Esterification of aromatic olefins with acetic acid in the presence of sulphuric acid as a catalyst
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Esterification of aromatic olefins with acetic acid in the presence of sulphuric acid as a catalyst (Abstract Nº 422)

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Abstract

In this researching work, esterification reactions of ethenyl benzene and its derivatives were carried out with acetic acid in the presence of sulphuric acid as a catalyst. These compounds have a double bond coupling with the aromatic ring and absorb strongly in the ultraviolet region, which permits a precise analysis when they are in very diluted concentrations. For it, the esterification reactions were carried out and followed in a thermostatized cell device of an ultraviolet-visible spectrophotometer.

A study was made on influence of temperature, catalyst concentration and type of substituted radical have on the conversion of all studied compounds. From the obtained results it can be deduced the following: an increase in temperature and catalyst concentration positively influences the conversion of the corresponding olefins. The substituted radical and the occupied position on the aromatic ring (*meta* or *para*) exert a very important influence on the reaction conversion. For identical substitute type, the substituted derivatives in position *para* present a bigger reactivity and olefin conversion than substituted derivatives in position *meta*.

The effect of the substitute on the ring benzene over the reaction rate constant of the esterification process was studied.

The effect of acidity medium over the reaction rate constant of the esterification process was studied by the application of the Hammett equation.

Finally, a thermodynamic and kinetic study has been done with the calculation of the corresponding parameters.

Keywords: esterification, styrene, kinetic, catalysis, olefins

1. Introduction

Most of the commercially available esters are obtained by the reaction between an alcohol and an organic acid, or an organic anhydride, generally in the presence of a strong mineral acid that acts as a catalyst. However, the direct esterification of an olefin by an organic acid should be the most appropriate, and therefore more economic method, to reach the same result of the classic reaction.

The addition of acetic acid to ethenyl benzene and its derivatives compounds in the presence of sulphuric acid as a catalyst registers inside the study of the homogeneous catalysis in solution. The practical importance of this type of reactions at present is due to the fact that numerous industrial processes take place for this way (Yoshihara 1982; Colombo 1983; Becker and Byrne 1999; Tipton 2000; Zeller and Walter 2001; Mass and Schwab 2001). Also, the concretely studied processes give place to specific components used in the formulation of new medications and cosmetics. On

the other hand it is necessary to highlight the industrial importance of esters in processes like the preparation of vinyl resins and their employment as solvent in the production of lacs (Mathys and Brown, 1997; Sapalidis, 1997).

In this sense, the scientific investigations of the last years are directed fundamentally toward the election of the most appropriate catalysts to carry out this type of processes, among those we can mention the polyphosphoric acid (Mebah, 1993); heteropolyacids, as the silicotungstic acid, molybdophosphoric acid, molybdosilicic acid (Higashi 2000), the tungstophosphoric acid and the molybdovanadophosphoric acid (Azuma 2000); the gallium silicate (Matsuoka 2000), or ion exchange resins (Chakrabarti and Sharma 1991; Mazzotti 1997):

In last years, we can observe there is a new group of catalysts used in olefins esterification, such as the cerium sulfate (Horiuchi, 2003), sulfamic acid (Wang, 2004), iridium complexes (Kiyooka, 2005).

Recently, the protic ionics liquids have been used as acidic catalyst for the esterification, such as SO_3H-functionalized ionic liquid (Gu, 2004), protic ionic liquids based on 2-methylpyridinium (Duan, 2006).

2. Experimental part

Ethenyl benzene and its derivative compounds, because of their double bond coupling with the aromatic ring, absorb strongly in the ultraviolet region, which permits a precise analysis when they are in very diluted concentrations, of the order of 10^{-4} mol/L. For it, the esterification reactions of ethenyl benzene and its derivative compounds by acetic acid in the presence of sulphuric acid as a catalyst were carried out and followed in a thermostatized cell device of an ultraviolet-visible spectrophotometer. Once the ethenyl benzene solution or its derivative compounds with acetic acid are prepared as well as of the catalyst, they are added into the ultraviolet-visible spectrophotometer quartz cell which is used as a reaction vessel. Then, the quartz cell temperature and the wavelength of the spectrophotometer are adjusted and the necessary quantity of olefin is injected, beginning the reaction at this time. On the other hand, the quartz cell of the spectrophotometer is playing the role of chemical reactor and in our concrete case, it is a micro reactor, of 3 ml of volume, in which the chemical reaction is developing and at the same time it is determining analytically the concentration of present olefin in the reaction medium.

