Electrode-Assisted Wacker Process: Phosphomolybdate-Mediated Oxidation of 1-Butene to Methyl Ethyl Ketone

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Received September 28, 2000

Keywords : Olefin oxidation, Wacker process, Phosphomolybdate, Electrochemistry, 1-Butene.

The Wacker process is important from an industrial point of view for synthesis of a large quantity of ketones and aldehydes. Since Wacker Chemie and Farbwerke Hoechst commercialized acetaldehyde synthesis process from ethylene,[1] the oxidation of other olefins has been extensively studied. The original process uses $PdCl_2$ to oxidize olefins (eq. 1, Scheme 1) and $CuCl_2$ to regenerate Pd(II) from Pd(0) (eq. 2). The produced Cu(I), in turn, is oxidized back to Cu(II) by molecular oxygen in acidic media (eq. 3).[2]

$$RCH{=}CH_2 + H_2O + Pd(II) \rightarrow RC(O)CH_3 + 2H^+ + Pd(0) \quad (1)$$

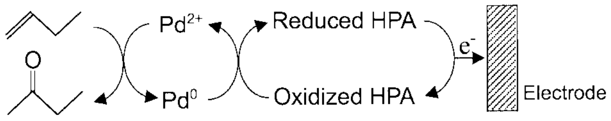
$$Pd(0) + 2CuCl_2 \rightarrow PdCl_2 + Cu_2Cl_2 \quad (2)$$

$$Cu_2Cl_2 + 2HCl + 1/2O_2 \rightarrow 2CuCl_2 + H_2O \quad (3)$$

Scheme 1

Since this scheme found disfavor due to the corrosion problem by copper chloride and safety hazard from the use of high pressure of oxygen, several alternatives have been developed. Smith III *et al.*[3] used substoichiometric amounts of $Cu(CH_3CO_2)_2$ instead of $CuCl_2$ to apply to the total synthesis of natural products. Monflier *et al.*[4,5] employed chemically modified β-cyclodextrin to selectively oxidize higher β-olefins to 2-ketones in high yields. Instead of using homogeneous catalysts, attempts have been made using heterogeneous catalysts, which include, for example, Cu/Pd-exchanged zeolites,[6] bulk and supported V_2O_5 impregnated with a Pd salt.[7,8] Recently, Stobbe-Kreemers *et al.*[9,10] showed Pd salts of Keggin-type, vanadium-substituted heteropoly acids (HPA) have high catalytic activities toward the oxidation of 1-butene. They explained catalytic activity as originated from the fact that the Pd center and the redox component are present in one molecule. Sim, in the mean time, showed the similar system could work even in solution phase.[11]

While most works so far have concentrated on the development of alternative catalytic systems in place of $CuCl_2$ but still used molecular oxygen to reoxidize these catalysts, we report in this communication that the Wacker process could proceed more efficiently by the assistance of an electrode in HPA-catalyzed systems. Since the rate-determining step is the oxidation of reduced HPA, it is possible to enhance the reaction rate by the electrochemical oxidation of reduced HPA, instead of molecular oxygen (Scheme 2).



Scheme 2

The electrochemical properties of various (un)substituted HPAs have been extensively studied because of their wide range of application.[12] Use of HPAs as a mediator may have advantage over other compounds in that a sequential reversible electron transfer takes place without destroying structure and their electrochemical properties is controllable simply by changing hetero- or addenda- atoms.[13]

Figure 1 shows the cyclic voltammetry of $H_3PMo_{12}O_{40}$ at a carbon sheet working electrode at pH 2.5 in the presence of Pd^{2+}. The details of experimentals are described in ref. 14. The rather distorted voltammogram is caused by the large ohmic polarization due to the low electrolyte concentration. Two redox peaks (A, A' and B, B') with formal potentials at 0.37 and 0.20 V are consecutive two-electron processes, making $PMo^{VI}_{11}Mo^{IV}O_{40}{}^{5-}$ and $PMo^{VI}_{10}Mo^{IV}_2O_{40}{}^{7-}$, respectively.[13] The added electrons are known to be localized on Mo.[15] The identical voltammogram was obtained in the absence of Pd^{2+} in the potential range examined. The color change depends on the oxidation state of phosphomolybdate. At 0.6 V or more positive potential where all Mo atoms are at +6 state, the solution takes yellowish green color. As the reduction takes place either chemically or electrochemically, the solution turns blue, indicating the formation of hetero-

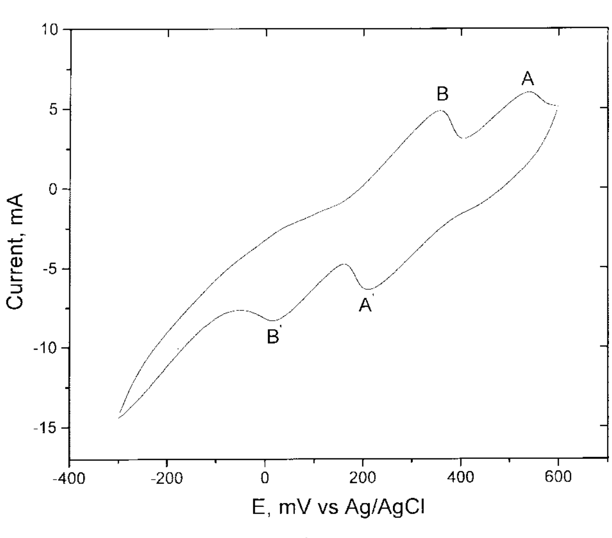


Figure 1. Cyclic voltammetry of 0.8 mM $H_3PMo_{12}O_{40}$ in pH 2.5 solution containing 0.2 mM $Pd(NO_3)_2$ and KCl at a carbon sheet electrode. Scan rate: 20 $mVsec^{-1}$; Apparent electrode area: 10 cm^2; Reference electrode: Ag/AgCl.

