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Reactions of Transition-Metal-Olefin Complexes. III. Kinetics of the Oxidation of Substituted Styrenes Catalyzed by Palladium Salts in an Aqueous Tetrahydrofuran Solution[*1]

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The kinetics of the oxidation of ring-substituted styrenes catalyzed by palladium(II) salts in a homogeneous aqueous tetrahydrofuran solution containing *p*-benzoquinone have been investigated at 30°C under a nitrogen atmosphere. The rate equation was found to be identical with the one previously found for styrene, *i. e.*, $-\mathrm{d}[\mathrm{olefin}]/\mathrm{d}t = (k_{\mathrm{I}}+k_{\mathrm{II}})[\mathrm{Pd}^{2+}][\mathrm{olefin}]$, where k_{I} is the rate constant for ketone-formation and k_{II} is the rate constant for aldehyde-formation. It was found that both the proton and the chloride ion affect the rate inhibition at high concentrations and the rate acceleration at low concentrations. The product ratio of the ketone to the aldehyde decreased monotonously with the increase in proton concentration and with the increase in chloride ion concentration. An increase in the ionic strength from 0.052 to 0.787 increased the rate constants, but the ratio of the products scarcely changed at all. The substituent effects for the sites of nucleophilic attack were specific; *i. e.*, the electron-releasing substituents facilitated the formation of substituted acetophenone and diminished the formation of substituted phenylacetaldehyde. The reverse trend was found for the electron-withdrawing substituents. From these results, there is proposed a mechanism in which two active species, $[\mathrm{ArCH{=}CH_2Pd(H_2O)(OH)Cl}]$ and $[\mathrm{ArCH{=}CH_2Pd(H_2O)(OH)Cl_2}]^-$, are involved and in which the rate-determining step is the decomposition of the σ-complexes with the hydride shift to the carbonyl products.

Since the report of the palladium(II) ion oxidation of olefins by Smidt *et al.*,1) many kinetic studies of the oxidation of ethylene and some olefins by palladium salts in aqueous solutions have been reported.2) However, few kinetic studies concerning the sites of nucleophilic attack in the above oxidation of substituted olefins have been reported.3) This study was undertaken to clarify the influences of such factors as proton concentration, chloride ion concentration, ionic strength, and the substituents on the sites of nucleophilic attack in the oxidation of ring-substituted styrenes by palladium salts in a homogeneous aqueous tetrahydrofuran (THF) solution at 30°C.

Results and Discussion

The oxidations of the substituted styrenes proceeded as is shown by the following equation;

$$\mathrm{X\text{-}C_6H_4CH{=}CH_2 + H_2O + Q \xrightarrow[\mathrm{THF\text{-}H_2O}]{\mathrm{Pd^{2+}}} \underset{\mathrm{I}}{\mathrm{X\text{-}C_6H_4COCH_3}} + \underset{\mathrm{II}}{\mathrm{X\text{-}C_6H_4CH_2CHO}} + H_2Q} \quad (1)$$

(X: *p*-$\mathrm{CH_3}$, *p*-Cl, *m*-$\mathrm{CH_3}$, *m*-Cl and H)

where Q indicates the *p*-benzoquinone used as an oxidizing agent for palladium in the system and where $\mathrm{H_2Q}$ indicates hydroquinone. The reaction rates were followed by the gas chromatography of the unreacted styrenes and of the produced substituted acetophenone (I) and substituted phenylacetaldehyde (II). The reaction was first order in styrene and in palladium salts, and the ratio of acetophenone to phenylacetaldehyde was almost constant throughout the reaction.3) For substituted styrenes, the kinetic relationships were identical with that of styrene. Thus, the rate expression is:

[*1] Reported at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967; Part II of this series: H. Okada and H. Hashimoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 2152 (1967).

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1) J. Smidt, W. Hafner, R. Jira, J. Sedlmeier and R. Sieber, *Angew. Chem.*, **71**, 176 (1959).

