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# Potassium Permanganate Oxidation of Organic Compounds

Ahmad Shaabani<sup>a</sup>, Farahnaz Tavasoli-Rad<sup>a</sup> & Donald G. Lee<sup>b</sup> <sup>a</sup> Chemistry Department, Shahid Beheshti University, Tehran, Iran <sup>b</sup> Department of Chemistry, University of Regina, Regina, Canada

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## Potassium Permanganate Oxidation of Organic Compounds

Ahmad Shaabani and Farahnaz Tavasoli-Rad Chemistry Department, Shahid Beheshti University, Tehran, Iran

Donald G. Lee

Department of Chemistry, University of Regina, Regina, Canada

**Abstract:** It has been discovered that potassium permanganate is an effective heterogeneous oxidant, even without resorting to the use of a solid support, if acetonitrile is employed as the solvent. Primary benzylic and secondary alcohols are converted to the corresponding aldehydes and ketones, alkyl arenes are oxidized to the corresponding  $\alpha$ -ketones in good yields using this procedure, and both alkyl and aryl sulfides are smoothly converted to the corresponding sulfones, also in excellent yields. When methylene chloride is used as the solvent, instead of acetonitile, the yields of aldehydes, ketones,  $\alpha$ -ketones, and sulfones are reduced. However, the oxidation of thiols to disulfides proceeds satisfactorily when methylene chloride is the solvent.

Keywords: Oxidation, permanganate, alkyl arene, sulfide, thiol, alcohol

#### INTRODUCTION

Potassium permanganate is a commercially available reagent, widely used for the oxidation of organic compounds.<sup>[1]</sup> The process is recognized as friendly to the environment because manganese dioxide, a coproduct formed by the reduction of permanganate, can be recycled.<sup>[2]</sup>

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Address correspondence to Ahmad Shaabani, Chemistry Department, Shahid Beheshti University, P.O. Box 19396-4716, Tehran, Iran. Fax: +98-21-2403041. E-mail: a-shaabani@cc.sbu.ac.ir

#### A. Shaabani, F. Tavasoli-Rad, and D. G. Lee

In spite of considerable knowledge with respect to the oxidation of organic compounds by  $KMnO_4$  under heterogeneous conditions, practical problems have been observed under some conditions. For example, over-oxidations and degradations, with the formation of a host of products, are known to occur occasionally. Reaction conditions, particularly the solvents, catalysts, and solid supports used are crucial to controlling the specificity of the products obtained.

It has recently been shown that organic compounds are oxidized selectively when treated under heterogeneous conditions with KMnO<sub>4</sub> adsorbed on solid supports such as  $CuSO_4 \cdot 5H_2O$ ,<sup>[3]</sup>  $Al_2O_3$ ,<sup>[3-5]</sup> zeolites,<sup>[6]</sup>  $SiO_2$ ,<sup>[7]</sup> ion exchange resins,<sup>[8]</sup> and montmorillonite K10.<sup>[9]</sup> Product yields are relatively good, but MnO<sub>2</sub> must be separated from the solid supports before it can be recycled. Although copper sulfate can be easily separated from MnO<sub>2</sub>,<sup>[2]</sup> separation of MnO<sub>2</sub> from most of the other solid supports such as silica, montmorillonite K10, alumina, ion exchange resin, and zeolites is very difficult. Therefore, the discovery of new conditions for the selectively transformation of organic compounds with KMnO<sub>4</sub>, in which there is no need to separate MnO<sub>2</sub> from supports, is of prime importance in synthetic organic chemistry.

In a continuation of our previous work on organic transformations using potassium permanganate as an oxidant,<sup>[9–11]</sup> we wish to report results which describe the selectively oxidation of alcohols, alkyl arenes, sulfides, and thiols by KMnO<sub>4</sub> under heterogeneous conditions without the use of solid supports. In these reactions, acetonitile was found to be a superior solvent for the oxidation of alkyl arenas, sulfides, and primary benzylic and secondary alcohols.

