

MECHANISM OF THE OXIDATION OF STYRENE BY PALLADIUM SALTS

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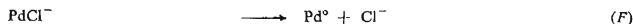
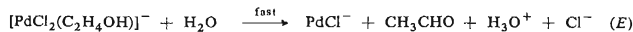
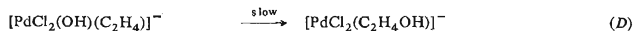
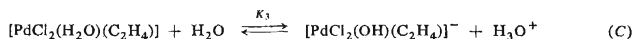
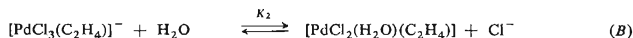
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The oxidation of styrene by palladium salts in excess of HCl has been investigated in homogeneous phase, using methanol as solvent. The degree of styrene conversion was followed polarographically. It was found that the reaction rate can be expressed by the rate equation corresponding to the transformation of a mononuclear complex with styrene coordinated to PdCl_4^{2-} , the kinetic term of which has the following form: $w = k_1[\text{styrene}][\text{PdCl}_4^{2-}]/[\text{H}_3\text{O}^+][\text{Cl}^-]^2$.

The oxidation mechanism of 1-alkenes by palladium salts has been the subject of intense research interest for long time, especially due to the industrial importance of this reaction. Most of the studies deal with mechanism of the oxidation of lower (gaseous) 1-alkenes, especially of ethylene, while the oxidation of higher (C_6 — C_{15}) 1-alkenes attracts less attention. Despite of a number of reports, interpretation of the mechanism of this oxidation is still controversial.

Thus it is stated^{1,2} that the mechanism of ethylene oxidation involves steps (A)—(F), with step (D) as rate determining. The overall reaction rate is then expressed by



Eq. (J), where k_{eff} includes the equilibrium constants of the fast established equilibrium steps (A) to (C):

$$w = k_{\text{eff}}[\text{C}_2\text{H}_4][\text{PdCl}_4^{2-}]/[\text{H}_3\text{O}^+][\text{Cl}^-]^2 \quad (\text{J})$$

On the other hand, some authors suppose³⁻⁵ that at higher alkene concentrations (0.04 to 0.02 mol/l), the reaction rate should be described better by relation (2) where the second term corresponds to the rearrangement of the binuclear palladiumalkene complex. According to this

assumption Eq. (1) is only a

$$w = k_1[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]/[\text{H}_3\text{O}^+][\text{Cl}^-]^2 + k_2[\text{PdCl}_4^{2-}]^2[\text{C}_2\text{H}_4]/[\text{H}_3\text{O}^+][\text{Cl}^-]^3 \quad (2)$$

specific case of the more general relation (2).

In the study of the oxidation of higher alkenes, the exact measurement of the oxidation is complicated by simultaneous isomerization of the starting 1-alkene as palladium salts catalyze also double bond migration. For that reason the oxidation of styrene, which hydrocarbon cannot be isomerized is more convenient for such a study.

The oxidation of styrene by palladium salts has been studied by only a few number of authors. Thus, it is reported^{6,7} that the rate of styrene oxidation measured potentiometrically at Pd^{2+} concentrations of 0.02 to 0.2 mol dm⁻³ can be expressed by the first order equation, it raises with increasing PdCl_4^{2-} concentration and becomes more complicated. The relationship between the second order rate equation and the concentration of H_3O^+ and Cl^- ions was described by Eq. (3). According to Eq. (1), the oxidation rate of styrene substituted on the

$$k_2 = 1/(a[\text{H}_3\text{O}^+][\text{Cl}^-] + b[\text{Cl}^-]^3) \quad (3)$$

benzene ring can be expressed by the second order rate equation.

In the present work we used styrene as the model compound for determining the oxidation rate of higher 1-alkenes by palladium salts with the aim to examine the role of mononuclear and binuclear palladium complexes in aqueous solution, which problem was examined in our previous papers by different methods⁸⁻¹⁰.

EXPERIMENTAL

Chemicals used. Styrene, redistilled b.p. 33.5°C/1.33 kPa; n_D^{20} 1.5467, d_4^{20} 0.9074, methanol, NH_4OH , HCl , Hg for polarography, gelatine and methoxyethanol were all of the analytical purity grade; PdCl_2 — 40% solution (Safina, Vestec near Prague).

