such as bleach kraft, sulphite etc. Unlike chlorine-based repulping agents, Oxone does not produce Absorbable Organic Halides (AOX) or other chlorinated organics. It also does not degrade the fiber or darken mechanical pulp.

Wool shrinkproofing

Oxone is used as an oxidizer for the treatment of wool, in preparation for the application of

shrinkproofing resins. In this process, Oxone disrupts the surface of the wool and oxidizes cystine linkages in the cuticle to give it anionic character, which is ideal for attracting polyacrylic and polyamide resins. Oxone causes less damage to wool fiber than chlorine processing and does not have the negative environmental impact associated with chlorine use.

Pool care

Oxone is used to keep the water clear, thus allowing chlorine in pools to sanitize the water rather than clarify the water, resulting in reduction of amount of chlorine requirement to keep the pools clean.

Conclusion

The increased use of Oxone in various fields these days implies the viability and ease of using this reagent under different experimental conditions and waste treatment sites in addition to other useful applications of the product. The reagent is being highly acknowledged for being cost effective, availability, simple handling and versatile nature. It is being used to study various chemical reactions and mechanisms involving substrates prone to oxidation. Synthesis of various compounds like carbamates, diaryliodonium salts, 2-aminoacylbenzenes, iodylarenes, triazolopyridines, hypervalent iodine compounds etc. have been undertaken. Oxone has been found to be extremely efficient in removal of various pollutants in waste water streams and soils laden with a variety of pesticides and herbicides like Hexachlorocyclohexane isomers (HCHs), tembotrione etc. Some investigations have been undertaken to validate the potential of OXONE in the removal of phenols, HAPs, pesticides and dyes from waste water streams. Sulfate radical-based advanced oxidation processes (SR-AOPs) are extending a great opportunity for the research work to be undertaken for oxone in the days to come. Oxone should be extensively explored in order to reap utmost benefits in the field of science and daily life.

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