COMMUNICATIONS TO THE EDITOR

Organic Sonochemsitry. Ne Ultrasound Reaction Apparatus Applied for Oxidation of Alcohols with $KMnO_4$

Byung Hee Han*, Dae Hyun Shin, Dong Gyu Jang, and Sung Nam Kim

**Department of Chemistry, College of Natural Science Chungnam National University, Daejeon 305 - 764.*

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There is a growing list of successful application of ultrasound to organic synthesis[1-4]. In the most of ultrasound procedures, the reactions are carried out under sonication in an ultrasound laboratory cleaner.

We found that irradiation from the ultrasonic cleaner is most effective when agitation mounts are to achieve maximum cavitation of the reagents. In practice, this focal spot moved around possibly because of changing temperature and distortion of the steel bottom caused by local heating of the transducer.[5] Moreover, the intensities of sound waves become weak during propagation through water media.

However, the rate enhancements can be improved greatly by using probe type sonicator. The primary advantages of the immersion tip is that the accoustic intensities available are much higher than bath type sonicator, and consequently the observed sonochemical rate enhancements are much greater. But sample contamination by probe erosion remains a problem[6].

In this paper, we describe a newly designed ultrasonic reactor which circumbents all the above disadvantages. A diagram of the apparatus used in the present experimental applications is shown in Figure 1.

The main improvement is that reactor is attached directly to transducer. The obvious advantages of this arrangement are elimination of substrate contamination by probe erosion and adjustment of reaction vessel on sweet spot in water bath. More importantly, a great rate acceleration over the traditional reaction setup was observed. In our first experiment with this ultrasonic reactor, permanganate oxidation of alcohols[7] was carried out in order to compare the effects of ultrasound irradiation by ultrasound laboratory cleaner as well as mechanical agitation. Typical results are presented in Table 1. As expected, the results listed in the Table clearly showed that the heterogeneous oxidation reaction proceeded smoothly under sonication with this reactor. Good yields were obtained in most cases (entry 2,4-9) and the oxidation proceeded essentialy to completion within 1 hr. Our yields generally are better than those obtained by the ultrasonic laboratory cleaner.

These results might be due to effective cavitation by directly attached transducer to reactor. As a result of this arrangement, strong cavitation occur constantly without interruption as in the bath type sonicator.

The best results were obtained with a sonicator at the maximum power (120 watt). Prolongation of the reaction time (entry 1,3,10) did not improve the yields. The overoxidation to carboxylic acid was completely suppressed as indicated by GC and proton NMR spectrum. However, we recognized that permanganate oxidation of cinnamyl alcohol gave decidedly different product ratios as a function of the irradiation of ultrasonic intensity. For example, the cinnamyl alcohol was treated with potassium permanganate and irradiated using ultrasonic reactor (Figure 1) with 120 watt, 37% of benzaldehyde, 42% of benzoic acid and 21% of cinnamoyl aldehyde were formed. But, under the exactly same reaction conditions except ultrasonic intensity (80 watt instead of 120 watt), 90% of cinnamoyl aldehyde was realized (entry 4). We also found that benzene was a superior solvent to hexane. When the same reaction was carried out with hexane (entry 1,2,5) instead of benzene, no reaction was observed.

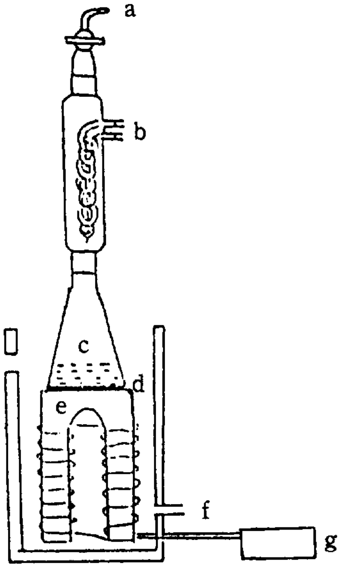

Figure 1. Schematic diagram of the apparatus. a. connected to N_2; b. condenser; c. glass reactor (4 cm dia. x 7 cm high); d. attached with epoxy glue; e. transducer (4 x 7 cm, 28 Khz); f. coolant inlet; g. ultrasound generator (110v, maximum 120 watt): h. coolant outlet.

In a typical experiment, a single necked static glass flask (Figure 1) was found, capable of withstanding vibration by

Table 1. $KMnO_4$ Oxidation of Alcohols using various setups[a]

Entry	Alcohol	Product	Yield (%, time in hr)		
			New reactor[b]	Ultrasound[c] Lab. Cleaner	Mechanical[c] Stirrer
1	Cyclohexanol	Cyclohexanone	87(3)[d]	53.2(5)	4.2(5)
2	2-Octanol	2-Octanone	93(1)	93(5)	2.6(5)
3	Cyclododecanol	Cyclododecanone	45(2)[d]	84.1(32)	
4	$PhCH = CHCH_2OH$	$PhCH = CHCHO$	90(2)[e]	82.8(3)	4.5(3)
5	1-Octanol	Octanal	92(1)	80.5(14)[f]	
6	$PhCH_2OH$	$PhCHO$	90(0.5)	29.7(1.5)	
7	$PhCH(OH)Ph$	$PhCOPh$	95(0.5)	98.9(5)	
8	Cycloheptanol	Cycloheptanone	85(1)	45.1(5)[g]	4.5(5)[h]
9	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CHO$	92(0.5)	73.8(3)[g]	16.5(5)[h]
10	1-Octene-3-ol	1-Octene-3-one	21(12)[d]	43.6(24)	

[a] 2:12.8 mmole of alcohol : $KMnO_4$ were employed at 15 °C in 6 m*l* of benzene. [b] isolated yield, otherwise noted. [c] same reaction conditions except temperature (50 °C) and solvent (entry 1,2,5) used hexane repectively. see : ref. 7b. [d] GC yields. [e] carried out with 80 watt. [f] octanoic acid. [g] our results at same reaction condition. [h] our results with magnetic stirrer.

transducer. Alcohol (0.01 mole), 2g (0.0128 mole) of powdered and dried $KMnO_4$ and 6 m*l* of benzene were added to the flask under nitrogen and the mixture was sonicated for 1-12 hrs. Reaction vessel temperature was maintained at 15 °C by using a running water bath.

A strong atomization phenomena (fogginess) was occurred during sonication. The reactions were monitored by GC. Isolation involved filtering to remove $KMnO_4$, ether washes of $KMnO_4$. The major product was isolated by simple distillation under reduced pressure or crystallization. The products were identified by GC, IR and NMR spectra. We are currently exploring a number of applications of this reactor and will report on them in due course.

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Enantioselective Inhibition Effect on Esterolytic Activity of β-Cyclodextrin by Inclusion with N-Benzoxycarbonyl-L-histidine

Burm-Jong Lee[†] and Iwhan Cho[*]

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131-650
[†]Department of Chemistry, Inje University, Kimhae 621-170.
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Fine processes in which substrates bind into cyclodextrin cavities and then undergo reactions with one of the secondary cyclodextrin's hydroxyl groups have attracted great attention as models of enzymatic reactions[1]. To improve the reaction rates[2-4] and stereoselectivities[3,4] for many types of reactions, particularly for the cleavage of activated esters, the derivatives of cyclodextrins[5-7] have also been studied. In those systems catalytic or reactive functional groups such as imidazole are present to attack the bound substrate. However, the alteration of cyclodextrins' own catalytic activity