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CATALYTIC HYDROCHLORINATION OF ACETYLENE ON MECHANOCHEMICALLY-ACTIVATED K_2PdCl_4

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We report the catalysis of the hydrochlorination of acetylene on the surface of dry K_2PdCl_4 subjected to prior mechanical activation in an atmosphere of acetylene or propylene. The stereochemistry of the reaction corresponds to trans addition of the halogen and hydrogen atoms to the C—C triple bond. The hydrogen halide is the source of the halogen atom in the reaction product. The mechanical activation of K_2PdCl_4, in contrast to the case of K_2PtCl_4, is also capable of activating the C—C double bond: propylene is hydrochlorinated under similar conditions to isopropyl chloride.

Key words: *acetylene, hydrochlorination, heterogeneous catalysis, potassium tetrachloropalladate(II), mechanical activation.*

Petroleum and natural gas are the major raw material sources for basic organic synthesis. Starting in the middle of the twentieth century, the use of these sources led to a change in the technology of the large-scale manufacture of many chemical products with reorientation to the use of olefinic raw materials and synthesis gas. Nevertheless, some processes for the large-scale manufacture of products such as vinyl ethers, pyrrolidone, N-methylpyrrolidone, and butanediol and the smaller-scale production of drugs, fragrances, and plant protection chemicals using acetylene have certain advantages and continue to be employed. Furthermore, acetylenic hydrocarbons are inevitably formed in the preparation of olefins from petroleum and natural gas. The use of these acetylenic hydrocarbons is dictated by the current scale of production and the cost of raw materials. On the other hand, in contrast to the case of petroleum, the reserves of coal and natural gas permit us to regard these materials as virtually inexhaustible sources of acetylene. In particular, the increasing interest in the chemistry of acetylene is clearly a function of these considerations (see the reviews of Beletskaya [1, 2]).

One of the industrial methods for the manufacture of vinyl chloride involves the hydrochlorination of acetylene catalyzed by $HgCl_2$ on activated charcoal [3]. The high toxicity of this mercury catalyst and its relative instability [4] have led to a search for other catalytic systems. The hydrochlorination of acetylene under homogeneous conditions is catalyzed by various metal salts containing Cu^I, Au^{III}, Pd^{II}, and Pt^{II} [3]. The Pt^{II} and Pd^{II} complexes in solution have high activity but are very unstable. Under heterogeneous conditions, Au^{III} [5, 6] and Rh^{III} complexes [7] on activated charcoal catalyze the hydrochlorination of acetylene but these reactions require elevated temperature (170-180 °C). Recently, we have discovered the catalysis of acetylene hydrochlorination on the surface of mechanically-activated K_2PtCl_6 [8] and K_2PtCl_4 [9]. We might

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assume that, similar to K_2PtCl_4, the palladium(II) chloride complex K_2PdCl_4, would display catalytic activity under analogous conditions in the hydrochlorination of acetylene. In the present work, we checked this hypothesis.

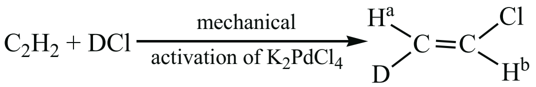
We discovered that prior mechanical activation of dry K_2PdCl_4 in an atmosphere of acetylene or propylene indeed leads to the formation of a catalyst for the hydrochlorination of acetylene by means of gaseous HCl. The catalytic reaction proceeds at room temperature also without continuous mechanical treatment.

The consumption of acetylene from the gas phase of a sealed reactor in an atmosphere of HCl corresponds to first-order kinetics. The observed rate constant for the loss of acetylene at 18 °C under the conditions given below is $(9.0 \pm 0.7)\cdot 10^{-5}$ s^{-1}. We note that prior treatment of K_2PdCl_4 in an atmosphere of acetylene or propylene is mandatory for the formation of an active catalyst form. This salt treated in the air displays much lower activity.

The yield of vinyl chloride relative to unreacted acetylene is close to quantitative. There is no significant drop in activity after more than 150 catalytic cycles relative to the palladium on the salt surface (more than 1.7 catalytic cycle relative to total palladium).

Vinyl bromide is predominantly isolated when the reaction is carried out in the presence of HBr on K_2PdCl_4 previously treated in an acetylene atmosphere.

The hydrochlorination of acetylene in an atmosphere of DCl leads to the formation of product, whose stereochemistry corresponds to *trans* addition of the chlorine and deuterium atoms to the C—C triple bond of acetylene. The ^1H NMR spectrum of this product in $CDCl_3$, δ, ppm: 5.52 (H^a), 6.31 (H^b), $J(H^aH^b)$ = 14.75, $J(H^bD)$ = 1.03 Hz.



K_2PdCl_4 mechanically-activated in an atmosphere of acetylene or propylene, in contrast to K_2PtCl_4 treated under similar conditions, is capable of activating not only the acetylene C—C triple bond but also the C—C double bond in propylene, which is quantitatively hydrochlorinated to isopropyl chloride. The ratio of the observed hydrochlorination rate constants measured under competitive conditions is close to 4.

