

LIQUID PHASE OXIDATION OF SUCROSE WITH H₂O₂ AND IRON TRIS(ACETYLACETONATE) AS CATALYST

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SUMMARY

D-glucarates are promising substances as chemopreventive agents against several different types of cancers, a practical synthesis of D-glucaric acid, is therefore of scientific and commercial interest. Since sucrose is in Vietnam an abundant and cheap raw material the reaction of sucrose with H₂O₂ and iron tris(acetylacetonate) as a catalyst to D-glucaric acid was investigated and the results are presented in this paper. The iron tris(acetylacetonate) catalyst was characterized by FT-IR, UV-Vis and AAS. The products of the oxidation reactions were analyzed by HPLC.

Keywords: sucrose oxidation, D-glucarate, glucaric acid, saccharic acid, Fe(acac)₃ catalyst.

I - INTRODUCTION

D-glucaric acid (or D-saccharic acid) is increasingly gaining scientific attention because its salts have found promising use as chemopreventive agents against several cancers [1, 2]. Therefore a practical synthesis of D-glucaric acid, starting from sucrose, which is an abundant raw material in Vietnam, is of scientific and economic value.

Among the numerous oxidative conversions of sucrose to D-glucaric acid catalytically reactions are the most promising for practical syntheses. According to recent preparative methods D-glucaric acid can, for example, be catalytically prepared by oxidation of D-glucose with O₂ and Pt/C [3], by the oxidation of molasses with nitric acid and V₂O₅ [4] and by oxidizing D-glucose with hypochlorite and 4-acetamido-TEMPO [5].

Since metal acetylacetonates with a transition metal, such as iron, as the central

metal ion, can be used effectively as a catalyst in oxidation reactions [6, 7] we investigated the oxidation of sucrose with H₂O₂ in the presence of iron tris(acetylacetonate) as a catalyst to D-glucaric acid.

The reaction products were analyzed by HPLC. The Fe(acac)₃ catalyst was characterized by FT-IR, UV-Vis and AAS.

II - EXPERIMENTAL

1. Catalyst preparation and characterization

Fe(acac)₃ was prepared by a modification of a general method [8]. 0.33 g of finely-ground iron(III) chloride hexahydrate were dissolved in 2.5 mL of distilled water. Over a period of 15 minutes a solution of 0.38 g of acetylacetonate in 10 mL methanol was added with constant magnetic stirring. To this mixture a solution of 0.51 g of sodium acetate dissolved in 1.5 mL of distilled water was added drop wise,

maintaining stirring throughout. The mixture was heated rapidly to about 80°C and was maintained at this temperature for 15 minutes, with rapid stirring. Then the reaction mixture was cooled to room temperature and subsequently in an ice bath. The product was isolated by suction filtration and washed with 10 mL of cold distilled water. Finally the catalyst was dried first by suction for 15 minutes, then by air-drying.

The FT-IR spectra were recorded on a Shimadzu FTIR 8000 Spectrophotometer. The UV-Vis spectrum was recorded on a GBC UV-Vis 2855. The Fe content of the catalyst was determined by AAS on AAS-SP9 Pye Unicam I.

2. Oxidation reaction

In a 250 ml round-bottomed flask placed in a thermostat, 17.1 g (0.05 mol) sucrose was dissolved in 10 ml of distilled water. Then the

required amount of the catalyst was added. The mixture was stirred with a magnetic stirrer and heated to the reaction temperature. Then 30% H₂O₂ was added drop wise. The reaction started immediately. The reaction was stopped when the H₂O₂ was used up.

The oxidation products were analyzed by HPLC on a Shimadzu LC-10AD using a Supelco H column with detection at 210 nm. 0.1% H₃PO₄ was used as the mobile phase. The flow rate was 0.3 ml/min at a pressure of 67 bar.

III - RESULTS AND DISCUSSION

1. Catalyst preparation and characterization

The FT-IR spectra and the frequencies of some characteristic absorption bands of acetylacetonone (Hacac) and the Fe(acac)₃ catalyst are shown in figure 1 and table 1, respectively.

