Transition metal carbene chemistry 6: Kinetic studies of the reactions of hydroxide ion with $(CO)_5Mo=C(XCH_2CH_2OH)(C_6H_5)$ (X = O and S) and $(CO)_5W=C(OCH_2CH_2OH)(C_6H_4–Z)$ ☆

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Abstract

A kinetic study of the reaction of hydroxide ion with $(CO)_5Mo=C(XCH_2CH_2OH)(C_6H_5)$ (X = O for **Mo–OR**, and X = S for **Mo–SR**), and $(CO)_5W=C(OCH_2CH_2OH)(C_6H_4–Z)$ (**W–OR(Z)**) is reported. The results are consistent with a pathway in basic solution that involves rapid deprotonation of the OH group followed by rate-limiting cyclization. The parameter k_1K^{OH} for the reaction of **W–OR(Z)** was determined as a function of the phenyl substituents. They were found to correlate well with the Hammett equation. The dependence of the reactivity on the metal atoms in the complexes **M–OR** (M = Cr, Mo and W) shows that the reactivity decreases slightly down the group of the Periodic Table, while for **M–SR** the reactivity increases slightly down the group. A plausible explanation of these results is offered based on electronegativity values of the metal atoms. The much higher $\rho(k_1K^{OH})$ value for **W–OR(Z)** over **W–SR(Z)** arises mainly due to the stabilization of the reactant carbene complex by the stronger π-donor effect of oxygen over sulfur.
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Keywords: Fischer carbene complexes; Kinetics; Intramolecular cyclization; Electronegativity; Periodic trends

1. Introduction

Studies of the effects of substituents on rates and equilibrium constants lie at the heart of understanding structure–reactivity relationships and probing transition state structures. The Fischer carbene complexes of the general type **M–OR(Z)** and **M–SR(Z)** undergo facile reversible intra-molecular nucleophilic addition reactions leading to the formation of cyclic adducts **M–ORO(Z)⁻** and **M–SRO(Z)⁻** [1,2].
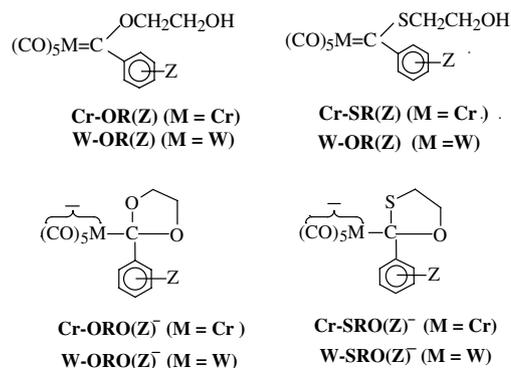
Cr-OR(Z) (M = Cr)
W-OR(Z) (M = W)

Cr-SR(Z) (M = Cr)
W-OR(Z) (M = W)

Cr-ORO(Z)⁻ (M = Cr)
W-ORO(Z)⁻ (M = W)

Cr-SRO(Z)⁻ (M = Cr)
W-SRO(Z)⁻ (M = W)

As reported earlier [1,2], the reversible cyclization reactions of **M–XR(Z)** (M = Cr and W, X = O or S) follow the general reaction (Scheme 1).

Scheme 1.
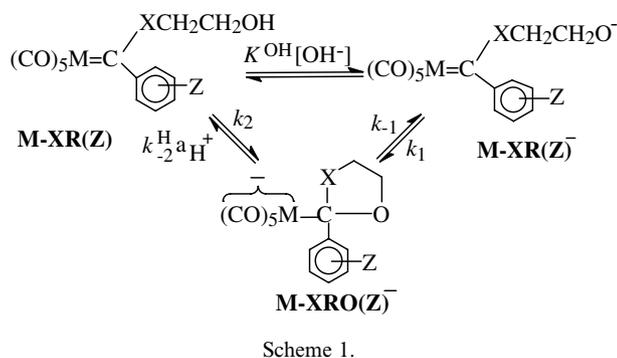
Rate and equilibrium constants for the various elementary steps were determined as a function of the phenyl substituents.

