

0.69,<sup>17</sup> Care was taken to match the optical density of the sample and the standard under the conditions of the measurement.

**Luminescence Lifetimes.** Emission lifetimes were measured using a TRW Model 75A decay time fluorometer equipped with a Xenon Corp. Model 437 Nanopulser exciting source. Appropriate filters were used on both the exciting and emission side to minimize scattered light from the excitation pulse. The RCA 931A photomultiplier tube (PMT) was powered by a Kepco Model ABC 2500 regulated high voltage power supply. The output of the PMT was monitored with a Tektronix 453 oscilloscope and recorded with a Polaroid camera. Plots of log (luminescence intensity) against time were linear in each case. Lifetimes at 298°K determined in degassed solution were difficult to obtain due to the weak emission intensity, spectral position, and the relatively long excitation pulse duration.

**Quenching of ClRe(CO)<sub>3</sub>X Luminescence.** Solutions (in 13 ×

100 mm test tubes) of the ClRe(CO)<sub>3</sub>X and the quencher (anthracene or *trans*-stilbene) were degassed by at least three freeze-pump-thaw cycles and the relative luminescence quantum yields determined using the Aminco-Bowman emission spectrophotometer. To determine the quantum yields for the ClRe(CO)<sub>3</sub>X sensitized *trans* → *cis*-stilbene reaction the samples were prepared such that all of the ClRe(CO)<sub>3</sub>X luminescence was quenched. The tubes were irradiated in parallel with actinometry tubes containing benzophenone (0.05 M) and *trans*-stilbene (~0.05 M) using a merry-go-round<sup>21</sup> equipped with a 550-W Hanovia lamp filtered with Corning filter no. 7-83 to isolate the 366-nm region of the Hg lamp output.

**Acknowledgment.** We thank the National Science Foundation for support of this research.

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## Kinetics of Olefin Oxidation by Tetrachloropalladate in Aqueous Solution

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Contribution from the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, Moscow, USSR. Received June 4, 1973

**Abstract:** Different possible forms of the kinetic equation for the reaction between PdCl<sub>4</sub><sup>2-</sup> and olefin in aqueous solution were analyzed. It was concluded that over a wide range of temperature, ionic strength, and concentrations of PdCl<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and H<sub>3</sub>O<sup>+</sup> the kinetics of olefin oxidation are described by a two-term equation (including a quadratic term in [PdCl<sub>4</sub><sup>2-</sup>]) rather than by a one-term equation, the latter being valid only for low Pd(II) concentration. The validity of the two-term equation extends over a wide range of variation of numerical values of the equilibrium constants of the π-complex formation used in calculations of the reaction rates. A comparison of the rates of ethylene oxidation in solutions of identical initial composition observed by the authors and by Henry leads to the conclusion that diffusion limitation seems to be appreciable in Henry's studies of the gaseous ethylene uptake by PdCl<sub>4</sub><sup>2-</sup> solutions.

The kinetics of olefin oxidation by palladium chloride in aqueous solutions have been studied by a number of authors.<sup>1-3</sup> It has been shown in our laboratory<sup>6,7</sup> that the rate of reaction between PdCl<sub>4</sub><sup>2-</sup> and olefin in solution obeys the equation

$$w = k_{\text{I}} \frac{[\text{PdCl}_4^{2-}][\text{C}_n\text{H}_{2n}]}{[\text{Cl}^-]^2[\text{H}_3\text{O}^+]} + k_{\text{II}} \frac{[\text{PdCl}_4^{2-}]^2[\text{C}_n\text{H}_{2n}]}{[\text{Cl}^-]^3[\text{H}_3\text{O}^+]} \quad (1)$$

The kinetic data related to the range of concentration of Pd(II) (0.01–0.2 M), temperature (25°), and ionic strength (3 M) have shown<sup>6</sup> that initial data are described better by eq 1 than by eq 2

$$W = k \frac{[\text{PdCl}_4^{2-}][\text{C}_n\text{H}_{2n}]}{[\text{Cl}^-]^2[\text{H}_3\text{O}^+]} \quad (2)$$

The difference between eq 1 and more complicated equations is (as it follows from the regression analysis)

(1) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1144, 1147 (1963).

