Kinetics and Mechanism of Oxidation of Styryl Biphenyl and Styryl Fluorenyl Ketones by Pyridinium Chlorochromate

Dae Dong Sung[*] **and P. Ananthakrishna Nadar**[†]

Department of Chemistry, Dong-A University, Pusan 604-714, Korea
[†]*Department of Chemistry, Annamalai University, Annamalainagar-608002 INDIA*
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The kinetics of oxidation of substituted styryl 4-biphenyl ketones and of substituted styryl 2-fluorenyl ketones by pyridinium chlorochromate (PCC) have been studied in 90% acetic acid- 10% water (v/v) containing perchloric acid and $NaClO_4$ at 10^0, 20^0, 30^0 and 40 °C. The reactions are first order in styryl ketones and PCC. The second order rate constants are well correlated only with σ^+ constants implying development of positive charge adjacent to benzene ring in the transition state. The effects of varying $[HClO_4]$ and the percentage of acetic acid on the reactions have also been analysed. A mechanism involving nucleophilic attack of PCC leading to an unsymmetric intermediate from which epoxides are formed is proposed.

Introduction

The kinetics of cycloalkanes,[1-5] bromination[6,7] and oxidation by chromic acid,[8] Tl(III),[9] perbenzoic acid,[10] Ce(IV)[11] and Ce(IV) catalysed by Ru(VI)[12] of chalcones have been extensively investigated by many workers. Even though those extensive investigation, the formulation of a detailed mechanism for chromium(VI) oxidation of olefins is rather difficult because of the diversity of reactions.[13-15] The reaction mechanism for chromium(VI) oxidations on the double bond is suggested to give an intermediate like in epoxidation or a kind of three membered ring product.[14]

These reactions on the double bond proceeds probably through a carbonium ion type intermediate. The conclusion which can be drawn from the kinetic data for chromium(VI) oxidation is that the transition state must be symmetrical. The chromium oxidation reaction does not seem to be very sensitive to steric effect. However the most significant rate effect which can be ascribed to steric effect hindrance is observed for α-*tert*-butyl-β,β-dimethylethylene which reacts almost three times slower than ethylene.[14]

The insensitivity of the chromium(VI) oxidation to steric effects would be caused that the formation of a direct chromium to carbon bond in the transition state is unlikely. A proposal for the reaction mechanism is consistent with most experimental data including the lack of stereospecificity in the formation of epoxides.

The chromium(VI) oxidation on the double bond is limited to alkenes or their derivatives. In contrast, the more electron rich enol ethers on allylic ketones react with pyridinium chlorochromate (PCC) at room temperature to give high yields of esters and epoxides.[16] This reaction would be involved initial attack upon to olefin by the reagent to afford an unstable cyclic intermediate which decomposes by chromium-oxygen bond cleavage in the carbonyl compound.

Recently the kinetics of oxidation of styryl phenyl and styryl methyl ketones using PCC has been reported.[17] The reactions are proceeded along with the change of substituent on the phenyl ring. Although the chromium oxidation is

expected to be seen a high stereospecificity in the formation of epoxides, the previous works have not investigated yet for different functional group linked to the ketone site in the styryl ketones. Furthermore the report has not brought out clearly the mechanism of the reaction. To investigate for structure-reactivity correlation precisely, the chromium oxidation by PCC are carried out for the oxidation reaction of styryl biphenyl and styryl fluorenyl ketones by PCC.

Experimental Section

Materials. The styryl 4-biphenyl ketones and the styryl 2-fluorenyl ketones were prepared by treating a mixture of the appropriate benzaldehyde (0.01 mol) in ethanol (50 mL) with 4-acetylbiphenyl (0.01 mol) and 2-acetylfluorene (0.01 mol) respectively in the presence of 10% sodium hydroxide solution (5 mL). All the compounds were recrystallized from ethanol and characterized by elemental analysis (Table 1). The literature procedures were employed to prepare 4-acetylbiphenyl[18] and 2-acetylfluorene.[19]

The PCC was prepared by the method of Corey and Suggs[20] as modified by Agarwal *et al*.[21] Other chemicals employed were of analytical grade.