The present investigation describes the reactions of OH^- ion in triethylamine and KOH buffers with $(CO)_5Mo=C(XCH_2CH_2OH)(C_6H_5)$ (**Mo–XR**) (X = O or S) and $(CO)_5W=C(OCH_2CH_2OH)(C_6H_4–Z)$ (**W–OR(Z)**) (Z = Cl, F, H, Me and OMe) leading to the formation of cyclic adducts. A major objective of this study is to establish a periodic trend of reactivity of the **Group 6** Fischer type carbene complexes for the formation of cyclic adducts. Another objective is to examine the substituent effects on the reactivity of **W–OR(Z)** towards OH^- ion.
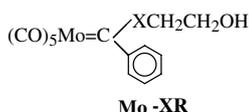
2. Results

Treatment of **Mo–XR** (X = S or O), or **W–OR(Z)** with 0.006 M KOH in 50% CH_3CN–50% H_2O(v/v) leads to an intermediate with the loss of the chromophoric M=C group. Based on precedent [1,2] this is most plausibly explained by a rapid deprotonation of the respective hydroxyl group followed by rate limiting intramolecular nucleophilic attack to form the cyclic adduct. This interpretation is supported by the following observations:

(i) Treatment with HCl or carboxylate buffers immediately after the generation of the cyclic adduct regenerates the original carbene complexes in more than 90% yield within 30 s of mixing. If the elapsed time is longer before addition of HCl or buffer, there is low recovery of the complex, presumably due to hydrolysis.

(ii) An alternative interpretation according to which the loss of the chromophoric M=C group is due to intermolecular nucleophilic attack by OH^- (Eq. (1)) is not attractive. It has been excluded on the basis that the addition of HCl or acidic buffer (pH 4–6) to the adduct would result in the formation of **W–OH(Z)**
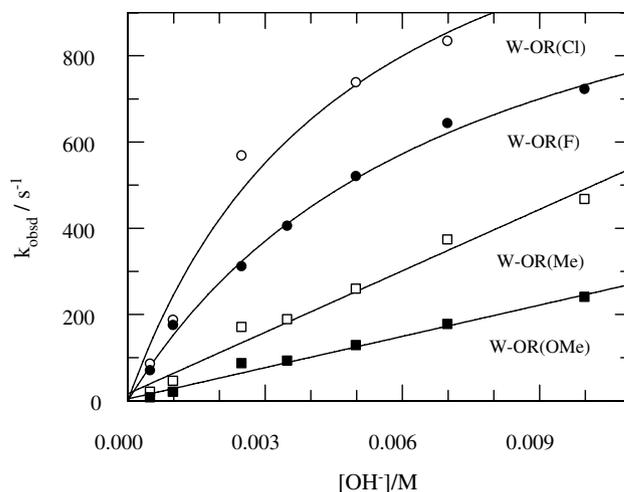
Fig. 1. Plot of k_{obsd} vs. $[OH^-]$ for the intramolecular cyclization of **W–OR(Z)** in 50% MeCN–50% H_2O.
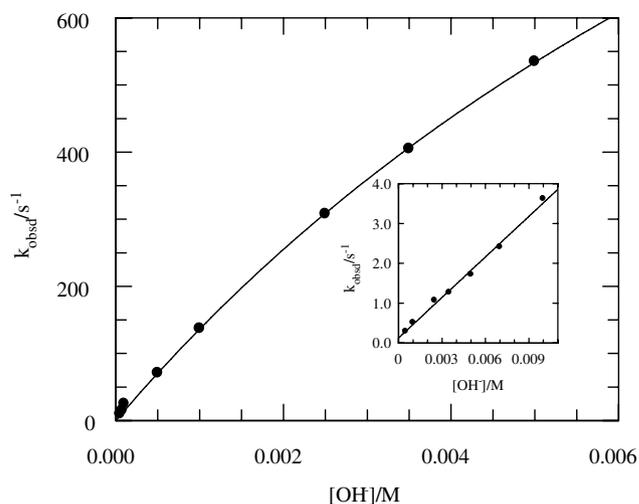
Fig. 2. Plot of k_{obsd} vs. $[OH^-]$ for the intramolecular cyclization of **Mo–OR** in 50% MeCN–50% H_2O. Inset is the same plot for **Mo–SR**.

rather than the recovery of the original complex because the thioethoxide or ethoxide ions are better leaving groups than the OH^-.