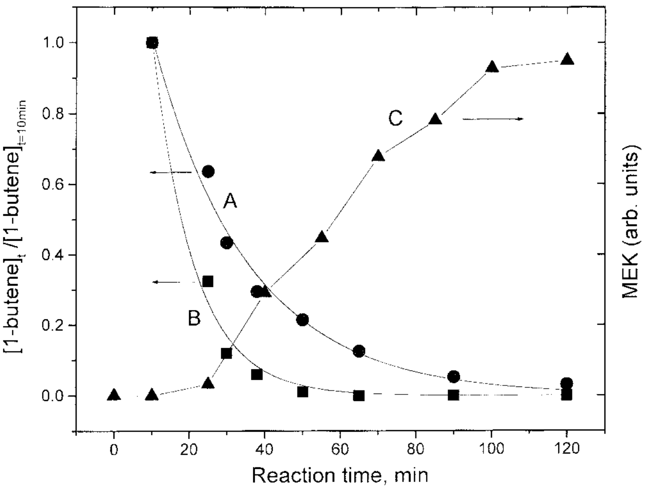


Figure 2. Plot of the normalized value of 1-butene remaining in the gas phase *vs* reaction time for Pd/HPA/O_2 (●) and Pd/HPA/electrode (■) systems. Solid lines are fitted results assuming the first order reaction. Measurements were made 10 min after the injection. Normalization was done with respect to the GC peak area at 10 min. +0.6 V was applied to the working electrode for curve B. Curve C (▲) represents the amount of MEK produced in the solution under the electrochemical condition as the reaction proceeds.

poly blue. Thus the examination of color change could be used as an indicator of the extent of the Wacker process.

Figure 2 shows how 1-butene oxidation proceeds as a function of time, depending on the reaction conditions. The y-values indicate the amount of unreacted 1-butene determined by GC. After injecting 1-butene into the solution, 10 min was allowed until it was equilibrated between the solution and the gas phase. Curve A was obtained without using an electrode but saturating the solution with oxygen as an oxidizing agent of phosphomolybdate. Assuming the first order reaction in 1-butene, the rate constant was calculated to be *ca*. 26 min^{-1} (solid line). However, when +0.6 V was applied to the electrode even in the absence of oxygen, with other conditions being the same, the rapid decrease in 1-butene was observed (curve B). Fitting to the first order reaction rate, the rate constant was only 11 min^{-1} (solid line). Virtually no 1-butene was detected in the gas phase in an hour. The difference in the reaction rates was also reflected in color changes. Starting with yellowish green color, the Pd/HPA/O_2 system rapidly turned deep blue and the recovery to the original color was very slow. But in the Pd/HPA/electrode system, the solution color was not that deep and the color recovery was much faster. After *ca*. 40 min, the solution took its original yellowish green color, which coincides with the 1-butene level remaining in the gas phase. At this time, almost all 1-butene was consumed (curve B, Fig. 2). When reaction products were identified with NMR and GC after extracting the solution with diethyl ether, exclusively methyl ethyl ketone was found, indicating high selectivity of this method. The amount of MEK monitored by GC gradually increased as the reaction proceeded. However the pattern does not show exponential behavior as expected from the decreasing pattern of 1-butene. Only a small amount of MEK was detected within first 30 min, indicating dissolved 1-butene was not immediately converted to MEK.

We have shown that the oxidation rate of 1-butene can be greatly enhanced by electrochemically oxidizing phosphomolybdate rather than by oxygen. The simplicity of this method may find some applications in an industrial area.

Acknowledgment. Financial support from Konkuk University in the program year 1999 is gratefully acknowledged.

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14. The reaction cell was made of a double-jacketed glass with internal volume of 50 mL. $Pd(NO_3)_2$ (Aldrich) and $H_3PMo_{12}O_{40}$ (Fluka) of reagent grade were used without further purification. Concentrated solutions of $Pd(NO_3)_2$ in HNO_3 and $H_3PMo_{12}O_{40}$ in HCl and KCl were prepared in separate vessels and taken to the reactor. Their final concentrations were adjusted 0.2 and 0.8 mM, respectively. We used KCl (0.2 mM) to provide Pd^{2+} with chloride ligands. In electrochemical experiments, the reactor was thoroughly degassed with high purity N_2 gas before introducing 1-butene and potential was applied. A typical three-electrode system, in which the working electrode was separated from the counter electrode by a salt bridge to avoid mixing of products, was employed. Ordinary Wacker oxidation was performed by saturating the solution with oxygen, instead using an electrode. In both experiments, 5 mL of 1-butene was injected. The reactor was only half-filled and the reaction progression was monitored by taking samples of 50 μL from the upper vapor to GC (Hewlett Packard 5890A). MEK was analyzed by taking 2 μL of liquid samples from the solution. Reaction temperature was maintained at 50 °C.
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