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Green oxidations. The use of potassium permanganate supported on manganese dioxide

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Abstract—Permanganate supported on active manganese dioxide can be used effectively for the oxidation of organic compounds under heterogeneous or solvent-free conditions. The residue that remains after extraction of the organic products, manganese dioxide, can be recycled, making the process infinitely sustainable, in theory. The use of this approach for the oxidation of arenes, alcohols and sulfides is described.

1. Introduction

During the past few decades, alternative experimental methods with reduced environmental impact have been developed for many reactions. However, similar progress has not been made on the modification of organic oxidations since the removal of electrons from stable molecules is relatively difficult, requiring vigorous reagents and/or forcing conditions. There is, therefore, little likelihood that it will ever be possible to use mild reagents and conditions for most oxidation reactions.

As an alternative to seeking gentle reactions that have low environmental impact, we have been searching for reactions that are easily insulated from the environment and which consume less material. For example, previously reported work from our laboratories and others has indicated that carrying out oxidation reactions under solvent-free conditions decreases environmental impact by reducing the need to deal with contaminated solvents.[1] When oxidation reactions are carried out under homogeneous conditions in polar solvents, such as aqueous acetone, the solvents must be cleaned up and disposed of or, preferably, recycled at the conclusion of the reactions. However, when the reactions are conducted under solvent-free conditions, no solvents are contaminated during the reaction. (Some solvent is usually required to separate the organic products from the spent oxidant; however, the amount of solvent required is reduced and it usually contains fewer contaminants.)

Homogeneous permanganate oxidations must be carried out in acidic or basic aqueous solutions,[2] and the corresponding heterogeneous reactions require the use of chemically inert solvents such as methylene chloride.[3–5] However, under solvent-free conditions, oxidations are done in the absence of solvent by using a reagent that consists of potassium permanganate and an approximately equal amount of a solid support such as alumina or silica. A minimum amount of organic solvent is then required to extract the products from the spent oxidant. In addition, solvents such as diethyl ether can be employed to extract the products, thus reducing the need to use chlorinated hydrocarbons.

It has recently been reported that the co-product obtained when organic compounds are oxidized, manganese dioxide, can be recycled under industrial conditions to regenerate permanganate.[6] Manganese dioxide is regenerated in a two-stage process that involves air oxidation to potassium manganate(VI) in a concentrated potassium hydroxide solution, followed by electrochemical oxidation to potassium permanganate.[7]

In previous descriptions of solvent-free permanganate reactions, procedures for separating manganese dioxide from solid supports, such as alumina or silica, have not been reported. Our experience with these reactions suggests that such a separation will not be easily achieved and we have, consequently, begun to investigate other approaches. The

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Keywords: Manganese dioxide; Potassium permanganate; Solid support; Arenes.

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most successful of our attempts, to date, has been realized by substituting manganese dioxide as the solid support.

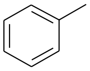
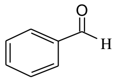
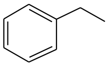
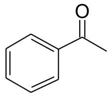
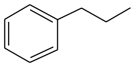
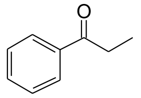
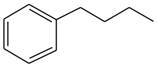
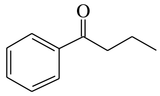
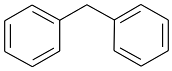
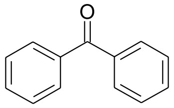
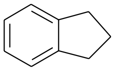
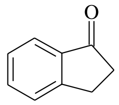
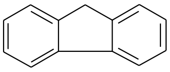
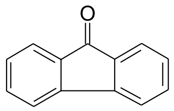
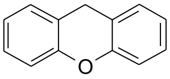
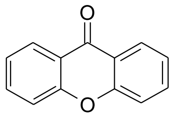
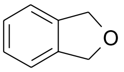
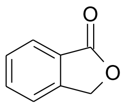
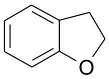
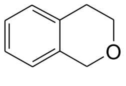
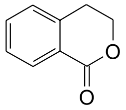
The combination of potassium permanganate and active manganese dioxide produces a reagent that can be used effectively for the oxidation of a variety of organic compounds. When organic compounds are oxidized by this reagent under solvent-free conditions, the solid coproduct remaining after the organic products have been separated is manganese dioxide containing residual amounts of potassium permanganate. This coproduct can then be recycled, making the process infinitely sustainable, in theory.