(1)
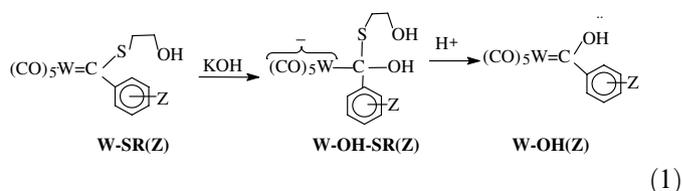
Kinetics were performed in 50% MeCN–50% water (v/v) at 25 °C by reacting **W–OR(Z)** or **Mo–XR** with a KOH or triethylamine buffer solutions which favors the formation of cyclic adducts **M–(ORO)(Z)⁻** or **Mo–XRO⁻**. Pseudo-first-order conditions have been used throughout with the carbene complexes as the minor component. Plots of the observed pseudo-first-order rate constants, k_{obs}, versus $[OH^-]$ are shown in Figs. 1 and 2.

3. Discussion

3.1. Mechanism

In our earlier papers several lines of evidence were presented in support of the mechanism shown in Scheme 1 and against some plausible alternatives [1].

Hence, it is expected that Scheme 1 will also be applicable to the present investigation. According to Scheme 1, and excluding the concerted route (k_2 and k_{-2}^H), which is important only in acidic solution, the rate law is given by Eq. (2).

$$k_{\mathrm{obs}} = \frac{k_1 K^{\mathrm{OH}}[\mathrm{OH}^-]}{1 + K^{\mathrm{OH}}[\mathrm{OH}^-]} + k_{-1} \qquad (2)$$

As the intercept values (k_{-1}) are negligible for all the reactions (Figs. 1 and 2) Eq. (2) simplifies to Eq. (3) which, in most cases, yields non-linear curves for the plot of k_{obs} versus [OH$^-$] showing the leveling off at

$$k_{\mathrm{obs}} = \frac{k_1 K^{\mathrm{OH}}[\mathrm{OH}^-]}{1 + K^{\mathrm{OH}}[\mathrm{OH}^-]} \qquad (3)$$

higher [OH$^-$] (Figs. 1 and 2). This is observed in the case of **M–OR** (M = Mo and W) and a non-linear regression analysis provides the values of k_1 and K^{OH}, which are listed in Table 1.

In a few cases $K^{\mathrm{OH}}[\mathrm{OH}^-] \ll 1$ and hence Eq. (3) becomes Eq. (4) yielding straight lines for the plot of k_{obs} versus [OH$^-$] with slope = $k_1 K^{\mathrm{OH}}$ (Figs. 1 and 2).

$$k_{\mathrm{obs}} = k_1 K^{\mathrm{OH}}[\mathrm{OH}^-] \qquad (4)$$

In the case of **M–OR** (M = Mo and W) values for both K^{OH} and k_1 could be determined experimentally (Eq. (3)) but the lack of k_{-1} made it impossible to get the values of K_1 (= k_1/k_{-1}). It is seen that K^{OH} ($\sim$77.0) for **Mo–OR** and **W–OR** are almost the same and hence the same value was assumed for **Cr–OR** [1]. For **M–SR** where K^{OH} was not experimentally accessible (Eq. (4)) a value of $\sim$7.70 M^{-1} was estimated in accordance with previous assumptions [1].

The reactions of **W–OR(Z)** with OH$^-$ ions gave $k_1 K^{\mathrm{OH}}$ values for Z = Me and OMe while for Z = Cl, F, H, k_1 and K^{OH} were determined separately. K^{OH} values for Z = Me and OMe were estimated by extrapolation of a plot of log-(K^{OH}) versus σ for Z = Cl, F and H; they are listed in Table 1.

3.2. Substituent effect

As there was uncertainty in the determination of K^{OH}, we used $k_1 K^{\mathrm{OH}}$ to determine the substituent effects for the intramolecular cyclization of **W–OR(Z)** (Fig. 3) which gives $\rho(k_1 K^{\mathrm{OH}}) = 2.19 \pm 0.18$. For the intramolecular cyclization of **W–SR(Z)** (Eq. (5)) under identical reaction conditions $\rho(k_1 K^{\mathrm{OH}}) = 0.96$ was extracted from the data obtained from reference [3].

