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Kinetic Studies of the Hydrolysis of Diketene Catalyzed by the Chloropalladium(II) Complex

Seichi Okeya* and Shinichi Kawaguchi*,†
Faculty of Education, Wakayama University, Fukiage, Wakayama 640
†*Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558*

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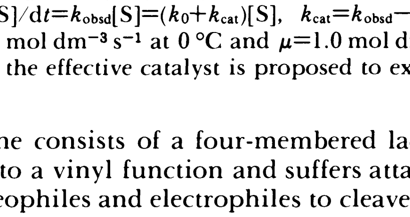
When diketene and sodium tetrachloropalladate(II) are mixed in aqueous solution, color of the solution changes promptly from dark red to yellow. During this fast primary reaction about one equivalent of diketene is consumed and acetoacetic acid (H_2A) is retained as a trihapto ligand in $[PdCl_2(HA)]^-$ (**2**). The succeeding steady hydrolysis of diketene (S) proceeds as a pseudo first-order reaction, obeying the rate law: $-d[S]/dt=k_{obsd}[S]=(k_0+k_{cat})[S]$, $k_{cat}=k_{obsd}-k_0=(k_1+k_2/[H^+])[Pd^{II}]/[Cl^-]$, where $k_1=2.0\times10^{-5}\,s^{-1}$ and $k_2=2.96\times10^{-6}\,mol\,dm^{-3}\,s^{-1}$ at 0 °C and $\mu=1.0\,mol\,dm^{-3}$ ($HClO_4$ and $NaClO_4$). A mechanism which postulates complex **2** as the effective catalyst is proposed to explain the observed two-term rate equation.

Diketene consists of a four-membered lactone ring adjacent to a vinyl function and suffers attack of various nucleophiles and electrophiles to cleave the ring.[1] Tezuka *et al.* found that sodium tetrachloropalladate catalyzes the alcoholysis of diketene to afford acetoacetic esters.[2] Ethyl acetoacetate (etacH) forms a stable dinuclear palladium(II) complex $[PdCl(etac)]_2$, in which the β-keto ester ligand was confirmed by X-ray analysis to be coordinated with palladium in the η-allylic fashion.[3] Okeya *et al.* also found that the solvolysis reactions of diketene in water and acetone are catalyzed by palladium(II) complexes.[4] Palladium(II) complexes of the reaction products, acetoacetic acid and 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one, were characterized and inferred to have the η-allylic structure. In fact the crystal and molecular structure of the former complex (**1**) was determined by X-ray crystallography.[5]



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Palladium(II) forms a lot of organometallic compounds and is useful as catalysts for synthetic reactions.[6] As is exemplified by the famous Wacker reaction,[7] palladium participates in redox processes in most of the catalytic reactions. The spontaneous reaction of diketene with water is very slow[8] but is catalyzed by acids to produce acetone and carbon dioxide *via* acetoacetic acid.[9] The tetrachloropalladate(II) is very effective as a catalyst for this hydrolysis reaction but shows no sign of redox process involved. With the aim of elucidating the mechanism of this interesting catalysis a kinetic study was undertaken.

Experimental

Materials. A stock aqueous solution of sodium tetrachloropalladate(II) was prepared by dissolving palladium(II) chloride and sodium chloride in the mole ratio of 1 : 5. The exact concentrations of palladium and total chloride were determined by chemical analysis. Diketene (99.9% in purity) was supplied by Daicel Co., Ltd. and vacuum-distilled just before use. Other reagents such as perchloric acid, sodium perchlorate, sodium hydroxide, sodium chloride, and palladium(II) chloride as well as analytical reagents and indicators were of the AR grade and used as supplied.