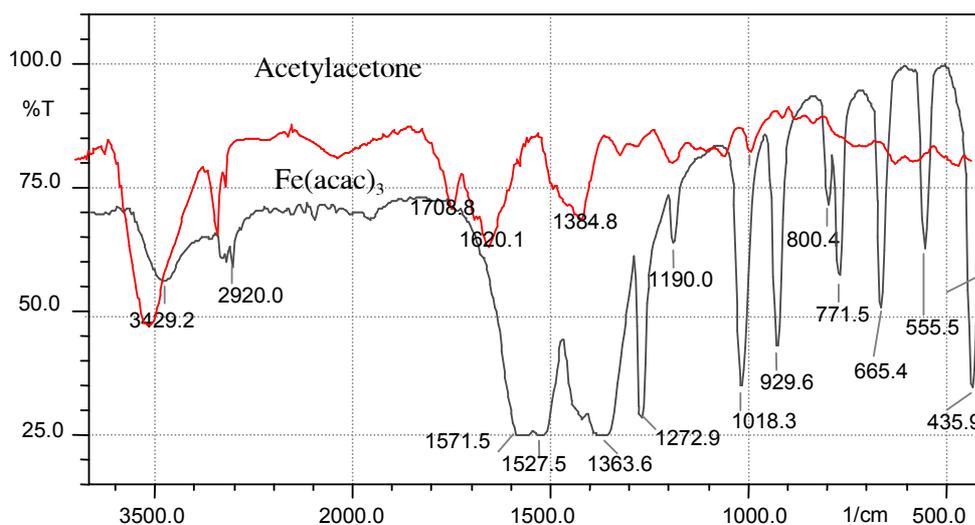
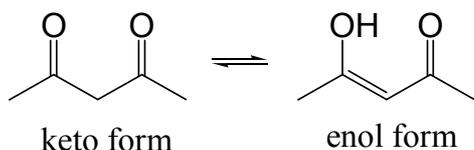


Figure 1: FT-IR spectra of acetylacetonone and Fe(acac)₃ catalyst

In the spectrum of the Fe(acac)₃ catalyst, absorption bands in the region of 400 - 700 cm⁻¹, which are absent in the free ligands, may be attributed to Fe-O vibrations. The C=O frequency of the complex is lowered compared to the corresponding frequency in the spectrum of the free ligand. In the spectrum of Hacac, bands at 1708 cm⁻¹ and 1620 cm⁻¹ were assigned

to C=O and C=C vibrations respectively. In the spectrum of Fe(acac)₃, bands at 1571 and 1527 cm⁻¹ were assigned to C=O and C=C vibrations respectively. The intensity of the O-H band at 3439 cm⁻¹ of Hacac is very strong, indicating that acetylacetonone is a mixture of keto and enol form. These absorption frequencies are in accordance with reported values [9].



Since the intensity of the OH band of the $\text{Fe}(\text{acac})_3$ catalyst is much weaker than the corresponding band of Hacac, one might assume that the enol form dominates the formation of the acetylacetonate complex.

Table 1: IR-frequencies of some characteristic adsorption bands of Hacac and $\text{Fe}(\text{acac})_3$

Sample	IR frequencies ν , cm^{-1}					
	$\nu_{\text{O-H}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$	ν_{CH_3}	$\nu_{\text{Fe-O}}$
Hacac	3431	2922	1708	1620	1384	-
$\text{Fe}(\text{acac})_3$	3429	2920	1571	1527	1363	435

The UV-Vis spectrum and the molar absorptivities of some adsorption peaks of the $\text{Fe}(\text{acac})_3$ catalyst are shown in figure 2 and table 2, respectively.

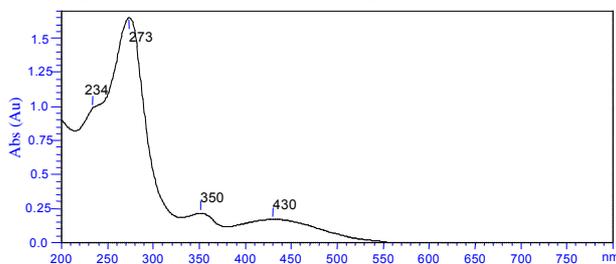


Fig. 2: UV-Vis spectrum of $\text{Fe}(\text{acac})_3$

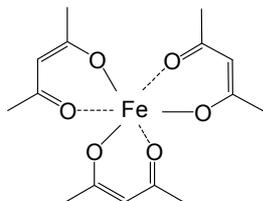
Table 2: Molar absorptivities of some adsorption peaks of $\text{Fe}(\text{acac})_3$