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(3) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964).

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(6) I. I. Moiseev, M. N. Vargaftik, S. V. Pestrikov, O. G. Levanda, T. N. Romanova, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **171**, 1365 (1966).

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within the scattering of kinetic experimental data (10–15%).

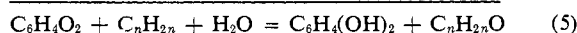
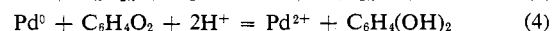
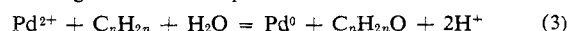
We report in this paper the kinetic data confirming the validity of eq 1 at all values of Pd(II), Cl<sup>-</sup>, and H<sub>3</sub>O<sup>+</sup> concentrations, ionic strength, and temperature where the PdCl<sub>4</sub><sup>2-</sup> form prevails.

### Experimental Section

All inorganic salts were reagent grade. PdCl<sub>2</sub> ("pure" grade) was purified by reduction in aqueous solution of sodium formate at 60° and pH 8–9, followed by thorough washing with water and HCl and dissolving in concentrated HCl and H<sub>2</sub>O<sub>2</sub>. PdCl<sub>2</sub> obtained from this solution was dried at 300–350° in dry HCl atmosphere. *Anal.* Calcd for PdCl<sub>2</sub>: Pd, 60.0; Cl, 40.0. Found: Pd, 59.9; Cl, 39.87. The purification of other chemicals and the procedure of solution preparation have been described previously.<sup>7</sup>

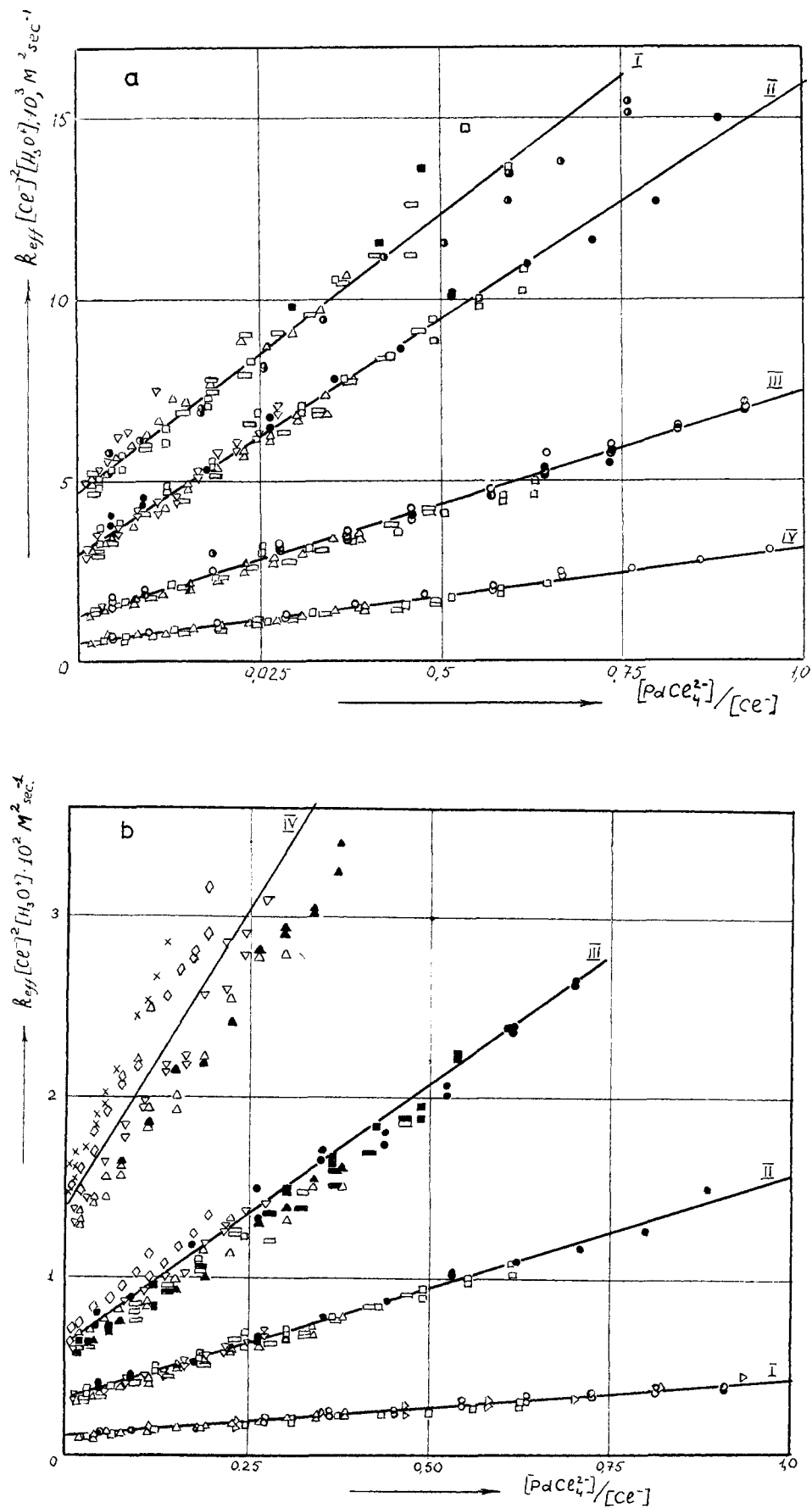
The kinetics of reaction between Pd(II) and dissolved olefin were studied in the presence of *p*-benzoquinone by measuring the emf of the following cell, one electrode of which was a quinone-hydroquinone (Q, QH<sub>2</sub>) electrode in the reactant medium, Pt|Q, QH<sub>2</sub>, Pd(II), HCl, LiClO<sub>4</sub>, olefin|Pd(II), HCl, LiClO<sub>4</sub>, Q, QH<sub>2</sub>|Pt.

