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The beneficial effect of manganese dioxide on the oxidation of organic compounds by potassium permanganate

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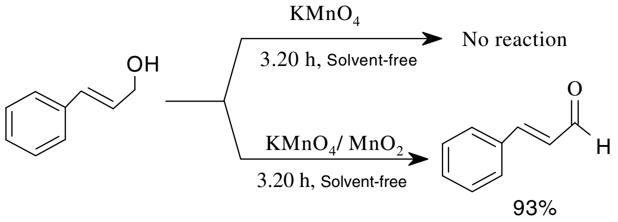

Addition of MnO_2 accelerates the oxidation of alkyl arenes, sulfides and allylic alcohols by potassium permanganate under solvent free and heterogeneous conditions.

KEY WORDS: catalytic effect; manganese dioxide; oxidation; potassium permanganate.

1. Introduction

Over the last 2 decades, chemistry under solvent free or heterogeneous conditions has become of increasing importance because it often produces improved reactivity and selectivity as well as facilitating product isolation [1]. When used in such reactions, the reagents are usually adsorbed on solid supports. One of the most striking examples of change in chemical reactivity associated with the use of solid supports is found with the well-known oxidant, potassium permanganate [2].

The use of potassium permanganate as an effective oxidant in organic chemistry has a long and extensive history [3]. Industrial applications have recently become more attractive environmentally by the introduction of a process for recycling MnO_2, a co-product of these reactions [4].

In the first reported example of the use of permanganate adsorbed on a solid support, aqueous $KMnO_4$ was added to molecular sieves and stirred until homogeneous, after which the excess water was evaporated [5]. The resulting permanganate impregnated molecular sieves were then used as a heterogeneous oxidant. Other solid supports such as alumina [6,7], silica [8], zeolites [9], montmorillonit K10 [10] and cation exchange oxidation resins [11] have also been used effectively as solid supports. Interestingly a number of hydrated salts of transition metals have also been found to work very well as promoters of heterogeneous permanganate oxidations. Of these, the most effective and most often used is copper sulfate pentahydrate [12,13].

The industrial utility of potassium permanganate as an oxidant is greatly enhanced if manganese dioxide, a co-product formed during the reduction of $KMnO_4$, can be separated and submitted for recycling at the conclusion of the reaction [2]. This is often difficult when solid supports, such as silica, montmorillonit K10, alumina or zeolites, are use in connection with oxidations under solvent free or heterogeneous conditions. Therefore the discovery of new approaches for the selective oxidation of organic compounds with $KMnO_4$, in which there is no need to separate MnO_2 from a solid support before recycling is of some importance in synthetic organic chemistry.

It is also well known that permanganate oxidation in aqueous media have been reported to take place autocatalytically [14] with either Mn^{2+} or MnO_2 acting as catalysts. With this in mind, we have studied the oxidation of organic compounds by MnO_2 when some solid manganese dioxide is present. In the approach taken, compounds were oxidized by $KMnO_4$ under solvent free conditions and under heterogeneous conditions, and the yields of products obtained with, and without, the addition of 20% MnO_2, all other conditions being held constant, were compared.

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Table 1
Comparison of the oxidation of organic compounds with $KMnO_4/MnO_2$ (5:1, w/w) and $KMnO_4$ under solvent-free conditions and in CH_2Cl_2 at room temperature

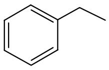
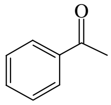
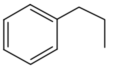
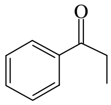
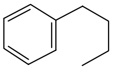
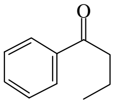
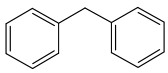
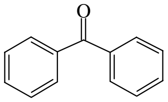
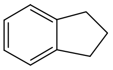
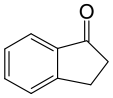
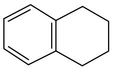
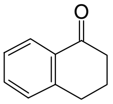
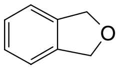
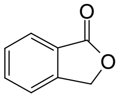
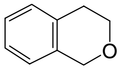
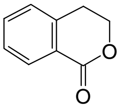
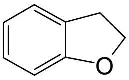
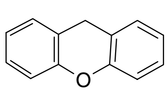
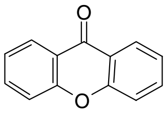
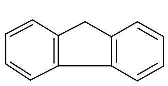
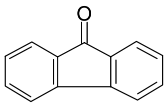
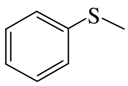
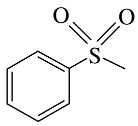
Entry	Substrate	Product	Time (h)	Yield (%)[a]		Time (h)	Yield (%)[b]	
				I[c]	II[d]		I[c]	II[d]
1[e]			17	10	23	51	20	70
2[e]			22	9	25	54	9	60
3[e]			27	14	30	53.5	10	48
4			7	23	44	143	15	72
5[e]			18	5	10	25	10	65
6[e]			21	10	24	60	23	63
7			5	41	55	41	40	52
8			18	32	61	20	39	76
9		No reaction	8	0	0	32	0	0
10			23	28	60	48	37	68
11			18	39	77	41	31	53
12			20	32	85	5	32	92

