A New System for Alkane Oxidation. Modification of Gif-type Reactions Using O_2/H_2 with a Pd Catalyst

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We have investigated the modification of Gif-type reactions using hydrogen peroxide formed *in situ* by the palladium catalyzed combining of oxygen and hydrogen. The oxidation of cyclohexane in the solvent mixture, acetone-acetic acid, gives cyclohexanol and cyclohexanone with rather high yields, but any solvent containing pyridine is not suitable for the modified system.

The development of new reaction systems for the oxidation of saturated hydrocarbons under mild conditions has become a stimulating research area in recent years.[1-8] In biomimetic oxidation systems, the Gif-systems[7,8] developed by Barton and co-workers are attractive because they consist of simple and readily available reagents. Two systems, Gif^{IV} and $GoAgg^{II}$, are known as the most practical members of the Gif family.[8] The Gif^{IV} system employs iron(II), molecular oxygen, acetic acid as a proton source, and zinc dust as a reducing agent while the $GoAgg^{II}$ system employs iron(III) and hydrogen peroxide as a shunt agent. Besides, in both systems, the pyridine-acetic acid mixture is used as a solvent. However, the modification that involes using molecular oxygen and avoiding a reducing agent like zinc should be valuable progress.

In this study, we have focused on the development of a new system based on Gif-systems and using hydrogen peroxide formed *in situ* by the palladium catalyzed combining of molecular oxygen and hydrogen.

We used iron chlorides like Gif-type reactions, but we did not use any metallic reducing agent or hydrogen peroxide; instead, hydrogen and oxygen gases were added together with a Pd/alumina. The reaction was conducted in a flask equipped with gas bubbler and refrigerated condenser as follows: $FeCl_2 \cdot 4H_2O$ (or $FeCl_3 \cdot 6H_2O$) and palladium on alumina (Aldrich, Pd content 1%) were added to cyclohexane in a solvent and the gases of hydrogen and oxygen were bubbled through the stirred reaction mixture. Various mixtures of acetic acid, pyridine and acetone were examined. Unless otherwise stated, the reaction time was 3 h. The products were analyzed by gas chromatograph (Shimadzu GC-14A) equipped with a 5% OV-17 on Chromosorb column with a flame ionization detector. The products were only cyclohexanol and cyclohexanone except for the reactions of extended time.

The reaction results using iron(II) chloride are summarized in Table 1. First we examined the original solvent of Gif-systems, pyridine-acetic acid, but it gave poor yield (entry 1 in Table 1) unlike Gif-systems. It is likely that the mixture of pyridine and acetic acid is not suitable for the hydrogen peroxide formation from oxygen and hydrogen. Moreover, there have been many attempts to substitute part or all of the pyridine by other solvents in Gif-systems[9,10] because their implementation on an industrial scale is undesirable due to the large quantities of pyridine required and its toxicity.

Therefore, we tried to add each component of the original Gif-type solvent on to acetone solvent that has been proven[11] to be suitable for the formation of hydrogen peroxide from oxygen and hydrogen. A little addition of acetic acid on to acetone solvent improves the yields for cyclohexanol and cyclohexanone greatly (entry 3, 4 in Table 1), showing the high selectivity for the alcohol formation, but addition of pyridine gives the opposite effects on the oxidation (entry 8, 9 in Table 1). As acetone is replaced with acetic acid gradually in the oxidation system, the yields increase up to the acetic acid/acetone ratio 3/17, and

Table 1. Oxidation of cyclohexane with $FeCl_2$-Pd/O_2-H_2^{a}

Entry	Solvent (ml)	Yield^b (mol %)		
		alcohol	ketone	total
1	pyridine 20 acetic acid 2	0.11	1.39	1.50
2	acetone 20	1.30	0.27	1.57
3	acetone 19 acetic acid 1	3.50	0.62	4.12
4	acetone 17 acetic acid 3	3.94	0.83	4.76
5	acetone 15 acetic acid 5	3.22	0.64	3.86
6	acetone 10 acetic acid 10	1.68	0.36	2.04
7	acetic acid 20	0.58	0.20	0.78
8	acetone 15 pyridine 5	0.15	0.08	0.23
9	pyridine 20	0.10	0.38	0.48

a)Condition: cyclohexane (59.4 mmol), $FeCl_2 \cdot 4H_2O$ (1.5 mmol), Pd/alumina (1 g), H_2 (20 ml/min), O_2 (20 ml/min), reaction temp. = 30°C, reaction time = 3 h. b)Yields are based on cyclohexane.