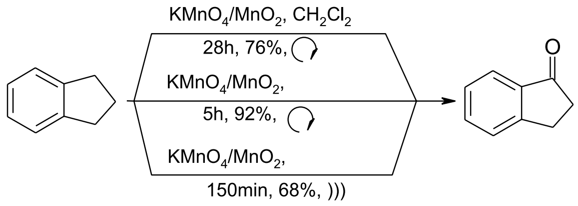
While recognizing that this approach may require further refining before it can be used commercially, we wish, at this time, to report the results that have been obtained for the oxidation of arenes, alcohols and sulfides. For comparison purposes, the results obtained for oxidation of the corresponding compounds under heterogeneous conditions is included.

2. Results and discussion

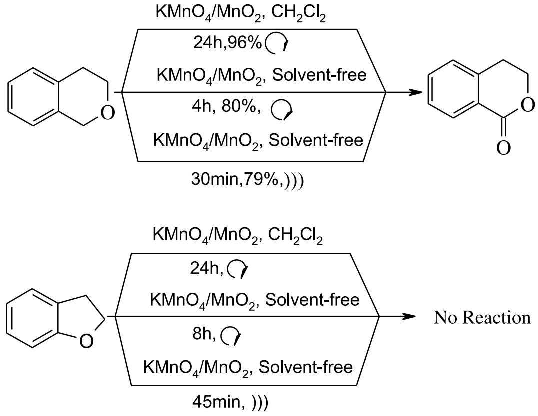
As can be seen from results reported in Table 1, alkyl arenes are converted into the corresponding α-ketones in good yields at room temperature. The products obtained under solvent-free conditions are identical to those obtained from heterogeneous reactions where the oxidant is dispersed in methylene chloride. In addition, the reaction times are reduced from a day or more to a few hours for many of the reactions, as summarized in Scheme 1.

Table 1. Oxidation of arenes to the corresponding carbonyl compounds by $KMnO_4/MnO_2$ under heterogeneous conditions (A), under conventional solvent-free conditions (B) and under solvent-free conditions assisted by ultrasonic irradiation (C)

Entry	Reactant	Product	Yield (%)		
			(A) (time, h)	(B) (time, h)	(C) (time, min)
1			25 (48)	21 (30)	0 (42)
2			89 (23)	56 (5.5)	62 (50)
3			85 (24)	62 (6)	65 (58)
4			92 (27)	70 (8)	78 (85)
5			93 (22)	85 (5)	85 (38)
6			76 (28)	92 (5)	68 (150)
7			96 (22)	85 (6)	82 (75)
8			93 (16)	94 (6)	80 (75)
9			81 (16)	80 (4)	70 (68)
10		No reaction	0 (24)	0 (8)	0 (45)
11			96 (24)	80 (4)	89 (30)



Scheme 1.



Scheme 2.

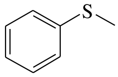
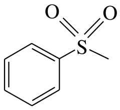
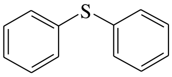
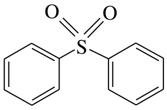
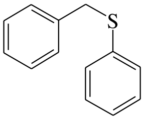
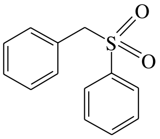
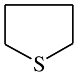
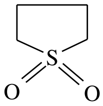
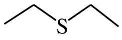
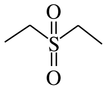
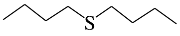
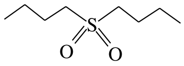
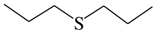
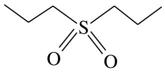
As indicated in Scheme 2, the reactions display a selectivity similar to that previously observed when oxygen is part of the bicyclic system. When oxygen is in the β-position, lactones are obtained in good yields; when it is in the α-position the reaction is completely inhibited.[4,5]