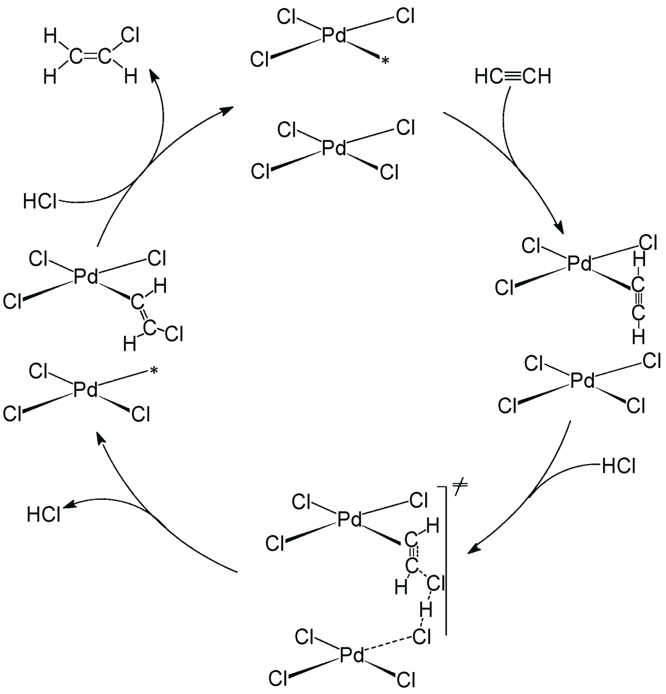
Thus, prior mechanical activation of K_2PdCl_4 in an acetylene or propylene atmosphere gives a catalyst for the hydrochlorination of acetylene and propylene by gaseous HCl. The reaction proceeds without continuous mechanical activation. The hydrogen halide is the source of the halogen atom in the product of the reaction with acetylene.

The electrophilic properties of the metal complexes probably play a key role in the activation of the C—C multiple bonds by these complexes. The capacity of K_2PdCl_4, in contrast to K_2PtCl_4, also to activate double bonds may be attributed to the greater electrophilicity of the Pd(II) acido complexes in comparison to the analogous Pt(II) complexes.

Mechanical activation of K_2PdCl_4 in an atmosphere of the indicated unsaturated hydrocarbons, similar to mechanical activation of K_2PtCl_4 [9], leads to the formation of complexes with coordination vacancies, acting as active sites for the heterogeneous catalyst. By analogy with hydrochlorination on mechanically-activated K_2PtCl_4 (platinum system) [9], the stepwise mechanism for the hydrochlorination of acetylene by gaseous HCl on previously treated K_2PdCl_4 (palladium system) may be presented as follows. Two adjacent surface palladium complexes take part in the reaction, one of which has a coordination vacancy $PdCl_3^-$. The π-coordination of acetylene to the Pd(II) complexes with a coordination vacancy and subsequent chloropalladation of π-coordinated acetylene by the action of an HCl molecule with the participation of the adjacent palladium complex leads to a Pd(II) σ-vinyl derivative and regenerates the complex with the coordination vacancy. The protodemetallation of the Pd(II) σ-vinyl derivative gives the final product. This stepwise scheme accounts for the high steric selectivity of the reaction and its catalytic mode.

The chloroplatination of acetylene proceeding with the participation of a hydrogen chloride molecule is rate-limiting for the catalytic reaction in the previously studied platinum system. This is seen in the significant kinetic isotope effect upon replacing HCl with DCl (KIE = 4) [9]. Using the analogy between the platinum and palladium systems, we should also expect a significant isotope effect for the palladium system. A study of the kinetics and mechanism of the catalytic reaction in the palladium system is the subject of further investigation.

The sample of K_2PdCl_4 was obtained by a standard procedure [10] and dried in a desiccator at 120-140 °C for 72 h. An increase in the drying time had no significant effect on the reaction kinetics. A sample of 0.25 g salt was subjected to prior



mechanical activation in the air or in an atmosphere of acetylene or propylene for 1 h, which is sufficient to obtain the limiting specific surface of 6 m^2/g. The specific surface was determined by the BET method relative to argon desorption. The mechanical activation of K_2PdCl_4 was carried out in a 13.7-mL glass vibroreactor containing glass milling beads. We used an MMVE-0.005 microvibromill with 50 Hz working frequency and 5.5 mm amplitude, which corresponds to a specific energy flux of about 15 W/kg.

After the prior mechanical treatment of the salt, the reactor was flushed with argon and with a five-fold excess of gaseous HCl or HBr relative to the volume of the reactor. The reactor was then hermetically sealed and 1 mL acetylene–ethane gas mixture was introduced with a syringe through a rubber stopper; ethane served as the internal standard. Gaseous hydrogen bromide was obtained by the bromination of anthracene, while hydrogen chloride (HCl or DCl) was obtained from roasted KCl and H_2SO_4 or D_2SO_4.

The ^1H NMR spectrum for vinyl chloride was taken in deuterochloroform on a Bruker BioSpin Avance II 400 spectrometer at 400 MHz.

The consumption of acetylene or propylene and the accumulation, respectively, of vinyl chloride or isopropyl chloride was monitored by gas-liquid chromatography using an LKhM-8-MD chromatograph with a flame ionization detector and a column packed with Silochrom C-120. The collection and treatment of the data was carried out using the Ampersand MultiChrom system.

The vinyl halides and isopropyl chloride were identified relative to their retention times *versus* authentic samples. A sample of vinyl chloride was obtained by the dehydrochlorination of 1,2-dichloroethane by the action of sodium methylate, while a sample of isopropyl chloride was obtained by the reaction of 2-propanol with hydrochloric acid. A commercial sample was used for the identification of vinyl bromide. An acetylene sample was obtained through a standard procedure [11].

The relative concentration of acetylene and vinyl chloride were determined relative to the areas of the corresponding chromatographic peaks and the ethane peak. The amount of compound was calculated using calibration curves for acetylene or vinyl chloride. The chromatograph was calibrated by introducing a known amount of C_2H_3Cl or C_2H_2 into the empty reactor and then the composition of the gas phase was subjected to chromatographic analysis. The amount of vinyl bromide liberated was determined taking account of the difference in sensitivity of the flame ionization detector relative to C_2H_3Cl and C_2H_3Br by a factor of 1.3.

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