Kinetic Measurement. A mixture of diketene and sodium tetrachloropalladate(II) in aqueous solution was stirred in a thermostated (±0.3 °C) reaction vessel. The solution was kept at $\mu=1.0\,mol\,dm^{-3}$ by virtue of sodium perchlorate and perchloric acid. By one minute after admixing the substrate with the catalyst color of the solution changed from dark red to yellow, indicating variation in the palladium(II) coordination sphere. Time zero for the steady reaction was set at this point and an aliquot was taken out from the reaction mixture and poured into an ethanol solution of about twice equivalents of dimethylglyoxime to quench the reaction. The mixture was titrated with a sodium hydroxide solution ($0.1\,mol\,dm^{-3}$). Bromothymol Blue was used as an indicator (color changing from yellow to green) and the solution was kept throughout in ice and handled promptly. The initial concentration of diketene (S) for the steady reaction was calculated from Eq. 1,

$$[S]_0 = [S]_a - \{[NaOH]_0-2[Pd^{II}]-[HClO_4]\}, \qquad (1)$$

where $[S]_a$ stands for the total concentration of diketene employed initially and $[NaOH]_0$ gives the concentration of alkali solution needed for neutralization of the aliquot. The amount of diketene consumed in the primary process is nearly equivalent to $[Pd^{II}]$. For each kinetic run diketene was used to make the $[S]_0$ value be in the region 0.15—0.20 $mol\,dm^{-3}$. Progress of the reaction thereafter was followed by taking aliquots at appropriate time intervals and titrating them in a similar way. The spontaneous hydrolysis of diketene in the absence of palladium(II) was also studied analogously.

Determination of the Hydrogen and Chloride Concentrations. It is usually rather difficult to determine accurately the hydrogen ion concentration in a solution with high ionic strength.[10] In this study an empirical method was used to relate an observed pH value to the hydrogen ion concentration. Solutions of hydrochloric acid at various concentrations were adjusted to $\mu=1.0\,mol\,dm^{-3}$ with sodium perchlorate and their pH values were determined. A calibration curve was thus drawn and the pH values of reaction mixtures were applied to this curve to evaluate their hydrogen ion concentrations.

As will be discussed shortly, the palladium(II) complex involved in the steady reaction is presumed to be $[PdCl_2(HA)]^-$ (H_2A=acetoacetic acid) and the concentration of free chloride ions was calculated from the equation,

$$[\mathrm{Cl}^-] = [\mathrm{Cl}^-]_t - 2[\mathrm{Pd}^{\mathrm{II}}],$$

where $[\mathrm{Cl}^-]_t$ represents the total concentration of chloride ions inclusive of those retained in the palladium(II) coordination sphere.

Instruments. The pH determination was performed with a Hitachi-Horiba M-5 pH meter. A reference electrode of the double junction type was used in order to prevent the perchlorate interference. Absorption spectra were measured by means of a Hitachi EPS-3T recording spectrophotometer.

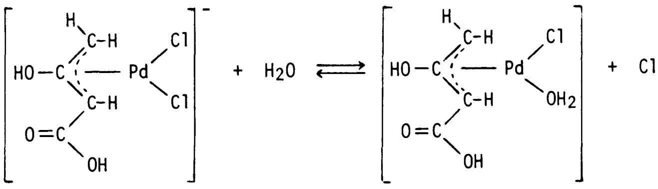
Results and Discussion

Spontaneous hydrolysis of diketene in the absence of the palladium(II) catalyst proceeds as a first order reaction and $k_0=1.67\times10^{-5}\,\mathrm{s}^{-1}$ at 0 °C and $\mu=1.0$ mol dm^{-3}. Addition of hydrochloric acid slightly lowers the rate, k_0 for example being $1.44\times10^{-5}\,\mathrm{s}^{-1}$ when [HCl] is 0.05 mol dm^{-3}. On the other hand the reaction is accelerated very remarkably by addition of sodium hydroxide.