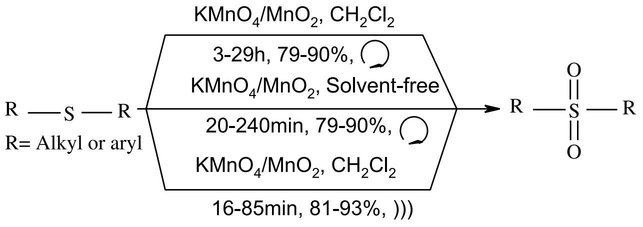
Application of ultrasonic irradiation in these reactions decreases the time required to obtain good yields by a factor of about 10. As a consequence, it is possible to select the most appropriate conditions for a particular application. If time is of little importance, the reaction can be completed without expenditure of additional energy; however, if time is an important factor, energy can be applied in the form of ultrasonic irradiation.

As can be seen from Table 2, aryl and alkyl sulfides are converted into the corresponding sulfones in good yields by $KMnO_4$ supported on MnO_2, with slightly shorter times being required when the reaction is subjected to ultrasonic irradiation.

This is a highly useful reaction for the preparation of sulfones which are important intermediates in the synthesis of many organic compounds.[8] The observation that benzyl phenyl sulfide (entry 3) is oxidized to the corresponding sulfone suggests that the reaction likely proceeds by way of an oxygen transfer mechanism. If the reaction involved electron transfer instead of oxygen transfer, substantial

Table 2. Oxidation of sulfides to the corresponding sulfones by $KMnO_4/MnO_2$ under heterogeneous conditions (A), under conventional solvent-free conditions (B) and under solvent-free conditions with the assistance of ultrasonic irradiation (C)

Entry	Reactant	Product	Yield (%)		
			(A) (time, h)	(B) (time, min)	(C) (time, min)
1			93 (3)	83 (25)	91 (24)
2			94 (8)	90 (60)	81 (45)
3			72 (29)	82 (240)	86 (85)
4			90 (4.5)	83 (25)	93 (25)
5			90 (3.5)	84 (20)	90 (16)
6			92 (4)	90 (45)	86 (38)
7			86 (4.5)	79 (30)	83 (27)
8	$[C_8H_{17}]_2$ S	$[C_8H_{17}]_2$ SO_2	89 (4)	85 (30)	93 (28)



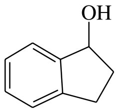
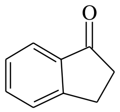
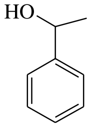
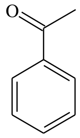
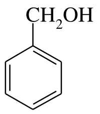
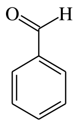
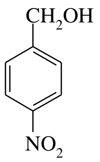
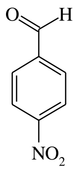
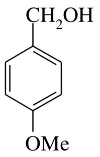
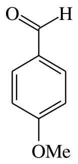
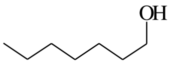
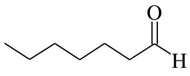
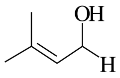
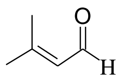
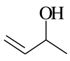
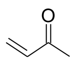
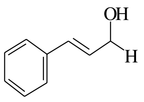
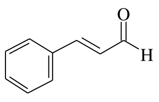
Scheme 3.

amounts of benzaldehyde would have been formed.[9,10] Most standard oxidations of sulfides under solvent-free conditions result in the formation of sulfoxides;[11–13] however, sulfoxides were not produced in these reactions.

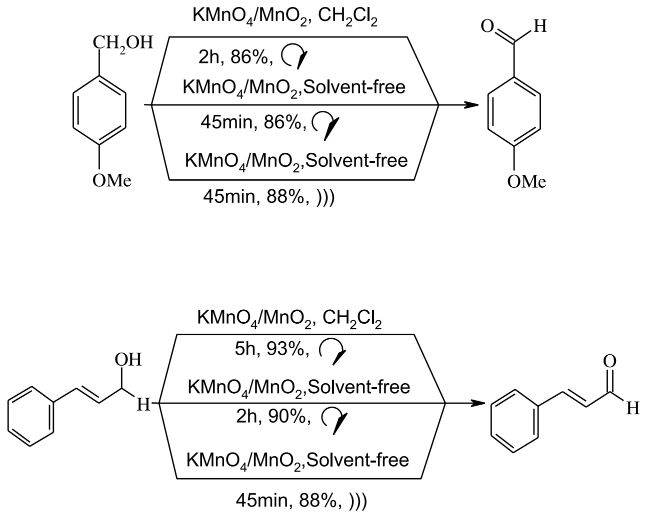
Both manganese dioxide and potassium permanganate will oxidize sulfides. However, the reaction of active manganese dioxide with sulfides is known to give only sulfoxides. Consequently, the observation that only sulfones are obtained in these reactions, as summarized in Scheme 3, suggests that the products are produced from the reaction of sulfides with $KMnO_4$, and not by a reaction of sulfides with MnO_2.

