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SHORT COMMUNICATIONS

Catalytic Hydrochlorination of Acetylen on the Surface of Mechanically Activated Salt K_2PtCl_4

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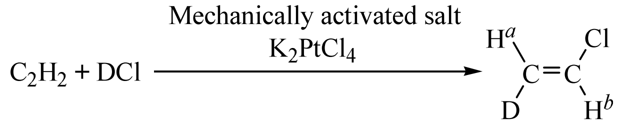
The catalytic hydrochlorination of acetylene is used in manufacturing of vinyl chloride, and the industrial catalyst is $HgCl_2$ on activated carbon [1]. The high toxicity of the mercury catalyst combined with its relatively low stability demands looking for other catalytic systems. Complexes of various metals {Cu(I), Au(III), Pd(II), Rh(III) [1], and Pt(II) [1, 2]} catalyze the reaction under homogeneous conditions. The complexes of Pt(II) and Pd(II) in solutions possess high activity but are fairly unstable. Under the heterogeneous conditions complexes of Pt(II), Au(III) [3, 4], and Rh(III) [5] on activated carbon catalyze the acetylene hydrochlorination but require high temperature for the process (170–180°C). We recently discovered [6] that the hydrochlorination of acetylene was catalyzed at room temperature on the surface of a mechanically activated salt K_2PtCl_6; the mechanically activated salt of Pt(II), K_2PtCl_4, was inactive under similar conditions. Note that in the homogeneous medium the situation is reverse: The chloride complexes of Pt(IV) do not catalyze acetylene conversion in solution.

The lack of catalytic activity in the chloride complexes of Pt(II) under mechanical activation was unexpected. It is known [7] that the mechanical treatment of K_2PtCl_4 powder results in the generation of $[PtCl_3]^-$, species with coordination vacancies, their fraction amounts to about 5% of the overall quantity of Pt(II) complexes on the surface, and they are capable of π-coordination with ethylene to form the Zeise's salt. It is presumable that acetylene would also enter into the coordination sphere of these species having coordination vacancies to form a π-complex whose subsequent transformations would finally lead to vinyl chloride. The goal of this study was to find conditions for acetylene hydochlorination catalyzed by mechanically activated Pt(II) chlorides.

We found that the dry K_2PtCl_4 salt preliminary mechanically activated under the dry acetylene atmosphere catalyzed the acetylene hydrochlorination with gaseous HCl without a continuous mechanical treatment. The kinetics of acetylene consumption from the gas phase of the closed reactor in an HCl atmosphere followed the kinetic equation of zero order unlike the similar reaction involving Pt(IV) (first order) [6]. The yield of vinyl chloride calculated on the reacted acetylene is close to quantitative. In the atmosphere HCl–DCl (at molar ratio ~1:1.5) formed mainly $H_2C{=}CHCl$ with a little admixture of monodeuterated vinyl chloride, where the deuterated product originated exclusively from *trans*-addition [^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.52 (H^a), 6.31 (H^b); $J(H^aH^b)$ 14.75, $J(H^bD)$ 1.03 Hz].



The estimation from the NMR data of the value of the kinetic isotope effect for the reaction of acetylene hydrochlorination in the system K_2PtCl_4 (solid)–DCl–HCl (gas) gives ~6 in contrast of the value of the kinetic isotope effect of 1.9 formerly evaluated [6] for the system K_2PtCl_6 (solid)–DCl (gas).

We did not observe any significant reduction of the catalytic activity after ~2.8 catalytic cycles were performed calculated on the "massive" platinum (or ~320 cycles calculated on the complex platinum anions on the surface of the catalyst). Introducing into the reactor of 20 μg of water as a steam results in inhibition of the reaction. The previously reported inactivity of the mechanically activated Pt(II) chloride complexes in acetylene hydrochlorination apparently originated from the inhibiting role of the water vapor. Note that in the system with Pt(IV) such a strong effect of inhibition with water vapor was not observed.

Thus the mechanical activation of the dry K_2PtCl_4 salt in an acetylene atmosphere provided a heterogeneous catalyst of acetylene hydrochlorination. The different character of kinetic relations and the considerable difference in the value of the kinetic isotope effect in the system K_2PtCl_4 (solid)–HCl (gas) compared with the previously studied [6] system K_2PtCl_6 (solid)–HCl (gas) indicates dissimilar mechanisms of catalytic acetylene hydrochlorination in the systems in question. The kinetics and mechanism of the discovered catalytic reaction will be the subject of further investigations.

K_2PtCl_4 salt was prepared by common procedure [8], recrystallized from water, dried at 120°C for 3 days, and all further operations with the salt were performed in the dry box. The reactions were carried out in a closed glass vibroreactor of 17 ml capacity containing glass beads. The platinum salt (0.3 g) was preliminary treated in a vibrating mill under acetylene atmosphere for 1.5 h. This time was sufficient to achieve the limiting specific surface of 2.7 m^2/g. Then the reactor was flushed from acetylene with a steam of dry argon and then it was filled with hydrogen chloride. We used vibrating micromill MMVE-0.005 of specific energy intensity 15 W/kg.

^{1}H NMR spectrun of vinyl chloride was registered from a solution in deuterochloroform on a spectrometer Varian GEMINI at operating frequency 200 MHz. The kinetics of acetylene consumption and vinyl chloride accumulation was measured by GLC on a chromatograph LKhM-8 MD equipped with a flame ionization detector, column packed with Silachrom C 120, and a system of data processing Multichrom of Ampere and Co.

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