$$\qquad (5)$$
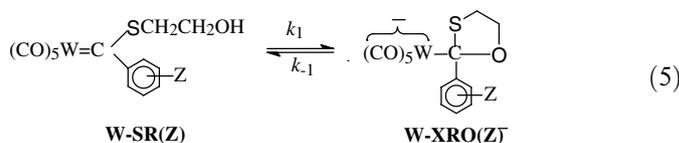
The positive ρ values imply that electron withdrawing substituents stabilize the adduct **W–XR(Z)**$^-$ and/or destabilize the carbene complexes. In fact, the main factor that can account for the positive ρ values is a destabilization of the carbene complexes by electron withdrawal, which is best understood in terms of an increased electron deficiency on the carbene carbon. Thus the key to an understanding of these findings is to consider the substituent effect not only on the transition state but also on the reactant. A major difference between **W–OR(Z)** (Eq. (7)) ($\rho = 2.19$) and **W–SR(Z)** (Eq. (5)) ($\rho = 0.96$) is that the π-donor effect of the oxygen is much stronger than that of the sulfur (σ(OMe) = -0.42, σ(SMe) = -0.15.) [4], which leads to a substantial contribution of the zwitterionic form **M–OR(Z)**$^{\pm}$ to the structure of **W–OR(Z)**.

$$\qquad (6)$$

Table 1
Summary of rate and equilibrium constants for the intramolecular cyclization of **Mo–XR** and **W–OR–Z** in 50% MeCN–50% H$_2$O

Complex	k_1 (s^{-1})	K^{OH} (M^{-1})	$k_1 K^{\mathrm{OH}}$ (M^{-1} s^{-1})
Cr–SR–H	30.5 ± 0.50	$\sim$7.7[a]	$(2.35 \pm 0.05) \times 10^2$
Mo–SR–H	44.0 ± 0.20	$\sim$7.7	$(3.39 \pm 0.11) \times 10^2$
W–SR–H	55.3 ± 0.11	$\sim$7.7[a]	$(4.26 \pm 0.11) \times 10^2$
Cr–OR–H	$(7.21 \pm 0.11) \times 10^3$	77.0[a]	$(5.55 \pm 0.04) \times 10^5$
Mo–OR–H	$(1.96 \pm 0.17) \times 10^3$	74.1	$(1.47 \pm 0.04) \times 10^5$
W–OR–H	$(1.80 \pm 0.11) \times 10^3$	77.0[a]	$(1.39 \pm 0.05) \times 10^5$
W–OR–Cl	$(1.45 \pm 0.33) \times 10^3$	204 ± 89	$(2.96 \pm 0.29) \times 10^5$
W–OR–F	$(1.26 \pm 0.17) \times 10^3$	138 ± 34	$(1.75 \pm 0.06) \times 10^5$
W–OR–Me	$(1.00 \pm 0.02) \times 10^3$	47.4 ± 4.0[b]	$(4.75 \pm 0.3) \times 10^4$
W–OR–OMe	$(0.75 \pm 0.02) \times 10^3$	32.2 ± 4.0[b]	$(2.42 \pm 0.14) \times 10^4$

[a] Ref. [1].
[b] Values are evaluated based on the best fit of Hammett plot.

Fig. 3. Hammett plot for $k_1 K^{\mathrm{OH}}$ for the intramolecular cyclization of **W–OR(Z)** and **W–SR(Z)**. For **W–SR(Z)** data adopted from Ref. [3].

$(CO)_5W=C$ ⟨OCH₂CH₂OH / Z⟩ $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ $(CO)_5\overset{-}{W}$—C⟨O—O / Z⟩ (7)

W–OR(Z)   **W–ORO(Z)⁻**
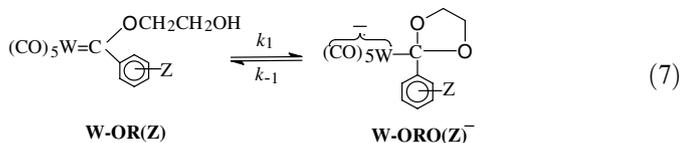
Since the positive charge on the oxygen is much more localized than the negative charge on the **(CO)₅W** moiety, the overall effect of an electron withdrawing phenyl substituent will be destabilization of the carbene complexes resulting in an increase in reactivity and hence higher ρ (2.19) for **W–OR(Z)**. Similar observations have been reported in the reactions of **W–OMe(Z)** with OH⁻ ($\rho = 1.78$), HC≡CCH₂O⁻ ($\rho = 1.73$) [5] (Eq. (6)), *n*-butyl-amine ($\rho = 1.79$) in 50% MeCN–50% water [6].

