# Catalysis of Trans-esterification Reactions in Model Ester Mixtures

V.A. Vasnev[1], G.D. Markova[1], B.A. Uvarov[1], W.Yu. Voytekunas[2] and M.J.M. Abadie[2]*

[1]A.N. Nesmeyanov Institute of Organo-Element Compounds - INEOS, Russian Academy of Science,
28 Vavilov str., Moscow, 117813, Russia

[2]Laboratory of Polymer Science & Advanced Organic Materials – LEMP/MAO – Université Montpellier 2,
Sciences et Techniques du Languedoc, Place Bataillon, 34095 Montpellier Cedex 05, France

## Abstract

Model trans-esterification reaction of n-butylbenzoate with phenyl-p-chlorobenzoate in the molar ratio of 20:1 has been studied.

In order to evaluate catalysts based on lanthanide system the activity of nyodymium compounds – neodymium acetate, neodymium acetylacetonate and nitrate complex with benzo-12-crown-4 (neodymium nitrate coronate) – has been studied in the model trans-esterification reaction of n-butylbenzoate with phenyl-p-chlorobenzoate.

The effect of the electronic structure of the metal on the catalytic activity of the coronates of lanthanum, cerium, praseodymium, neodymium, samarium, terbium and erbium nitrates has been studied.

In order to estimate the optimum concentration of the catalysts, a study of the dependence of the trans-esterification reaction on concentration of neodymium nitrate coronate was carried out. An asymptotic nature of the concentration dependence on the catalytic activity of lanthanide compounds has been observed.

In order to look for new classes of inhibitors of trans-esterefication reaction, the model trans-esterificatiom reaction of n-butylbenzoate with phenyl-p-chlorbenzoate has been studied in the presence of some carborane derivatives: cesium salts of bis-1,2-(dicarbollyl) complexes of iron, cobalt and nickel(3+) and bis-1,2-(dicarbollyl)nickel(4+) $[(C_2B_9H_{11})_2Me]$. Some of these compounds were found to be effective inhibitors.

The dependence of the constant rate of the model trans-esterification reaction of n-butylbenzoate with phenyl-p-chlorobenzoate on the concentration of cerium salt of bis-1,2-(dicarbollyl) complex of nickel has been studied to determine the optimum concentration of inhibitors.

The influence of the ester chemical structure on the activity of ester groups in the trans-esterification activity has been determined in the reaction of di-n-butylterephthalate with different p-substituted derivatives of phenylbenzoate (phenyl-p-methoxybenzoate, phenyl-p-methylbenzoate, phenylbenzoate, phenyl-p-chlorobenzoate, phenyl-p-nitrobenzoate, p-methoxyphenylbenzoate, p-methylphenylbenzoate, p-chlorophenylbenzoate, p-nitrophenylbenzoate, n-butylbenzoate, di-n-butylterephthalate) in presence of the samarium nitrate coronate.

## Introduction

Some published studies of exchange reactions (included trans-esterification) in blends of conventional industrial polyesters indicate the possibility of producing new polymer materials with valuable properties [1-4]. It should be noted that further development of this method and its practical application in the field of polyesters is hardly possible without an exhaustive understanding of the basic exchange reactions in polyester mixtures, entailing the related mechanisms and factors which determine the reactivity of ester groups. The relatively slow rate of trans-esterification reaction enables to look for new catalytic systems with higher efficiency.

It should be mentioned here that, to produce blends of copolysters with a given block or random microstructure from a certain motherbatch polyester, it is essentially both to catalyze the trans-esterification reaction, and terminate this process at a certain stage. In addition, using of the inhibitors may expect to stabilize the mixtures of polyesters during their processing and application.

*corresponding  authors. E-mail: abadie@univ-montp2.fr

The objective of this investigation was to find new and efficient catalysts and inhibitors in order to control reactivities of ester groups during the process of trans-esterification. On the first stage of this work the model reaction of trans-esterification of n-butylbenzoate with phenyl-p-chlorobenzoate in the molar ratio of 20:1 (reaction 1) has been studied (Scheme 1)

In order to determine the influence of the chemical structure on the activity of ester groups, the reaction of di-n-butylterephthalate with different p-substituted derivatives of phenylbenzoate (20:1 molar ratio) has been studied (reaction 2 − Scheme 2)
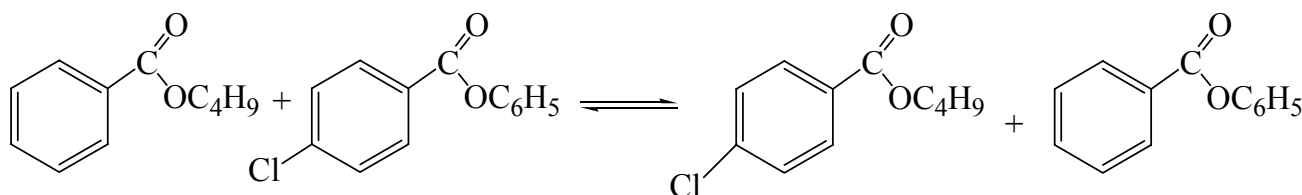


