

Organic Solvent Controlling the Oxidativity of Potassium Permanganate

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It has been discovered that potassium permanganate can be a homogenous weak oxidant in organic solvent without the addition of water. If acetone is employed as the only solvent, among some common organic substrates included alkenes, alcohols, arenes, aldehydes and phenols, secondary alcohols are converted to the corresponding ketones and aldehydes to the corresponding acid. Compared with oxidation reaction of potassium permanganate in water, in anhydrous acetone system, potassium permanganate as a weaker oxidant has no influence on the alkyls in benzene rings, double bonds and so on. So potassium permanganate can exhibit selectivity by solvent controlling. Especially, when aldehydes are oxidized, the oxidation process is a green organic reaction for nearly all coproducts and solvent can be recycled.

Key Words: Homogeneous oxidation, Solvent controlling, Potassium permanganate, Organic compounds.

INTRODUCTION

Potassium permanganate, as a traditional oxidant is often used in oxidizing some organic compounds¹. The process is recognized as friendly to the environment because manganese dioxide, a by product formed by the reduction of permanganate, can be recycled². As a familiar strong oxidant, scholars have done few studies on how to control its oxidativity³. Almost all oxidation reactions concerted with potassium permanganate are occurred in water system with acid or base as catalysts⁴⁻⁷. It has recently been found when traded under heterogeneous conditions with potassium permanganate absorbed on some solid supports organic compounds are oxidized selectively⁸. Those methods bring such a problem that it is difficult to separate reaction by product manganese dioxide with the solid support. Shaabani *et al.*⁹ studied potassium permanganate as a heterogeneous oxidant in organic solvent without the use of solid support and other catalysts. Their method simplified the reaction system and needn't separate by product manganese dioxide with solid supports. In spite of their study results showed primary benzylic and secondary alcohols were converted to the corresponding aldehydes and ketones, alkyl arenes are oxidized to the corresponding α -ketones in good yields in presence of acetonitrile⁹, the reaction time is more than 10 h and it is known to all that acetonitrile is not an environmentally benign oxidant and harmful to human being. Recently, we found potassium permanganate does not dissolve in all organic solvents except acetone at room temperature¹⁰. If acetone is employed as the

only solvent, many organic compounds especial some molecules with bigger molecular weight are easier to dissolve so that oxidation reaction could proceed in a homogeneous system. Adopting this idea, we prepared a series of oxidation products of bigger molecular weight with potassium permanganate as homogeneous oxidant in acetone system without addition of water and other catalysts. Not only the oxidation reaction completed with better yield, but also the anhydrous acetone converts potassium permanganate into a weak oxidant, while potassium permanganate is strong one in other homogeneous solvent as water. Therefore, some different oxidative products will be gotten by solvent controlling the oxidativity of potassium permanganate. For example, with anhydrous acetone as the only solvent, potassium permanganate can oxidize aldehydes and not oxidize alkyls on the benzene rings. These suggested that the oxidation activity of potassium permanganate can be controlled by solvents. Particularly, some reactants of higher aldehydes can be easier to convert into the corresponding acids. However, in this organic solvent system, what potassium permanganate will do to common organic substrates such as cycloalkanes, alkenes, alcohols, aldehydes, arenes have been not done enough research. In this paper, an attempt has been made to investigate the oxidative degree of potassium permanganate to common organic substrates in anhydrous acetone system and which kind of selectivity that potassium permanganate reaches will be studied. Some of results of the reaction differ from the ones obtained with KMnO_4 as a heterogeneous oxidant in acetonitrile system.

EXPERIMENTAL

Initial reactants used in the synthesis such as 4-methylbenzaldehyde, 4-(4-ethylcyclohexyloxy)benzaldehyde and 4-(4-propylbenzyloxy)benzaldehyde were prepared in our laboratory as reported in literature¹⁰ with purity higher than 99 % and characterized by IR, GC-MS and ¹H NMR methods. Other reagents were analytical reagent from commercial sources and used without further purification.

The purities of compounds were detected by LC-10A instrument with methanol as eluent and flowing rate was 1 mL/min. Elemental analyses were conducted on a PE-2400 analyzer (Perkin-Elmer). IR (KBr) spectra were recorded on a Prestige-21 FTIR spectrophotometer (Shimadzu). Mass data were recorded on a GCMS-QP2010 (Shimadzu) and IE was 70 eV. ¹H NMR was obtained on a Bruker Avance 300 spectrometer (300 MHz, solvent CDCl₃). The DSC experiments were carried out on DSC Q1000 instrument (TA) and the determination condition was: the sample mass less than 5 mg; heating rate, 10 °C/min and samples were protected by nitrogen.

