Kinetic and catalytic aspects of dimethylterephtalate transesterification also through the use of model molecules

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Abstract

Kinetic and catalytic aspects of DMT transesterification reaction, key step in the industrial production of polyethylen-terephtalate (PET), have been deepened also through the use of model molecules such as $CH_3COO–Ph–X$. These molecules give the same reactions with ethylene glycol occurring in the DMT transesterification too. The use of model molecules in the study of this reaction seems therefore to be promising in perspective. As we observed, however, the nature of the para-substituent X has a very strong influence on the reaction rate, when salts of bivalent metals such as Zn, Cd, Co, Mg, Mn, are used as catalysts, while this influence is much smaller when a tetravalent metal, as Ti, is used. This fact suggests that the transesterification mechanism operating in the two cases is different and this suggestion has been confirmed by applying Hammett's approach to the available kinetic data. Experimental kinetic runs were all performed at 193°C, by withdrawing small samples of the reaction mixture at different reaction times. These samples were gaschromatographically analyzed. We found volcano shaped curves of the reaction rates as a function of the metal ion acidities and we obtained different trends with a maximum of activity shifted from a metal to another for different substrates. A comparison of the kinetic results obtained, respectively, with the model molecules and DMT will be reported too. © 1998 Elsevier Science B.V.

1. Introduction

Dimethylterephtalate (DMT) transesterification is a key step in the industrial production of polyethylenterephtalate (PET). As the production of this polymer is continuously growing in the world [1], many papers dealing with the kinetic and catalytic aspects of DMT transesterification have been published [2–6]. On the basis of these papers it is possible to conclude that the reaction is catalyzed by metal salts whose activity strongly depends on the acidity of the different metal ions. On this purpose some authors [2,3] reported volcano shaped curves of the reaction rates as a function of the metal ion acidities. As it will be seen, these volcano shaped curves should be considered with caution because the reaction order with respect to the catalyst can notably change with the concentra-

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tion, in a different way for each metal [2,4,6,7]. Besides, in recently published papers [7–9] it has been shown that DMT transesterification occurs with the formation of three types of oligomers having different terminal groups (HO–OH, CH_3O–OH, CH_3O–OCH_3) mixtured with the predominant monomer bis(hydroxyethyl) terephtalate (BHET). Oligomers can reach to the maximum 6–10 monomeric units in industrial conditions [6,7]. These facts require an elaboration of the kinetic data more complicated than in the past, taking sometimes to different conclusions.
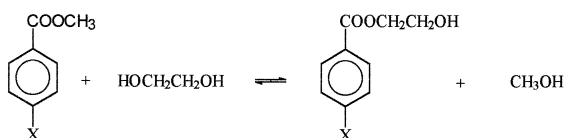
In this paper, kinetic and catalytic aspects of DMT transesterification reaction will be deepened also through the use of model molecules such as:
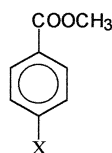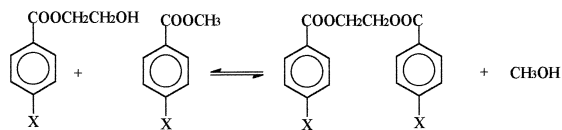

$$(1)$$

where X = H, CH_3, NO_2, OCH_3.

Transesterification reactions occurring with these molecules are:

$$(2)$$

$$(3)$$

In other words, two reactions occur with different rates and equilibrium constants, the former involving one hydroxyl of the free ethylene glycol molecules, the latter the residual hydroxyl of the bonded ethylene glycol. These reactions are the same occurring in the DMT transesterification too. The use of model molecules in the study of this reaction seems therefore to be promising in perspective. As we observed, however, the nature of the para-substituent X has a very strong influence on the reaction rate, when salts of bivalent metals such as Zn, Cd, Co, Mg, Mn, are used as catalysts, while this influence is much smaller when a tetravalent metal, as Ti, is used. This fact suggests that the transesterification mechanisms operating in the two cases are different and this suggestion will be confirmed by applying Hammett's approach [10] to the available kinetic data.

Another observation reported in this paper is the different trends we obtained with a maximum of activity shifted from one metal to another, plotting activities obtained for each model molecule as a function of the acidities of the bivalent metals.

A comparison of the kinetic results obtained with the model molecules and DMT, respectively, is also reported.

