

## Green Oxidations. Manganese(II) Sulfate Aided Oxidations of Organic Compounds by Potassium Permanganate

Ahmad Shaabani<sup>1,\*</sup>, Abbas Rahmati<sup>1</sup>, Masoumeh Sharifi<sup>1</sup>, Jafar Mogimi Rad<sup>1</sup>, Behnaz Aghaaliakbari<sup>2</sup>, Elham Farhangi<sup>1</sup>, and Donald G. Lee<sup>3,\*</sup>

<sup>1</sup> Department of Chemistry, Shahid Beheshti University, Tehran, Iran

<sup>2</sup> Department of Chemistry, University of Kashan, Kashan, Iran

<sup>3</sup> Department of Chemistry and Biochemistry, University of Regina, Regina SK, Canada

Received January 23, 2007; accepted February 14, 2007; published online May 11, 2007

© Springer-Verlag 2007

**Summary.** The oxidation of arenes and sulfides by potassium permanganate was accomplished in good yields under solvent free and heterogeneous conditions when manganese(II) sulfate is used as a solid support. After extraction of the organic products, the inorganic products can be reoxidized to permanganate. This result is important because it provides an approach to oxidation reactions that is, in theory, infinitely sustainable.

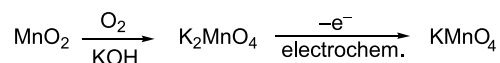
**Keywords.** Oxidation; Solvent free; Permanganate; Arene; Sulfide.

### Introduction

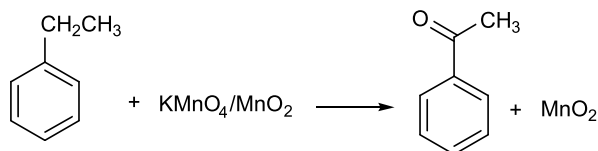
Although oxidation reactions play a central role in organic chemistry, many are known to be environmentally destructive because they require vigorous reagents and harsh conditions. Therefore, there are substantial benefits to be realized from the development of oxidation processes that are sustainable and, as a consequence, more environmentally acceptable.

In an attempt to find sustainable oxidation procedures, we have previously examined the use of potassium permanganate under various conditions. It is a most attractive oxidant on which to base a sustainable process because its reduction product, manganese dioxide, can be reoxidized to potassium

permanganate, as outlined in the following reaction [1].



Therefore, if ways to recover the manganese dioxide (in sufficiently pure form) can be found, the process becomes infinitely sustainable. An approach to the exploitation of this idea that we have previously discussed in literature involves the use of potassium permanganate as an oxidant under solvent free or heterogeneous conditions [2]. When used under such conditions, potassium permanganate must be activated using a solid support. Unfortunately, many of the common solid supports (such as alumina [3, 4], silica [5], zeolite [6], montmorillonite K10 [7], cation exchange resins [8], molecular sieves [9], or copper sulfate pentahydrate [10]) interfere with the reoxidation process. However, we have found that activated manganese dioxide is an excellent solid support that can be recycled, as in the following example [11].



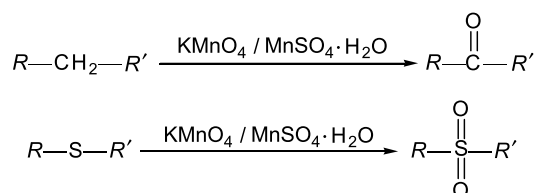
\* Corresponding author. E-mail: a-shaabani@cc.sbu.ac.ir

After the organic product (acetophenone in this example) has been extracted, the manganese product can be oxidized to potassium permanganate, making the process infinitely sustainable, in theory.

One of the difficulties with this approach is the need to prepare activated manganese dioxide by the oxidation of manganese(II) sulfate with potassium permanganate. In an attempt to bypass this step, and thereby improve the efficiency of this process, we have now investigated the use of manganese(II) sulfate as a solid support for these reactions under both solvent free and heterogeneous conditions.

## Results and Discussion

The results obtained from the oxidation of a number of products of these reactions are the corresponding ketones and sulfones, as indicated in the following equations.



The yields under three sets of conditions are reported in Table 1. The first column gives the yields obtained when an oxidant consisting of equal amounts (by weight) of  $KMnO_4$  and  $MnSO_4 \cdot H_2O$  was used under solvent free conditions. The second column gives the yields obtained when  $KMnO_4$  and  $MnSO_4 \cdot H_2O$  were combined in a 5:1 ratio (by weight) and used under solvent free conditions. The third column gives the yields obtained when equal amounts (by weight) of  $KMnO_4$  and  $MnSO_4 \cdot H_2O$  were combined and used under heterogeneous conditions with methylene chloride as the solvent. In the absence of any added manganese(II) sulfate, the yields were abysmally low.

Although there are individual variations, it appears that the use of an oxidant consisting of  $KMnO_4$  and  $MnSO_4 \cdot H_2O$  in a 5:1 ratio (by weight) under solvent free conditions is generally the most satisfactory approach. The yields are comparable to those obtained when equal amounts of  $KMnO_4$  and  $MnSO_4 \cdot H_2O$  were used under solvent free conditions and the reaction times are much shorter than those required for similar yields under heterogeneous conditions. Therefore, the use of  $KMnO_4$  and  $MnSO_4 \cdot H_2O$  in a 5:1 ratio is environmentally appealing for two reasons: (1) less material is used, and (2) the reduced oxidant can be recycled.