Preparation of 4-(4-methylbenzyloxy)benzaldehyde:

The acyl chloride of 4'-methylbenzoic acid was prepared by stirring a mixture of 4'-methylbenzoic acid (2.72 g, 20 mmol), SOCl₂ (5.9 g, 50 mmol) and at reflux temperature for 4 h, then the solvent was removed under reduced pressure. A brown liquid (acyl chloride) was obtained and used to next step without further purifying. 4-(4-Methylbenzyloxy)benzaldehyde was obtained by dissolving of 4'-methylbenzoic acylchloride in CH₂Cl₂ (40 mL) and dropped the solution into a solution of *p*-hydroxybenzene aldehyde (2.4 g, 20 mmol) and triethylamide (4 mL, 20 mmol) in CH₂Cl₂ (40 mL) and stirred at ambient temperature for 1d, then the reacting mixture was washed with 5 % NaOH and water. After being dried by Na₂SO₄, the solvent was removed under reduced pressure. The residue was recrystallized with ethanol, then a white crystal (2.22 g) was obtained in yield of 87 % (two steps). The 4-(4-ethylcyclohexyloxy)benzaldehyde and 4-(4-propylbenzyloxy)benzaldehyde were prepared by the same method with yields of 85 and 83 %.

Preparation of 4-(4-methylbenzyloxy)benzoic acid:

4-(4-Methylbenzyloxy)benzoic acid was prepared by heating and stirring a mixture of 4-(4-(methylbenzyloxy)benzaldehyde (0.37 g, 1 mmol) with acetone (40 mL) and some KMnO₄ (1.5 mmol) until reflux and continue 4 h. Then filtered the reaction solution, the acetone was remained to find if there is some other products. The residue was then washed many times by acetone and water to remove oil-soluble and water-soluble compounds. The residue dried was acidified for certain time by 10 % (v/v) hydrochloric acid. After filtered, the residue was washed by water until the filtrate without any acidity was dried under vacuum condition. The residue was extracted by acetone (50 mL) as solution. The extraction was concentrated and the solid was recrystallized with mixed solution of ethyl acetate and ethanol (v:v = 5:1). 4-(4-methylbenzyloxy)benzoic acid was then gained as white crystals. The other two products 4-(4-ethylcyclohexyloxy)benzoic acid and 4-(4-propylbenzyloxy)benzoic acid were obtained with the same method.

Oxidation of other organic compounds in anhydrous acetone system: Cyclohexene (0.82 g, 1.0 mmol) was dissolved

in 40 mL of acetone and potassium permanganate (2.35 g, 1.5 mmol) in a round-bottomed flask until reflux and continue 4 h. Then filtered the reaction solution, the acetone was remained to find if there is some other products by GC-MS. The residue was then washed many times by acetone and water to remove oil-soluble and water-soluble compounds. The residue dried was acidified for certain time by 10 % (v/v) hydrochloric acid. After filtered, the residue was washed by water until the filtrate without any acidity was dried under vacuum condition. The residue was extracted with acetone (50 mL) as solution so that the acidifying solid phase was obtained to examine if there was some other product by GC-MS.

Spectral data of some acids

4-(4-Methylbenzyloxy)benzoic acid: White needle crystal, m.p. 240-241 °C; IR (cm⁻¹): 2918, 2617, 2556, 1732, 1693, 1674, 1607, 1504, 1427, 1319, 1277, 1209, 1178, 1165, 1074, 1020, 928, 885, 847, 762, 742, 683. ¹H NMR (300 MHz, CDCl₃): 2.410 (s, 3H), 7.391-7.413 (m, 4H), 8.012-8.039 (m, 4H). Ms: 32 (0.46), 39 (5.29), 45 (0.31), 51 (1.96), 55 (0.37), 62 (4.52), 65 (14.98), 69 (2.06), 77 (0.67), 81 (2.06), 89 (3.66), 91 (32.12), 103 (0.05), 109 (0.67), 118 (0.03), 119 (100), 128 (0.10), 137 (0.36), 147 (5.3), 164 (0.09), 181 (0.06), 211 (0.03), 239 (0.36), 276 (5.3). Anal. calcd. for C₁₅H₁₂O₄: C, 70.31; H, 4.72. Found: C, 70.10, H, 4.91.

