

УДК 542

Products of Homogeneous Two-Stage Oxidation of 1-Butene to Butanone with O₂ over the Catalyst Pd + Heteropoly Acid

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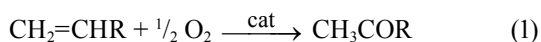
Received 20.05.2009, received in revised form 27.05.2009, accepted 04.06.2009

Oxidation of 1-butene to butanone in the presence of homogeneous catalyst Pd + HPA (H₁₂P₃Mo₁₈V₇O₈₅) followed by regeneration of the catalyst with O₂ proceeds with selectivity 97.5%. Side products of the process are acetic acid (1.4%) and condensed compounds C₇H₁₂O₂, C₈H₁₄O₂, C₆H₆O₂, and C₈H₁₀O₂ (total 1.1%). In the course of the catalyst regeneration at 170°C under O₂ pressure, the compounds C₆–C₈ are completely oxidized to CO₂ and acetic acid. n-Butanal is absent in the reaction products, that permits readily to separate butanone as a water azeotrope from the reduced catalyst.

Keywords: Oxidation of 1-butene to butanone, homogeneous catalyst Pd + HPA, reaction products.

Introduction

The processes of oxidation of lower alkenes C₂–C₄ to carbonyl compounds with dioxygen by reaction (1) are of great practical importance:



Here R = H, CH₃, or C₂H₅. In the late 1950s the Wacker company had suggested for such processes a homogeneous catalyst, which was an aqueous solution of PdCl₂ + CuCl₂ [1, 2]. CuCl₂ here is a reversible oxidant, which reduced form is readily oxidized with dioxygen. Such catalyst had a high concentration of chlorides (up to 2 M), that led to formation of toxic chloroorganic side products. Their amount strongly increased in the series C₂ (ca. 2% [3]) < C₃ (ca. 4%) < C₄ (> 6%) [2, 4]. Amount of chloroorganics strongly increased also at elevated temperature [4] but decreased after dehydrochlorination (see later). Besides,

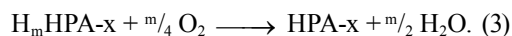
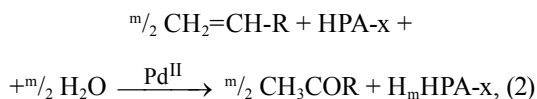
various amounts of aldehydes, RCH₂CHO, were formed together with ketones, CH₃COR. When propene or 1-butene were oxidized, yield of RCH₂CHO varied from 3 to 18% [2, 5]. Only in oxidation of 2-butene, butanone was the single reaction product [1]. Now only the oxidation of C₂H₄ to CH₃CHO is implemented with the Wacker catalyst on industrial scale [6].

To eliminate formation of chlorinated products in oxidation of lower alkenes C₂–C₄ with dioxygen in the presence of any Pd-containing catalysts, in the mid-1970s Matveev and co-authors suggested *chloride-free* Pd + heteropoly acid catalysts. In this case, aqueous solutions of the Keggin type Mo-V-P heteropoly acids, H_{3+x}PMo_{12-x}V_xO₄₀ (HPA-x, 2 ≤ x ≤ 6), were reversible oxidants [7]. The reversibility of oxidative properties of the HPA-x solutions favorably distinguishes them from non-

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reversible oxidants, such as CrO_3 , KMnO_4 , or NaIO_4 . To provide maximal selectivity and nonexplosiveness, processes (1) in the presence of such catalysts are carried out in two steps (2) + (3) in separate reactors:



At oxidation of lower alkenes, the target products of reaction (2), CH_3COR , are easily separated from the reduced $\text{Pd} + \text{H}_m\text{HPA-x}$ catalyst by evaporation. At step (3), that is common for all processes (1), the catalyst is regenerated at 130–145°C under O_2 or air pressure [8].

The chloride-free $\text{Pd} + \text{HPA-x}$ catalysts were highly selective (97–99%) in oxidation of alkenes $\text{C}_2\text{--C}_4$ to CH_3COR [7]. In particular, the selectivity of 1-butene oxidation to butanone exceeded 97%. However, it was later found that thermostability of the aqueous solutions of Keggin-type HPA-x was not high. So, the often used 0.2 M HPA-4 solution gradually evolved vanadium-containing deposits during operations at $t > 140^\circ\text{C}$ [9]. For oxidation of 1-butene to butanone, later we have developed catalysts $\text{Pd} + \text{HPA-x'}$ based on *modified* non-Keggin HPA-x' solutions, $\text{H}_a\text{P}_z\text{Mo}_y\text{V}_{x'}\text{O}_b$ (HPA-x' , $1 \leq z \leq 3$; $8 \leq y \leq 16$; $4 \leq x' \leq 12$; $a = 2b - 6y - 5(x' + z)$; $40 \leq b \leq 89$). Certain solutions from this series had high concentration of vanadium (2.0–2.2 M) and improved thermostability [10]. Among them, 0.25 M solution of total composition $\text{H}_{12}\text{P}_3\text{Mo}_{18}\text{V}_7\text{O}_{85}$ (HPA-7') was the most promising. It was recommended by us as a main components of the homogeneous $\text{Pd} + \text{HPA-7'}$ catalyst for the 1-butene oxidation to butanone [10].