Kinetic Methods. The kinetic measurements were carried out spectrophotometrically in a Perkin-Elmer-Hitachi 200 UV/visible spectrophotometer whose cell was connected to a glass bulb through the tail of the latter. Two side arms with stopcocks were fused into the bulb. The bulb and the arms, including stopcocks and tail were coated with teflon tape. The whole assembly was flushed with nitrogen gas and thermostated. The solutions of styryl ketones in aqueous acetic acid were taken in one arm and that of PCC and an appropriate amount of $HClO_4$ and $NaClO_4$ in the same solvent was taken in the other. Nitrogen gas was bubbled through the solutions to exclude oxygen. After thermal equilibration the solutions from the arms were run into the bulb and mixed thoroughly and made to flow quickly into the thermostated cell of the spectrophotometer. The rate of the reaction was followed at 350 nm. The variation of rate

Table 1. Analytical Data for Styryl Ketones Synthesized for The Oxidation Reaction

Substituent	Formula	m.p (°C)	Found	% (Required)
			C	H
Substituted Styryl 4-Biphenyl Ketones				
H	$C_{21}H_{16}O$	153-154[a]	_	_
p-OH	$C_{21}H_{16}O_2$	109-110	84.01	5.30
			(84.00	5.33)
p-OCH$_3$	$C_{22}H_{18}O_2$	123-124	84.03	5.70
			(84.08	5.73)
p-CH$_3$	$C_{22}H_{18}O$	141-142	88.52	6.01
			(88.59	6.04)
m-CH$_3$	$C_{22}H_{18}O$	150-151	88.53	6.06
			(88.59	6.04)
p-Cl	$C_{21}H_{15}ClO$	182-183	79.00	4.75
			(79.12	4.71)
m-Cl	$C_{21}H_{15}ClO$	152-153	79.10	4.68
			(79.12	4.71)
m-NO$_2$	$C_{21}H_{15}NO_3$	183-184	76.52	4.52
			(76.60	4.56)
p-NO$_2$	$C_{21}H_{15}NO_3$	190-191	76.53	4.51
			(76.60	4.56)
Substituted Styryl 2-Fluorenyl Ketones				
H	$C_{22}H_{16}O$	150-151[b]	-	-
m-Cl	$C_{22}H_{15}ClO$	43-44	79.81	4.56
			(79.88	4.54)
p-Cl	$C_{22}H_{15}ClO$	84-85	79.80	4.52
			(79.88	4.54)
p-OH	$C_{22}H_{16}O_2$	92-93	84.58	5.18
			(84.62	5.13)
p-OCH$_3$	$C_{23}H_{18}O_2$	94-95	84.70	5.56
			(84.66	5.52)
m-NO$_2$	$C_{22}H_{15}NO_3$	77-78	77.45	4.45
			(77.42	4.40)
p-NO$_2$	$C_{22}H_{15}NO_3$	85. 86	77.40	4.35
			(77.42	4.40)

[a]Lit.[10a] m.p., 156. [b]Lit.[11a] m.p., 150.

Figure 1. Plot of k_{obs} against the concentrations of styryl 4-biphenyl ketone for the chromium oxidation reactions

where λ' is the measurement of optical density at 350 nm and at the time, t' on the spectrum of the chromium oxidation reaction and λ is the measurement of optical density at the time, t and at the same wavelength.

The pseudo-first-order rate constants, k_{obs} are linearly correlated with the concentrations of styryl ketones. The second order rate constants, k_2 have been determined from the following Eq. (3),

$$k_{obs} = k_2[\text{styryl ketone}] \qquad (3)$$

For example, under the condition given in Table 3, 3.60 $\times 10^{-3}$ L $\cdot$ mol^{-1}sec^{-1} for the second-order rate constant of styryl 4-biphenyl ketone at 30 °C was obtained from the slop on the graph which was plotted by the variation of the pseudo-first-order rate constants against the concentrations of styryl 4-biphenyl ketone as shown in Figure 1. Good straight line plots of k_{obs} versus the concentration of styryl 4-biphenyl ketone or styryl 2-fluorenyl ketone were obtained in all cases.

