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Vanadium Catalyzed Partial Oxidation of Some Saturated Hydrocarbons to Functionalized Products Under Mild Conditions

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Abstract

Partial oxidation of cyclopentane, cyclohexane, cycloheptane and propane to oxygenated products has been investigated using vanadyl acetylacetonate catalyst in presence of oxidant $K_2S_2O_8$ in CF_3COOH (TFA) solvent. It has been observed that the primary products were alcohols and carbonyl compounds. However, in the reaction of cycloheptane and propane, carbonyl was not formed. Alcohols subsequently reacted with TFA and produced esters. In case of propane, two esters were observed where *iso*-propyl trifluoroacetate was the dominant product and *n*-propyl trifluoroacetate was the minor product. In this case, about 89 mol% conversion was achieved. The conversion of cycloalkanes is found lower than that of propane. For the cyclohexane functionalization, the optimum condition found 7.5 mmol of $K_2S_2O_8$, 5 mL of CF_3COOH , 0.1 mmol of catalyst, 80°C reaction temperature and 1 mmol of cyclohexane.

Key words: Partial oxidation, Homogeneous catalysis, Hydrocarbon functionalization, Potassium persulfate and Trifluoroacetic acid

Introduction

The functionalization of saturated hydrocarbons to valuable oxygen-containing compounds is a very important subject of both fundamental and technological significance (Sheldon and Kochi, 1981). However, the replacement of H of C-H bond of alkanes by oxygen is challenging due to high bond strength (Hill 1989; Schuchardt *et al.*, 2001; Batiot and Hodnett, 1996; Labinger, 2004).

Cyclohexane is one of the available saturated hydrocarbons and oxidation of which in the liquid phase is of great industrial importance.

In the solution phase catalytic oxidation of cycloalkane by direct attack of oxygen, two drawbacks can be encountered. One is the low solubility of oxygen in the solution and

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the other one is the energy-consuming by oxygen activation. To overcome those problems various oxidants have been explored and alternative sources of active oxygen such as iodobenzene (Groves and Nemo, 1983), hydrogen peroxide (Tung *et al.*, 1992), alkylhydroperoxide (MacFaul *et al.*, 1997) are used. The kinetics of cyclohexane and cyclopentane oxidation by hydrogen peroxide catalyzed by iron porphyrins in acetonitrile solutions is studied at room temperature (Karasevich and Karasevich, 2002). The cyclohexane is oxidized to the corresponding alcohol, ketone, and hydroperoxide. The alcohol and ketone are formed by the molecular pathway in a ratio of 7 : 1. The catalytic activity of redox metals such as Ti, Co, Fe and Cr supported on mesoporous silicate are tested in the liquid phase oxidation of cyclohexane with tert-butylhydroperoxide (TBHP) as oxidant. Supported Cr and Co showed excellent performance in the oxidation of cyclohexane, Cr being highly selective to cyclohexanone (Anand *et al.*, 2006).

Oxidation of cyclohexane by hydrogen peroxide in the presence of catalytic amounts of the Keggin-type heteropolytungstates was found to produce cyclohexanol, cyclohexanone and, in certain cases, cyclohexyl hydroperoxide (Simoes *et al.*, 1999). The reactions were carried out in acetonitrile, using tetra *n*-butylammonium salts of the catalysts and aqueous 30% hydrogen peroxide as oxidant. The polyanions of the het-

eropoly acids showed higher catalytic activity and different selectivity for the oxidation of cyclohexane. Polychlorophthalocyanine and tetrasulfophthalocyanine complexes of iron are employed as catalysts for the oxidation of cyclohexane using tert-butyl hydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA) and hydrogen peroxide as oxidants. Catalysis using the catalyst was performed in a dimethylformamide:dichloromethane (3:7) solvent mixture. The products of the catalysis are cyclohexanone, cyclohexanol and cyclohexanediol. The relative yields of the products depended on oxidant and the catalyst. TBHP was found to be the best oxidant since minimal destruction of the catalyst and higher selectivity in the products were observed when this oxidant was employed (Grootboom and Nyokong 2002).