As indicated from the results reported in Table 3, secondary alcohols are efficiently converted into the corresponding ketones in good yields and aldehydes are selectively obtained from the oxidation of primary alcohols. The preparation of both aliphatic and aromatic aldehydes from the corresponding primary alcohols has not previously been easily achieved using permanganate or other strong oxidants because aldehydes are readily converted to carboxylic acids under oxidizing conditions. In addition, it was found that both primary and secondary α,β-unsaturated alcohols were oxidized to the corresponding carbonyl compounds without disruption of the double bond (entries 8–10). These results are summarized in Scheme 4.

Table 3. Oxidation of alcohols to the corresponding carbonyl compounds by $KMnO_4/MnO_2$ under heterogeneous conditions (A), under conventional solvent-free conditions (B) and under solvent-free conditions assisted by ultrasonic irradiation (C)

Entry	Reactant	Product	Yield (%)		
			(A) (time, h)	(B) (time)	(C) (time, min)
1			83 (4)	94 (50 min)	90 (43)
2			92 (5)	91 (35 min)	86 (30)
3			74 (5)	78 (60 min)	94 (63)
4			52 (14)	67 (3 h)	46 (150)
5			86 (2)	86 (45 min)	88 (45)
6			93 (24)	90 (6 h)	68 (120)
8			82 (17)	79 (4 h)	64 (150)
9			87 (8)	90 (2.5 h)	72 (45)
10			93 (5)	90 (2 h)	95 (105)

Active manganese dioxide in the absence of permanganate is able to oxidize primary and secondary alcohols to the corresponding aldehydes and ketones under solvent-free conditions.[14] However, the time required to complete the reaction is often a few days instead of 1 h or less as observed when permanganate is present.



Scheme 4.

3. Conclusions

1. A mixture of potassium permanganate (1 g) and activated manganese dioxide (3 g) can be used as an effective oxidant for arenes, sulfides and alcohols under both heterogeneous and solvent-free conditions. Removal of the organic products by extraction leaves a residue that consists primarily of manganese dioxide containing small amounts of potassium permanganate.
2. Ultrasound irradiation increases the rate at which products are formed.