The following reactions take place in the emf cell



As we have found earlier<sup>8</sup> this reaction proceeds quantitatively

(9) M. N. Vargaftik, O. G. Levanda, A. P. Belov, L. M. Zakharova and I. I. Moiseev, *Kinet. Katal.*, **10**, 1016 (1969); English translation p 828.



**Figure 1.**  $k_{eff}[Cl^-]^2[H_3O^+]$  vs.  $[PdCl_4^{2-}]/[Cl^-]$ : (a) for various ionic strengths ( $\mu = 1.1 M$  (I),  $2.0 M$  (II),  $3.0 M$  (III),  $4.0 M$  (IV)) and (b) temperatures (temp =  $15.0$  (I),  $25.0$  (II),  $32.0$  (III),  $40.0^\circ$  (IV)) for ethylene. Concentration ( $M$ ) of  $Cl^-$  ions:  $\circ$ ,  $0.2$ ;  $\square$ ,  $0.3$ ;  $\square$ ,  $0.4$ ;  $\triangle$ ,  $0.5$ ;  $\nabla$ ,  $0.7$ ;  $\diamond$ ,  $1.0$ ;  $\times$ ,  $1.4$ . All unfilled circles correspond to  $[H_3O^+] = 0.2 M$ ; all black circles correspond to  $[H_3O^+] = 0.5 M$ ;  $\bullet$ ,  $[H_3O^+] = 0.1 M, [Cl^-] = 0.2 M$ ;  $\ominus$ ,  $[H_3O^+] = 0.8 M, [Cl^-] = 0.2 M$ ;  $\odot$ ,  $[H_3O^+] = 1.0 M, [Cl^-] = 0.2 M$ ; and  $\ominus$ ,  $[H_3O^+] = 1.5 M, [Cl^-] = 0.2 M$ .

without any by-processes, the variation of emf being determined solely by the conversion of the olefin.

The apparatus for emf measurements and the procedure of treatment of results have been described in ref 9.