$(CO)_5M=C$ ⟨XCH₂CH₂OH / Z⟩ ⟷ $(CO)_5\overset{-}{M}$—C⟨$\overset{+}{X}$CH₂CH₂OH / Z⟩

M–XR(Z)   **M–XR(Z)⁺⁻**
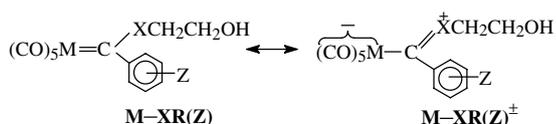
3.3. Chromium, molybdenum and tungsten complexes

It was observed that in the cyclization reaction of **M–OR** (M = Cr and W), the cyclic adduct of the chromium complex is thermodynamically as well as kinetically favored over that of the tungsten complex [K_1(Cr)/K_1(W) = 2.35, k_1(Cr)/k_1(W) = 3.98 [1]. This contrasts with the β-mercaptoethanol derivatives, **M–SR**, where the reactivity pattern follows exactly the reverse trend (K_1(Cr)/K_1(W) = 0.35, k_1(Cr)/k_1(W) = 0.55, k_2(Cr)/k_2(W) = 0.37) [1]. Similar observations were also made for other systems, as for example, for MeO⁻ addition to **Cr–OMe** and **W–OMe** in methanol k_1(Cr)/k_1(W) = 2.41 and for HC≡CCH₂O⁻ addition in 50% MeCN–50% H₂O it is 1.79 [5]; for the addition of various thiolate ions to these carbenes as well as their corresponding ethoxy derivatives in 50% MeCN–50% H₂O k_1(W)/k_1(Cr) varies between 2.56 and 3.16 [7,8]. The extension of this study to the **Mo–XR** system also conforms to the above reactivity pattern i.e., the order of kinetic reactivity is: Cr < Mo < W for **M–SR** and Cr > Mo > W for **M–OR** (Table 1).

To explain the reactivity order Cr < Mo < W for the intramolecular cyclization of **M–SR**, it is necessary to consider a number of factors that may potentially affect the transition state (Eq. (8))

$(CO)_5M=C$ ⟨XCH₂CH₂O⁻ / Z⟩ $\rightleftharpoons$ $\left((CO)_5\overset{\delta-}{M}$══C⟨$\overset{X}{\cdots}O\,\delta-$ / Z⟩ $\right)^{\#}$ $\rightleftharpoons$ $(CO)_5\overset{-}{M}$—C⟨X—O / Z⟩

M–XR   **(M–XRO)^#**   **M–XRO⁻**

(8)
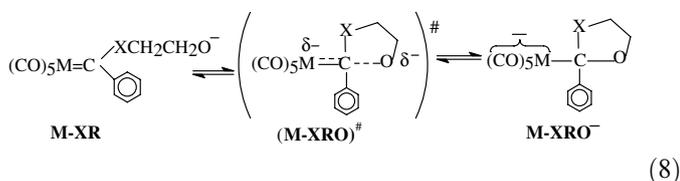
In the transition state **(M–XRO)^#** the negative charge mostly resides on the metal atom [9]. The stabilization of this negative charge may occur either through its dispersion into the 5 CO groups or through the electron-withdrawing inductive/field effect of the X atom. As the charge delocalization has made very little progress in the transition state [9], the stabilization of the **TS** by charge dispersion into the 5 CO groups will be insignificant. Regarding the influence of X, for a particular X atom the electron withdrawing inductive/field effects are expected to contribute about equally in all the carbene complexes in a series with a common X (**M–XR**). A third potential factor is the electronegativity of the metals. It is well known that down the group in the Periodic Table, the electronegativity of the Group VI elements increases. The experimental electronegativity (χ/amu) values are 0.137, 0.143 and 0.162 for Cr, Mo and W respectively [10]. This indicates a gradual increase in the attractive force between the valence electron of the atom and its nuclear charge. So the control of the nucleus on the additional negative charge on the metal and hence stabilization of the negative charge in the transition state **(M–XRO)^#** will increase down the group and consequently an enhanced reactivity trend down the group is apparent. Such a trend in reactivity has also been seen in the *intrinsic* rate constants ($\log(k_0)$) [11] which are 2.56 for **Cr–SR** and 2.76 for **W–SR** [1].

