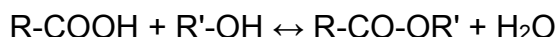


Mechanism for Esterification Reactions Catalyzed by Reaxis C188

Esterification reactions are equilibrium reactions as represented by the following formula:



The reaction velocity of the ester formation can be influenced by several factors, including:

- excess of one of the educts, normally the alcohol,
- the rate of removal of the volatile by-product water,
- using a catalyst for faster formation of the reaction equilibrium.

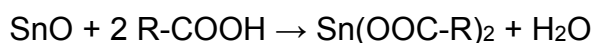
Many different catalysts can catalyze esterification reactions. Inorganic and organic tin catalysts are widely used in this application.

Reaxis C188 belong to the group of inorganic tin catalysts where tin is present in an oxidation state of +2. Chemically, Reaxis C188 is stannous oxide. Like all other tin(II)-catalysts Reaxis C188 is a Lewis-Acid at the borderline between hard and weak acids and catalysis is believed to follow the rules of Lewis-Acid-catalysis /1/. Tin(II) species have vacant d-orbitals in low energy levels and they can accept up to four ligands to work well as a metal template /2/.

It has to be mentioned that the reaction mechanism of tin(II)-catalysts is still not completely understood. Various hypothetical models have been presented in the literature to date. The following description of the catalytic mechanism is based on information presented in the literature and on our own observations.

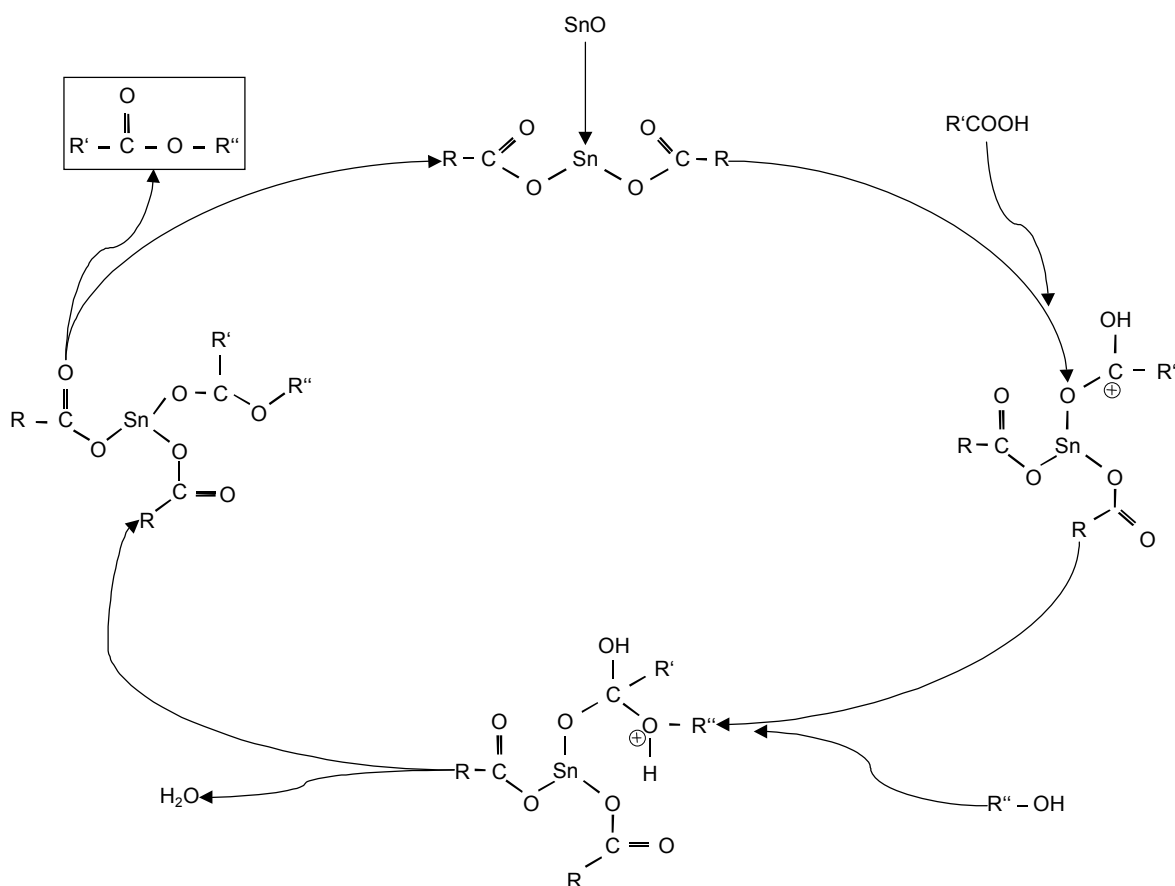
Reaxis C188 is a black powder that is added to the reaction mixture at the beginning of the reaction. Normally the catalyst is fed into the reactor together with the other raw materials. Following addition, the reaction is initiated by heating.

It can be observed that the black powder dissolves during the heating process. Due to the fact that the acid value is initially very high, it is very likely that Reaxis C188 reacts with the acid to form a stannous carboxylate as represented below.



Reaction between stannous oxide and the alcohol component can be disregarded given the fact that the solubility in pure alcohols is very low, whereas the solubility in pure acids is very high /3/.

This stannous carboxylate is believed to be the catalytic active species in the esterification reaction. The following figure shows the assumed catalytic cycle of the tin catalyst.



The catalytic cycle starts by forming a complex of the stannous carboxylate and two molecules of the acid via bonding of p- or d-orbitals of Sn(II) to the carbonyl group of the acid /4/. It is not quite clear whether during this complex formation that one of the initial carboxylic groups is replaced by the new complex ligand or not. Both scenarios are presented in the literature /4/,/5/. It is believed that the most favored geometrical

configuration is for the tin to be centered in a pyramidal structure, having a coordination number of three and a non-bonding electron pair.

Formation of this complex imparts a positive charge on the carbon atom of the carbonyl group thus enabling the hydroxyl group of the alcohol to undergo a nucleophilic attack. In the next step hydrogen is transferred from the hydroxyl group of the alcohol to the carboxylic acid, which subsequently leads to the liberation of water. The resulting ester molecule is still complexed to the tin(II)-center unless it is replaced by a new molecule of carboxylic acid whereby the catalytic cycle can start again.

Alternatively, it has been presented that the alcohol does not directly attack the positively charged carbonyl-C-atom, but first bonds to the non-bonding electron pair present on the tin and is then transferred to the positive C-atom /4/. Given the present state of knowledge, it cannot be determine which model is represents the real mechanism.

Literature:

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- /5/ P. In't Veld, E. Velner, P. van de Witte, J. Hamhuis, P. Dijkstra, J. Feijen, *J. Polym. Sci. Part A PolyChem.*, 35 (1997) 219-226
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