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Journal of Organometallic Chemistry 689 (2004) 3520–3527

Journal of Organometallic Chemistry

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Transition metal carbene chemistry 2: kinetic studies on the nucleophilic substitution reactions of $(CO)_5M{=}C(SCH_3)CH_3$ (M = Cr and W) with morpholine in aqueous acetonitrile

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Received 9 July 2004; accepted 6 August 2004
Available online 15 September 2004

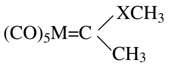
Abstract

Kinetic studies of the aminolysis of [methyl(thiomethyl)carbene]pentacarbonyl chromium(0),$(CO)_5Cr{=}C(CH_3)(SCH_3)$ **(1-Cr(S))** and [methyl(thiomethyl)carbene]pentacarbonyltungsten(0), $(CO)_5W{=}C(CH_3)(SCH_3)$ **(1-W(S))**, with morpholine, a secondary amine, in 50% acetonitrile–50% H_2O (v/v at 25 °C) is reported. The second-order rate constant (k_A in $m^{-1}\ s^{-1}$) increases with amine concentration, giving a linear dependence with an intercept on the rate axis and a tendency towards leveling off at higher amine concentration. The reaction was found to undergo general base catalysis. The mechanism proposed is very similar to those for ester reactions, involving a nucleophilic addition of amine to the substrate to yield a zwitterionic tetrahedral intermediate ($T_A^{\pm}$) in the first step, followed by deprotonation to form T_A^- in the second step, which, in the third step, converted to product by H_2O and/or conjugate acid of the base (BH^+), assisted MeS^- expulsion. The reactivity (k_1) of **1-W(S)** was found to be higher than that of **1-Cr(S)**, whereas, comparable ($k_3^{H_2O}K_a^{\pm}/k_{-1}K_w$), water catalyzed and ($k_3^{BH}K_a^{\pm}/k_{-1}K_a^{BH}$), BH^+ catalyzed, leaving group departure were found for both the carbenes complexes. All these observations have been explained successfully.

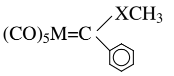
Keywords: Fischer carbenes; Nucleophilic substitution; Morpholine; Three steps reactions

1. Introduction

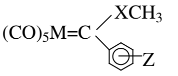
The carbene carbon of Fischer type carbene complexes of the general type **1-M** – **3-M** is electrophilic in nature [1] and undergoes facile substitution of CH_3X group (X = S and O; in general, M = Cr and W, unless otherwise mentioned) with nucleophiles, such as OH^- [2], water [2], MeO^- [3], amines [4], thiolate ions [5], carbanion [6] and others [7] (Eq. (2)). In general, the reactions proceed in stepwise fashion with the formation of a tetrahedral intermediate **(4-M)** [1,8]. In few cases, direct detection of intermediate **(4-M)** has been reported [5d,3(b)].



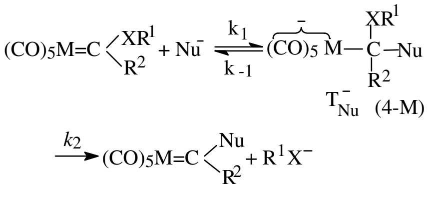
X= S, M =Cr&W, 1-M(S)
X= O, M = Cr&W,1-M(O)



X= S, M=Cr&W, 2-M(S)
X= O, M =Cr&W, 2-M(O)



X= S, M = Cr & W, 3-M(S)-Z
X= O, M = Cr & W, 3-M(O)-Z



$$(CO)_5M{=}C\langle^{XR^1}_{R^2} + Nu^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CO)_5\overset{-}{M}-\overset{XR^1}{\underset{R^2}{C}}-Nu \qquad T^-_{Nu}\ (4\text{-}M) \qquad (1)$$

$$\xrightarrow{k_2} (CO)_5M{=}C\langle^{Nu}_{R^2} + R^1X^-$$

In recent reports, Bernasconi et al. [4(f,g),9,10] demonstrated that the mechanism of reactions of **2-Cr(O)** and **3-M(O)-Z** with amine nucleophiles (Scheme 1) also applies to the reactions of corresponding thiomethyl analogue. However, there are differences in the rate

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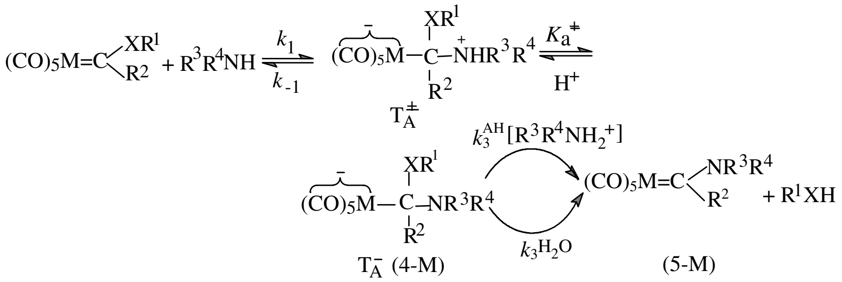
doi:10.1016/j.jorganchem.2004.08.012



