

Transition metal carbene chemistry 5: Kinetic studies on the nucleophilic substitution reactions of $(\text{CO})_5\text{M}=\text{C}(\text{SCH}_3)\text{CH}_3$ ($\text{M} = \text{Cr}$ and W) with primary amines in aqueous acetonitrile [☆]

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Abstract

A kinetic study of the aminolysis of [methyl(thiomethyl)carbene]pentacarbonyl chromium(0), $(\text{CO})_5\text{Cr}=\text{C}(\text{CH}_3)(\text{SCH}_3)$ (Cr–S) and [methyl(thiomethyl)carbene]pentacarbonyltungsten(0), $(\text{CO})_5\text{W}=\text{C}(\text{CH}_3)(\text{SCH}_3)$ (W–S), with primary aliphatic amines namely aminoacetonitrile (AA), glycylethyl ester (GEE) and glycinamide (GA) in 50% MeCN–50% H_2O (v/v) at 25 °C is reported. The second-order rate constant (k_A , $\text{M}^{-1}\text{s}^{-1}$) increases with amine concentration, leveling off at higher amine concentration. The general base catalysis was confirmed from the dependence of k_A on $[\text{AA}]_f$, $[\text{NMM}]_f$ (*N*-methylmorpholine) and also on $[\text{OH}^-]$ for the M–S–AA reaction. The mechanism proposed is very similar to those for ester reactions, proceeding in a step-wise fashion. $\beta_{\text{nuc}}(k_1)$ for the reactions of primary amines was found to be 0.31 ± 0.02 and 0.29 ± 0.02 for Cr–S and W–S, respectively, which are of the same order as that for the reaction of Cr–SR, but lower than Cr–OR reactions with $\beta_{\text{nuc}}(k_1) = 0.60$. The reactivity of W–S was found to be higher than Cr–S. All these observations have been explained successfully.

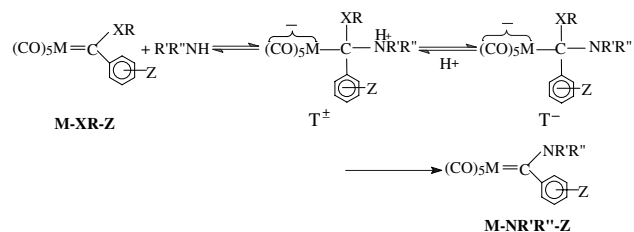
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1. Introduction

The extensive and ever increasing activity in the area of transition metal carbene complexes has been mainly driven by their usefulness in synthesis. The electrophilic nature at the carbene carbon [1–3] has been exploited to modify the carbene fragment which resulted in the emergence of chemistry of carbene complexes as an important branch of organometallic chemistry. Nucleophilic substitution of an alkoxy or alkylthio group of carbene complexes such as $\text{M}-\text{XR}-\text{Z}$ is one of the prototypical

reactions of Fischer carbene complexes. It has generally been assumed that these reactions proceed in a step-wise manner via tetrahedral intermediates, T^\pm , in an analogy to the reactions of carboxylic esters with nucleophiles in polar solvent. Eq. (1) involves the reactions of Fischer carbene complexes with amines, it includes a proton transfer as additional step compared to their reactions with anionic species like MeO^- , RS^- , carbanions, etc.



