

Brief Communications

Kinetic isotope effects in oxidation reaction of C_2H_4 and C_2D_4 by *p*-benzoquinone in the Pd^{2+} — $HClO_4$ — CH_3CN — H_2O system

I. V. Martynov, G. E. Efremov, and O. N. Temkin*

Moscow Technological University, Institute of Fine Chemical Technology,
86 prosp. Vernadskogo, 119571 Moscow, Russian Federation.
E-mail: olegtemkin@mail.ru

Kinetic isotope effects (KIE) have been measured for oxidation reactions of ethylene by *p*-benzoquinone in Pd^{2+} — $MeCN$ — H_2O — $HClO_4$ system. Under the conditions of preferred formation of complex $Pd(MeCN)(H_2O)_3^{2+}$ the ratio between the initial reaction rates $R^0_{C_2H_4}/R^0_{C_2D_4}$ is equal to 1.14 ± 0.06 and is close to the KIE for classical chloride systems. Based on the obtained results and previous data for C_2H_4 — C_2D_4 and H_2O — D_2O (0.97 ± 0.12) systems, the slow step was proposed in the reaction mechanism — a *trans*-addition of water molecule to the cationic π -complex $LPd(H_2O)_2(CH_2CH_2)^{2+}$ with formation of metalcarbenium ion solvated by water molecule ($LPd(H_2O)_2(CH_2CH_2O^+H_2)^+$).

Key words: oxidation of olefins, cationic palladium complexes, kinetic isotope effect.

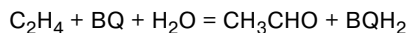
Cationic complexes and π -complexes of Pd^{II} are of high interest for scientists due to their activity and increased reactivity towards nucleophiles in dimerization, oxidative amidation, oxidation, and polymerization reactions.¹ The study of cyclohexene oxidation reaction in Pd^{2+} — $HClO_4$ — CH_3CN — H_2O system by *p*-benzoquinone (BQ)² disclosed specific features for mechanism and kinetic model of this reaction. It was shown,³ for example, that kinetic isotope effect (KIE) (H_2O/D_2O) for cyclohexene and ethylene oxidation reactions is close to one in case of this system, in contrast with $KIE = 4$ for ethylene oxidation reaction in classical chloride system.⁴ It was also found, that the initial rate of cyclohexene oxidation in this system increases with increasing acid concentration up to 0.2 mol L^{-1} and is almost independent from

$[H^+]$ for interval of $HClO_4$ concentrations between 0.2 and 1.0 mol L^{-1} at the constant ionic strength $[LiClO_4] + [HClO_4] = 1.0 \text{ mol L}^{-1}$, and is also having a weak maximum for [BQ]. In contrast with ethylene oxidation kinetics, the independence from $[H^+]$ was observed for cyclohexene oxidation also in chloride systems.⁵

The KIE for C_2H_4/C_2D_4 pair have been measured to gain additional information about the mechanism of the process in cationic palladium complexes solutions.

Experimental

The ethylene oxidation was carried out according to the reaction



in the $\text{Pd}(\text{OAc})_2$ ($0.0005 \text{ mol L}^{-1}$)— HClO_4 (0.2 mol L^{-1})—BQ (0.2 mol L^{-1})—MeCN— H_2O system under conditions of cationic palladium(II) complexes existence.⁶ The molar fraction of water was $\alpha = 0.66$; the ionic strength was kept constant $I = 0.5$ ($[\text{HClO}_4] + [\text{LiClO}_4] = 0.5 \text{ mol L}^{-1}$). Commercial acetonitrile ("SuperGradient LabScan") and C_2D_4 (grade A from FSUE RSC "Applied chemistry", containing 99% C_2D_4 , USSR standard 25070-87) were used. The catalytic system was prepared in three steps.⁶ Initial solution $\text{Pd}_3(\text{OAc})_6$ —MeCN ($[\text{Pd}(\text{OAc})_2] = 0.005 \text{ mol L}^{-1}$) kept for 7 days. Before an experiment the solution CH_3CN (5 mL)— H_2O (4 mL)— LiClO_4 (0.3190 g)—BQ (0.2160 g) was prepared inside the reactor and the reactor was blown through ethylene (deuteroethylene). Then perchloric acid (0.182 mL of 70%) was added to 1 mL of the prepared before $\text{Pd}_3(\text{OAc})_6$ —MeCN solution, this mixture was stored for 20 min and injected into the reactor by syringe; the time counting was started. The catalytic system composition was $\text{Pd}(\text{OAc})_2$ ($0.0005 \text{ mol L}^{-1}$)— HClO_4 (0.2 mol L^{-1})—BQ (0.2 mol L^{-1})— LiClO_4 —(0.3 mol L^{-1})—MeCN— H_2O (the molar fraction of water in the solution was $\alpha = 0.66$).

