

# Review on modified solid supported potassium permanganate and its reaction mechanism for solvent-free heterogeneous oxidation of organic functional groups

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## Abstract

Potassium permanganate adsorption on the surface of solid support changes the selectivity and reactivity in several reactions leading to environmentally sustainable and greener prospects. Potassium permanganate supported alumina acts efficiently in the oxidation of urazoles to triazolinediones, dehydrogenation of 2-imidazolines to corresponding imidazoles, conversion of oximes into carbonyl compounds under solid-state conditions, chemical cleavage reactions of DNA on silica support, oxidation of alcohols to aldehydes and ketones under solvent-free conditions, oxidations of sulfides and thiols to sulfoxides and disulfides, and oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers and of ethylene acetals to the corresponding carbonyl compounds. Addition of manganese dioxide accelerates the oxidation of alkyl arenes, sulfides and allylic alcohols by potassium permanganate under solvent-free and heterogeneous conditions. Almost in all the cases, the reaction times is shorter and yields of the product is higher. When used in solution, permanganate reacts rapidly with alkenes, converting them into diols, ketols or cleavage products. When permanganate is adsorbed onto an inert solid support and used as a heterogeneous oxidant, however, some alkenes are resistant to oxidation and may actually inhibit the rate of oxidation of other reductants.

**Keywords:** Reaction Mechanism, Functional group transformation, Chemo-selective oxidant, Permanganate

## 1. Introduction

It is the focus of modern science to make kinetic experiments sustainable by applying modified methodologies for metal mediated oxidation kinetics meanwhile recycling the used reagents and catalysts after completion of reactions [1-5].

Redox reactions especially oxidation reaction is a very fundamental organic functional group transformation reaction in synthetic chemistry and likely plays a vital role in the production of value-

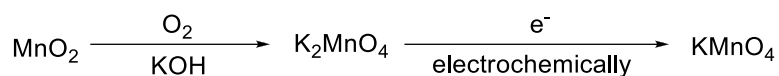
added chemicals from varied biomass and precursors. The endlessly increased pollution, increased petroleum prices as well as its reduced natural availability invoking a growing need for clean energy sources. Researchers have already been directed to find an alternate to this global crisis. In connection to this, the solid support oxidation has gained tremendous attention in the research area over the last few years. The use of solid supported reagents in synthetic chemistry has become popular due to their especially able altered reactivity, chemo selectivity and convenient product isolation they provide [6-11].

One of the most fascinating examples of a change in chemical reactivity and selectivity that has been reported to date is with the well-known oxidant, potassium permanganate [12]. Over the last two decades, chemistry under solvent free or heterogeneous conditions has become of increasing importance because it often produces enhanced reactivity and selectivity as well as facilitating product isolation [13]. This kind of reactions is not only important for it benefits from ecological point of view, but in most of the cases also offers significant synthetic advantages in terms of yield, selectivity and simplicity of the procedure. These factors are especially important in industry. Oxidation of organic compounds by permanganate adsorbed on a solid support has two major advantages over the corresponding reactions that takes place under homogeneous conditions: (a) the product can be easily isolated by filtration, followed by evaporation of the solvent; and (b) heterogeneous permanganate oxidation often exhibits better reactivity and selectivity [14]. This oxidant is an inexpensive, water-soluble and stable oxidizing reagent that is commercially available quite easily [15]. The role of permanganate as a heterogeneous oxidant adsorbed on solid support in solvent free condition is thus a very good field of study.

## **2. Chemistry of $\text{KMnO}_4$ : Preparation and modification**

Potassium permanganate ( $\text{KMnO}_4$ ) is one of the most versatile and vigorous oxidizing agent that is used to study the oxidation kinetics of several organic substrates. The permanganate ( $\text{MnO}_4^-$ ) ion in potassium permanganate has a tetrahedral geometry with extensive  $\pi$ -bonding; and manganese in permanganate has +7 oxidation state. It is stable in neutral or slightly alkaline pH range but in strong alkaline medium, it slowly disproportionate with hydroxide ion to form manganese(V) (hypomanganate) or manganese(VI) (manganate). At high pH, it is sometimes difficult to confirm whether an oxidation is proceeding via a one- or a two- electron process [16].

Permanganate is produced by the oxidation of manganese dioxide ( $\text{MnO}_2$ ) ore in a two-stage process. At first  $\text{MnO}_2$  is oxidized to potassium manganate(VI) by oxygen in a concentrated solution of potassium hydroxide and then to potassium permanganate electrochemically as shown-



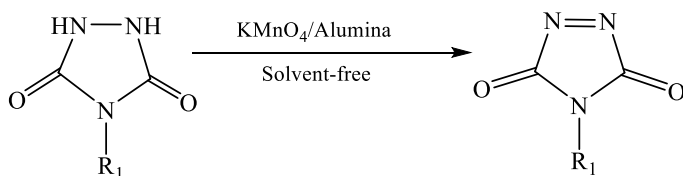
During organic synthesis reaction by permanganate oxidations, often a co-product manganese dioxide is produced. This manganese dioxide can be economically and effectively re-oxidized to permanganate by this process [17]. Thus, the use of potassium permanganate as an oxidant must be carried out under solvent-free or heterogeneous conditions [18] and the permanganate should be activated by using a solid support. But most of the solid supports like alumina [19,20], silica [21], zeolite [22], montmorillonite K10 [23], cation exchange resins [24], molecular sieves [25], or copper sulfate pentahydrate [26] interfere with the re-oxidation process.

Later activated manganese dioxide was found to be a good solid support that can be recycled [27], but preparation of activated  $\text{MnO}_2$  is difficult. Hence in order to bypass activated  $\text{MnO}_2$ , a new method has been developed for carrying out the reaction on a manganese(II) sulfate support [28]. The oxidant consisting of  $\text{KMnO}_4$  and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in a 5:1 ratio (by weight) is believed to be the most satisfactory approach.