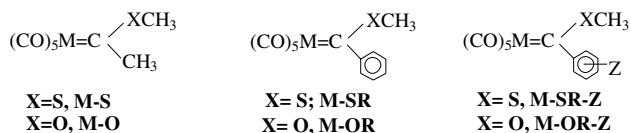
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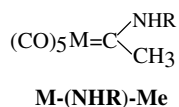
Though in most synthetic applications common nucleophiles such as amines [1,3–7], hydrazine [1,8] oximes [1,9], alkoxide ions [1,3,10] thiolate ions [1,3,11–13], carbanions [13–18], (mainly aryl and alkyl lithium) as well as others [1,19–21] were involved, there have been relatively few kinetic studies in the early literature. These investigations focused mainly on reactions with amines [3,22–24] and phosphines [3,25,26] in non-polar organic solvents. The nucleophilic substitution reaction of M–OR with several primary amines (*n*-BuNH₂, C₆H₁₁NH₂, C₆H₅CH₂NH₂) were carried out in *n*-decane, dioxane, methanol and dioxane–methanol (1/1) mixtures [23]. In *n*-decane the rate was found to be third-order with respect to amine concentration and in dioxane it is second-order. In non-polar solvents the mechanism was complicated due to hydrogen binding. More recently, a number of rate studies with alcohol [27,28], alkoxide ions [27,28], water [29–33], OH[−] [29–33], thiols [34–36], thiolate ions [34–36], amines [33,37–42] and carbanion [43] in polar (mainly water–acetonitrile mixtures) solvent were reported on M–XR and M–XR–Z. Because, in this highly polar solvent there are no hydrogen bonding association as observed in non-polar solvents, which unduly complicate the situation, more clear cut conclusion could be drawn about the mechanistic details. However, the kinetic studies on the nucleophilic substitution involving methoxymethyl (M–O) or methylthiomethyl carbene complexes (M–S) are limited [41,42].



In the present paper, we report a detailed kinetic study of the aminolysis of M–S with three primary aliphatic amines, namely, aminoacetonitrile (AA), glycylethyl ester (GEE) and glycinamide (GA) in 50% MeCN–50% H₂O (v/v).

2. Results and discussion

The reaction of primary aliphatic amines with methylthiomethyl carbene complexes (M–S) lead to corresponding amino carbene complexes (M–(NHR)–Me) in quantitative yield. The conversion of M–S to M–(NHR)–Me produces a blue shift in the UV–Vis region which is typical for the reaction of amines with Fischer carbene complexes.



The kinetics was performed under pseudo-first-order conditions with the carbene complexes as the minor

component. In all cases, plots of observed pseudo-first-order rate constants, k_{obsd} , vs. $[\text{RNH}_2]_f$ (f stands for free amine base) showed upward curvatures with increasing slope (Fig. 1), which is reminiscent of the reactions of M–OR with primary and secondary amines [37,38]. Plots of k_A vs. $[\text{RNH}_2]$ in the absence of external buffer showed an initial rapid increase in k_A with the increase in amine concentration followed by leveling off at higher amine concentration. A representative plot for M–S–GEE reaction is shown in Fig. 2.

As the carbene complexes undergo deprotonation [Eq. (2)] under the reaction conditions ($\text{p}K_a^{\text{CH}} = 9.05$ for Cr–S and 8.37 for W–S [44]) and the deprotonated species do not participate in nucleophilic reaction, k_A was corrected by Eq. (3).

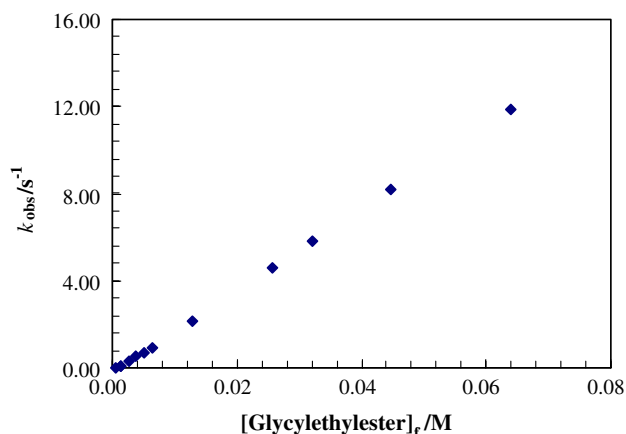
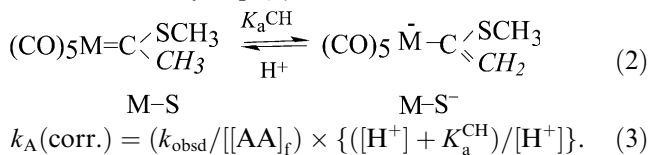


Fig. 1. Dependence of k_{obsd} on amine concentration for the reaction W–S with glycylethylester at pH 7.68.

