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Physical Organic Chemistry of Transition Metal Carbene Complexes. 21.[1] Kinetics and Mechanism of Hydrolysis of $(CO)_5M{=}C(SR)Ar$ ($M = Cr$ and W; $R = CH_3$ and $CH_3CH_2CH_2$; $Ar = C_6H_5$ and 3-ClC_6H_4) in Aqueous Acetonitrile. Important Differences Relative to Complexes with Alkoxy Leaving Groups

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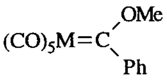
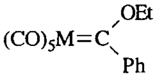
Abstract: A kinetic study of the hydrolysis of $(CO)_5M{=}C(SMe)Ph$ ($M = Cr$ and W) in 50% MeCN−50% water (v/v) at 25 °C over a pH range from 1.7 to 14.2 is reported. The reaction occurs in two stages: the first is formation of $(CO)_5M{=}C(O^-)Ph$ or $(CO)_5M{=}C(OH)Ph$ while the second stage leads to the formation of $PhCH{=}O$ and $(CO)_5MOH^-$. This paper is concerned with the first stage. The rate−pH profiles are complex and consistent with a mechanism (Scheme 1) that involves water/OH^- addition to the substrate to form a tetrahedral intermediate (T_{OH}^{-}), followed by product formation via five potential pathways whose relative importance depends on the pH. A more limited study of the reactions of $(CO)_5M{=}C(SCH_2CH_2CH_3)Ph$ ($M =$ Cr and W) and $(CO)_5M{=}C(SMe)C_6H_4$-3-Cl ($M = Cr$ and W) with OH^- is also reported. The main focus of the discussion is aimed at understanding the reactivity differences between $(CO)_5M{=}C(SMe)Ph$ and the corresponding methoxy analogues studied earlier. This understanding is in large measure based on an analysis of how the *intrinsic* rate constants are affected by the interplay of steric, inductive, and π-donor effects and the potential imbalances of these effects at the transition state. It is also shown that the much lower sensitivity to H^+-catalysis of RS^- compared to RO^- leaving group departure from the tetrahedral intermediate is responsible for the more complex rate−pH profile for the hydrolysis of $(CO)_5M{=}C(SMe)Ph$ than for the hydrolysis of the methoxy analogue.

Introduction

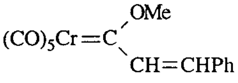
A kinetic study of the hydrolysis of the Fischer type transition metal carbene complexes **1-M**,[2] **2-M**[2], and **3-Cr** in 50%



1-Cr (M = Cr)
1-W (M = W)

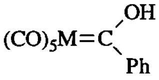


2-Cr (M = Cr)
2-W (M = W)



3-Cr

MeCN−50% water has recently been reported.[3] As had been shown by Aumann et al.,[4] the reaction occurs in two stages. The first stage involves conversion of the alkoxy carbene complex into the corresponding hydroxy complex, e.g., **4-M**,



4-Cr (M = Cr)
4-W (M = W)

the second stage leads to benzaldehyde and $(CO)_5MOH^-$. The reported kinetic study dealt with the first stage. The results were shown to be consistent with the mechanism described by Scheme 1 (X = O); k_{-1}^{H} and k_2^{H} refer to H^+-catalyzed OH^- and RX^- departure from T_{OH}^{-}, respectively, k_3^{H} to H^+-catalyzed RX^- departure from T_{OH}^{2-}, and k_2^{i} to intramolecular acid catalysis of RX^- departure from T_{OH}^{-} by the OH group. The rate law, given by

$$k_{obsd} = k_1^{H_2O} + k_1^{OH}[OH^-] + k_1^{B}[B] \tag{1}$$

indicated that formation of the tetrahedral intermediate, T_{OH}^{-}, by water attack at low pH and by OH^- attack at high pH is rate limiting; the $k_1^{B}[B]$ term refers to general base catalysis by buffer bases.[5]

The reason Scheme 1 includes an intramolecular pathway (k_2^{i}) as well as a pathway through the dianionic intermediate T_{OH}^{2-} is that these additional pathways provide faster conversion of T_{OH}^{-} to products than the $k_2^{H_2O} + k_2^{H}a_{H^+}$ reactions and explain why T_{OH}^{-} does not accumulate to detectable levels during the reaction.[6]

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[1] Part 20: Bernasconi, C. F.; Whitesell, C.; Johnson, R. A. *Tetrahedron* **2000**, *56*, 4917.

[2] When using the symbols **1-M**, **2-M**, etc. both the Cr and W derivatives will be meant. When only one of the derivatives is referred to, we will use the symbols **1-Cr**, **1-W**, **2-Cr**, etc.

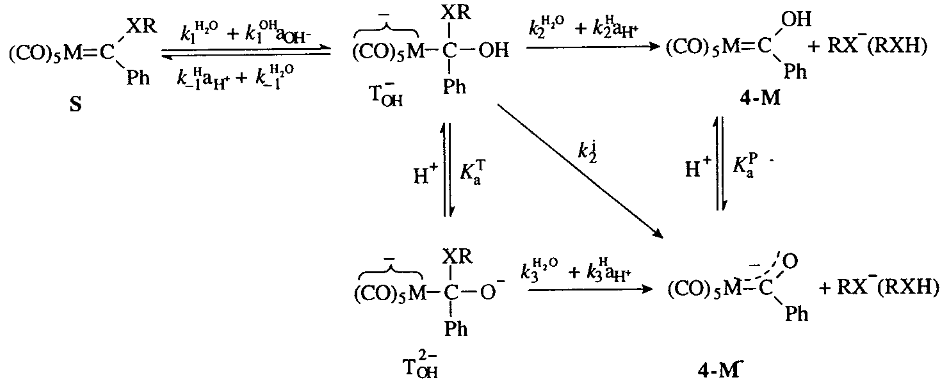
[3] Bernasconi, C. F.; Flores, F. X.; Kittredge, K. W. *J. Am. Chem. Soc.* **1997**, *119*, 2103.