### 3. Varied established oxidation kinetics applying solid binded $\text{KMnO}_4$

#### 3.1. Oxidation of Nitrogenous Compounds

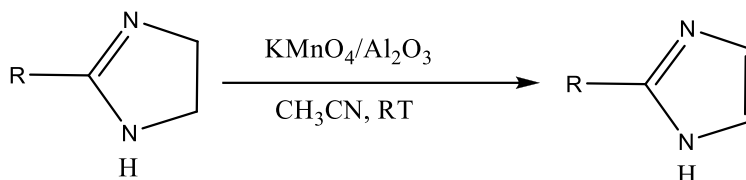
Potassium permanganate supported on solid alumina surface has been used for the oxidation of urazoles to triazolinediones. The novelty of the reaction lies on the fact that it is carried out under solvent-free conditions. The chemoselectivity of the reaction enhances the rate and yield in the reaction with a simple work-up procedure [29]. The modification is sustainable and green due to using no harmful solvent as well minimising the time for the completion.



**Scheme 1: Conversion of urazoles to triazolinediones**

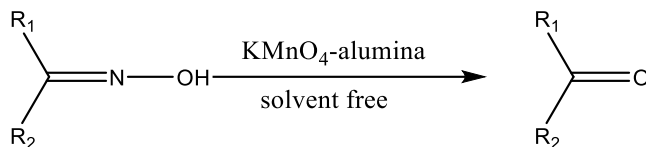
In another such reaction, dehydrogenation of 2-imidazolines to their corresponding imidazoles can be effectively carried out by potassium permanganate supported on solid alumina with high yields, it also happened to shorten the reaction times and made the full organic transformation a easy work-up.

The formation of a ring double bond by this process requires very mild reaction condition and has excellent chemoselectivity [30].



**Scheme 2: Conversion of 2-imidazolines to imidazoles**

Oximes, a class of nitrogen containing hydroxo compound, can effectively be converted into carbonyl compounds by alumina supported potassium permanganate under solid-state conditions [31].



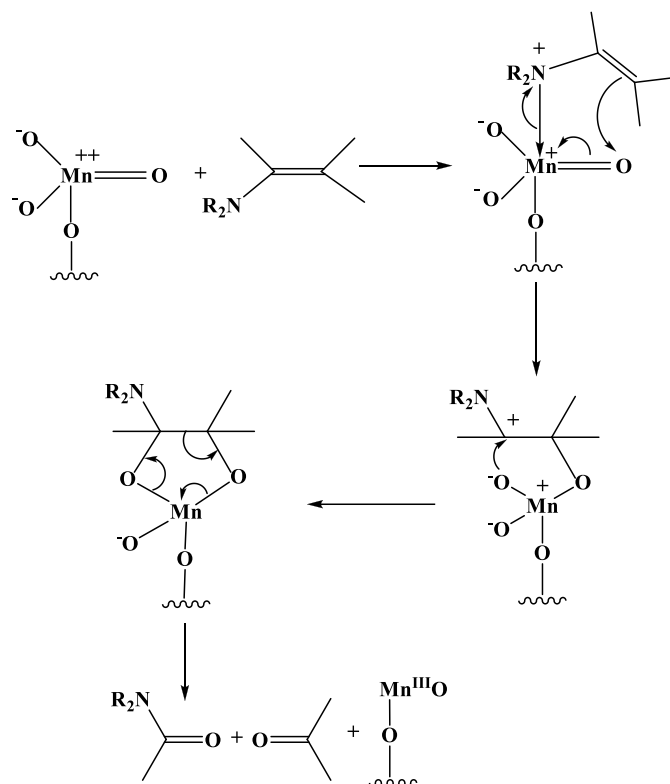
**Scheme 3: Conversion of oximes into carbonyl compounds**

The solvent free reaction condition along with no consumption of external heat energy is a better of its kind. The usefulness of the reaction lies in the fact that the genre of a nitrogenous substrate can be changed into a carbonyl non-nitrogenous compound and thus is very much useful in modern organic synthesis.

### Chemical cleavage reaction of DNA on solid-supported permanganate

DNA samples to be tested were loaded on to silica beads and the DNA bound to the solid supports went chemical modification reactions with potassium permanganate and hydroxylamine in 3M tetraethylammonium chloride (TEAC) solution. Piperidine then simultaneously cleaved the modified DNA, which was removed from the solid supports to achieve DNA fragments without the requirements of DNA purification between reaction steps. Thus time-consuming DNA purification at each reaction step could be omitted, resulting a much faster cleavage reaction [32].

In the case of enamines, the reaction is thought to begin by bond formation between nitrogen and manganese, followed by oxidative attack on the contiguous double bond (**Scheme 4**) [33]. The reaction introduces a five-membered chelate-type ring with the olefinic compound and Mn-centre. A complete anhydrous condition is maintained throughout the reaction.



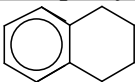
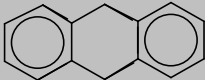
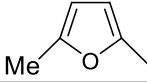
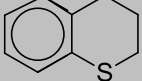

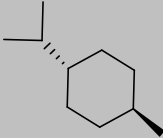
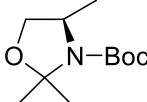
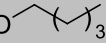
**Scheme 4: Possible reaction scheme for the oxidative cleavage of enamines**

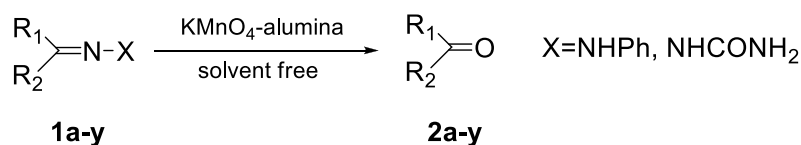
### Conversion of semicarbazones and phenylhydrazones to carbonyl compounds

Wet silica-supported potassium permanganate was used as a cheap and efficient reagent for the conversion of semicarbazones **1a-q** and phenylhydrazones **1r-y** into the consequent carbonyl compounds **2a-y** under solid-state conditions [34]. This reaction method is simple and easy with shorter reaction time (15-45 min) and product isolation is straightforward (**Table 1 and Scheme 5**). The very high amount of yield was recorded for such oxidation reactions.