2) For example, K. Teramoto, T. Oga, S. Kikuchi and M. Ito, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Synth. Chem. Japan)*, **21**, 298 (1963); T. Dozono and T. Shiba, *Bull. Japan Petrol. Inst.*, **5**, 8 (1963); P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964); 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).

3) H. Okada and H. Hashimoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 2137 (1966).

$$-\frac{d[\text{olefin}]}{dt} = \frac{d[\text{I}]}{dt} + \frac{d[\text{II}]}{dt} = (k_{\text{I}} + k_{\text{II}})[\text{Pd}^{2+}][\text{olefin}] \qquad (2)$$

where k_{I} and k_{II} are the second-order rate constants for substituted acetophenone (I) and substituted phenylacetaldehyde (II) respectively.

TABLE 1. THE EFFECT OF PROTON CONCENTRATION ON THE RATE CONSTANTS IN THE OXIDATION OF *p*-CHLOROSTYRENE*

$[\text{H}^+]\times10^2$ (M)	$k_{\text{I}}\times10^2$ (l/M·sec)	$k_{\text{II}}\times10^2$ (l/M·sec)
3.01	1.80	2.40
3.83	2.06	2.89
8.63	1.94	5.53
9.73	1.58	4.56
25.6	0.55	1.65

* $[\text{Pd}^{2+}]=4.41\times10^{-3}$ M
$[p\text{-ClC}_6\text{H}_4\text{CH=CH}_2]_0=[\text{Q}]_0=5.34\times10^{-2}$ M
$[\text{Cl}^-]/[\text{Pd}^{2+}]=2.00$

When the perchloric acid concentration was changed from 0.03 M to 0.25 M in the oxidation of *p*-chlorostyrene by palladium chloride in THF-water (60 : 40 vol/vol) in the absence of added salts, the values of k_{I} and k_{II} reached their maxima, as shown in Table 1. The effect of the proton concentration on the rate constants in the oxidation of *m*-methylstyrene at a constant ionic strength of 0.44 and a constant chloride ion concentration (Cl/Pd=2) in the same solvent system is shown in Fig. 1. The rate constants, k_{I} and k_{II}, had their

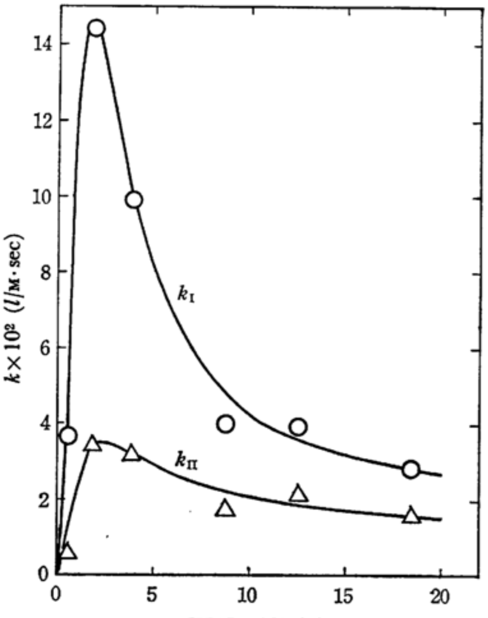

Fig. 1. The effects of proton concentration on the rate constants in the oxidation of *m*-methylstyrene.
$[m\text{-CH}_3\text{C}_6\text{H}_4\text{CH=CH}_2]_0=[\text{Q}]_0=5.34\times10^{-2}$ M;
$[\text{Pd}^{2+}]=4.41\times10^{-3}$ M; $[\text{Cl}^-]/[\text{Pd}^{2+}]=2.00$;
$\mu=0.44$
○: *m*-methylacetophenone
△: *m*-methylphenylacetaldehyde

