

Kinetics of One-Stage Wacker-Type Oxidation of C₂–C₄ Olefins Catalysed by an Aqueous PdCl₂–Heteropoly-Anion System

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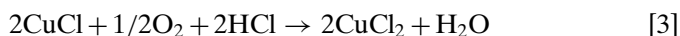
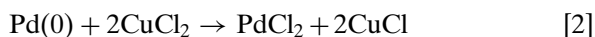
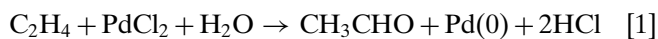
The steady-state kinetics of the one-stage Wacker oxidation of gaseous olefins such as ethene, propene, and 1-butene by oxygen (1 : 2 stoichiometric mixture of O₂ and olefin) to form acetaldehyde, acetone, and methyl ethyl ketone, respectively, was studied in a semicontinuous reactor. The catalytic system involves an aqueous solution of Pd(II) chloride (0.05–2 mM Pd(II), [Pd(II)]/[Cl⁻] = 1 : 50) and Keggin-type heteropoly anions [PMo₉V₃O₄₀]⁶⁻ (50 mM), at 20–50°C. Under these conditions in a steady state, the reactivity of olefins increases in the order ethene ≤ 1-butene < propene, but the total range is only a factor of 3. The oxidation of 1-butene is accompanied by the double-bond migration to form 2-butene.

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Key Words: Wacker oxidation; olefin; palladium; heteropoly anion; kinetics.

INTRODUCTION

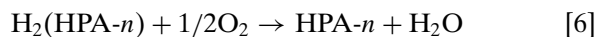
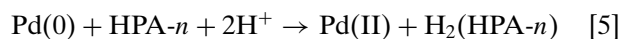
The oxidation of ethene by oxygen catalysed by PdCl₂–CuCl₂ in aqueous solution to produce acetaldehyde was developed and commercialised by Wacker-Chemie in 1959 (1). The Wacker process can be described by a simplified scheme involving reactions [1]–[4] (1–4):



Industrially, the reaction is usually performed in two-stage plants where the reduction of the catalyst by ethene (steps [1] and [2]) and the reoxidation of the catalyst by oxygen (step [3]) are conducted in separate reactors. This process, however, suffers a major drawback; that is, high levels of chloride are required to render the oxidation of Pd(0) by Cu(II) thermodynamically possible (3, 5) and to avoid Pd(0) deposition. As a result of the high chloride concentration, besides the requirement of using titanium-lined re-

actors to limit corrosion, up to 5% chlorinated by-products are formed in the oxidation of ethene, arising mainly from oxychlorination of acetaldehyde by Cu(II) chloride. The percentage of chlorinated by-products increases when the oxidation of higher olefins is attempted, hence only ethene oxidation is exploited on a commercial scale.

Matveev *et al.* (6–8) addressed this problem by using Keggin-type molybdovanadophosphate heteropoly anions [PMo_{12-n}V_nO₄₀]⁽³⁺ⁿ⁾⁻ (HPA-*n*, *n* = 2, . . . , 6) instead of copper chloride to reoxidise Pd(0) to Pd(II) in a chloride-free system. This allowed avoidance of the chlorination in the course of oxidation of olefins. With HPA-*n*, the reaction occurs through steps [5] and [6] instead of [2] and [3]:



Here H₂(HPA-*n*) is the reduced form of HPA-*n* (heteropoly blue) of the formula H₂[PMo_{12-n}V_{n-2}V₂O₄₀]⁽³⁺ⁿ⁾⁻. Steps [5] and [6] involve redox transformations of vanadium V⁵⁺ ⇌ V⁴⁺ inside the HPA-*n* heteropoly anion. However, the absence of chloride ions led to a rather poor palladium stability in solution, resulting in deactivation of the system because of formation of colloidal and metallic palladium. Maitlis *et al.* (9) studied the oxidation of 1-butene to methyl ethyl ketone (MEK) in this system. More recently, Grate *et al.* (10, 11) at Catalytica showed that by adding small amounts of chloride to that system catalyst deactivation could be avoided and much higher palladium turnover frequencies could be achieved than in the original Wacker process. The concentrations of Pd(II) and Cl⁻ used in this system are much lower than in the Wacker process, and it is claimed that the production of chlorinated by-products in the two-stage oxidation of ethene is reduced by over 99%. Propene, butene, and higher olefins can be oxidised in addition to ethene to give the corresponding ketones with very high selectivities and low levels of chlorinated by-products (7, 9, 10).

