



Features of the mechanism of oxidative dehydrodimerization of propynol

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ABSTRACT

Analysis of kinetic regularities for the propynol oxidative coupling under the action of cupric salts in pyridine and in the presence of a buffer is undertaken. The reaction mechanism, including the formation of Cu(I) acetylides, is considered.

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1. Introduction

Oxidative dehydrodimerization (oxidative coupling) of terminal acetylenes (Scheme 1) is an important modern method for preparing highly unsaturated dimeric, polymeric, and macrocyclic structures.^{1–3}

The importance of this method prompts a necessity to study the mechanism of this complex multicomponent catalytic reaction. Earlier, the dehydrodimerization of phenyl acetylene under the action of Cu(II) in pyridine in the presence of a buffer (amine–AcOH) was shown to be zero order with respect to Cu(I), second order with respect to both the substrate and Cu(II) and reverse second order with respect to AcOH.⁴ The application of the buffer was necessary to avoid retardation of the reaction by the developing acidity. On the basis of experimental results and calculations we proposed a mechanism for the oxidative coupling.⁴ The key step was synchronous oxidation of two acetylide anions by two Cu²⁺ ions with simultaneous formation of the C–C bond. This mechanism is valid for a number of acetylenes of various structures.⁵ The reactivity of acetylenes increases with enhanced acidity. Meanwhile, the oxidative coupling of propynol (P) under the same conditions is known to be an autocatalytic process that follows quite different kinetic parameters.^{6,7} At [Cu(I)]/[Cu(II)] ratios of ≥ 5 , the reaction is zero order with respect to Cu(II), less than first order with respect to the substrate, and approximately first order with respect to Cu(I). At initial time of P oxidation, the mechanism was shown to be the same as for other acetylenes, and the reaction

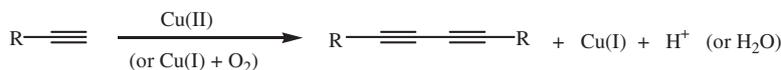
does not involve Cu(I). When Cu(I) is formed, an ‘anomalous’ mechanism with its participation is implemented. When $[P]_0 \gg [Cu(II)]_0$, the final rate of P oxidation becomes constant. It should be noted that oxidative coupling in aqueous ammonia under the action of Cu(II) follows the same patterns as those for phenyl acetylene in a buffer solution.⁸ The rate of dehydrodimerization of terminal acetylenes was earlier shown to depend on the Cu(I) concentration if the reaction conditions were favorable for the formation of Cu(I) acetylides and their dimeric complexes.⁹ The formation of acetylides and their dimeric complexes in a buffer containing AcOH seems to be unlikely. Herein, an attempt was made to elucidate the reasons behind the ‘anomalous’ kinetics of P oxidation in the buffer.

2. Results and discussion

Our study of the rate of P oxidative coupling versus [AcOH] at constant [AcO⁻] revealed unexpectedly that it increased with a rise in the acidity of the reaction medium (Fig. 1).⁷ This dependence is the key for understanding the features of P oxidative coupling. Indeed, P can be considered as a bidentate ligand for Cu⁺ forming complex (A) with participation of the π -electrons of the triple bond and the n -electrons of the O atom (Scheme 2). This complexing enhances the liability of the hydroxy proton, whereas formation of the alkoxide ion decreases the acidity of the ethynyl group. However, dissociation of the hydroxy group is reversible and the acid in the buffer shifts the equilibrium to the left. Experimentally, this results in a linear dependence of the reaction rate on [AcOH]. On the contrary, dissociation of the ethynyl group of A is irreversible. Deprotonation of the ethynyl group leads to the formation of Cu(I) acetylides, which are highly inclined to give dimeric associates

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Scheme 1.