[4] Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145.

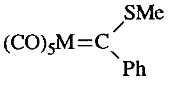
[5] For simplicity, the buffer terms for all steps ($k_1^{B}[B]$, $k_{-1}^{BH}[BH]$, $k_2^{BH}[B]$, and $k_3^{BH}[BH]$) have been omitted from Scheme 1.

10.1021/ja002371l CCC: $19.00

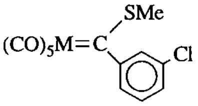
Scheme 1



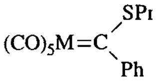
In the present paper we report a detailed kinetic study of the hydrolysis of the thiomethyl analogues to compound **1-M**, i.e., **5-M**, and a more limited study of **6-M** as well as the *n*-propyl derivatives **7-M**. It will be shown that the same mechanistic scheme applies for these reactions as for the hydrolysis of **1-M** and **2-M**, but that for the thioalkyl carbene complexes changes in pH induce multiple changes in the rate-limiting step not observed with the alkoxy derivatives. These changes in rate-limiting step can be attributed to the much weaker response to acid catalysis of thioalkyl compared to the alkoxy leaving groups.



5-Cr (M = Cr)
5-W (M = W)



6-Cr (M = Cr)
6-W (M = W)



7-Cr (M = Cr)
7-W (M = W)

Results

All experiments were performed in 50% MeCN−50% water (v/v) at 25 °C and an ionic strength of 0.1 M maintained with KCl. The reaction manifests itself by a distinct change in the absorption spectrum as shown in Figure 1 for a representative example. The presence of sharp isosbestic points indicates a clean reaction. For **5-M**, rates were measured under pseudo-first-order conditions in KOH and HCl solutions, and in triethylamine, *N*-methylmorpholine, and acetate buffers, spanning a pH range from 1.7 to 14.2. Figure 2 shows the rate−pH profiles. The rate constants derived from the experiments in the triethylamine and *N*-methylmorpholine buffers represent values that were extrapolated to zero buffer concentration.

For **6-M** and **7-M** rate measurements were restricted to KOH solutions. Plots of k_{obsd} vs [KOH] were linear with intercepts that were too small for an accurate determination.

Discussion

Mechanism. As mentioned in the Introduction, the reason the k_2^i step and the pathway via T_{OH}^{2-} were added to the scheme for the reactions of **1-M** and **2-M** (X = O in Scheme 1) was that they are necessary to explain why T_{OH}^- does not accumulate to observable levels at high pH.[3] This conclusion was reached based on an estimate of K_1^{OH}, the equilibrium constant for formation of T_{OH}^- by addition of OH⁻ to **1-M**, and an estimate of the $k_1^{OH}/k_2^{H_2O}$ ratio. These estimates led to the conclusion that, at high pH, $K_1^{OH}[OH^-] > (\gg) 1$ and $k_1^{OH}[OH^-]/k_2^{H_2O} > (\gg) 1$; these are the two necessary conditions for T_{OH}^- to become observable. The additional pathways must therefore lead to a more rapid conversion of T_{OH}^- to products than the $k_2^{H_2O}$ pathway, turning T_{OH}^- into a steady-state intermediate.

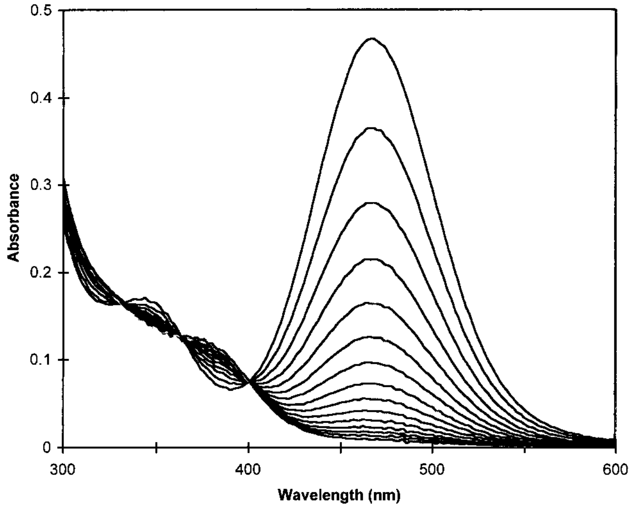


Figure 1. Time-dependent absorption spectra of $(CO)_5Cr{=}C(SMe)$-Ph (**5-Cr**) in 50% MeCN−50% water at pH 14.0. Scans taken every 20 s.

