Kinetics and Mechanism of Alkaline Hydrolysis of [(Methoxy)(*p*-substituted styryl)-carbene] Pentacarbonyl Chromium(0) Complexes in Aqueous Acetonitrile

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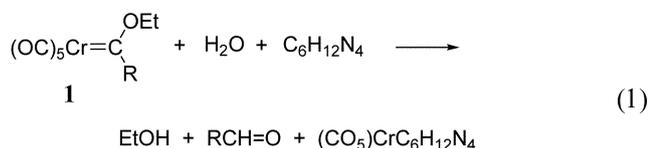*[‡]Department of Chemistry, Inha University, Incheon 402-751, Korea*
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Kinetic studies have been performed for alkaline hydrolysis of a series of [(methoxy)(*p*-substituted styryl)carbene]pentacarbonyl chromium(0) complexes $((CO)_5Cr=C(OCH_3)CH=CHC_6H_4X$, X = *p*-$OCH_3$, *p*-$CH_3$, H, *p*-Cl, *p*-$NO_2$). Second-order rate constants (k_{OH^-}) for the alkaline hydrolysis in 50% acetonitrile-water (v/v) were determined spectrophotometrically at various temperatures. At a low pH region (pH < 7.5), the observed rate constant (k_{obs}) remained constant with a small value, while in a high pH region (pH > 9.5), k_{obs} increases linearly with increasing the pH of the medium. The second-order rate constants (k_{OH^-}) increase as the substituent X changes from a strong electron donating group to a strong electron withdrawing group. The Hammett plot obtained for the alkaline hydrolysis is consisted of two intersecting straight lines. The nonlinear Hammett plot might be interpreted as a change in the rate-determining step. However, the fact that the corresponding Yukawa-Tsuno plot is linear with ρ and r values of 0.71 and 1.14, respectively indicates that the nonlinear Hammett plot is not due to a change in the rate-determing step but is due to ground-state stabilization through resonance interaction. The positive ρ value suggests that nucleophilic attack by OH^- to form a tetrahedral addition intermediate is the rate-determining step. The large negative $\Delta S^{\neq}$ value determined in the present system is consistent with the proposed mechanism.
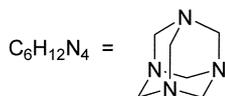
Key Words : Kinetic study, Hydrolysis, Activation parameters, Hammett equation, Yukawa-Tsuno equation

Introduction

Fischer carbene complexes such as (Methoxymethylcarbene) pentacarbonylchromium(0) and (ethoxymethylcarbene) pentacarbonylchromium(0) have become a major focus of many synthetic groups and the chemistry of these complexes has developed an important branch of organometallic chemistry over the last 20 years.[1-4] The first study on the hydrolysis of Fischer carbene complexes we are aware of is that reported in 1993 by Aumann *et al.*,[5] who investigated the reaction of **1** in THF containing small quantities of water as shown in eq. (1).
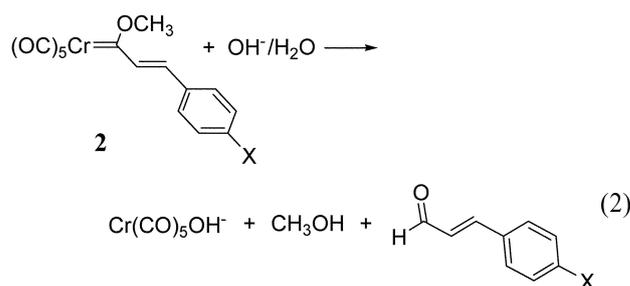
$$(OC)_5Cr=C \begin{matrix} OEt \\ R \end{matrix} + H_2O + C_6H_{12}N_4 \longrightarrow$$

1

$$EtOH + RCH=O + (CO_5)CrC_6H_{12}N_4$$

$$(1)$$

R = Ph (**1a**), PhCH=CH (**1b**), $C_4H_3SCH=CH$ (**1c**), PhC≡C (**1d**).