Apparatus and analytical methods used. Kinetic measurements were carried out in a discontinual isothermal reactor of the shape of sealed ampoules placed in a rotating stand. These were immersed into a thermostated bath, the temperature of which was kept constant within $\pm 0.1^\circ\text{C}$. The reaction was stopped by flashing the contents to 0°C . The initial palladium and HCl concentrations were determined by potentiometric titration using palladium electrode (the reference electrode was s.c.e.); KJ or NaOH were used as titrating agents.

Kinetics of the oxidation of styrene by palladium salts was followed on the basis of Pd(II) ions consumption which was determined polarographically¹¹ using ammonia buffer. Under these condition, Pd determined as $\text{Pd}(\text{NH}_3)_4^+$ ions showed the half wave potential $E_{1/2}^0 = -0.72 \text{ V}$. The measurements were made on a LP 60 instrument (Laboratorní přístroje, Prague).

RESULTS

The measurements were performed at a temperature of 75°C . This temperature was chosen on the basis of preliminary experiments. PdCl_2 and styrene were always used in the 1 : 1 molar ratio. Methanol was used as the solvent since it homogenized the

reaction medium and was also inert to the reactants under given reaction conditions. The initial concentrations of individual components were as follows: 0.075M-PdCl₂, 0.075M styrene, 0.225M-HCl, 15M-H₂O, the residue was methanol. The PdCl₂ : HCl : H₂O mol. ratio was 1 : 3 : 200. The results of 5 independent measurements are summarized in Table I.

Further measurements were made by using PdCl₂ : HCl : H₂O mol. ratio = 1 : 4 : 100. The H₂O to PdCl₂ ratio was decreased due to the fact that at PdCl₂ : H₂O mol. ratio = 1 : 200 the reaction mixture contained two phases. The initial concentrations the following: 0.075M-PdCl₂, 0.075M styrene, 0.3M-HCl, 7.5M-H₂O,

TABLE I
Time Dependence of Pd(II) Conversion at 75°C for PdCl₂ : HCl : H₂O Molar Ratio = 1 : 3 : 200

<i>t</i> , min	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₄	<i>x</i> ₅	\bar{x}
10	0.360	0.360	0.385	0.381	0.365	0.370
20	0.462	0.378	0.458	0.460	0.469	0.465
30	0.499	0.505	0.495	0.525	0.518	0.508
45	0.572	0.577	0.585	0.580	0.571	0.577
60	0.628	0.623	0.607	0.615	0.620	0.619
120	0.395	0.704	0.711	0.700	0.690	0.700
180	0.747	0.762	0.752	0.763	0.763	0.757
240	0.785	0.791	0.785	0.785	0.780	0.785
300	0.815	0.799	0.801	0.811	0.820	0.809

TABLE II
Time Dependence of Pd(II) Conversion at 75°C for PdCl₂ : HCl : H₂O Molar Ratio = 1 : 4 : 100

<i>t</i> , min	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	\bar{x}
10	0.059	0.059	0.062	0.060
20	0.116	0.124	0.125	0.122
30	0.169	0.177	0.173	0.173
45	0.204	0.216	0.222	0.214
60	0.267	0.251	0.258	0.259
120	0.359	0.352	0.347	0.353
180	0.418	0.418	0.420	0.419
240	0.467	0.461	0.463	0.464
300	0.486	0.489	0.490	0.488

the residue was methanol. The results obtained by 3 independent measurements are presented in Table II.

Analogous measurements were made also by using the components in the molar ratio $\text{PdCl}_2 : \text{HCl} : \text{H}_2\text{O} = 1 : 5 : 100$. The initial concentration in the solution before oxidation was the same as in the preceding cases except that HCl concentration was increased to $0.375 \text{ mol/dm}^{-3}$. The results of 3 independent measurements are presented in Table III.

DISCUSSION

As already mentioned, we examined in the present work kinetics of the styrene oxidation with palladium chloride and with $[\text{PdCl}_2]_4^-$ to get a deeper insight into the mechanism of this oxidation in the case of higher 1-alkenes. Compared to the so far reported measurements of this oxidation kinetics, the principal change in this work is the use of the method of conversion curves. In previous works hydroquinone was used as the reoxidant, the overall concentration of chloride and hydrogen ions being thus constant in the course of the oxidation. In our case, the concentration of PdCl_4^{2-} ions decreases during the reaction and the concentration of both chloride and hydrogen ions increases proportionally as the result of formation of metallic palladium. Both ions exhibit rate-retarding effect⁷⁻⁹ on the velocity of the reaction. Thus, their formation can be utilized — *via* comparison of theoretical with experimental conversion curves — in proving or disproving the ideas about mechanism of this oxidation reaction.