Scheme 1.

constants of the individual steps leading to the occurrence or absence of base catalysis by OH^- and amines [9,10]. Generally, base catalysis is observed when leaving group (MeX^-) departure is rate limiting, i.e., when $(k_3^{H_2O}K_a^{\pm}/k_{-1}K_w)[OH^-] < 1$ and $(k_3^{BH}K_a^{\pm}/k_{-1}K_a^{BH})[BH] < 1$; $K_w(= 18.19)$ is the ionic product of water in 50% H_2O–50% CH_3CN (v/v) at 25 °C, and K_a^{BH} is the acidity constant of BH^+, the conjugate acid of the amine base. With methoxy analogue **2-M(O)** and **3-M(O)-Z**, the general base catalysis was observed for a wide variety of amines [4(f,g)]. However, a change from methoxy to the corresponding thiomethyl analogue induces a large decrease in k_{-1}, a moderate decrease in $k_3^{H_2O}$ and $K_a^{\pm}/K_w$ and a slight decrease in k_3^{AH} and $K_a^{\pm}/K_a^{BH}$. As a consequence, a situation arises where $(k_3^{H_2O}K_a^{\pm}/k_{-1}K_w)[OH^-]$ and $k_3^{BH}K_a^{\pm}/k_{-1}K^{BH})[B] > 1$ and k_1 becomes the rate limiting step. This situation is quite apparent for the reaction of **2-Cr(S)** with *n*-butylamine, 2-chloroethylamine, 2-methoxyethylamine, glycinamide, piperidine, piperazine and 1(2-hydroxyethyl) piperazine, where, a strict second-order dependence, first-order in **2-Cr(S)** and first-order in the amine was apparent [9]. In contrast, with morpholine, general base catalysis, and with aminoacetonitrile only OH^- catalysis were observed [9]. In the reaction of **3-Cr(S)-Z** with both primary and secondary amines nucleophilic attachment of the amines to the carbene carbon is rate limiting and no base catalysis was observed [10]. Thus, varying mechanistic features were observed for the reactions of phenyl thiomethyl carbene complexes with different amines, whereas, a general behaviour was observed for all the aminolysis reaction of methoxy phenyl carbene complexes. Though, there are few reports on the aminolysis reactions of methoxy phenyl or phenyl thiomethyl carbene complexes (**2-M(X)** or **3-M(X)-Z**) [4(f,g),9,10], no such detailed study on the corresponding methoxy methyl or methyl thiomethyl carbene complexes (**1-M(X)**) is reported thus far. The Fischer carbene complexes, **1-M(S)**, behave as carbon acids and kinetic and thermodynamic acidities are reported very recently [11]. In a subsequent study, pK_a^{CH} of **1-Cr(S)** was re-determined by exploiting the aminolysis reaction with morpholine, a secondary amine [12]. In the present paper, we report a detailed kinetic study on the aminolysis of **1-M(S)** with morpholine. The reaction of **2-Cr(S)** with thiolate ions showed a significant change in rate constants of all elementary steps [11] compared to the corresponding reactions of **2-Cr(O)** [4(f,g)]. Taking this as a guide, it is expected that in Scheme 1 with X = S, in the present investigation too, there would be a substantial effect of MeS^- as leaving group on rates and equilibrium constants.

Table 1

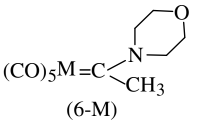
Summary of pseudo-first-order rate constant for the nucleophilic substitution reaction of $(CO)_5M{=}C(SCH_3)(CH_3)$ (M = Cr and W) with morpholine in 50% MeCN–50% H_2O at pH 8.70, [**1-M(S)**] = $(5.0–9.0) \times 10^{-5}$ M, $I = 0.10$ M KCl, $t = 25$ °C

[Morpholine]/M	$10^2 \times k_{obs}/s^{-1}$(Cr)	$10^2 \times k_{obs}(W)/s^{-1}$	$k_{A(corr)}/m^{-1}\ s^1$(Cr)	$k_{A(corr)}/m^{-1}\ s^1$(W)
0.001	0.052	0.52	0.76	16.4
0.002	0.123	1.14	0.90	17.8
0.004	0.289	2.68	1.06	21.0
0.005	0.382	3.75	1.12	23.5
0.015	2.21	18.2	2.16	38.0
0.025	5.40	40.6	3.17	50.8
0.035	9.70	71.5	4.06	63.9
0.050	19.5	135	5.72	84.5
0.060	25.2	190	6.16	99.1
0.075	33.0	265	6.45	110.6
0.085	46.2	320	7.97	117.8
0.100	51.0	406	7.47	127.1

$k_A(corr)(Cr) = (k_{obs} - k_h)/[morp] \times ([H^+] + K_a^{CH}(M)/[H^+])(M = Cr,\ pK_a^{CH} = 9.05, M = W,\ pK_a^{CH} = 8.37$, k_h (W) (at pH 8.70) = 1.04×10^{-4}, s^{-1}; k_h (Cr) (at pH 8.70) = 2.90×10^{-4}, s^{-1}.