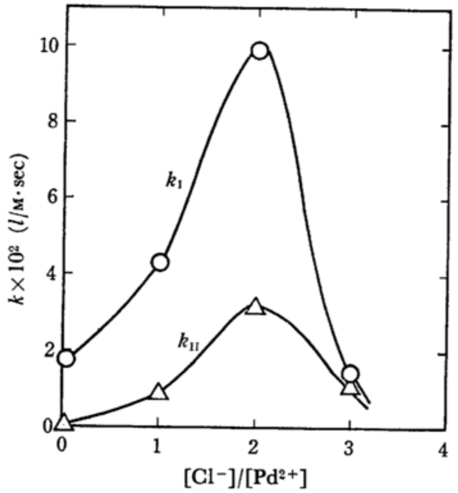

Fig. 2. The effects of chloride ion concentration on the rate constants in the oxidation of *m*-methylstyrene.
$[m\text{-CH}_3\text{C}_6\text{H}_4\text{CH=CH}_2]_0=[\text{Q}]_0=5.34\times10^{-2}$ M;
$[\text{H}^+]=3.83\times10^{-2}$ M; $[\text{Pd}^{2+}]=4.41\times10^{-3}$ M;
$\mu=0.44$
○: *m*-methylacetophenone
△: *m*-methylphenylacetaldehyde
The chloride ion concentration was varied by addition of NaCl.

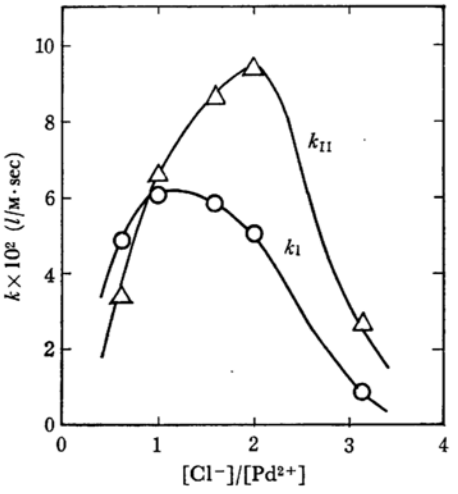

Fig. 3. The effects of chloride ion concentration on the rate constants in the oxidation of *m*-chlorostyrene.
$[m\text{-ClC}_6\text{H}_4\text{CH=CH}_2]_0=[\text{Q}]_0=5.34\times10^{-2}$ M;
$[\text{H}^+]=0.74\times10^{-2}$ M; $[\text{Pd}^{2+}]=4.41\times10^{-3}$ M;
$\mu=0.90$
○: *m*-chloroacetophenone
△: *m*-chlorophenylacetaldehyde

maximum values in a proton concentration of about 0.02 M. Therefore, it appears that k_{I} and k_{II} generally have their maximum values at low proton concentrations in these systems.

Figures 2 and 3 show the effect of the chloride ion concentration on the rate constants in the oxidation of *m*-methylstyrene and *m*-chlorostyrene at a constant ionic strength ($\mu=0.44$ and 0.90 respectively) and at a constant proton concentration (0.038 M and 0.0074 M respectively). It is obvious that, in these cases, the maximum points appear in the curves of k_{I} and k_{II} at low chloride ion concentrations, when the ratio of chloride ions to palladium ions is 2 : 1 or less.

In the oxidations of ethylene and propylene by palladium chloride in aqueous solutions in the presence of excess chloride ions, the first-order proton inhibition and the second-order chloride inhibition have been established.[4] Also, in the oxidation of styrene by palladium chloride in aqueous tetrahydrofuran, the logarithm of the rate constants of acetophenone-formation is approximately proportional to the values of the acidity function, H_0, of the system in high proton concentrations,[3] showing a first-order proton inhibition similar to that of ethylene. However, Smidt *et al.*[5] has recently reported, regarding the aqueous palladium chloride oxidation of ethylene in the presence of *p*-benzoquinone, that the rate constants have maximum values both in low proton concentrations and in low chloride concentrations; they obtained the experimental rate expression of Eq. (3):

$$-\frac{d[CH_2{=}CH_2]}{dt}=\frac{a[H^+][Cl^-]}{b+[H^+]^2[Cl^-]^3} \tag{3}$$

Although the influences of the acid concentration and the anion concentration on the rate were not independently analyzed, similar results were obtained in the oxidation of carbon monoxide by palladium chloride in aqueous dioxane in the presence of *p*-benzoquinone,[6] and in the acetoxylation of ethylene by palladium chloride or palladium acetate in acetic acid containing sodium acetate and *p*-benzoquinone.[7] Therefore, it may be concluded to be generally true in these reactions that protons and chloride ions have both effects of the rate inhibition and acceleration. These facts suggest that, under the conditions of low proton concentrations and of limited amounts of chloride ions, the mechanisms of these oxidation processes or the reaction species may differ from those proposed previously.[3,8]