**Table 1: Conversion of semicarbazones 1a–q and phenylhydrazones 1r–y to the carbonyl compounds 2a–y using KMnO<sub>4</sub>/wet SiO<sub>2</sub> under solvent-free conditions**

| Entry    | R <sub>1</sub>                     | R <sub>2</sub> | Time(min) | Yield (%) |
|----------|------------------------------------|----------------|-----------|-----------|
| <b>a</b> | Ph                                 | Me             | 15        | 90        |
| <b>b</b> | Ph                                 | H              | 15        | 85        |
| <b>c</b> | 3-ClC <sub>6</sub> H <sub>4</sub>  | H              | 25        | 80        |
| <b>d</b> | 3-MeOC <sub>6</sub> H <sub>4</sub> | H              | 20        | 91        |
| <b>e</b> | PhCH=CH                            | H              | 20        | 75        |

|          |  |    |    |    |
|----------|--|----|----|----|
| <b>f</b> | 4-BrC <sub>6</sub> H <sub>4</sub>  | Me | 25 | 70 |
| <b>g</b> | 4-PhC <sub>6</sub> H <sub>4</sub>  | Me | 30 | 75 |
| <b>h</b> | 4-Pyridyl  | Me | 20 | 80 |
| <b>i</b> | 1-Naphthyl   | H  | 15 | 78 |
| <b>j</b> |         | –  | 15 | 90 |
| <b>k</b> |         | –  | 15 | 88 |
| <b>l</b> |         | H  | 20 | 76 |
| <b>m</b> |         | –  | 25 | 91 |
| <b>n</b> |         | –  | 30 | 80 |
| <b>o</b> |         | –  | 45 | 85 |
| <b>p</b> |        | H  | 35 | 81 |
| <b>q</b> | THPO  | H  | 45 | 82 |
| <b>r</b> | 3-MeOC <sub>6</sub> H <sub>4</sub>   | H  | 40 | 70 |
| <b>s</b> | 3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>                                     | H  | 25 | 77 |
| <b>t</b> | Ph   | H  | 30 | 72 |
| <b>u</b> | Ph   | Me | 30 | 70 |
| <b>v</b> | 2-HOC <sub>6</sub> H <sub>4</sub>  | H  | 40 | 85 |
| <b>w</b> | 2-HO(CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>                        | Me | 45 | 78 |
| <b>X</b> | 4-HOC <sub>6</sub> H <sub>4</sub>  | H  | 20 | 90 |
| <b>y</b> | 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>  | H  | 25 | 90 |

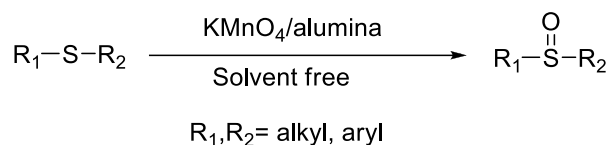


**Scheme 5: Conversion of semicarbazones and phenylhydrazones to carbonyl compounds**

The oxidative cleavage of these derivatives occurs at room temperature in the absence of solvent. Also, this oxidation system can convert complicated semicarbazones in the presence of other oxidizable functional groups into the parent carbonyl compounds.

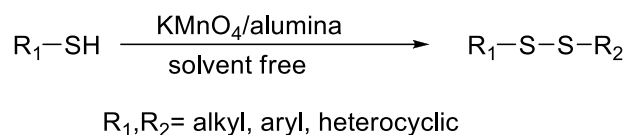
### 3.2. Oxidation kinetics of Non-Nitrogenous Compounds

Sulfoxides which play an important role in organic chemistry can be prepared by alumina supported potassium permanganate oxidation compared to the older procedures which were expensive and not that safer. Solid state permanganate oxidation of sulfides is less expensive, safer with faster reaction rates and higher yield [14].



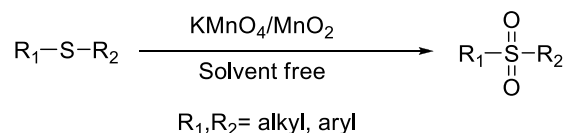
**Scheme 6: Conversion of sulfides to sulfoxides**

Disulfides bond formation is also important in organic synthesis, in biological active molecules and for protein stabilization and in peptides [35]. Most of the methods for coupling of thiols uses solvents that are toxic in nature. But alumina supported potassium permanganate solid-state oxidation of thiols to disulfides eliminates the toxic factor with higher yields and faster reaction time [14].



**Scheme 7: Conversion of thiols to disulfides**

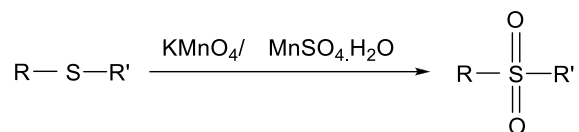
Most of the oxidation reaction of sulfides under solvent free condition results in the formation of sulfoxides. But sulfones can be efficiently produced from the oxidation of sulfides by permanganate with added  $\text{MnO}_2$  under both solvent-free and heterogeneous conditions. The yield is also improved in the presence of  $\text{MnO}_2$  [18].