2. Results and discussion

As reported earlier [12], the products formed in these reactions are **(6-M)** quantitative, and the conversion of **[1-M(S)]** into the amine carbene complex **(6-M)** produces a blue shift in the UV–Vis region.



(6-M)

The kinetic conditions adopted for the reaction of **1-M(S)** with morpholine are: **[1-M(S)]** = (5.0–9.0) × 10^{-5} M, $[\text{morpholine}]_f$ (subscript ‘f’ indicates the free morpholine) = 0.001–0.10 M, pH 8.70 and 9.10–11.65 (Table 1). In all cases, plots of the observed pseudo-first-order rate constants, k_{obs}, vs. $[\text{morpholine}]_f$ showed upward curvature (Fig. 1) with negligible or no intercepts on the rate axes, which is reminiscent of the reactions of **[2-M(O)]** with primary and secondary amines [4f]. The carbene complexes undergo auto-decomposition (hydrolysis) and hydrolysis rate constants at all pH of reactions were determined separately. For this purpose, concentration of different bases (NMM, TEA, etc) were varied at particular pH, and intercepts of the plots of k_{obs} vs. [base] give k_h, the water hydrolysis rate constant. Data were analyzed based on Eq. (2)

$$k_A = (k_{\text{obs}} - k_h)/[\text{morpholine}]_f. \tag{2}$$

As the carbene complexes undergo deprotonation (Eq. (3)) under the reaction conditions [$\text{p}K_a^{\text{CH}} = 9.05$ for **1-Cr(S)** and 8.37 for **1-W(S)**] [11], and the deprotonated carbene complexes do not undergo nucleophilic attack, $k_A$was corrected further by Eq. (4).

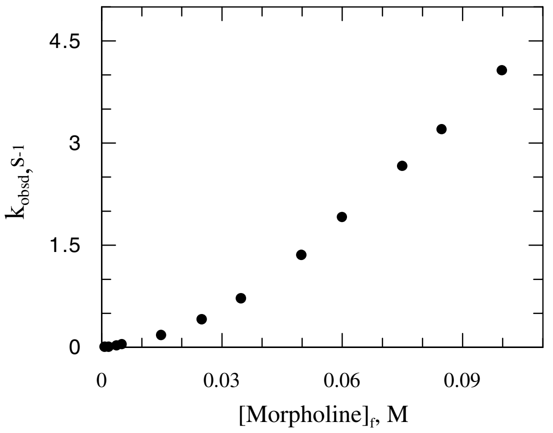
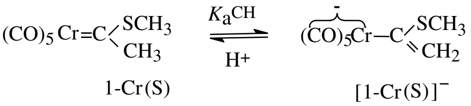


Fig. 1. Plot of k_{obs} vs. $[\text{morpholine}]_f$ for the reaction between morpholine and **1-W(S)** in 50% CH_3CN–50% H_2O. Conditions are: **[1-W(S)]** ~ 6.0 × 10^{-5} M, pH 8.70, I = 0.10 M (KCl) and temperature, 25 °C.



$$(CO)_5Cr{=}C(SCH_3)CH_3 \underset{H^+}{\overset{K_a^{CH}}{\rightleftharpoons}} [(CO)_5Cr{-}C(SCH_3){=}CH_2]^- \tag{3}$$

1-Cr(S) [1-Cr(S)]$^-$

$$k_A(\text{corr}) = k_A\{([H^+] + K_a^{\text{CH}})/[H^+]\}. \tag{4}$$

The hydrolysis of these carbene complexes was also carried out in KOH medium. Plots of $k_{\text{obsd}}(\text{corr})$ $(= k_{\text{obsd}}\{([\text{H}^+] + K_a^{\text{CH}})/[\text{H}^+]\})$ vs. [KOH] for **1-M(S)** are shown in Fig. 2. The Plots of k_A(corr) vs. $[\text{morpholine}]_f$ at pH 8.70 were straight lines with a slight tendency towards curvature at the tail for both the complexes. A representative plot for **1-W(S)** is shown in Fig. 3.