## Results

The experimental data indicate first-order kinetics of olefin conversion

$$k_1^{\text{obsd}} = \frac{1}{t} \ln \frac{[C_nH_{2n}]_{\Sigma}^0}{[C_nH_{2n}]_{\Sigma}^t} \quad (6)$$

where  $[C_nH_{2n}]_{\Sigma}^0$  and  $[C_nH_{2n}]_{\Sigma}^t$  are the total concentrations of olefin initially and at time  $t$ . Relating  $k_1^{\text{obsd}}$  to the total concentration of  $PdCl_4^{2-}$ , one can obtain the second-order rate constant

$$k_2^{\text{obsd}} = \frac{k_1^{\text{obsd}}}{[PdCl_4^{2-}]_{\Sigma}} \quad (7)$$

The effective rate constant  $k_{\text{eff}}$  is equal to

$$k_{\text{eff}} = \frac{W}{[C_nH_{2n}][PdCl_4^{2-}]} = \frac{k_1^{\text{obsd}}}{[PdCl_4^{2-}]_{\Sigma}} (1 + K[PdCl_4^{2-}]_{\Sigma}) \quad (8)$$

since the concentrations of  $PdCl_4^{2-}$  and  $Cl^-$  exceed considerably that of olefin in our experiments.  $[C_nH_{2n}]$  and  $[PdCl_4^{2-}]$  are equilibrium concentrations which have been achieved as a result of hydrolysis of  $PdCl_4^{2-}$  and of  $\pi$ -complex formation (eq 10 and 11, see below). In eq 8

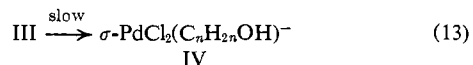
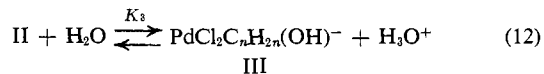
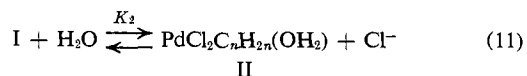
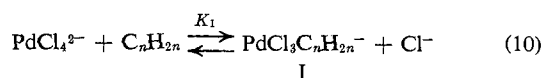
$$K = K_1/[Cl^-] + K_1K_2/[Cl^-]^2 \quad (9)$$

where  $K_1$  and  $K_2$  are equilibrium constants of  $\pi$ -complex formation.

The kinetic data obtained in seven series of experiments (experimental data for three of them have been published partly in ref 6 and 7) at different temperature and ionic strength values show that eq 1 is valid for the whole range of variables studied (Figure 1).

## Discussion

The kinetic data together with data concerning formation of Pd(II)-olefin  $\pi$ -complexes<sup>10-14</sup> and decomposition of possible  $\sigma$ -organopalladium intermediates<sup>15</sup> permit us to propose the following mechanism<sup>2,6</sup>



(10) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **152**, 147 (1963).

(11) S. V. Pestrikov and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 349 (1965).

(12) S. V. Pestrikov, I. I. Moiseev, and T. N. Romanova, *Zh. Neorg. Khim.*, **10**, 2203 (1965).

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(15) I. I. Moiseev and M. N. Vargaftik, *Dokl. Akad. Nauk SSSR*, **166**, 370 (1966).

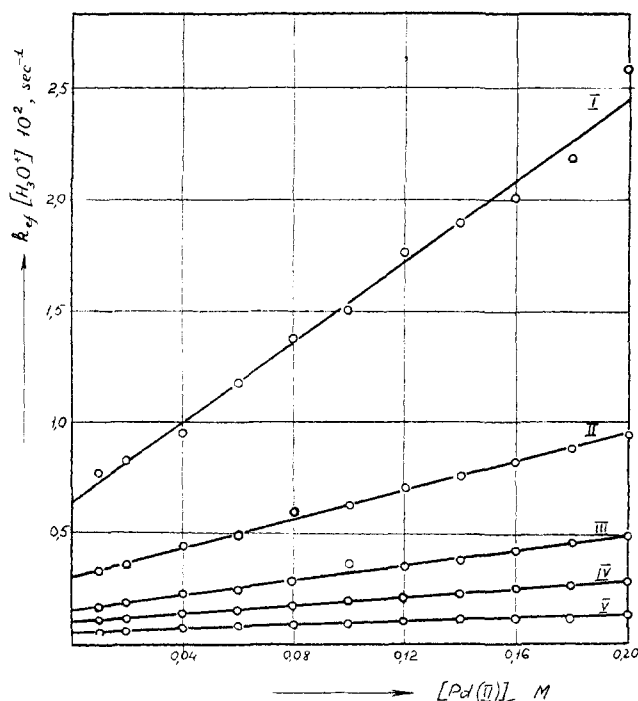
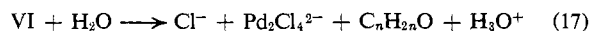
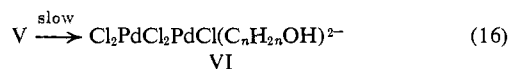
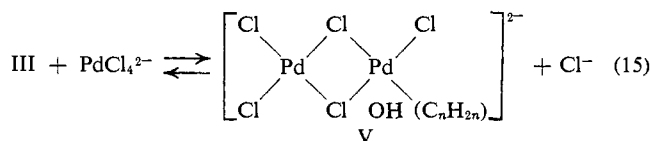
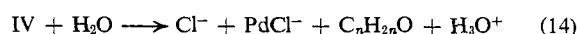