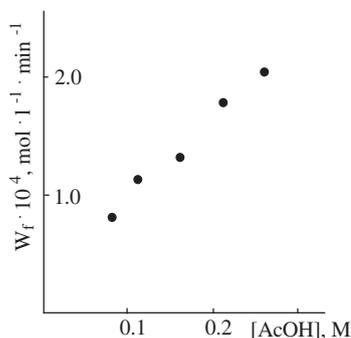


Figure 1. Dependence of W_f on $[\text{AcOH}]$ with constant $[\text{AcO}^-]$, maintained by adding $[\text{NEt}_4]^+\text{OAc}^-$; 40 °C, $[\text{P}]=1.0\text{ M}$, $[\text{HN}(\text{CH}_2)_3]=1.0\text{ M}$, $[\text{Cu(II)}]_0=4 \times 10^{-3}\text{ M}$.

$$A = \frac{[\text{P}]_t}{1 + \frac{1}{K'_1[\text{Cu(I)}_s]} + K_2 \frac{[\text{B}]}{[\text{BH}^+]}} \quad (2)$$

Therefore,

$$\begin{aligned} W_f &= \frac{k_3[\text{B}][\text{P}]_t}{1 + \frac{1}{K'_1[\text{Cu(I)}_s]} + K_2 \frac{[\text{B}]}{[\text{BH}^+]}} \\ &= \frac{k_3 K'_1 [\text{B}][\text{P}]_t [\text{Cu(I)}_s]}{1 + K'_1 [\text{Cu(I)}_s] + K'_1 K_2 [\text{Cu(I)}_s] [\text{B}]/[\text{BH}^+]} \end{aligned} \quad (3)$$

Along with Cu(I)_s , other copper complexes, which do not in practice react with the acetylene, are present in the solution. Thus,

$$[\text{Cu(I)}]_t = [\text{Cu(I)}_s] + \sum K_i [L'_i][\text{Cu(I)}_s] + [\text{A}] + [\text{A}^-] \quad (4)$$

where $[\text{Cu(I)}]_t$ = total concentration of Cu(I) , K_i = constant for the complexing of Cu(I) with all ligands (L_i) except acetylene, $L'_i = [L_i]/[\text{Py}]$.

$$[\text{Cu(I)}]_t = [\text{Cu(I)}_s] + \sum K_i [L'_i][\text{Cu(I)}_s] + K'_1 [\text{P}]_t \cdot [\text{Cu(I)}_s] (1 + K_2 [\text{B}]/[\text{BH}^+]) ([\text{P}] \approx [\text{P}]_t) \quad (5)$$

$$[\text{Cu(I)}_s] = \frac{[\text{Cu(I)}]_t}{1 + \sum K_i [L'_i] + K'_1 [\text{P}]_t (1 + K_2 [\text{B}]/[\text{BH}^+])} \quad (6)$$

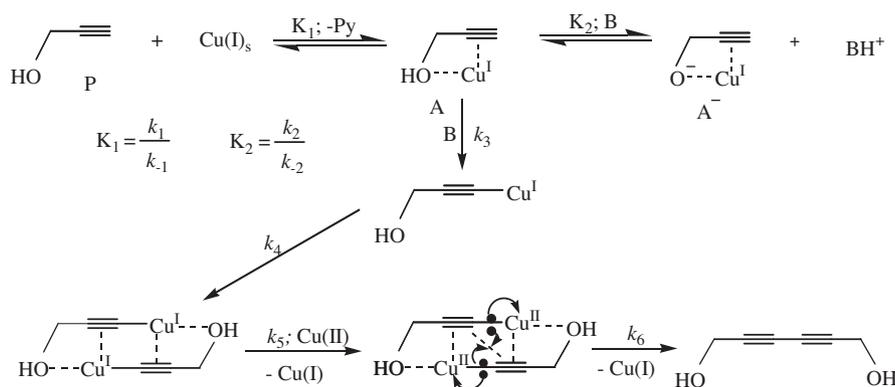
$$W_f = \frac{k_3 K'_1 [\text{B}] \cdot [\text{Cu(I)}]_t \cdot [\text{P}]_t}{1 + \sum K_i [L'_i] + K'_1 [\text{P}]_t + K'_1 K_2 [\text{P}]_t \cdot [\text{B}]/[\text{BH}^+] + K'_1 [\text{Cu(I)}]_t + K'_1 K_2 [\text{Cu(I)}]_t \cdot [\text{B}]/[\text{BH}^+]} \quad (7)$$

with the participation of hydroxy groups (Scheme 2). As a result, the reaction pathway, including the formation of dimeric Cu(I) acetylides and their oxidation by Cu(II) into dimeric Cu(II) acetylides, becomes prevalent.