The stepwise stability constants (K_n in dm^3 mol^{-1}) of the complexes $\mathrm{PdCl}_n(\mathrm{H_2O})_{4-n}^{(2-n)+}$ were determined by Elding[11] at 25 °C and $\mu=1.00$ mol dm^{-3}: $K_1=(2.98\pm0.06)\times10^4$, $K_2=(1.92\pm0.13)\times10^3$, $K_3=(2.6\pm0.2)\times10^2$, and $K_4=(2.37\pm0.10)\times10$. When the chloride ion concentration lies in the 0.02—0.2 mol dm^{-3} region as is the case for the present study, the chloropalladium(II) complex seems to exist as a mixture of $[\mathrm{PdCl_4}]^{2-}$, $[\mathrm{PdCl_3(H_2O)}]^-$, and $[\mathrm{PdCl_2(H_2O)_2}]$.

When an aqueous solution of diketene is added to an aqueous solution of $\mathrm{Na_2[PdCl_4]}$, color of the solution changes in one minute from dark red to yellow. The absorption spectrum of this solution has a maximum at 360 nm (ε=*ca.* 1200), and does not change during the progress of reaction. As is seen in Fig. 1, the $\lambda_{\max}$ slightly shifts to longer wave length side with increasing chloride concentration. It may be presumed that the dichloropalladium(II) complex coordinated with acetoacetic acid in an η-allylic fashion, $[\mathrm{PdCl_2(HA)}]^-$ (**2**), is produced by the following fast reactions and works as an effective catalyst for the succeeding steady reaction. Complex **2** may be contaminated with a small amount of aqua counterpart **2′** in equilibrium 3. Since the chloride ion is a weaker ligand than the aqua ligand in the spectrochemical series, shift of the equilibrium 3 to the left hand side causes red shift of the absorption maximum. Thus $[\mathrm{PdCl(H_2O)(en)}]^+$ and $[\mathrm{PdCl_2(en)_2}]$ absorb at 360 and 370 nm, respectively.[12]

$$\left.\begin{array}{lcl} [\mathrm{PdCl_4}]^{2-} + \mathrm{S} + \mathrm{H_2O} & \xrightarrow{\text{fast}} & [\mathrm{PdCl_2(HA)}]^- + \mathrm{H}^+ + 2\mathrm{Cl}^- \\ [\mathrm{PdCl_3(H_2O)}]^- + \mathrm{S} & \xrightarrow{\text{fast}} & [\mathrm{PdCl_2(HA)}]^- + \mathrm{H}^+ + \mathrm{Cl}^- \\ [\mathrm{PdCl_2(H_2O)_2}] + \mathrm{S} & \xrightarrow{\text{fast}} & [\mathrm{PdCl_2(HA)}]^- + \mathrm{H}^+ + \mathrm{H_2O} \end{array}\right\} \quad (2)$$



2 **2′** (3)

When diketene is used up, color of the solution returns to red gradually. On being cooled below 0 °C the yellow solution deposits complex **1** but the red solution does not. The ^{1}H NMR assay indicates that complex **1** is converted into **2** in aqueous solution containing excess chloride ions, but either of them is not thermodynamically stable under these circumstances. Even when sodium acetoacetate is added to aqueous solution of $\mathrm{Na_2[PdCl_4]}$, no sign of reaction is observed. Thus complex **2** is not formed by the reaction of $[\mathrm{PdCl_4}]^{2-}$ with acetoacetic acid, but seems to be involved as an intermediate in the catalytic reaction.

The succeeding rather slow hydrolysis of diketene was followed by the titration method. The hydrogen ion concentration of the reaction mixture remained almost constant during the progress of reaction, indicating that acetoacetic acid, the reaction product, hardly ionizes in the acidic solution. Contributions from added perchloric acid and produced hydrochloric acid were subtracted from the observed hydrogen ion concentration, and the remaining part was related to the ionization of the η^3-coordinated acid in complex **2**.