To check the general base catalysis of these reactions, variation of $[\text{TEA}]_f$ (TEA = triethylamine, 0.001–0.20 M) at pH 10.78 and $[\text{morpholine}]_f$ = 0.02 M for

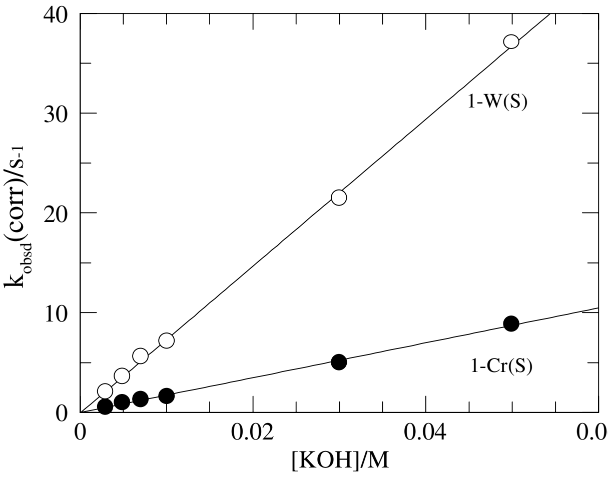


Fig. 2. Plots of $k_{\text{obs}}(\text{corr})(= k_{\text{obs}} \times \{([\text{H}^+] + K_a^{\text{CH}})/[\text{H}^+]\})$ vs. [KOH] for the hydrolysis of **1-M(S)** (M = Cr and W) in 50% CH_3CN–50% H_2O. Conditions are: **[1-M(S)]** ~ 6.0 × 10^{-5} M,, I = 0.10 M (KCl) and temperature, 25 °C.

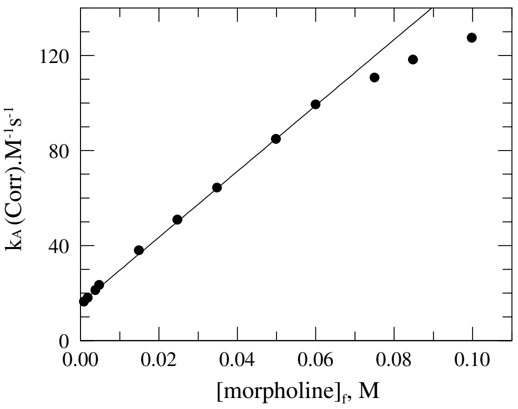


Fig. 3. Plot of k_A(corr) vs. $[\text{morpholine}]_f$ for the reaction between morpholine and **1-W(S)** in 50% CH_3CN–50% H_2O. Conditions are: **[1-W(S)]** ~ 6.0 × 10^{-5} M, pH 8.70, I = 0.10 M (KCl) and temperature, 25 °C.

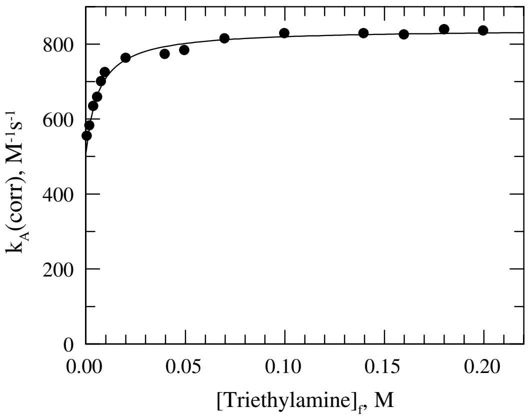


Fig. 4. Plot of k_A(corr) vs. [triethylamine] for the reaction between morpholine and **1-W(S)** in 50% CH_3CN–50% H_2O. Conditions are: [**1-W(S)**] ~ 6.0×10^{-5} M, [morpholine]$_f$ = 0.01 M, pH 10.78, M, I = 0.10 M (KCl) and temperature, 25°.

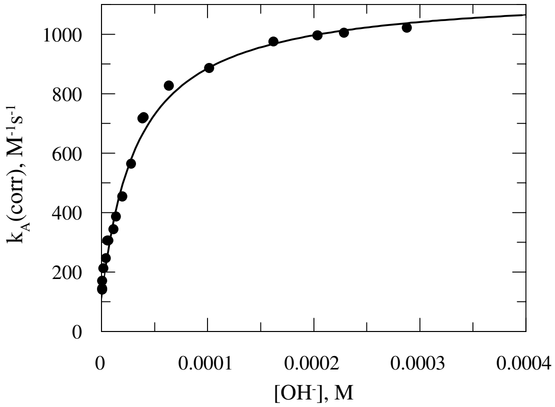


Fig. 5. Plot of k_A(corr) vs. [OH^-] for the reaction between morpholine and **1-W(S)** in 50% CH_3CN–50% H_2O. Conditions are: [**1-W(S)**] ~ 6.0×10^{-5} M, [morpholine]$_f$ = 0.01 M, [TEA]$_f$ = 0.01 M, I = 0.10 M (KCl) and temperature, 25 °C.

1-Cr(S) and 0.01 M for **1-W(S);** and also a variation of pH (9.10–11.65) at constant [TEA]$_f$ = 0.02 M and [morpholine]$_f$ = 0.02 M for **1-Cr(S)** and [TEA]$_f$ = 0.01 M and [morpholine]$_f$ = 0.01 M for **1-W(S)** were carried out. Plots of k_A vs. [TEA]$_f$ and. [OH^-] are shown in Figs. 4 and 5 for **1-W(S)**, respectively.

2.1. Mechanism

The reactions can best be represented by Scheme 2; k_3^{BH} (B = morpholine and/or TEA), and $k_3^{H_2O}$ refer to conjugate acid of the amine and solvent catalyzed pathways, respectively.