In this study potassium persulfate ($K_2S_2O_8$) is used as an oxidant for the oxidative functionalization of cycloalkanes specially cyclohexane in the presence of $VO(acac)_2$ catalyst in trifluoroacetic acid solvent. The reaction conditions such as reaction temperature, amount of $K_2S_2O_8$, TFA and reaction time.

Materials and Methods

Various types of saturated hydrocarbons such as propane (Bangladesh Oxygen Company, 97%); cyclopentane (BDH

Chemicals, 99.5%), cyclohexane (BDH Chemicals, 99.5%), cycloheptane (BDH Chemicals, 99.5%) and other chemicals such as vanadyl acetyl acetonate (Wako, 99.0%), trifluoroacetic acid (E-Merk, Germany, 99.8%), potassium persulfate (E-Merk, Germany, 99.9%) etc. were used without further purification.

Equipment

High pressure stirred autoclave (Buchi Glass Uster 350, Switzerland) was used for experimental purpose and Gas chromatograph 14B was used for product analysis.

Procedure

The reactions were carried out in 200 mL high pressure stainless steel magnetic coupled autoclave. In this functionalization reaction, vanadyl acetyl acetonate, $\text{VO}(\text{acac})_2$ was used as catalyst and potassium persulfate was used as oxidant which release oxygen to the hydrocarbon molecules. Trifluoroacetic acid (CF_3COOH , TFA) was used as a solvent. About 0.1 mmol of catalyst and 5 mmol of $\text{K}_2\text{S}_2\text{O}_8$ were placed in the stainless steel autoclave equipped with magnetic coupled mechanical stirrer. Then 5 mL of TFA and 5 mmol of cycloalkanes were introduced into the reactor. Then the reactor was closed and ensured the complete seal. In the case of propane, a 25 mL autoclave was used. It was flashed with propane after clos-

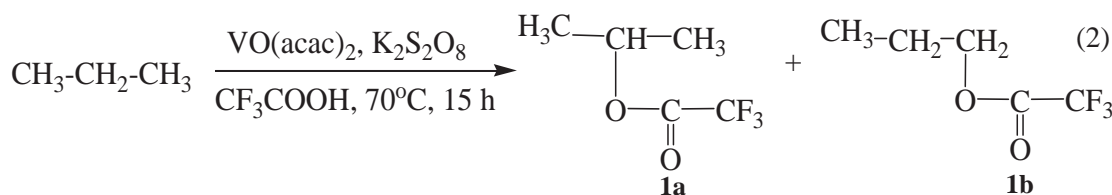
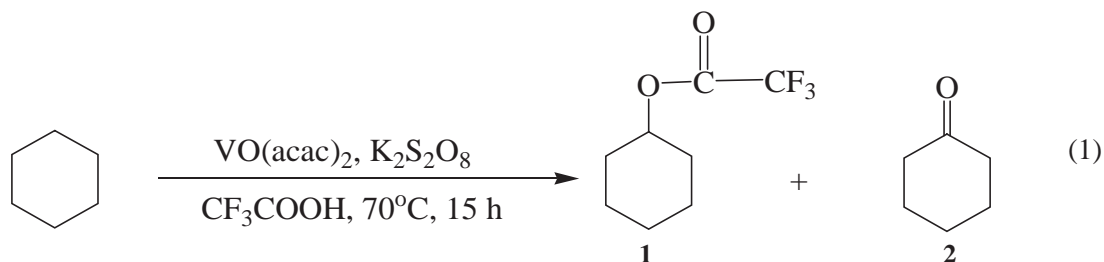
ing and pressurized to 5 atm. Then the autoclave was heated to a desired temperature with stirring. The reaction was proceeded under different conditions such as temperature, amount of oxidant, amount of TFA, amount of cycloalkane etc. to optimize them. This is because the conditions mentioned usually affect the yield of products in the hydrocarbon functionalization reaction (Asadullah *et al.*, 2000).

After 15 h (Asadullah *et al.*, 2000), the autoclave was cooled on an ice bath for 15 min and then opened. About 80 mg of an internal standard (*n*-butanol for the product of propane and cyclooctanol for the product of cycloalkane) was added into the reaction mixture and stirred for 5 minutes. Contents of the reaction mixture were analyzed by gas chromatograph (GC 14B).