**Scheme 8a: Conversion of sulfides to sulfones (with added  $\text{MnO}_2$ )**

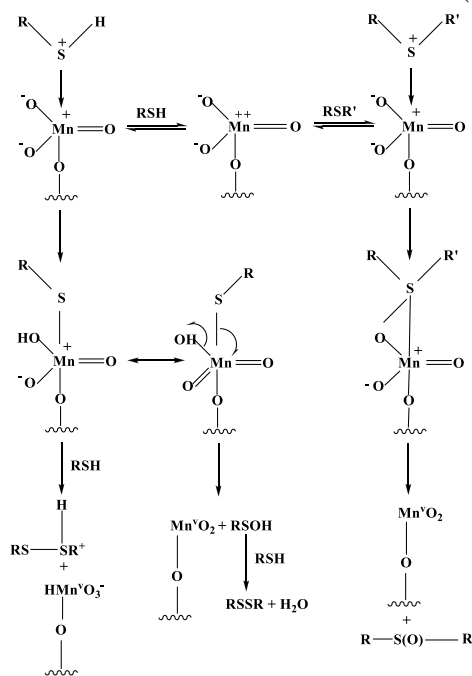
Activated  $\text{MnO}_2$  is a very good solid support that can be recycled [27], but it is difficult to prepare activated  $\text{MnO}_2$ . Hence to bypass activated  $\text{MnO}_2$ , a new method to conduct the oxidation on a manganese(II) sulfate support was developed.  $\text{KMnO}_4$  and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in a 5:1 ratio (by weight)

acts as the oxidant which can successfully convert sulfides into sulfones in good yields and shorter reaction times, under solvent-free and heterogeneous conditions [28].



**Scheme 8b: Conversion of sulfides to sulfones (with added MnSO<sub>4</sub>)**

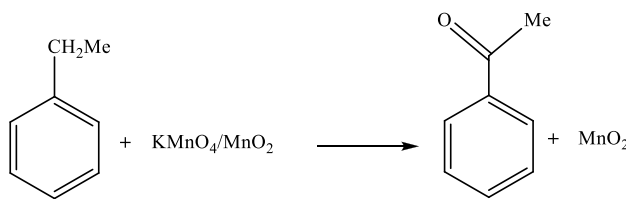
Lee et al. proposed a mechanism for the oxidation of thiols and sulfides. The oxidation of thiols lead to the formation of disulfides, which could be formed either by the nucleophilic attack on the complexed thiol or after it has been oxidized to a sulfenic acid (RSOH) [33].



**Scheme 9: Oxidation of thiols and sulfides by solid supported permanganate**

### Conversion of arenes into carbonyl compounds

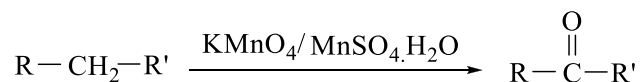
a) Addition of MnO<sub>2</sub> accelerates the process of oxidation of alkyl arenes into carbonyl compounds by potassium permanganate under solvent-free and heterogeneous conditions [18].



**(Scheme 10a)**

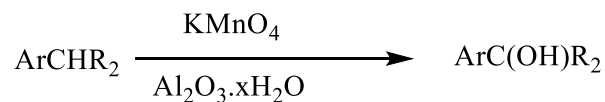
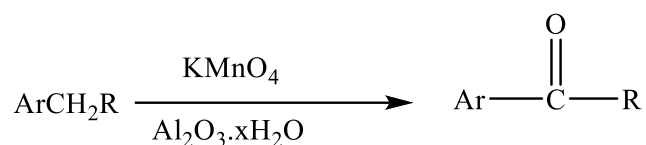


b) Arenes can also be rapidly oxidised into carbonyl compounds in high yields by potassium permanganate with manganese(II) sulfate as a solid support under solvent-free and heterogeneous conditions [28].



(Scheme 10b)

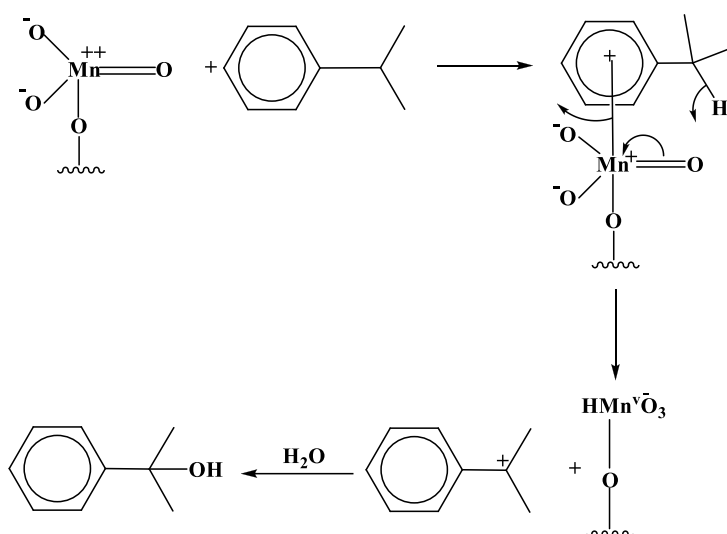
c) Normally benzoic acid results from the oxidation of Aromatic side-chain derivatives by permanganate in solution. But in the presence of a solid support like alumina, the oxidation leads to the formation of aromatic alcohols or ketones, depending upon the nature of benzylic carbons, i.e., the products are ketones when benzylic carbons are secondary and alcohols when they are tertiary. The reaction is very selective in nature and occurs under mild conditions [33].



(Scheme 10c)

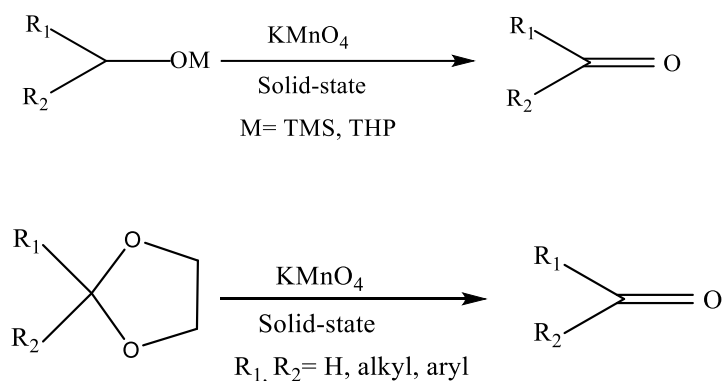
**Scheme 10(a, b & c): Conversion of arenes into carbonyl compounds**

The rates of homogeneous hydrocarbon oxidations are usually controlled by the ease of C-H or C-C bond cleavage. Heterogeneous oxidations can be dependent upon the adsorption rate of the reactants or desorption rate of the product and the need for proper orientation of the adsorbed reactant [36]. The oxidation of arenes like cumene whose benzylic position have only one C-H bond, forms tertiary alcohols. The proposed mechanism of cumene oxidation is thought to initiate between the electron-rich benzene ring and the electron-deficient manganese, i.e., electron donation takes place from the aromatic HOMO to the manganese LUMO. Hydride transfer then takes place, resulting a carbocation, which reacts with water to give an alcohol [33].