Application of steady-state approximation to $T_A^{\pm}$ leads to the rate law of Eq. (5).

The general second-order rate constant, $k_A(\text{corr}) = \{(k_{obs} - k_h)/[B]\} \times \{(K_a^{CH} + [H^+])/[H^+]\}$ is given as Eq. (6)

$$k_{obs} = \frac{k_1\left(\frac{k_3^{BH}K_a^{\pm}}{k_{-1}K_a^{AH}}[B] + \frac{k_3^{H_2O}K_a^{\pm}}{k_{-1}K_w}[OH^-]\right)}{1 + \frac{k_3^{BH}K_a^{\pm}}{k_{-1}K_a^{BH}}[B] + \frac{k_3^{H_2O}K_a^{\pm}}{k_{-1}K_w}[OH^-]}[RR'NH], \qquad (5)$$

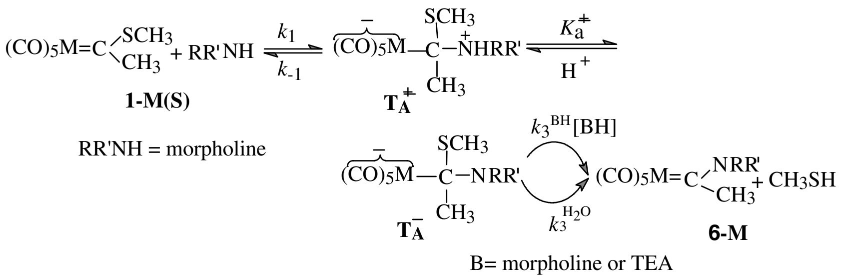
$$k_{A(corr)} = \frac{k_1\left(\frac{k_3^{BH}K_a^{\pm}}{k_{-1}K_a^{BH}}[B] + \frac{k_3^{H_2O}K_a^{\pm}}{k_{-1}K_w}[OH^-]\right)}{1 + \frac{k_3^{BH}K_a^{\pm}}{k_{-1}K_a^{BH}}[B] + \frac{k_3^{H_2O}K_a^{\pm}}{k_{-1}K_w}[OH^-]}. \qquad (6)$$

2.2. Data analysis

For both the carbene complexes plots of k_A(corr) vs. [morpholine]$_f$ at pH 8.70 were straight lines with a slight tendency towards curvature at the tail. Linear regressions for the linear part of the plots give slope = (99.9 ± 1.4) $m^{-2}\,s^{-1}$ and intercept = (0.06 ± 0.02) $m^{-1}\,s^{-1}$ for **1-Cr(S)** and slope = (1384 ± 18) $m^{-2}\,s^{-1}$ and intercept = (15.8 ± 0.44) $m^{-1}\,s^{-1}$ for **1-W(S)**. The nature of dependence indicates that under these conditions $(k_3^{BH}K_a^{\pm}/k_{-1}K_a^{BH}[B] + k_3^{H_2O}K_a^{\pm}/k_{-1}K_w[OH^-] \ll 1)$ and Eq. (7) is applicable, and slopes and intercepts correspond to $k_1(k_3^{B}/k_{-1})$ and $k_1(k_3^{OH}/k_{-1})[OH^-]$, respectively.

$$k_{A(corr)} = k_1\left(\frac{k_3^{BH}K_a^{\pm}}{k_{-1}K_a^{BH}}[B] + \frac{k_3^{H_2O}K_a^{\pm}}{k_{-1}K_w}[OH^-]\right). \qquad (7)$$

Non-linear least-squares fit of data to Eq. (6) for [TEA]$_f$ and [OH^-] variations yielded parameters which are listed in Table 2. The k_1 values obtained from [TEA]$_f$ variation are somewhat lower than from the



Scheme 2.

Table 2
Summary of rates and equilibrium constants for the reaction of $(CO)_5M{=}C(SCH_3)(CH_3)$ (M = Cr and W) with morpholine

Parameters	$(CO)_5Cr{=}C(SCH_3)(CH_3)$	$(CO)_5W{=}C(SCH_3)(CH_3)$
k_1, m^{-1} s^{-1}	(79.7 ± 1.30)[a] (62.7 ± 0.82)[b]	(1140 ± 20)[a] (883 ± 5.0)[b]
$k_3^{OH}/k_{-1}, M^{-1}$	$(3.85 \pm 0.27) \times 10^4$	$(3.39 \pm 0.27) \times 10^4$
$k_3^{TEA}/k_{-1}, M^{-1}$	(228 ± 31)	(386 ± 42)
$k_3^{morp}/\mathrm{k}_{-1}, M^{-1}$	(1.25 ± 0.01)	(1.22 ± 0.01)
k_3^{OH}/k_3^{TEA}	169	87.7
k_3^{OH}/k_3^{morp}	3.08×10^4	2.78×10^4

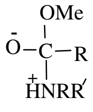
[a] Data extracted from $[OH^-]$ variation.
[b] Data extracted from [triethylamine] variation.

determination of $[OH^-]$ dependence, and this was also found in many reactions of other carbene complexes with different primary as well as secondary amines. From the knowledge of k_3^{OH}/k_{-1} it is possible to determine the k_3^B/k_{-1} for morpholine catalysis of the reaction. Data are listed in Table 2.