$C_6H_{12}N_4$ =

In the presence of hexamethylenetetraamine ($C_6H_{12}N_4$) aldehydes RCH=O were reported[5] to be formed over 90% yield except when R is PhC≡C; in this latter case the triple bond was reported to undergo nucleophilic attack by the amine. Aumann *et al.*[5] found that the aldehyde formed was

RCD=O in the presence of D_2O, and proposed a two step mechanism. More systematic studies have been performed for alkaline hydrolysis of **1** and its related complexes by Bernasconi *et al.*[3,4,7] However, the reaction mechanism, especially the rate-determining step (RDS) has not been clearly understood.

We have performed hydrolysis of a series of Fischer carbene complexes, **2a-e** in a wide range pH range at three different temperatures to investigate reaction mechanism, as shown in eq. (2). The change in the substituent X from a strong electron donating group (EDG) to a strong electron withdrawing group (EWG) would be expected to influence the reactivity of **2a-e** as well as reaction mechanism including the RDS. In this paper we report the nature of the RDS for alkaline hydrolysis of **2a-e** on the basis of the results of the kinetic study (the Yukawa-Tsuno ρ and r values,[8] activation parameters).

$$(OC)_5Cr= \begin{matrix} OCH_3 \end{matrix} + OH^-/H_2O \longrightarrow$$

2

$$Cr(CO)_5OH^- + CH_3OH + \quad (2)$$

X = *p*-OCH_3(**2a**), *p*-CH_3(**2b**), H(**2c**), *p*-Cl(**2d**), *p*-NO_2(**2e**)
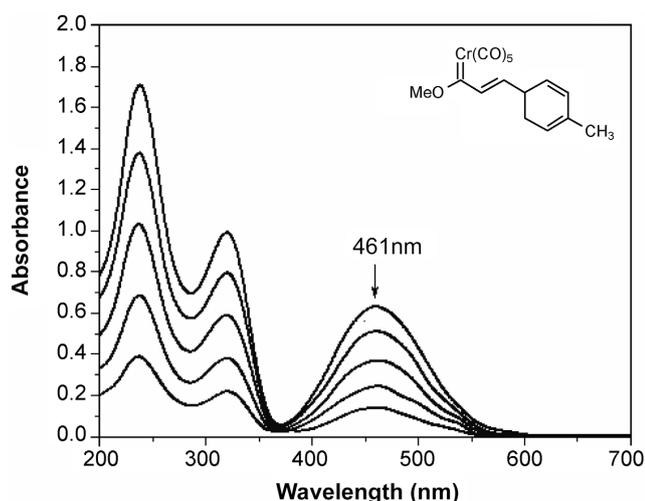
Figure 1. Time-dependent UV-Vis spectra of **2c** in 50% MeCN-H_2O at pH 12.4. Scan taken every 20s.

Results

All the experiments were carried out in 50% acetonitrile-50% water (v/v) and an ionic strength of 0.05 M maintained with KCl at 25.0, 30.0, and 35.0 °C. The reaction manifests itself by distinct changes in the absorption spectra as shown in Figure 1 for a typical example. Presence of an isosbestic point suggests that no stable intermediate is accumulating during the reaction.