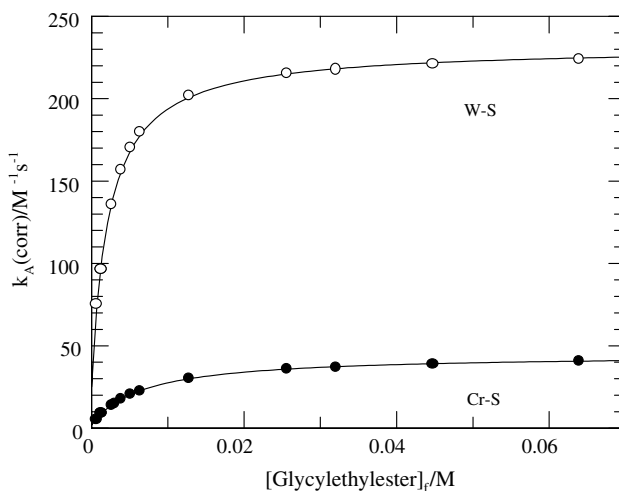


Fig. 2. Dependence of k_A on amine concentration for the reaction M–S with glycylethylester at pH 7.68.

In the experimental range of pH (6.18–8.14) rate constants for the hydrolysis of carbene complexes fall in the range $(0.2\text{--}2.0) \times 10^{-4} \text{ s}^{-1}$ for Cr-S and $(0.4\text{--}4.0) \times 10^{-4} \text{ s}^{-1}$ for W-S which were found to be insignificant compared to the aminolysis reactions and hence were neglected.

As was found earlier, the reaction of primary amines with M-S is best described by a step-wise mechanism as depicted in Scheme 1.

As the intermediate does not accumulate to a detectable level, application of steady-state approximation to T_A^\pm leads to the rate law of Eq. (4)

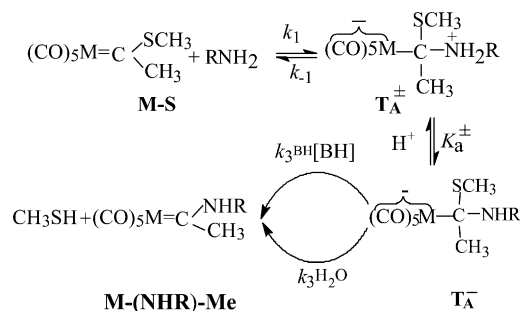
$$k_{\text{obsd}} = \frac{k_1 \left(\frac{k_3^{\text{BH}} K_a^\pm}{k_{-1} K_a^{\text{BH}}} [\text{B}] + \frac{k_3^{\text{H}_2\text{O}} K_a^\pm}{k_{-1} k_w} [\text{OH}^-] \right)}{1 + \left(\frac{k_3^{\text{BH}} K_a^\pm}{k_{-1} K_a^{\text{BH}}} [\text{B}] + \frac{k_3^{\text{H}_2\text{O}} K_a^\pm}{k_{-1} k_w} [\text{OH}^-] \right)} [\text{RNH}_2], \quad (4)$$

$$k_A = \frac{k_1 \left(\frac{k_3^{\text{BH}} K_a^\pm}{k_{-1} K_a^{\text{BH}}} [\text{B}] + \frac{k_3^{\text{H}_2\text{O}} K_a^\pm}{k_{-1} k_w} [\text{OH}^-] \right)}{1 + \left(\frac{k_3^{\text{BH}} K_a^\pm}{k_{-1} K_a^{\text{BH}}} [\text{B}] + \frac{k_3^{\text{H}_2\text{O}} K_a^\pm}{k_{-1} k_w} [\text{OH}^-] \right)}. \quad (5)$$

In the reactions of RNH_2 with M-S, variation of $[\text{RNH}_2]_f$ at pH 6.18 for AA, 7.68 for GEE and 8.14 for GA were carried out in the absence of external buffer which yielded non-linear curves for the plot of k_A vs. $[\text{RNH}_2]_f$, and were solved to get k_1 , (k_3^{B}/k_{-1}) and (k_3^{OH}/k_{-1}) . The percentage of error for the parameter k_3^{OH}/k_{-1} obtained thereby may be little bit high compared to the other parameters (k_1 , (k_3^{B}/k_{-1})).