Selectivity of this process over the $\text{Pd} + \text{HPA-7'}$ catalyst is as high as that over $\text{Pd} + \text{HPA-x}$ catalysts. At that, high concentration of vanadium in the new catalyst provides a 3-fold higher productivity in the total process (1). High

thermostability of the $\text{Pd} + \text{HPA-7'}$ catalyst allows us readily to regenerate this catalyst by reaction (3) at higher temperature (160–170°C) [11]. This also increases efficiency of the catalyst. We have demonstrated that the $\text{Pd} + \text{HPA-7'}$ catalyst is capable of stable operation for at least several months of continuous work.

Kinetics of the 1-butene oxidation to butanone in the presence of the $\text{Pd} + \text{HPA-x}$ and $\text{Pd} + \text{HPA-x'}$ catalysts was reported in our previous works [11, 12]. Physicochemical properties of the HPA-x' solutions were thoroughly discussed in [13]. In the present work, we give detailed information on products of the 1-butene oxidation over the new $\text{Pd} + \text{HPA-7'}$ catalyst.

Experimental

The 0.25 M solution of $\text{H}_{12}\text{P}_3\text{Mo}_{18}\text{V}_7\text{O}_{85}$ (HPA-7') was synthesized by the method described elsewhere [14]. Palladium was introduced into the HPA-7' solution as PdSO_4 to obtain the concentration $[\text{Pd}] = 6 \times 10^{-3}$ M.

For oxidation reaction (2), we used 99.6% 1-butene from Budyonnovsk Chemical Plant (Russia) having only 2-butenes and *n*-butane as admixtures. 1-Butene used in our work contains no butadiene or acetylenes that hinder oxidation of alkenes in the presence of Pd. The oxidation of 1-butene was performed in a shaken thermostated reactor at 30–70°C for 15–17 min to the complete reduction of the catalyst solution [12]. The resulting butanone was evaporated from the reduced catalyst as a water azeotrope containing 89% of butanone and boiling at 73.4°C [15]. Degree of the butanone evaporation (ca. 97%) was controlled by the GLC method (see later). Regeneration of the catalyst with dioxygen by reaction (3) was carried out for 20 min in a stainless steel autoclave at 170°C and $P_{\text{O}_2} = 4$ atm [8].

The reaction products were analyzed by the GLC method using a Tsvet 500 chromatograph

with glass capillary column (40 m × 0.25 mm) and flame-ionization detector. Methyl silicone rubber SE-30 was used as a stationary phase, and helium as a carrier gas. The analysis was made via thermoprogrammed heating from 60 to 160°C with a ramp rate of 20°/min. The chromatograms were recorded and analyzed using a Mul'tikhrom computer system. In the study, we have analyzed: a) the reduced Pd + H_mHPA-7' catalyst solution containing products of reaction (2); b) the condensate of the products evaporated from this catalyst; c) the Pd + HPA-7' catalyst solution oxidized by reaction (3).

For identification, the reaction products were analyzed also by GC-MS method using a capillary quartz column (30 m × 0.25 mm) in the temperature range of 50–200°C. Non-polar methylpolysiloxane CP-SIL 8 (Chrompack) was used as a stationary phase intended for chromatomass spectrometers.

Results and Discussion

The composition of products of the 1-butene oxidation in reaction (2) in the presence of the tested chloride-free Pd + HPA-7' catalyst is presented in Table 1. For comparison, Table 1 shows also products of oxidation of butene-butane fractions in the presence of other catalysts. In the presence of the Wacker PdCl₂ + CuCl₂ catalyst, content of the side chlorine-containing organics was > 6% [2, 4]. In the presence of the Catalytica's catalyst PdCl₂ + Na_xHPA-x containing acidic salts of HPA-x (x = 3–6) and small amount of HCl, yield of chlorinated products was only 0.15% [18]. However, even so small amount of chloroorganics hampered purification butanone from by-product, *n*-butanal (see later).