Figure 2. Dependence of  $k_{\text{eff}}[H_3O^+]$  on Pd(II) concentration for different  $Cl^-$  concentrations at  $25^\circ$  and  $2.0 M$  ethylene: I,  $0.2 M [Cl^-]$ ; II,  $0.3 M [Cl^-]$ ; III,  $0.4 M [Cl^-]$ ; IV,  $0.5 M [Cl^-]$ ; V,  $0.7 M [Cl^-]$ . The values  $K_1 = 17.4$  and  $K_2 = 0.3^8$  were used for computing  $k_{\text{eff}}$ .



At low  $PdCl_4^{2-}$  concentrations (up to  $0.04 M$ ) reactions (eq 15-17) are negligible and the kinetics are described satisfactorily by eq 2 which is in fact the first term of eq 1.<sup>1,2</sup> This is in accord with the observations of other authors.<sup>3-5</sup> At higher Pd(II) concentrations (from  $0.04$  to  $0.20 M$ ), especially if  $Cl^-$  concentration is low, it is the second term of eq 1 which is predominant (Figure 1).

Recently Henry<sup>8</sup> has raised doubt as to the existence of the second term of kinetic eq 1 on the ground that he has observed no systematic growth of the first-order rate constant on increasing Pd(II) concentration up to  $0.2 M$  in his study of absorption of gaseous olefins by aqueous  $PdCl_4^{2-}$  solutions. He was inclined to ascribe this term to "systematic deviation in the calculations of rate constants from the experimental data," due to the use of erroneous constants  $K_1$  and  $K_2$ .

**The Form of the Kinetic Equation.** Let us consider the effect of numerical values of  $K_1$  and  $K_2$  on the form of kinetic equation. Leaving out for the moment the question of correct values of the equilibrium constants (ours or Henry's), let us accept, according to Henry,<sup>3,8</sup>  $K_1 = 17.4$  and  $K_2 = 0$  at  $25^\circ$ . It can readily be seen from Figure 2 that the effective rate constants,  $k_{\text{eff}}$ , calculated from our data with the use of these  $K_1$  and

**Table I.** Comparison of Ethylene Oxidation Rates Observed by Henry<sup>8</sup> and Computed from Eq 1 at 25° by the Data from Our Laboratory