Table 4. Characterization of products

Product	^{1}H NMR (ppm)	IR (cm^{-1})	Melting points
Benzaldehyde	7.20–7.79 (m, 5H), 9.94 (s, 1H)	3030, 2778, 2703, 1695, 1667, 1587, 1449, 1389, 1299, 1205, 1163, 1075	2,4-DNP derivative 234–236 °C (lit. 237 °C)[15]
Acetophenone	2.43 (s, 3H), 7.15–7.80 (m, 5H)	3100, 1700, 1600, 1580, 1450, 1360, 1300, 950	2,4-DNP derivative 247–250 °C (lit. 250 °C)[16]
Propiophenone	1.18 (t, $^{3}J_{\mathrm{HH}}=5.1$ Hz, 3H) 2.94 (q, $^{3}J_{\mathrm{HH}}=5.2$ Hz, 2H) 7.47–7.92 (m, 5H)	2980, 1690, 1595, 1450, 1215, 950	2,4-DNP derivative 187–188 °C (lit. 187–189 °C)[15]
Butyrophenone	0.95 (t, $^{3}J_{\mathrm{HH}}=5.1$ Hz, 3H) 1.41–1.96 (m, 2H) 2.82 (t, $^{3}J_{\mathrm{HH}}=5.1$ Hz, 2H) 7.12–7.87 (m, 5H)	2960, 1700, 1610, 1455, 1220, 1010, 700	2,4-DNP derivative 198–200 °C (lit. 200 °C)[16]
Benzophenone	7.20–7.78 (m, 10H)	3060, 1655, 1600, 1450, 1270, 800	2,4-DNP derivative 237–238 °C (lit. 239 °C)[16]
1-Indanone	2.63 (t, $^{3}J_{\mathrm{HH}}=6.1$ Hz, 2H) 3.09 (t, $^{3}J_{\mathrm{HH}}=6.1$ Hz, 2H) 7.08–7.80 (m, 4H)	2925, 1710, 1600, 1450, 1270, 750	2,4-DNP derivative 253–256 °C (lit. 258 °C)[16]
9-Fluorenone	7.10–7.70 (m, 8H)	3050, 1700, 1600, 1440, 1290, 860	81–82 °C (lit. 84 °C)[17]
Xanthone	7.36–8.32 (m, 8H)	1655, 1610, 1480, 1450, 1340, 1140, 760	172–173 °C (lit. 174 °C)[17]
Phthalide	5.32 (s, 2H) 7.35–7.86 (m, 4H)	1760, 1460, 1440, 1310, 1050, 745	73–74 °C (lit. 75 °C)[17]
1-Isochromaone	3.10 (t, $^{3}J_{\mathrm{HH}}=8.5$ Hz, 2H) 4.56 (t, $^{3}J_{\mathrm{HH}}=8.5$ Hz, 2H) 7.20–8.20 (m, 4H)	2945, 1716, 1602, 1455, 1389, 1289, 1237, 1115	175–176 °C (lit. 176 °C)[15]
Methyl phenyl sulfone	3.05 (s, 3H) 7.61–7.94 (m, 5H)	3091, 3066, 2928, 1585, 1480, 1449	85–87 °C (lit. 86 °C)[18]
Diphenyl sulfone	7.94 (m, 4H) 7.56–7.41 (m, 6H)	1450, 1310, 1150, 1110, 1000	128–129 °C (lit. 128 °C)[17]
Benzy phenyl sulfone	4.32 (s, 2H) 7.08–7.68 (m, 10H)	3088, 3006, 2969, 1606, 1495	144–145 °C (lit. 146 °C)[17]
Tetramethylene sulfone	2.20 (m, 4H) 3.01 (m, 4H)	3436, 2973, 2882, 1669, 1464, 1309	—
Diethyl sulfone	1.42 (t, $^{3}J_{\mathrm{HH}}=7.50$ Hz, 4H) 3.00 (q, $^{3}J_{\mathrm{HH}}=7.47$ Hz, 6H)	3241, 2996, 1672, 1479, 1378, 1286	73–75 °C (lit. 74 °C)[15]
Dibutyl sulfone	0.97 (t, $^{3}J_{\mathrm{HH}}=6.7$ Hz, 6H) 1.17–1.96 (m, 8H) 2.95 (t, $^{3}J_{\mathrm{HH}}=10.1$ Hz, 4H)	2960, 2880, 1460, 1410, 1300, 1130	45–46 °C (lit. 46 °C)[17]
Dipropyl sulfone	1.09 (t, $^{3}J_{\mathrm{HH}}=6.5$ Hz, 6H) 1.46–2.11 (m, 4H) 2.95 (t, $^{3}J_{\mathrm{HH}}=6.7$ Hz, 4H)	2960, 2880, 1460, 1410, 1280, 1125	29–30 °C (lit. 30 °C)[15]
Dioctyl sulfone	0.89 (t, $^{3}J_{\mathrm{HH}}=5.93$ Hz, 6H) 1.20–1.92 (m, 24H) 2.88–3.00 (m, 4H)	2910, 1463, 1313, 1264, 1122, 771	74–76 °C (lit. 74 °C)[17]
4-Nitrobenzaldehyde	8.09–8.39 (m, 4H) 10.18 (s, 1H)	2850, 2720, 1705, 1600, 1540, 1350, 1200	104–105 °C (lit. 106 °C)[15]
4-Methoxybenzaldehyde	3.83 (s, 3H) 6.92–7.72 (m, 2H) 9.80 (s, 1H)	2850, 2750, 1700, 1610, 1510, 1255	2,4-DNP derivative 190–191 °C (lit. 191 °C)[16]
Cyclohexanone	1.79–2.25 (m, 10H)	2940, 1710, 1450, 1310, 1220, 1120	2,4-DNP derivative 160–161 °C (lit. 162 °C)[19]
3-Methyl-2-butenal	9.96 (d, 1H) 5.87 (m, 1H) 2.18 (m, 3H) 1.99 (m, 3H)	3360, 3302, 2855, 2722, 1890, 1693	—
Acrolein	6.11–6.68 (m, 3H) 9.54 (m, 1H)	3360, 3060, 2800, 1690, 1420, 1360	—
Cinnamaldehyde	6.29–6.91 (m, 1H) 7.30–7.58 (m, 1H) 9.67 (d, $^{3}J_{\mathrm{HH}}=6.7$ Hz, 1H)	3025, 2805, 2740, 1680, 1630, 1450	2,4-DNP derivative 252–254 °C (lit. 255 °C)[16]
Heptanal	0.90 (t, $^{3}J_{\mathrm{HH}}=5.1$ Hz, 3H) 1.34–2.50 (m, 8H) 4.60–4.90 (m, 2H) 9.72 (t, $^{3}J_{\mathrm{HH}}=5.1$ Hz, 1H)	2950, 2725, 1750, 1460	2,4-DNP derivative 106–107 °C (lit. 108 °C)[16]