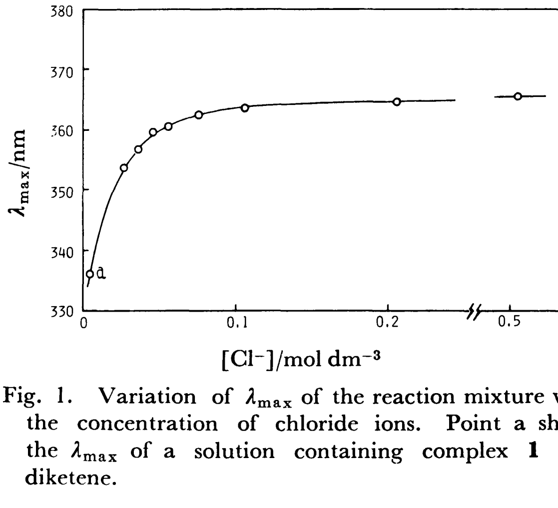


Fig. 1. Variation of $\lambda_{\max}$ of the reaction mixture with the concentration of chloride ions. Point a shows the $\lambda_{\max}$ of a solution containing complex **1** and diketene.

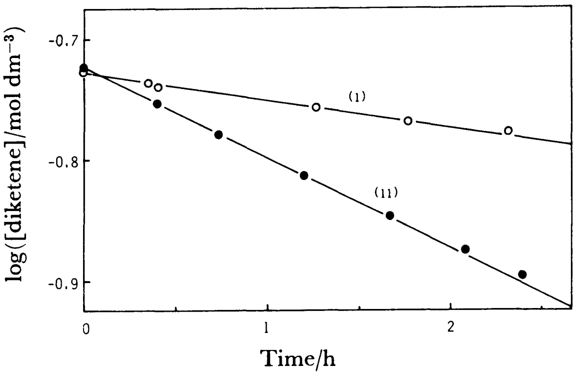


Fig. 2. The first-order plots for the hydrolysis of diketene in the absence (i) and presence (ii) of the Pd$^{\mathrm{II}}$ catalyst at 0 °C and $\mu=1.0$ mol dm^{-3}. $[\mathrm{Cl}^-]=0.050$ mol dm^{-3}, $[\mathrm{H}^+]=0.021\pm0.001$ mol dm^{-3}, and $[\mathrm{Pd}^{\mathrm{II}}]=0.0100$ mol dm^{-3}.

In this way the acid dissociation constant K_a (1) of **2** was estimated to be in the range 10^{-2}—10^{-3} mol dm^{-3} and is a little smaller than that of complex **1** (3.2×10^{-2} mol dm^{-3} at 18 °C).[4,5]

As is shown in Fig. 2, the reaction proceeds as a pseudo first order reaction up to 30—50% conversion. Since the spontaneous uncatalyzed hydrolysis is also a first order reaction, contribution of the catalyzed reaction is given by Eq. 4.

$$-\frac{d[S]}{dt} = k_{obsd}[S] = (k_0+k_{cat})[S],\ k_{cat} = k_{obsd} - k_0. \qquad (4)$$

Both of the rate constants k_{obsd} and k_0 for the overall and uncatalyzed reactions, respectively, were measured more than four times under the same conditions and averaged.

Figures 3 and 4 show that ($k_{obsd}-k_0$) is proportional to the palladium(II) concentration and also to reciprocal of the chloride concentration. Dependence of ($k_{obsd}-k_0$) on the hydrogen ion concentration at constant palladium(II) and chloride concentrations is shown in Fig. 5. If the rate constants are plotted against the reciprocal of hydrogen ion concentration, a straight line is obtained (Fig. 6). Thus the pseudo first order rate constant for the catalyzed reaction is expressed by Eq. 5, and k_1=2.0×10^{-5} s^{-1} and k_2=2.96×10^{-6} mol dm^{-3} s^{-1} at 0 °C and μ=1.0 mol dm^{-3}.

$$k_{obsd} - k_0 = \left(k_1+\frac{k_2}{[H^+]}\right)\frac{[Pd^{II}]}{[Cl^-]}. \qquad (5)$$

The Eyring plots of rate data in Table 1 for the catalyzed and spontaneous reactions gave $\Delta H^{\neq}$=53 kJ mol^{-1} for both reactions. It should be added that the rate data reported in this paper may be accurate to ±10%.