An attempt on the explanation of the observed phenomena, on the basis of reasonable reaction mechanisms, concludes the paper.

2. Experimental section

2.1. Methods, techniques and reagents

The reactor used to perform the transesterification of the mentioned model molecules has already been described elsewhere [7] in detail. Methanol formed during the reaction was stripped by a nitrogen stream of 2 l/h while vaporized ethylene glycol was refluxed. Kinetic runs were all performed at 193°C, by withdraw-

ing small samples of the reaction mixture at different reaction times. These samples were gaschromatographically analyzed by injecting a solution of the sample diluted with CH_2Cl_2 (about 0.05 g of the sample in 4 cm^3 of CH_2Cl_2) into a HP1 column of the Crompack (25 m in length, 0.32 mm i.d. containing 100% dimethylpolysiloxane gum). FID was used as a detector. The temperature of the oven was gradually increased by an opportune program. Catalysts used were acetates of Mg, Mn, Zn, Co, Cd and titanium butoxide. All reagents and catalysts were supplied by the Aldrich at the highest purity available.

Kinetic runs related to DMT transesterification, reported in this paper, have been performed as indicated in a previous work [7].

3. Results and discussion

The reactions occurring with model molecules (Eqs. (2) and (3)) have been performed by stripping methanol. Therefore, those reactions can be considered far from the equilibrium conditions, consequently, we can write in a simpler way:

$$SUB + EG \rightarrow M + CH_3OH\uparrow$$

$$SUB + M \rightarrow D + CH_3OH\uparrow$$
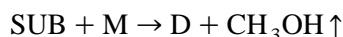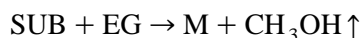
with SUB being a model molecule, that is methyl *p*-toluate (MT), methyl *p*-nitrobenzoate (MNB), methyl *p*-anisate (MA), methyl benzoate (MB), while M is the compound $X\text{-}\phi\text{-}COOCH_2CH_2OH$ and D is $X\text{-}\phi\text{-}COOCH_2CH_2OOC\text{-}\phi\text{-}X$. By assuming, as a first approximation, a second order kinetic law, we can write the differential equations system:

$$d[SUB]/dt = -K_M[SUB][EG]$$
$$- K_D[SUB][M]$$

$$d[M]/dt = K_M[SUB][EG] - K_D[SUB][M]$$

$$d[D]/dt = K_D[SUB][M]$$

By integrating these equations simultaneously it is possible to reproduce the evolution with time of reagents and products concentration provided the kinetic parameters are known. Kinetic pa-

Table 1

List of the kinetic runs performed on methyl *p*-toluate (MT) with related operative conditions and obtained kinetic parameters

Run	Metal	Metal concentration (10^3 mol/l)	Mol SUB/mol EG	K_M (10^3 l min^{-1} mol^{-1})	K_D (10^3 l min^{-1} mol^{-1})
1	Zn	5.78	1	1.33	0.29
2	Cd	5.87	1	8.04	2.41
3	Co	5.78	1	0.98	0.17
4	Mg	5.68	1	2.61	0.57
5	Mn	5.68	1	7.55	2.04
6	Zn	0.38	0.5	0.62	0.15
7	Cd	0.37	0.5	1.57	0.39
8	Mn	0.36	0.5	1.87	0.39
9	Zn	1.03	0.5	0.41	0.05
10	Cd	1.04	0.5	3.34	1.05
11	Mn	1.04	0.5	3.47	1.02
12	Mg	1.04	0.5	1.35	0.4
13	Zn	2.62	0.5	0.47	0.08
14	Cd	2.57	0.5	4.27	1.44
15	Mn	2.57	0.5	5.14	1.54
16	Mg	2.57	0.5	2.49	0.54
17	Zn	4.17	0.5	0.63	0.17
18	Cd	4.17	0.5	6.96	0.83
19	Mn	4.17	0.5	6.80	1.54
20	Mg	4.20	0.5	2.60	0.21
21	—	—	1.0	less than 1e − 6	1e − 12
22	Ti	5.82	1.0	1.40	0.29

Table 2

List of the kinetic runs performed on methyl *p*-nitrobenzoate (MNB) with related operative conditions and obtained kinetic parameters