Results and Discussion

The $\text{VO}(\text{acac})_2$ has been used for functionalization of cycloalkanes and *n*-alkane in the presence of $\text{K}_2\text{S}_2\text{O}_8$ as oxidant and CF_3COOH as solvent. Equation (1) shows the representative reaction of cycloalkanes and equation (2) shows the representative reaction of *n*-alkane. The results of the functionalization reaction are summarized in Table I.

In equation (1), the ester product was formed as dominant product and carbonyl compound



was formed as minor product as shown in Table I. However, as shown in equation (2) the carbonyl product was not formed. In both of the reactions the alcohols were the primary products which in turn produced ester products by esterification with trifluoroacetic acid. Propane produced two types of esters, the dominant one was the *iso*-propyl trifluoroacetate (1a) and the minor one was the *n*-propyl trifluoroacetate (1b).


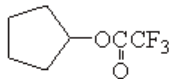
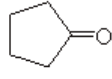

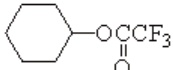
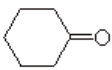

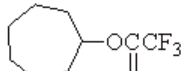

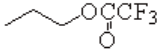
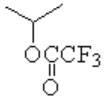
Cyclopentane underwent this reaction to yield cyclopentanol, 0.18 mmol and cyclopentanone, 0.1 mmol, giving a total yield of 5.6 mol% (based on cyclopentane, entry 1). Cyclohexane gave a remarkably high yield (14.8 mol%) (entry 2). On the other hand, cycloheptane gave only ester product in 3.4 mol% yield. Propane also underwent this reaction to yield 15 mol%. From the data of this table, it is obvious

that among the cycloalkanes, cyclohexane undergoes the reaction most effectively. In terms of product selectivity, cycloheptane gave only one product; however, the yield was very low. On the other hand, propane did not give carbonyl compound but a mixture of the esters of two alcohols. The yield obviously depends on the reaction conditions and thus, this reaction was optimized in terms of temperature, amount of $\text{K}_2\text{S}_2\text{O}_8$, amount of CF_3COOH and amount of alkanes.

Effect of temperature

We have investigated the effect of temperature on the yield of reaction from room temperature to 90°C while the other conditions remained fixed as before. The results are represented in Fig. 1. It can be seen from this figure that the yields of **1** and **2** at room temperature are minor (0.01 and 0.01 mmol,

Table I. Functionalization of various hydrocarbons^a

Hydrocarbon	Products		Amount of products (mmol)		Total yield, (mol%) ^b
	1	2	1	2	
			0.18	0.10	5.6
			0.56	0.18	14.8
			0.17	--	3.4
			0.55 ^c	--	15.0
			0.20 ^d		

^aReaction conditions: 200-ml autoclave, cycloalkane (5 mmol), propane (5 mmol, 25 mL autoclave), VO(acac)₂ (0.1 mmol), K₂S₂O₈ (5 mmol) and CF₃COOH (5 ml) at 70°C. ^bGC yields based on hydrocarbons. ^cProduct **1a**, *iso*-propyl trifluoroacetate and ^dproduct **1b**, *n*-propyl trifluoroacetate.

respectively). The total yield of products **1** and **2** substantially increased as the reaction temperature increased and attained the maximum values of **1** and **2** (0.60 and 0.20 mmol, respectively) at 80°C. The yields of both of them decreased suddenly at high temperature beyond 80°C. The decreasing trend may be due to the thermal or catalytic decomposition of all products at high temperature to the smaller molecular products

which are actually obtained on the GC chart as several peaks. The other possibility is the thermal decomposition of K₂S₂O₈ at high-temperature which would cause the insufficiency of the oxidant to reoxidize vanadium species to the higher oxidation state in the reaction mixture. Therefore, it is apparent that 80°C is the convenient temperature for the functionalization of cyclohexane.