Rate constants were measured in buffers with a pH range from 2.5 to 12.4. Observed pseudo-first-order rate constant, k_{obs}, was almost constant at a low pH range (pH < 8.0). However, k_{obs} increases with increasing hydroxide ion concentration at a higher pH range (pH > 9.5). The hydrolysis of Fischer carbene complexes **2a-e** in 50% acetonitrile-water (v/v) at 25.0 °C obeys clean second-order kinetics at a high OH$^-$ concentration region as shown Figure 2. The plot of k_{obs} *vs.* [OH] was linear with a positive intercept in all cases, indicating that eq. (3) can be applied to the present system. The k_{OH^-} values were determined from the slope of the linear plot of k_{obs} vs. hydroxide ion concentration, respectively. The k_{OH^-} values determined in this way are summarized in Table 1.
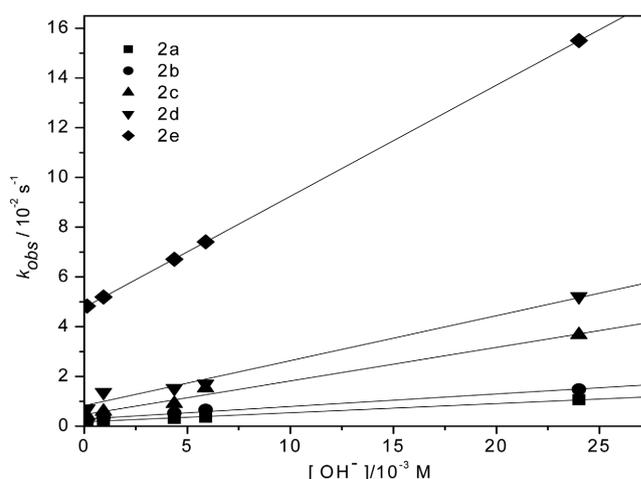

Figure 2. Plot of k_{obs} *vs.* hydroxide ion concentration for the alkaline hydrolysis of compounds **2a-e** at 25 °C.
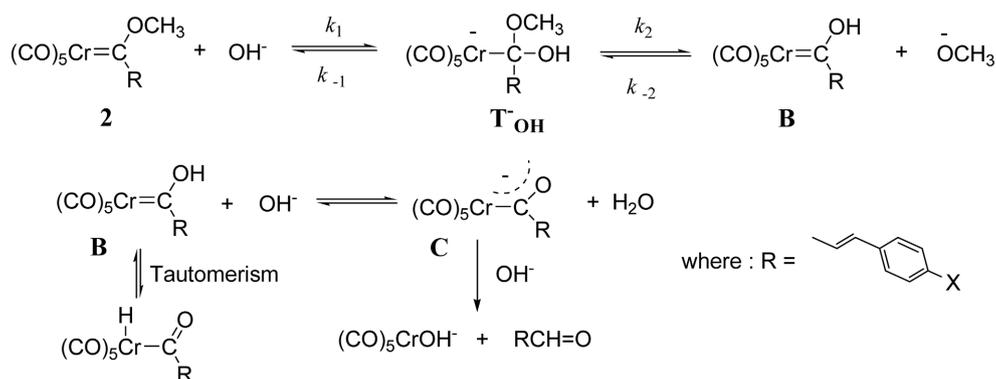
Table 1. Second order rate constants (k_{OH^-}) for the alkaline hydrolysis of compounds, **2a-e**

Substituent	k_{OH^-} $(M^{-1}s^{-1})$		
	25 °C	30 °C	35 °C
p-OCH$_3$, **2a**	0.0366	0.526	0.684
p-CH$_3$, **2b**	0.0505	0.553	1.04
H, **2c**	0.135	0.949	1.72
p-Cl, **2d**	0.181	1.58	2.50
p-NO$_2$, **2d**	0.447	4.64	5.24

$$k_{obs} = k_{H_2O} + k_{OH^-}[OH^-] \tag{3}$$

Discussion

Reaction Mechanism. Bernasconi *et al.*[4] proposed that alkaline hydrolysis of **1** proceeds through the mechanism shown in Scheme 1 based on the observed pH – rate profile, kinetic solvent isotope effect, and the law of mass action. The first step is nucleophilic substitution by OH$^-$ through a tetrahedral intermediate, **T**$^-_{OH}$. Then, the enol **B** is formed directly by loss of CH$_3$O$^-$ from **T**$^-_{OH}$. The enol intermediate **B** tautomerizes to its keto form and/or equilibrates to the