The kinetics of the two-stage ethene oxidation has been extensively studied both under Wacker conditions (high [Cl⁻]) (2–4) and in the absence of Cl⁻ (6, 12), showing that

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different reaction mechanisms are operative in these two extreme cases (7). However, little is known regarding the oxidation of olefins in the presence of an intermediate level of chloride except Catalytica's results for the oxidation of ethene (10, 11). Alternatively, the oxidation of olefins can be carried out as a one-stage process, i.e., when steps [1]–[3] occur simultaneously in one reactor. Such a process has the advantage of a much lower concentration of HPA-*n* in the catalyst, and the stability of the catalyst may be better than that in the two-stage process. To the best of our knowledge, no kinetics for the one-stage oxidation of C₂–C₄ olefins by the O₂/Pd(II)/HPA-*n* system has been reported.

The aim of this work is to study the kinetics of the one-stage oxidation of ethene, propene, and 1-butene by oxygen to acetaldehyde, acetone, and MEK, respectively, using a catalytic system based on Pd(II)/HPA-3, similar to that developed by Catalytica.

EXPERIMENTAL

Materials. The gases ethene, propene, and 1-butene of >99% purity were purchased from BOC (N2.0 grade). 2-Butene (99+%) was purchased from Aldrich. A 50 mM aqueous stock solution of the sodium salt of HPA-3, Na₄H₂[PMo₉V₃O₄₀], pH 1.3, was prepared as described elsewhere (10, 11). A 2.0 mM Pd(II) chloride aqueous solution with a molar ratio Pd(II)/Cl⁻ = 1 : 50 (NaCl) containing 50 mM HPA-3, pH 1.3, was used as a source of palladium.

Kinetic measurement. Oxidation of gaseous olefins was carried out at atmospheric pressure in a specially designed semicontinuous reactor with intense stirring, which allowed avoidance of diffusion control of reaction rates. The reactor was a 125-cm³ double-jacketed cylindrical glass vessel with baffles on the inside wall of the reactor to enhance gas–liquid mixing (Fig. 1). A gas flow (olefin + O₂) was fed into and removed from the reactor at a steady rate, whereas the products were accumulated inside the vessel. The reactor was heated by circulating thermostated (±0.05°C) water, and the temperature was controlled with a

thermometer (not shown). The reaction mixture was stirred using a PTFE blade attached to a glass rod connected to an overhead stirrer. Mass flow controllers were used to control the oxygen and olefin flows into the reactor. The gas flow out of the reactor was monitored by online GC analysis (Varian 3380 instrument, 2-m Carbopak C packed column and TCD) through an automated valve, and the flow rate was measured using a manual bubble flow meter. For reactions with 1-butene, the olefin feed line was heated to 40°C to prevent condensation of 1-butene in the line.

The following conditions were used for measuring the reaction kinetics: [Pd(II)] = 0.05–0.2 mM; [Pd(II)]/[Cl⁻] = 1 : 50 (NaCl); [HPA-3] = 50 mM; pH 1.3; stoichiometric molar ratio O₂/olefin = 1 : 2 in the gas feed (4.0 cm³/min O₂ and 8.0 cm³/min olefin); *T* = 20–50°C; and the volume of reaction solution, 100 cm³. The pH was adjusted to 1.3 at each temperature by adding NaOH or H₂SO₄. In a typical experiment ([Pd(II)] = 0.10 mM), 95 cm³ of HPA-3 stock solution was introduced into the reactor thermostated to a required temperature with slow stirring (250 rpm), and a 1 : 2 stoichiometric gas mixture of oxygen (4 cm³/min) and olefin (8 cm³/min) was fed into the reactor to replace air until constant gas-phase composition was achieved, as monitored by GC. Once the system equilibrated, the stirring was stopped, and 5.0 cm³ of the 2.0 mM Pd(II) stock solution was added. Stirring was then resumed at a speed ≥1200 rpm, and GC analysis was automatically performed every 5 min. The gas flow out was measured every 5 min as well. GC analysis with absolute calibration for O₂ and olefins in conjunction with flow measurements in and out of the reactor permitted the calculation of the amount of olefin and oxygen consumed in the reactor, using the perfect-gas equation. The rate of gaseous olefin or O₂ consumption (mol/dm³ min) was calculated as a difference of moles of the reactant in and out of the reactor per unit time divided by the volume of the reaction mixture (0.100 dm³). The oxidation products were not studied in detail. Occasional GC tests confirmed that the main products were acetaldehyde, acetone, and MEK from, respectively, ethene, propene, and 1-butene, as expected. Small amounts of acetic acid were also found.