[Pd(II)], <sup>a</sup> <i>M</i>	[NaCl], <sup>a</sup> <i>M</i>	[PdCl <sub>4</sub> <sup>2-</sup> ], <sup>b</sup> <i>M</i>	[PdCl <sub>3</sub> ·H <sub>2</sub> O <sup>-</sup> ], <sup>b</sup> <i>M</i>	[PdCl <sub>3</sub> ·C <sub>2</sub> H <sub>4</sub> ], <sup>c</sup> <i>M</i>	[PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )·H <sub>2</sub> O], <sup>b</sup> <i>M</i>	[Cl <sup>-</sup> ], <sup>b</sup> <i>M</i>	10 <sup>5</sup> <i>W</i> , <sup>c</sup> <i>M</i> sec <sup>-1</sup>	10 <sup>5</sup> <i>W</i> , <sup>d</sup> <i>M</i> sec <sup>-1</sup>
0.20	0.2	0.1498	0.0146	0.0232	0.0123	0.262	30.75	14.9
0.10	0.2	0.0723	0.0079	0.0124	0.0074	0.235	12.31	9.53
0.05	0.2	0.0353	0.0041	0.0065	0.0042	0.219	5.03	4.81 (4.54)
0.01	0.2	0.0068	0.0009	0.0014	0.0010	0.204	0.75	1.07 (0.96)
0.20	0.3	0.1613	0.0120	0.0190	0.0076	0.346	16.42	8.40
0.10	0.3	0.0796	0.0062	0.0098	0.0043	0.325	6.26	3.79
0.05	0.3	0.0395	0.0032	0.0051	0.0023	0.313	2.50	2.48 (2.16)
0.01	0.3	0.0078	0.0006	0.0010	0.0005	0.303	0.37	0.44 (0.45)
0.20	0.4	0.1693	0.0100	0.0157	0.0050	0.436	9.58	6.11
0.10	0.4	0.0840	0.0052	0.0082	0.0027	0.419	3.61	3.22
0.05	0.4	0.0418	0.0026	0.0042	0.0014	0.410	1.44	1.70 (1.28)
0.01	0.4	0.0083	0.0005	0.0008	0.0003	0.402	0.22	0.31 (0.23)
0.20	0.5	0.1745	0.0085	0.0134	0.0036	0.529	6.10	3.79
0.10	0.5	0.0870	0.0043	0.0068	0.0018	0.515	1.85	2.09
0.05	0.5	0.0434	0.0222	0.0035	0.0010	0.508	0.92	1.10 (0.86)
0.01	0.5	0.0087	0.0004	0.0007	0.0002	0.502	0.15	0.24 (0.18)

<sup>a</sup> Initial concentrations in Henry experiments. <sup>b</sup> Equilibrium concentrations computed with account of hydrolysis of PdCl<sub>4</sub><sup>2-</sup> ( $pK = 1.59^{17}$ ):  $K_1 = 15.0$ ,  $K_2 = 0.14 M$ , the solubility of ethylene  $2.7 \times 10^{-3} M$ . <sup>c</sup> Ethylene oxidation rate computed from eq 1 with constants  $k_{I1} = 2.94 \times 10^{-3} M^{-2} \text{sec}^{-1}$ ,  $k_{II1} = 1.31 \times 10^{-2} M^{-2} \text{sec}^{-1}$ . <sup>d</sup> Ethylene oxidation rate from data of ref 8. The rate observed in the earlier work of the same author<sup>8</sup> is given in parentheses.

$K_2$  values vary as a result of increasing PdCl<sub>4</sub><sup>2-</sup> concentration, which should not have been the case if the kinetic equation did not contain the second term. Analysis shows that  $k_{\text{eff}}$  changes in agreement with eq 18

$$k_{\text{eff}} = A + B[\text{PdCl}_4^{2-}] \quad (18)$$

where constants  $A$  and  $B$  depend upon Cl<sup>-</sup> and H<sub>3</sub>O<sup>+</sup> concentrations ( $A = 2.61 \times 10^{-3}/[\text{Cl}^-]^2[\text{H}_3\text{O}^+]$ ;  $B = 1.56 \times 10^{-2}/[\text{Cl}^-]^2.58[\text{H}_3\text{O}^+]$ ).

Thus, the use of Henry's constants also leads to the equation with a quadratic term in [PdCl<sub>4</sub><sup>2-</sup>]. The difference between such an equation and the one proposed by us is only a slight change in the values of coefficients and a slight decrease of the reaction order with respect to [Cl<sup>-</sup>]. The analysis shows that the second term in eq 1 disappears only for  $K_1 = 2$  and  $K_2 = 0$ , which is far beyond the experimental error, and even in this case eq 2 describes the kinetic data worse than eq 1. Thus, the principal argument proposed by Henry<sup>8</sup> against our equation cannot be considered as a correct one.