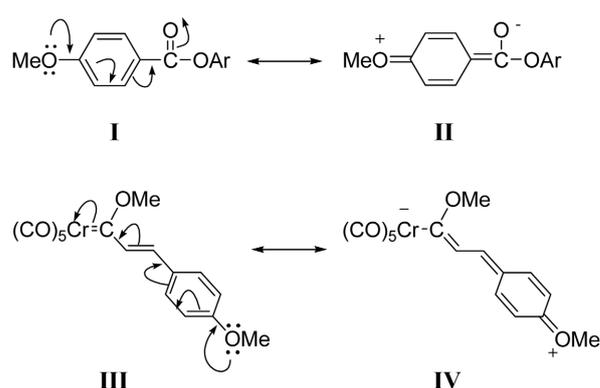**Scheme 1**

enolate **C**. Finally, the enolate **C** is converted to an aldeyde and $(CO)_5CrOH^-$ by hydroxide ion attack on the metal carbene. The RDS for this reaction has been suggested to be dependent on the reaction conditions but not clearly understood. The principle aim of this study is to investigate detailed reaction mechanism together with the nature of the RDS by studying the effect of substituent X in the substrates **2a-e** on the reaction rate.

Effect of Substituent X on Rate. As shown in Table 1, the second-order rate constant increases as the substituent X changes from a strong EDG to a strong EWG, *i.e.*, k_{OH^-} increases from 0.0366 to 0.135 and 0.447 $M^{-1}s^{-1}$ as the substituent X changes from *p*-MeO to H and *p*-NO$_2$, respectively for alkaline hydrolysis of **2a-e** at 25.0 °C. A similar result can be seen for the corresponding reactions at 30.0 and 35.0 °C. The effect of substituent X on rates is illustrated in Figure 3. As shown, the Hammett plot[9] is not linear but exhibits two intersecting straight lines. Traditionally such a nonlinear Hammett plot has been interpreted as a change in the reaction mechanism or the RDS, *i.e.*, a concave upward curvature is indicative of a change in the reaction mechanism, while a convex downward curvature is suggestive of a change in the RDS.[11]

One can notice that the points for π-electron donor substituents deviate negatively on the Hammett plot. Such a nonlinear Hammett plots has recently been reported by Um *et al.*[10] They have found that the Hammett plots for aminolysis of aryl X-substituted benzoates and their related compounds are nonlinear but the corresponding Yukawa-Tsuno plots[8] are linear. Thus, ground-state stabilization through resonance interaction has been suggested to be responsible for the negative deviation as shown in resonance structures **I** $\leftrightarrow$ **II**.[10a,d] A similar argument can be applied to the present system since the ground-state stabilization through resonance interaction is also possible in the present system as shown in resonance structures **III** $\leftrightarrow$ **IV**.

The presence of such resonance structures would stabilize the ground-state of the Fischer carbene complexes **2** and

cause rate retardation as well as negative deviations from the Hammett plot. Thus, the nonlinear Hammett plot shown in Figure 3 is probably not due to a change in the RDS but is due to the ground-state stabilization through resonance interaction which causes the negative deviations for electron donor substituents in the Hammett plot.

$$\log(k/k_0) = \rho[\sigma + r(\sigma^+ - \sigma)] \qquad (3)$$

The above argument can be confirmed by applying to present kinetic data the Yukawa-Tsuno eq. (3).[8] As shown in Figure 4 the Yukawa-Tsuno plot for the hydrolysis of **2a-e** is linear with an *r* value of 1.14. The *r* value in the Yukawa-Tsuno eq represents the extent of resonance contribution. The r value of 1.14 indicates that the ground-state stabilization through resonance is significant in the present system. The ρ value determined in Figure 4 is +0.71. Such a positive ρ value indicates that a negative charge develops at the reaction center at the rate-determining transition-state. If the departure of MeO^- group from the tetrahedral intermediate occurred in the RDS, one should have obtained a negative ρ value. The fact that the ρ value is positive suggests that the departure of MeO^- from the tetrahedral intermediate occurs after the RDS. Thus, we suggest that the alkaline hydrolysis of **2a-e** proceeds through rate-determining OH^- ion attack to the carbon atom bonded to the chromium metal in the
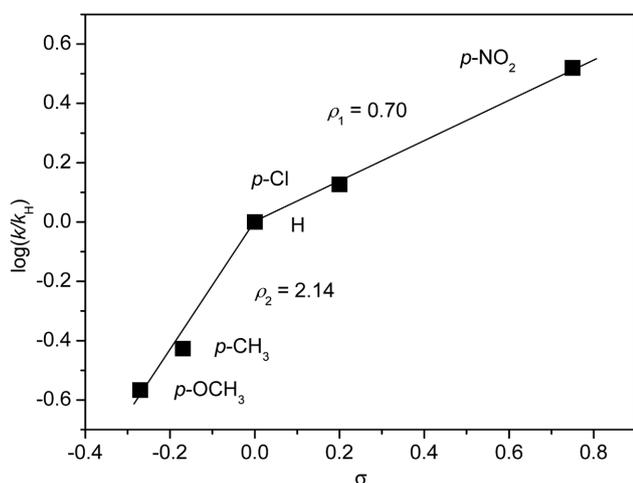