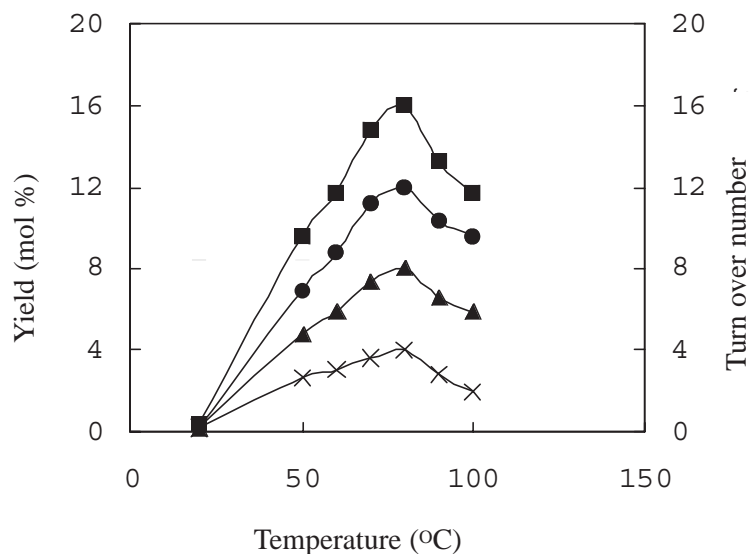


Fig. 1. Effect of temperature on the yield of products and turnover number of catalyst. (■) total yield, (●) yield of ester, (X) yield of ketone, (▲) turn over number.

Effect of the amount of $K_2S_2O_8$

The oxidant such as $K_2S_2O_8$ in this reaction plays a key role for reoxidation of active species of the vanadium (Piao *et al.*, 1999). Therefore, the effect of the amount of oxidizing agent, was investigated in this reaction where cyclohexane (5 mmol), $VO(acac)_2$ (0.1 mmol) and CF_3COOH (5 ml) were used at 80°C for 15 h. The results are shown in Fig. 2. It is seen from this figure that the reaction of cyclohexane in the absence of $K_2S_2O_8$ did not take place. The reaction proceeded significantly when at least 1 mmol of $K_2S_2O_8$ was used. The total yield and the turnover number increased sharply with increasing the amount of $K_2S_2O_8$ up to 8 mmol. Further increase of the amount of

$K_2S_2O_8$ is the cause of a slight decrease in yield and also in turn over number. The use of excess $K_2S_2O_8$ beyond 8 mmol will be wasteful. In the presence of large amounts of $K_2S_2O_8$, two possibilities for decreasing the yields of **1** and **2** have been encountered: one is lower efficiency of stirring and the other one is complex reaction.

Effect of the amount of CF_3COOH

The experiments were carried out with the variation of the volume of CF_3COOH between 2 and 15 ml while the other conditions were held constant as earlier. The results are shown in Fig. 3. The reaction of propane did not take place when the amount of CF_3COOH used was less than 2 ml. The

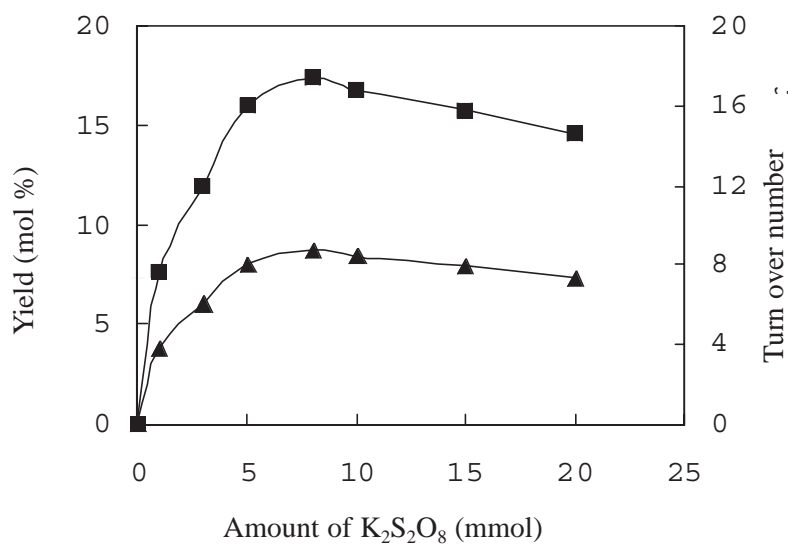


Fig. 2. Effect of the amount of K₂S₂O₈ on the yield of products and turn over number of catalyst. (■) total yield, (▲) turn over number.