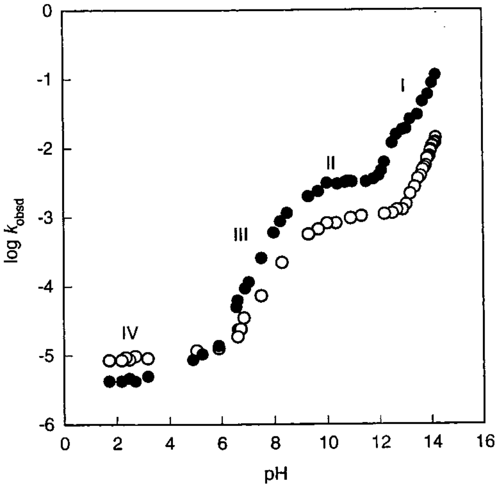


Figure 2. Rate−pH profiles for the hydrolysis of **5-Cr** (○) and **5-W** (●).

The situation for **5-M** (X = S in Scheme 1) is probably different in that the two additional pathways are not necessary

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(6) T_{OH}^- would accumulate to detectable levels at high pH without these additional pathways because the equilibrium of the first step is expected to favor T_{OH}^- over the reactants and $k_1^{OH}a_{OH^-} \gg k_2^{H_2O}$, as discussed in detail in ref 3.

Table 1. Rate Constants for OH^- and Water Attack on Fischer Carbene Complexes in 50% MeCN−50% Water at 25 °C

carbene complex	k_1^{OH}, $M^{-1}\,s^{-1}$	$k_1^{H_2O}$, s^{-1}	k_1^{PrS}, $M^{-1}\,s^{-1}$	K_1^{PrS}, M^{-1}
$(CO)_5Cr{=}C(OMe)Ph$ (**1-Cr**)	26.6[a]	2.9×10^{-3} [a]	1.34×10^{4} [b]	1.06×10^{4} [b]
$(CO)_5W{=}C(OMe)Ph$ (**1-W**)	26.3[a]	2.8×10^{-3} [a]	4.21×10^{4} [b]	1.35×10^{4} [b]
$(CO)_5Cr{=}C(SMe)Ph$ (**5-Cr**)	$(1.27 \pm 0.03) \times 10^{-1}$	$(1.03 \pm 0.06) \times 10^{-3}$	5.33×10^{2} [c]	1.10×10^{6} [c]
$(CO)_5W{=}C(SMe)Ph$ (**5-W**)	1.00 ± 0.03	$(3.24 \pm 0.05) \times 10^{-3}$	1.58×10^{3} [c]	4.75×10^{6} [c]
$(CO)_5Cr{=}C(SMe)C_6H_4$-3-Cl (**6-Cr**)	$(3.40 \pm 0.10) \times 10^{-1}$			
$(CO)_5W{=}C(SMe)C_6H_4$-3-Cl (**6-W**)	2.04 ± 0.10			
$(CO)_5Cr{=}C(SPr)Ph$ (**7-Cr**)	$(7.25 \pm 0.17) \times 10^{-2}$			
$(CO)_5W{=}C(SPr)Ph$ (**7-W**)	$(3.10 \pm 0.10) \times 10^{-1}$			

[a] Reference 3. [b] Reference 9. [c] Reference 12.

to turn T_{OH}^- into a steady-state intermediate. This is because one would expect the $k_1^{OH}/k_2^{H_2O}$ ratio to be smaller than that for X = O for two reasons: k_1^{OH} is lower (Table 1), as discussed in more detail below, and $k_2^{H_2O}$ is expected to be higher because MeS^- is a better leaving group that MeO^-.[9] This means that the $k_1^{OH}[OH^-]/k_2^{H_2O}$ ratio is probably <(≪)1 even at the highest pH (14.2) used in this study, ensuring that T_{OH}^- is a steady-state intermediate irrespective of the contribution of the other pathways. Nevertheless, since the additional pathways are crucial for the alkoxy carbene complexes they should be included in the scheme for the thioalkyl complexes as well, irrespective of their relative contribution to the rate of conversion of T_{OH}^- to products (more on this below).

In relating our kinetic results to Scheme 1 we note an important contrast with the kinetic behavior of the alkoxy complexes. For these latter, nucleophilic attack by OH^- or water is rate limiting over the entire pH range[3] while for the thioalkyl complexes the reaction undergoes several pH-dependent changes in rate-limiting step. These changes are apparent from the complex rate−pH profiles (Figure 2). We offer the following interpretation for the four regions of the rate−pH profiles; the general expression of k_{obsd} and its derivation are given in the Supporting Information.[10]

Region I (pH ≳12.5 for **5-Cr**, pH ≳11.5 for **5-W**). In this pH-range, OH^- attack is rate limiting, i.e., the observed pseudo-first-order rate constant, k_{obsd}, is given by

$$k_{obsd} = k_1^{OH}[OH^-] \tag{2}$$

This means that the relationships shown in eqs 3 and 4 apply. Note that in eq 4 the $k_2^{H}a_{H^+}$ term has been omitted because, as shown below, it is negligible down to pH 6.