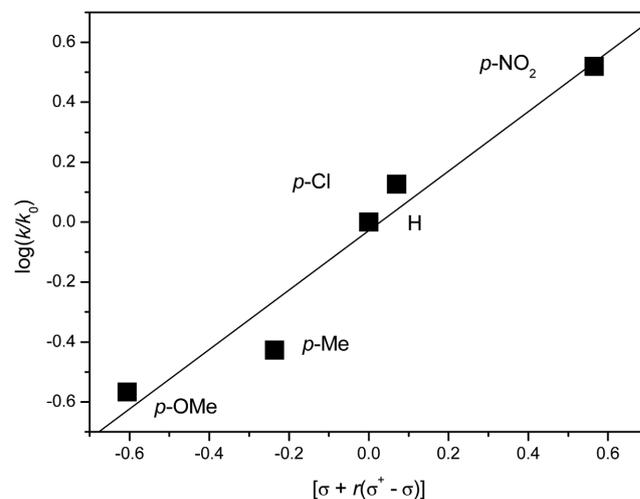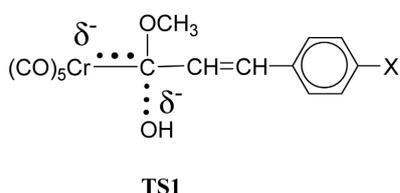**Figure 3.** The Hammett plot for the alkaline hydrolysis of compounds, **2a-e** at pH 12.4.

Figure 4. The Yukawa-Tsuno plot for the alkaline hydrolysis of compounds, **2a-e** at pH 12.4.

Table 2. Activation parameters for the hydrolysis of compounds, **2a-e** in 50% acetonitrile-50% water (v/v) at pH 11.80

Substituents	E_a (kJ·mol^{-1})	$\Delta H^{\neq}$ (kcal·mol^{-1})	$-\Delta S^{\neq}$ (cal·mol^{-1}·K^{-1})
p-OCH$_3$	18.0	4.1	70
p-CH$_3$	16.3	4.5	73
H	14.7	4.1	74
p-Cl	13.7	3.9	76
p-NO$_2$	6.8	2.2	91

Fischer carbene complexes.

The ρ value in the present system is much smaller than the one reported for other Fischer carbene complexes (*e.g.*, r = 1.5-2.5).[12,13] However, this is not surprising since the reaction center in the present system is further away from the substituent X due to the presence of the –CH=CH– group between the phenyl ring and the electrophilic carbon atom of **2a-e**. The fall-off factor, *f*, for –CH=CH– is 2.16,[14] which is nearly the same as that for –CH$_2$– (2.19). The correction of the present ρ using this fall-off factor, the ρ value becomes 1.53 which agrees well with those for other Fischer carbene complexes. On the basis of the ρ value, we propose the transition-state structure similar to TS1 in the present system. To examine this proposal, activation parameters have been determined in the following section.