3.- Results
## 3.1 Influence of variables

For the different processes of acetic acid addition to ethenyl benzene and its derivatives compounds in the presence of sulphuric acid as a catalyst that were carried out, a study was made of the influence that temperature, catalyst concentration and type of substituted radical have on the conversion of all studied compounds.

In the specific case of 1-ethenyl-4-chloro benzene esterification, Graph 1 shows the influence of temperature on the reactions carried out at 20ºC, 25ºC, 30ºC, 35ºC and 40ºC respectively, with a catalyst concentration of 2 mol/L and an initial olefin concentration of $1.2 \cdot 10^{-4}$ mol/L, respectively. It is observed that an increment of the temperature influences positively the conversion of this compound. Similar results were obtained on the influence of this variable on the remainder olefins mentioned previously.
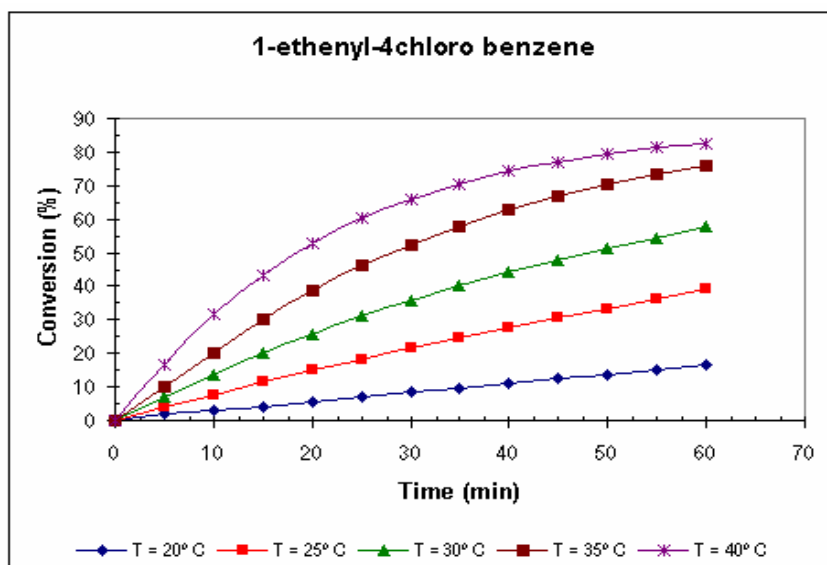
Graph 1 : 1-ethenyl-4-chloro benzene. Influence of temperature over olefin conversion.

When the catalyst concentration influence on the olefin conversion was studied, it was observed that catalyst concentration effects positively the conversion of olefin, just as it is demonstrated in the Graph 2, for the specific case of 1-ethenyl-3-chloro benzene esterification reactions that were carried out with catalyst concentrations of 2, 3 and 4 mol/L, respectively at temperature of 35ºC, with an initial olefin concentration of $1.2 \cdot 10^{-4}$ mol/L. Similar results were obtained with the remaining studied olefins.
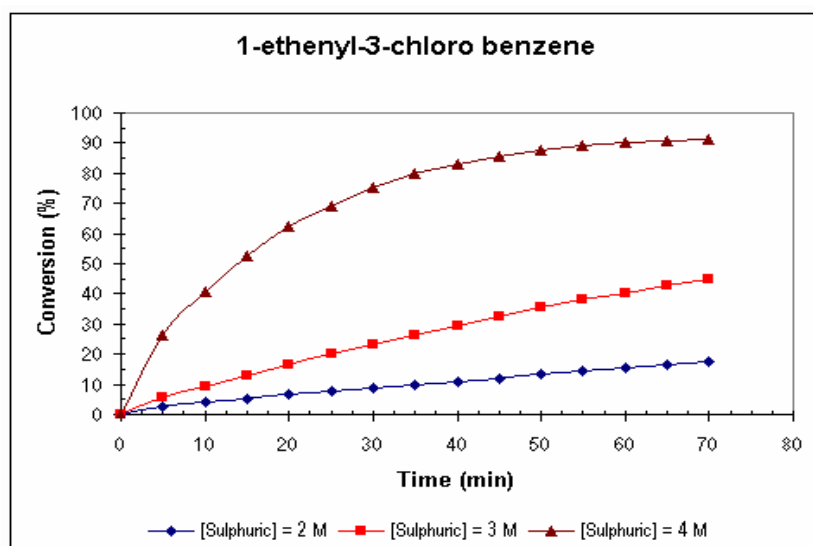
Graph 2 : 1-ethenyl-3-chloro benzene. Influence of catalyst concentration over olefin conversion.