Table 1
Continued

Entry	Substrate	Product	Time (h)	Yield (%)[a]		Time (h)	Yield (%)[b]	
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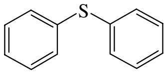
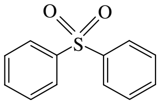
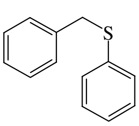
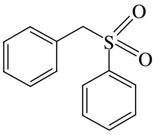
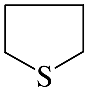
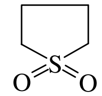
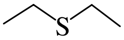
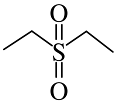
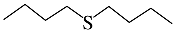
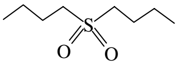
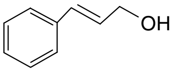
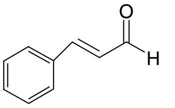
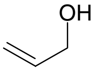
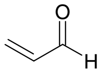
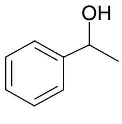
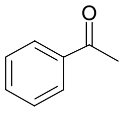
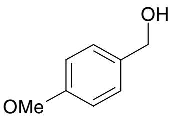
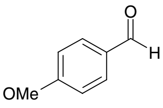
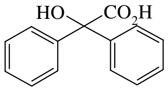
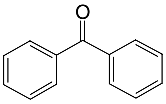
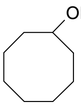
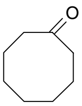
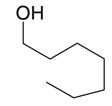
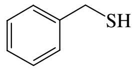
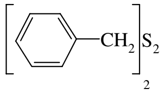
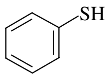
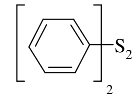
13			40	38	74	22	14	96
14			19	11	61	72	25	68
15			3	0	82	6	10	70
16			1	20	50	16	48	94
17			2.30	20	88	23	42	96
18	$[C_8H_{17}]_2S$	$[C_8H_{17}]_2SO_2$	12	0	35	4.5	17	85
19			3.20	0	93	5	0	60
20[e]			1.30	22	96	1.30	16	46
21			2	86	84	3	85	88
22			1	74	74	3	68	65
23			0.45	29	65	1.30	48	55
24			18	34	35	69	68	72

Table 1
Continued

Entry	Substrate	Product	Time (h)	Yield (%)[a]		Time (h)	Yield (%)[b]	
				I[c]	II[d]		I[c]	II[d]
25		No reaction	24	0	0	24	0	0
26			0.05	96	96	0.6	96	98
27			0.04	94	94	0.5	91	86

[a] Isolated yields under solvent free conditions.
[b] Isolated yields in CH_2Cl_2.
[c] In the absence of MnO_2.
[d] In the presence of MnO_2.
[e] Yield determined by GLC.

2. Experimental

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H-NMR spectra was recorded on a BRUKER DRX-500 AVANCE spectrometer at 500.13 MHz. NMR spectra were obtained on solutions in $CDCl_3$ using TMS as internal standard.

The oxidant was prepared by grinding potassium permanganate (1.0 g), using a pestle and mortar, until a fine powder was obtained. A second sample of the oxidant was prepared in exactly the same way, with the exception that MnO_2 (0.2 g) was added to the mixture. For the solvent free reactions, these oxidants were placed in two separate round bottom flasks in the absence of solvent and to each flask was added reductant (1 mmol). 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 in one of the flasks had been completely reacted or until a reasonable amount of time had elapsed. Methylene chloride (15 mL) was then added to each flask and the reaction mixtures were filtered through a sintered glass funnel. The residues were washed with additional methylene chloride (2 × 10 mL) and the solvent collected from each reaction was combined and evaporated on a flash evaporator. The yield was determined by GC analysis or from the integrals of the ^{1}H-NMR spectrum of the material obtained when most of the solvent had been evaporated. All products are known compounds with well-defined ^{1}H-NMR spectra.

The heterogeneous reactions were carried out in an identical way, except that 15 mL of methylene chloride was added to the oxidants prior to introduction of the reductants.

3. Results and discussion

As indicated from the data in Table 1, addition of MnO_2 increases the yields of ketones obtained from the oxidation of alkyl arenes (Entries 1–11) by up to 50%. The effect of MnO_2 is maximal when the alkyl arenes are oxidized under heterogeneous conditions in methylene chloride.

Sulfones are obtained very efficiently from the oxidation of sulfides. The beneficial effect of adding MnO_2 is significant for the oxidation of sulfides under both of solvent free and heterogeneous conditions (Entries 12–18). This is a highly useful reaction for the preparation of sulfones which are important intermediates in the synthesis of many organic compounds [15].

The observation that benzyl phenyl sulfide (Entry 14) is oxidized to the corresponding sulfone suggests that the reaction likely proceeds by way of an oxygen transfer mechanism. If the reaction involved a single electron transfer (SET) mechanism instead of an oxygen transfer mechanism, substantial amounts of benzaldehyde would have been formed [16,17]. Most other oxidations of sulfides under solvent-free conditions result in the formation of sulfoxides [18,19]; however, sulfoxides were not produced in these reactions.

As indicated by the results of reactions 19 and 20 in Table 1, it can be seen that the yields of carbonyl compounds obtained from the oxidation of allylic alcohols under both solvent-free and heterogeneous conditions are greatly increased when MnO_2 is added. However, no similarly improved yields were found for the oxidation of benzylic alcohols (Entries 21–23), aliphatic alcohols (Entries 24 and 25) or thiols (Entries 26–29).

4. Conclusions

1. The oxidation of organic compounds by $KMnO_4$, with and without added MnO_2, has been studied under solvent-free and heterogeneous conditions at room temperature. The yields form the oxidation of arenes, sulfides and allylic alcohols are improved when MnO_2 is present.
2. These reactions produce a coproduct that could be recycled under industrial conditions without further purification.
3. These results, which will be of practical use in synthetic organic chemistry, also present an interesting challenge for physical organic chemists who may wish to study their mechanisms.

Acknowledgment

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References

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