#### **RESULTS AND DISCUSSION**

Alkyl arenes are converted into the corresponding carbonyl compounds in good yields when oxidized heterogeneously by potassium permanganate in acetonitrile at room temperature. The products are identical to those obtained under heterogeneous conditions when the KMnO<sub>4</sub> is supported on CuSO<sub>4</sub> · 5H<sub>2</sub>O<sup>[3]</sup> or alumina.<sup>[3,4]</sup> However, as indicated by the data in Table 1, the yields are reduced if methylene chloride is used as the solvent. The reaction exhibited a strong selectivity for the oxidation of  $\alpha$ -methylene groups. No reaction was observed for the oxidation of toluene derivatives where the  $\alpha$ -carbon is primary. The observation that no oxidation occurs when dihydrobenzofuran,  $\alpha$ -phenylacetophenone, or o-ethylpyridine are the reductants is reminiscent of other heterogeneous oxidations.<sup>[3,5]</sup>

As indicated by the data in Table 2, alkyl and aryl sulfides are also converted into the corresponding sulfones in excellent yields at room

#### **Potassium Permanganate Oxidation**

*Table 1.* Oxidation of alkyl arenes to the corresponding carbonyl compounds by  $KMnO_4$  in  $CH_3CN$  and  $CH_2Cl_2$  at room temperature

| Entry | Reactant | Product     | CH <sub>3</sub> CN<br>(Yield %)<br>(Time, h) | CH <sub>2</sub> Cl <sub>2</sub><br>(Yield %)<br>(Time, h) |
|-------|----------|-------------|--|---|
| 1     |          |             | 56(29)                                       | 20(51)  |
| 2     |          |             | 58(30)                                       | 9(54)   |
| 3     |          |             | 58(32)                                       | 14(53.5)  |
| 4     |          |             | 75(24)                                       | 8(27)   |
| 5     |          |             | 80(24)                                       | 23(60)  |
| 6     |          |             | 78(27)                                       | 15(143)   |
| 7     | C        |             | 77(22)                                       | 10(28)  |
| 8     |          |             | 72(15)                                       | 31(41)  |
| 9     |          | No reaction | 0(24)  | 0(24)   |

(continued)

| Entry | Reactant | Product     | CH <sub>3</sub> CN<br>(Yield %)<br>(Time, h) | CH <sub>2</sub> Cl <sub>2</sub><br>(Yield %)<br>(Time, h) |
|-------|----------|-------------|--|---|
| 10    |          | No reaction | 0(24)  | 0(24)   |
| 11    |          | No reaction | 0(24)  | 0(24)   |
| 12    | Br       | No reaction | 0(24)  | 0(24)   |
| 13    |          | No reaction | 0(24)  | 0(24)   |
| 14    | O<br>N   | No reaction | 0(24)  | 0(24)   |

Table 1. Continued

temperature when acetonitrile is used as the solvent. This is a highly useful reaction for the preparation of sulfones, which are important intermediates in the synthesis of many organic compounds.<sup>[12]</sup>

As can be seen from the results reported in Table 3, primary benzylic and secondary alcohols are converted into the corresponding carbonyl compounds in relatively high yields in  $CH_3CN$  at room temperature; however, the yields of these reactions are reduced if  $CH_2Cl_2$  is used and the reaction is completely inhibited when the electron withdrawing group is in *para*-position of alcohol (Entry 6).

Under homogenous conditions, thiols are converted into sulfonic acids.<sup>[13,14]</sup> However, under heterogeneous conditions, both aromatic and aliphatic thiols are oxidized to the corresponding disulfides in good yields at room temperature, as indicated by the data in Table 4. For these reactions, methylene chloride proved to be a satisfactory solvent.