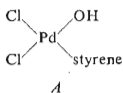
The approach used to derive the corresponding kinetic equations can be illustrated on the validity of the rate determining equation (I). In this case, we assumed that

TABLE III

Time Dependence of Pd(II) Conversion at 75°C for $\text{PdCl}_2 : \text{HCl} : \text{H}_2\text{O}$ Molar Ratio = 1 : 5 : 100

t, min	x_1	x_2	x_3	\bar{x}
10	0.035	0.020	0.038	0.031
20	0.055	0.051	0.061	0.056
30	0.094	0.067	0.082	0.081
45	0.120	0.119	0.105	0.115
60	0.139	0.144	0.137	0.140
120	0.239	0.235	0.219	0.231
180	0.275	0.314	0.290	0.293
240	0.337	0.330	0.341	0.336
300	0.376	0.373	0.378	0.376

equilibrium steps (A), (B) and (C) are fast compared to the rate determining step (D). In such a case, the rate determining step is the decomposition of the mononuclear complex A, provided



that the equilibrium constants of the equations (A)–(C) are shifted to the left and the initial concentrations are the following: $\text{PdCl}_4^{2-} = c_p^0$, styrene = $c_s^0 = c_p^0$, chlorides = $c_{\text{Cl}}^0 = c_p^0$, hydrogen ions = $c_{\text{H}}^0 = 3c_p^0$.

In time t , when the degree of palladium conversion will be x , the concentrations of the above compounds will be as follows: palladium: $c_p^t = c_p^0(1 - x)$, styrene: $c_s^t = c_p^0(1 - x)$, chlorides: $c_{\text{Cl}}^t = c_p^0(1 + 4x)$, hydrogen ions: $c_{\text{H}}^t = c_p^0(3 + 2x)$. After introducing these expressions into Eq. (1) we obtain Eq. (4), the modification of which yields Eq. (5) which after integration acquires the form (6).

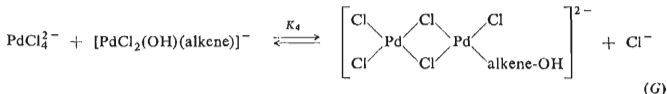
$$w = c_p^0 \cdot dx/dt = [k_1 \cdot c_p^0(1 - x) c_p^0(1 - x)] [c_p^{02}(1 + 4x)^2 \cdot c_p^0(3 + 2x)]^{-1} \quad (4)$$

$$dx/dt = k_1 c_p^{0-2} [(1 - x)^2] [(3 + 2x)(1 + 4x)^2]^{-1} \quad (5)$$

$$k_1 (c_p^0)^{-2} = t^{-1} (16x^2 + 128x + 125 \frac{x}{1 - x} - 250 \ln(1/1 - x)). \quad (6)$$

Further equations for the mononuclear mechanism were derived analogously and that for the case where the equilibrium constant of Eq. (A) is shifted to the right, the other two to the left, etc., until the equilibrium constants of the reactions (A)–(C) are all shifted to the right. The resulting integrated kinetic equations are listed in Table IV.

Because the binuclear complexes prevail³⁻⁵ over the mononuclear ones, at alkene concentrations higher than 0.04, we derived also the rate equations for the binuclear mechanism. In this case the first three equations are identical with the previous case (Eqs (A)–(C) for the mononuclear mechanism); the reaction mechanism involves, however, one additional step (G).



The example of the derivation of kinetic equations for the binuclear mechanism is the case where the equilibrium constants of Eqs (A)–(C) and (G) are shifted

TABLE IV
Differential and Integrated Kinetic Equations for "Mononuclear" Mechanism
For conditions see Table I.

