

## THE OBTAIN OF PROPYL FORMATE THROUGH THE ESTERIFICATION OF THE FORMIC ACID AND OF THE PROPYLIC ALCOHOL

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### SUMMARY

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This article includes series of synthesis achieved for obtain the propyl formate. It is used in large quantities for obtaining the top notes (initially perceived smell) and it achieves through the direct esterification of the formic acid and of ethyl carbinol. There were been studied the change of reactants ratio on reactions efficiency and the change of reaction time respective reaction catalyzer ( $H_2SO_4$  and formic acid).

Keywords: propyl formate, ester, esterification

### INTRODUCTION

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The perfume is a fugitive impression, but its study can take a life time: exhausting hours of distinguishing the formulas, the combinations and retrials of essences, lots of false tracks in one target – untying of making a grand perfume, discovering the essences and proportions which give the absolute character [1].

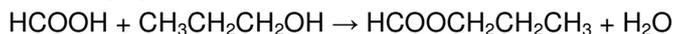
The odours of flowers and fruits owe to some simple organic agents: ethers, esters, nonsaturated alcohols which can be obtained in the laboratory too.

The usual method of obtaining the esters is the reaction of direct esterification between the acid and appropriate alcohol [2].

The reaction of esterification is a balance reaction. The chemical balance can move to the development of the ester, using an excess of reactants or cutting one of reaction products contained from the system.

The propyl formate is used in big quantities for obtaining the fresh top notes (initially perceived smell) and it is obtained through the direct esterification of the formic

acid and propyl alcohol [10].



The esterification of the formic acid with the propane can be made only with dipping acid, sulfurobenzen acid or exceptionally direct estification.

If it is not added the catalyst, the reaction time is a little long. In this case, it is considered the formic acid constitute reaction catalyst too [1].

## MATERIALS AND METHODS

The working materials used for obtaining the propyl formate are represented in Table I, next to the main physico-chemical characteristic properties of them.

**Table I. The characteristic properties of the utilized working materials**

No.	Characteristic property	Unit of measure	Formic acid	1-propanol	H2SO4
1	Aspect	-	Clear liquid	Clear liquid	Viscid liquid
2	Density at 20° C	g/cm <sup>3</sup>	1.226	0.804	1.84
3	Melting-point	°C	8.4	-127	0
4	Boiling-point	°C	100.5	97.1	0
5	Index of refraction	-	-	1.3853	-
6	Gram-molecular weight	-	46.02	60	98
7	Concentration	%	85	98	96

The obtained ester was characterized by the determination of :

- the acid number;
- the density;
- the distillation range;
- the index of refraction.

The acid number is definite as the number of milligrams of the kalium hydroxide necessary for the neutralization of the free acids from a gram of test.

The acid number calculates with the next formula:  $I.A = 5.61 \cdot V/m$  [ mg KOH/g ]

V = the volume of the solution of the potassium hydroxide 0.1 N utilized at titration (ml)

m = the mass of ester weighing in grams

5.61 = constant

The density's read directly with a densymeter.

The determination of the distillation range fulfils in a distillation plant

Experimental method used consists in the reaction of the direct esterification of formic acid with 1- propanol ,in attendance of a catalyst of reaction. It is worked at the reflux temperature 96-100° C.

The utilized compounds in the laboratory synthesizes are represented in Table II.

**Table II. The utilized compounds in the laboratory synthesizes**

Synthesis no	Starting materials: Formic acid 1-propanol	Catalyst [%]	Temperature of reaction [°C]	Reaction time [hours]
1	1 : 0.5	-	99	8
2	1 : 0.75	H <sub>2</sub> SO <sub>4</sub> 0.15	100	8
3	1 : 1	-	95	8
4	1 : 0.25	H <sub>2</sub> SO <sub>4</sub> 0.5	90	8
5	1 : 0.75	ABS 0.5	100	8

The mode of action is the following : in a reaction balloon which has a refrigerant of reflux, it is inserted the formic acid and 1-propanol. It is refluxing a certain reaction time. In the case of using of catalyst , it is inserted before warming the system.

After the end of the reaction , the warming the installation is turned off. It is let to cool off. It is appended a reflux cooler and a column of fractionation and the reaction product – propyl formate- is distilled [5].

The synthesis instillation of teh propyl formate is composed of :

- a warming system;
- a reaction baloon ;
- a reflux cooler;
- a thermometer.

The distillation plant of he propyl formate is composed of :

- a reaction balloon;
- a heating pocket ;
- thermometer ;
- a reflux cooler;
- a collecting recipient of the propyl formate.

## RESULTS

It is determined the influence of the formate acid excess, the influence of the reaction catalyst and the influence of the reaction time. For determining the excess of formic acid on the reaction efficiency the were been made 4 synthesis using molar ratio formic acid : 1-propanol of: 1:1;1:0.75; 1:0.5; 1:0.25. It wasn't been used any catalyst , considering the excess of formic acid has catalyst role. The reaction temperature was of 99°C -100°C.