The oxidation of alkene (*trans*-stilbene) and alkyne (diphenylacetylene) gives cleavage product (benzaldehyde) in high yields (GC yield) in CH<sub>3</sub>CN

*Table 2.* Oxidation of sulfides to sulfones by  $KMnO_4$  in  $CH_3CN$  and  $CH_2Cl_2$  at room temperature

| Entry | Reactant  | Product   | CH <sub>3</sub> CN<br>(Yield %)<br>(Time, h) | CH <sub>2</sub> Cl <sub>2</sub><br>(Yield %)<br>(Time, h) |
|-------|---|---|--|---|
| 1     | $C_2H_5$ -S- $C_2H_5$   | $C_2H_5$ - $SO_2$ - $C_2H_5$  | 85(5)  | 48(16)  |
| 2     | $C_3H_7$ -S- $C_3H_7$   | C <sub>3</sub> H <sub>7</sub> -SO <sub>2</sub> -C <sub>3</sub> H <sub>7</sub> | 92(6)  | 40(18)  |
| 3     | C <sub>4</sub> H <sub>9</sub> -S- C <sub>4</sub> H <sub>9</sub>   | $C_4H_9$ - $SO_2$ - $C_4H_9$  | 92(7)  | 42(23)  |
| 4     | C <sub>8</sub> H <sub>17</sub> -S- C <sub>8</sub> H <sub>17</sub> | $C_8H_{17}$ -SO <sub>2</sub> - $C_8H_{17}$                                    | 93(7)  | 35(8)   |
| 5     | ⊂s  | o∭ <sup>s</sup> ≈₀  | 93(4)  | 8(6)  |
| 6     | s –   | S S S   | 95(4)  | 32(5)   |
| 7     | s - C   |   | 95(55)                                       | 25(72)  |
| 8     | S S   |   | 96(22)                                       | 14(22)  |
| 9     |   |   | 85(24)                                       | 38(28)  |

at room temperature. However, these reactions are completely inhihibited in  $CH_2Cl_2$  after a few days.

The oxidation of oximes and aromatic amines was also investigated. However, the oxidation of these compounds does not result in the formation of significant amount of useful product.

In conclusion we have introduced an economically and environmentally friendly procedure for the selectively oxidation of organic compounds by  $KMnO_4$  in  $CH_3CN$  or  $CH_2Cl_2$  without using of any solid supports. We have found in  $CH_3CN$  sulfones are obtained from sulfides,  $\alpha$ -ketones from arenas, aldehydes, and ketones from primary benzylic and secondary alcohols, benzaldehyde from alkene or alkyne and in  $CH_2Cl_2$  disulfides are obtained from thiols.

| Entry | Reactant  | Product    | CH <sub>3</sub> CN<br>(Yield %)<br>(Time, h) | CH <sub>2</sub> Cl <sub>2</sub><br>(Yield %)<br>(Time, h) |
|-------|-----------|------------|--|---|
| 1     | ОН        | H O        | 98(1)  | 45(3.30)  |
| 2     | OH<br>OMe | H O<br>OMe | 77(0.40)                                     | 67(3.15)  |
| 3     | ОН        | H O        | 78(0.35)                                     | 68(3)   |
| 4     | OH        | OMe<br>H O | 75(0.45)                                     | 60(4.30)  |
| 5     | OMe<br>OH |            | 70(0.30)                                     | 58(5)   |
| 6     | OH        |            | 75(3.30)                                     | No reaction(5)  |
| 7     | OH        |            | 98(0.50)                                     | 72(3.30)  |

*Table 3.* Oxidation of alcohols to the corresponding carbonylcompounds by  $KMnO_4$  in  $CH_3CN$  and  $CH_2Cl_2$  at room temperature

(continued)

| Table 3. Continued |          |            |  |   |
|--------------------|----------|------------|--|---|
| Entry              | Reactant | Product    | CH <sub>3</sub> CN<br>(Yield %)<br>(Time, h) | CH <sub>2</sub> Cl <sub>2</sub><br>(Yield %)<br>(Time, h) |
| 8                  | OH       | °          | 85(1)  | 78(2.15)  |
| 9                  | ОН       |            | 81(6)  | 17(192)   |
| 10                 | ОН       | → °        | 85(1.30)                                     | 65(4)   |
| 11                 | ОН       | ОН         | 70(0.30)                                     | 47(5)   |
| 12                 | OH       |            | 65(6)  | 5(6)  |
| 13                 | ОН       | $\bigcirc$ | 40(16)                                       | No reaction(18)   |
| 14                 | OH<br>C  |            | 60(6)  | 10(6)   |