We assume that formation of the Cu(I) acetylide determines the reaction rate, that is, $k_3 \ll k_1, k_{-1}, k_2, k_{-2}, k_4, k_5$. Therefore, the reaction rate is expressed as

$$W_f = k_3 [\text{B}][\text{A}] \quad (1)$$

where $W_f = -\frac{d[\text{Cu(II)}]}{dt}$ – the final reaction rate. The total P concentration is equal to the sum of the concentrations of free P, A and A^- : $[\text{P}]_t = [\text{P}] + [\text{A}] + [\text{A}^-]$. Using the equations for equilibrium constants $K'_1 = \frac{[\text{A}]}{[\text{P}][\text{Cu(I)}_s]}$, where $K'_1 = \frac{K_1}{[\text{Py}]}$, and $K_2 = \frac{[\text{A}^-][\text{BH}^+]}{[\text{A}][\text{B}]}$, it can be derived that



Scheme 2. $\text{Cu(I)}_s = \text{Cu(I)}$ solvated by pyridine; B-base (amine) k_i = the rate constants for the reaction steps.

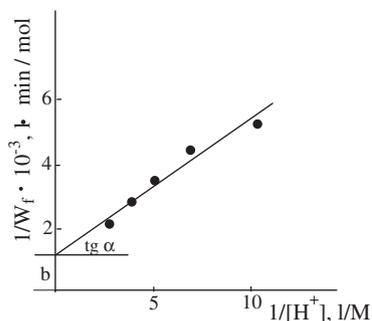


Figure 2. Dependence of $1/W_t$ on $1/[\text{AcOH}]$ with constant $[\text{AcO}^-]$, maintained by adding $[\text{NEt}_4]^+\text{OAc}^-$; 40 °C, $[\text{P}]=1.0$ M, $[\text{HN}(\text{CH}_2)_5]=1.0$ M, $[\text{Cu}(\text{II})]_0=4 \times 10^{-3}$ M.

$$b = \frac{1 + \sum K_i [L'_i] + K'_1 [P]_t}{k_3 K'_1 [B] \cdot [P]_t \cdot [\text{Cu}(\text{I})]_t}; \quad \text{tg} \alpha = \frac{K_2}{k_3 [\text{Cu}(\text{I})]_t} [P]_t \gg [\text{Cu}(\text{I})]_t \quad (8)$$

The data obtained can be used to explain the 'unusual' behavior of P in Cu-catalyzed cross-coupling with aryl iodides.¹⁰ Unlike phenyl acetylene and heptyne, P does not react with aryl iodides in a $\text{CuI}-\text{PPh}_3-\text{K}_2\text{CO}_3$ system in DMSO and is regenerated in 80% yield. However, protection of P with THP, *t*-butyl and acetyl groups enabled the reaction to give the corresponding coupled products in 37–90% yields. According to the accepted scheme of the reaction mechanism, aryl iodide interacts with $\text{Cu}(\text{I})$ acetylde formed in situ. In the case of propynol, the formation of $\text{Cu}(\text{I})$ acetylde was shown to be impeded. Therefore it can be assumed that the $\text{Cu}(\text{I})$ -catalyzed cross-coupling of other α -acetylenic alcohols with aryl iodides would also be impeded, for the same reasons.^{11–13}

The reactivity of terminal acetylenes in oxidative couplings is determined not only by their acidity, but also by the ability of existing functional groups to form complexes with $\text{Cu}(\text{I})$. This complexing facilitates the formation of a multicentered transition state in the process of synchronous electron transfer. This feature results in kinetic regularities in the oxidative coupling of some functionalized acetylenes.

3. Experimental

Cuprous chloride partially oxidized with O_2 in the buffer solution was used as the oxidizing agent. The reaction was monitored by a change in optical density of the solution in the region of the absorption maximum of $\text{Cu}(\text{II})$ at λ 680 nm. A 42 mm long thermostated cuvette provided with a stirrer was used. The cuvette was filled, under N_2 , with the buffer solution containing the partially oxidized cuprous chloride, placed in a spectrophotometer (SF-10) and thermostated. The acetylene was then introduced rapidly into the cuvette, the reaction mixture was stirred and the measurements were recorded.

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