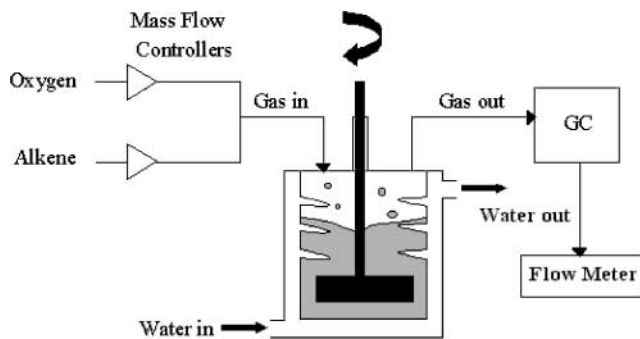


FIG. 1. Schematic diagram of the reactor setup used for the study of kinetics of gaseous olefin oxidation by O₂/Pd(II)/HPA-3 system.

RESULTS AND DISCUSSION

Catalytica's typical catalyst solution for the two-stage oxidation of ethene at 110–130°C and 10-bar pressure consists of an aqueous solution with 0.1 mM Pd(II), 5–25 mM Cl⁻, and 300 mM HPA-*n* (*n* = 2–3) at pH ≤ 1 (10, 11). The HPA-*n* solution is a complex equilibrium mixture of Keggin polyanions containing one to four vanadium atoms (10, 11, 13, 14). Hence the formula {PMo_{12-n}V_n} refers only to the average composition of the solution. It was suggested (7, 10) that the molybdophosphate matrix serves two purposes, namely to solubilize high levels of V(V) in acidic aqueous solution (VO₂⁺ has a limited solubility at low pH) and to provide for

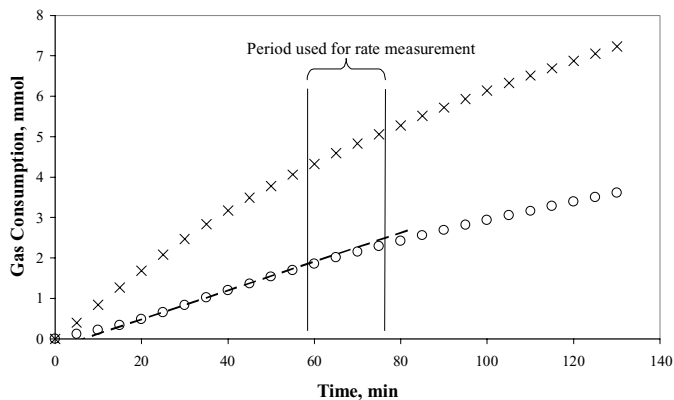


FIG. 2. Amount of 1-butene (x) and oxygen (o) consumed versus time. An induction period for O₂ consumption can be seen. Reaction conditions: 50 mM HPA-3, 0.10 mM Pd(II), 5.0 mM Cl⁻, 30°C, 1500-rpm stirring speed, 4.0 cm³/min oxygen, 8.0 cm³/min 1-butene.

the rapid oxidation of V(IV) by O₂ (VO²⁺ is oxidised very slowly at low pH).

The typical catalyst solution used in this study for the one-stage oxidation consisted of 0.10 mM Pd(II), 5.0 mM Cl⁻, and 50 mM HPA-3. The ratio Pd(II)/Cl⁻ = 1 : 50 gave the best results in Catalytica's system. The HPA-3 concentration was lowered to 50 mM, which was sufficient for the one-stage oxidation. This allowed for a greater solubility of olefins and oxygen in the catalyst solution compared to Catalytica's system due to reducing the salt-out effect on the gas solubility.