Run	Metal	Metal concentration (10^3 mol/l)	Mol SUB/mol EG	K_M (10^3 l min^{-1} mol^{-1})	K_D (10^3 l min^{-1} mol^{-1})
23	—	—	1	0.326	4.97e − 6
24	Zn	5.1	1	13.50	1.35
25	Cd	5.1	1	10.80	2.16
26	Co	5.1	1	9.18	0.92
27	Ti	5.1	1	7.56	0.97
28	Mn	5.1	1	12.42	0.97

Table 3

List of the kinetic runs performed on methyl *p*-anisate (MA) with related operative conditions and obtained kinetic parameters

Run	Metal	Metal concentration (10^3 mol/l)	Mol SUB/mol EG	K_M (10^3 l min^{-1} mol^{-1})	K_D (10^3 l min^{-1} mol^{-1})
29	Zn	5.68	1	0.38	0.005
30	Mn	5.68	1	5.98	0.92
31	Mg	5.68	1	1.60	0.22
32	—	—	1	1×10^{-9}	1×10^{-15}
33	Ti	5.68	1	1.51	0.0005

rameters have been determined by mathematical regression analysis of the data collected, at different times, in each run. Runs performed are summarized, respectively, in Tables 1–4, being Table 1 related to MT, Table 2 to MNB, Table 3 to MA and Table 4 to MB.

In the tables are reported the adopted operative conditions as the type of catalyst used, the catalyst concentration and the initial molar ratio between the reagents. In the same tables are also reported the kinetic constants K_M and K_D determined by mathematical regression analysis. The adopted second order kinetic law proved to be correct, as it appears by observing the agreement obtained in the simulation of the kinetic runs. Examples of such simulations are reported in Figs. 1–4, corresponding, respectively, to one run for each considered substrate.

The agreement obtained in the simulation of all the runs, with the kinetic parameters reported in Tables 1–4, is similar to that observable in the previously mentioned Figs. 1–4.

As can be seen from data reported in Table 1, runs with MT have been made by using different catalysts concentrations. It is opportune to define an overall catalyst activity as $K_M + K_D$, and selectivities as $K_M/(K_M + K_D)$ and $K_D/(K_M + K_D)$. In Fig. 5 the activities obtained for different catalyst concentrations of Mn, Cd, Mg and Zn, respectively, are reported for comparison purpose.

It is surprising that the Zn catalyst has very low activity in promoting MT transesterification if compared, for instance, with Cd and Mn, in contrast with the behavior observed for DMT, at 180°C, that is reported in Fig. 6 for the catalysts

Table 4

List of the kinetic runs performed on methylbenzoate (MB) with related operative conditions and obtained kinetic parameters

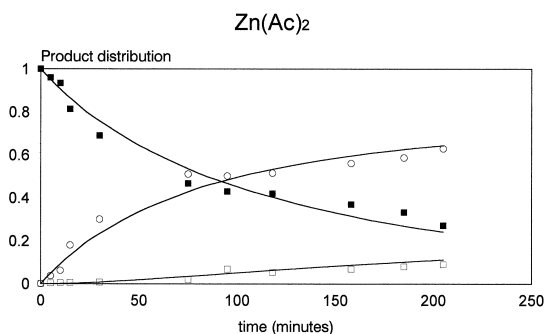| Run	Metal	Metal concentration (10^3 mol/l)	Mol SUB/mol EG	K_M (10^3 l min^{-1} mol^{-1})	K_D (10^3 l min^{-1} mol^{-1})
34	Mn	5.8	1.0	3.15	0.33
35	Mg	5.6	1.0	1.12	0.056
36	Co	5.7	1.0	2.05	0.326
37	Zn	5.7	1.0	4.47	0.838
38	Ti	5.7	1.0	2.55	0.337
39	Cd	5.7	1.0	2.30	0.057

Fig. 1. Simulation of a kinetic run performed on methyl *p*-toluate (MT) with $Zn(Ac)_2$ as a catalyst.
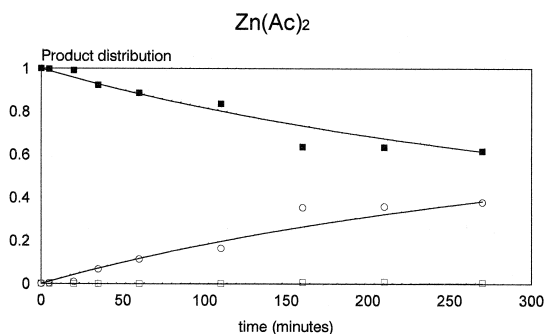

Fig. 3. Simulation of a kinetic run performed on methyl *p*-anisate (MA) with $Zn(Ac)_2$ as a catalyst.