**Scheme 1**
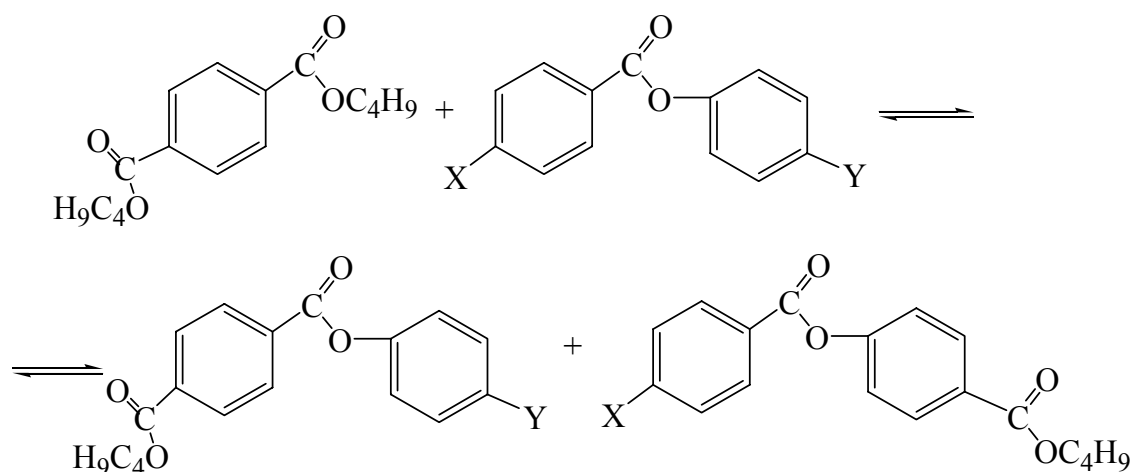


where, X and Y = $OCH_3$, $CH_3$, H, Cl, $NO_2$

**Scheme 2**

## Experimental

All the solvents and starting chemicals were thoroughly purified using traditional purification techniques and the properties of purified chemicals corresponded very well with the literature data [5].

A number of substances which are listed in Table 1 were obtained by the method of acceptor-catalytic esterification, following the next procedure.

Solution of 7.3338 g (0.0364 mole) of p-nitrobenzoyl chloride in 50 ml of benzene was added to the solution in 100 ml benzene of 3.4216 g (0.0364 mole) of phenol and 4.4117 g (0.0385 mole) of triethylamine. The reaction was allowed to proceed for 2 hours. Ttriethylamine hydrochloride was precipitated out, filtered and washed with water. Esters were purified by crystallization from hexane or from its mixture with benzene in the volume ratio 5:1. Measured properties of the purified esters agreed very well with the literature values [5].

Complexes of lanthanide nitrates with benzo-12-crown-4 were synthesized in the Moscow State University using the following procedure [6]: solution of 3.32 g of neodymium nitrate in 29.2 ml of acetonitrile was added to solution of 2.24 g of benzo-12-crown-4 in 12.7 ml of acetonitrile. The resulting precipitate was filtered, washed with acetonitrile and methylene chloride and dried over $P_2O_5$ for 3 days. The obtained compounds were identified by elemental analysis and IR-spectroscopy.

Cesium salts of bis-1,2-(dicarbollyl) complexes of iron, cobalt, nickel (III) and nickel (IV) salt of

**Table 1**

Esters, obtained by the method of acceptor-catalytic
esterification

| No | Compound | Reference |
|----|----------|-----------|
| 1 | phenyl-p-methoxybenzoate | [5] |
| 2 | phenyl-p-methylbenzoate | "-" |
| 3 | phenylbenzoate | "-" |
| 4 | phenyl-p-chlorobenzoate | "-" |
| 5 | phenyl-p-nitrobenzoate | "-" |
| 6 | p-methoxyphenyl-benzoate | "-" |
| 7 | p-methylphenylbenzoate | "-" |
| 8 | p-chlorophenylbenzoate | "-" |
| 9 | p-nitrophenylbenzoate | "-" |
| 10 | n-butylbenzoate | "-" |
| 11 | di-n-butylterephthalate | "-" |

bis-1,2-(dicarbollyl) were synthesized in the Institute of Organo-Element Compounds of the Russian Academy of Sciences using the method described in Ref. [7].