With our chlorine-free Pd + HPA-7' catalyst, no chloroorganics is produced, and selectivity of butanone formation attained 97.5%, with the total amount of side products not exceeding 2.5%. However, composition of side products

significantly differs from composition of them in the presence of other catalysts.

In our case, the main side product of the 1-butene oxidation is acetic acid (HOAc), its content attains to 1.4%. Other side products, accounting for ca. 1.1%, are C₇H₁₂O₂ (**I**, 0.3%), C₈H₁₄O₂ (**II**, 0.1%), C₆H₆O₂ (**III**, 0.3%), and a mixture of C₈H₁₀O₂ isomers (**IV**, 0.4%). Note that *n*-butanal (*n*-C₃H₇CHO) is not found among these products, thus indicating that its content in the products mixture does not exceed 0.05%.

It is known that HOAc is formed at oxidation of butanone with vanadium(V) compounds in strongly acidic media [19]. Our catalyst based on the HPA-7' solution is characterized indeed by high acidity and has pH₀ < 0. Acidity of our catalyst is comparable with acidity of concentrated solutions of heteropoly acids as H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ [20], and far exceeds acidity of other catalysts intended for oxidation of *n*-butene fractions with dioxygen. For comparison, pH values of the Pd-containing catalysts based on Na_xHPA-x [21] or CuCl₂ [2] varied from 0.4 to 1.0.

As for other side products, compound **II** with high probability is 3-methylheptane-2,4-dione (C₈), and compound **I** is 3-methylhexane-2,4-dione (C₇). Then, isomers **IV**, being hydrogen-poorer in comparison with β-diketone **II**, can be interpreted as products of dehydrogenation or dehydrocyclization of the diketone. In that case, compound **III** is the product of β-diketone C₆H₁₀O₂ dehydrogenation or dehydrocyclization. But this β-diketone is not detected in our study, probably due to its low concentration. Note that β-diketone C₆H₁₀O₂ is a lower homologue of β-diketones **II** (C₇H₁₂O₂) and **I** (C₈H₁₄O₂).

We believe that products of the 1-butene oxidation had initially contained also *n*-butanal, which further turned into compounds **II**, **I**, **IV**, and **III** according to Fig. 1. Earlier, when C₄ fractions contained 1-butene were oxidized in the presence of other catalysts such as Pd + Na_xHPA-x or

Table 1. Composition of products of *n*-butene fractions oxidation in the presence of various homogeneous Pd-containing catalysts