To check the general base catalysis of these reactions, variation of $[\text{NMM}]_f$ (NMM = *N*-methylmorpholine) (0.001–0.090 M) at pH 7.56 and $[\text{AA}]_f = 0.003 \text{ M}$ for Cr-S and 0.0018 M for W-S; and also a variation of pH (6.40–8.78) at constant $[\text{NMM}]_f = 0.01 \text{ M}$ and $[\text{AA}]_f = 0.003 \text{ M}$ were carried out for M-S-AA reactions. Plots of $k_A(\text{corr})$ vs. $[\text{NMM}]_f$ and $[\text{OH}^-]$ are shown in Figs 3 and 4, respectively, for M-S-AA reaction.

A variation of $[\text{GA}]_f$ at pH 10.2 for M-S-GA reaction with triethylamine as an external buffer showed a linear dependence of $k_{\text{obsd}}(\text{corr}) (=k_{\text{obs}} - k^{\text{OH}}[\text{OH}^-])$, where k^{OH} is the OH^- catalyzed decomposition of M-S,



Scheme 1.

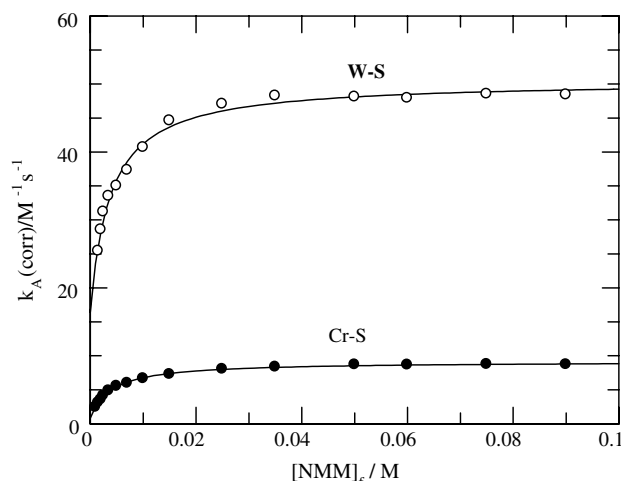


Fig. 3. Dependence of k_A on $[\text{NMM}]_f$ for the reaction M-S with Aminoacetonitrile at pH 7.56.

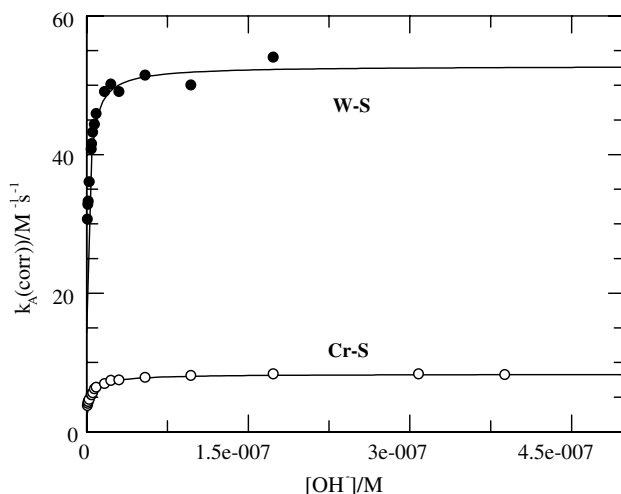


Fig. 4. Dependence of k_A on $[\text{OH}^-]$ for the reaction M-S with Aminoacetonitrile.