4-(4-Ethylcyclohexyloxy)benzoic acid: White needle crystal, m.p. 220-221 °C; IR (cm⁻¹): 2961, 2932, 2855, 2669, 2552, 2365, 2181, 2046, 1931, 1749, 1702, 1603, 1506, 1448, 1425, 1379, 1315, 1290, 1261, 1205, 1163, 1121, 1067, 1015, 993, 932, 850, 806, 760. ¹H NMR (300 MHz, CDCl₃): 0.904 (m, 6H) 1.243 (s, 3H), 1.539 (q, 2H, *J* = 4.0 Hz), 1.879 (d, 2H, *J* = 3.9 Hz), 2.131-2.170 (d, 2H, *J* = 3.9 Hz), 2.500 (t, 1H, *J* = 3.8 Hz), 7.177-7.203 (m, 2H), 8.127-8.153 (m, 2H). Ms: 29 (7.64), 36 (0.05), 39 (8.56), 41 (25.05), 45 (0.67), 51 (0.50), 55 (35.16), 57 (0.10), 63 (0.21), 67 (8.42), 69 (89.97), 79 (2.07), 81 (15.68), 85 (0.05), 91 (0.07), 95 (0.10), 107 (0.06), 111 (100), 121 (10.01), 147 (1.95), 140 (1.05), 147 (1.95), 165 (0.10), 173 (0.02), 185 (0.02), 213 (0.02), 239 (0.03), 247 (0.02), 259 (0.09), 267 (0.02), 276 (0.69): Anal. calcd. for C₁₇H₂₂O₄: C, 70.32; H, 7.64. Found: C, 70.21; H, 7.62.

4-(4-Propylbenzyloxy)benzoic acid: White needle crystal, m.p. 247-248 °C; IR (cm⁻¹): 2918, 2885, 2816, 2671, 2556, 2419, 2318, 1732, 1693, 1674, 1607, 1504, 1427, 1319, 1209, 1178, 1165, 1074, 1020, 928, 885, 847, 762, 743, 683, 665. ¹H NMR (300 MHz, CDCl₃): δ: 0.843 (t, *J* = 7.5 Hz, 3H), 1.568-1.589 (m, 2H), 2.609 (t, *J* = 8.0 Hz, 2H), 7.357 (m, 4H), 8.010-8.023 (m, 4H); Ms: 29 (1.33), 41 (4.78), 51 (2.04), 65 (3.72), 77 (4.16), 87 (0.06), 91 (18.95), 103 (2.15), 115 (2.26), 119 (8.53), 131 (1.08), 139 (0.90), 147 (100), 161 (0.14), 181 (0.15), 211 (0.07), 227 (0.07), 255 (0.21), 267 (0.14), 284 (0.32). Anal. calcd. for C₁₇H₁₆O₄: C, 71.82; H, 5.67. Found: C, 71.69, H, 5.82.

RESULTS AND DISCUSSION

Initial attempts to optimize the reaction conditions for the oxidation of aldehydes to the corresponding carboxylic acids were done using benzaldehyde as a suitable substrate. The optimum conditions of reaction were molar ratio of KMnO₄

to reactant is 1.5 to 1.0, the reaction time of 4 h and acidifying time of 1.5 h with the yield of 87 %. All reactions in this study were performed in the optimum conditions.

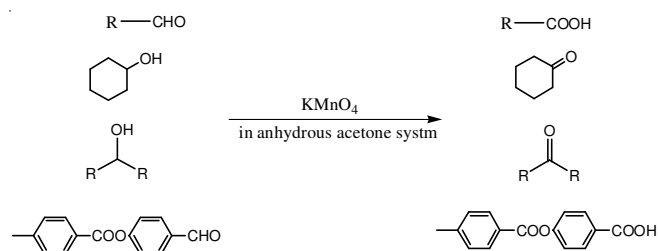
As indicated by the experimental results (Table-1), the cyclohexane, alkenes, aliphatic alcohols, ketones and arenes are difficult to be oxidized in this system, while aldehydes and secondary alcohols are oxidized in such surroundings. This shows that this solvent system without any water has reduced the oxidative ability of potassium permanganate. We know that all those compounds above, for example cyclohexane, alkenes¹¹ and arenes¹² will be oxidized by potassium permanganate with water as solvent. Acetone has lower polarity than water. The lower polarity makes it difficult for potassium permanganate to be ionized. However, the higher oxidativity of potassium permanganate is performed by its permanganate anion. The experimental result also shows the oxidativity of potassium permanganate would be controlled by changing the polarity of reaction solvent.