**Scheme 11: Mechanism for the oxidation of cumene**

One of the cheap process for the oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers and deprotection of ethylene acetals to the corresponding carbonyl compounds in high yields is carried out by potassium permanganate under solvent-free conditions. The inexpensive reagents, simple work-up, mild reaction conditions, and high yield of the products, make this process a good and useful method for the oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers and deprotection of ethylene acetals to achieve the corresponding carbonyl compounds [15].

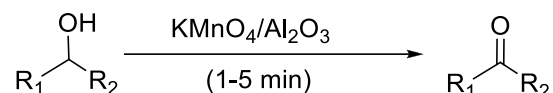


**Scheme 12: Oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers and deprotection of ethylene acetals**

### 3.3. Conversion of alcohols to carbonyl compounds

#### a) Oxidations with KMnO<sub>4</sub> supported on alumina

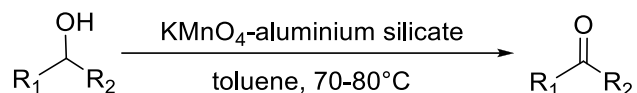
A very fast and simple method for the oxidation of alcohols to carbonyl compounds was accomplished in high yields by potassium permanganate oxidation on solid support alumina under solvent-free conditions. It may be noted that in a mixture of primary and secondary alcohol, the primary one is selectively oxidized. No overoxidation to carboxylic acids or double bond cleavage as in the case of allylic alcohols is found [37].



**Scheme 13a: Oxidation of alcohol**

#### b) Oxidations with KMnO<sub>4</sub> supported on aluminium silicate

Again, permanganate adsorbed on solid support aluminium silicate can selectively oxidize primary alcohols to aldehydes, also oxidizes secondary alcohols to ketones. Thus, this reagent competes successfully over those reagents reported only for oxidizing secondary alcohols [38].

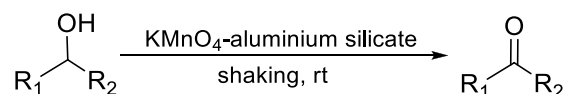


**Scheme 13b: Oxidation of alcohol**

Comparing with the supported KMnO<sub>4</sub> reagents that oxidizes primary alcohols, this KMnO<sub>4</sub>-aluminium silicate has extra advantages of shorter reaction times and higher yields over KMnO<sub>4</sub>-kieselgurh.

#### c) Oxidations with KMnO<sub>4</sub> supported on aluminium silicate and with shaking

Lou et al. reported a new and efficient method for the selective oxidations of alcohols to the corresponding aldehydes and ketones by aluminium silicate supported potassium permanganate under solvent-free conditions and with shaking [39].



**Scheme 13c: Oxidation of alcohol**

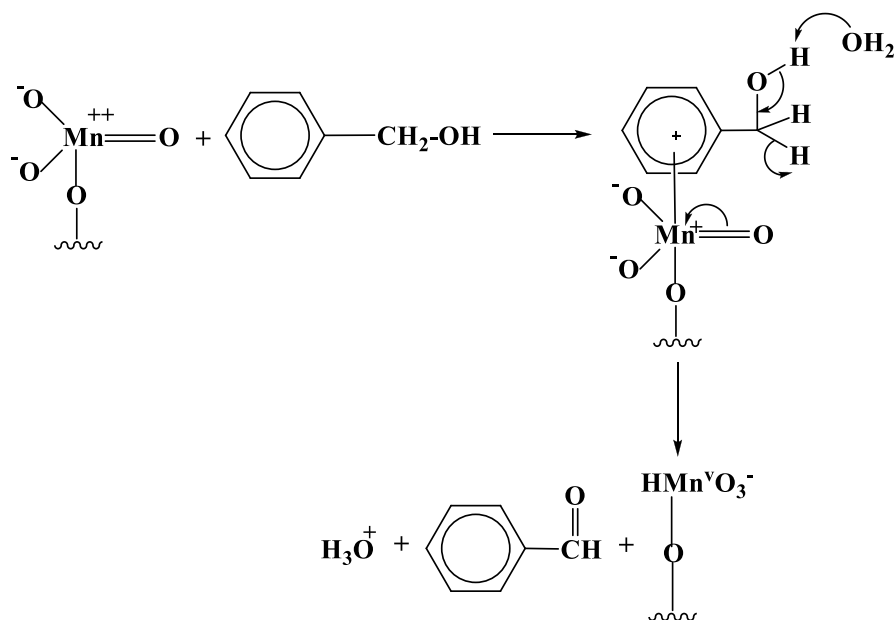
This oxidation method is excellent because it is completed within 60 min time period, with high yields of the products and of its applicability to a range of alcohols, as can be seen in **Table-2**.