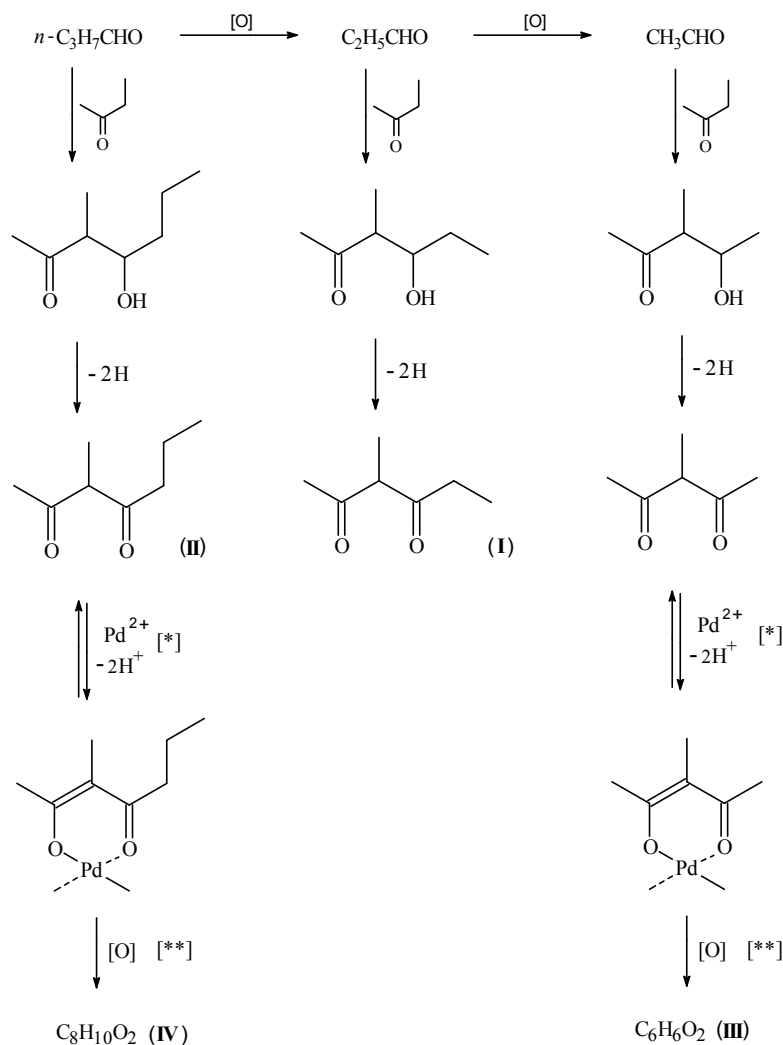
Patent holder	Catalyst composition	Total <i>n</i> -butenes part in C ₄ fraction, % ^a	Selectivity on butanone, %	Side products, %	Refs.
Wacker-Chemie, BRD	PdCl ₂ + CuCl ₂ + HCl; [Cl ⁻] = 1.2–2.0 M	94 ^{at}	85–88	<i>n</i> -butanal: 2–4; 3-chloro- and 3,3-dichloro-2-butanone: 4–6; diacetyl ^b and other Cl-free compounds: 2–3.5	[2]
BashNIIPN, USSR	PdCl ₂ + CuCl ₂ + Cu(OAc) ₂ + HOAc; [Cl ⁻] = 0.6–0.75 M	72 ^{at}	70–90	acetone; 3-chloro- and 3,3-dichloro-2-butanone; diacetyl ^b , <i>tert</i> -butanol ^d	[16] ^c
Catalytica of Mountain View, USA	PdCl ₂ + HCl + Na _x HPA- <i>x</i> ; [Cl ⁻] = 0.035 M	68 ^{at}	93.4	AcOH: 2.9; <i>n</i> -butanal: 0.63; C ₃ H ₅ CHO + AcH: 0.57; Cl-derivatives: 0.15; 1- and 2-butanols: 0.23; other ketones: 0.09; nonvolatile compounds: ~2.0	[18]
Institute of Catalysis, SB RAS, Russia	PdSO ₄ + HPA- <i>x</i> ^c ; [Cl ⁻] = 0	99.8 ^{at, at}	97.5	AcOH: 1.4; 3-methyl-2,4-hexanedione (I): 0.3; 3-methyl-2,4-heptanedione (II): 0.1; C ₆ H ₆ O ₂ (III): 0.3; isomers of C ₈ H ₁₀ O ₂ (IV): 0.4	the present work

^a All C₄ fractions contain other components: ^{at} *n*-butane; ^{at} *n*-butane, *iso*-butane, and *iso*-butene (ca. 10%) [17], ^{at} *n*-butane, *iso*-butane, trace amounts of C₃, butadiene, and C₅. ^{at} Including 99.6% of 1-butene and 0.2% of 2-butenes.

^b Product of 3,3-dichloro-2-butanone hydrolysis.

^c In [16], only qualitative composition of side oxidation products was reported.

^d It was formed through hydration of *iso*-butene presented in the C₄ fraction.



[*] The Pd^{II} complex is in equilibrium with β -diketone and contains two β -ketoenol ligands. (Only one ligand is shown in the Fig.). Every ligand detaches H^+ at the complex formation with Pd^{II} .

[**] Every ligand loses 3 H atoms at the oxidative decomposition of the Pd^{II} complex.

Fig. 1. Formation of side products in reaction (2)

$\text{PdCl}_2 + \text{CuCl}_2$, n -butanal was always detected in products of oxidation. Thus, in the presence of the $\text{PdCl}_2 + \text{Na}_x\text{HPA-x}$ catalyst, products of oxidation of the fraction with ratio 1-butene : 2-butenes ~ 0.5 contained 0.63% of n -butanal and no β -diketones **I** and **II** [18]. Taking into account the chemical properties of n -butanal and composition of the observed products of reaction (2), we think that a part of n -butanal, $n\text{-C}_3\text{H}_7\text{CHO}$, is subjected to partial oxidative degradation [22, 23] yielding $\text{C}_2\text{H}_5\text{CHO}$ and CH_3CHO (Fig. 1). Further each of

the three aldehydes condenses with butanone [24, 25] forming β -hydroxyketones ('aldols') with composition $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}(\text{OH})\text{R}$, where $\text{R} = n\text{-C}_3\text{H}_7$, C_2H_5 , or CH_3 . These 'aldols' contain the secondary alcohol group $-\text{CH}(\text{OH})-$.