Based on observations in many nucleophilic substitution reactions the kinetic data are best described in terms of stepwise mechanism depicted in Scheme 2. The compelling evidence is that there is a reasonable agreement between the plateau values of the curvilinear plots of k_A vs. $[OH^-]$ and $[TEA]_f$. General base catalysis of reactions may also be accounted for by Scheme 3.

Scheme 3 represents the base B and OH^- catalyzed deprotonation of $T_A^{\pm}$ followed by leaving group departure [1,8,13,14] which typically observed in the aminolysis of esters **(7)** [15] and in numerous S_NAr reactions where general base catalysis occurs [16]. From the Scheme 2 and 3, one can equate $k_3^B = k_{3P}^B$ and $k_3^{OH} = k_{3P}^{OH}$.

In contrast, the deprotonation of the corresponding zwitterionic intermediate **(8)** of a strongly activated vinylic compounds, e.g., β-methoxy-α-nitrosostilbene **(9)** in its aminolysis reactions, is fast and methoxide ion departure is rate *determining* [17].



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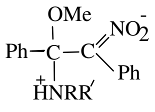

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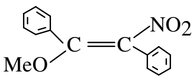

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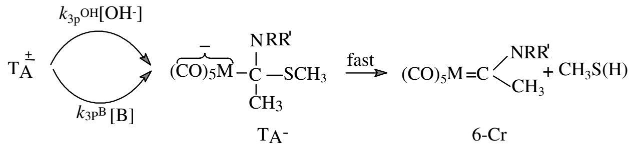
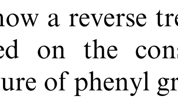
In the reaction of morpholine with **1-M(S)**, Scheme 2 is operative and several lines of reasoning in support of this and against Scheme 3 are discussed elsewhere [4(f,g),9,10,12].



Scheme 3.

In the reaction of **2-M(O)** with thiolate ions [5d] direct detection of intermediate **(11-M)** was encountered. This arises because the equilibrium of the first step is quite favorable i.e., $k_1[RS^-] \gg 1$ and the conversion of the intermediate to products is slower than its formation from the reactants i.e., $k_1[RS^-]/k_2 > 1$ (Eq. (2)).



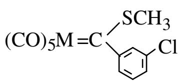
(11-M)

The critical inspection of the Table 2 reveals that k_3^B/k_{-1} for morpholine is smaller than k_3^B/k_{-1} for triethylamine catalysis. This leads to k_3^{OH}/k_3^B morpholine $\gg k_3^{OH}/k_3^B$(triethylamine) for both the carbene complexes. The strong increase in the k_3^{OH}/k_3^B ratios with decreasing basicity of the amine is easily accounted for in terms of the mechanism in Scheme 2, which successfully explains the general base catalysis.

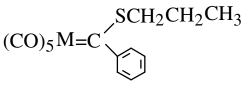
Though, there will be no direct correlation between the catalytic activities of morpholine and triethylamine, as they belong to different class of amines (secondary and tertiary, respectively), the observed result appears mainly as the consequence of the decreased catalytic activity of BH^+ as it becomes less acidic and hence lower k_3^{BH}.

CH_3 vs. Ph: With respect to nucleophilic attack **1-M(S)** was found to be more reactive than **2-M(S).** As for example, for morpholine as nucleophile, k_1(1-Cr(S)/k_1(2-Cr(S) ~ 200 while for leaving group departure, the reverse trend is prevailing: $((k_3^{BH}K_a^{\pm}/k_{-1}K_a^{B\ H})(\mathbf{1-C\ r(S)})/(k_3^{B\ H}K_a^{\pm}/k_{-1}K_a^{B\ H})(\mathbf{2-C\ r(S)}) \sim 0.24$ and $(k_3^{H_2O}K_a^{\pm}/k_{-1}K_w)(\mathbf{1-Cr(S)})/(k_3^{H_2O}K_a^{\pm}/k_{-1}K_w)(\mathbf{2-Cr(S)}) \sim 0.12$. This implies that the formation of $T_A^{\pm}$ with morpholine is thermodynamically more favorable for **1-Cr(S)** than **2-Cr(S)**, though, based on inductive (*I*) effect it should show a reverse trend. The compelling explanation is based on the consideration of steric crowding. Bulky nature of phenyl group over the methyl group disfavors this process. Here, the steric effect predominates over the inductive effect and hence the observed reaction trend.

