

Stepan Melnyk

PERFLUOROOXASULPHONATES OF METALS – THE CATALYSTS OF ESTERS MANUFACTURE

*Lviv Polytechnic National University**12, S. Bandery str., 79013 Lviv, Ukraine; st_melnyk@yahoo.com**Received: December 28, 2012 / Revised: February 06, 2013 / Accepted: March 23, 2013*

© Melnyk S., 2013

Abstract. The process of obtaining of aliphatic dibasic esters from dicarboxylic acids and C₄-C₅ alcohols in the presence of perfluoro(4-methyl-3,6-dioxaoctane)sulphonates of different metals has been researched. For the comparative estimation of catalysts their concentration was chosen identical and of such value that the rate of the process was limited exactly by the rate of chemical reaction. The dependences of technological characteristics of esterification process on catalyst nature and concentration and on reagents nature have been determined. High activity of the investigated catalysts has been found out, which is probably caused by the synergetic effect of metal cation and perfluoroic fragment, which provides decreasing of electron density on metal ion and at the same time good solubility of catalyst in the substrate, thus providing its high active concentration.

Keywords: esterification, dicarboxylic acids, perfluoro-oxasulphonates, catalysts, C₄-C₅ alcohols.

1. Introduction

The Lewis acids are effective catalysts of esterification due to their mildness and sometimes specificity of their action. Nowadays a large number of different organometallic compounds have been investigated as catalysts, which allowed to improve many processes of esters manufacturing [1-4]. Apparently, a prerequisite for ensuring of the efficiency of esterification in the presence of homogenous catalyst – Lewis acid – is its good solubility in reaction medium. For example, isotridecanol is used to improve the solubility of catalyst – salts of trifluorometansulfoacid – in the process of obtaining esters of lactic acid [5]. However, high boiling point of aliphatic dicarboxylic acid diesters renders applying of these catalytic solutions impossible due to complexity of the recovery catalyst from the mixture of reaction

products. That is why perfluorooxasulfoacid salts, which are sufficiently soluble in organic substrates and could be extracted by water from the reaction mixture, were chosen for the study. High activity of these compounds in obtaining esters reactions is caused either by the nature of metal cation or by anion of acid residue. The last one due to having electrophilic perfluoro chain reduces the electron density on the active center of the catalyst – cation of metal – and increases its electrophilic properties. The aim of the research was to determine the influence of cation of perfluorooxasulfoacid salt nature on the rate of reaction and on technological characteristics of the esterification process of aliphatic dicarboxylic acids with alcohols C₄-C₅.

2. Experimental

We have used catalysts – perfluoro(4-methyl-3,6-dioxaoctane)sulphonates of different metals (CF₃CF₂OCF₂CF(CF₃)OCF₂CF₂SO₃)_nMe (Me(pfos)_n, where Me is Ca, Be, Zn, Sn, Co, Ni, Al, and Cu) and reagents – 1-butanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 1-pentanol, succinic (SA), and adipic (AA) acid.

The laws of esterification have been investigated in an open system with stripping of water, formed in the reaction [6]. The experiments were carried out until the accumulation of water in Dean-Stark trap was completely stopped. The reaction products were analyzed by titration and by gas-liquid chromatography. According to analysis results conversion of the carboxylic groups of dibasic acid and its monoester as well as composition of the reaction mixture were calculated.

3. Results and Discussion

The influence of the nature of the catalyst, its concentration and composition of the reaction mixture on the laws of diesters obtaining have been investigated.

Esterification in an open system combines chemical reaction and mass transfer process of water stripping from the reactor. At the high catalyst concentrations the rate of esterification reaction is limited by stripping of water from the reaction system. To eliminate the influence of this factor when comparing the effect of the catalyst nature on the esterification of dibasic acids, sufficiently low catalyst concentration was used. This allowed us to calculate the highest rate of esterification from the curve of water accumulation in the Dean-Stark trap (Fig. 1).

In general, investigations of esterification of succinic acid with 1-butanol showed that the aluminium perfluoro(4-methyl-3,6-dioxaoctane)sulphonate is the most active catalyst. Activity of the catalysts decreases in the row of cations $Al^{3+} > Co^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Sn^{2+} > Be^{2+} > Ca^{2+}$ (Fig. 1). Such a law can be explained by the influence of cation size and its relative electronegativity (Fig. 2). The role of the cation charge, obviously, is of less importance, since for triply charged cation, surrounded by three ligands of large size, large steric hindrance in the catalyst–reagent complexes formation may occur.