Figure 2 shows typical plots for the consumption of 1-butene and O₂ as a function of time under the preceding conditions. An induction period of 5 to 10 min for the O₂ consumption is observed, as expected for a consecutive reaction. The flow out drops immediately once the Pd(II) has been introduced (zero time) (Fig. 3). As seen from GC counts, this is mainly because of olefin absorption, which causes a compensating increase in O₂ concentration in the

gas flow. The red catalyst solution turns dark green, indicating reduction of HPA-3. The system reaches a steady state in 40–50 min with an average degree of HPA-3 reduction <0.2 e⁻ per polyanion, which is estimated from absorption of olefin and O₂. Similar gas-consumption profiles, including the induction period for oxygen, were observed with both ethene and propene. Unless otherwise stated, the reaction rates were therefore measured at a time onstream of 60 to 75 min to ensure a quasi-steady state of the system. The slopes of the plots for olefin and oxygen consumption (Fig. 2) obtained by linear regression in that interval (typically R² > 0.98) were used for calculating the reaction rates.

To eliminate diffusion control the reaction was performed at different stirring speeds. At speeds ≥600 rpm no significant increase in reaction rate was observed for any of the olefins at 20–50°C (Fig. 4), indicating that the diffusion of olefins into the catalyst solution was fast enough to avoid mass-transfer limitation. However, the oxygen diffusion could still affect the reaction regime at stirring speeds over 600 rpm. This was shown by an incremental increase of stirring speed while monitoring the gas flow rate and composition (Fig. 5). Each increment caused a drop in both the flow rate and O₂ composition, the latter being offset by an increase in olefin content. An additional amount of O₂ was therefore consumed to reach another steady state with a lower degree of reduction of HPA-3. This effect weakened as the stirring speed increased, and at stirring speeds ≥1000 rpm stirring ceased to affect the reaction regime. For this reason, rate measurements were performed at stirring speeds ≥1200 rpm. The slower O₂ transfer compared to that of olefin was also found by Grate *et al.* (10).

The oxidation of 1-butene was complicated by the double-bond migration to form 2-butene, especially at lower temperatures. The 1-butene feed did not contain any 2-butene. In the steady-state oxidation at 20°C, the flow out contained 1-butene and 2-butene in a ratio of 5 : 1 to 10 : 1, which was determined by GC. In the absence of palladium

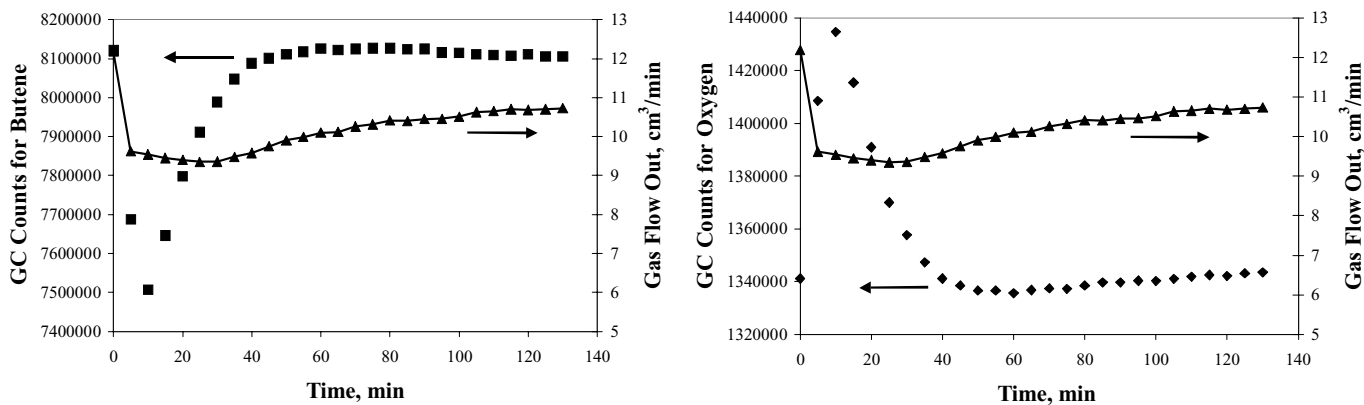


FIG. 3. 1-Butene (left) and oxygen (right) concentrations in the gas flow (GC counts) versus time online. Reaction conditions: 50 mM HPA-3, 0.10 mM Pd(II), 5.0 mM Cl⁻, 30°C, 1500-rpm stirring speed, 4.0 cm³/min oxygen, 8.0 cm³/min 1-butene.