Cr vs. W: As has been noted earlier, the tungsten carbene complexes are usually slightly more reactive than their chromium counterpart, though in some cases almost the similar reactivity were observed, particularly for the reaction of **2-Cr(O)** and **2-W(O)** with OH^- and water [2], and the reasons for which are not clear. The higher reactivity of tungsten carbene complexes over the chromium is particularly true for thioalkyl carbene complexes, as is borne out by the results for the reaction of **2-M(S), 11-M(S)** and **12-M(S)** with OH^- and water [3,18]. This is also expected to be valid for the reactions of **1-M(S)** with morpholine. The k_1 value for the reaction of morpholine with tungsten complex is about 14-fold higher than that of chromium complex. Similar $k_1(W)/k_1(Cr)$ ratios have been reported for the reactions with MeO$^-$ in MeOH [3] and with various thiolate ions in 50% MeCN–50% H_2O with **3-M(X)-Z** [5d,19]. They show a consistent pattern of somewhat enhanced electrophilic reactivity of tungsten complexes. On the other hand, k_3^{OH}/k_{-1} and k_3^{TEA}/k_{-1} or k_3^{morp}/k_{-1} are almost the same for chromium and tungsten complexes, falling almost within the limit of experimental errors.



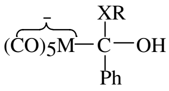
11-M(S)



12-M(S)

M= Cr and W

MeO vs. MeS as leaving group – As there is no report on the reaction of **1-M(O)** with amine as nucleophile, a direct comparison of reactivity **1-M(O)** and **1-M(S)** is not possible. Based on the reactivity of water, OH$^-$ and thiolate ions toward **2-M(O) and 2-M(S)** [2,3,5d,19] complexes an indirect comparison can be drawn for the reactivity of **1-M(O)** and **1-M(S)** towards morpholine. Very similar reactivity of **2-M(O)** and **2-M(S)** towards water to form tetrahedral intermediate (**13**) was observed: $k_1^{H_2O}(2 - Cr(S))/k_1^{H_2O}(2 - Cr(O)) = 0.355$ while the ratio $k_1^{H_2O}2 - W(S))/k_1^{H_2O}(2 - W(O)) = 1.16$ [3,18]. This is in contrast with the reactions of OH$^-$ and thiolate ion, where **2-M(S)** is substantially more reactive than **2-M(O)**, which apparently violate the *Reactivity-selectivity principle*



(13), X = O or S

[20] or Hammond [21]–Leffler [22] postulates but understandable in the context of Hammond–Leffler postulate. Several factors that may affect the reactivity include steric, inductive and π-donor effects. Specially, the steric effect is expected to lower the reactivity of **2-M(O)** relative to **2-M(S)** due to larger size of MeS group. While the stronger electron-withdrawing inductive effect of the MeO group should enhance the reactivity of **2-M(O)** over **2-M(S)**, the stronger π-donor effect of the MeO group compared to that of MeS group should lower the reactivity of **2-M(O)**. The relative importance of these factors can be evaluated by comparing the effect of changing leaving group on the rates and equilibrium constants. For the reaction of propanethiolate ion, PrS$^-$ with **2-M(O)** and **2-M(S)** K_1^{PrS} [5d] values showed a trend that was opposite to that of k_1^{PrS}, i.e., K_1^{PrS} was larger for the thiomethyl than for methoxy derivatives, e.g., $K_1^{PrS}[2 - Cr(S)]/K_1^{PrS}[2 - Cr(O)] = 1.04 \times 10^2$ or $K_1^{PrS}[2 - W(S)]/K_1^{PrS}[2 - W(O)] = 3.52 \times 10^2$. The opposite trends in rate and equilibrium constants imply that the intrinsic rate constant (k_0) for the thiomethyl derivatives are substantially lower than those of the methoxy derivatives. This is an indication of 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. This means that the transition states of these reactions are imbalanced in the sense that the development of these factors is not synchronous with bond formation [11]. 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 are the consequences of the development of the steric effect at the transition state being more advanced than bond formation [23]. Similar explanation should also be valid for **1-M(O)** and **1-M(S)** reactions. We are currently investigating the reactions of **1-M(O)** towards different amines and thiols to support this proposition.

3. Conclusions

(i) The reaction of **2-M(X)** with morpholine leads to the nucleophilic substitution of the thiomethyl group by a three step mechanism of Scheme 2. The general base catalysis was detected which is in the same line for reaction of morpholine with **2-Cr(S)**.

(ii) The intermediates $T_A^{\pm}$ and T_A^- remain undetectable even at high amine concentration and high pH due to the fact that the rate of its conversion to product is faster than its formation i.e. $k_1[R^3R^4NH]/(k_3^{H_2O} + k_3^{AH}[R^3R^4NH_2^{3+}]) < (\ll)1$.

(iii) With respect to nucleophilic attack **1-M(S)** was found to be more reactive than **2-M(S)** while for leaving group departure the reverse trend is prevailing: This implies that the formation of $T_A^{\pm}$ with morpholine is thermodynamically more favorable for **1-Cr(S)** than **2-Cr(S)**, though based on inductive effect it should show a reverse trend. Bulky nature of phenyl group over the methyl group disfavors this process. Steric effect predominates over the inductive effect and hence the observed reaction trend.