Mechanism of Catalyzed Hydrolysis. Hydrolysis reactions of aliphatic lactones in weakly acidic solutions have been studied rather extensively.[13] For example, rates of hydrolysis of β-propiolactone and

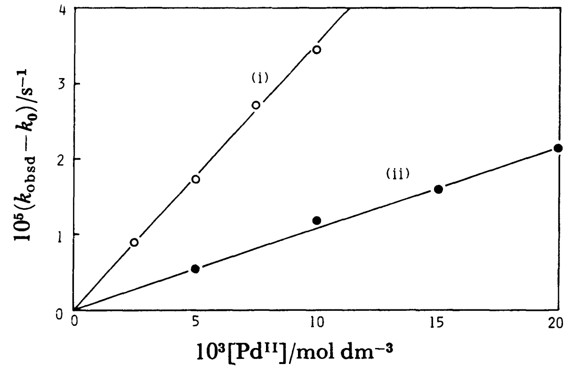


Fig. 3. Dependence of ($k_{obsd}-k_0$) on the palladium(II) concentration at 0 °C, μ=1.0 mol dm^{-3}, and [H$^+$]=0.021±0.001 mol dm^{-3}. (i) [Cl$^-$]=0.050 mol dm^{-3}. (ii) [Cl$^-$]=0.180 mol dm^{-3}.

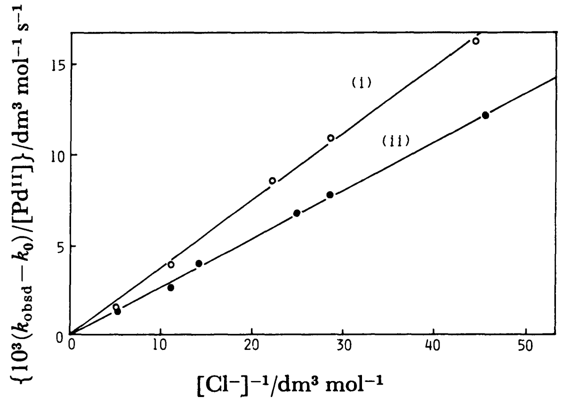


Fig. 4. Dependence of ($k_{obsd}-k_0$) on the reciprocal of chloride concentration at 0 °C and μ=1.0 mol dm^{-3}. (i) [Pd^{II}]=0.0050 mol dm^{-3} and [H$^+$]=0.0080 ±0.0002 mol dm^{-3}. (ii) [Pd^{II}]=0.0100 mol dm^{-3} and [H$^+$]=0.0123±0.0005 mol dm^{-3}.

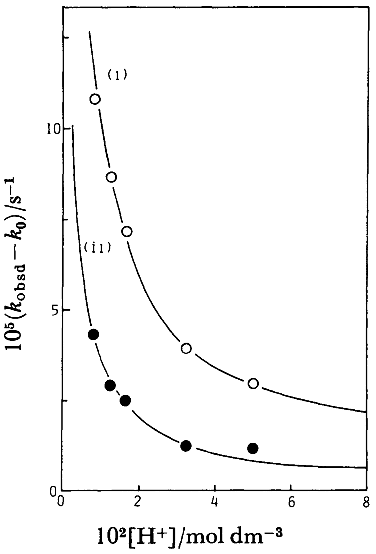


Fig. 5. Dependence of ($k_{obsd}-k_0$) on the hydrogen ion concentration at 0 °C, μ=1.0 mol dm^{-3}, and [Pd^{II}]=0.0050 mol dm^{-3}. (i) [Cl$^-$]=0.015 mol dm^{-3}. (ii) [Cl$^-$]=0.045 mol dm^{-3}.