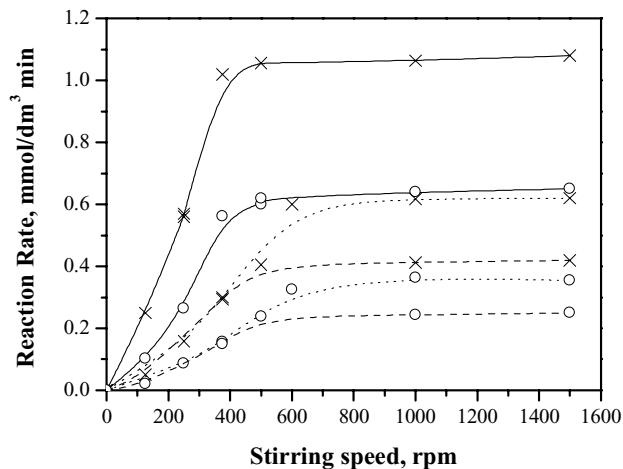


FIG. 4. Olefin (x) and oxygen (o) reaction rates versus stirring speed: ethene (broken lines), propene (solid lines), and 1-butene (dotted lines). Reaction conditions: 50 mM HPA-3, 0.10 mM Pd(II), 5.0 mM Cl⁻, 30°C (50°C for butene), 4.0 cm³/min oxygen, 8.0 cm³/min olefin.

no double-bond migration was observed which rules out the acid-catalysed isomerisation of 1-butene. The butenes were also collected from the flow out by saturating a CDCl₃ solution and subjected to ¹H NMR analysis, which clearly showed the presence of both isomers. The double-bond migration is suggested to occur via π -allyl complexes (Eq. [7]) (4). The formation of π -allyl Pd(II) complexes may affect the kinetics of 1-butene oxidation (see the following discussion):

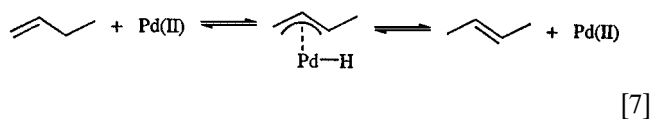


Table 1 shows the kinetic data for the oxidation of ethene, propene, and 1-butene with O₂. Most of these data are mean values of three or more parallel measurements. The results include the steady-state rates of absorption of olefins and O₂ as well as the initial rates of olefin absorption in the temperature range of 20–50°C and [Pd(II)] = 0.05–0.2 mM. The reactions were typically carried out until 1–2 V(V) turnovers (750–1500 Pd(II) turnovers). For comparison, the rate of stoichiometric oxidation of olefins by Pd(II)/HPA-3 in the absence of O₂ was measured. The measurement of olefin absorption was more accurate than that of O₂, hence the rates discussed here were typically obtained from the olefin absorption unless stated otherwise.

Figure 6 shows the time course for the stoichiometric oxidation of olefins by Pd(II)/HPA-3 in the absence of O₂. The absorption of olefins was calculated both from the combined GC and flow-rate measurements and from the flow-rate measurements only. Both methods gave practically the same results, which proves the accuracy of our methodology. The curves for ethene and propene fit well

TABLE 1

Kinetics of Oxidation of Gaseous Olefins by O₂/Pd(II)/HPA-3 System^a

Pd(II) (mM)	T (°C)	Reaction rate ^b (mmol/dm ³ min)					
		Ethene	O ₂	Propene	O ₂	1-Butene	O ₂
0.05	30	0.203	0.116	0.613	0.339	0.243	0.141
0.10	20	0.145	0.09	1.06	0.51		
0.10 ^c	20	0.16		1.17			
0.10	30	0.413	0.243	1.24	0.685	0.475	0.283
0.10 ^c	30	0.461		1.56		0.878	
0.10 ^{c,d}	30	0.632		1.58		0.929	
0.10	40	1.12	0.70	1.97	1.16	0.55	0.32
0.10 ^c	40	1.48		2.64		1.27	
0.10	50	2.07	1.26	3.16	1.74	0.622	0.36
0.10 ^c	50	2.73		3.56		1.47	
0.20	30	0.755	0.439	2.29	1.19	0.860	0.485

^a Reaction conditions: 50 mM HPA-3, [Pd(II)]/[Cl⁻] = 1 : 50 mol/mol, 4.0 cm³/min oxygen, 8.0 cm³/min olefin, 1200–1500-rpm stirring speed.

