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Study of Chromium Containing Oxidants for Oxidation of Organic Compounds

[1]Kamal Raj Sapkota*, [2]Arun Kumar

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ABSTRACT

Studies on redox behavior of inorganic and organic substrates is an important area of research. Potassium dichromate (K2Cr2O7), the orange crystalline solid is an excellent oxidant for inorganic substrates. Nevertheless, this issue arises with organic substrates because of their inadequate solubility in organic solvents, prompting efforts to substitute the K+ cation with alternative cations. A range of onium ions has been used to design several Cr(VI) oxidants, with di-tertiary butyl chromate (TBC) being the key oxidant utilized in this study.

Keywords: *Chromium, Onium, Oxidation, TBC.*

INTRODUCTION

The effectiveness of the oxidizing scheme and oxidation potential of anionic oxidants like Ce(IV), Mn(VII), W(VI), Mo(VI), Cr(VI), and Ru(VII) are significantly changed by the presence of onium ions as counterions (Liang et al., 2021; Fawzy et al., 2021; Priyadarshini et al., 2017). These ions enhance the lipid solubility of the oxidants, making them milder and more chemo-selective. Various customized onium ions, including bismuthenium, ammonium, arsonium, phosphonium, and tellurium were utilized as counterions for anionic oxidants (Panday et al., 2009; Hajipour et al., 2009; Song, 2006; Patnail & Muralidhar; 2000; Yoshihiro et al., 2008l; D'Orazio et al., 2021; Moradi et al., 2022). Under varying reaction states, these

[1]Research Scholar, University Department of Chemistry, B. R. A. Bihar University, Muzaffarpur, Bihar, India

[2]Professor of Chemistry & Principal, L. N. D. College, Motihari, B.R.A. Bihar University, Muzaffarpur, Bihar, India

**Corresponding Email:*

oxidants can exhibit biomimetic properties influenced by the counterions, which create a microheterogeneous environment. This environment forms distinct solubilization pockets for substrates, similar to those found in micelles, microemulsions, reverse micelles, vesicles in artificial frameworks, and lipid or protein membranes within biological systems (Patel & Mishra ; 2006). The presence of onium counterions plays a crucial role in enhancing the solubility of oxidants within the reaction medium. Significant research efforts have focused on creating new oxidants incorporating these onium ions. Numerous research centers have fabricated various asymmetric and symmetric tetraalkylammonium ions with different alkyl chain lengths to develop more effective oxidation methods. These ions function as transporters for oxidants and assist in processing organic substrates within organic solvents. They have occasionally been used in solvent-free setups, solid-state transformations, and microwave-assisted methods. Tetraalkylammonium ions' impact on changes in water's shape is still unclear. On the other hand, smaller alkyl groups and a more exposed charge on the onium ion cause the water structure to be disrupted (Turner et al, 1992; Patel et al., 2022), whereas large alkyl groups improve the structural organization of water (Marciacq-Rousselot et al., 1972).

Alkyl Ammonium Ions as cr(vi) Oxidant Carriers

Water-soluble potassium (K) or sodium (Na) dichromates are commonly employed in laboratories as oxidizing agents or oxidants for organic compounds. They work especially well when strong acids are present. The Sarett School of Scholars attempted to oxidize certain steroidal alcohols in organic solvents by utilizing pyridine to create a salt with CrO_3, a Lewis acid, following the advent of organic phase transferring agents (Poos et al., 1953). Subsequent researchers employed this reagent without analyzing the oxidant's structure (Heravi et al., 2016; Chawala et al., 1974; Gilbert et al., 1976). In his pioneering work to confirm pyridinium chlorochromate as an adaptable oxidant, Corey reconsidered the reagent utilized by Sarett and identified it as pyridinium dichromate (Heravi et al., 2016; Barot et al., 2025; Corey et al., 1979). Henceforth, several Cr(VI) oxidants based on heterocyclic ammonium ions were prepared, as well as their oxidation capabilities with respect to different substrates were examined. A comprehensive review of this subject (oxidants) as reported previously (Patel et al., 2007). Several oxidative reagents were designed in the contemporary era, achieving irregular success (Sadeghy et al., 2005).