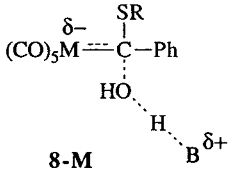
$$k_1^{OH}[OH^-] \gg k_1^{H_2O} \text{ and } k_{-1}^{H_2O} \gg k_{-1}^{H}a_{H^+} \tag{3}$$

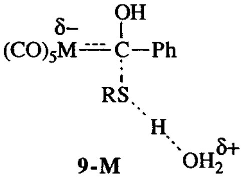
$$k_2^{H_2O} + k_2^{i} + K_a^{T}\,k_3^{H_2O}/a_{H^+} + K_a^{T}\,k_3^{H} \gg k_{-1}^{H_2O} \tag{4}$$

Region II (pH ∼10 to ∼12.5 (**5-Cr**) or ∼10 to ∼11.5 (**5-W**)). Nucleophilic attack by water is rate limiting, eq 5. The

$$k_{obsd} = k_2^{H_2O} + k_1^{B}[B] \tag{5}$$

$k_1^{B}[B]$ term refers to buffer base catalyzed water attack, most likely via a class n concerted reaction[7] whose transition state is shown as **8-M**. The rate law implies that relationships 6 and 7 apply; the $k_2^{H}a_{H^+}$ term is again negligible and omitted from eq 7.


8-M


9-M

$$k_2^{H_2O} \gg k_1^{OH}[OH^-] \text{ and } k_{-1}^{H}a_{H^+} \gg k_{-1}^{H_2O} \tag{6}$$

$$k_2^{H_2O} + k_2^{i} + K_a^{T}\,k_3^{H_2O}/a_{H^+} + K_a^{T}\,k_3^{H} \gg k_{-1}^{H}a_{H^+} \tag{7}$$

Region III (pH ∼6 to ∼10). In this region eq 6 remains valid but eq 7 changes to eq 8, which means that the nucleophilic

$$k_{-1}a_{H^+} \gg k_2^{H_2O} + k_2^{i} + K_a^{T}\,k_3^{H} \tag{8}$$

attack step is now a rapid preequilibrium and hence k_{obsd} is given by eq 9, with $K_1^{H_2O} = k_1^{H_2O}/k_{-1}^{H}$ being the equilibrium constant for nucleophilic attack by water. The fact that the slope of the

$$k_{obsd} = \frac{K_1^{H_2O}}{a_{H^+}}(k_2^{H_2O} + k_2^{i} + K_a^{T}\,k_3^{H}) \tag{9}$$

rate−pH profile is approximately unity indicates that neither the $k_2^{H}a_{H^+}$ term nor the $K_a^{T}\,k_3^{H_2O}/a_{H^+}$ term contribute significantly to k_{obsd} in this region and hence these terms have been omitted from eqs 8 and 9.

Region IV (pH ≲6). Below pH 6 the $k_2^{H}a_{H^+}$ term finally becomes important; it now represents the dominant pathway for the rate-limiting collapse of T_{OH}^- (eq 10), eq 8 becomes eq 11, and eq 9 becomes eq 12.

$$k_2^{H}a_{H^+} \gg k_2^{H_2O} + k_2^{i} + K_a^{T}\,k_3^{H} \tag{10}$$

$$k_{-1}a_{H^+} \gg k_2^{H}a_{H^+} \tag{11}$$

$$k_{obsd} = K_1^{H_2O}\,k_2^{H} \tag{12}$$

Could the Reaction be Concerted? A referee has raised the possibility that the hydrolysis of **5-M**, **6-M**, and **7-M** might not involve a tetrahedral intermediate (T_{OH}^-) but could conceivably be concerted. This suggestion is based on theoretical calculations which indicate that tetrahedral intermediates formed by attachment of thiolate ions to carbonyl or acyl compounds are much less stable than those formed by attachment of OH^-.[11] The following observations are inconsistent with a concerted reaction.

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[7] Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345.

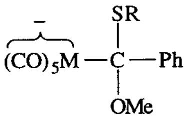
[8] Bernasconi, C. F.; Ketner, R. J.; Brown, S. D.; Chen, X.; Rappoport, Z. *J. Org. Chem.* **1999**, *64*, 8829.

[9] Bernasconi, C. F.; Kittredge, K. W.; Flores, F. X. *J. Am. Chem. Soc.* **1999**, *121*, 6630.

[10] See paragraph concerning Supporting Information at the end of this paper.

[11] (a) Arad, D.; Langridge, R.; Kollman, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 491. (b) Shokhen, M.; Arad, D. *J. Mol. Mod.* **1996**, *2*, 399.

(1) Tetrahedral intermediates derived from nucleophilic attack on Fischer carbene complexes are much more stable than those derived from nucleophilic attack on esters. In fact, these intermediates are so stable that, under the right conditions, they accumulate to detectable levels, even those that contain alkyl thio groups, e.g. **10-M** (R = n-Pr, $HOCH_2CH_2$, $MeO_2CCH_2CH_2$, MeO_2CCH_2).[9]



$$\overset{-}{(CO)_5M}-\underset{OMe}{\overset{SR}{C}}-Ph$$

10-Cr(M = Cr)
10-W(M = W)

(2) The pH−rate profile requires the postulate of an intermediate because, if a reaction does not involve an intermediate, there cannot be changes in rate-limiting steps.