The ampoules method has been used for kinetics measurement [8]. All catalysts and inhibitors involved were soluble in the reaction mixture at the temperature range 523-563 K.

The samples were analyzed by chromatographic separation in "Hewlett-Packard" liquid Chromatograph: column with "Nucleosil 120C18", particle size 5 micron, UV-detector. The mixture of methanol/water/isopropanol (volume ratio 8/4/3) was used as an eluent. Flow rate was 0.4 ml/min at room temperature. The estimated error in the observed reaction rate constant ($k_0$) is equal to be 5%.

## Results and Discussion

It was been found that non-catalytic trans-esterification reaction 1 follows first-order kinetics at a 20-fold molar excess of butyl benzoate at temperatures 523 K, 538 K, 548 K and 563 K [8]. The activation energy values and the pre-exponential factor in the Arrhenius equation were found to be 108.9 kJ/mol and $1.8 \cdot 10^6$ s$^{-1}$, respectively. The high activation energy of the non-catalytic reaction 1 is the cause of the low rate constant for the trans-esterification ($k_0 = 0.82 \cdot 10^{-5}$ s$^{-1}$) reaction. The degree of reaction 1 at 523 K

was found to be only 50% in 24 hours. This prompted us to look for efficient catalytic systems for trans-esterification reactions.

Previously, the catalytic activity of a series of metal containing catalysts, partly being used in organic chemistry and in some polycondensation processes had been studied by our group [9]. Some of these results are listed in Table 2. The data show that not every compound listed exhibit catalytic activity in the trans-esterification reaction. In addition, tetra-butoxytitanium and tributoxyantimony, which are effective catalysts in the reaction of alcoholysis of ester bond [8], exhibit relatively low catalytic activity in the reaction of esterification. Therefore, it was necessary to continue search for new catalysts suitable for trans-esterification reactions. Literature reports that lanthanide compounds are effective catalysts for polymerization processes, due to coordination of lanthanide atom with the carbon-carbon double bond of the diolefin molecule [10]. Since this coordination is also possible in the carbon-oxygen double ester group's bond, the catalytic activity of such a compounds also could be expected in trans-esterification reactions.

In quest for further evaluation of lanthanide system's based catalysts, the activity of neodymium compounds has been studied at the first step. The constant rates of reaction 1 have been found in the presence of neodymium acetate, neodymium acetylacetonate and nitrate complex with benzo-12-crown-4 (neodymium nitrate coronate). These constants are listed in Table 3.

Catalytic activity of neodymium compounds was found to be higher than that ones studied before (Table 2). So, it confirms the hypothesis of the high catalytic activity of lanthanide compounds during esterification reaction. Our results show that the rate of trans-esterification reaction is not significantly affected by the chemical structure of the ligand in the neodymium complexes involved. As it was proved by IR-spectra, ligands of all neodymium catalysts (Table 3), after heating at 523 K during 7 hours (reaction 1) were substituted by benzoate groups. Thus, during the trans-esterification reaction, substitution of ligand in the initial catalyst imparts equal catalytic activity to different neodymium's compounds.

In order to determine the optimum concentration of the catalyst, the dependence of the trans-esterification reaction on neodymium nitrate coronate's concentration has been studied. The dependence was found to be asymptotic (Fig. 1), *i.e.* a considerable

**Table 2**

Observed rate constants for catalytic reaction 1 at 523 K

| No | Catalyst | Content of catalyst − mol.% with respect to phenyl-p-chlorobenzoate chlorobenzoate | $k_0 \cdot 10^{-5}$ s$^{-1}$ |
|----|----------|-----------------------------------------|------------------|
| 1 | Non-catalytic reaction | 0 | 0.8 |
| 2 | $B(OC_4H_9)_3$ | 1.98 | 0.8 |
| 3 | $As(OC_4H_9)_3$ | 2.00 | 0.8 |
| 4 | $Ti(OC_4H_9)_4$ | 1.99 | 1.2 |
| 5 | $Sb(OC_4H_9)_3$ | 1.97 | 1.9 |
| 6 | $Mn(OOCCH_3)_2$ | 2.00 | 2.1 |
| 7 | $Co[CH_3C(O)CHC(O)CH_3]_3$ | 2.02 | 2.4 |
| 8 | $Pb(OOCCH_3)_2$ | 2.01 | 2.5 |
| 9 | $Mn[CH_3C(O)CHC(O)CH_3]_2$ | 1.98 | 2.7 |
| 10 | PbO | 2.02 | 2.8 |