In all the experiments, the ratio of the acetophenone (I) to the products, *i. e.*, $k_{\mathrm{I}}/(k_{\mathrm{I}}+k_{\mathrm{II}})$, decreased monotonously with any increase in either the proton or chloride ion concentration, independently of the maximum values of k_{I} and k_{II}, for example, from 0.86 to 0.63 in Fig. 1, from 1.00 to 0.57 in Fig. 2, and from 0.59 to 0.25 in Fig. 3. With palladium perchlorate in the absence of chloride ions, no oxidation of styrenes occurred in very low proton concentrations. While higher proton concentrations generally caused side reactions to produce ring-substituted benzaldehydes (substituents: *p*-CH_3, *m*-CH_3, *p*-Cl and *m*-Cl)

TABLE 2. THE INFLUENCE OF IONIC STRENGTH ON THE RATE CONSTANTS IN THE OXIDATION OF *m*-CHLOROSTYRENE*

μ	$k_{\mathrm{I}}\times10^2$ (l/M·sec)	$k_{\mathrm{II}}\times10^2$ (l/M·sec)	$k_{\mathrm{I}}/(k_{\mathrm{I}}+k_{\mathrm{II}})$
0.052	2.53	3.33	0.431
0.393	4.21	5.16	0.450
0.787	7.49	9.69	0.436

* $[H^+]=3.84\times10^{-2}$ M
$[m\text{-}ClC_6H_4CH{=}CH_2]_0=[Q]_0=5.34\times10^{-2}$ M
$[Cl^-]/[Pd^{2+}]=2.00$

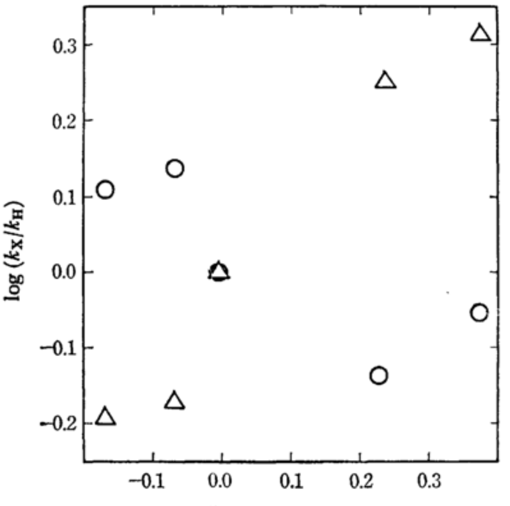

Fig. 4. The Hammett plots of the rate constants.
[substituted styrene]$_0$=[Q]$_0$=5.34×10^{-2} M;
$[H^+]=3.83\times10^{-2}$ M; $[Pd^{2+}]=4.41\times10^{-3}$ M;
$[Cl^-]/[Pd^{2+}]=2.00$; $\mu=0.052$
○: substituted acetophenone
△: substituted phenylacetaldehyde