TS1

Activation Parameters. Alkaline hydrolysis of **2a-e** has also been performed at 30.0 and 35.0 °C to determine activation parameters. The Ea, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ values determined in the present system are summarized in Table 2. As shown in the table, $-\Delta S^{\neq}$ values are much larger than $\Delta H^{\neq}$ values regardless of the electronic nature of substituent X. Furthermore, the $-\Delta S^{\neq}$ value increases as the substituent X becomes a stronger EWG. Such large negative $\Delta S^{\neq}$ values and the dependence of $-\Delta S^{\neq}$ on the electronic nature of substituent X suggest that the hydrolysis of **2a-e** proceeds through a typical rate-determining nucleophilic addition.[15] This is consistent our preceding proposal that the alkaline hydrolysis of **2a-e** proceeds through rate-determining OH$^-$ attack to the carbon atom bonded to the chromium metal of **2a-e** to form a tetrahedral intermediate.

Conclusion

The present study has allowed us to conclude the following: (1) The electron donating substituents *p*-MeO and *p*-Me exhibit negative deviations from the Hammett plot for the alkaline hydrolysis of **2a-e**. Ground-state stabilization through resonance interaction has been suggested to be responsible for the negative deviations on the basis of the

fact that the corresponding Yukawa-Tsuno plot is linear with an *r* value of 1.14. (2) The large *r* value determined in the present system indicates that the ground-state resonance contribution is significant. (3) The positive ρ and large negative $\Delta S^{\neq}$ values obtained in the present system suggest that the nucleophilic attack by OH$^-$ ion to the carbon atom bonded to the chromium metal of **2a-e** is the RDS.

Experimental Section

General procedure. Triethylamine and diethyl ether were refluxed and distilled over sodium metal prior to use. Acetonitrile was purchased from Merck and used without distillation. Water was taken from an Elga purification system. Melting points were measured using a Tomas Hoover 6427-H10. Infrared spectra were taken using a Hitachi Series IR spectrophotometer. ^{1}H NMR spectra were recorded on Bruker DRX 500 and AC 200 instruments using CDCl$_3$ as solvent, unless otherwise stated, with TMS as an internal standard. UV-Vis spectra were obtained on a Shimadzu UV-2401PC spectrophotometer. Kinetic experiments were performed using an applied photophysics DX.18MV stopped-flow apparatus for fast reactions or a Shimadzu UV-2401PC spectrophotometer for slow reactions.

Synthesis of substrates.

[(Methoxy)(methyl)carbene]pentacarbonyl chromium (0). A 100 mL round-bottomed flask equipped with an inlet for nitrogen was charged with 5.00 g (22.7 mmol) of chromium hexacarbonyl and 50 mL of freshly distilled diethyl ether over sodium metal. The dropping syringe was then charged with 1.4 M methyllithium solution (27.2 mmol) in dried diethyl ether. The methyllithium solution was then added in a drop wise fashion to the ethereal solution of chromium hexacarbonyl during a period of *ca.* 55 min. During the course of the reaction the color of the reaction mixtures changed from yellow to dark-brown. The following operations were performed in the open air. The solvent was completely removed with an evaporator, leaving behind the salt Li [Cr(CO)$_5$(COCH$_3$)]. At this point approximately 20 mL of water was added to dissolve the salt. The solution was stirred for a few minutes and then filtered by gravity. Solid trimethyloxonium tetrafluoroborate was added in small portions to the stirred solution until the solution was neutralized. The extract was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The filtrate was evaporated *in vacuo* to afford the crude product, which was purified by flash column chromatography on silica gel with *n*-hexane to give a yellow solid compound (3.5 g). mp 33-35 °C, IR (KBr): 1940 (C=O) ^{1}H NMR (500 MHz, CDCl$_3$) (δ) 2.97 (s, 3H, CH$_3$), 4.71 (s, 3H, OCH$_3$).