Finally, it was possible to prove the important influence of the substituted radicals in the m- or p- positions on the conversion of the studied olefins, presenting growing reactivity in the following order: 1-ethenyl-3-nitro benzene, 1-ethenyl-3-chloro benzene, 1-ethenyl-4-chloro benzene, 1-ethenyl-3-methyl benzene and 1-ethenyl-4-methyl benzene. This effect can be appreciated in the Graph 3 for the reactions carried out at temperature of 25ºC and a sulphuric acid concentration 1.5 mol/L, with all the mentioned olefins.
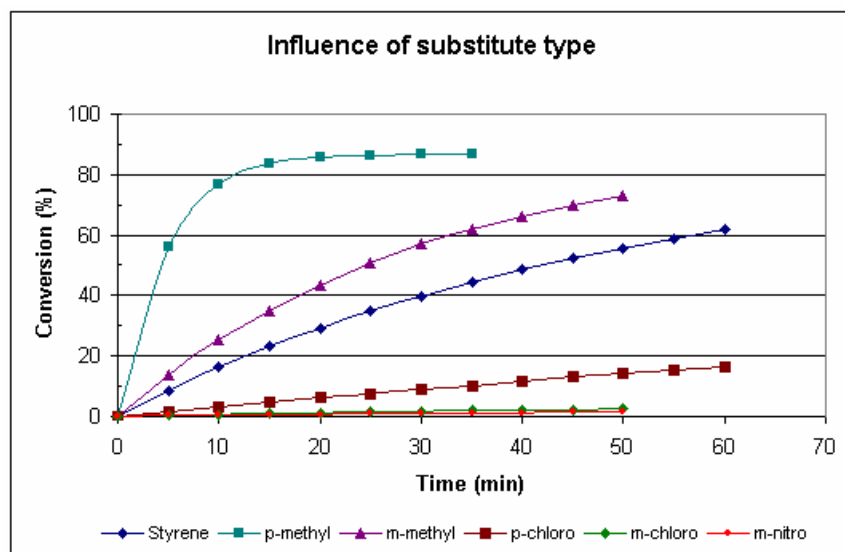
Graph 3: Influence of substitute type over olefin conversion. T = 25ºC; [Sulphuric] = 1.5 mol/L

3.2 Kinetic study

The addition of acetic acid to ethenyl benzene and its derivative compounds in the presence of sulphuric acid as a catalyst, it registers in the field of the homogeneous catalysis in solution. The study of the olefins esterification has taken to diverse authors to establish that these processes can be considered like catalyzed reactions by acids or bases. The corresponding reaction for the studied processes can be represented in the following way, in case of ethenyl benzene:

Ethenyl benzene
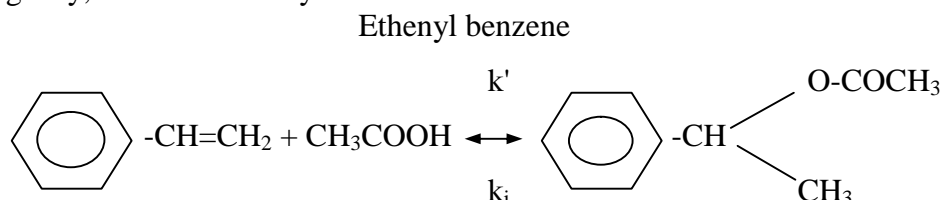
3.3 Determination of kinetic parameters

The determination of kinetic parameters has been done using mathematical expressions developed in previous works (Martínez and Rus 1992), which resulted in the following equation:

$$Ln\frac{D_o - D_e}{D - D_e} = (k + k_i) \cdot t \qquad (1)$$

where D_o, D and D_e are the optical densities of the olefins in the initial instant, in any instant t and in the equilibrium respectively, considering that the optical density of the olefin is proportional to its concentrations, by the law of Lambert-Beer.