Zn and Mn, respectively. The values of $K_M + K_D$ reported in Fig. 6 have been recalculated from data reported in previous works [7,11].

Another important observation is that the overall activities $K_M + K_D$ have for all the metals a similar trend growing with the catalyst concentration until a maximum value is reached. Thus, the reaction order related to the catalyst changes gradually from one to zero, probably because two phenomena occur increasing the catalyst concentration: the association between the glycoxide complexes [12] and the decrease in the ionic dissociation factor [7]. Both the phenomena contribute to change the catalyst reaction order, but it is difficult to forecast quantitatively the behavior of each metal.

It is useful to point out that MT transesterification activities observed are much lower than the ones for DMT, despite that in the first case the temperature used is higher. The decrease in

activity observed must be attributed essentially to the inductive and resonance effect of the methyl group in *para* position. In fact, the situation changes abruptly when in place of the methyl group we introduce NO_2 or OCH_3. With NO_2 we obtained an increase in the overall activity for all the catalysts, a decrease with OCH_3, both compared with CH_3. Particularly in the presence of the nitro-group the reaction of transesterification occurs also in the absence of the catalyst, as can be appreciated in Fig. 7. In the same figure, for comparison purpose, the behavior of MT and MA, in the absence of a catalyst, is reported too. As can be seen, for MT only 2% of the substrate is converted beyond four hours and for MA only 0.8%. The differences observed in the presence of proven catalysts can be better appreciated in Fig. 8 where all the activities shown by MT, MNB, MA and
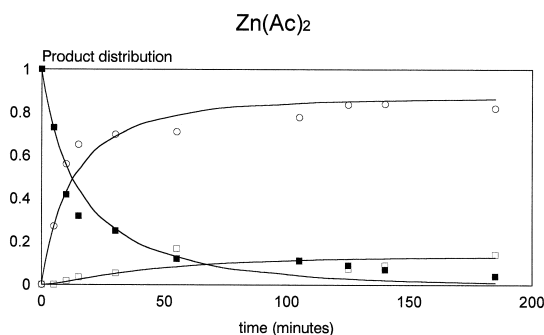

Fig. 2. Simulation of a kinetic run performed on methyl *p*-nitro-benzoate (MNB) with $Zn(Ac)_2$ as a catalyst.
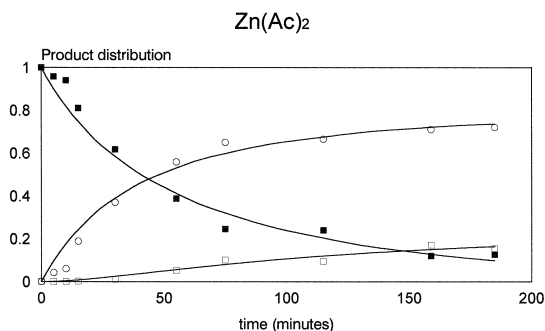

Fig. 4. Simulation of a kinetic run performed on methylbenzoate (MB) with $Zn(Ac)_2$ as a catalyst.
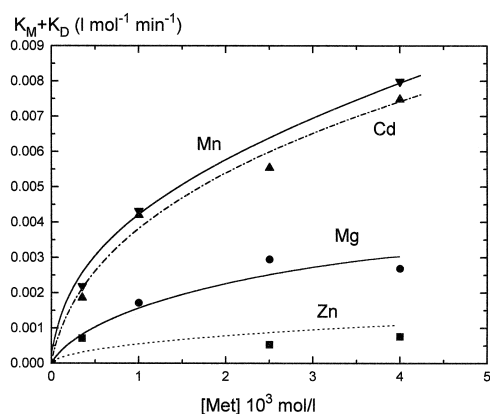
Fig. 5. Overall catalyst activities obtained for different catalyst concentrations of Mn, Cd, Mg and Zn, respectively, with methyl *p*-toluate (MT) as a reagent.

Fig. 7. Reaction of MT and MA with EG in the absence of a catalyst.