Designation	Differential kinetic equation	Integrated kinetic equation	Note
I0	$\frac{dx}{dt} = k_1 \frac{C_P^{0.2}(1-x)^2}{C_P^{0.4}(4+x)(3+2x)^2}$	$\frac{k_1}{C_P^{0.2}} = \frac{1}{t} \left(2x^2 + 42x + 155 \frac{x}{1-x} - 161 \ln \frac{1}{1-x} \right)$	equilibrium constants of Eqs (1)–(3) shifted to the right
I1	$\frac{dx}{dt} = k_1 \frac{C_P^{0.2}(1-x)^2}{C_P^{0.4}(3+2x)^3}$	$\frac{k_1}{C_P^{0.2}} = \frac{1}{t} \left(8x^2 + 64x + 155 \frac{x}{1-x} - 192 \ln \frac{1}{1-x} \right)$	equilibrium constants of Eqs (1) and (2) shifted to the right, Eq. (3) shifted to the left
I2	$\frac{dx}{dt} = k_1 \frac{C_P^{0.2}(1-x)^2}{C_P^{0.4}(3+2x)(2+3x)^2}$	$\frac{k_1}{C_P^{0.2}} = \frac{1}{t} \left(9x^2 + 87x + 125 \frac{x}{1-x} - 200 \ln \frac{1}{1-x} \right)$	equilibrium constant of Eq. (1) shifted to the right, that of Eqs (2) and (3) shifted to the left
I3 = 6	$\frac{dx}{dt} = k_1 \frac{C_P^{0.2}(1-x)^2}{C_P^{0.4}(3+2x)(1+4x)^2}$	$\frac{k_1}{C_P^{0.2}} = \frac{1}{t} \left(16x^2 + 128x + 125 \frac{x}{1-x} - 250 \ln \frac{1}{1-x} \right)$	equilibrium constants of Eqs (1), (2) and (3) shifted to the left

TABLE V

Differential and Integrated Kinetic Equation
For conditions see Table I.

Designation	Differential kinetic equation	Integrated kinetic equation	Note
14	$\frac{dx}{dt} = k_{11} \frac{C_p^3(1-x)^3}{C_p^0(4+x)^4}$	$\frac{k_{11}}{C_p^0} = \frac{1}{t} \left(-\frac{x^2}{2} - 19x + 312.5 \frac{x(2-x)}{(1-x)^2} - 500 \frac{x}{1-x} + 150 \ln \frac{1}{1-x} \right)$	equilibrium constants of Eqs (1)–(3) and (13) shifted to the right
15	$\frac{dx}{dt} = k_{11} \frac{C_p^3(1-x)^3}{C_p^0(4+x)(3+2x)^2}$	$\frac{k_{11}}{C_p^0} = \frac{1}{t} \left(-4x^2 - 92x + 312.5 \frac{x(2-x)}{(1-x)^2} - 875 \frac{x}{1-x} + 350 \ln \frac{1}{1-x} \right)$	equilibrium constants of Eqs (1)–(3) shifted to the right, that of Eq. (13) shifted to the left
16	$\frac{dx}{dt} = k_{11} \frac{C_p^3(1-x)^3}{C_p^0(3+2x)^4}$	$\frac{k_{11}}{C_p^0} = \frac{1}{t} \left(-8x^2 - 144x + 312.5 \frac{x(2-x)}{(1-x)^2} - 1000 \frac{x}{1-x} + 625 \ln \frac{1}{x-1} \right)$	equilibrium constants of Eqs (1) and (2) shifted to the right, the constants of Eqs (3) and (13) to the left
17	$\frac{dx}{dt} = k_{11} \frac{C_p^3(1-x)^3}{C_p^0(3+2x)(2+3x)^3}$	$\frac{k_{11}}{C_p^0} = \frac{1}{t} \left(-27x^2 - 351x + 312.5 \frac{x(2-x)}{(1-x)^2} - 1375 \frac{x}{1-x} + 1125 \ln \frac{1}{x-1} \right)$	equilibrium constant of Eq. (1) shifted to the right, the constants of Eqs (2), (3) and (13) shifted to the left
18	$\frac{dx}{dt} = k_{11} \frac{C_p^3(1-x)^3}{C_p^0(3+2x)(1+4x)^3}$	$\frac{k_{11}}{C_p^0} = \frac{1}{t} \left(-64x^2 - 672x + 312.5 \frac{x(2-x)}{(1-x)^2} - 1750 \frac{x}{1-x} + 1800 \ln \frac{1}{1-x} \right)$	equilibrium constants of Eqs (1)–(3) and (13) shifted to the left

TABLE VI
 Differential and Integrated Kinetic Equations for "Mononuclear" and "Binuclear" Mechanism
 For conditions see Table II and III.