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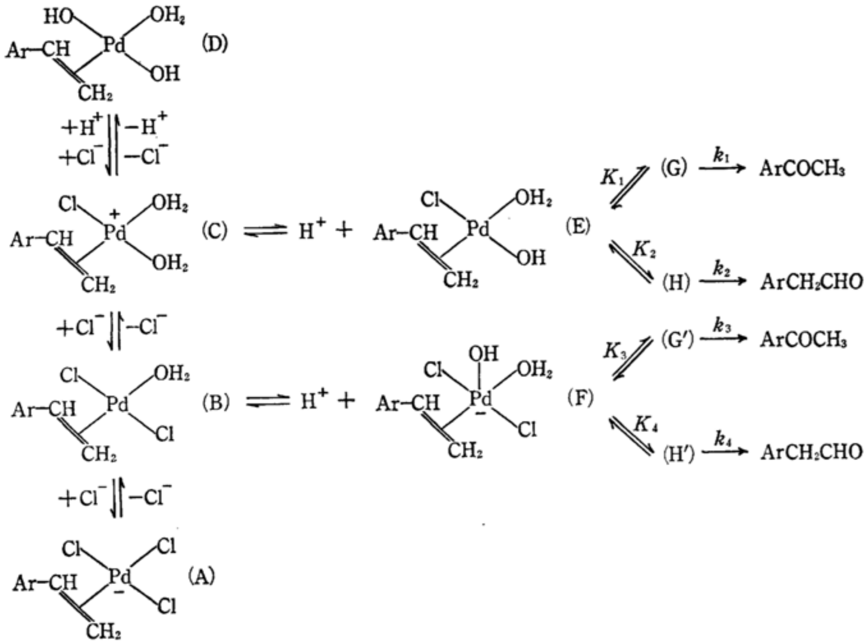
[4] I. I. Moiseev, M. N. Vargaftik and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR.*, **153**, 140 (1963); P. M. Henry, *J. Am. Chem. Soc.*, **88**, 1595 (1966).

[5] R. Jira, J. Sedlmeier and J. Smidt, *Liebigs Ann. Chem.*, **693**, 99 (1966).

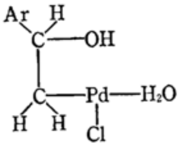
[6] A. B. Fasman, V. A. Golodov and D. V. Sokol'skii, *Zhur. Fiz. Khim.*, **38**, 1545 (1964).

[7] R. Ninomiya, M. Sato and T. Shiba, *Bull. Japan Petrol. Inst.*, **7**, 31 (1965); A. P. Velov, I. I. Moiseev and N. G. Uvarova, *Izv. Akad. Nauk SSSR., Ser. Khim.*, **1966**, 1642; I. I. Moiseev, A. P. Velov, V. A. Igoshin and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR.*, **173**, 863 (1967).

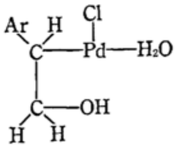
[8] J. P. Collman, in "Transition Metal Chemistry," Vol. II, ed. by R. L. Carlin, Marcel Dekker, New York (1966), p. 73.



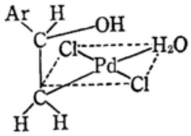
(G):



(H):



(G′):



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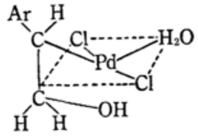

in the oxidation of the corresponding substituted styrenes, their amounts were no more than 5%.

Table 2 shows the effect of the ionic strength in the oxidation of *m*-chlorostyrene under comparable conditions. The results indicate that an increase in ionic strength considerably increases the values of both k_{I} and k_{II}, whereas it has little effect on the ratio of the products, that is to say, the value of $k_{\mathrm{I}}/(k_{\mathrm{I}}+k_{\mathrm{II}})$.

In order to obtain further information regarding the mechanism of the reaction, we have investigated the effects of the ring-substituents on the oxidation rates. One example of the Hammett plots of the rate constants under typical experimental conditions is shown in Fig. 4. The rates roughly follow the Hammett $\rho\sigma$ equation. However, the sign of ρ is opposite for the α- and β-positions; that is, it is negative for the substituted acetophenone-formation and positive for the substituted phenylacetaldehyde-formation. This shows that electron-releasing substituents accelerate the reaction at the α-position and diminish the rate at the β-position. The reverse relationship holds for electron-withdrawing substituents. When the reaction conditions, especially the proton concentration and the chloride ion concentration were varied, the ρ-values changed somewhat, but the general tendency was the same. The reverse signs of ρ-values for the α- and β-positions have also been found in the hydroboration of substituted styrenes.[9,10]

The following reaction scheme is proposed to explain all of the results obtained: 1) the effects of both rate acceleration and retardation by protons and chloride ions; 2) the influence of the proton and chloride ion concentrations on the product ratio and 3) the opposite effects of the substituents on the reaction sites. In this scheme some assumptions are involved because of the complexity of the chemical species concerned.