[(Methoxy)(*p*-Substituedstyryl)carbene]pentacarbonyl chromium(0), 2a-e. A solution of the *p*-substitued benzaldehyde (3.52 mmol; *p*-OCH$_3$, *p*-CH$_3$, H, *p*-Cl, *p*-NO$_2$) with [(methoxy)(methyl)carbene]pentacarbonyl chromium (0) (3.2 mmol) and Me$_3$SiCl (9.6 mmol) and Et$_3$N (12.8 mmol) in diethyl ether (30 mL) was stirred at room temperature. The mixture was refluxed under a nitrogen atmo-

sphere for 40 h. The reaction controlled by TLC showed quickly disappearance of the starting material ([(methoxy)-(methyl)carbene] pentacarbonyl chromium(0)). The mixture was washed with water and extracted with CH_2Cl_2. The extract was dried over anhydrous magnesium sulfate and the solvent was removed under a reduced pressure. The filtrate was evaporated *in vacuo* to afford the crude product, which was purified by column chromatography on silica gel with *n*-hexane-CH_2Cl_2 to give [(methoxy)(*p*-Substituedstyryl)-carbene] pentacarbonyl chromium(0). The substrates synthesized were confirmed by spectral analysis as follows.

[(Methoxy)(*p*-methoxystyryl)carbene]pentacarbonyl chromium(0) (2a): mp 76-78 °C, IR(KBr): 1940 (C=O), 1600 (C=C), ^1H NMR (500 MHz, $CDCl_3$) (δ) 3.86 (s, 3H, OCH_3), 4.78 (s, 3H, OCH_3 (aromatic)), 6.93 (d, J = 7.8 Hz, 2H (aromatic)), 7.03 (d, J = 15.2 Hz, 1H (olefin)), 7.65 (d, J = 7.8 Hz, 2H (aromatic)), 7.86 (d, J = 15.2 Hz, 1H (olefin)).

[(Methoxy)(*p*-methylstyryl)carbene]pentacarbonyl chromium(0) (2b): mp 82 °C, IR (KBr): 1940 (C=O), 1600 (C=C), ^1H NMR (500 MHz, $CDCl_3$) (δ) 2.39 (s, 3H, CH_3), 4.80 (s, 3H, OCH_3), 6.99 (d, J = 12.8 Hz, 1H (olefin)), 7.23 (m, 2H (aromatic)), 7.49 (m, 2H (aromatic)), 7.93 (d, J = 12.8 Hz, 1H (olefin)).

[(Methoxy)(styryl)carbene]pentacarbonyl chromium (0) (2c): mp 76-78 °C, IR (KBr): 1940 (C=O), 1600 (C=C), ^1H NMR (500 MHz, $CDCl_3$) (δ) 2.96 (s, 3H, OCH_3), 6.97 (d, J = 15.2 Hz, 1H (olefin)), 7.41 (m, 3H (aromatic)), 7.59 (m, 2H (aromatic)), 7.96 (d, J = 15.2 Hz, 1H (olefin)).

[(Methoxy)(*p*-chlorostyryl)carbene]pentacarbonyl chromium(0) (2d): mp 82 °C, IR (KBr): 1940 (C=O), 1600 (C=C), ^1H NMR (δ) 4.83 (s, 3H, OCH_3), 6.89 (d, J = 15.2 Hz, 1H (olefin)), 7.38 (d, J = 7.0 Hz, 2H (aromatic)), 7.51 (d, J = 7.0 Hz, 2H (aromatic)), 7.92 (d, J = 15.2 Hz, 1H (olefin)).

[(Methoxy)(*p*-nitrostyryl)carbene]pentacarbonyl chromium(0) (2e): mp 82 °C, IR (KBr): 1940 (C=O), 1600 (C=C), 1400 (-NO_2) ^1H NMR (δ) 4.88 (s, 3H, OCH_3), 6.84 (d, J = 15.02 Hz, 1H (olefin)), 7.71 (brs, 2H (aromatic)), 7.99 (d, J = 15.02 Hz, 1H (olefin)), 8.25 (brs, 2H (aromatic)).