**Table 3**

Observed rate constants for reaction 1 in the presence of neodymium compounds at 523 K (2 mol.% with respect to phenyl-p-chlorobenzoate)

| No | Catalyst | $k_0 \cdot 10^{-5}$ s$^{-1}$ |
|----|----------|------------------|
| 1 | Non-catalytic reaction | 0.82 |
| 2 | $Nd(OOCCH_3)_2$ | 3.14 |
| 3 | $Nd[CH_3C(O)CHC(O)CH_3]_3$ | 3.17 |
| 4 | $Nd(NO_3)$ Benzo-12-Crown-4 | 3.23 |



Fig. 1. Dependence of the observed rate constants ($k_0$) for reaction 1 on the concentration of catalyst (neodymium nitrate coronate) at 523 K.

(over 0.5 mol.%) increase of catalyst concentration results only in minor changes in the catalytic reaction 1 rate. So, the further kinetic studies in the presence of compounds of neodymium and other lanthanide have been done for catalyst concentration of 0.5 mol.% with respect to phenyl-p-chlorobenzoate.

In order to estimate the effect of the electronic structure of the metal on the catalytic activity of nitrates, the coronates of lanthanum, cerium, praseodymium, neodymium, samarium, terbium and erbium (0.5 mol.%) has been studied at 523 K. These results, presented in Fig. 2, show higher catalytic activity of samarium, terbium and terbium nitrate coronates.

In order to determine the electron-donor property effect of the substituents X and Y in the ester on the reactivity of the ester group, the model reaction of di-n-butylterephthalate with p-substituted derivatives of phenylbenzoate (reaction 2) has been investigated.
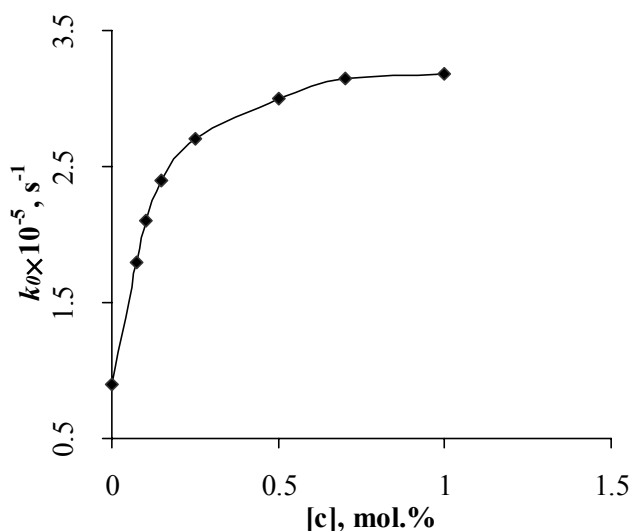
The reaction has been carried out at 523 K and a 20-fold molar excess of di-n-butylterephthalate in the presence of 0.5 mol.% of samarium nitrate coronate. Under these conditions, the reaction was found to obey the first-order kinetics law.

Figure 3 shows the Hammet dependence obtained for esters with different substituents X and Y in the acid and phenol fragments in the given reaction. The results indicate a greater extent affection of the changes in the donor-acceptor properties of the substituents located in the aromatic ring of acid residual
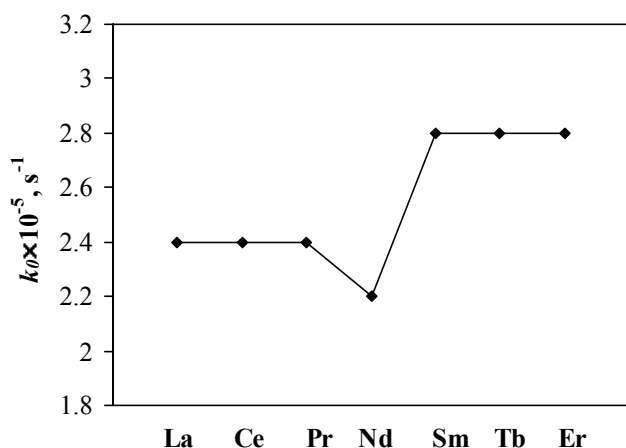
Fig. 2. Effect of the nature of lanthanides on the observed rate constants ($k_0$) for reaction 1 at 523 K (0.5 mol.% of lanthanide nitrate coronate).