In the above scheme, the A, B, C, D, E and F π-complexes are in a state of equilibrium. Both

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9) J. Klein, E. Dunkelblum and M. A. Wolff, *J. Organometal. Chem.*, **7**, 377 (1967).

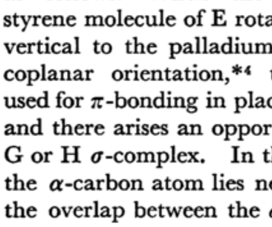
10) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

the A and D complexes may be considered to be inactive species, for at a very high chloride ion concentration the reaction almost stopped, and in the complete absence of chloride ions, *i. e.*, in a palladium perchlorate or palladium hydroxide solution, the reaction scarcely proceeded at all. The specific effects of the protons and chloride ions on the rate and on the product distribution described above suggest that at least two active species participate in the reaction, because it is difficult to explain those effects in terms of only one reactive species. We propose that the E and F π-complexes are active species, with E more reactive than F. Although a five-coordinated species such as F could not be isolated, it seems reasonable to assume its existence, as has been proposed by Khan *et al.*11) for the stereospecific hydrogenation of benzyl derivatives.*3 At lower proton and chloride ion concentrations, the reaction path through the E complex is predominant. The higher the chloride ion concentration, the more does the reaction proceed through the F complex. The net effects will result the maximum of the rate constant at a given proton concentration and at a given chloride ion concentration respectively.

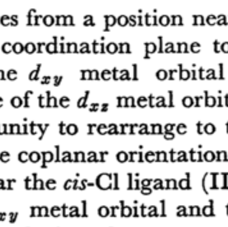
From the observed substituent effects, it is reasonable to consider that the transformation of the π-complex to the σ-complex is probably a reversible step and that the decomposition of the σ-complex to carbonyl compounds, involving a hydride shift, is the rate-determining step. If the conversion of the π-complex to the σ-complex were rate-determining, the electron-withdrawing substituents would facilitate this transformation and the same sign of the ρ-value would be observed in the Hammett plots regardless of the reaction sites.

In the σ-complexes the effects of the ring-substituents may be stronger at the α-carbon than at the β-carbon. Thus, the electron-releasing groups increase the electron density at the α-carbon in the G and G′ σ-complexes and facilitate the hydride transfer from the α-carbon to the β-carbon atom and interrupt the hydride transfer from the β-carbon to the α-carbon in the H and H′ σ-complexes. The tendency is the reverse in the case of the electron-withdrawing groups.

The ratio of the ketone to the aldehyde produced is determined by the ratio of the product of the rate constant and the equilibrium constant, for example, k_1K_1 to k_2K_2 and k_3K_3 to k_4K_4. The monotonous decrease in the ratio of $k_{\rm I}/(k_{\rm I}+k_{\rm II})$ with increases in both the proton and chloride ion concentrations means that, in the reaction path through the F π-complex, k_3K_3 may be considered to be nearly equal to k_4K_4. The reason for this may be as follows. When the coordinated substituted styrene molecule of E rotates from a position nearly vertical to the palladium coordination plane to a coplanar orientation,*4 the d_{xy} metal orbital is used for π-bonding in place of the d_{xz} metal orbital, and there arises an opportunity to rearrange to the G or H σ-complex. In the coplanar orientation, if the α-carbon atom lies near the *cis*-Cl ligand (III), the overlap between the d_{xy} metal orbital and the π-antibonding orbital of substituted styrene will be prevented by the steric hindrance resulting from the interaction between the aryl group and chloride ions. Moreover, since the β-carbon atom lies far from the *cis*-OH ligand,*5 the conversion from the E π-complex to the H σ-complex, which is preferable for aldehyde formation, would be difficult. On the contrary, if the β-carbon atom lies near the *cis*-Cl ligand (IV), the $p_\pi{}^*$-d_{xy} overlap will not be prevented and then the α-carbon atom will lie near the *cis*-OH ligand.*5 Thus, transformation to the G σ-complex, which is preferable for ketone formation, would be predominant.