Table 2. Oxidation of cyclohexane with $FeCl_3$-Pd/O_2-H_2^{a}

Entry	Solvent (ml)	Yield^b (mol %)		
		alcohol	ketone	total
1	acetone 20	1.43	0.24	1.67
2	acetone 19 acetic acid 1	2.89	0.49	3.39
3	acetone 17 acetic acid 3	4.22	0.80	5.02
4	acetone 15 acetic acid 5	1.90	0.37	2.27
5	acetone 10 acetic acid 10	1.18	0.20	1.38
6	acetic acid 20	0.06	0.02	0.08

a)Condition: cyclohexane (59.4 mmol), $FeCl_3 \cdot 6H_2O$ (1.5 mmol), Pd/alumina (1 g), H_2 (20 ml/min), O_2 (20 ml/min), reaction temp. = 30°C, reaction time = 3 h. b)Yields are based on cyclohexane.

subsequently decrease. With using iron(III) chloride, the same effects of acetic acid addtion to acetone solvent are seen (Table 2).

To understand the promoting effect of acetic acid, first of all, the solubilities of iron chlorides in the reaction solvents were checked. $FeCl_2 \cdot 4H_2O$ is slightly soluble in acetone while 0.15 mmol of $FeCl_2 \cdot 4H_2O$ can be dissolved completely in the solvent mixture of acetone (17 ml) and acetic acid (3 ml). However, the solubility test of $FeCl_3 \cdot 6H_2O$ showed that it is readily soluble in both solvents. Therefore, we can exclude the possibility that the promoting effect of acetic acid is due to the change of solubility. We also examined the possibility of the increasing of hydrogen peroxide formation by acetic acid addition: hydrogen peroxide was determined iodimetrically after the reaction using pure acetone or the solvent mixture, acetone-acetic acid (17:3), under the same conditions as the oxidation except that cyclohexane was not added. However, the amount of hydrogen peroxide formed in the acetone-acetic acid mixture was almost same as that in pure acetone (that corresponded to 36.7 mmol of peroxide). The promoting effect of acetic acid could be explained by the active species like iron-oxo complex is stabilized by acetate ligand or a possibility of the formation of peracetic acid. To clarify the effect of acetic acid addition, futher investigations are needed.

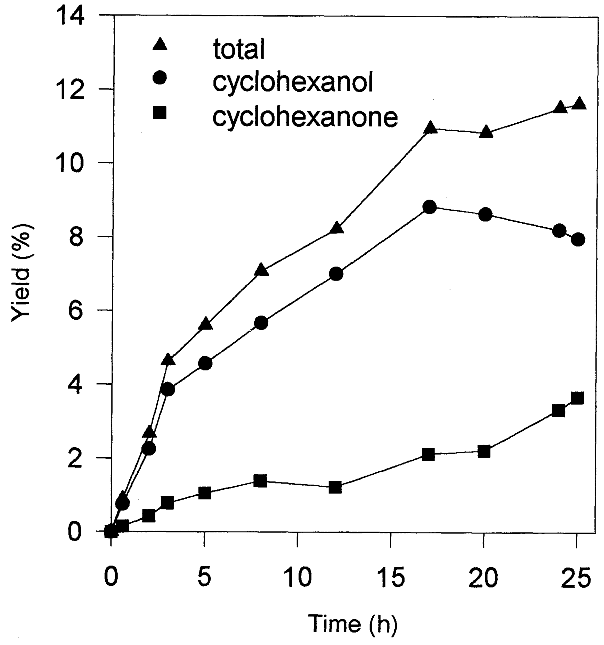

Figure 1. Time dependence of cyclohexane oxidation. Conditions : cyclohexane (59.4 mmol), acetone (17 ml), acetic acid (3 ml), $FeCl_2 \cdot 4H_2O$ (2.5 mmol), Pd/alumina (1 g), H_2 (20 ml/min), O_2 (20 ml/min), Temperature = 30°C.

The Pd/alumina used in the oxidation was recycled by filtering and drying, and showed no loss of activity as being reused. However, reusing of recovered iron salt from the oxidation using iron(II) chloride gave yield decrease of 20%. Recently, it has been reported that iron catalysts are deactivated by the formation of iron hydroxide in the Gif-type reactions.[9] Indeed, in the measurements of atomic absorption spectroscopy, the recovery rate of iron ions as soluble forms after the oxidation was 83 % as using the acetone-acetic acid (17:3) mixture. Now, we are doing further work to develop more useful systems.

The results on varying reaction time are shown in Figure 1. Yields increase with the time and then reaches up to ca. 12 mole %. It is to be noted that the modified system showed high selectivity for alcohol formation being contrary to original Gif-systems. Seeing change of yields for alcohol and ketone with reaction time, it is likely that cyclohexanol is converted to cyclohexanone by further oxidation. This is in agreement with a previous report.[12] Besides, traces of byproducts like 1,3-cyclohexanediol and 2-hydroxycyclohexanone were detected in the reaction time more than 16 h.

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