Product Analysis. Maintaining all kinetic experimental conditions each styryl ketone and PCC were mixed together under nitrogen excluding light and kept at 30 °C for two days. After this period, the acid was neutralised with NaHCO$_3$ and the products were extracted with ether. The extract was dried (MgSO$_4$) and the residues obtained after evaporation of ether were subjected to column chromatography employing alumina to separate the products from the unreacted ketones. The products showed single spots on TLC plate. They were recrystallized and analysed and found to be epoxides. Their elemental data are presented in Table 2.

Stoichiometry. An excess of PCC was allowed to react with each styryl ketone under kinetic conditions. The unreacted PCC remained after completion of the reaction showed
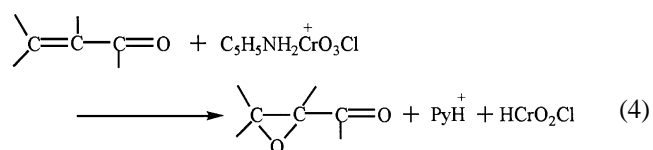
constant with the concentration of perchloric acid, [HClO$_4$] shows the order in perchloric acid as one. This means that the chromium oxidation is acid-catalysed reaction. Therefore the kinetic expression predicted as follows,

$$\text{rate} = k_{obs}[\text{styryl ketone}][\text{PCC}][\text{HClO}_4] \qquad (1)$$

where [styryl ketone] is the concentration of styryl 4-biphenyl ketones or styryl 2-fluorenyl ketones. A pseudo-first-order reaction is observed when the concentration of styryl ketone is so high as 24 times more compared to the concentration of PCC. The initial concentration of PCC in all kinetic runs was about 1.0×10^{-3} mol $\cdot$ L^{-1} and that of styryl ketones was about 2.4×10^{-2} mol $\cdot$ L^{-1}. Here the concentration of perchloric acid [HClO$_4$] is 90 to 210 times compared to [PCC] and [styryl ketone]. The observed rate constants are obtained by the following Eq.[22] (2),

$$\ln(\lambda'-\lambda) = -k_{obs}t + \text{constant} \qquad (2)$$

$$(4)$$

Table 2. Analytical Data of Epoxides Produced from the Oxidation of Substituted Styryl Ketones

Substituent	Formula	m.p (°C)	Found C	% (Required) H
Epoxides	From Substituted Styryl	4-Biphenyl	Ketones	
H	$C_{21}H_{16}O_2$	70-71	83.92	5.21
			(84.00	5.33)
p-OH	$C_{21}H_{16}O_3$	86-87	79.68	5.00
			(79.75	5.06)
p-OCH₃	$C_{22}H_{18}O_3$	80-81	79.62	5.13
			(80.00	5.45)
p-CH₃	$C_{22}H_{18}O_2$	77-78	84.01	5.68
			(84.08	5.73)
m-CH₃	$C_{22}H_{18}O_2$	69-70	84.00	5.69
			(84.08	5.73)
p-Cl	$C_{21}H_{15}ClO_2$	101-102	75.21	4.40
			(75.34	4.48)
m-Cl	$C_{21}H_{15}ClO_2$	114-115	75.22	4.41
			(75.34	4.48)
m-NO₂	$C_{21}H_{15}NO_4$	74-75	73.00	4.29
			(73.04	4.35)
p-NO₂	$C_{21}H_{15}NO_4$	64-65	73.00	4.30
			(73.04	4.35)
Epoxides	From Substituted Styryl	2-Fluorenyl	Ketones	
H	$C_{22}H_{16}O_2$	61-62	84.56	5.02
			(84.62	5.13)
m-Cl	$C_{22}H_{15}ClO_2$	68-69	76.12	4.27
			(76.19	4.33)
p-Cl	$C_{22}H_{15}ClO_2$	78-79	76.11	4.28
			(76.19	4.33)
p-OH	$C_{22}H_{16}O_3$	90-91	80.41	4.79
			(80.49	4.88)
p-OCH₃	$C_{23}H_{18}O_3$	86-87	80.62	5.20
			(80.70	5.26)
m-NO₂	$C_{22}H_{15}NO_4$	95-96	73.89	4.16
			(73.95	4.20)
p-NO₂	$C_{22}H_{15}NO_4$	65-66	73.90	4.15
			(73.95	4.20)