Given that, under the conditions in which the esterification processes were carried out, the reactions were completely displaced toward the corresponding formation of ester, and considering the process to be an irreversible elemental process, Equation (1) can be expressed in the following form:

$$Ln\ D = Ln\ D_o - k \cdot t \qquad (2)$$

Table 1 shows the experimental results obtained for the ethenyl benzene and its derivatives, being k_{exp} the direct reaction constant, with an experimental error of 1%.

OLEFIN	T (ºC)	[H₂SO₄] (mol/L)	k_{exp} (min⁻¹)	Corr. Coef.
1-ethenyl benzene	15	2	0.01094	0.99993
1-ethenyl benzene	25	1.5	0.01584	0.99945
1-ethenyl-4-methyl benzene	20	1	0.04684	0.99482
1-ethenyl-4-methyl benzene	25	1.5	0.14654	0.99681
1-ethenyl-3-methyl benzene	25	2	0.06092	0.99667
1-ethenyl-3-methyl benzene	30	1.5	0.05462	0.99443
1-ethenyl-4-chloro benzene	30	2	0.01411	0.99971
1-ethenyl-4-chloro benzene	35	2.5	0.03899	0.99506
1-ethenyl-3-chloro benzene	40	3	0.01639	0.99815
1-ethenyl-3-chloro benzene	50	4	0.08056	0.99800
1-ethenyl-3-nitro benzene	50	4.5	0.00372	0.99967
1-ethenyl-3-nitro benzene	60	5	0.02370	0.99561

Table 1: Determination of experimental direct reaction constant in the esterification of ethenyl benzene and its derivatives. $[S_o] = 1.2 \cdot 10^{-4}$ mol/L

3.4 The influence of medium acidity

The addition of acetic acid on the olefins and their inverse reactions are visibly similar to the hydration and dehydration of their corresponding esters. This analogy is demonstrated by the influence that acidity of the medium exerts on the reaction rate constant, which suggests the following reaction scheme for ethenyl benzene and its derivative compounds:

$$S + H^+ \underset{k'_1}{\overset{k_1}{\rightleftharpoons}} SH^* \underset{k'_2}{\overset{k_2}{\rightleftharpoons}} S^* \overset{k_3}{\longrightarrow} Products$$
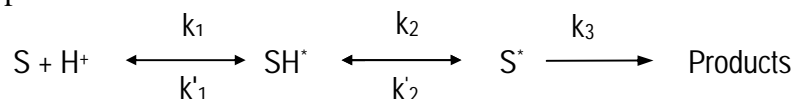
where S represents the ethenyl benzene concentration or its derivative compounds, SH* is an intermediate complex formed quickly, but in small concentration, by the addition of one proton to the double bond, and S* represents another activated complex, from which the products reaction are irreversibly formed.

On the other hand, if ionization equilibrium of a neutral base B (introduced in the medium) is considered and expressed by the following equation:

$$B + H^+ \longleftrightarrow BH^+$$
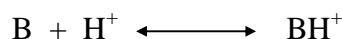
The acidity of the reacting medium can be characterized by the Hammett equation:

$$h_o = a_{H^+} \frac{f_B}{f_{BH^+}} \tag{3}$$

From mathematical expressions developed in previous works (Martínez and Rus, 1992) and with the values of the Hammett constant (H_o) taken from the bibliography (Mollard et al., 1966), it has been proven that, for various concentrations of catalyst, the experimental data fits the following equation:

$$\log k = -\alpha \cdot H_o - \beta \qquad (4)$$

where
k = direct reaction constant
$H_o = - \log h_o$
$\alpha = 1$

$$\beta = - \left(\log k^0 + \log \frac{f_{BH^+} f_S}{f_{S^*} f_B} \right)$$

and f_i is the fugacity of the component i.