$k^{\text{OH}} = 175$ and $736 \text{ M}^{-1} \text{ s}^{-1}$ for Cr-S and W-S, respectively [43] on $[\text{GA}]_f$ with slope value $= (70.8 \pm 4.7) \text{ M}^{-1} \text{ s}^{-1}$ for Cr-S and $356 \pm 10 \text{ M}^{-1} \text{ s}^{-1}$ for W-S. This observation indicates that condition (6) holds good and Eq. (5) reduces to (7)

$$\left(\frac{k_3^{\text{BH}} K_a^\pm}{k_{-1} K_a^{\text{BH}}} [\text{B}] + \frac{k_3^{\text{H}_2\text{O}} K_a^\pm}{k_{-1} k_w} [\text{OH}^-] \right) \gg 1, \quad (6)$$

$$k_A(\text{corr}) = k_1. \quad (7)$$

Non-linear least squares fit of data to Eq. (5) for $[\text{RNH}_2]_f$, $[\text{NMM}]$ and $[\text{OH}^-]$ variations yielded the parameters, which are listed in Table 1. The respective k_1 values obtained from $[\text{AA}]_f$ variation at constant pH 6.18 is somewhat lower than those determined from the dependence of k_A on $[\text{NMM}]$ and $[\text{OH}^-]$ at constant $[\text{AA}]_f$; and this was also found in many reactions of other carbene complexes with different primary as well

Table 1
Summary of rate and equilibrium Constants

Amines	Rate parameters	Cr-S	W-S
Aminoacetonitrile (5.29)	$k_1, \text{M}^{-1} \text{s}^{-1}$	6.89 ± 0.10^a 9.16 ± 0.10^b 8.26 ± 0.10^c $k_1(\text{Av}) = 8.71 \pm 0.10^d$	44.5 ± 0.20^a 50.5 ± 0.60^b 52.8 ± 0.52^c $k_1(\text{Av}) = 51.5 \pm 0.55^d$
	$(k_3^{\text{AA}}/k_{-1}), \text{M}^{-1}$	23.8 ± 0.10	69.8 ± 0.20
	$(k_3^{\text{NMM}}/k_{-1}), \text{M}^{-1}$	274 ± 14	397 ± 48
	$(k_3^{\text{OH}}/k_{-1}), \text{M}^{-1}$	$(2.60 \pm 0.13) \times 10^8$	$(6.06 \pm 0.70) \times 10^8$
	$(k_3^{\text{OH}}/k_3^{\text{AA}})$	$(1.09 \pm 0.10) \times 10^7$	$(8.68 \pm 0.40) \times 10^6$
	$(k_3^{\text{OH}}/k_3^{\text{NMM}})$	$(9.49 \pm 0.10) \times 10^5$	$(1.53 \pm 0.40) \times 10^6$
Glycylethylester (7.70)	$k_1, \text{M}^{-1} \text{s}^{-1}$	44.7 ± 0.22	230 ± 0.44
	$(k_3^{\text{GEE}}/k_{-1}), \text{M}^{-1}$	156 ± 3.4	498 ± 25
	$(k_3^{\text{OH}}/k_{-1}), \text{M}^{-1}$	1.48×10^6	3.88×10^6
	$(k_3^{\text{OH}}/k_3^{\text{GEE}})$	9.49×10^3	7.79×10^3
Glycinamide (8.03)	$k_1, \text{M}^{-1} \text{s}^{-1}$	70 ± 0.2 60.5 ± 0.4 $k_1(\text{Av}) = 65.3 \pm 0.3$	355.7 ± 2.9 324 ± 4.0 $k_1(\text{Av}) = 339.9 \pm 3.5$
	$(k_3^{\text{GA}}/k_{-1}), \text{M}^{-1}$	268.5 ± 8.1	693 ± 62
	$(k_3^{\text{OH}}/k_{-1}), \text{M}^{-1} \text{s}^{-1}$	4.51×10^5	3.37×10^5
	$(k_3^{\text{OH}}/k_3^{\text{GA}})$	1.68×10^3	4.86×10^2

^a From the dependence of $k_A(\text{corr})$ on $[\text{AA}]$.