To explain the reactivity trend (Cr > Mo > W) for the intramolecular cyclization of **M–OR** system it is not only necessary to consider the same factors as for **M–SR**, i.e., (i) electron withdrawing inductive/field effect of OR, (ii) delocalization of the negative charge in the transition state, (iii) the electonegativity of the metal but also (iv) the resonance stabilization of the ground state through the π-donation by the hetero-atom (**(M–XR)**). The electron-withdrawing field/inductive effect of alkoxy group (RO) is common to all carbene complexes in a particular series and expected to contribute equally. As the delocalization of negative charge in the transition state (TS) has made very little progress, this effect would have little importance towards its stabilization. The enhanced stabilization of the negative charge in the **TS** by the increased electronegativity down the group should be the same as in **M–SR**, and should follow the same trend as in **M–SR**, i.e. the reactivity order should follow the order Cr < Mo < W. So the observed reverse trend in reactivity indicates that the dominating factor must be the ground state stabilization of **M–OR** through the π-donation by the hetero-atom and the better stabilization of negative charge on the metal atom by the more electronegative metal atom which follows the trend: Cr < Mo < W. Higher ground state stability implies lower reactivity down the group in this series. This reactivity trend is also reflected in *intrinsic* rate constants with $\log k_0 \approx 1.19$ for **Cr–OR** and ≈0.78 for **W–OR** [1]. It is to be mentioned here that ground state stabilization may also be present in the **M–SR** carbene complexes, but the sulfur atom being a poor π-donor, this effect is probably of minor significance. The poor π-donor effect of S over O is evidenced from the σ values of XMe (vide infra) [4], and lower ground state acidity of the $(CO)_5M$=C(OCH₃)CH₃ (pK_a = 12.5 for M = Cr and 12.36 for M = W) compared to that of $(CO)_5M$═C(SCH₃)CH₃ (pK_a = 9.03 for M = Cr and 8.37

for M = W) [17] as well as the lower acidity of **CH₃COOEt** ($pK_a = 26.5$) [18] over **CH₃COSEt** ($pK_a = 21.0$) [19].

3.4. Oxa versus Thia

The rate constants for the nucleophilic attack are lower for thia than oxa complexes: $k_1(O)/k_1(S) = 43$ for **Mo–XR**. Similar results were also obtained for the **Cr–XR** and **W–XR** complexes with $k_1(O)/k_1(S) = 238$ and $k_1(O)/k_1(S) = 32$, respectively [1]. The reversal order of reactivity (k_1) of **M–SR** to that of **M–OR** is apparent from these ratios. Though intrinsic rate constants, $\log(k_0)$, for **Mo–XR** complexes are not known, based on $\log(k_0)$ values for **Cr–OR** (~ 1.19) **Cr–SR** (~ -1.53) and **W–OR** (~ 0.78) and **W–SR** (~ -1.50) [1] it is apparent that the transition states are imbalanced in the sense that the development of stabilizing/destabilizing factors such as resonance effects, steric effects, π-donor effects and possibly others is not synchronous with bond formation [9,12]. Specifically steric hindrance in the adducts, **M–XRO⁻**, probably develops ahead of bond formation [13] which according to the principle of non-perfect synchronization (PNS) reduces $\log(k_0)$ [14]. With respect to resonance effects, there is strong evidence that the negative charge in the adducts is highly delocalized, while in the transition state, **M–XRO#**, it has made little progress. As a consequence of the lag in charge delocalization, the inductive effect of **X** leads to a disproportionately strong stabilization of the transition state relative to that of the adduct. This enhances k_0, and more so for the reaction of **M–ORO⁻** than for **M–SRO⁻**, because of the stronger inductive effect of the oxygen. The oxygen being a stronger π-donor than the sulfur, may also lead to the difference in k_0 for the reactions of **M–OR** and **M–SR** [3]. However, there are two potential opposing interactions, which makes the prediction as to which interaction benefits the most from this effect difficult [9]. Another potential factor is the anomeric effect. Early development of this adduct stabilizing effect should lead to an increase in k_0 for **M–ORO⁻** and contribute to enhancing the difference in k_0 values for **M–ORO⁻** and **M–SRO⁻**.