Table 2 shows some of the obtained results. As can be observed, an adequate fitting is obtained, since the correlation coefficients is sufficiently acceptable. However, the value of α is higher than the theoretical. This is in agreement with the results obtained by other scientific investigators who studied these type of reactions (Corriu and Guenzet, 1970; Corriu et al., 1970; Corriu and Reye, 1974) that attribute the deviation regarding the equation (4), on one hand to the olefin's own nature and for other, to the degree of transfer of the proton on the same one.

OLEFIN	[H_2SO_4] (mol/L)	H_o	K_{exp} (min^{-1})	α β
1-ethenyl-4-methyl benzene (*)	1	- 3.10	0.02480	$\alpha = 1.51629$
	1.5	- 3.42	0.06775	$\beta = 6.32042$
	2	- 3.65	0.17141	R = 0.99746
1-ethenyl-3-methyl benzene(**)	1.5	- 3.42	0.07377	$\alpha = 1.38880$
	2	- 3.65	0.17827	$\beta = 5.86122$
	2.5	- 3.86	0.29991	R = 0.99260
1-ethenyl-4-chloro benzene (***)	1.5	- 3.42	0.00305	$\alpha = 1.42404$
	2	- 3.65	0.00823	$\beta = 7.33777$
	2.5	- 3.86	0.01567	R = 0.99131
	3	- 4.08	0.02685	
1-ethenyl-3-chloro benzene (**)	2	- 3.65	0.00249	$\alpha = 1.33545$
	3	- 4.08	0.00835	$\beta = 7.49468$
	4	- 4.53	0.03721	R = 0.99887
1-ethenyl-3-nitro benzene (***)	1.5	- 3.42	0.00026	$\alpha = 1.36850$
	2	- 3.65	0.00054	$\beta = 8.26445$
	2.5	- 3.86	0.00104	R = 0.99998

Table 2: Influence of the medium acidity. Fitting of experimental results to the Hammett equation. [S_o] = 1.2 · 10^{-4} mol/L. (*) T = 15ºC; (**) T = 35ºC; (***) T = 25ºC and R = Correlation coefficient.

3.5 Thermodynamic study

From the equation of Arrhenius, as well as the values of k obtained experimentally at different temperatures for each compound, the activation energy was determined for the esterification of ethenyl benzene and its derivatives by acetic acid, in presence of sulphuric acid as a catalyst.

The activation Arrhenius energy can be related with ΔH^o through the equation:

$$E_{act} = \Delta H^o + R \cdot T \qquad (5)$$

On the other hand, applying the transitional state theory, substituting the value of ΔH^o from Equation (5) and taken into account that $R << E/T$, for this type of processes, the ΔS^o can be expressed as follows:

$$\qquad (6)$$

where h is Planck's constant and k_B is Boltzman's constant.

The values of ΔH^o, ΔS^o and activation energy had been calculated. From the observation of the ΔH^o values, it can be deduced that the esterification of the ethenyl benzene and its derivatives is an endothermic process. On the other hand, the activation energy values increase as the olefin reactivity decreases. Finally, as was expected, negative values from ΔS^o have been obtained.

3.6 The influence of the type of substitute

The effect of the substitute on the ring benzene over the reaction rate constant of the esterification process can be studied by the application of the Hammett equation:

$$\log k = \log k_o + \sigma \cdot \rho \qquad (7)$$

where k is the reaction rate constant of substituted compound and k_o is the reaction rate constant of non-substituted compound (ethenyl benzene in this case) that takes as reference value. The parameter σ is called the substitution constant, it is characteristic of the nature and position of the substitute. The parameter ρ is called the reaction constant, it depends on reaction family and the external conditions in which the reaction occurs. The Hammett equation is valid for a series of compound aromatic that has in common a reaction centre. The Hammett equation, just as we have expressed is applicable only to substitute in position m- or p- on the ring benzene. On the position o-, particular geometric effects give important irregularities.