3. Since industrial processes for recycling and reoxidizing manganese dioxide to permanganate are well established, the reactions are infinitely sustainable, in theory.

4. Experimental

4.1. Preparation of oxidant

The oxidant was prepared by grinding potassium permanganate (1.0 g, 6.3 mmol) and active manganese dioxide (3.00 g, 34.5 mmol) in a mortar until a homogeneous powder was obtained. This reagent was used for all of the oxidations described herein. Active manganese dioxide, obtained commercially, is a reagent that is produced by the Carus Chemical Company of La Salle, Il, USA.

4.2. Procedure A. The oxidation of organic compounds by $KMnO_4/MnO_2$ under heterogeneous conditions

Substrate (2.0 mmol) was dissolved in CH_2Cl_2 (25 mL) and placed in a round-bottomed flask fitted with a magnetic stirrer. The oxidant, finely grounded $KMnO_4/MnO_2$ reagent (4.0 g), was added in small portions over a period of 15 min. The mixture was stirred vigorously at room temperature while the progress of the reaction was monitored by TLC. Upon completion of the reaction, the product was filtered through a sintered glass funnel to remove spent oxidant. The residue was then washed successively with CH_2Cl_2 (2× 20 mL). Evaporation of the solvent gave product that was characterized by the use of spectroscopy and melting points, as described below.

4.3. Procedure B. The oxidation of organic compounds by $KMnO_4/MnO_2$ under solvent-free conditions

Substrate (2.0 mmol) was added to the oxidant, a mixture of $KMnO_4$ and MnO_2 (4.0 g), in a 25 mL round bottomed flask. These reactants were then mixed by magnetic stirring at room temperature. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the residue was washed with a minimum amount of methylene chloride or diethyl ether. After filtration to remove any spent oxidant, the solvent was evaporated. Product of acceptable purity for most purposes was obtained. If greater purity is required, the product can be distilled or recrystallized. The products were characterized as described below.

4.4. Procedure C. The oxidation of organic compounds by $KMnO_4/MnO_2$ under solvent-free conditions and assisted by ultrasound irradiation

Substrate (2.0 mmol) and oxidant, a mixture of $KMnO_4$ and MnO_2 (4.0 g), were thoroughly mixed together and the reaction mixture was irradiated in a 25 mL beaker for an appropriate period at room temperature. The progress of the reaction was monitored by TLC. When complete, the reaction mixture was washed with methylene chloride or diethyl ether (2×20 mL). After filtration to separate spent oxidant, the solvent was evaporated. Relatively pure product was obtained and characterized as described below.

4.5. Characterization of products

The products of these reactions were characterized from their ^1H NMR and IR spectra and by comparison of their melting points (or those of their derivatives) with known compounds, as indicated in Table 4.

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