^b The rates measured by consumption of olefin and O₂ for a time on stream of 60–75 min.

^c Initial rate for the time onstream of 0–15 min.

^d Reaction in the absence of O₂: 50 mM HPA-3, [Pd(II)]/[Cl⁻] = 1 : 50 mol/mol, 4.0 cm³/min nitrogen, 8.0 cm³/min olefin.

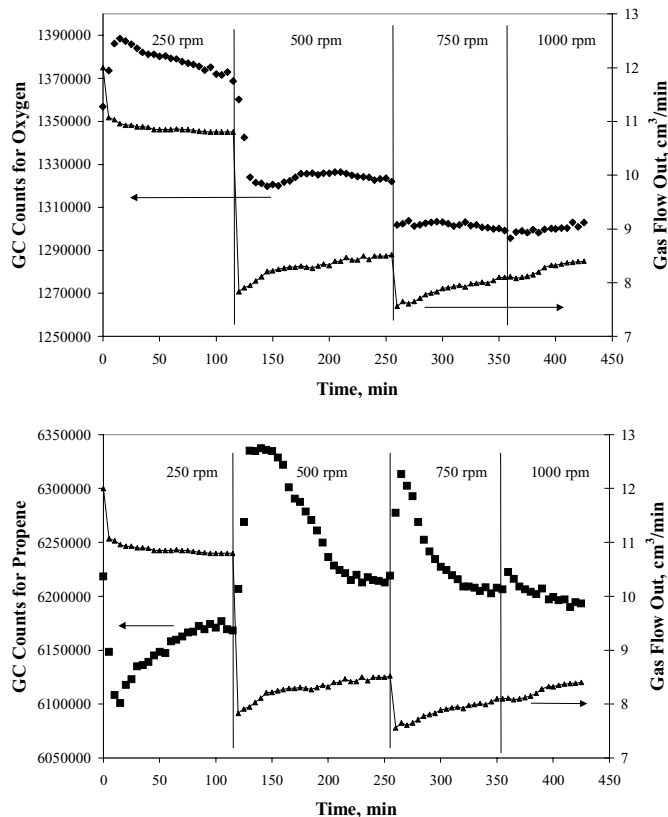


FIG. 5. Gas flow out and its oxygen (top) and propene (bottom) contents as a function of time and stirring speed. Reaction conditions: 50 mM HPA-3, 0.10 mM Pd(II), 5.0 mM Cl⁻, 50°C, 4.0 cm³/min oxygen, 8.0 cm³/min propene.

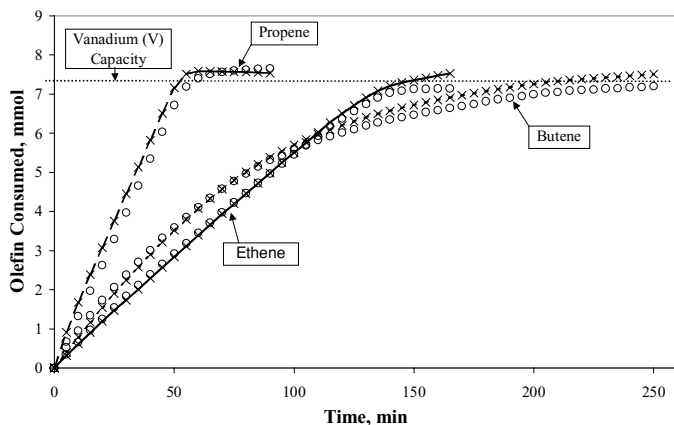


FIG. 6. Olefin consumption from GC and flow measurement (\times) and flow measurement only (\circ) as a function of time for the stoichiometric oxidation of olefins by Pd(II)/HPA-3 system. Reaction conditions: 50 mM HPA-3, 0.10 mM Pd(II), 5.0 mM Cl^- , 30°C, 1500-rpm stirring speed, 4.0 cm^3/min nitrogen, 8.0 cm^3/min olefin.