**Table 2: Oxidation of alcohols by aluminium silicate supported potassium permanganate and with shaking**

| Substrate   | Reaction-time<br>(min) | Product   | Yield (%) |
|---|------------------------|---|-----------|
| Me(CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OH            | 60                     | Me(CH <sub>2</sub> ) <sub>4</sub> CHO                   | 81        |
| MeCCI=CHCH <sub>2</sub> OH                                      | 40                     | MeCCI=CHCHO   | 93        |
| PhCH <sub>2</sub> OH  | 40                     | PhCHO   | 97        |
| PhCH=CHCH <sub>2</sub> OH                                       | 30                     | PhCH=CHCHO  | 97        |
| <i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub> OH | 30                     | <i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -CHO        | 95        |
| H <sub>2</sub> C=CHCH(OH)Me                                     | 30                     | H <sub>2</sub> C=CHC(O)Me                               | 90        |
| MeCH <sub>2</sub> CH(OH)Me                                      | 40                     | MeCH <sub>2</sub> C(O)Me                                | 93        |
| Cyclohexanol  | 40                     | Cyclohexanone   | 97        |
| PhCH(OH)Ph  | 40                     | PhC(O)Ph  | 98        |
| PhCH(OH)COOEt   | 40                     | PhCOCOEt  | 93        |
| C <sub>15</sub> H <sub>31</sub> CH(OH)CH <sub>2</sub> COOEt     | 50                     | C <sub>15</sub> H <sub>31</sub> COCH <sub>2</sub> COOEt | 89        |
| PhCH(OH)CH <sub>2</sub> OH                                      | 40                     | PhCOCH <sub>2</sub> OH                                  | 93        |
| Cyclopropylmethanol   | 50                     | Cyclopropylformaldehyde                                 | 89        |
| Dicyclopropylmethanol   | 50                     | Dicyclopropylketone                                     | 90        |

**d) Oxidation of allyl and benzyl alcohols by KMnO<sub>4</sub> supported on copper(II) sulfate pentahydrate or hydrated alumina**

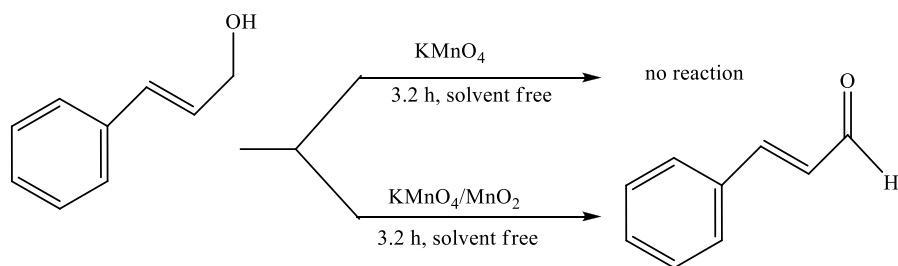
Potassium permanganate adsorption onto solid supports like copper(II) sulfate pentahydrate or hydrated alumina promotes the oxidation of alcohols, particularly allyl and benzyl alcohols. The positioning of the  $\alpha$ -H closer to permanganate, resulting in an easy hydride transfer facilitates the oxidation of benzyl alcohols as illustrated in the **Scheme 13d**. Similarly,  $\alpha$ - $\beta$  unsaturated alcohols can be oxidized if their double bonds are complexed with manganese in an analogous manner. Other unsaturated alcohols with one or more methylene groups between the double bond and carbon bearing the hydroxyl group cannot be oxidized due to such  $\alpha$ -H positioning [33].



**Scheme 13d: Oxidation of alcohol**

#### e) Oxidation of allylic alcohols (with added $\text{MnO}_2$ )

Addition of manganese dioxide ( $\text{MnO}_2$ ) accelerates the oxidation of allylic alcohols by potassium permanganate under solvent-free and heterogeneous conditions. The yields of the product greatly increased when  $\text{MnO}_2$  was added under both solvent-free and heterogeneous conditions [18].



**Scheme 13e: Oxidation of alcohol**

#### 4. Future prospect

Not only the mentioned functional groups but also many other oxidation reactions may be performed for having profound effect in solvent free media. Interestingly the reaction can also be performed under the catalytic presence of supramolecular nano-reactors, like surfactants or other nanoparticles. There are several reactions using Mn or Cr are reported to produce significant important improvement in organic functional group transformation reaction in association with micellar

catalysis. Solid supported  $\text{MnO}_4$  might be an option to investigate for further sustainable development of this type of reactions in either solvent free or in aqueous media. The proposed mechanism may invoke that the active oxidant preferably may get accumulated in the aqueous phase in presence of ionic surfactants but partitioned between water and micellar phase in presence of non-ionic surfactant and thus will have higher chance of faster kinetics superior yield.

## 5. Conclusions

$\text{KMnO}_4$  supported on solid alumina or silica has been established for its efficient oxidising ability of urazoles to triazolinediones, dehydrogenation of 2-imidazolines to their corresponding imidazoles, oxidation of alcohols to aldehydes and ketones under solvent-free conditions and superior stereo and chemo-selectivity. The oxidation of sulfides and thiols to sulfoxides and disulfides, oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers and of ethylene acetals to the corresponding carbonyl compounds has also been reported. This method offers several advantages including high yields, short reaction times, easy work-up, very mild reaction conditions and excellent chemoselectivity, and finally its 'benign by design' nature made it an ideal for the use in modern organic synthesis. The studies of oxidation of organic compounds by  $\text{KMnO}_4$  with and without added  $\text{MnO}_2$ , under solvent-free and heterogeneous conditions at room temperature provided its utility in modern organic synthesis. Solvent free oxidation of primary and secondary alcohols using  $\text{KMnO}_4$  supported on aluminium silicate at room temperature by shaking is a new and efficient method for the preparation of the corresponding aldehydes and ketones. The oxidation of arenes and sulfides by potassium permanganate was accomplished in good yields again under solvent free and heterogeneous conditions.