Table 3. Continued

#### EXPERIMENTAL

#### Oxidation of Fluorene in Acetonitrile. A Typical Procedure

Fluroene (0.16 g, 1.0 mmol) was dissolved in 25 mL of  $CH_3CN$  and placed in a round-bottomed flask. Finely ground  $KMnO_4$  (1.0 g, 6.3 mmol) was added

| Entry       | Reactant   | Product  | % Yield<br>Time (min)      |
|-------------|--|--|----------------------------|
| 1           | ————————————————————————————————————   | S <sub>2</sub>   | 90(30)                     |
| 2           | SH   |  | 81(35)                     |
| 3           | √∽ы  |  | 83(60)                     |
| 4           | СІ   |  | 93(40)                     |
| 5           | SH<br>NH <sub>2</sub>  |  | 82(45)                     |
| 6           | SH   | $\left[ \bigcirc \right] s_2$  | 95(53)                     |
| 7<br>8<br>9 | [C <sub>8</sub> H <sub>17</sub> ]SH<br>[C <sub>5</sub> H <sub>11</sub> ]SH<br>[C <sub>3</sub> H <sub>7</sub> ]SH | $\begin{array}{c} {}^{2}\\ [C_{8}H_{17}]_{2}S_{2}\\ [C_{5}H_{11}]_{2}S_{2}\\ [C_{3}H_{7}]_{2}S_{2}\end{array}$ | 94(60)<br>92(55)<br>78(45) |

Table 4. Oxidation of thiols by KMnO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature

in small portions over a period of 15 min. The mixture was stirred vigorously at room temperature for 15 h. The product was filtered through a celite pad and the residue washed successively with  $CH_3CN$  (2 × 10 mL). The filtrate was treated with three to four drops of  $NH_2$ - $NH_2 \cdot 2HCl$  in order to reduce any residual oxidant. After filtering and evaporating the solvent, pure 9-fluorenone (0.13 g, 0.72 mmol, 72%), mp = 83–84°C (Lit.<sup>[15]</sup> 82.5–85°C) was isolated.

#### Oxidation of Diphenylsulfide in Acetonitrile: A Typical Procedure

Diphenyl sulfide (0.16 g, 1.0 mmol) was dissolved in 25 mL of CH<sub>3</sub>CN and placed in a round-bottomed flask. Finely ground KMnO<sub>4</sub> (1.0 g, 6.3 mmol) was added in small portions over a period of 15 min. The mixture was stirred vigorously at room temperature for 22 h. The product was filtered

#### **Potassium Permanganate Oxidation**

through a celite pad and the residue washed successively with  $CH_3CN$  (2 × 10 mL). The filtrate was treated with three to four drops of  $NH_2$ - $NH_2 \cdot 2HCl$  in order to reduce any residual oxidant. After filtering and evaporating the solvent, pure diphenyl sulfone (0.21 g, 0.98 mmol, 98%), mp =  $127-128^{\circ}C$  (Lit.<sup>[16]</sup>  $126-128^{\circ}C$ ) was isolated.

#### **Oxidation of 1-Indanol in Acetonitrile: A Typical Procedure**

1-Indanol (0.134 g, 1 mmol) was dissolved in 25 mL of CH<sub>3</sub>CN and placed in a round-bottomed flask and cooled to  $+5^{\circ}$ C using an ice-water bath and stirred magnetically. Finely ground KMnO<sub>4</sub> (1.0 g, 6.3 mmol) was added in small portions over a period of 15 min and after stirring for 5 min, the flask was removed from the cooling bath and stirred for an additional 50 min. The product was filtered through a celite pad and the residue washed successively with CH<sub>3</sub>CN (2 × 10 mL). The filtrate was treated with three to four drops of NH<sub>2</sub>-NH<sub>2</sub> · 2HCl in order to reduce any residual oxidant. After filtering and evaporating the solvent, pure 1-indanone (0.129 g, 0.98 mmol, 98%), mp = 41-42^{\circ}C (Lit.<sup>[17]</sup> 42°C) was isolated.