**Table III. The obtained resultants in effected synthesis**

No.	Formic acid : 1- propanol Molar ratio	Temperature of reaction [°C]	Reaction time [hours]	Reaction efficiency [%]
1	1 : 1	95	8	32.5
2	1 : 0.75	100	8	50.45
3	1 : 0.5	99	8	68.3
4	1 : 0.25	98	8	88.9

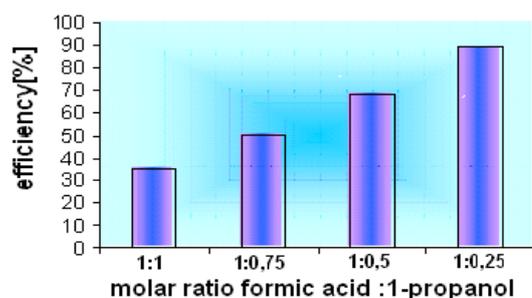


Figure 1. The efficiency variation term molar ratio formic acid : 1-propanol

There are obtaining good results at a molar ratio formic acid : 1- propanol of 1 : 0.75, respectively 1 : 0.5, at a formic acid excess.

At a stoichiometric ratio of 1 : 1 it is determined the obtainof a small efficiency ( 35% ).

For observing the influence of the reaction catalyst there were effected various synthesis for obtaining the propyl formate using as catalyst : formic acid, dipping acid and sulfurobenzen acid [10].

The synthesis was obtained at the reaction temperature of  $\sim 100^{\circ}\text{C}$ .

In Table IV there are represented the obtained results at utilization of different reaction catalysts.

**Table IV. The obtained results at utilization of different reaction catalysts**

Crt. No.	Starting materials Formic acid 1-propanol Molar ratio	Catalyst [%]	Reaction time [h]	Temperature of reaction [°C]	Efficiency [%]
1	1 : 0.5	AF	8	99	68.30s
2	1 : 1.75	H <sub>2</sub> SO <sub>4</sub> 0.5	8	100	30.25
3	1 : 1.75	ABS 0.5	8	100	50.12

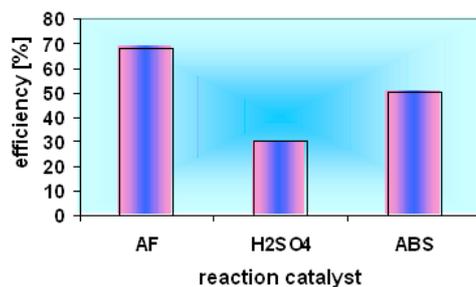


Figure 2. The influence variation of reaction catalyst on the reaction efficiency (Where: H<sub>2</sub>SO<sub>4</sub>-dipping acid, ABS- sulfurobenzen acid, AF-formic acid).

It is observed there are obtaining high efficiencies of 68% in case of using the formic catalyst too. If it is used the catalyst  $H_2SO_4$  there are obtaining low efficiencies of 30% & thing owes to the dispersion of a certain quantity of formic acid in the attendance of  $H_2SO_4$  utilization of a sulfurobenzen acid there are obtaining efficiencies of 50%.

For following the influence of reaction time on the efficiency of esterification reaction of the formic acid with - propanol there were been used as reaction parameters : temperatures of  $100^\circ C$  and a molar ratio formic acid : 1- propanol of 1 : 0.5.

**Table V. The obtained experimental data at the synthesis of propyl formate**

No.	Starting materials Formic acid 1-propanol Molar ratio	Reaction time [h]	Temperature of reaction [ $^\circ C$ ]	Efficiency [%]
1	1 : 0.5	30	100	10.10
2	1 : 0.5	60	100	25.30
3	1 : 0.5	180	100	40.50
4	1 : 0.5	360	100	50.21
5	1 : 0.5	480	100	68.30
6	1 : 0.5	1440	100	84.50

In Figure 3 there are represented the obtained experimental data , respectively the reaction efficiency variation reaction time.

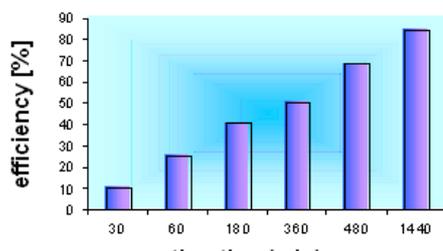


Figure 3. Reaction efficiency variation term reaction time

It is observed from the diagram that the more the refluxing time is high, the more reaction efficiency's is more higher. It accomplishes a good efficiency of ~ 84% using a reaction time of 24 hours.

## DISCUSSION

The ester obtained in all the experimental synthesis was distilled and it were been determined his physical-chemical characteristics

These are represented in Table VI.

**Tabelul VI. The physico-chemical characteristics of the obtained propyl formate.**

No.	Characteristic property	Unit of measure	Obtained propyl formate	Literature propyl formate
1	aspect	-	Clear liquid	Clear liquid
2	acid number	Mg KOH/g	0.01	0.01
3	boiling-point	°C	80.5 - 82	82
4	Index of refraction	-	1.377	1.3771
5	Density at 20°C	g/cm <sup>3</sup>	0.901	0.901

Next, there are represented the spectral data of the propyl formate [6].