Why Are the Rate−pH Profiles Different for Complexes with Thio and Alkoxy Leaving Groups? For the hydrolysis of **1-M**, **2-M**, and **3-Cr** there are no changes from rate-limiting nucleophilic attack at high pH to rate-limiting collapse of T_{OH}^- at low pH, i.e., nucleophilic attack is rate limiting over the entire rate−pH profile. The key feature responsible for the difference between the two types of carbene complexes is that oxyanion (OH^- as well as RO^-) departure from T_{OH}^- is very sensitive to H^+-catalysis while for thiolate ion departure the sensitivity to H^+-catalysis is much weaker. Hence, for the hydrolysis of the alkoxy carbene complexes, H^+-catalysis of conversion of T_{OH}^- to products and of conversion back to reactants becomes important in similar pH ranges. This means that lowering the pH affects the rates of conversion of T_{OH}^- to reactants and products in a comparable way so that no change in rate-limiting steps occurs. In contrast, for the hydrolysis of the thioalkyl carbene complexes, k_2^H is so small that at pH values where the $k_{-1}^H a_{H^+}$ term starts to become important, the $k_2^H a_{H^+}$ term is still negligible. Hence in the pH range from 6 to 10 where H^+-catalysis of OH^- departure ($k_{-1}^H a_{H^+}$) is already strong, H^+-catalysis of RS^- departure ($k_2^H a_{H^+}$) is insignificant which renders the $k_{-1}^H a_{H^+}$ process to be faster than the conversion of T_{OH}^- to products and leads to the observed change in rate-limiting step. As the pH is lowered further, the $k_2^H a_{H^+}$ term eventually becomes significant but the $k_{-1}^H a_{H^+}$ has also increased so that the collapse of T_{OH}^- to products remains rate limiting.

The lower sensitivity to H^+-catalysis of thiolate compared to alkoxide ion departure has been observed in other reactions and is a general phenomenon; a detailed discussion has been presented in connection with the study of the acid-catalyzed breakdown of alkoxide and thiolate ion adducts of benzylidene Meldrum's acid type adducts.[8] The main reason for this reduced sensitivity appears to be the lower basicity of RS^- compared to RO^- or OH^- ions. However, the mechanism for H^+-catalysis is probably the same for all leaving groups and most likely represents a concerted reaction with a transition state such as **8-M** (B = H_2O) or **9-M**.

The low sensitivity of thiolate ion departure to acid catalysis has implications regarding the relative importance of the intramolecular pathway (k_2^i) and the pathway via T_{OH}^{2-} in converting T_{OH}^- to products. Just as is the case for k_2^H, k_2^i and k_3^H are expected to be much smaller for X = S than for X = O, while $k_3^{H_2O}$, just as $k_2^{H_2O}$, should be much larger for X = S than for X = O. Hence the $K_a^T k_3^{H_2O}/a_{H^+}$ term is probably quite significant and perhaps dominant at high pH (e.g., in eq 4) while the k_2^i and $K_a^T k_3^H$ terms may very well be negligible (e.g. in eq 9).

Structure−Reactivity Relationships. Table 1 summarizes the k_1^{OH} and $k_{-1}^{H_2O}$ values for **1-Cr**, **1-W**, **5-Cr**, and **5-W**; also included are the k_1^{OH} values for **6-Cr**, **6-W**, **7-Cr**, and **7-W**.

k_1^{OH}: MeO vs MeS as Leaving Group. The reactivity of the MeS complexes toward OH^- is significantly lower than that of the methoxy derivatives; for example, the k_1^{OH}(**5-Cr**)/k_1^{OH}(**1-Cr**) ratio is 4.77×10^{-3} and the k_1^{OH}(**5-W**)/k_1^{OH}(**1-W**) ratio is 3.80×10^{-2}. These results are reminiscent of the lower reactivity of the thiomethyl compared to the methoxy carbene complexes toward thiolate ions;[9,12] for example, for the reaction with n-PrS$^-$, the k_1^{PrS}(**5-Cr**)/k_1^{PrS}(**1-Cr**) ratio is 4.00×10^{-2} and the k_1^{PrS}(**5-W**)/k_1^{PrS}(**1-W**) ratio is 3.75×10^{-2}; for the reaction with $HOCH_2CH_2S^-$, the corresponding ratios are 2.93×10^{-2} and 4.52×10^{-2}, respectively.

There are several factors that may affect these reactivity ratios. They include steric, inductive, and π-donor effects; for the reactions of **1-M** with OH^- they may also include an anomeric effect.[13] Specifically, the steric effect is expected to lower the reactivity of **5-M** relative to **1-M** due to the larger size of the MeS group;[16] the stronger electron-withdrawing inductive effect of the MeO group[18] should enhance the reactivity of **1-M** relative to that of **5-M**; the anomeric effect may increase the reactivity of **1-M** toward oxyanion nucleophiles; the stronger π-donor effect of the MeO group compared to that of the MeS group[20] should lower the reactivity of **1-M** relative to that of **5-M.**

How can one evaluate the relative importance of these factors? For the reactions of **1-M** and **5-M** with thiolate ions, valuable insights into this question were obtained by comparing the effect of changing leaving group not only on the rate but on the equilibrium constants for nucleophilic addition (K_1^{PrS}) as well. It is therefore useful to briefly review the situation for these reactions.[12] The K_1^{PrS} values showed a trend that was opposite to that for k_1^{PrS}, i.e., K_1^{PrS} was *larger* for the thiomethyl than for the methoxy derivatives, e.g. K_1^{PrS}(**5-Cr**)/K_1^{PrS}(**1-Cr**) = 1.04×10^2 or K_1^{PrS}(**5-W**)/K_1^{PrS}(**1-W**) = 3.52×10^2. These opposite trends in the rate and equilibrium constants imply that the *intrinsic* rate constants (k_o)[21] for the thiomethyl derivatives are substantially lower than those for the methoxy derivatives. This is an indication that the relative contributions of the steric, inductive, and π-donor effects in affecting the rate constants are different from those that affect the equilibrium constants, i.e., the transition states of these reactions are imbalanced in the sense that the development of these factors is not synchronous with bond formation.[22]

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(12) Bernasconi, C. F.; Ali, M. *J. Am. Chem. Soc.* **1999**, *121*, 11384.