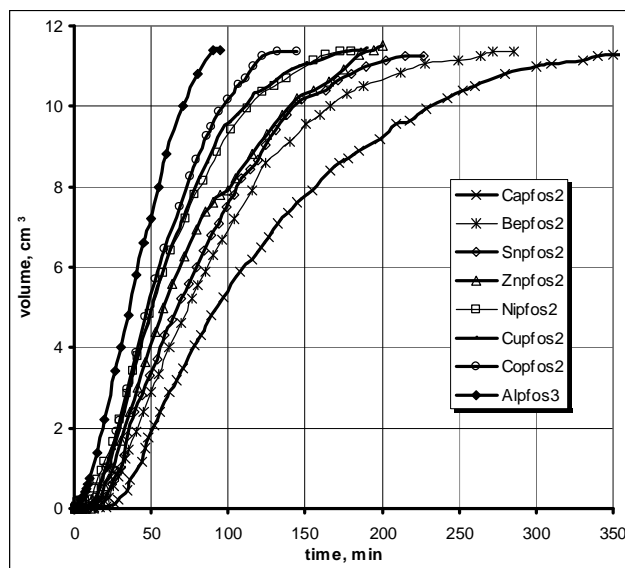


Fig. 1. Dynamics of water accumulation in Dean-Stark trap by esterification of succinic acid with 1-butanol in the presence of various catalysts. Catalyst concentration – $1.1 \cdot 10^{-3}$ mol/dm³

A similar dependence has been obtained for the process of esterification of adipic acid with 1-butanol.

In the presence of any investigated catalyst at different time carboxylic acid groups of succinic acid and monobutylsuccinate (MBS) conversion of more than 90 % was achieved (Table 1). However, the feature of all catalysts is the fact that in their presence the ratios between intermediate and final reaction products as well as MBS and dibutylsuccinate (DBS) yields are somewhat different at close values of conversion.

By increasing the catalyst concentration, the rate of diesters obtaining has been increased and the duration of the esterification process of dibasic acids with C₄–C₅ alcohols has been decreased. Apparently, the catalyst concentration, at which the rate of water stripping is equal to the rate of its formation by the chemical reaction, is the optimal one.

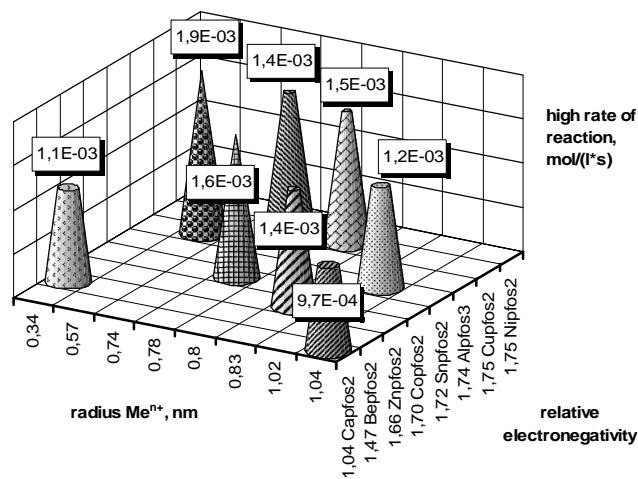


Fig. 2. The influence of the metal ion radius and the relative electronegativity of the element on the high rate of the esterification reaction

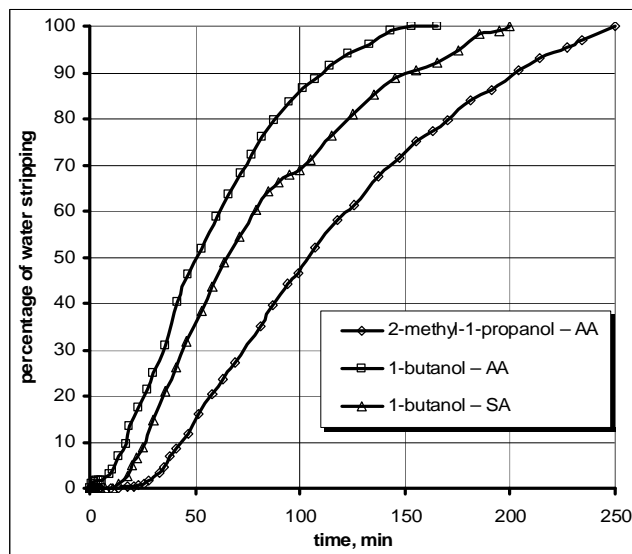


Fig. 3. The influence of the reagents nature on the esterification process. Dibasic acid:alcohol molar ratio – 2.5/1. $C(Zn(pfos)_2) = 1.1 \cdot 10^{-3}$ mol/dm³