Knowing the reaction rate constants of ethenyl benzene (Martinez de la Cuesta et al., 1995) and its derivatives (1-ethenyl-3-chloro benzene, 1-ethenyl-3-methyl benzene and 1-ethenyl-3-nitro benzene respectively) as well as the normal substitution constants (Corriu and Reye 1974) it was possible to determine the exalted substitution constants, σ^*, for the derivatives 1-ethenyl-4-chloro benzene and 1-ethenyl-4-methyl benzene, respectively. Later on the numeric value of the reaction constant, ρ, is calculated. Tables 4 and 5 show the corresponding results. An adequate fitting is obtained, since the correlation coefficients are sufficiently acceptable. The values of the substitution constants are in agreement with the expected results.

OLEFIN	T (ºC)	[H$_2$SO$_4$] (mol/l)	k$_{exp}$ (min^{-1})	σ*
1-ethenyl-4-methyl benzene	25	1.5	0.14654	σ* = 0.056 R = 1
	25	2	0.40988	
	25	2.5	0.89611	
1-ethenyl-4-chloro benzene	25	2	0.00823	σ* = 0.241 R = 0.99946
	30	2	0.0144	
	35	2	0.02441	

Table 4: Influence of the substitute type. Determination of the substitution constant

of the p-substituted derivatives compounds. [S$_o$] = 1.20 · 10^{-4} mol/L. R = Correlation coefficient

T (ºC)	ρ
20	4.665
25	4.654
30	4.644
35	4.634

Table 5: Esterification of p- or m- substituted derivatives.

Determination of reaction constant. [H$_2$SO$_4$] = 2 mol/L

4. Conclusions

From the obtained results it can be deduce the following conclusions: an increase in temperature and catalyst concentration positively influences the conversion of the corresponding olefins.

On the other hand it has been proven that the substituted radical and the position that it occupies on the aromatic ring (m- or p-) exert a very important influence on the conversion of the studied olefins, presenting growing reactivity in the following order: 1-ethenyl-3-nitro benzene, 1-ethenyl-3-chloro benzene, 1-ethenyl-4-chloro benzene, 1-ethenyl-3-methyl benzene and 1-ethenyl-4-methyl benzene. For the same substitute type, those derivatives substituted in position p- present a bigger reactivity and a bigger conversion of the olefin than derivatives substituted in position m-.

The values α and β, which appears in Hammett equation, has been calculated, as well as the reaction constant and the substitution constant (σ and ρ) of each one of derivatives compounds of ethenyl benzene.

Finally, a kinetic and thermodynamic study has been done, and the corresponding kinetic parameters have been calculated in each one of the cases with an adequate fitting.

5.- Nomenclature

a$_H^+$ = activity of proton in the reaction medium, (mol/L)

BH^+ = ionic compound formed from the reaction between a neutral base with a proton

Conversion % = percentage of olefin conversion = $\left(\dfrac{D_o - D}{D_o} \right) \cdot 100$

Corr. Coef. = Correlation coefficient in linear fitting

E_{act} = activation energy, (Kcal/mol)

$[H_2SO_4]$ = sulphuric acid concentration, (mol/L)

h_o = Hammett function

H_o = Hammett constant

$k = k_{exp}$ = direct reaction constant of pseudofirst order in esterification reaction, (min^{-1})

k_i = inverse reaction constant of esterification reaction, (min^{-1})

k' = direct reaction constant of first order of esterification reaction, $(L \cdot mol^{-1} \cdot min^{-1})$

k^o = parameter in the Hammett equation

k_1 = direct reaction constant of the formation reaction of intermediate complex SH*, $(L \cdot mol^{-1} \cdot min^{-1})$

k_2 = direct reaction constant of the formation reaction of activated complex S*, (min^{-1})

k'_1 = reaction constant in the decomposition reaction of the intermediate complex SH* to form S and H^+, (min^{-1})

k'_2 = reaction constant in the decomposition reaction of the activated complex S* to form SH*, (min^{-1})

k_3 = reaction constant of the irreversible reaction of the activated complex S* to form the corresponding products, (min^{-1})

R = molar constant of gases, $(J \cdot mol^{-1} \cdot K^{-1})$

$[S_o]$ = initial concentration of olefina, (mol/L)

T = temperature, (ºC)

t = time, (min)

Greek letters

α = Parameter in the Hammett equation

β = Parameter in the Hammett equation

σ = Substitution constant

ρ = Reaction constant

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