1 : 1 stoichiometry and thus the oxidation is believed to proceed according to Eq. (4) involving two electron transfer.

Polymerization Test. Under the kinetic conditions, the reaction was carried out in the presence of added acrylonitrile. No polymerization occurred to acrylonitrile indicating the absence of radicals in the reaction.

Results and Discussion

The plots of log[PCC] versus time in all cases were linear indicating that the reaction is first order in PCC. The first-order rate constants are independent of the initial concentration of PCC. The rate measurements studied by varying the concentration of styryl ketones show that the order in all the ketones is one . It is observed that perchloric acid influences the rate very much. The rate constants are increased nearly

Table 3. The Second Order Rate Constants ($k_2 \times 10^3$ L·mol^{-1}·sec^{-1}) and Activation Parameters for the Oxidation of Substituted Styryl Ketones

Substituent X	Temp (°C) 10	20	30	40	Ea (kcal/mol)	$\Delta H^{\ddagger}_{283}$ (kcal/mol)	$\Delta S^{\ddagger}_{283}$ e.u
X—C₆H₄—CH=CH—CO— (biphenyl)							
H	0.86	1.75	3.60	7.23	12.8	12.2	-36.1
p-OH	6.52	13.40	27.60	53.70	12.4	11.8	-30.1
p-OCH₃	4.05	8.20	16.50	33.15	12.5	11.9	-31.1
p-CH₃	1.70	3.54	7.17	13.98	12.6	12.0	-32.5
m-CH₃	1.12	2.19	4.41	8.70	12.0	11.4	-35.4
p-Cl	0.69	1.40	2.86	6.41	13.7	13.1	-30.2
m-Cl	0.48	0.98	1.91	3.77	12.9	12.3	-33.9
m-NO₂	0.26	0.49	1.02	2.26	13.6	13.0	-32.7
p-NO₂	0.20	0.41	0.84	1.78	13.7	13.1	-32.8
X—C₆H₄—CH=CH—CO— (fluorenyl)							
H	1.14	2.21	4.50	9.07	11.9	11.3	-35.7
m-Cl	0.54	1.13	2.27	4.76	12.8	12.2	-34.0
p-Cl	0.95	1.81	3.58	7.26	12.0	11.4	-35.7
p-OH	8.24	16.65	33.40	67.00	11.2	10.6	-34.2
p-OCH₃	5.20	10.60	21.65	42.36	11.3	10.7	-34.8
m-NO₂	0.34	0.63	1.30	2.85	13.4	12.8	-32.8
p-NO₂	0.26	0.57	1.08	2.25	13.5	12.9	-30.9

1.5 times at 30 °C when there is an increase of 2.5 fold in the concentration of perchloric acid in both the series of styryl ketones (Table 4). The plots of logk_1 versus the concentration of HClO₄ are linear with unit slope showing the order with respect to HClO₄ as one. This suggests that HClO₄ is involved in protonating PCC in the reaction and that the protonated form of the PCC takes part in the rate determining step.[23]

The rate of oxidation of the parent styryl ketones was studied by changing the solvent mixtures from 70% acetic acid-30% H₂O (v/v) to 90% acetic acid-10% water (v/v). It was observed that the increase in the proportion of acetic acid increased the rate. For example, as given in Table 5, $10^5 k_1$

Table 4. Dependence of Rate Constants on [HClO₄] for the Oxidation of Substituted Styryl Ketones