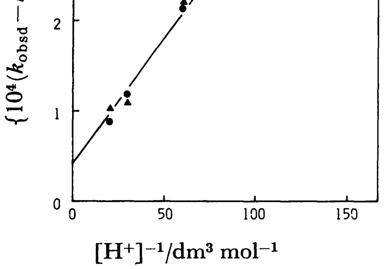


Fig. 6. Plot of ($k_{obsd}-k_0$)[Cl$^-$]/[Pd^{II}] against reciprocal of the hydrogen ion concentration. Rate data are the same as those of Fig. 5, [Cl$^-$] being 0.015(●) or 0.045(▲)mol dm^{-3}.

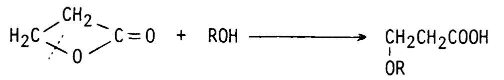
TABLE 1. RATES OF HYDROLYSIS OF DIKETENE AT VARIOUS TEMPERATURES AND $\mu = 1.0$ mol dm^{-3}, $[Cl^-] = 0.195$ mol dm^{-3}, $[H^+] = 0.008$ mol dm^{-3}

T / K	$10^5 k_0$ / s^{-1}	$10^5 k_{obsd}$ / s^{-1}	$10^3(k_{obsd}-k_0)/[Pd^{II}]$[a)] / dm^3 mol^{-1} s^{-1}
303	17.3	27.2	19.8
293	8.45	13.3	9.70
283	3.76	5.89	4.26
278	2.34	3.74	2.80
273	1.56	2.37	1.62

a) $[Pd^{II}] = 0.0050$ mol dm^{-3}.

γ-butyrolactone were reported to be 1.88×10^{-4} and 5.00×10^{-5} s^{-1}, respectively, in neutral solutions at 37 °C.[14] The β-lactone is usually less stable and hydrolyzed more readily than the γ-lactone. In the molecule of diketene, the C=C function is attached to the β-lactone ring and the strain energy was estimated[15] as 94.1 kJ mol^{-1}. The rotational spectrum suggested that diketene is not planar.[16] Thus diketene is thermodynamically less stable and more reactive than β-propiolactone. In fact the hydrolysis rate of diketene was reported by van Duuren *et al.*[14] to be 2.0×10^{-3} s^{-1} at 25 °C and pH 7. This value is much larger than the present data in Table 1, but does not allow a direct comparison because of lacking in description of ionic strength. Higher ionic strength decreases the hydrolysis rate, k_0 at 0 °C being 3×10^{-5} s^{-1} at $\mu \approx 0$ and 1.56×10^{-5} s^{-1} at $\mu = 1.0$ mol dm^{-3}.

β-Propiolactone reacts with alcohol both in the absence and presence of acid catalysts to give 3-alkoxypropionic acid.[17] The alkyl-oxygen bond seems to be cleaved in this reaction (Eq. 6) as well as in hydrolysis.[18] On the other hand the reaction between diketene and alcohol results in the acetoacetic ester[1] probably by virture of the acyl-oxygen fission (Eq. 7).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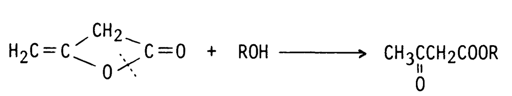
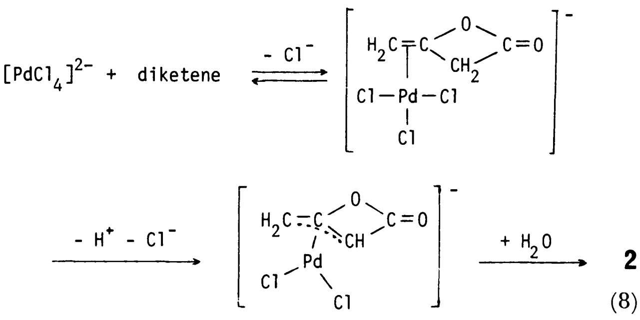