Assuming the reaction to follow only the first route (eq 10–14) the analysis of kinetic data leads to values of equilibrium constants that are too low. It was this fact which had earlier<sup>2</sup> made us conclude that under the experimental conditions steps 10 and 11 did not attain equilibrium. However, in fact, these steps approach equilibrium.<sup>16</sup>

**The Technique of the Kinetic Experiment.** The discrepancy between the results of ref 6 and 7 and those of 3, 4, and 8 is apparently due to the different experimental techniques employed by Henry and by us. In our laboratory the reaction kinetics between PdCl<sub>4</sub><sup>2-</sup> and dissolved olefin were studied by a potentiometric method. Henry used a volumetric method, measuring the absorption of gaseous olefin by aqueous palladium chloride solutions. Under the conditions of a two-phase system used in<sup>3,8</sup> diffusion limitations could be

appreciable, but they were eliminated in our experiments.

It is well known that it is a very difficult task to prove the absence of the diffusional effects in a gas-liquid system especially for a stirrer reactor. Independence of the reaction rate on the number of the stirrer revolutions even over a wide range of values cannot always serve as a sufficient proof that the reaction occurs under kinetic conditions. A large variation of the degree of filling of the vessel in such reactors leads to a change in conditions of the gas-liquid contact, which is difficult to be controlled quantitatively. There was mention in ref 8 that the reaction rate did not change with twofold decreasing of the liquid-phase volume at constant stirring rate. However, this fact cannot serve as unequivocal demonstration of the absence of the diffusion and/or gas-dynamic limitations.

In view of this it is of interest to compare the rate of ethylene oxidation by palladium chloride determined by Henry and by us for solutions of similar concentrations. As one can see from Table I, at low Pd(II) concentrations the rates of gaseous ethylene uptake as determined<sup>3,8</sup> coincide satisfactorily with the oxidation rates of dissolved ethylene determined by us. At higher concentrations of Pd(II) (0.1–0.2 *M*) and low Cl<sup>-</sup> concentrations (0.2–0.5 *M*) the oxidation rates of the dissolved ethylene exceed ethylene uptake by a factor of 1.5–2. The difference between the two rates remains practically the same when Henry's values for equilibrium constants<sup>3,8</sup> of  $\pi$ -complex formation are used for calculations.

These discrepancies may be ascribed to the increasing part played by diffusion factors with increasing rate of the chemical reaction in the transition region which was the probable region in which Henry worked. It is, therefore, not surprising that there should have been a fall in the order of the reaction with respect to [PdCl<sub>4</sub><sup>2-</sup>] and [Cl<sup>-</sup>] as observed in ref 8. Reduced orders for the reaction kinetics with reference to the dissolved reactant are not unusual for the transition region in which the

(16) I. I. Moiseev, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**, B49 (1969).

(17) O. G. Levanda, *Zh. Neorg. Khim.*, **12**, 3311 (1968).

chemical reaction rates are comparable with those of diffusion.<sup>18-20</sup>

In general, it is difficult to accept Henry's results also because of the considerable scatter in his data resulting in deviations of the rate constant values of up to 50%. In some cases these deviations seem to be of a systematic nature.

**Equilibrium Constants.** In our experiments the equilibrium of the  $\pi$ -complex formation was investigated under suppressed oxidation reaction conditions. This method permits one to eliminate possible errors arising from uptake due to the oxidation reaction. The particular design of the apparatus and the method of gas and liquid mixing excluded noncontrolled absorption of ethylene in the initial stage of reaction.<sup>10</sup> A shortcoming of our experiments could be the noticeable difference between the  $\text{Cl}^-$  as well as  $\text{H}_3\text{O}^+$  concentration in the equilibrium and kinetic experiments. In the equilibrium studies at constant ionic strength  $\text{Cl}^-$  concentration was varied in some cases up to 75% of the overall ionic strength. Careful analysis<sup>16</sup> showed, however, that even if these factors are of significance their effect is within the experimental error. It should be pointed out that the equilibrium constants determined by a volumetric method are in satisfactory agreement with those obtained from kinetic data<sup>21</sup> (Table II).