III



IV

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11) A. M. Khan, F. J. McQuillin and I. Jardine, *Tetrahedron Letters*, **1966**, 2649.

*3 A five-coordinated complex is well known for some group VIII metals; for example: $[Pt(SnCl_3)_5]^{3-}$ and $[HPt(SnCl_3)_4]^{3-}$,12) $[CH_3(CH_2)_4CORhCl_2(PPh_3)_2]$,13) $[RuCl_2(PPh_3)_3]$,14) and so on.15)

12) R. V. Lindsey, Jr., G. W. Parshall and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965); G. W. Parshall, *ibid.*, **88**, 704 (1966).

13) J. Tsuji and K. Ohno, *ibid.*, **88**, 3452 (1966).

14) S. J. L. Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 782 (1965).

15) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York (1958), p. 186.

*4 It is supposed that the substituted styrene molecule rotates with the coordination bond as axis, as in the case of ethylene rotation in bis-ethylene-π-cyclopentadienyl rhodium(I).16)

16) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

*5 Although in $[C_2H_4PdCl_2]_2$ the axis of the ethylene molecule is perpendicular to the plane of the dimer and the center of the ethylene double bond lies on the plane of the dimer,17) in $[C_6H_5CH{=}CH_2PdCl_2]_2$ the styrene molecule coordinates to palladium(II) not at the center of the double bond but at the point near β-carbon atom.18) The NMR spectra of such assymmetrically-substituted ethylene complexes as $K[(C_6H_5CH{=}CH_2)PtCl_3]$19) and $[CH_3CH{=}CH_2PtCl_2(C_5H_5NO)]$20) suggest that the CH_2 groups are positioned nearer to the platinum atom and that the olefin molecules are slightly twisted out of the original ethylene plane, with the bulky group away from and the *trans*-hydrogen atom toward the platinum.

17) J. N. Dempsey and N. C. Baenziger, *ibid.*, **77**, 4984 (1955).

18) J. R. Holden and N. C. Baenziger, *ibid.*, **77**, 4987 (1955).

19) H. P. Fritz, K. E. Schwarzhans and D. Sellman, *J. Organometal. Chem.*, **6**, 551 (1966).

20) P. D. Kaplan and M. Orchin, *Inorg. Chem.*, **6**, 1096 (1967).

In a vertical orientation such as in the F complex, the overlap between the p_π* orbital of olefin and the d_{xz} palladium orbital is at a maximum and an interaction with a fifth hydroxide ligand above or below the square plane of the four-coordinated planar complex may be expected. Because of the rapid rotation of olefin and/or the two coordination sites for the hydroxide ligand, the probability of an attack of the hydroxide ion on either the α-position or the β-position will be nearly equal. This may decrease the selective formation of either carbonyl compound from F. The transformation of the E π-complex to the G or H σ-complex may involve a four-center-type transition state. The four-center-type transition state has also been proposed for the rearrangement of the hydrido-π-olefin complex to a σ-alkyl complex in the hydrogenation of fumaric acid by ruthenium(II) chloride.[21]

Experimental

Materials. In the oxidation of *p*-chlorostyrene, *p*-dibromobenzene was used as an internal reference in the gas chromatographic quantitative analysis. It was the same material as was employed in the oxidation of styrene.[3] Bromomesitylene was used as an internal reference in the oxidations of the other three substituted styrenes; it was prepared by the bromination of mesitylene,[22] bp: 136—137°C/50 mmHg. Ring-substituted styrenes were prepared by the dehydration of the alcohols which were formed by the action of the corresponding ring-substituted phenylmagnesium bromide and acetaldehyde[23]; *p*-methylstyrene, bp: 61.5—62.5°C/13 mmHg; *m*-methylstyrene, bp: 61.0—62.0°C/13 mmHg; *p*-chlorostyrene, bp: 90.5—91.3°C/30 mmHg; *m*-chlorostyrene, bp: 62.0—63.0°C/7—8 mmHg. All the substituted styrenes described above were confirmed to be pure by means of g.l.c. and by means of their NMR spectra.