(7)

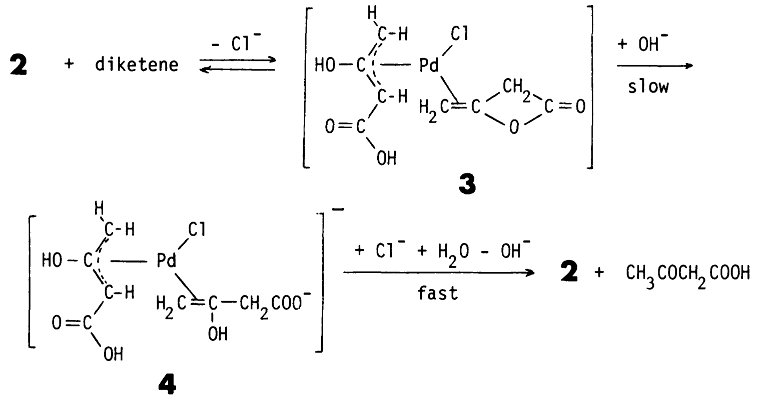
Alcoholysis of diketene catalyzed by palladium(II) seems to proceed according to the same mechanism and analogously hydrolysis of diketene both in the absence and presence of palladium(II) may involve the acyl-oxygen fission.

Since either of β-propiolactone and γ-butyrolactone shows no sign of interaction with $[PdCl_4]^{2-}$ in aqueous solution, diketene must coordinate with palladium(II) not through the oxygen atom(s) but through the C=C bond in the primary step of catalysis. Displacement of two chloride ligands and a methylene proton of diketene may give rise to a trihapto complex of the diketene anion, which in turn will be hydrolyzed rapidly to give complex **2** (Eq. 8).

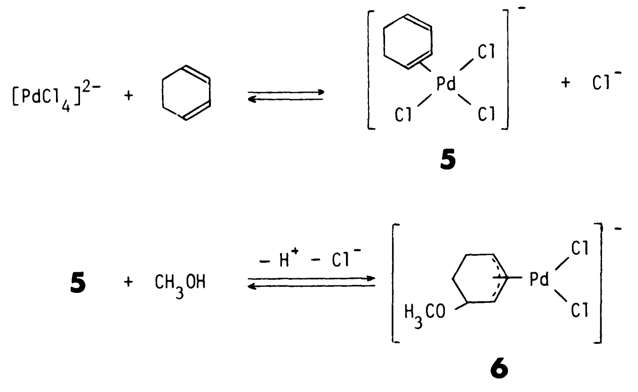

(8)

The succeeding steady reaction obeys the two term rate equation 5. The rate-determining step may be the nucleophilic attack of a water molecule (k_1) or a hydroxide anion (k_2) on the diketene ligand in the intermediate complex **3** as is shown in Eq. 9 for the k_2 path.

The enol tautomer of acetoacetic acid in the presumed complex **4** must be very unstable and rapidly displaced by a chloride anion to recover complex **2** and the product acetoacetic acid. Although the intermediate complexes postulated in this scheme have not been characterized, the rate equation 5 is readily interpreted on the assumption that complex **2** functions as the effective catalyst for hydrolysis of diketene. Pietropaolo *et al.*[19] studied kinetically the reaction between $[PdCl_4]^{2-}$ and 1,3-cyclohexadiene to form an η-allylic complex and proposed the following mechanism which involves the nucleophilic attack of methanol on the coordinated olefinic double bond as the rate-determining step in accordance with the observed rate law, rate=$k[PdCl_4^{2-}][\text{diene}]/[Cl^-]$. The mechanism is


(9)

quite similar to that proposed here for the steady hydrolysis of diketene.



We thank Daicel, Ltd. for the generous gift of diketene.

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