($\rho = 0.62$) to the activity of ester groups in trans-esterification reactions compare to redistribution of the electron density in the phenol fragment ($\rho = 0.45$).
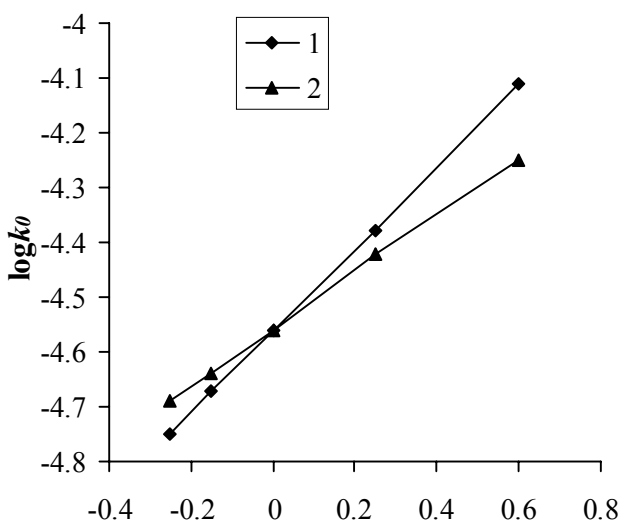


Fig. 3. Effect of electron-donor properties of the substituents X and Y on the reactivity of the ester groups in reaction 2 – log$k_0$ versus $\sigma$ (H), (X and Y = $OCH_3$, $CH_3$, H, Cl, $NO_2$): 1 – Substituent in the acid fragment. 2 – Substituent in the phenol fragment.

As it was mentioned above, to have a proper control on overall reaction rate, the inhibition of transesterification reactions is equally important. In order to look for new classes of inhibitors (carborane derivatives) of trans-esterification reaction, reaction 1 in the presence of cesium salts of bis-1,2-(dicarbollyl) complexes of iron, cobalt and nickel (3+) and bis-1,2-(dicarbollyl) nickel (4+) [($C_2B_9H_{11})_2$Me] has been studied. The results of the major kinetic studies (Table

4) show the effectiveness of some of the compounds involved, as inhibitors of trans-esterification. They reduce the reaction rate by a factor of 4, compared to that one – in the case of non-catalytic reaction.

**Table 4**
Observed rate constants for trans-esterification reaction 1 in the presence of ($C_2B_9H_{11})_2$Me (0.5 mol.%)

| Metal | Concentration | $k_0 \cdot 10^{-5}$ s$^{-1}$ |
|---|---|---|
| None | 0 | 0.8 |
| $Co^{3+}Cs^{1+}$ | 0.502 | 1.32 |
| $Ni^{4+}$ | 0.497 | 0.39 |
| $Ni^{3+}Cs^{1+}$ | 0.500 | 0.28 |
| $Fe^{3+}Cs^{1+}$ | 0.499 | 0.21 |

To determine the optimum concentration of inhibitors, the dependence of the observed constant rate of reaction 1 on the concentration of the cerium salt of bis-1,2-(dicarbollyl) complex of nickel has been studied. As one can see from Fig. 4, the results are rather complicated – with a minimum of the inhibitor concentration equal to be 0.15 mol.% and, with 4 times lower reaction rate compared to the one, without catalyst. Nevertheless, the results obtained must be studied in greater detail.
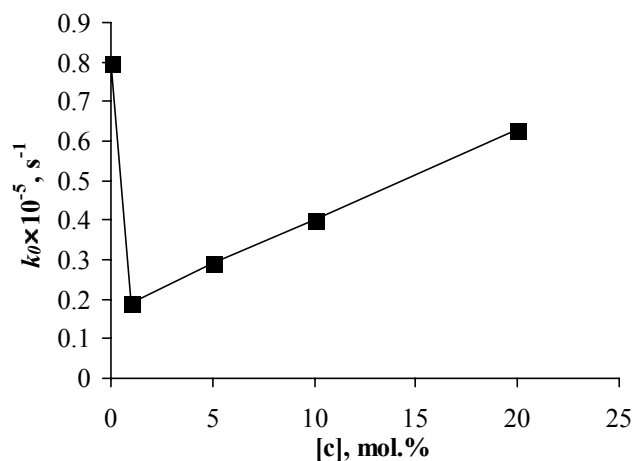


Fig. 4. Effect of the inhibitor concentration [($C_2B_9H_{11})_2$ NiCs] on the values of the observed constant rates ($k_0$) of reaction 1 at 523 K.

## Conclusions

The catalytic activity of the metal-containing compounds on the basis of trans-esterification's model

reactions has been studied. The concentration dependence of lanthanide (neodymium)' catalytic activity was found to be an asymptotic. A new class of inhibitors of trans-esterification reactions, namely, boron containing compounds of metals of the iron group has been found. The effect of the inhibitor concentration on the trans-esterification reaction rate seems to be enough complicated and needs further investigation.

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