Kinetic Runs. The unreacted styrenes and reaction products were analyzed by means of g.l.c., using a 3-m copper column packed with 20% silicon DC 550 on Diasolid, at a hydrogen gas flow rate of 80 m*l*/min at 130°C. The other experimental techniques used in this study have been described previously.[3]

Identification of the Products. The ring-substituted acetophenones, phenylacetaldehydes, and benzaldehydes were identified by means of g.l.c. and their IR and/or NMR spectra in comparison with those of the authentic samples synthesized by the methods cited below or by similar methods. The boiling points of the authentic samples are also given below. The IR spectra were taken on neat liquid or on KBr tablets. The NMR spectra were measured by a Japan Electron Optics C-60 chemical analyzer at 60 Mc in carbon tetrachloride, containing tetramethylsilane as an internal reference.

Compounds Obtained in the Oxidation of p-Methylstyrene. *p-Methylacetophenone.*[24] bp: 225—226.5°C/760 mmHg. IR: 1184, 1285, 1385 and 1677 cm^{-1}.

p-Methylphenylacetaldehyde.[25] bp: 104—129°C/20 mmHg. IR: 810, 1725 and 2718 cm^{-1}.

p-Methylbenzaldehyde.[26] bp: 107.0—109.0°C/32 mmHg. IR: 1389, 1690, 2736 and 2816 cm^{-1}.

Compounds Obtained in the Oxidation of m-Methylstyrene. *m-Methylacetophenone.*[27] bp: 107.0—107.5°C/18 mmHg. NMR: 7.60 τ (3H, singlet); 7.50 τ (3H, singlet); 2.10—2.70 τ (4H, multiplet).

m-Methylphenylacetaldehyde.[28] bp: 84.5—85.0°C/8 mmHg. IR: 703, 783, 1740 and 2710 cm^{-1}. NMR[*6]: 7.77 τ (3H, singlet); 6.62 τ (2H, doublet); 2.80—3.20 τ (4H, multiplet).

m-Methylbenzaldehyde.[26] bp: 93.0—94.0°C/17 mmHg. IR: 685, 780, 1700 and 2710 cm^{-1}. NMR: 7.55 τ (3H, singlet); 2.10—2.60 τ (4H, multiplet); -0.17 τ (1H, singlet).

Compounds Obtained in the Oxidation of p-Chlorostyrene. *p-Chloroacetophenone.*[29] bp: 136.0—136.5°C/36 mmHg. IR: 1177, 1264, 1359 and 1690 cm^{-1}. NMR: 7.42 τ (3H, singlet); 2.10—2.55 τ (4H, multiplet).

p-Chlorophenylacetaldehyde.[28] bp: 134—136°C/29 mmHg. IR: 1721, 2740 and 2820 cm^{-1}.

p-Chlorobenzaldehyde. mp: 46.0—47.0°C, bp: 108.0—110.0°C/ 25 mmHg. IR: 769, 1325 and 1690 cm^{-1}. NMR: 2.10—2.70 τ (4H, multiplet); 0.03 τ (1H, singlet).

Compounds Obtained in the Oxidation of m-Chlorostyrene. *m-Chloroacetophenone.*[27] bp: 109°C/12 mmHg. IR: 670, 800, 1280, 1360 and 1690 cm^{-1}. NMR: 7.55 τ (3H, singlet); 2.20—2.90 τ (4H, multiplet).

m-Chlorophenylacetaldehyde. NMR: 6.51 τ (2H, doublet); 2.70—3.10 τ (4H, multiplet); 0.45 τ (1H, triplet). All of the compounds listed above had the same retention time as the authentic samples in g.l.c.

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