λ_{max} , nm	234	273	350	430
ϵ	3937	8517	765	603

The absorption peak of $\text{Fe}(\text{acac})_3$ at $\lambda_{\text{max}} = 234$ nm has the molar absorptivity of 3937. This demonstrates a charge transfer from the oxygen atom of acetylacetone (the donor) to the d-orbital of Fe^{3+} (the acceptor). The very high molar absorptivity of the peak at $\lambda_{\text{max}} = 273$ nm ($\epsilon = 8517$) indicates the $\pi \rightarrow \pi^*$ transitions. This means that the $\text{Fe}(\text{acac})_3$ contains a conjugate system of C=C and C=O double bonds.

The Fe content (% by weight) of the catalyst determined by AAS is 15.3. Whereas the calculated value of Fe content obtained from the formula $\text{Fe}(\text{acac})_3$ is 15.8. It proves that one Fe^{3+} ion is bonded with 3 $(\text{acac})^{-1}$ ions.

From the above results, the formula of $\text{Fe}(\text{acac})_3$ catalyst can be presented as follows:



2. The oxidation reaction

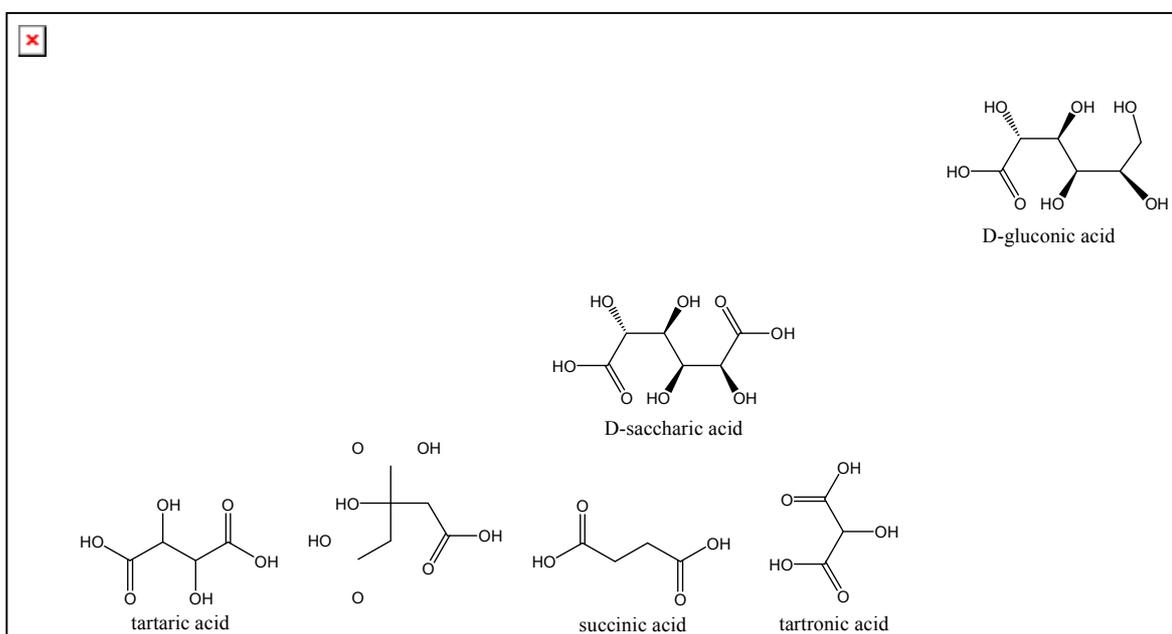
The results of the influence of the H_2O_2 /sucrose ratio on the oxidation of sucrose are shown in table 3.