MB are plotted as a function of the acidity of the metals as suggested by Tomita and Ida [2], introducing the acidity factor β corresponding to the stability constant of dibenzoyl methane complex for metal species. This factor is used for the titanium too [13], considering it is the most acid metal of the other proven ones even when you use Chung's approach based on chemical–physical parameters of metallic ions [3].

As can be seen, the optimal acidity level is different according to the *para* substituent and the promoting effect of zinc is quite low for MA and MT, intermedium for MB and the best for
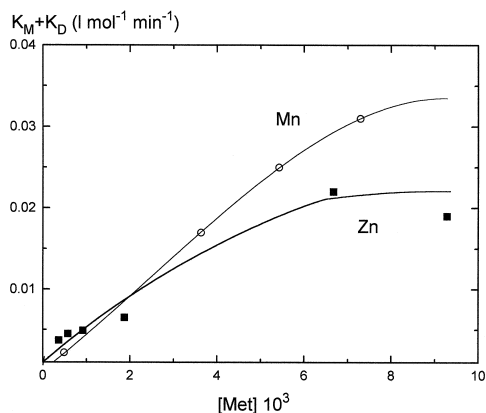
MNB. By observing Fig. 8 it is easy to recognize volcano shaped trends of the activities as a function of the bivalent metal acidities as the one observed for DMT by other authors [2,3] and by ourselves [7] (see Fig. 9). Titanium catalysts do not show this behavior. Particularly, in the case of MA, for example, the activity shown by this catalyst is higher than the one shown by zinc despite the increased acidity level. The peculiarity of this behavior suggests the intervention of a different reaction mechanism in agreement with the suggestions found in the literature [14,15]. Then we made an attempt to confirm that the reaction mechanisms operating, respectively, in the presence of bivalent

Fig. 6. Overall catalyst activities obtained for different catalyst concentrations of Mn and Zn, respectively, with dimethylterephtalate (DMT) as a reagent.
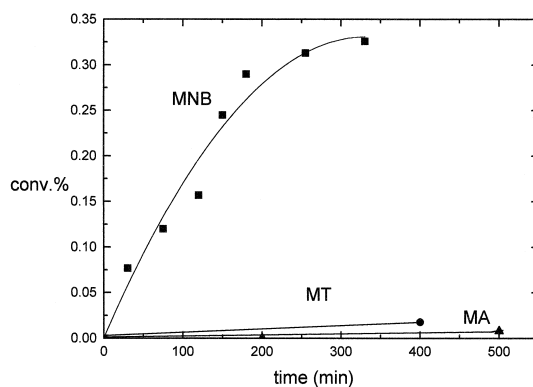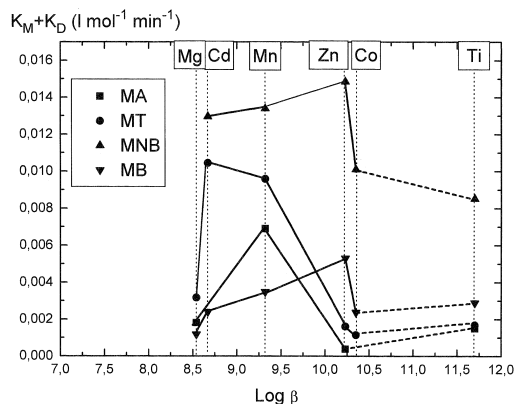

Fig. 8. Overall activities of proven catalysts shown by methyl *p*-toluate (MT), methyl *p*-nitrobenzoate (MNB), methyl *p*-anisate (MA) and methylbenzoate (MB) as a function of the acidity factor β.

metals or titanium are different by interpretating the kinetic data with the introduction of Hammett's correlation. This correlation could also be used to interpret semiquantitatively the effect of the *para* substituent on the activities. In Fig. 10, the activities obtained for the different substrates for any given catalyst are reported as a function of the normal substituent constants σ^n, Hammett's parameters characteristic of the *para* substituent in case of negligible through-resonance interaction [10].

This figure shows that only for titanium a linear trend is obtained. This fact suggests that in case of titanium the specialized long range interactions in the transition state are negligible. On the contrary bivalent metals seem to be strongly involved in the effect of resonance induced by the substituent, in agreement with the mechanisms suggested in the literature, according to which bivalent metals attack preferably the carbonyl oxygen [2,11,14] and titanium complexes interact with the acylic oxygen coordinating it [15].