TABLE-1
REACTION RESULTS OF OTHER SUBSTRATES UNDER
THE OPTIMUM OXIDATION CONDITION

Reactant	Product		Yield (%)
	Liquid phase	Acidifying of solid phase	
	No reaction	No reaction	0
	No reaction	No reaction	0
	No reaction	No reaction	0
	No reaction	No reaction	0
	No reaction	No reaction	0
	No product		72
	No product		70
	No product		87
	No reaction	No reaction	0
	No reaction	No reaction	0
	No reaction	No reaction	0
		No product	67
		No product	65
		No product	72
CH_3COCH_3	No reaction	No reaction	0
	No reaction	No reaction	0
	No reaction	No reaction	0
	No reaction	No product	0

Under this homogenous condition, all reaction types that could process are shown in **Scheme-I**. Aldehydes could be converted to corresponding carboxylic acids. However, during the reaction process the acid is not produced directly, instead we first got the intermediates as the form of potassium salt of carboxylic acid, which were absorbed by MnO_2 so that intermediates and reaction solvent could be separated by filter operation. The intermediates were then acidified, filtered and

washed by water to remove acid. The solid was last extracted by acetone to give the corresponding carboxylic acids with high purity. The process is easier to separate products and reactants and solvent acetone can be used circularly. Because aldehyde oxidation is an important reaction for the manufacture of organic acids¹³, the separating methods of aldehyde and its corresponding acids is also very important. As usual, separating both of them first exact by organic solvent and then purify chromatography using dichloromethane as eluent¹⁴. The oxidation process can provide a simpler method to separate both of them and reaction solvent can be recycled.



Scheme-I The oxidation reaction that can process in anhydrous acetone system

In particular, when the method is used to oxide other reactants as 4-(4-methylbenzoyloxy)benzaldehyde, 4-(4-propylbenzoyloxy)benzaldehyde, which have aldehyde and alkyl groups both localized in benzene rings. The corresponding acids, which were the intermediates to synthesize a kind of liquid crystals^{15,16}, are obtained with good yields. Those structures of products also show the oxidation process would not affect the alkyls localized in benzene rings. It indicates that the oxidation process has the opportunity to fulfill selective oxidation between aldehyde and aromatic alkyl groups. The better yields must have some relationships with the acyloxy groups localized in *para*-position of aldehyde group. The acyloxy groups as an electron-donating group could increase the electron density of benzaldehyde in order to increase the opportunity of aldehyde group to be oxidized. To prove this, we will further study a series of reactants which have the structure of benzaldehyde with other group for example methoxy, nitro, chloro groups on the benzene rings to know how the electronic effect works to such oxidation process. The target compound 4-(4-ethylcyclohexacyloxy)benzoic acid still proves this oxidation process could not oxidize the cyclohexane structure. Potassium permanganate also has selective oxidativity between benzaldehyde and cyclohexane (Table-2).

TABLE-2
REACTION RESULTS OF SELECTIVE
OXIDATION IN THIS SYSTEM

Reactant	Product		Yield /%
	Liquid phase	Acidifying of solid phase	
		No product	32
	No product		75
	No reaction		77
	No product		90
	No product		92
	No product		89

Except for the aldehyde compounds, we find the system convert the secondary alcohols to corresponding ketones and aromatic alcohol to corresponding aldehydes, which would not be further oxidized in the same system. This result also shows the secondary alcohols and aromatic alcohols are easier to be oxidized than aliphatic and alicyclic primary alcohols. This reaction process could get the same result as other oxidation reactions of alcohols with the present of catalysts^{17,18}. The oxidation process also have the chance to carry out selective oxidize between primary and secondary alcohols (Table-2). It is noteworthy that those function selective oxidations can be achieved with this method, which is generally problematic in classical oxidation process of potassium permanganate.

Conclusion

The present study found anhydrous acetone system itself gives potassium permanganate an opportunity to fulfill a homogeneous oxidation of organic compound. Further research of this reaction shows this oxidation has greatly simplified the experiment and purified procedure without the addition of water. In this system, anhydrous acetone, as a solvent of weaker polarity, has controlled the oxidativity of KMnO_4 so that some selective oxidations can carried out.

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