**Table II.** Equilibrium Constants of Reactions 10 and 11 Obtained by Different Authors

Temp, °C	$\mu$ , M	$K_1$	$K_2$ , M	Ref
13.4	4.5	16.3	0.4	10
13.3	3.0	15.9	0.18	14
13.3	2.0	15.5	0.033	14
20	4.0	15.2	0.28	12
25	4.0	13.1	0.21	12
15	2.0	18.7		3
25	2.0	17.4	$10^{-3}$	3, 8
35	2.0	9.4		3
25	2.0	15.5	0.05	3, a
25	1.1	13.9	0.029	21
25	2.0	15.0	0.14	21
25	3.0	14.8	0.22	21
25	4.0	15.0	0.32	21
15	2.0	15.8	0.11	21
32	2.0	14.2	0.16	21
40	2.0	12.7	0.18	21

<sup>a</sup> Data of ref 3 recalculated with account of  $\text{PdCl}_4^{2-}$  hydrolysis ( $pK_{\text{hydr}} = 1.59^{17}$ ).

(18) P. Danckwert, "Gas-Liquid Reactions," McGraw-Hill, New York, N. Y., 1970.

(19) Z. Šterbacek and P. Tausk, "Mechani v chemickém průmyslu," Státní nakladatelství technické literatury, Praha, 1961.

(20) G. Astarita, "Mass-Transfer with Chemical Reaction," Elsevier, Amsterdam, 1967.

(21) O. G. Levanda, and I. I. Moiseev, *Kinet. Katal.*, **12**, 354 (1971).

There are no indications in ref 3 of taking into account the possible ethylene uptake in the evacuated reactor prior to switching on the stirrer. The amount of ethylene dissolved was determined in this work by extrapolation. Furthermore at low  $\text{Cl}^-$  concentrations  $\text{PdCl}_4^{2-}$  is hydrolyzed to a considerable extent<sup>17, 22-24</sup>



(The constant of hydrolysis  $K_h = 0.0256 \pm 0.002 M$  at ionic strength  $2 M^{17}$ .) The resulting decrease of  $\text{PdCl}_4^{2-}$  and increase of  $\text{Cl}^-$  concentrations were taken into account neither in the analysis of kinetic data nor in computing of the equilibrium constants in ref 3. These errors accumulate since the ratios of these concentrations are used when treating experimental results. The actual value of the  $\text{PdCl}_4^{2-}$  concentration corrected on account of hydrolysis may be calculated by

$$[\text{PdCl}_4^{2-}] = \frac{[\text{Pd(II)}] - [\pi]_{\Sigma}}{1 + K_h/[\text{Cl}^-]} \quad (20)$$

where  $[\pi]_{\Sigma}$  is the total equilibrium concentration of  $\pi$ -complexes I and II,  $[\text{Pd(II)}]$  is total concentration of Pd(II), and  $[\text{Cl}^-]$  is equilibrium concentration of  $\text{Cl}^-$  ions coinciding approximately with the total one in kinetic experiments.

The values of equilibrium constants of  $\pi$ -complex formation may be determined by using<sup>10</sup>

$$\varphi = K_1 K_2 + K_1 [\text{Cl}^-] \quad (21)$$

where

$$\varphi = \frac{[\pi]_{\Sigma} [\text{Cl}^-]^2}{[\text{PdCl}_4^{2-}] [\text{C}_n\text{H}_{2n}]} \quad (22)$$

If Henry's data<sup>3</sup> are treated by this procedure (albeit without sufficient statistical grounding), the values for  $K_1$  ( $=15.5$ ) and  $K_2$  ( $=0.05$ ) considering all mentioned above are reasonably close to the values obtained by us (Table II).

Probably at present there is no other way for a more accurate determination of the equilibrium constants and there seems to be no basis for Henry's assertion that the values of equilibrium constants obtained by him are more reliable than those determined by the authors of the present work.

Two-term equations (1) have also been found to be valid for the oxidation rates of propylene and butene-1.<sup>6</sup> Further insight into mechanism of Pd(II)-olefin reaction may be obtained only by the use of more accurate and reliable kinetic data together with their treatment by means of computers.

(22) D. Dyrssen and K. Burger, *Acta Chem. Scand.*, **17**, 1489 (1963).

(23) E. D. Weed, *Diss. Abstr.*, **25**, 795 (1964).

(24) V. I. Shlenskaja and A. A. Biriukov, *Z. Neorg. Khim.*, **11**, 54 (1966).