There is ongoing investigation concentrated on creating novel chromium (VI) reagents that can selectively and efficiently oxidize organic compounds under mild conditions (Hajipour et al., 2005).

Recent advancements were made by utilizing unique (novel) oxidizing agents that feature tetralkylammonium ions, such as tetraethylammonium, tetrahexylammonium, tetramethylammonium, tetrabutylammonium, and tetrapropylammonium. These agents are used alongside various chromate-based oxidants, including dichromate, chlorochromate, fluorochromate, and bromochromate.

Alkylammonium Ions as Carriers of Chromates

Tetrabutylammonium ion was vastly utilized as a component in several water-lipid systems because of its (Tetrabutylammonium ion) balanced amphiphilic natures. Several oxidants containing tetrabutylammonium ion have been developed, such as TBAFC (tetrabutylammonium fluorochromate) (Ghammami et al., 2005), TBACC (chlorochromate) (Santaniello et al., 1983), and TBAC (chromate) (Pourali et al., 2006). TBAFC ((C4H9)4NCrO3F) was utilized for the selective and efficient oxidation of alcohols under gentle conditions (Santaniello et al., 1983; Ghammami et al., 2005). The preparation of the reagent involves reacting tetrabutylammonium fluoride with CrO3 in equal molar (1:1 ratio) amounts. TBAFC in acetonitrile facilitates the oxidation of triphenylphosphine to its corresponding oxide, offering clear proof of an oxygen-transfer reaction in the oxidation (Ghammami et al., 2005). Tetrabutylammonium bromochromate (TBABC: (Bu)4.NCrO3Br) (Pourali et al., 2006) and tetrapropylammonium bromochromate (TPABC: (Pr)4NCrO3Br) (Ghammamy et al., 2007) are two efficient reagents that could oxidize alcohols to their complementary carbonyl compounds under mild reaction conditions (Scheme 1.1). According to Pourali et al., oximes were transformed into carbonyl by employing TBAC (tetrabutylammonium chromate) in inhomogeneous, moderately acidic, and aprotic conditions. Recent research has demonstrated the use of TBAC for nitrating phenolic compounds with sodium nitrite and for oxidizing hydroquinones into quinones in the presence of dichloromethane (Pourali et al., 2011; Dipti et al., 2012; Tomar et al., 2006; 2007; Ghammamy et al., 2008). The identical reaction could occur in the presence of TBAD (tetrabutylammonium dichromate) under neutral aprotic conditions when utilizing methylene chloride (CH2Cl2) (Scheme 1.2).

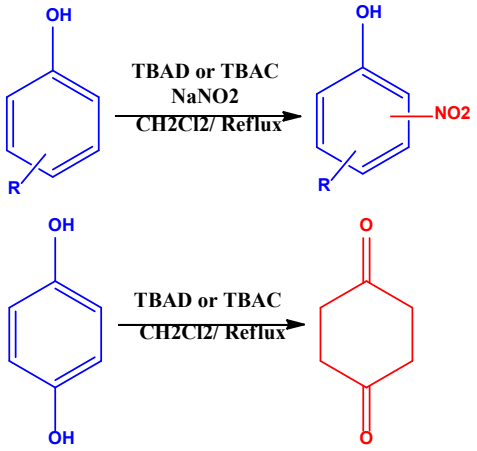
Scheme 1.1

TBC as a Variable Oxident

Di-tert-butyl chromate (TBC), a chromium (VI)-based oxidant, is commonly utilized for oxidation processes, frequently resulting in the breakdown of various organic compounds. In 1949, R.P. Oppenauer and H. Obberauch synthesized TBC for the first time and used it as an oxidant for one-degree alcohols. TBC is obtained from tertiary butyl alcohol (2-methyl-2-propanol). While it is not a widely used compound, TBC is listed under CAS number 1189-85-1 with the following information.

TBC has the molecular formula $C_8H_{18}O_4Cr$ and a molecular weight of 230. Its structural formula is represented by H3C. The compound melts at temperatures between 22 and 32°F.

Di-tertiary butoxy chromyl, di-tertiary butyl ester chromic acid, and di-tertiary butyl chromate are some more names for TBC too. Several organic molecules have been oxidized using this chemical.