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## References

1. Mondal, M. H., Malik, S., Roy, A., Saha, R., Saha, B., Modernization of surfactant chemistry in the age of Gemini and bio-surfactants: a review in the age of gemini and bio-surfactants: a review; RSC Adv. 5 (2015) 92707-92718, DOI: 10.1039/C5RA18462B
2. Mondal, M. H., Malik, S., De, S., Bhattacharyya, S. S., Saha, B., Employment and resurrection of surfactants in bipyridine promoted oxidation of butanal using bivalent copper at NTP; Res. Chem Intermed. 43 (2017) 1651-1670, DOI: 10.1007/s11164-016-2721- 6
3. Mondal, M. H., Roy, A., Malik, S., Ghosh, A., Saha, B., Review on chemically bonded geminis with cationic

- heads: second-generation interfactants; Res. Chem. Intermed. 42 (2015) 1913-1928, DOI: 10.1007/s11164-015-2125-z
4. Malik, S., Saha, D., Mondal, M. H., Sar, P., Ghosh, A., Mahali, K., Saha, B., Micellar effect on hetero-aromatic nitrogen base promoted chromic acid oxidation of 1,3-propanediol in aqueous media at room temperature; J. Mol. Liq. 225 (2017) 207-216, DOI: 10.1016/j.molliq.2016.11.033
  5. Sar, P., Ghosh, A., Saha, R., Saha, B., Micellar effect on pentavalent vanadium oxidation of formaldehyde to formic acid in aqueous acid media at room temperature; Res. Chem. Intermed. 41 (2015) 5331-5352, DOI: 10.1007/s11164-014-1635-4
  6. Mondal, M. H., Malik, S., Garain, A., Mandal, S., Saha, B., Extraction of Natural Surfactant Saponin from Soapnut (*Sapindus mukorossi*) and its Utilization in the Remediation of Hexavalent Chromium from Contaminated Water; Tenside Surf. Det. 54 (2017) 519-529, DOI: 10.3139/113.110523
  7. Malik, S., Mondal, M. H., Ghosh, A., De, S., Mahali, K., Bhattacharyya, S. S., Saha, B., Combination of Sodium Dodecylsulfate and 2,2'-Bipyridine for Hundred Fold Rate Enhancement of Chromium(VI) Oxidation of Malonic Acid at Room Temperature: A Greener Approach; J. Solut. Chem. 45 (2016) 1043-1060, DOI: 10.1007/s10953-016-0494-6
  8. Ghosh, A., Saha, R., Saha, B., Effect of CHAPS and CPC micelles on Ir(III) catalyzed Ce(IV) oxidation of aliphatic alcohols at room temperature and pressure; J. Mol. Liq. 196 (2014) 223-237, DOI: 10.1016/j.molliq.2014.03.037
  9. Ghosh, A., Sar, P., Malik, S., Saha, B., Role of surfactants on metal mediated cerium(IV) oxidation of valeraldehyde at room temperature and pressure; J. Mol. Liq. 211 (2015) 48-62, DOI: 10.1016/j.molliq.2015.06.056
  10. Ghosh, A., Saha, R., Sar, P., Saha, B., Rate enhancement via micelle encapsulation for room temperature metal catalyzed Ce(IV) oxidation of formaldehyde to formic acid in aqueous medium at atmospheric pressure: A kinetic approach; J. Mol. Liq. 186 (2013) 122- 130, DOI: 10.1016/j.molliq.2013.07.003
  11. Ghosh, S. K., Basu, A., Saha, R., Nandi, R., Saha, B., Kinetics and Mechanism of 2, 2'- Bipyridyl Catalyzed Chromium(VI) Oxidation of Formic Acid in the Presence and Absence of Surfactants; Current Inorganic Chemistry, 2 (2012) 86-91, DOI: 10.2174/1877944111202010086
  12. Lee, D. G., In Encyclopedia of Reagents for Organic Synthesis; Paquette, L. A., Ed.; Wiley: New York, NY, 1995; pp 4274-4281.
  13. (a) Smith, K., (ed.), Organic Synthesis (Ellis Horwood and PTR Prentice Hall, New York, 1992) ; (b) Laszlo, P., in Comprehensive Organic Synthesis, Vol. 7, ed. B.M. Trost (Pergamon, New York, 1991) p. 893.
  14. Hajipour, A. R., Mallakpour, S. E., Adibi, H., A facile and selective method for oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides with alumina-supported potassium permanganate under solvent-free conditions; Sulfur Lett. 25 (2002), 155-160, DOI: 10.1080/02786110213976