Solvent : Acetic acid-water (90 : 10% v/v)
[Styryl 4-biphenyl ketone] = [Styryl 2-fluorenyl ketone] = 0.024 mol·L⁻¹
[PCC] = 0.00 1mol·L⁻¹; [NaClO₄] = 0.09 mol·L⁻¹

Temp. 30 °C			Temp. 30 °C		
Styryl 4-biphenyl ketone			Styryl 2-fluorenyl ketone		
[HClO₄] mol·L⁻¹	$k_1 \times 10^5$ sec⁻¹	$k_2 \times 10^3$ L·mol⁻¹·sec⁻¹	[HClO₄] mol·L⁻¹	$k_1 \times 10^5$ sec⁻¹	$k_2 \times 10^3$ L·mol⁻¹·sec⁻¹
0.084	6.16	2.57	0.084	7.70	3.21
0.126	6.92	2.88	0.126	8.65	3.60
0.168	7.59	3.16	0.168	9.49	3.95
0.210	8.64	3.60	0.210	10.80	4.50

Table 5. Dependence of Rate Constants for the Oxidation of Substituted Styryl Ketones on Acetic acid-Water Composition at 30 ºC

[Styryl 4-biphenyl ketone] = [Styryl 2-fluorenyl ketone] = 0.024 mol · L⁻¹
[PCC] = 0.001 mol · L⁻¹; [NaClO₄] = 0.09 mol · L⁻¹
[HClO₄] = 0.210 mol · L⁻¹

Solvents*	Styryl 4-biphenyl ketone		Styryl 2-fluorenyl ketone	
	$k_1 \times 10^5$ sec⁻¹	$k_2 \times 10^3$ L · mol⁻¹ · sec⁻¹	$k_1 \times 10^5$ sec⁻¹	$k_2 \times 10^3$ L · mol⁻¹ · sec⁻¹
90	8.64	3.60	10.8	4.50
85	7.48	3.12	9.02	3.76
80	6.31	2.63	7.61	3.17
75	5.40	2.25	6.20	2.58
70	4.79	2.00	5.48	2.28

*Acetic acid composition (v/v %)

values increased from 4.79 to 8.64 s⁻¹ and $10^3 k_2$ values increased from 2.00 to 3.60 L · mol⁻¹ · sec⁻¹ for styryl 4-biphenyl ketone when the percentage of acetic acid was increased from 70 to 90%. For the same change in solvent composition the increase in $10^5 k_1$ was from 5.48 to 10.8 s⁻¹ and the increase in $10^3 k_2$ was from 2.28 to 4.50 L · mol⁻¹ · sec⁻¹ for styryl 2-fluorenyl ketone. As the dielectric constant increases the rate falls. A plots of log$k$ versus (ε–1/2ε) is linear with negative slope suggesting that the reaction investigated is one of ion-dipole type[24] and that PCC is protonated.

Substituent Effects. The second order rate constants for the oxidation of substituted styryl 4-biphenyl ketones and substituted styryl 2-fluorenyl ketones at different temperatures in 90% acetic acid-10% water (v/v) containing 0.21 mol · L⁻¹ HClO₄ and 0.09 mol · L⁻¹ NaClO₄ are presented in Table 5. The data show that the reaction is accelerated by electron releasing substituents while electron withdrawing substituents retard the reaction. A correlation of logk_2 with Hammett σ constants in the case of substituted styryl 4-biphenyl ketones gives the correlation coefficient r = 0.956 with standard deviation s = 0.133 at 10 ºC. The electron releasing groups such as *p*-OH, *p*-OCH₃ and *p*-CH₃ deviate considerably from the linear plot and they demand more negative σ values for correlation. A similar correlation for the same ketones with σ^0 values is very much poor with r = 0.910 and s = 0.170 at 10 ºC. In the case of substituted styryl 2-fluorenyl ketones the correlation with σ constants gives r = 0.968 and s = 0.127 and that with σ^0 constants gives r = 0.938 with s = 0.152 at 10 ºC. Here too, the electron releasing substituents like *p*-OH and *p*-OCH₃ deviate considerably and demand large negative σ values for correlation. However, all substituents show excellent fit with Brown's σ^+ values generating equations (5) and (6) for styryl 4-biphenyl ketones and styryl 2-fluorenyl ketones respectively at 10 ºC.