Designation	Differential kinetic equation	Integrated kinetic equation
19	$\frac{dx}{dt} = \frac{k_1 C_P^{0^2} (1-x)^2}{C_P^0 (4+2x)(2+4x)^2}$	$\frac{k_1}{C_P^{0^2}} = \frac{1}{t} \left(16x^2 + 160x + 216 \frac{x}{1-x} - 360 \ln \frac{1}{1-x} \right)$
20	$\frac{dx}{dt} = \frac{k_1 C^{0^2} (1-x)^2}{C_P^0 (5+2x)(3+4x)^2}$	$\frac{k_1}{C_P^{0^2}} = \frac{1}{t} \left(16x^2 + 192x + 319 \frac{x}{1-x} - 466 \ln \frac{1}{1-x} \right)$
21	$\frac{dx}{dt} = k_{II} \frac{C_P^{0^3} (1-x)^3}{C_P^0 (4+2x)(2+4x)^3}$	$\frac{k_{II}}{C_P^{0^2}} = \frac{1}{t} \left(-4x^2 - 112x + 1196 \frac{x(2-x)}{(1-x)^2} - 1512 \frac{x}{1-x} + 648 \ln \frac{1}{1-x} \right)$
22	$\frac{dx}{dt} = k_{II} \frac{C_P^{0^3} (1-x)^3}{C_P^0 (5+2x)(3+4x)^3}$	$\frac{k_{II}}{C_P^{0^2}} = \frac{1}{t} \left(-64x^2 - 992x + 2401 \frac{x(2-x)}{(1-x)^2} - 4802 \frac{x}{1-x} + 3528 \ln \frac{1}{1-x} \right)$

to the left. In time $t = 0$, the initial concentrations of the substances are following: $\text{PdCl}_4^{2-} = c_p^0$, styrene $= c_s^0 = c_p^0$, free chlorides $c_{Cl}^0 = c_p^0$, hydrogen ions $c_H^0 = 3c_p^0$. In time t the actual concentrations are the following: $\text{PdCl}_4^{2-} : c_p^t = c_p^0(1-x)$, styrene: $c_s^t = c_p^0(1-x)$, chlorides: $c_{Cl}^t = c_p^0(1+4x)$, hydrogen ions: $c_H^t = c_p^0(3+2x)$.

After introducing the second term of Eq. (2) we obtain relation (7) which can be transformed to Eq. (8) which after integration yields Eq. (9).

$$w = c_p^0 \cdot dx/dt = k_{11}[c_p^{0^2}(1-x)^2 c_p^0(1-x)] [c_p^0(3+2x)(c_p^0)^3(1+4x)^3]^{-1} \quad (7)$$

$$dx/dt = k_{11}[(c_p^0)^{-2}(1-x)^3] [(3+2x)(1+4x)^3]^{-1} \quad (8)$$

$$k(c_p^0)^{-2} = t^{-1} \left(-64x^2 - 627x + 312.5 \frac{x(2-x)}{(1-x)^2} - 1750 \frac{x}{1-x} 1800 \ln + \frac{1}{1-x} \right) \quad (9)$$

Further possible types of kinetic equations for the binuclear mechanism were derived analogously. It was assumed that the equilibrium constants of Eqs (A)–(C) and (G) are successively shifted to the right until all the equilibrium constants of the reaction mechanism are shifted to the right hand side. The equations in integrated form are presented in Table V.

The integrated relations (10)–(18) were used to calculate the rate constants $k_1/(c_p^0)^2$ or $k_{11}/(c_p^0)^2$ for individual mechanisms from experimental data. The values of these constants in dependence on the conversion of styrene are represented graphically in Fig. 1 for the mononuclear mechanism and in Fig. 2 for the binuclear one. From Figs 1 and 2 it becomes evident that the values of $k_1/(c_p^0)^2$ and of $k_{11}/(c_p^0)^2$ remain constant for Eq. (13) (identical with Eq. (6)), which corresponds to the transformation of the mononuclear palladium complex during which all the preceding equilibrium steps are shifted to the left.