with zero-order kinetics in vanadium ($[\text{Pd(II)}] = \text{const}$) until almost complete reduction of vanadium(V) in HPA-3, as expected. Similar results were obtained for the oxidation of ethene by Pd(II)/HPA-3 by Grate *et al.* (10, 11). The oxidation of 1-butene follows a more complex course with a monotonous decrease of the reaction rate, although it reaches the complete conversion of V(V) to V(IV). The different behaviour of 1-butene may be explained by the isomerisation of 1-butene to less-reactive 2-butene and by the formation of relatively strong π -allyl Pd(II) complexes (Eq. [7]), which could decrease catalyst activity toward 1-butene oxidation.

The steady-state reactions of all the olefins are first-order in Pd(II) (Fig. 7). The reaction orders in olefin and O_2 were not measured here; Grate *et al.* (10, 11) found the order

to be first in both olefin and O_2 for the two-stage oxidation of ethene. The reactivity of olefins in the steady-state oxidation is found to be in the following order: ethene \leq 1-butene < propene; but the total range is only a factor of 3 at 30°C. The same order was obtained for the initial rates of stoichiometric oxidation by Pd(II)/HPA-3 (Table 1, Fig. 6). These rates are close to the steady-state rates of the corresponding catalytic reactions, although somewhat lower. The difference between the two rates is probably because part of palladium in the steady-state catalyst system is present as inactive Pd(0). The effect of olefin structure on the reaction rate is quite unexpected. For the stoichiometric oxidation with PdCl_4^{2-} at $[\text{Cl}^-] > 0.1 \text{ M}$ and 25°C, Henry (15) found a different order: ethene > propene > 1-butene; the total range was a factor of 6. This order is mainly governed by the steric hindrance of the olefin structure to the Pd(II) attack. In our system, Pd(II) mainly exists as PdCl_2 and PdCl_3^- (with $[\text{PdCl}_3^-]/[\text{PdCl}_2] = 1.3$ at 5 mM $[\text{Cl}^-]$) (10, 16). These Pd(II) species are more electrophilic than PdCl_4^{2-} and hence more reactive toward the more nucleophilic propene and 1-butene than toward ethene. Also at the low chloride concentrations, more than one olefin might bind to Pd(II) producing an unreactive Pd(II) species, which would happen more readily with ethene. It should be noted that in a chloride-free system, the highly electrophilic Pd^{2+} aqua-ion oxidises propene significantly faster than ethene, as found by Matveev *et al.* (17).

From the steady-state reaction rates of gaseous olefins in the temperature range of 20–50°C (Table 1) apparent activation energies E were calculated to be 71 ± 7 , 29 ± 4 , and 11 ± 4 kJ/mol for ethene, propene, and 1-butene, respectively. The corresponding E values estimated from the initial rates (before the steady state had been reached) are 76, 30, and 24 kJ/mol. The two values for ethene and propene are quite close and also similar to the activation energies 88 (18) and 44 kJ/mol (19) for the oxidation of ethene and propene in the Wacker system ($\text{PdCl}_2/\text{CuCl}_2$). The reason for the low activation energy for the steady-state oxidation of 1-butene is not clear. Diffusion control can be ruled out because of the high efficiency of mass transfer in the system. Apparently, the complexity of the system associated with the formation of the π -allyl Pd(II) complexes, as evidenced by the double-bond migration in 1-butene, could be the cause. If the enthalpies of solubility of the olefins were taken into account, the activation energies thus obtained would be higher (by ca. 20 kJ/mol). Unfortunately the solubilities of olefins in the catalysts solution are not available. Other contributions to the activation energies from a number of equilibria involved in the process, such as $\text{PdCl}_2 + \text{Cl}^- \rightleftharpoons \text{PdCl}_3^-$, olefin-Pd(II) π -complexes formation, etc., should be noted.