15. Hajipour, A. R., Mallakpour, S. E., Mohammadpoor-Baltork, I., Backnezhad, H., An easy and fast method for oxidative deprotection of trimethylsilyl ethers, tetrahydropyranyl ethers, and ethylene Acetals with  $\text{KMnO}_4$  supported on alumina under solvent-free conditions; *Synth. Commun.* 32 (2002) 771-779, DOI: 10.1081/SCC-120002518
16. Freeman, F., Postulated intermediates and activated complexes in the permanganate ion oxidation of organic compounds; *Rev. React. Species Chem. React.* 1 (1973), 179-226, DOI: 10.1007/BF03155668
17. Singh, N., Lee, D. G., Permanganate: A Green and Versatile Industrial Oxidant; *Org. Process Res. Dev.* 5 (2000) 599-603, DOI: 10.1021/op010015x
18. Shaabani, A., Mirzaei, P., Lee, D. G., The Beneficial Effect of Manganese Dioxide on the Oxidation of Organic Compounds by Potassium Permanganate; *Catal. Lett.* 97 (2004) 119-123, DOI: 10.1023/B:CATL.0000038572.73523.bd
19. Toda, F., Takum, H., Yamaguchi, H., *Chem. Express* 4 (1989) 507.
20. Tanaka, K., Kishigami, S., Toda, F., Reformatsky and Luche reaction in the absence of solvent; *J. Org. Chem.* 56 (1991) 4333-4334, DOI: 10.1021/jo00013a055
21. Toda, F.; Tanaka, K.; Hamai, K. *J. Chem. Soc., Perkin Trans. 1* 1999, 3307.
22. Toda, F., Takumi, H., Akehi, M., Efficient solid-state reactions of alcohols: dehydration, rearrangement, and substitution; *J. Chem. Soc., Chem. Commun.* 0 (1990) 1270-1271, DOI: 10.1039/C39900001270
23. (a) Rao, P. S., Venkataratnam, R. V., Zinc chloride as a new catalyst for knoevenagel condensation; *Tetrahedron Lett.* 32 (1991), 5821-5822, DOI: 10.1016/S0040-4039(00)93564- 0
24. (a) Ballini, R., Marziali, P., Mozzicafreddo, A., Amberlyst A-27, an Efficient Heterogeneous Catalyst for the Michael Reaction of Nitroalkanes with  $\beta$ -Substituted Alkene Acceptors; *J. Org. Chem.* 61 (1996) 3209-3211, DOI: 10.1021/jo9520553
25. Shaabani, A., Lee, D. G., Solvent free permanganate oxidations; *Tetrahedron Lett.* 42 (2001) 5833-5836, DOI: 10.1016/S0040-4039(01)01129-7
26. (a) Regen, S. L., Koteel, C., Activation through impregnation. Permanganate-coated solid supports; *J. Am. Chem. Soc.* 99 (1977), 3837-3838, DOI: 10.1021/ja00453a053; (b) Lai, S., Lee, D. G., Heterogeneous Permanganate Oxidation of Styrene and Cinnamic Acid Derivatives: A Simple and Effective Method for the Preparation of Benzaldehydes; *Synthesis* 11 (2001) 1645-1648, DOI: 10.1055/s-2001-16760
27. Shaabani, A., Mirzaei, P., Naderi, S., Lee, D. G., Green oxidations. The use of potassium permanganate supported on manganese dioxide; *Tetrahedron* 60 (2004) 11415-11420, DOI: 10.1016/j.tet.2004.09.087
28. Shaabani, A., Rahmati, A., Sharifi, M., Rad, J. M., Aghaaliakbari, B., Farhangi, E., Lee, D. G., Green Oxidations. Manganese(II) Sulfate Aided Oxidations of Organic Compounds by Potassium Permanganate;



Monatshefte für Chemie 138 (2007) 649-651, DOI: 10.1007/s00706-007-0667-5

29. Hajipour, A. R., Mallakpour, S. E., Adibi, H., Oxidation of urazoles to triazolinediones under solvent-free conditions using permanganate and alumina-supported permanganate; *Indian J. Chem.* 41B (2002) 2425-2427, DOI: 10.1002/chin.200310137
30. Abdollahi-Alibeik, M., Mohammadpoor-Baltork, I., Zolfigol, M. A., Alumina supported potassium permanganate: an efficient reagent for chemoselective dehydrogenation of 2- imidazolines under mild conditions; *Bioorg. Med. Chem. Lett.* 14 (2004) 6079-6082, DOI: 10.1016/j.bmcl.2004.09.070
31. Imanzadeh, Gh., Hajipour, A. R., Mallakpour, S. E., Solid State Cleavage of Oximes with Potassium Permanganate Supported on Alumina; *Synth. Commun.* 33 (2003) 735-740, DOI: 10.1081/SCC-120016316
32. Bui, C. T., Lambrinakos, A., Babon, J. J., Cotton, R. G., Chemical cleavage reactions of DNA on solid support: Application in mutation detection; *BMC Chem. Biol.* 3 (2003) 1, DOI: 10.1186/1472-6769-3-1
33. Noureldin, N. A., Zhao, D., Lee, D. G., Heterogeneous Permanganate Oxidations. 7. The Oxidation of Aliphatic Side Chains; *J. Org. Chem.* 62 (1997) 8767-8772, DOI: 10.1021/jo971168e
34. Hajipour, A. R., Adibi, H., Ruoho, A. E., Wet Silica-Supported Permanganate for the Cleavage of Semicarbazones and Phenylhydrazones under Solvent-Free Conditions; *J. Org. Chem.* 68 (2003) 4553-4555, DOI: 10.1021/jo034217y
35. a) Ogawa, A., Nishiyama, T., Kambe, N., Murai, S. and Sonada, N., Selenium, carbon monoxide and water as a new reduction system: Reductive cleavage of disulfides and diselenides to thiols and selenols; *Tetrahedron Lett.*, 28 (1987) 3271-3274, DOI: 10.1016/S0040-4039(00)95490-X; b) Johnson, J. R., Bruce, W. F., and Dutcher, J. D., Gliotoxin, The Antibiotic Principle of *Gliocladium fimbriatum*. I. Production, Physical and Biological Properties<sup>1</sup>; *J. Am. Chem. Soc.*, 65 (2005) 2005-2009, DOI: 10.1021/ja01250a051; c) Bodansky, M., Principle of Peptide Synthesis; Springer-Verlag, Berlin. (1984) 158- 201, DOI: 10.1007/978-3-642-96763-4\_5
36. Atkins, P., Physical Chemistry, 5th ed.; Freeman: New York, NY, 1994; pp 993–997.
37. Hajipour, A. R., Mallakpour, S. E., Imanzadeh, Gh., Oxidation of Alcohols to Carbonyl Compounds under Solvent-Free Conditions Using Permanganate Supported on Alumina; *Chem. Lett.* 28 (1999) 99-100, DOI: 10.1246/cl.1999.99
38. Lou, J. D., Zhu, L. Y., Wang, L. Z., Efficient Oxidation of Alcohols with Potassium Permanganate Adsorbed on Aluminum Silicate Reagent; *Monatsh. Chem.* 135 (2004) 31-34, DOI: 10.1007/s00706-003-0098-x
39. Lou, J. D., Gao, C. L., Li, L., Fang, Z. G., An Efficient Selective Oxidation of Alcohols with Potassium Permanganate Adsorbed on Aluminum Silicate under Solvent-free Conditions and Shaking; *Monatsh. Chem.* 137 (2006) 1071-1074, DOI: 10.1007/s00706-006-0506-0