3.5. Conclusion

(1) The present reaction is best described by Scheme 1 excluding the $k_2/k_{-2}^H a_{H^+}$ path.
(2) The ρ ($k_1 K^{OH}$) value corresponding to the reaction (5) is 0.96 while that for reaction (7) is 2.19. An explanation is offered by considering the substituent effect not only on the transition state but also on the reactant. The stronger π-donor effect of the oxygen over sulfur [4] and much more localization of positive charge on it than the negative charge on the **(CO)₅W** moiety leads to destabilization of carbene complexes by electron withdrawing phenyl substituents and hence an increase in reactivity by the electron withdrawing substituents.

(3) The order of kinetic reactivity are: Cr < Mo < W for **M–SR** and Cr > Mo > W for **M–OR**. For **M–SR** a plausible explanation is offered based on electronegativity of the central metal atom, which increases down the group. The higher the electronegativity, the higher is the attraction between the negative charge on the metal atom and the effective nuclear charge of the atom thereby stabilizing the transition state and hence increasing the reactivity of the carbene complexes. On the other hand, for the **M–OR** series it is the ground state stabilization of the carbene complexes which is the highest for **W–OR** and least for **Cr–OR**.

(4) The rate constants for the nucleophilic attack are lower for *thia* than *oxa* complexes. $k_1(O)/k_1(S) = 43$ for **Mo–XR**, indicating that the intrinsic rate constants are higher for oxa complexes than for the thia complexes. This result can be understood in terms of PNS effects that result from the transition state imbalances. Specifically early development of the steric effect reduces $k_0(S)$ and hence $k_1(S)$ more than $k_0(O)$ and hence $k_1(O)$; and a disproportionately strong transition state stabilization by the inductive effect of X that is the result of the lag in charge delocalization into the (CO)₅M moiety increases $k_0(O)$ and hence $k_1(O)$ more than for the sulfur analogue.

4. Experimental

4.1. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded in CDCl₃ on a 500 MHz Varian Unity instrument. UV–Vis spectra were obtained on Agilent 8453 diode array spectrophotometer. Kinetic experiments were performed on a Applied Photophysics DX.17MV stopped-flow spectrophotometer.

4.2. Reagents

Triethylamine was refluxed and distilled over Na/CaH₂ prior to use. All solvents and chemicals were of Reagent grade and used as received. KOH and HCl stock solutions were prepared by using "dilut it" from Baker Analytical. Water was taken from a Milli-Q purification system.

5. Synthesis

5.1. Synthesis of [(2-hydroxyethoxy)(phenyl)carbenepentacarbonyl]molybdenum(0) (Mo–OR)

This compound was prepared by following the method of Bernasconi and Ali [3] by reacting a solution of [(methoxy)(phenyl)carbenepentacarbonyl]molybdenum(0) (**Mo–OMe**) with NaOCH₂CH₂OH. The starting material,

Mo–OMe was prepared using the method of Senoff et al. [15]. In a typical procedure a NaOCH$_2$CH$_2$OH solution was prepared by adding 0.27 g (11.7 mmol) of clean sodium metal to a mixture of 13 ml of ethylene glycol and 7 ml dry THF under argon and stirring for 30 min until all the sodium had reacted. This solution was then added to a solution of 1.0 g (4 mmol) of **Mo–OMe** in 30 mL of dry THF over a period of 10 min during which time the solution turned light yellow. A 35 mL solution of HCl in THF (prepared from 6 mL of concentrated HCl in 100 mL of THF) was added dropwise over a period of 15 min whereupon the solution turned red-brown. The resulting solution was stirred for about 20 min. All the above procedures were carried out in an argon atmosphere. The following treatments were carried out in open air. The volume of the reaction solution was reduced to a minimum in a roto-evaporator, 70 mL water followed by 100 mL CHCl$_3$ was added. The organic extract was separated from the aqueous phase, washed with water and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under vacuum to get the oily residue. Attempt was taken to purify the product by passing through flash silicagel column but every time the compound decomposes rapidly in the column precluding the possibility to get the ^{1}H and ^{13}C-NMR spectra of the pure product. But the electronic spectrum of the required carbene complex was found to be comparable to those for the corresponding Cr and W complexes.