The reaction kinetic was studied in a closed volumetric installation under the constant partial pressure of ethylene and temperature 30°C . The ethylene and deuteroethylene contents in gas phase was at least 95% (measured by chromatography).³

Results and Discussion

The kinetic curves (Fig. 1) have two parts for the studied C_2H_4 system, as also for cyclohexene oxidation reaction,² which is probably related with formation of catalyzing the process quinone Pd^{I} complexes and quinone Pd^0 complexes.^{2,3}

The initial rates of oxidation reaction (R_0) decrease slightly from C_2H_4 to C_2D_4 (Table 1), and the KIE is 1.14 ± 0.06 .

This result and previously obtained values $\text{KIE} \approx 1$ for $\text{H}_2\text{O}/\text{D}_2\text{O}$ pair allow to propose that in the solution of $\text{Pd}(\text{H}_2\text{O})_x(\text{L})_{4-x}(\text{L}-\text{MeCN})$ complexes (under conditions of preferred formation of complexes with $x = 3$ and molar fraction of water $\alpha = 0.66$ in acetonitrile—water solvent composition) the *anti*-addition of water from the solution to the cationic π -complex of Pd^{2+} with formation of solvated by water metalcarbenium cation $\text{LPd}(\text{H}_2\text{O})_2(\text{CH}_2\text{CH}_2\text{O}^+\text{H}_2)^+$ takes place. This step is a slow one. Then a fast redox decomposition of the obtained intermediate results in formation of acetaldehyde and Pd^0 complexes.

Therefore, we have found that the experimental extreme dependence of the initial rate for ethylene oxidation from $[\text{BQ}]_0$ concentration is the result of $\text{Pd}(\text{BQ})^0$ and $\text{Pd}(\text{BQ})_2^0$ complexes participation in palladium complexes composition and a possible presence of an additional slow

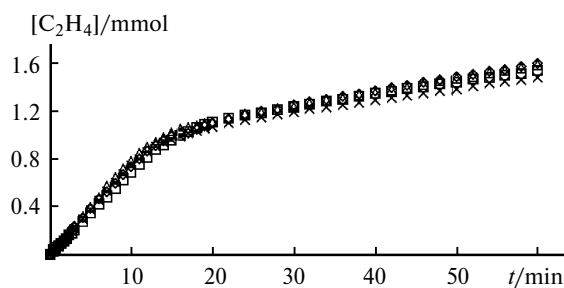


Fig. 1. Dependence of amount of consumed ethylene from time for five experiments.

Table 1. Initial rates of oxidation reaction (R_0) C_2H_4 and C_2D_4

Entry	$R_0 \cdot 10^2 / \text{mol L}^{-1} \text{ min}^{-1}$		$R_{\text{H}}/R_{\text{D}}$
	C_2H_4	C_2D_4	
1	6.37	5.57	1.14
2	6.42	5.41	1.18
3	6.33	5.18	1.22
4	6.20	5.60	1.11
5	6.30	5.80	1.08

step of quinone palladium(0) complexes oxidation. The kinetic model of ethylene oxidation will be published later.

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References

- O. N. Temkin, *Kinet. Catal. (Engl. Transl.)*, 2014, **55**, 181–220.
- O. N. Temkin, L. G. Bruk, D. S. Zakharova, K. Yu. Odintsov, E. A. Katsman, I. V. Petrov, O. Yu. Istomina, *Kinet. Catal. (Engl. Transl.)*, 2010, **51**, 1.
- D. S. Zakharova, O. A. Chertkova, A. A. Chelkin, L. G. Bruk, O. N. Temkin, *Russ. Chem. Bull. (Int. Ed.)*, 2013, **62**, 844.
- I. I. Moiseev, M. N. Vargaftik, Ya. K. Syrkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1963, **12**, 144.
- M. N. Vargaftik, I. I. Moiseev, Ya. K. Syrkin, *Dokl. Chem. (Engl. Transl.)*, 1961, **139**, 3196.
- D. S. Zakharova, I. V. Martynov, V. M. Nosova, O. N. Temkin, *Fine Chemical Technologies*, 2016, **11**, 57.

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