$$\log k_2 = -1.168\sigma^+ - 3.526 \qquad (5)$$
$$(\pm 0.0295) \quad (\pm 0.0899)$$
$$r = 0.998; \quad s = 0.0422$$

$$\log k_2 = -1.160\sigma^+ - 3.384 \qquad (6)$$
$$(\pm 0.0740) \quad (\pm 0.0247)$$
$$r = 0.999 \qquad s = 0.0348$$

Mechanism of the Reaction. A considerable amount of work has been done to understand the mechanism of oxidation of olefins[25] and chalcones[8] by chromic acid. Several mechanisms have been proposed under a variety of conditions. In many cases epoxides are isolated as reaction products and in some cases the reaction products obtained are explained in terms of epoxide intermediates.[26] The epoxides are formulated either through a carbonium ion intermediate or through a cyclic chromium (IV) ester. It has also been reported that in the oxidation of olefins by chromic acid in acetic acid solution, besides epoxides, diols and diacetates are also isolated and depending on reaction conditions complex mixtures of products are isolated.[27]

Awasthy and Roček[28] in their investigation on the oxidation of olefins by chromium (VI) propose that the rate-limiting step is a symmetric eletrophilic attack of chromium (VI) on the double bond and formulate the reaction similar to the epoxidation of olefins by peracids and consider that the oxygen transferred to the olefin comes from an OH group.

It is important to mention here that no investigation on the oxidation of styryl ketones by protonated PCC, which has shed light clearly on the mechanism of the reaction, is available in the literature so far. Further, the systems investigated by Awasthy and Roček contain double bonds to which are attached a number of activating alkyl groups. But the systems under consideration are chalcones which contain olefinic double bonds to which strong deactivating carbonyl group is attached whose polarization creates positive charge at the double bond. Furthermore, the chromium in protonated PCC has a net positive charge while in chromic acid it does not possess such a charge.

As the second-order rate constants excellently correlate with σ^+ constants, in this study, giving negative ρ values, there is reason to believe that positive charge is created in the transition state which is stabilised by resonance. Under such circumstances only a mechanism involving nucleophilic attachment is probable. But the formation of transition state I leading to an intermediate II is highly unlikely, for I visualises development of positive charge at adjacent atoms and in II there is a direct linkage between carbon and chromium.

I   II
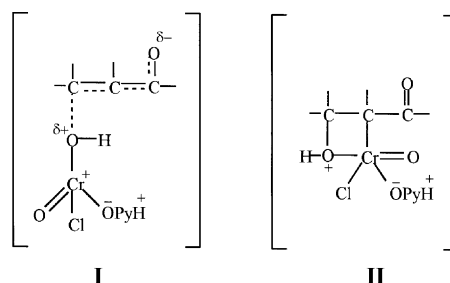
Such a linkage would result in large steric effect as has