At the same concentration of catalyst in the 1-butanol–AA, 1-butanol–SA and 2-methyl-1-propanol–AA systems intensity of water stripping and the chemical

reaction rate are different (Fig. 3). In general, such a different effect of alcohols and dibasic acids on the esterification can be explained by the differences in their chemical and physical properties as well as the properties of their monoesters. The physical properties of the alcohols first of all determine the different boiling points of the mixture in the reaction that affects the rate of chemical transformation. Therefore, to achieve the same acid number of the reaction products (the same conversion of carboxylic groups) the reaction time should be different and should increase in the row of:

1-butanol – AA < 1-butanol – SA < 2-methyl-1-propanol – AA.

The yield of the monoester at the esterification of adipic acid with 1-butanol was slightly higher compared to the yield at esterification of adipic acid with 1-butanol at the same conversion of carboxyl groups (~ 95–96 %). The unreacted dicarboxylic acid weight content in the reaction products is practically constant and is 2 %.

Thus, in the esterification reaction of dibasic acids both the nature of the alcohol (its reactivity and physical properties) and the nature of dicarboxylic acid affect the rate of reagents conversion. Undoubtedly, the change in the composition of the reaction mixture (different reactivity of the monoesters) and the polarity of the reaction medium also influences the reaction of the diesters obtaining.

Table 1

Indicators of the esterification process of succinic acid with 1-butanol

Catalyst	Time, min	Acid number, mg KOH/g	Degree of carboxylic groups conversion, %	Composition of the reaction mixture, %			Yield of the products, %		Maximum reaction rate, $r \cdot 10^3$, mol/(dm ³ ·s)
				SA	MBS	DBS	MBS	DBS	
Al(pfos) ₃	95	32.7	91.1	4.0	1.5	78.7	2.2	88.9	1.9
Co(pfos) ₂	145	7.1	98.1	0.9	3.7	82.2	5.5	92.6	1.6
Cu(pfos) ₂	190	10.4	97.2	1.3	0.9	85.2	1.4	95.8	1.5
Ni(pfos) ₂	180	28.1	92.4	3.5	5.1	76.3	7.6	84.8	1.4
Sn(pfos) ₂	230	10.1	97.3	1.3	4.6	80.8	6.8	90.5	1.2
Zn(pfos) ₂	200	15.0	96.0	1.9	4.7	79.8	6.9	89.1	1.4
Be(pfos) ₂	285	11.3	97.0	1.4	2.3	83.3	3.3	93.6	1.1
Ca(pfos) ₂	355	32.7	94.9	2.4	16.2	63.7	23.9	71.0	0.97