Mo–OMe   **M–OMe(Z)**
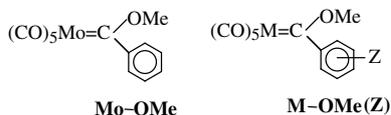
Kinetic studies were carried out with this crude material after filtration through a bio-gel filtering kit and the impurities produced due to decomposition of the complex were found to be insoluble in MeCN and had no influence on reaction kinetics.

5.2. Synthesis of [(2-hydroxythioethyl)(phenyl)carbenepentacarbonyl]molybdenum(0)(Mo–SR)

This compound was prepared by following the method of Bernasconi and Ali [3] by reacting a solution of [(methoxy)(phenyl)carbenepentacarbonyl]molybdenum(0) (**Mo–OMe**) with NaSCH$_2$CH$_2$OH. A NaSCH$_2$CH$_2$OH solution was prepared by adding 0.60 g (15 mmol) of solid NaOH to 15 mmol of 2-mercaptoethanol in 20 mL of methanol saturated with argon. This solution was added to 10 mmol of **Mo–OMe** dissolved in 50 mL dry diethylether and stirred for 10 min. A 35 mL 0.7 M HCl solution in methanol was added drop wise for 20 min in argon atmosphere. The solution turned red-brown and the precipitated NaCl was filtered out. The subsequent steps are similar as described above. Here also we could not get the pure product.

5.3. Synthesis of W–OR(Z)

The synthesis of the phenyl substituted carbene complexes, **W–OR(Z)** was carried out by the method used for the synthesis of **W–OR(Z)** [1] and purity in most cases were checked by ^{1}H and ^{13}C NMR studies:

W–OR(H), ^{1}H NMR: δ(ppm) OH, s 1.89; CH_2O: 4.27(t); OCH_2: 5.06(t); Ph: 7.44 and 7.58. ^{13}C NMR: CO(*cis*): 197.2; CO(*trans*): 203.6; CH$_2$O: 61.2; OCH2: 77.1; Ph: 126.2, 128.2, 131.8, 155.5, =C: 321.2.

W–OR–Cl, ^{1}H NMR: OH, s 1.64(s); CH_2O: 4.26(t); OCH_2: 5.04 (t); Ph: 7.37,7.41,7.53 and 7.57. ^{13}C NMR: CO(*cis*): 197.07; CO(*trans*): 203.17; SCH2: 61.1; OCH2: 84.5; Ph: 127.65 128.04 and 128.53, =C: 318.21.

W–OR–Me, ^{1}H NMR: OH, s 1.58(s); CH_2O: 2.46(t); OCH_2: 3.49 (t); Ph: 7.28,7.34,7.36; CH$_3$: 1.22. ^{13}C NMR: CO(*cis*): 192.2; CO(*trans*): 197.63; SCH2: 66.1; OCH2: 84.5; Ph: 127.87 127.9, 129.1 and 129.5, =C: 318.6; CH$_3$: 15.5.

6. Kinetic measurements

All kinetic runs were conducted under pseudo-first-order conditions ensured by a large excess of KOH or buffer over the substrate. The reactions were monitored at or near λ_{max} (430–450 nm) of the neutral carbene complexes. Stock solutions of the carbene complexes were prepared in anhydrous CH$_3$CN in which they were found to be fairly stable for several hours.

All kinetic experiments were conducted in 50% CH$_3$CN–50% H$_2$O (v/v) under pseudo-first-order conditions with the carbene complexes as the minor component and with I = 0.10 mol dm^{-3} (KCl) at 25 °C by monitoring the disappearance of the substrate. Typical substrate concentrations were $(5.0–9.0) \times 10^{-5}$ M. The pH in triethylamine buffer (0.05 M) in 50% MeCN–50% H$_2$O was measured with Systronics digital pH meter model-335 (Systronics India) or Orion Model 611) pH-meter equipped with glass electrode and actual pH of the solution was calculated according to Allen and Tidwell [16] as: pH$_{actual}$ = pH$_{observed}$ + 0.18. The buffer catalysis of these reactions was found to be insignificant and was ignored. The pH for the reactions in KOH medium was directly calculated from the relationship: pH = pK_w + pOH, with pOH = $-\log$[OH$^-$] and pK_w = 15.19 in 50% MeCN–50% water [17].

The pseudo-first-order rate constants (k_{obs}, s^{-1}) were obtained by fitting the kinetic traces with suitable computer-fit program and the results were found to fall within the error limit ±5%.

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