# Oxidation of Benzyl Thiol in Methylene Chloride: A Typical Procedure

Benzyl thiol (0.24 g, 2.0 mmol) was dissolved in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> and placed in a round-bottomed flask with a magnetic stirring bar. Finely ground KMnO<sub>4</sub>, (1.0 g, 6.3 mmol) was added in small portions over a period of 15 min. The mixture was stirred vigorously at room temperature for 35 min. The product was filtered through sintered glass and the residue washed successively with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The solvent was evaporated to give product (0.20 g, 0.81 mmol, 81%), which produced only one TLC spot and was identified as dibenzyl disulfide, mp = 70–71°C (Lit.<sup>[18]</sup> 71–72°C).

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#### REFERENCES

 Fatiadi, A. J. The classical permanganate ion: still a novel oxidant in organic chemistry. *Synthesis* 1987, 85–127.

- Singh, N.; Lee, D. G. Permanganate: A green and versatile industrial oxidant. Org. Proc. Res. and Develop. 2001, 5, 599–603.
- Noureldin, N. A.; Zhao, D.; Lee, D. G. Heterogeneous permanganate oxidations. 7. The oxidation of aliphatic side chains. J. Org. Chem. 1997, 62, 8767–8772.
- 4. Quici, S.; Regen, S. Alumina as a triphase catalyst. J. Org. Chem. 1979, 44, 3436–3437.
- Zhao, D.; Lee, D. G. Heterogeneous permanganate oxidations; Part 6: Selective oxidation of arenes. *Synthesis* 1994, 915–916.
- Streekmar, R.; Padmakumar, R. Zeolite supported permanganate: An efficient catalyst for selective oxidation of enamines, alkylarenes and unsaturated alcohols. *Tetrahedron Lett.* 1997, *38*, 5143–5146.
- 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. 2003, 68, 4553–4555.
- Joshi, P. L.; Hazra, B. G. Cation exchange resin supported oxidation of alkylbenzenes and defines using potassium permanganate. *J. Chem. Res. (S)* 2000, 38–39.
- Shaabani, A.; Bazgir, A.; Teimori, F.; Lee, D. G. Selective oxidation of alkyl arenes in dry media with potassium permanganate supported on montmorillonite(K10). *Tetrahedron Lett.* 2002, *43*, 5165–5167.
- Shaabani, A.; Bazgir, A.; Teimori, F.; Lee, D. G. Ion exchange catalysis in oxidation of organic compounds with potassium permanganate. *Synth. Commun.* 2003, 33, 1057–1065.
- Shaabani, A.; Lee, D. G. Solvent free permanganate oxidations. *Tetrahedron Lett.* 2001, 42, 5833–5836.
- 12. Simpkius, N. A. Sulphones in Organic Synthesis; Pergamon Press: Oxford, 1993.
- Doerr, I. L.; Wempen, I.; Clarke, A.; Fox, J. J. Thiation of nucleosides. III. oxidation of 6-Mercaptopurines. J. Org. Chem. 1961, 26, 3401–3409.
- Arndt, D. Manganese Compounds as Oxidizing Agents in Organic Chemistry; Open Court: La Salle, 1981; pp. 272–273.
- 15. Walter, W. *Handbook of Organic Chemistry*; Prentice Hall: New York, 1996; pp. 624–626.
- Cohen, V. I. A new and simple synthesis of alkyl, cycloalkyl, and aralkyl diselenides from aliphatic and aromatic aldehydes. Aliphatic ketones and cycloketones. *J. Org. Chem.* 1977, 42, 2510–2511.
- Huang, X.; Chan, C. C. Synthesis and applications of Bis[benzyltriethylammonium] dichromate: A new selective oxidation reagent. *Synthesis* 1982, 1091–1092.
- Iranpoor, N.; Firouzabadi, H.; Zolfigol, M. A. Dinitrogen tetroxide copper nitrate complex [Cu(NO<sub>3</sub>)<sub>2</sub> · N<sub>2</sub>O<sub>4</sub>] as a new nitrosating agent for catalytic coupling of thioles via thionitrite. *Synthetic Communications* **1998**, 28, 367.