With respect to the fact that in aqueous solution there exist only mononuclear palladium complexes^{8,9}, the most likely seems to be the mechanism described by the rate equation (13).

Therefore we measured further the oxidation rate of styrene with PdCl_4^{2-} , in which case we increased the initial HCl concentration and determined the rate equations with the corresponding initial composition. For data given in Table II we calculated Eqs (19), (20) and (21), (22), the differential and integrated forms of which are presented in Table VI. Eqs (19) and (21) are rate equations of the type (13) and (18) for data from Table III. From Eqs (19), (20) and Eqs (21), (22) we calculated the rate constants summarized in Fig. 3. From their values it follows that also for another $\text{PdCl}_2 : \text{HCl}$ ratio the reaction course according to the mononuclear



mechanism is more likely compared to the binuclear one. Even the ratio of the apparent rate constants to the initial palladium concentration, $k_1/(c_p^0)^2$ (excess 4M-HCl and excess 5M-HCl with respect to PdCl_2 in the initial composition of the solution) has in both cases the practically identical absolute values which could indicate that in such solutions also the equilibrium constants have constant values.

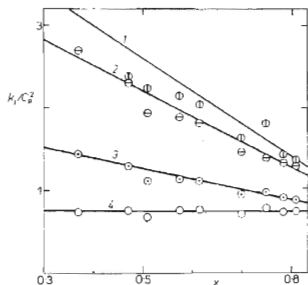


FIG. 1

Values of Apparent Rate Constants for "Mononuclear" Mechanism Calculated from Data Presented in Table I

1 Eq. (10), 2 Eq. (11), 3 Eq. (12), 4 Eq. (13).

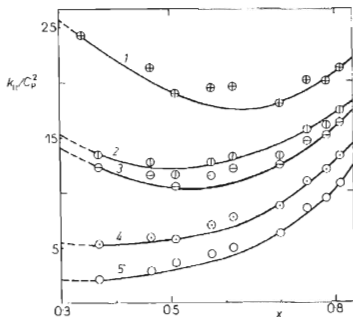


FIG. 2

Values of Apparent Rate Constants for "Binuclear" Mechanism Calculated from Data Summarized in Table I

1 Eq. (14), 2 Eq. (15), 3 Eq. (16), 4 Eq. (17), 5 Eq. (18).

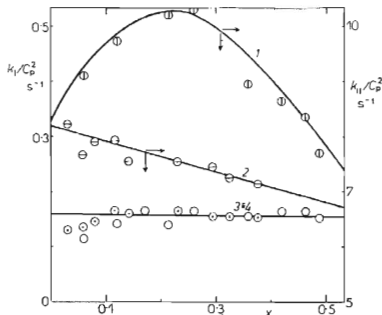


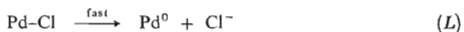
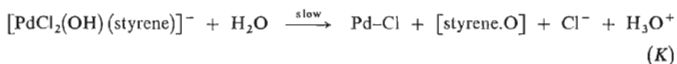
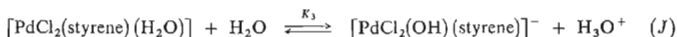
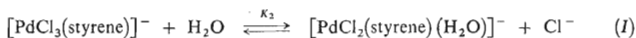
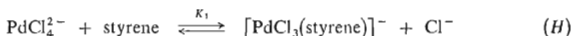
FIG. 3

Values of Apparent Rate Constants for "Mononuclear" and "Binuclear" Mechanism Calculated from Data Listed in Tables II and III

1 Eq. (21), 2 Eq. (22), 3 Eq. (19), 4 Eq. (20).

It could be deduced from experimental data that the most probable reaction mechanism of the oxidation of styrene involves steps (H)–(L), the constants $K_1 - K_3$ being smaller than 1. The rate of the oxidation is controlled by Eq. (23), where $k_1 = K_1 K_2 K_3 k$

$$w = k_2 [\text{PdCl}_4^{2-}] [\text{styrene}] ([\text{H}_3\text{O}^+] [\text{Cl}^-]^2)^{-1} \quad (23)$$



Note: $[\text{styrene.O}] = \text{acetophenone and phenylacetaldehyde}$.

The rate equation just mentioned should describe also the oxidation of higher alkenes with PdCl_4^{2-} , although in these cases the description of the reaction rate is complicated by simultaneous double bond isomerization.

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