Another interesting result is that in the steady-state system the oxygen absorption rates are always slightly higher (by 4–25%) than those expected from the 1:2 O_2/olefin stoichiometry (Fig. 8). The surplus rate is in the order

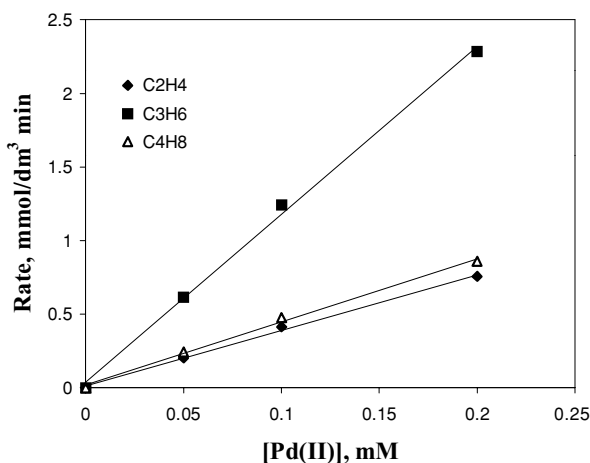


FIG. 7. Reaction rate versus Pd(II) concentration (50 mM HPA-3, 0.10 mM Pd(II), 5.0 mM Cl^- , 30°C, 4.0 cm^3/min oxygen, 8.0 cm^3/min olefin).

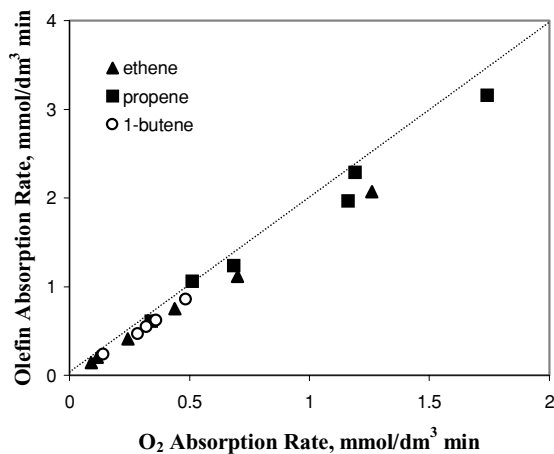


FIG. 8. Olefin absorption rate versus O₂ absorption rate (50 mM HPA-3, 0.10 mM Pd(II), 5.0 mM Cl⁻, 20–50°C, 4.0 cm³/min oxygen, 8.0 cm³/min olefin). The straight line corresponds to 2:1 stoichiometry.

ethene \geq 1-butene $>$ propene, which correlates with the oxidisibility of the corresponding products (acetaldehyde \geq MEK $>$ acetone). This may be explained by the co-oxidation of HPA-3 blue and the products by O₂, leading to overoxidation of products. Indeed, some acetic acid was found among the products by GC analysis. It was shown that the oxidation of HPA-*n* blues with a low average degree of reduction ($<1 e^-$ per Keggin anion) occurs through the formation of free radicals (HO \cdot) that can initiate the aerobic oxidation of organic compounds if they are present in the system (13, 20). Use of a flow reactor with continuous removal of the products could reduce their overoxidation.

CONCLUSIONS

The steady-state kinetics of the one-stage Wacker oxidation of gaseous olefins such as ethene, propene, and 1-butene by oxygen catalysed by the Pd(II)/HPA-3 redox system to form, respectively, acetaldehyde, acetone, and MEK in aqueous solution has been studied in a semicontinuous reactor by reacting a stoichiometric 1:2 mixture of O₂ and olefin at 20–50°C. The chosen catalyst composition matches Catalytica's system and involves Pd(II) chloride (0.05–2 mM Pd(II), [Pd(II)]/[Cl⁻] = 1:50) and Keggin-type heteropoly anions [PMo₉V₃O₄₀]⁶⁻ (50 mM) at pH 1.3. Under these conditions in a steady state, the reactivity of olefins increases in the following order: ethene \leq 1-butene $<$ propene; but the total range is only a factor of 3. The oxidation of ethene and propene occurs without any complication. The oxidation of 1-butene is accompanied by

double-bond migration to form 2-butene, apparently proceeding through relatively stable π -allyl Pd(II) complexes. This complicates the kinetics of 1-butene oxidation. Some overoxidation of reaction products takes place in the semi-continuous reactor. Use of a flow reactor with continuous removal of the products from the catalyst solution could reduce their overoxidation.

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