Scheme 1.2

Isolation and Synthesis

The first isolation of 1,2-dihydroxybenzene was made in 1839 by Edgar Hugo Emil Reinsch (1809–1884), who did it by distilling catechin, a solid substance obtained from catechu, the boiled or condensed juice of the Mimosa catechu (Acacia catechu L.f.) tree. Reinsch originally referred to this material as Brenz-Katechusaure (burned catechu acid), which sublimated as a white crystalline deposit when catechin was heated above its disintegration temperature. This substance was created when the catechin's flavanols broke down thermally. Wackenroder and Zwenger separately rediscovered catechol in 1841. The molecule was eventually dubbed 'pyrocatechin' by Philosophical Magazine. Erdmann identified catechol in 1852 as

a chemical made up of two oxygen atoms and benzene. Catechol was formally known as pyrocatechol by 1868 after August Kekulé postulated in 1867 that it was a diol derivative of benzene. The term 'catechol,' which was first proposed in the Journal of the Chemical Society in 1879, was officially approved and documented the following year. Natural sources of 1,2-Dihydroxybenzene in its free form include kino and beechwood tar. Human and equine urine was found to contain its sulfonic acid derivative.

1,2-Dihydroxybenzene can be synthesized on an industrial scale through the hydroxylation of phenol, employing hydrogen peroxide as the oxidizing agent.

$$C_6H_5OH + H_2O_2 \rightarrow C_6H_6(OH)_2 + H_2O$$

In the previous work, 1,2-dihydroxybenzene was produced by alkaline hydrolysis of 2-substituted phenols, including 2-chlorophenol, in the presence of hot aqueous alkali solutions or by oxidizing salicylaldehyde with hydrogen peroxide. The derivative of methyl ether (Guaiacol) transforms into catechol through the hydrolysis of its CH3-O bond, catalyzed by hydroiodic acid.

DISCUSSION

1,2-dihydroxybenzene is oxidized using TBC

For a long time, organic chemistry researchers have sought efficient oxidants that can function under normal conditions for organic compounds. In this pursuit, TBC appears to be a promising solution. Since its introduction by Obberaunch and Oppenaurer, it has garnered significant interest from organic chemistry researchers over the past few decades. Recently, Di tert-butyl chromate (TBC) has found applications in the selective oxidation and degradation of diverse organic compounds, such as substituted olefins, fatty acids (both unsaturated and saturated), esters, ethers, enol-acetates, terpenoids, alkyl groups, carbohydrates, and steroids, under several reaction conditions. Mishra et al. explored several facets of TBC oxidation. The oxidation of 1,2-dihydroxybenzene (B-12) with TBC in THF (tetrahydrofuran) has been investigated in this work. DHB-122, DHB-121, and DHB-123 were the different products that were formed from the reaction of (DHB-12) with TBC in molar ratios of 1:0.5, 1:1, and 1:0.33. Suppliers include Sigma Aldrich, Sisco, E-merk, and BDH provided the AR-grade compounds used in the tests. Elemental analysis was performed with a C (carbon), H (hydrogen), and N (nitrogen) analyzer at CDRI, Lucknow, and chromium (Cr) were estimated using a titration technique. FTIR studies were accomplished by executing the FTIR instrument at B.R.A. Bihar

University, Muzaffarpur. The compounds' structures were suggested based on the formula obtained from elemental analysis and the identification of functional group signals in the IR spectra. These suggested structures were confirmed with TGA data.

CONCLUSION

In the present work, we have used TBC and TAC as oxidizing agents to investigate the oxidation of several organic compounds, including vanillin (4-hydroxy-3-methoxybenzaldehyde) and 1,2-dihydroxybenzene (benzene-1,2-diol). We even utilized a range of solvents, such as dioxane, dichloromethane, tetrahydrofuran, and acetonitrile, to investigate how different oxidants affect the same substrate and to evaluate the influence of solvents on the oxidation of organic compounds. We varied the substrate-to-oxidant ratio in our experiments for a more comprehensive comparison. The obtained oxidation products displayed disparities in composition, color, structural arrangement, and magnetic characteristics.

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