SYNTHESIS AND MECHANISM OF ACTION OF ANTHRACEN-9-YL ACETATE

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Abstract. The article presents information on the methods and mechanism of synthesis of anthracen-9-yl acetate from anthracene isolated from tar product – a waste formed during the processing of natural gas.

Keywords: pyrolysis, tar product, anthracene, lead(IV) acetate, anthracen-9-yl acetate, acetic acid, acetonitrile.

In today's rapidly developing oil and gas industry, as well as in natural gas processing, tar products – considered pyrolysis by-products – are of relatively low importance. This is mainly due to the complexity of purifying this raw material and the high energy consumption involved in the process[1]. The presence of dozens of fuel-related compounds in its composition, as well as the high content of hydrocarbons such as naphthalene, phenanthrene, and anthracene, has been attracting the attention of industry specialists [2-3].

The reaction of anthracene with lead tetraacetate ($Pb(CH_3COO)_4$) was investigated in this work. Acetic acid and CH_3CN were used as solvents. The reaction was carried out at 60–80 °C for 4 hours, resulting in a yield of 65.25%. Anthracene-9-yl acetate crystals with a melting point of 130–134 °C were obtained[4].

The mechanism of the reaction between anthracene and lead tetraacetate ($Pb(CH_3COO)_4$) in the presence of acetic acid involves acetoxylation at the 9-position of anthracene, leading to the formation of anthracene-9-yl acetate. This is an electrophilic substitution reaction driven by the oxidizing properties of lead tetraacetate[5].

Acetic acid and CH_3CN act as polar solvents, facilitating the dissolution of both anthracene and lead tetraacetate, thereby enabling a more efficient reaction. This provides a homogeneous reaction medium[6].

In this reaction, anthracene reacts with lead tetraacetate ($Pb(CH_3COO)_4$), and a hydrogen atom at the 9-position of anthracene is removed. This hydrogen combines with acetate ions (CH_3COO^-), formed during the decomposition of lead tetraacetate, to produce acetic acid (CH_3COOH)[7].

The reaction proceeds through the following steps:

Formation of acetate radicals:

Lead tetraacetate ($Pb(CH_3COO)_4$) decomposes to form highly reactive species – acetoxy radicals ($CH_3COO\bullet$).

In this step, lead(IV) acetate decomposes into lead(II) acetate ($Pb(CH_3COO)_2$) and two acetoxy radicals ($CH_3COO\bullet$)[8].

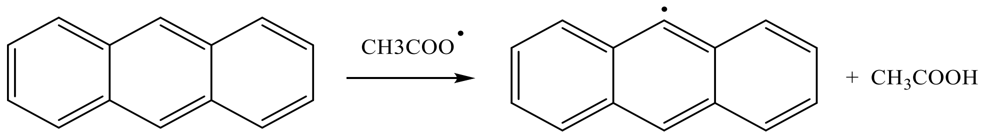
Abstraction of hydrogen atom from the 9-position of anthracene:

Acetic acid can donate protons (H^+) to facilitate specific stages of the reaction, particularly proton transfer processes. This helps stabilize intermediate species formed during the acetoxylation or oxidation of anthracene. Acetic acid also stabilizes acetate radicals ($CH_3COO\bullet$) or acetate ions (CH_3COO^-) generated from the decomposition of lead tetraacetate, ensuring a smooth reaction pathway without side reactions[9].

During the reaction, the hydrogen atom removed from the 9-position of anthracene combines with acetate ions (CH_3COO^-) to form acetic acid (CH_3COOH). Thus, acetic acid is regenerated as a by-product within the reaction system. Lead tetraacetate is typically used in combination with acetic acid because the acetate medium provided by CH_3COOH helps maintain the oxidizing ability of $Pb(CH_3COO)_4$ and prevents its premature decomposition[10].

Formation of the 9-anthracenyl radical:

The acetate radical ($CH_3COO\bullet$) abstracts a hydrogen atom from the 9-position of anthracene, leading to the formation of a 9-anthracenyl radical. The removal of this hydrogen leaves an unpaired electron on the 9-carbon atom of anthracene[11].



In this step, the acetoxy radical abstracts a hydrogen atom from the 9-position, and acetic acid (CH_3COOH) is formed as a by-product[12].