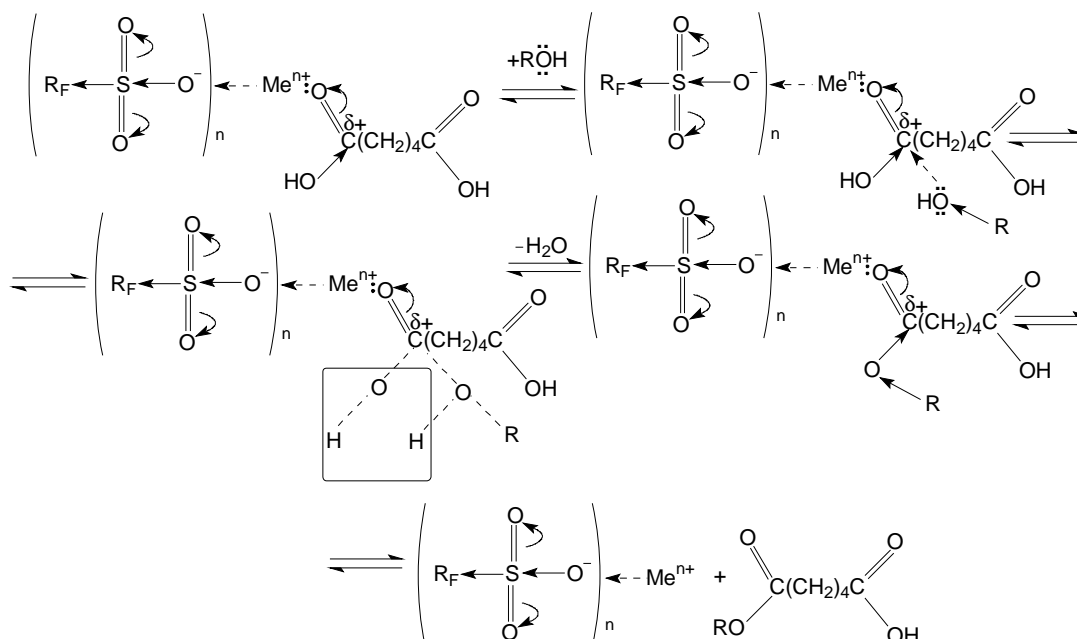


Fig. 4: The scheme of transformations in the esterification reaction, catalyzed by metals perfluoro(4-methyl-3,6-dioxaoctane)sulphonate

For the explanation of the catalyst action the scheme shown in Fig. 3 is offered.

It is obvious that the ligand environment of the cation not only improves the solubility of the salt in the reaction medium but also increases the polarization of covalent bonds C–S–O in its molecule (Fig. 4) due to the high electronegativity of the fluorine atoms.

Due to this fact, there is a significant shift of electron density from the metal cation, which makes it much more electrophilic. Probably, the first catalytic act is coordination of the oxygen atom of the dicarboxylic acid molecule on such activated cation. This coordination causes decrease of electron density on the carbon atom of its carboxyl group forming δ^+ -charge on it, which facilitates the interaction with the alcohol. After coordination of the alcohol molecule on the carboxyl C-atom the redistribution of the chemical bonds and the cleavage of water molecules take place. The final stage is decay of the catalytic complex formed by the catalyst and the ester.

We should not also exclude the possibility of simultaneous coordination of O-atoms of the acid molecules and alcohol on the electrophilic metal cation with the removal of water and the emergence of a new bond between the carboxyl C-atom of the acid and the RO-fragment of the alcohol molecule.

4. Conclusions

The investigations carried by us showed that the salts of perfluorooxasulfoacids have high activity in esterification process. It was determined that the composition of the catalyst, in particular the nature of the cation of catalyst significantly affects the technological parameters of the esterification process, namely the conversion of carboxyl groups of the reagents, the final acid number of the products, the duration of the reaction and the composition of the reaction mixture. The dependence between the relative electronegativity, radius of cation of the catalyst and the rate of chemical reaction has been found. It was established that the minimal radius

of cation and high relative electronegativity are optimal for an intensive course of chemical reactions. The same factors allow to achieve the best technological parameters of the process, particularly to reduce the time of reaction and achieve high conversion of dicarboxylic acid (91.1–98.1 %) and yield of diester (88.9–95.8 %).

References

- [1] Otera J.: Esterification. Methods, Reactions and Applications. Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim 2003.
- [2] Garaleh M.: Eur. J. Sci. Res., 2011, **3**, 383-387.
- [3] Ridland J. and Wesley L.: Pat. US 2002/6372929. Publ. Apr. 04, 2002.
- [4] Ishihara K. and Yamamoto H.: Pat. US 2011/7973193. Publ. Jul. 5, 2011.
- [5] Finmans P. et. al: Pat. WO 2005/049556. Publ. Jun. 02, 2005.
- [6] Odabashyan G. and Shvets W.: Laboratornyi Practicum po Khimii i Technologii Osnovnogo Organicheskogo i Neftekhimicheskogo Sinteza. Khimiya, Moskva 1992.

ПЕРФТОРОКСАСУЛЬФОНАТИ МЕТАЛІВ – КАТАЛІЗАТОРИ ОДЕРЖАННЯ ЕСТЕРІВ

Анотація. Досліджено процес одержання естерів аліфатичних дикарбонових кислот і спиртів C_4 - C_5 у присутності перфтор(4-метил-3,6-діоксаоктан)сульфонатів різних металів. Для порівняльної оцінки каталізаторів їх концентрація вибрана однаковою і такою, щоб швидкість процесу лімітувалася саме швидкістю хімічної реакції. Отримано залежності впливу концентрації та природи каталізатора, природи дикарбонової кислоти та спирту на технологічні показники процесу естерифікації. Виявлена досить висока активність досліджених каталізаторів, яка, ймовірно, обумовлена синергічним ефектом дії катіону металу і перфторованого фрагмента, який забезпечує як зменшення електронної густини на йоні металу, так і добру розчинність каталізатора в субстраті і створення його високої активної концентрації.

Ключові слова: естерифікація, дикарбонові кислоти, перфтороксасульфونات, каталізатор, спирти C_4 - C_5 .