Interaction of carbon dioxide with ditoluenetitanium

E. F. Kvashina

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

The interaction of ditoluenetitanium with CO_2 has been studied. Based on hydrolysis, thermolysis, and IR spectral data, the conclusion is drawn that a low-valent titanium oxalate is formed.

Key words: carbon dioxide; ditoluenetitanium, interaction.

The reduction of CO_2 under mild conditions mostly results in one-carbon compounds.[1] We studied the interaction of a Ti^0 complex with CO_2 under mild conditions. Ditoluenetitanium (DTT) was synthesized by cocondensation of titanium atoms evaporated in a high vacuum with a solid toluene matrix cooled with liquid nitrogen.[2]

The starting compound and the reaction products are moisture and oxygen-sensitive; therefore, all of the experiments were conducted in a vacuum or in an inert atmosphere.

It was found that DTT dissolved in toluene (λ_{max} = 512 nm) reacts with CO_2 at −60 to +20 °C to give a black product **1** insoluble in toluene. The IR spectrum of the product recorded in an inert atmosphere contains an intense absorption band at 1550 cm^{-1}, which is attributable to vibrations of the C=O group. This product is hydrolyzed with water, which is accompanied by the evolution of comparable amounts of hydrogen and toluene. When D_2O is used, D_2 is evolved, which implies that the oxidation state of titanium in product **1** is low. The composition of the hydrolysis products of compound **1** demonstrates that the latter contains toluene. However, the IR spectrum of **1** does not contain an intense absorption band at 966 cm^{-1}, which is observed in the IR spectrum of DTT.[3] This is probably due to a change in the coordination of toluene in complex **1**.

The action of 2 *M* HCl on product **1** results in its dissolution, but no CO_2 is evolved. This fact demolishes the hypothesis that compound **1** is a titanium—CO_2 complex or has a carbonate-like nature; hence, the most probable assumption is that this compound is an oxalate complex of titanium. This is confirmed by the IR spectrum of a solution of compound **1** in 2 *M* HCl, which displays absorption bands at 3380, 1630, 1380, 1200, 1070, and 880 cm^{-1}. The spectrum observed is typical of metal—oxalate complexes.[4] The absorption bands at 3380 and 1650 cm^{-1} corresponding to the OH group vibrations imply that compound **1** undergoes hydrolysis on dissolution.

The gaseous products of the thermal decomposition of complex **1** at 300 °C consist of CO_2 and CO. These products have been observed in the thermolysis of titanium oxalates.[5] This process can afford CO due to decomposition of the oxalate ion.[5]

The results obtained allow us to conclude that the dimerization of CO_2 in the system studied results in an oxalate of low-valent titanium.

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