Scheme 1
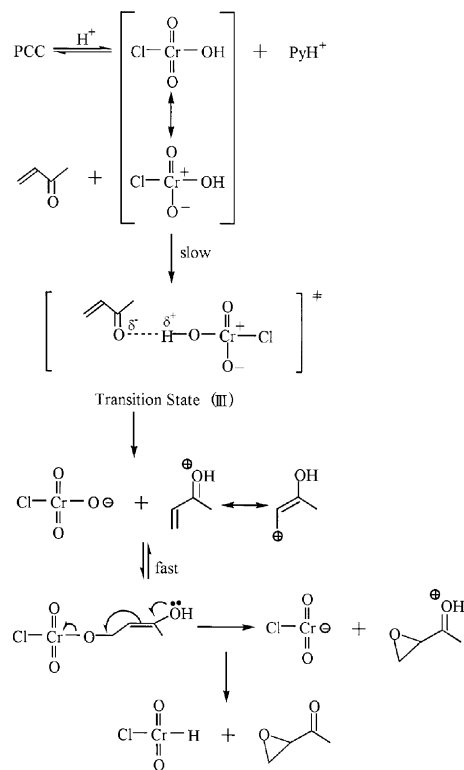
been observed in the case of the formation of Ag$^+$ complexes and in the Pd(II) oxidation with olefins where direct linkage between metals and carbon exists. Thus we believe that the rate-determining step in the oxidation of chalcones by protonated PCC is the approaching step of the hydrogen atom of protonated PCC to the carbonyl oxygen of styryl ketone as shown in Scheme 1.

To find out the electronic effect by adjacent functional group to keto-carbon, the second-order rate constants for different functional groups are compared. The order of magnitude of second-order rate constant for the oxidation reaction of styryl ketone is fluorenyl > biphenyl > phenyl[17] > methyl[17] in the same condition.

It is predicted that the proton transfer occurs firstly from the hydroxychromate to the oxygen of the styryl ketone. In order to draw a more detailed mechanistic conclusion, the activation thermodynamic parameters are compared to the results in Table 3 and in data reported previously.[17] The activation energies show in the range of 50.4-57.5 kJ $\cdot$ mol^{-1} (12.0-13.7 kcal $\cdot$ mol^{-1}) for biphenyl, 47.0-56.7 kJ $\cdot$ mol^{-1} (11.2-13.5 kcal $\cdot$ mol^{-1})[17] for fluorenyl, 51.9-69.3 kJ $\cdot$ mol^{-1} for phenyl[17] and 57.2-87.6 kJ $\cdot$ mol^{-1} for methyl. Also the activation enthalpies show in the range of 47.9-55.0 kJ $\cdot$ mol^{-1} (11.4-13.1 kcal $\cdot$ mol^{-1}) for biphenyl, 44.5-54.2 kJ $\cdot$ mol^{-1} (10.6-12.9 kcal $\cdot$ mol^{-1}) for fluorenyl, 49.3-66.7 kJ $\cdot$ mol^{-1} for phenyl[17] and 54.6-85.0 kJ $\cdot$ mol^{-1} for methyl.[17]

In the case of methyl, the activation energy and enthalpy show higher ranges than other functional groups (biphenyl, phenyl and fluorenyl) adjacent to keto carbon of substituted styryl ketone. This means that the oxidation reaction for substituted styryl methyl ketone is influenced by the methyl

group much more than other functional groups.

The isokinetic relationship[27] is applied to this study in other to obtain the isokinetic temperature. However, the linearity does not appear when the variation in activation entropies are plotted against activation enthalpies. On the other hand the difference of activation enthalpy ($\Delta\Delta H^{\neq}$) and the difference activation entropy ($\Delta\Delta S^{\neq}$) are well correlated to the isokinetic relationship. The isokinetic temperatures are calculated as high as 364-497 K for biphenyl, 347-446 K for fluorenyl, 420-741 K[17] for phenyl and 472-2249 K[17] for methyl compared to the much lower experimental temperatures. This trend means that the oxidation reactions of substituted styryl ketones are controlled mainly by the enthalpy factor.[28] Therefore the reaction series would be affected by the internal reaction energy. This internal energy may contribute to the activation enthalpy much more than does the external energy affected by solvent effect, etc.. On this view, the order of the magnitude of the enthalpy controlling effect estimates as methyl > phenyl > biphenyl > fluorenyl.

In the case of fluorenyl the the low enthalpy contribution to the oxidation reaction might be due to the proton transfer which occurs easily, and then in the next step the reaction would be proceeded through the unsymmetric intermediate as shown in Scheme 1.

Therefore the reactivity of chromium oxidation by PCC could be controlled by the electronic effect linked with adjacent functional group to the keto-carbon.

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