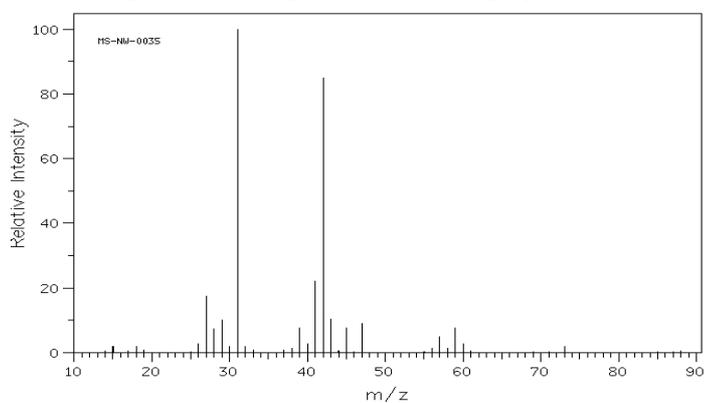


Figure 4. The mass spectrum of propyl formate.  
Source temperature : 220°C Sample temperature : 25°C  
The RMN spectrum of propyl formate is represented in Figure 5.

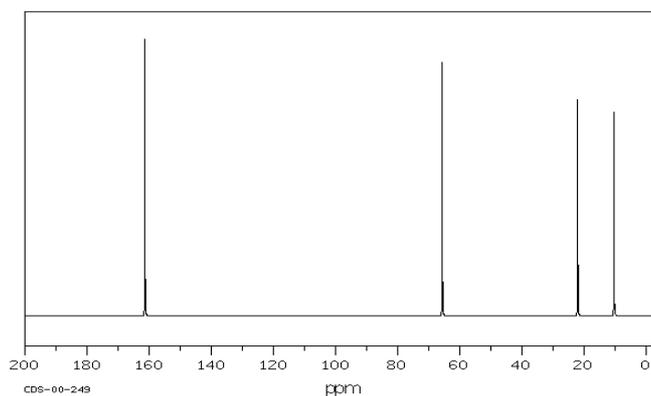


Figure 5. The RMN spectrum of propyl formate

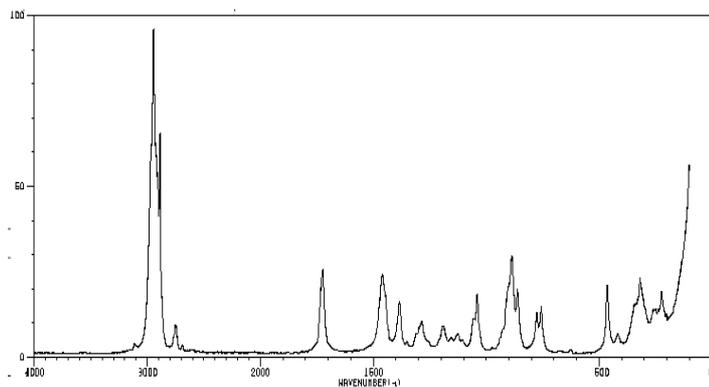


Figure 6. The RAMAN spectrum of propyl formate

All these methods of structural determination of organic compounds demonstrate the experimental obtain of propyl formate.

## CONCLUSION

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After the finish of the synthesis there were determined the followings:

1. It can obtain good efficiencies ( 68% ) in the case of utilizing a formic acid excess, in this case it representing also the reaction catalyst .
2. It can be worked in good conditions with a molar ratio formic acid : 1-propanol of 1 : 0.5
3. The temperature of reaction is the one of reflux, about 100°C and the time reaction is about 8 hours .
4. The obtained ester – propyl formate – is pureness of 99.9%.
5. It was been collected only the fraction with boiling-point 81-82°C.
6. The ester has a nice fruity smell. It is used as top note in various perfumes.

## REFERENCES

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1. Hădărugă D., "Compuși odoranți și aromatizanți", Ed. Politehnică, Timișoara 2003.
2. A.Steffen, J.Powliszyn, "Analysis of Flavor Volatiles Using Headspace Solid-Phase Microextraction" *J. Agric.Food Chem.* **44** (1996) 2187.
3. K.Héberger; "Evaluation of polarity indicators and stationary phases by principal component analysis in gas-liquid chromatography", *Chemometrics and Intelligent laboratory systems*, **47** (1998) 41-49.

4. K.Ishihara; M.Makayama; "A Green Method for the Selective Esterification of Primary Alcohols in the Presence of Secondary Alcohols or Aromatic Alcohols" *Synlett*, **7** (2001), 1117-1120; through C.C. 2001.
5. F.Augusto; A.L A.Steffen, J.Powliszyn, "Sampling and sample preparation for analysis of aromas and fragrances " *Trends in Analytical Chemistry*, **22(3)**, (2003), 160-169.
6. K. Ramalinga; P. Vijayalakchmi; T.N.B. Kaimal; "A mild and efficient method for esterification and transesterification catalyzed by iodine", *Tetrahedron Letters* **43** (2002) 879-882