We also tried unsuccessfully to apply Hammett's [10] and Taft's [16] approaches, in order to evaluate the effect of the resonance interaction in the transition state.

The conclusion, however, is that bivalent metals strongly affect the resonance of the transition state in a complicated way. This fact well
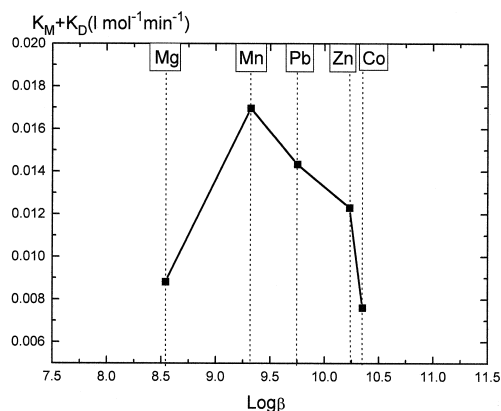

Fig. 10. Overall activities obtained for different model molecules and different catalysts as a function of the normal substituent constants σ^n.

explains the difficulties found in the quantitative interpretation of all the observed phenomena occurring together that is the influence of the para substituent, the shift of the maximum of activity with the metal acidity and the change of reaction order with the catalyst concentration.

Another remarkable achievement reached is that the model reaction can be useful to interpret the reaction mechanism, but the transfer of the results obtained to the DMT transesterification should be made with caution by using the model molecule that is the most similar to DMT such as, for example, MNB.

4. Conclusions

By comparing the kinetic behaviors shown by different bivalent metals, such as Zn, Cd, Co, Mg, Mn in the transesterification with ethylene glycol and model molecules, such as MT, MNB, MA, MB we observed, first of all, a very strong influence of the *para* substituent in affecting both the activities of the reaction and the

Fig. 9. Volcano shaped curve of overall catalyst activities as a function of the bivalent metal acidities for dimethylterephtalate (DMT) as a reagent.
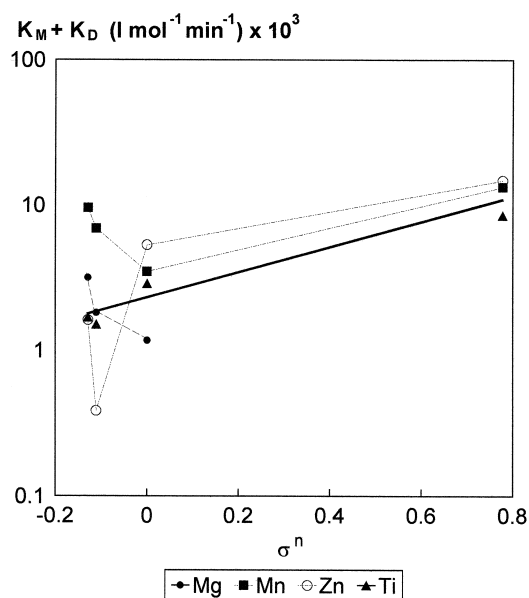
position of the maximum of the activity as a function of the metal acidity. For example, the catalyst based on Zn shows the smallest activity, compared with the other metals, as for MA. This behavior has been explained as a consequence of the strong resonance effect induced by the *para* substituent that is affected by the metal. All the bivalent metals show a variable reaction order from 1 to 0 with the concentration, probably as a consequence of the combined effect of association of the glycoxide complexes formed 'in situ' and the change in the ionic dissociation. This behavior has also been observed in the case of DMT. DMT shows activities that are comparable only with MNB, that is the $COOCH_3$ *para* substituent has an electron withdrawing effect similar to that of NO_2. Notwithstanding volcano shaped curves of Figs. 8 and 9, concerning MNB and DMT, respectively, have a maximum value for a different metal acidity.

Moreover, Fig. 8 shows zinc is the most active metal only for the two reagents without an electron-donor group in *para* position.

At last, we showed the behavior of the catalyst based on titanium is different from that of bivalent catalysts and we attributed the observed differences to a different catalytic mechanism. Titanium shows only the inductive field effect and not the resonance one. As a consequence we suggest, in agreement with other authors [15], that bivalent metals intervene by attacking the oxygen in the carbonyl group favoring the nucleophilic attack of the corresponding carbon atom, while titanium complexes coordinate acylic oxygen favoring transesterification through a concerted mechanism.

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