When the H_2O_2 /sucrose ratio is low, the total acid yield is low but the selectivity of the production of D-saccharic acid is the highest. With a higher H_2O_2 /sucrose ratio, the total acid yield raises and the selectivity for D-saccharic acid is lowered. A reasonable mechanism for the production of D-saccharic acid could proceed as follows. Under the reaction conditions, sucrose is hydrolyzed to give D-glucose and D-fructose which are further oxidized to D-gluconic acid. In the next step D-gluconic acid is easily oxidized to D-saccharic acid. An excess of H_2O_2 can subsequently oxidize the produced D-saccharic acid to secondary products such as tartaric acid, citric acid, succinic acid, tartronic acid, oxalic acid and formic acid. This mechanism explains why the total acid yield increases and the selectivity

of D-saccharic acid decreases with an increasing excess of H₂O₂.

Table 3: Influence of H₂O₂/sucrose ratio on the oxidation of sucrose at 80°C (with 0.075 mol of the Fe(acac)₃ catalyst per mol sucrose)

H ₂ O ₂ /sucrose ratio (mol/mol)	1/1	1.2/1	1.5/1	2/1	4/1	6/1	7/1
Total acid yield (mol%)	27	30	34	48	65	74	75
Selectivity (mol%)							
- D-saccharic acid	90.1	88.8	85.3	79.5	57.2	43.9	37.1
- Formic acid	5.3	7.1	8.9	12.0	27.6	42.2	51.6
- Other products	4.6	4.1	5.8	8.5	15.2	13.9	11.3



The influence of the reaction temperature on the selectivity of the products is shown in table 4.

Table 4: The influence of the reaction temperature on the selectivity of the oxidation of sucrose (mol ratios: Fe(acac)₃/sucrose = 0.075/1, H₂O₂/sucrose = 1.2/1)

Reaction temperature, °C	Reaction time, min	Selectivity (%wt.)		
		D-saccharic acid	Formic acid	Other products
90	15	86.37	11.29	2.38
80	25	88.80	7.10	4.10
70	30	92.33	3.84	3.83
50	45	89.40	7.84	2.77

The reaction started immediately after the addition of H₂O₂. At low temperature, H₂O₂ decomposes slowly and it took a long time for the active oxygen to be used completely. This

explains the long reaction time at low temperature. At higher reaction temperatures, D-saccharic acid produced as primary product is oxidized further to the secondary oxidation products such as oxalic acid, formic acid, etc. If the reaction temperature is too high, oxygen is released too fast from H₂O₂ to be consumed smoothly by the oxidation reaction. Under these conditions more than the necessary amount of H₂O₂ is used and in addition more of the unwanted secondary products are produced.

IV - CONCLUSIONS

1. Fe(acac)₃ catalyst has been characterized by IR, UV-Vis and AAS. Evidence is given that the enol form of acetylacetone is responsible for the formation of the acetylacetonate complex. The structure of the Fe(acac)₃ catalyst has been confirmed by spectroscopic methods.

2. During the oxidation of sucrose, if the temperature and reaction time as well as the H₂O₂/sucrose ratio increase, D-saccharic acid formed as primary product is oxidized further to give the secondary oxidation products such as oxalic acid and formic acid.

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REFERENCES

1. M. Hanausek, Z. Walaszek, T. Slaga. *Integrative Cancer Therapies*, 2(2), 139 (2003).
2. A. B. Caragay. *Food Technology*, 46(4), 65 (1992).
3. J. M. Dirx, H. S. Van der Baan, J. M. Van den Broek. *Carbohydrate Research*, 59(1), 63 (1977).
4. V. Pamuk, M. Yilmaz, A. Alicilar. *J. Chem. Technol. Biotechnol.*, 76(2), 186 (2001).
5. N. Merbouh, J. F. Thaburet, M. Ibert, F. Marsais, J. M. Bobbitt. *Carbohydrate Res.*, 336, 75 (2001).
6. A. Valente, A. M. Botelho do Rego, J. M. Reis, I. F. Silva, A. M. Ramos, J. Vital. *Appl. Catal. A: General*, 207, 221 (2001).
7. L. I. Matienko, L. A. Mosolova. *Kinetics and Catalysis*, 46(3), 328 (2005).
8. R. N. Prasad, M. Agrawal, M. J. Sharma. *Chil. Chem. Soc.*, 48(1), 1 (2003).
9. L. J. Bellamy, L. J. Beecher. *Chem. Soc.*, 4487 (1954).