(13) In the present context, the anomeric effect[14] refers to the stabilization exerted by geminal oxygen atoms,[15] e.g., in dialkoxy adducts such as T_{OH}^- (X = O).

(14) (a) Kirby, A. G. *The Anomeric Effect and Related Stereoelectronic Effects of Oxygen*; Springer-Verlag: Berlin, 1983. (b) Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393.

(15) (a) Hine, J.; Klueppl, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 2924. (b) Wiberg, K. B.; Squires, R. R. *J. Chem. Thermodyn.* **1979**, *11*, 773. (c) Harcourt, M. P.; More O'Ferrall, R. A. *Bull. Soc. Chim. Fr.* **1988**, 407.

(16) Taft's[17] steric substituent constants, E_s, are −0.55 for MeO and −1.07 for MeS, respectively.

(17) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 91.

(18) σ_F = 0.30 and 0.20 for MeO and MeS, respectively.[19]

(19) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

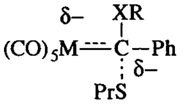
(20) σ_R = −0.43 and −0.15 for MeO and MeS, respectively.[19]

(21) The intrinsic rate constant for a reaction with a forward rate constant k_f and a reverse rate constant k_r is defined as $k_o = k_f = k_r$ when $K_f = k_f/k_r = 1$.

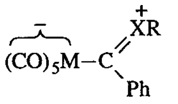
(22) For more details see ref 12.

A summary of the specific interpretation of the dependencies of K_1^{PrS} and k_1^{PrS} on the leaving group is as follows. The fact that K_1^{PrS} is larger for the thiomethyl carbene complexes implies that the stronger reactant-stabilizing π-donor effect of the methoxy group compared to the thiomethyl group is the dominant factor on K_1^{PrS}, overriding the steric and inductive effects. The lower intrinsic rate constants and hence lower k_1^{PrS} values for the thiomethyl derivatives are mainly a consequence of the development of the steric effect at the transition state being more advanced than bond formation.[23]

Another contribution to the differences in intrinsic rate constants is the stronger inductive effect of the methoxy group; this inductive effect increases the intrinsic rate constant more for the methoxy derivative than for the thiomethyl derivative because, at the transition state, the negative charge, which in the intermediate is delocalized into the CO ligands (T_{OH}^- in Scheme 1), is mainly localized on the metal (**11-M**).[25]



11-M(X = O or S)



12-M(X = O or S)

Regarding the possible contribution of the π-donor effect to the difference in the intrinsic rate constants, the situation is more complex because there are two opposing interaction mechanisms that partially or completely offset each other. One is the loss of resonance stabilization of the reactants that is expected to run ahead of bond formation and hence lower the intrinsic rate constant.[23] The π-donor ability of oxygen being stronger than that of sulfur,[20] there will be a stronger reduction of k_o for **1-M** than for **5-M**. The other interaction mechanism is the preorganization of the structure of the $(CO)_5M$ moiety in **5-M** or **1-M** toward its electronic configuration in the adducts that results from the π-donor effect (**11-M**). As a consequence, the lag in the charge delocalization into the CO ligands at the transition state[25] is reduced and the intrinsic rate constant for **1-M** is not as strongly depressed by the effect associated with this lag as that for **5-M**. Observations regarding the effect of changing π-donor strength in the deprotonation of alkoxyalkyl carbene complexes[27] suggest that the two factors essentially cancel each other, i.e., the π-donor effect on the intrinsic rate constant is negligible.

Can the reasoning regarding the relative rate constants for the reactions of **1-M** and **5-M** with thiolate ions be applied in explaining why OH^- reacts more slowly with **5-M** than with **1-M**? The answer is yes. As is the case for K_1^{PrS}, the equilibrium constants for OH^- addition, K_1^{OH}, are expected to be higher for **5-M** than for **1-M**, although the K_1^{OH}(**5-M**)/K_1^{OH}(**1-M**) ratios may not be as large as the K_1^{PrS}(**5-M**)/K_1^{PrS}(**1-M**) ratios for two reasons. (a) The steric effect is probably smaller because OH^- is a smaller nucleophile than the thiolate ions. (b) The anomeric effect should mainly increase K_1^{OH}(**1-M**) but not K_1^{OH}(**5-M**). These two factors should also enhance k_1^{OH}(**1-M**) relative to k_1^{OH}(**5-M**), potentially making the k_1^{OH}(**5-M**)/k_1^{OH}(**1-M**) ratios smaller than the k_1^{PrS}(**5-M**)/k_1^{PrS}(**1-M**) ratios. However, these factors should be partially or completely offset because the reduced steric effect will be less effective in decreasing the intrinsic rate constants for **5-M** relative to those for **1-M**. Indeed, the actual k_1^{OH}(**5-W**)/k_1^{OH}(**1-W**) ratio (3.80×10^{-2}) is almost the same as the k_1^{PrS}(**5-W**)/k_1^{PrS}(**1-W**) ratio (4.00×10^{-2}), while the k_1^{OH}(**5-Cr**)/k_1^{OH}(**1-Cr**) ratio (4.77×10^{-3}) is somewhat lower than the k_1^{PrS}(**5-Cr**)/k_1^{PrS}(**1-Cr**) ratio (3.75×10^{-2}).

