CATALYTIC OXIDATION OF TOLUENE BY Pd(I) COMPLEXES IN PdSO₄–H₂SO₄ SOLUTIONS. DIFFERENTIATION OF ROUTES INVOLVING Pd(I) AND Pd(II)

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The oxidation mechanism of toluene in PdSO₄–H₂SO₄ (80.0 wt.%) solutions at 298 K via routes involving Pd(I) and Pd(II) has been studied. Addition of benzene was found to inhibit the reaction due to the binding of Pd(I). The routes involving Pd(II) and Pd(I) were distinguished.

In the interaction of arenes with PdSO₄–H₂SO₄ solutions, besides the oxidative coupling products, π-complexes Pd(II)...ArH /1/ and (Pd(I)...ArH)₂ dimer /1, 2/ are formed. A complex mechanism for the activation of arenes in these reactions which includes routes involving Pd(II), and a catalytic mechanism involving Pd(I) have been discovered recently /3/. The concentration of Pd(I) complexes is much lower than that of Pd(II) and is determined by the steady-state conditions. The first-order rate constants k measured according to the substrate consumption at

\[ k = k^s + k^t + k^{\text{II}} \]

consist of the contributions of reactions with H₂SO₄ (k^s), Pd(II) (k^{\text{II}}) and Pd(I) (k^t).

Two independent ways to distinguish the contributions of k^t and k^{\text{II}} are suggested, based on the new effects of inhibiting the reaction of toluene with Pd(I) owing to the binding of Pd(I) with benzene to an inactive complex (method A) or due to the oxidation of Pd(I) to Pd(II) (method B). The kinetics was studied by the distribution method /4/ in PdSO₄ (80.0 wt. %) solutions at 298 K.
**Method A.** The oxidation rates of toluene and deuterotoluene are decreased by the additions of benzene (PhH) in amounts much smaller than the PdSO₄ concentration but considerably higher compared with the substrate. Under these conditions the rate of benzene oxidation is very low. Since [PhH]₀ ≪ [Pd(II)], and the stability constant of the Pd(II) ... PhH complex is small (K = 20 kg/mol /5/), the concentration of the uncomplexed Pd(II) does not practically decrease. The (Pd(I) ... PhH)₂ complex is much more stable /1, 2/. Therefore, the effect discovered is due to the inhibition of kᵢ contributions rather than of kᵢ₁ upon adding benzene. These data indicate that in the kᵢ₁ route of the toluene-Pd(I) reaction, uncomplexed Pd(I) species, apparently Pd₂⁺ dimers, participate, and the added benzene acts as a trap for Pd(I), thus inhibiting the reaction. Assuming that benzene, due to complex formation transforms the active complex Pd₂⁺ PhCH₃ to an inactive species, provided that [Pd(II)] ≫ [PhH]₀ ≫ [Pd₂⁺ CH₃Ph], kᵢ₁ = kᵢ/(1 + K₁ [PhH]) and

\[
1/(k - kₐ) = 1/k₁ + 1/k₁K₁ [PhH],
\]

where K₁ is the effective equilibrium constant taking into account inhibition, k and kₐ are the rates upon adding benzene, k and k₁ are the rates without PhH, [PhH] = [PhH]₀/(1 + K [Pd(II)]) is the benzene concentration in solution allowing for its complex formation with Pd(II), and [PhH]₀ is the total benzene concentration. Equation (2) agrees with the experimental data (Fig. 1). Hence K₁ = (1.3±0.2) × 10⁴ kg/mol and k₁ values (Table 2) are determined.

![Fig. 1. Validity of eq. (2) for the oxidation of CH₃C₆H₅ (I, II, III) and CD₃C₆D (IV) by PdSO₄−H₂SO₄ solutions at [PdSO₄] = 1.52 × 10⁻² (I), 1.13 × 10⁻² (II, IV) and 0.534 × 10⁻² mol/kg](image)