(iv) The tungsten carbene complex is slightly more reactive than its chromium counterpart. The k_1 values for the reaction of morpholine with tungsten complex are about 14-fold higher than that of chromium complex. On the other hand, $(k_3^{BH}K_a^{\#}/k_{-1}K_a^{BH})$ and $(k_3^{H_2O}K_a^{\#}/k_{-1}K_w)$ are almost the same for chromium and tungsten complexes. This arises due the combination of a somewhat greater thermodynamic driving force as well as probably a greater intrinsic rate constant ($\log k_0$) of **1-W(S)** over **1-Cr(S)** for adduct formation [21].

4. Experimental section

4.1. Materials

[Methyl(thiomethyl)carbene]pentacarbonylchromium (0), $(CO)_5Cr{=}C(CH_3)(SCH_3)$ (1-Cr(S)) and [Methyl(thiomethyl)carbene]pentacarbonyltungsten(0), $(CO)_5W{=}C(CH_3)(SCH_3)$ (1-W(S)) were synthesized by the method of Lam and Senoff [5b] used for the synthesis of phenylmercapto derivatives. Instead of using CH_3SH gas, as used by Fischer and coworkers [5a], CH_3SNa was used in this process. The carbene complexes were characterized by ^1H and ^{13}C NMR in $CDCl_3$ with 250 MHz Bruker NMR spectrophotometer as follows: δ 2.65 (s, 3H, CH_3S) and 3.50 (s, 3H, CH_3). ^{13}C NMR δ 26.87 (CH_3S), 46.03 (CH_3), 216.0 (CO, *cis*), 227.4 (CO, *trans*), 366.9 (C=), for **1-Cr(S)** and δ 2.54 (s, 3H, CH_3S) and 3.34 (s, 3H, CH_3). ^{13}C NMR δ 27.46 (CH_3S), 48.07 (CH_3), 197.8 (CO, *cis*), 207.6 (CO, *trans*), 332.6 (C=), for **1-W(S)** which are very similar to those reported by Fischer et al. [5a] in $CDCl_3$: UV–Vis (50% MeCN–50% H_2O): (**1-Cr(S)**), λ_{max} 448 nm ($\varepsilon = 8455$ m^{-1} cm^{-1}); (**1-W(S)**), 432 nm ($\varepsilon = 13{,}300$ m^{-1} cm^{-1}). M.p. 31–32 °C (lit. 34 0 °C) for **1-Cr(S)** and 33–34 °C (lit. 34 0 °C) for **1-W(S)**.

Reagent grade morpholine (Aldrich) was distilled over CaH_2 before use. The spectrum of the reaction product was found to be identical with **6-M**, prepared separately by using the method described by Fischer and Leupold [4f].

4.2. pH measurements

The pH in 50% MeCN–50% H_2O (v/v) at an ionic strength 0.10 mol dm^3 mol^{-1} (KCl) at 25 °C (maintained by using water-jacketed container and flowing water through it from a thermostatic water bath) was determined by following Eq. (2) according to Allen and Tidwell [25] where, $pH_{measured}$ referring to the reading of the pH-meter. A digital pH-meter (Systronics-335, India) equipped with a glass electrode and a reference electrode calibrated with standard aqueous buffers before use was used to measure the pH of the reaction solutions: $pH_{actual} = pH_{measured} + 0.18$.

4.3. Kinetic runs and spectra

Stock solutions of the carbene complexes were prepared in anhydrous acetonitrile in which it was found to be fairly stable for several hours. Agilent 8453 diode array spectrophotometer equipped with peltier temperature controller (Agilent 89090 A) was used for kinetic studies. For few faster reactions ($k_{obs} > 0.10$ s^{-1}) Applied Photophysics DX.17W stopped flow apparatus was used. All kinetic experiments were conducted in 50% CH_3CN–50% H_2O (v/v) under pseudo-first-order conditions with the carbene complexes as the minor component and monitored by the disappearance of the substrate at 448 nm at lower pH while at 355 nm at higher pH for **1-Cr(S)**, and at 432 nm at lower pH and at 335 nm at higher pH for **1-W(S)**. All reactions were found to give excellent first-order kinetics over at least 4 half-lives and pseudo-first-order rate constants (k_{obs}, s^{-1}) were obtained by the integration method, fitting the experimental absorbance-time data with the equation of the form: $\ln(A_t - A_\infty) = \ln(A_o - A_\infty) - k_{obs} \times t$, and the results were found to fall within the error limit ± 5 %. Typical substrate concentrations were $(5.0–9.0) \times 10^{-5}$ M. The study of reactions at two different wave lengths (say 432 and 335 nm for **1-W(S)** does not show any visible wavelength dependency of rates.

Acknowledgements

Thanks are due to the DST, New Delhi, for financial assistance and Professor C.F. Bernasconi, Department of Chemistry and Biochemistry, UCSC, Santa Cruz for helpful discussion.

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