$k_1^{H_2O}$: MeO vs MeS as Leaving Group. The reactivity of the MeS complexes toward water is very similar to that of the MeO derivatives: the $k_1^{H_2O}$(**5-Cr**)/$k_1^{H_2O}$(**1-Cr**) ratio is 0.355, the $k_1^{H_2O}$(**5-W**)/$k_1^{H_2O}$(**1-W**) ratio is 1.16. This contrasts with the reactions of OH^- and thiolate ions discussed above, where **5-M** is substantially less reactive than **1-M**. At first sight, this result would appear to be in clear violation of the Reactivity–Selectivity Principle[27] or the Hammond[29]–Leffler[30] postulate. The following interpretation shows that the results are actually understandable in the context of the Hammond–Leffler postulate.

The equilibrium constants for water addition, $K_1^{H_2O}$, are related to K_1^{OH} for OH^- addition by eq 13, with K_w being the ionic product of the solvent. Hence the $K_1^{H_2O}$(**5-M**)/$K_1^{H_2O}$(**1-M**) ratios must be equal to the K_1^{OH}(**5-M**)/K_1^{OH}(**1-M**) ratios. In the previous section it was argued that these ratios are >(≫)1 although probably not as large as the K_1^{PrS}(**5-M**)/K_1^{PrS}(**1-M**) ratios (100 to 350); and the fact that the k_1^{OH}(**5-M**)/k_1^{OH}(**1-M**) ratios are ≪1, i.e., do not follow the trend of the equilibrium constant ratios, was attributed to transition state imbalances. For the water reaction, the $k_1^{H_2O}$(**5-M**)/$k_1^{H_2O}$(**1-M**) ratios of approximately unity do not follow the trend in the K_1^{OH}(**5-M**)/K_1^{OH}(**1-M**) ratios either. This must again be the result of transition state imbalances but the less dramatic discrepancy between the rate and equilibrium constant ratios suggests that these imbalances are smaller and hence have a smaller effect on $k_1^{H_2O}$ than on k_1^{OH} or k_1^{PrS}.

$$K_1^{H_2O} = K_1^{OH} K_w \tag{13}$$

A plausible reason for the smaller imbalances is that, due to the lower reactivity of water, the transition state is later in the sense that bond formation between the nucleophile and the carbene carbon is more advanced than in the reactions with OH^- or thiolate ions, as predicted by the Hammond–Leffler postulate. This has the effect of reducing the imbalance between the development of the steric effect or the delocalization of negative charge into the carbonyl ligands on one hand and bond formation on the other, i.e., the impact on the intrinsic rate constants and hence on the actual rate constants is reduced.

It should be noted that this is a conclusion that not only pertains to the reactions discussed in this paper but is the general validity. In other words, a more advanced transition state will

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(23) This is a manifestation of the principle of nonperfect synchronization (PNS).[24] With respect to the factors relevant to the present study, the PNS states that the intrinsic rate constant decreases if (a) the development of a product destabilizing factor (e.g., a steric effect) runs ahead of bond changes at the transition state, (b) a product stabilizing factor (e.g., resonance) lags behind bond changes, or (c) the loss of a reactant stabilizing factor is ahead of bond changes (π-donor effect).

(24) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9. (c) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119.

(25) This lag of the charge delocalization behind bond changes is another example of a transition state imbalance. The resulting PNS[23] effect is a major factor why the intrinsic rate constants for reactions of Fischer carbene complexes with nucleophiles or bases (deprotonation of carbene complexes with protons on the α-carbon) are relatively small.[26]

(26) For a review, see: Bernasconi, C. F. *Chem. Soc. Rev.* **1997**, *26*, 299.

(27) Bernasconi, C. F.; Leyes, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5169.

(28) (a) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *16*, 69. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 125. (c) Rappoport, Z., Ed. *Isr. J. Chem.* **1985**, *26*, 303–428 (RSP-issue).

(29) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(30) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963; p 156.

always leave less room for imbalances of any kind. This is best appreciated by considering the limiting case where the transition state is almost completely product-like since for such a transition state all processes will have approached 100% completion.

k_1^{OH}: Effect of Metal, Size of Leaving Group, and Phenyl Substituent. As has been noted before, the tungsten carbene complexes are usually slightly more reactive than their chromium counterparts.[9,12,26,31] This is particularly true for the thioalkyl carbene complexes,[11] as is borne out by the results for the reactions of **5-M**, **6-M**, and **7-M** with OH^- and water. As discussed elsewhere, the higher reactivity of the tungsten derivatives results from a combination of a somewhat greater thermodynamic driving force as well as a greater intrinsic rate constant for adduct formation.[9]

In some cases, e.g. for the reactions of **1-Cr** and **1-W** with OH^- and water, the reactivities of the chromium and tungsten complexes are about the same.[3] The reasons for this are not entirely clear.