Kinetic Measurement. The rate constants for the hydrolysis of [(methoxy)(*p*-substituted styryl)carbene] pentacarbonyl chromium(0), **2a-e** were measured spectrophotometrically in 50% acetonitrile-50% water (v/v) at 25 °C ± 0.1 °C by monitoring the decrease in absorbance due to disappearance of the substrate at their maximum wavelengths (**2a**; 465 nm, **2b**; 461 nm, **2c**; 458 nm, **2d**; 460 nm, **2e**; 480 nm). The solvent used is 50% acetonitrile-50% water mixture. Buffer solutions were maintained at a constant ionic strength of 0.05 M with KCl. The buffer solutions employed were NaOH, sodium bicarbonate-sodium carbonate, sodium dihydrogen phosphate-sodium carbonate, acetic acid-sodium acetate and HCl, spanning a pH range from 2.50 to 12.4. Rate constants for hydrolysis of **2a-e** were measured in the pH range 2.50-12.40. All the kinetic determinations were made under pseudo-first-order kinetic conditions with **2a-e** as the minor component.

Product analysis. The reaction mixtures, compounds **2a-e** in 50% acetonitrile-50% pH 12.40 buffer solution were

stirred at 25 °C. After evaporation of solvent, the product was isolated by silica gel column chromatography. Analytical data of the product gave the following results: ^1H-NMR spectral analysis of the product gave the following results.

***p*-MeO-C_6H_4CH=CHCHO, 2a:** ^1H NMR (δ) 3.91 (s, 3H, OCH_3), 6.76-6.81 (q, J_{AB} = 12.0 Hz, $J_{AB'}$ = 6.0 Hz, 1H (olefin)), 6.94-7.01 (m, 2H (aromatic)), 7.41 (t, J = 15.0 Hz, 2H (aromatic)), 7.84 (d, J = 12.0 Hz, 1H (olefin)), 9.69 (d, J = 6.0 Hz, 1H (CHO). ^{13}C NMR (δ) 55.58, 111.30, 120.89, 123.01, 128.89, 129.12, 132.68, 148.21, 158.31, 194.58.

***p*-Me-C_6H_4CH=CHCHO, 2b:** ^1H NMR (δ) 2.41 (s, 3H, CH_3), 6.63 (q, J_{AB} = 12.0 Hz, $J_{AB'}$ = 6.0 Hz, 1H (olefin)), 7.18 (d, J = 9.01 Hz, 2H (aromatic)), 7.39 (d, J = 9.01 Hz, 2H (aromatic)), 7.58 (d, J = 12.0 Hz, 1H (olefin)), 9.68 (d, J = 6.0 Hz, 1H (CHO).

C_6H_5CH=CHCHO, 2c: ^1H NMR (δ) 6.63 (q, J_{AB} = 12.0 Hz, $J_{AB'}$ = 6.0 Hz, 1H (olefin)), 7.33-7.54 (m, 5H (aromatic)), 7.58 (d, J = 12.0 Hz, 1H (olefin)), 9.68 (d, J = 6.0 Hz, 1H (CHO).

***p*-Cl-C_6H_4CH=CHCHO, 2d:** ^1H NMR (δ) 6.63 (q, J_{AB} = 12.0 Hz, $J_{AB'}$ = 6.0 Hz, 1H (olefin)), 7.24 (d, J = 9.0 Hz, 2H (aromatic)), 7.62 (d, J = 9.1 Hz, 2H (aromatic)), 7.58 (d, J = 12.1 Hz, 1H (olefin)), 9.7 (d, J = 6.0 Hz, 1H (CHO).

***p*-NO_2-C_6H_4CH=CHCHO, 2e:** ^1H NMR (δ) 6.92 (q, J_{AB} = 12.0 Hz, $J_{AB'}$ = 6.0 Hz, 1H (olefin)), 7.56 (d, J = 9.0 Hz, 2H (aromatic)), 8.14 (d, J = 9.0 Hz, 2H (aromatic)), 7.72 (d, J = 12.0 Hz, 1H (olefin)), 9.68 (d, J = 6.0 Hz, 1H (CHO).

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