**Table 1.** Yields/% (react time/h) obtained from the manganese(II) sulfate aided oxidations of arenes and sulfides by potassium permanganate

Reductant	$KMnO_4:MnSO_4 \cdot H_2O = 1:1$ (solvent free)	$KMnO_4:MnSO_4 \cdot H_2O = 5:1$ (solvent free)	$KMnO_4:MnSO_4 \cdot H_2O = 1:1$ (heterogeneous)
Ethylbenzene	90 (4.45)	67 (5.4)	70 (35)
Propylbenzene	75 (5.30)	70 (6)	32 (45)
Butylbenzene	79 (5.45)	80 (6)	50 (47)
Diphenylmethane	55 (5)	96 (6)	87 (43)
Indane	80 (6)	76 (18)	61 (53)
Tetralin	85 (4)	80 (7.30)	80 (56)
Phthalan	81 (4)	65 (4)	65 (20)
Isochroman	90 (5)	82 (10)	70 (51)
Xanthene	85 (4)	80 (5)	100 (24)
Fluorene	91 (3.30)	89 (5.30)	68 (51)
Diphenylsulfide	92 (1)	93 (2)	95 (10)
Benzylphenylsulfide	96 (1)	95 (1)	86 (42)
Methylphenylsulfide	83 (0.75)	87 (0.5)	90 (1.15)
Methyl(4-nitrophenyl)sulfide	100 (0.5)	97 (1.10)	100 (12)
Bis(4-hydroxyphenyl)sulfide	80 (2)	86 (1.30)	64 (11)
Phenoxathin	86 (0.5)	95 (0.75)	95 (11)
Dibenzylsulfide	95 (1.25)	90 (1.30)	90 (51)
Dipropylsulfide	90 (0.17)	92 (1.10)	33 (5)
Dibutylsulfide	95 (0.25)	91 (1.20)	45 (5)
Tetrahydrotiophene	93 (0.25)	18 (6)	30 (5)

## Experimental

The oxidant for the reactions reported in the first column of Table 1 was prepared by grinding together potassium permanganate (1.0 g) and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (1.0 g). This oxidant was placed in a round bottom flask (in the absence of solvent) and reductant (1.0 mmol) was added. The reactants were stirred continuously at room temperature using a magnetically controlled stirring bar. Progress of the reactions was monitored by TLC until the reductant had completely reacted or until a reasonable amount of time had elapsed. Methylene chloride ( $15 \text{ cm}^3$ ) was then added to the flask and the reaction mixture was filtered through a sintered glass funnel. The residue was washed with additional methylene chloride ( $2 \times 10 \text{ cm}^3$ ) and the solvent collected was combined and evaporated on a flash evaporator. The yields were determined by GC analysis or from the integrals of the  $^1\text{H}$  NMR spectrum of the material obtained when most of the solvent had been evaporated. All products are known compounds with well-defined  $^1\text{H}$  NMR spectra [11].

The results reported in the second column of Table 1 were obtained in the same way except that the oxidant consisted of  $\text{KMnO}_4$  (1.0 g) and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (0.20 g).

The results reported in the third column of Table 1 were obtained using heterogeneous conditions.  $\text{KMnO}_4$  (1.0 g) and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (1.0 g) were ground together and placed in a round bottom flask, followed by methylene chloride ( $15 \text{ cm}^3$ ) and reductant (1.00 mmol). The reaction was then monitored and worked up as described above.

## Acknowledgements

Financial assistance from the Research Council of Shahid Beheshti University of Iran is gratefully acknowledged.

## References

- [1] Singh N, Lee DG (2000) *Org Process Res Dev* **5**: 599
- [2] Shaabani A, Mirzaei P, Lee DG (2004) *Catal Lett* **97**: 119
- [3] Toda F, Takum H, Yamaguchi H (1989) *Chem Exp* **4**: 507
- [4] Tanaka K, Kishigami S, Toda F (1991) *J Org Chem* **54**: 4333
- [5] Toda F, Tanaka K, Hamai K (1999) *J Chem Soc Perkin Trans 1*: 3307
- [6] Toda F, Takumi H, Akehi M (1990) *Chem Commun* 1270
- [7] a) Rao PS, Venkataratnam RV (1991) *Tetrahedron Lett* **32**: 5821; b) Sugino T, Tanaka K (2001) *Chem Lett* 110; c) Bose DS, Narsaiah AV (2001) *J Chem Research (S)* 36; d) Sabitha G, Reddy BVS, Sathesh RS, Yadav JS (1998) *Chem Lett* 773; e) Bogdal D (1998) *J Chem Research (S)* 468; f) Balalaie S, Nemat N (2000) *Synth Commun* **30**: 869
- [8] a) Ballini R, Marziali P, Mozzicafreddo A (1996) *J Org Chem* **61**: 3209; b) Christoffers J (1997) *J Chem Soc Perkin Trans 1*: 3141; c) Diez-Barra E, dela Hoz A, Merino S, Rodriguez A, Sanchez-Verdu P (1998) *Tetrahedron* **54**: 1835; d) Kotsuki H, Arimura K, Ohishi T, Maruzasa R (1999) *J Org Chem* **64**: 3770; e) Loupy A, Sansoulet J, Zaparucha A, Merienne C (1998) *Tetrahedron Lett* **30**: 333; f) Michaud D, Boulet FT, Hamelin J (1997) *Tetrahedron Lett* **38**: 7563; g) Ranu BC, Saha M, Bhar S (1997) *Synth Commun* **27**: 621
- [9] Shaabani A, Lee DG (2001) *Tetrahedron Lett* **42**: 5833
- [10] a) Regen SL, Koteel C (1977) *J Am Chem Soc* **99**: 3837; b) Lai S, Lee DG (2001) *Synthesis* 1645
- [11] Shaabani A, Mirzaei P, Naderi S, Lee DG (2004) *Tetrahedron* **60**: 11415