The dependence on the RS group, **7-M** vs **5-M**, shows a small reduction in k_1^{OH} for the carbene complexes with the n-PrS group, indicating a steric effect. The somewhat larger k_1^{OH} values for **6-M** compared to **5-M** (k_1^{OH}(**6-Cr**)/k_1^{OH}(**5-Cr**) = 2.68, k_1^{OH}(**6-W**)/k_1^{OH}(**5-W**) = 2.04) indicate stabilization of the incipient negative charge on the transition state by the electron-withdrawing *m*-Cl group. These ratios are similar to the k_1^{RO}(**8-W**)/k_1^{RO}(**1-W**) ratio of 3.01 for the reactions with $CF_3CH_2O^-$ in 50% MeCN−50% water, where **8-W** = $(CO)_5W{=}C(OMe)C_6H_4$-3-Cl.[31]

Conclusions

(1) The hydrolysis of **5-M** and, presumably, that of **6-M** and **7-M** as well proceed by the mechanism shown in Scheme 1, the same mechanism postulated for the hydrolysis of alkoxy carbene complexes (**1-M**). However, the k_2^{i} and $K_a^{T}k_3^{H}$ pathways are probably negligible while the $k_2^{H_2O}$ pathway should be much more important than for **1-M**.

(2) The rate-limiting step changes from nucleophilic attack by OH^- (region I of the pH rate profiles) and by water (region II) to breakdown of T_{OH}^- via the combined $k_2^{H_2O}$, k_2^{i}, and $K_a^{T}k_3^{H}$ pathways (region III) and finally to the k_2^{H} pathway (region IV). This contrasts with the hydrolysis of **1-M** where nucleophilic attack by OH^- (high pH) or water (low pH) is rate limiting over the entire pH range.

(3) The key feature responsible for the difference between how the hydrolysis of the two types of complexes respond to pH changes is that OH^- and MeO^- departure from T_{OH}^- is very sensitive to H^+-catalysis while for RS^- departure the sensitivity to H^+-catalysis is much weaker.

(4) For the reaction with OH^-, the MeS complexes are kinetically much less reactive than the MeO derivatives yet the equilibrium constants for intermediate formation are probably larger for the MeS than for the MeO complexes. This indicates that the intrinsic rate constants are much lower for the reactions of the MeS complexes than for the MeO complexes due to imbalances in the development of the steric effects and the delocalization of the negative charge into the CO ligands.

(5) For the reaction with water, the MeS and MeO complexes show comparable kinetic reactivities. This can be understood in terms of a later transition state than in the reactions with OH^-, which leads to smaller imbalances.

Experimental Section

Materials. **5-Cr** and **5-W** were synthesized as described previously[12] by reacting **1-Cr** and **1-W**, respectively, with NaSMe in a benzene−methanol mixture. The same procedure was used to prepare **6-Cr** and **6-W** from $(CO)_5M{=}C(OMe)C_6H_4$-3-Cl (M = Cr and W) with the latter complexes being available from a previous study.[31] ^{1}H NMR ($CDCl_3$) for **6-W**: δ 2.16 (s, 3H, CH_3S), 6.61 (d, 1H, Ar), 6.73 (s, 1H, Ar), 7.37 (m, 2H, Ar). ^{1}H NMR ($CDCl_3$) for **6-Cr**: δ 2.33 (s, 3H, CH_3S), 6.53 (d, 1H, Ar), 6.65 (s, 1H, Ar), 7.23 (d, 1H, Ar), 7.40 (t, 1H, Ar). ^{13}C NMR ($CDCl_3$) for **6-W**: δ 28.26 (CH_3S), 116.46, 126.51, 129.39 and 158.52 (Ar), 196.34 (CO, cis), 208.08 (CO, trans), 324.21 (=C). ^{13}C NMR ($CDCl_3$) for **6-Cr**: δ 28.54 (CH_3S), 117.01, 126.90, 130.27, and 158.09 (Ar), 215.43 (CO, cis), 228.58 (CO, trans), 358.89 (=C). **7-Cr** and **7-W** were available from a previous study.[9]

Instrumentation, Procedures, and Kinetic Experiments. NMR spectra were recorded on a Bruker 250 MHz instrument. UV spectra were obtained on a Hewlett-Packard 8562 diode array spectrophotometer. Kinetic experiments were performed on a Perkin-Elmer Lambda 2 or the 8562 diode array spectrophotometer. pH measurements were made with an Orion Research 611 digital pH meter and calibrated with standard aqueous buffers at pH 4.00, 7.00, and 10.00. Actual pH values were calculated by adding 0.18 to the measured pH, according to Allen and Tidwell.[32] All rates were measured under pseudo-first-order conditions as described under Results; the reactions were monitored at 466 and 450 nm, respectively, corresponding to the λ_{max} of the Cr and W complexes, respectively. For the slowest reactions the method of initial rates was used where k_{obsd} was determined by using eq 14 where

$$k_{obsd} = \frac{slope}{A_o - A_\infty} \qquad (14)$$

slope is the slope of a plot of absorbance, A, vs time for the first 1−5% of reaction, and A_o is the initial absorbance and A_∞ the absorbance after the reaction is complete. This latter was obtained from runs in KOH solutions.

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Supporting Information Available: General rate expression for Scheme 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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