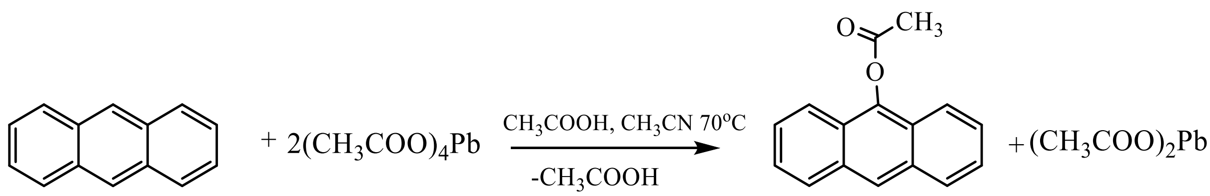
Acetoxylation of the 9-anthracenyl radical:

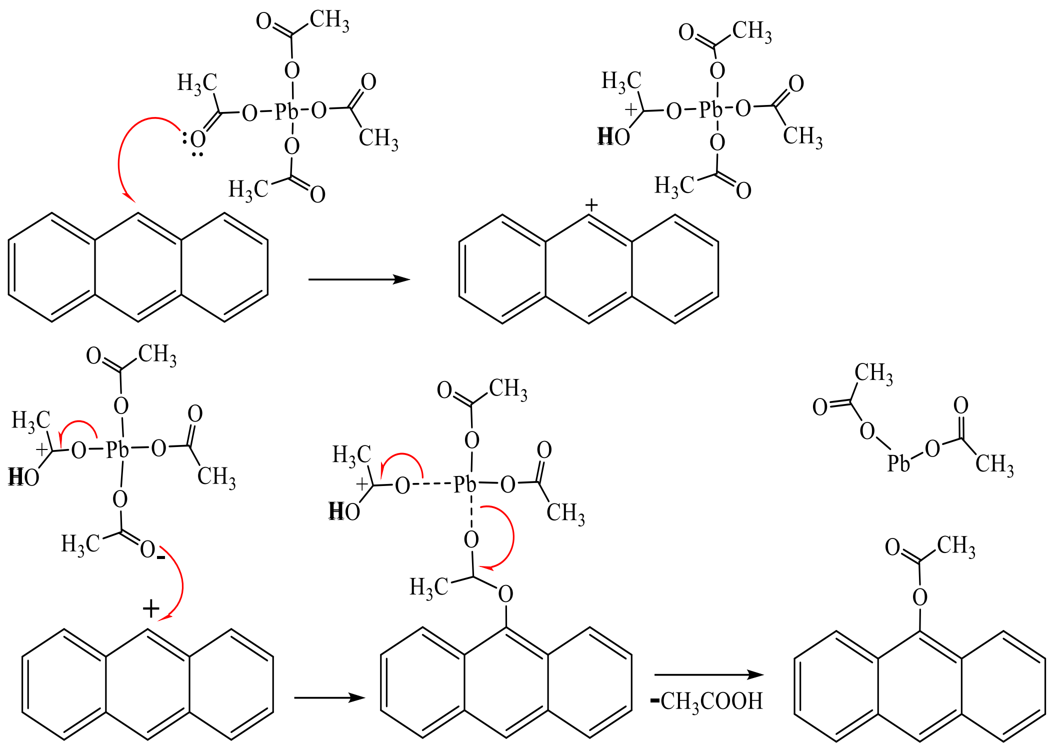
The 9-anthracenyl radical is highly reactive and readily reacts with another acetoxy radical ($CH_3COO\bullet$). Radical coupling at the 9-position leads to the formation of anthracene-9-yl acetate, where an acetoxy group ($–OCOCH_3$) is attached to the 9-position of the anthracene ring.

Regeneration of lead(II) acetate:

Lead tetraacetate is reduced during the process, forming lead(II) acetate ($Pb(CH_3COO)_2$) as a by-product. The regeneration of $Pb(CH_3COO)_2$ occurs simultaneously with the formation of anthracene-9-yl acetate[13].

Overall reaction mechanism of anthracene with $Pb(CH_3COO)_4$:





In conclusion, it can be stated that the investigated tar-product secondary fraction, due to its high content of aromatic and polyaromatic compounds, is recommended as a raw material for the synthesis of various water- and oil-soluble organic compounds. Currently, our research is continuing in the direction of synthesizing cation-exchange resins (cationites) based on the physicochemical properties of the above-mentioned industrial waste.

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