

The Effect of 1,3-Dicarbonyl Compounds on Alkane Oxidation in Gif-Type Reactions

Warinthorn Chavasiri*[†] and Doo Ok Jang*[‡]

[†]Surface Chemistry and Catalysis Research Unit, Department of Chemistry, Chulalongkorn University, Phayathai Rd., Bangkok 10330, Thailand

[‡]Department of Chemistry, Yonsei University, Wonju 222-710, Korea

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The selective oxidation of hydrocarbons under mild conditions is an industrially and biologically important problem.¹ In industry, the oxidation of cyclohexane to cyclohexanol or cyclohexanone is an important commercial process for the production of caprolactam and/or adipic acid and then to nylon.² In nature, the selective functionalization of hydrocarbons occurs *via* enzymatic catalysis. Among them, the interesting enzymes are methane monooxygenase,³ *iso*-penicillin *N* synthase,⁴ deacetoxycephalosporin *C* synthase,⁵ and clavaminat synthase.⁶ They all require iron in a non-heme active site.

Gif-type reactions are one of promising candidates among non-heme chemical models attempting to mimic biological systems,⁷ Under these particular conditions, saturated hydrocarbons are generally oxidized to ketones; alcohols are observed as minor products of the reaction. The ligand coordinated around iron was found to be one of crucial factors to control the outcome of the oxidation reaction.^{7,8} For instance, picolinic acid and its congeners were reported to have a profound effect on the rate of the oxidation under GoAgg^{II} conditions.⁹

Very recently, it has clearly been demonstrated that in the absence of suitable carboxylate ligands, Gif chemistry was not observed.¹⁰ We report herein the effect of 1,3-dicarbonyl compounds on alkane oxidation in Gif-type system.

The ratio of Fe (III) to 1,3-dicarbonyl compound was found to be significant effect on the rate of the oxidation reaction. Using acetylacetone (**3**) as a representative, it was observed that the fastest rate and the yield of the desired products was obtained when the mole ratio of Fe (III) to acetylacetone was 1 : 3 (Table 1). Addition of more ligand (5 or 10 mole ratio to Fe (III)), although the rate increased, the yield of the products decreased. Compared with the system without acetylacetone, the rate of the oxidation in the presence of acetylacetone (3 mole ratio to Fe (III)) was found to be approximately 14 times faster although it is twice slower than the system with picolinic acid which is the most active ligand so far found.

According to the results mentioned above, a series of 1,3-dicarbonyl compounds was selected to examine their ability to promote the alkane oxidation (Table 2). It was observed that the product distribution and the total amount of the products obtained (cyclohexanone and cyclohexanol) from each set of the reaction were nearly similar except for the case of dibenzoylmethane (**8**) (entry 7). Nonetheless, the rate of the oxidation reaction greatly influenced by types of 1,3-dicarbonyl compounds. To illustrate this, the system comprising of iron (III) and 1,3-dicarbonyl ligands bearing electron releasing group could enhance the rate of oxidation (entries 2, and 6-8). On the other hand, the system containing iron (III) and 1,3-dicarbonyl compounds which have electron withdrawing groups revealed almost no difference in the rate enhancing efficiency from that without 1,3-dicarbonyl ligands (entries 3-5 and 9-10). Moreover, the systems with 1,3-dicarbonyl ligands holding strong electron

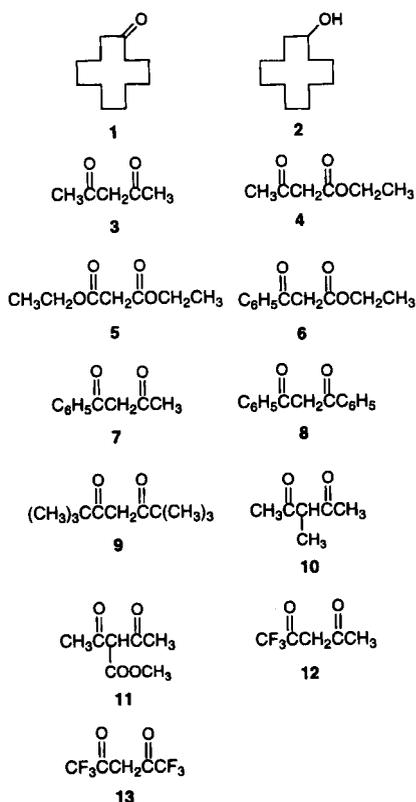


Table 1. The Total Amount of the Oxidized Products and the Half-lives of the Oxidation Reaction of Cyclohexane in the Presence of Various Iron (III) to Acetylacetone (**3**) Ratio¹²

Ratio Fe(III) : Acetyl Acetone (3) (mol : mol)	Total Amount of Oxidized Product (mmol)	Half-life (min)
1:0	2.43	210.0
1:1	2.48	57.7
1:2	2.50	39.0
1:3	2.60	15.0
1:5	1.30	4.5
1:10	1.03	—*

*Not determined

Table 2. The Effect of 1,3-Dicarbonyl Compounds on the Oxidation of Cyclohexane.¹²

Entry	1,3-Dicarbonyl Compound	Product (mmol)					
		30 min			12hr		
		1	2	Σ	1	2	Σ
1	None	0	0	0	2.90	0.20	3.10
2	3	0.92	0.25	1.17	3.01	0.32	3.33
3	4	0.11	0.05	0.16	2.49	0.23	2.72
4	5	0.11	0.05	0.16	3.09	0.23	3.32
5	6	0.16	0.07	0.23	2.58	0.14	2.72
6	7	0.76	0.20	0.96	2.96	0.29	3.25
7	8	1.08	0.29	1.37	3.40	0.34	3.74
8	9	0.90	0.23	1.13	3.05	0.23	3.28
9	10	0.05	0.20	0.25	3.01	0.27	3.28
10	11	0.18	0.65	0.83	2.93	0.29	3.12
11	12	0	0	0	2.49	0.23	2.72
12	13	0	0	0	3.14	0.18	3.32

Σ: Summation of the oxidized products

withdrawing groups such as **12** and **13** were found to retard the rate of oxidation reaction (entries 11 and 12). These results were obviously in good agreement with the previous postulation that the iron species responsible for alkane oxidation in Gif-type reactions possess its electrophilic character.¹¹

In summary, this study reinforces the conception that the ligands around iron are important for Gif-type chemistry. The ligands bearing electron donating group could provide an enhancing effect on the rate oxidation reaction. This work also offers the insight for the further design of ligands that could provide the faster and more selective oxidation reaction for saturated hydrocarbons.

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- In a typical experiment: To a solution of FeCl₃·6H₂O (54 mg, 0.2 mmol), the 1,3-dicarbonyl compound (0.6 mmol) and cyclohexane (1.68 g, 20 mmol) in pyridine (30.0 mL)-acetic acid (3.0 mL), 30% aqueous H₂O₂ (15.0 mL) was added in one portion. The solution was stirred at room temperature in a closed flask. Aliquots taken were acidified (50% H₂SO₄), extracted with ether and then analyzed by GLC.