As was shown in [26], secondary alcohols are readily oxidized to ketones in the presence of the catalytic system $\text{Pd} + \text{HPA-x}$. Hence, the system $\text{Pd} + \text{HPA-7'}$ would certainly oxidize β -hydroxyketones to β -diketones $\text{CH}_3\text{COCH}(\text{CH}_3)\text{COR}$. It is known that various

metal ions, in particular Pd^{2+} , form complexes with enolic forms of β -diketones, for example, with enol form of well-known acetylacetone, $\text{CH}_3\text{COCH}_2\text{COCH}_3$, *i.e.* with $\text{CH}_3\text{C}(\text{OH})=\text{CHCOCH}_3$ [27]. However, as the enol forms of β -diketones shown in Fig. 1 are weak acids, their complexation with Pd^{2+} in strongly acidic media is reversible. This feature offers to explain why GLC analysis of products of the 1-butene oxidation reveals not all β -diketones, but only those from them which complexes with Pd^{2+} are less stable. In turn, β -diketones are partially dehydrocyclized to form non-identified compounds of type **III** or **IV** with a lower content of hydrogen.

In strongly acidic media, the oxidative transformations of *n*-butanal into lower aldehydes, 'aldols' and β -diketones shown in Fig. 1 are rather readily. The dehydrocyclization of β -diketones into compounds **III** and **IV** proceeds more slowly. This is the reason why *n*-butanal, which supposedly was among initial side products of the 1-butene oxidation in the presence of the $\text{Pd} + \text{HPA-7'}$ catalyst, was not detected in our products of reaction (2).

The $\text{C}_6\text{--C}_8$ compounds from Fig. 1, being less volatile as compared to butanone, are evaporated not completely with butanone. The remaining part of these compounds goes further to the reactor for catalyst regeneration. At ca. 170°C under the O_2 pressure, these compounds are gradually oxidized to HOAc and CO_2 .

Thus, the interaction of the reduced $\text{Pd} + \text{H}_m\text{HPA-7'}$ catalyst at step (3) with O_2 at high temperature results in its regeneration with simultaneous oxidation of all side products except HOAc. As was revealed earlier, small amounts of HOAc (up to 10%) do not hinder the 1-butene oxidation at step (2) in the presence of the $\text{Pd} + \text{HPA-x}$ catalyst. On the contrary, HOAc increases rate of this reaction due to improved solubility of 1-butene in the catalyst [28].

During the long-term cyclic testing via Fig. (2) + (3), the amount of HOAc in the solution of catalyst $\text{Pd} + \text{HPA-7'}$ gradually increases to 8–10% and then remains at a stationary level, because HOAc begins to evaporate from the reduced catalyst together with butanone. Note also that the real absence of *n*-butanal in the products of the 1-butene oxidation strongly facilitates separation of butanone from the reaction products. It is known that *n*-butanal forms an azeotrope with water that boils at 68.0°C and is difficultly separable from the (butanone + water) azeotrope boiling at 73.4°C [15]. Thus, if *n*-butanal was really formed at the oxidation of *n*-butenes in the presence of the $\text{Pd} + \text{Na}_x\text{HPA-x}$ catalyst, then there was a need to reduce it to *n*-butanol in a separate reactor [18]. At that, the reduction of *n*-butanal was accompanied by a partial reduction of butanone to *sec*-butanol, that indeed decreased total selectivity of the Catalytica butanone process [21].

The use of the Wacker chloride catalyst gave even a more complicated mixture of products of the *n*-butenes oxidation. The mixture was also treated with dihydrogen in a separate reactor, where both reduction of *n*-butanal to *n*-butanol and dehydrochlorination of side 3-chloro- and 3,3-dichloro-2-butanone to butanone occurred [2]. Since at our 1-butene oxidation over the $\text{Pd} + \text{HPA-7'}$ catalyst, *n*-butanal is really absent in the reaction products, there is no necessity of its reduction. This significantly simplifies process (1) of butanone production over the $\text{Pd} + \text{HPA-7'}$ catalyst developed in our work.

Conclusion

Selectivity of butanone formation at the 1-butene oxidation with dioxygen over the homogeneous $\text{Pd} + \text{HPA-7'}$ catalyst attains 97.5%. Side products of this oxidation are acetic acid (1.4%) and the condensed compounds of $\text{C}_6\text{--C}_8$ series (1.1%) that are formed in the strongly acidic medium. During regeneration of the catalyst at

170°C and $P_{O_2} = 4$ atm, the C_6-C_8 compounds are almost completely oxidized to CO_2 and HOAc. Small amounts of HOAc in the catalyst solution do not hinder the 1-butene oxidation, since they increase solubility of 1-butene in the catalyst. An

important advantage of the Pd + HPA-7' catalyst is the absence of *n*-butanal in products of the 1-butene oxidation. This considerably facilitates separation of butanone from the reduced catalyst without decrease of total productivity of process (1).

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