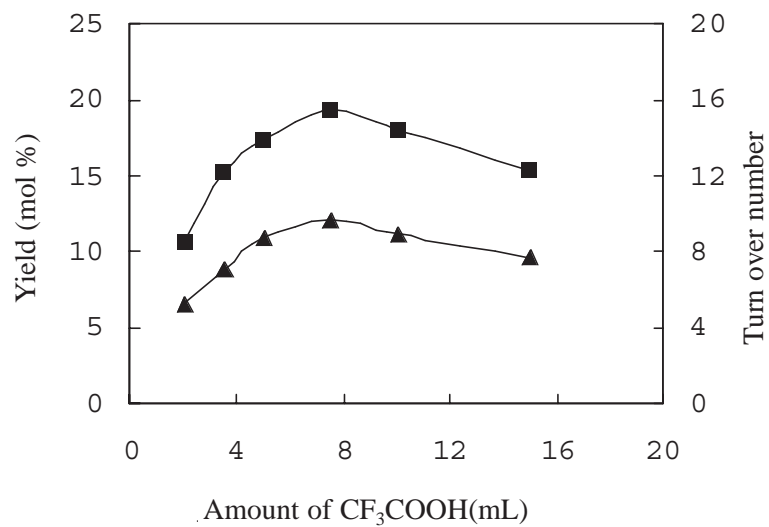


Fig. 3. Effect of the amount of CF₃COOH on the yield of products and turn over number of catalyst. (■) total yield, (▲) turn over number.

reaction significantly proceeded when at least 2 ml of CF_3COOH was used.

It can be seen that the total yield and the turn over number increased with increasing the amount of CF_3COOH up to 7.5 ml where the maximum total yield is 19.4 and the turn over number of the catalyst is 9.7. Then the yield and turn over number decreased with increasing the amount of CF_3COOH . The large volume of the solvent diluted the reaction mixture and decreased the yield. Considering the results of this experiment it is concluded that 7.5 ml of CF_3COOH is the optimum amount for this reaction.

other conditions constant. The results are summarized in Table II. The results show that the use of 1 mmol cyclohexane gave moderately high yields, giving 0.32 and 0.09 mmol of **1** and **2**, respectively. The amounts **1** and **2** increased constantly with increasing the amount of cyclohexane. It is obvious from these findings that increasing the concentration of cyclohexane facilitates the functionalization reaction. The yield of the total products based on cyclohexane is the highest (about 41 mol% yield) when 1 mmol of cyclohexane was used in this reaction. Then the yield of the total products decreases constantly with increasing the amount of cyclohexane.

Table II. Effect of the amount of cyclohexane on the yields of products and turn over number of catalyst^a

Entry	Amount of cyclohexane (mmol)	Product (mmol)		TON ^b	Yield ^c
		1	2		
1	1	0.32	0.09	4.1	41.0
2	2	0.47	0.13	6.0	30.0
3	3	0.59	0.16	7.5	25.1
4	4	0.67	0.22	8.9	22.3
5	5	0.71	0.25	9.7	19.4
6	6	0.75	0.26	10.1	16.8
7	7	0.76	0.26	10.2	14.6

^aReaction conditions: 200-ml autoclave, $\text{VO}(\text{acac})_2$ (0.1mmol), $\text{K}_2\text{S}_2\text{O}_8$. (10 mmol) and CF_3COOH (5 ml) at 80°C for 15 h. ^bTurnover number based on $\text{VO}(\text{acac})_2$.

^cGC yields based on cyclohexane.

Effect of the amount of cyclohexane

The reaction was carried out by adding different amounts of cyclohexane, keeping the

Conclusion

Alkanes including *n*-alkane and cycloalkane have been functionalized in the presence of

VO(acac)₂, K₂S₂O₈ and CF₃COOH under mild conditions. The reaction conditions for cyclohexane functionalization has been optimized. The optimum reaction conditions were 7.5 mmol of K₂S₂O₈, 5 mL CF₃COOH, 0.1 mmol of catalyst and 80°C reaction temperature. The maximum yield of the products has been found to be 41 mol% when 1 mmol of the reactant was used.

Acknowledgement

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