^b From the dependence of $k_A(\text{corr})$ on $[\text{NMM}]_f$.

^c From the dependence of $k_A(\text{corr})$ on $[\text{OH}^-]$.

^d Average of b and c.

as secondary amines [37–42]. It is to be noted that k_1 values obtained from this experiment is somewhat lower for GA than those obtained from the dependence k_{obs} on $[\text{GA}]_f$ at pH 10.2 with triethylamine as external buffer. This is also in the same line as observed for aminoacetonitrile reactions as well as for the reaction of both primary and secondary amines with different carbene complexes [37–42].

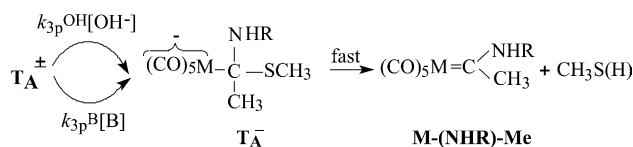
Nature of base catalysis. The fact that the reaction is catalyzed not only by OH^- but also by the amine (NMM and AA) demonstrates a general base catalysis. The most likely mechanism that can account for general base catalysis is shown in Scheme 1, which indicates a rapid acid–base equilibrium between T_A^\pm and T_A^- followed by general acid catalyzed rate-limiting leaving group departure. In terms of this mechanism, the following relationships hold good

$$k_3^{\text{B}} = k_3^{\text{BH}} K_a^\pm / K_a^{\text{BH}}, \quad (8)$$

$$k_3^{\text{OH}} = k_3^{\text{H}_2\text{O}} K_a^\pm / K_w. \quad (9)$$

General base catalysis of these reactions may also be accounted for by Scheme 2.

Scheme 2 represents the base B and OH^- catalyzed deprotonation of T_A^\pm followed by leaving group departure, which typically observed in the aminolysis of esters (1) [45] and in numerous $\text{S}_{\text{N}}\text{Ar}$ reactions (2) [46,47], where general base catalysis occurs. From the Scheme 2, one can equate $k_3^{\text{B}} = k_{3p}^{\text{B}}$ and $k_3^{\text{OH}} = k_{3p}^{\text{OH}}$. In the reaction of AA with M-S, the rate-limiting deprotonation of T_A^\pm



(Scheme 2) can be excluded on the basis of $k_3^{\text{OH}}/k_3^{\text{B}}$ ratios. The ratio increases from 1.68×10^3 for glycinamide to 1.09×10^7 for aminoacetonitrile for the Cr-S, whereas, this increases from 4.86×10^2 for glycinamide to 8.68×10^6 for aminoacetonitrile for W-S and fits a pattern observed earlier [33,37]. Based on Scheme 2, the reactions of OH^- and B are expected to be a diffusional encounter controlled proton transfer, and hence k_{3p}^{OH} and k_{3p}^{B} should have a value around $10^{10} \text{M}^{-1} \text{s}^{-1}$ [48]. If proton transfer is rate limiting, the $k_{3p}^{\text{OH}}/k_{3p}^{\text{B}} = k_3^{\text{OH}}/k_3^{\text{B}}$, it can be said that $k_3^{\text{OH}}/k_3^{\text{B}}$ ratios should be independent of amines and have values between 5 and 25 [49,50]. This contrasts with our experimental observations.

3. Structure–reactivity relationship and transition-state structure

For the nucleophilic attack step (k_1), Bronsted plots for k_1 are shown in Fig. 5. There is a good correlation between $\log(k_1)$ and $\text{p}K_a^{\text{BH}}$ with $\beta_{\text{nuc}} = 0.31 \pm 0.02$ and 0.29 ± 0.02 for Cr-S and W-S, respectively. The $\beta_{\text{nuc}} = 0.30 \pm 0.02$ was obtained for the reaction of

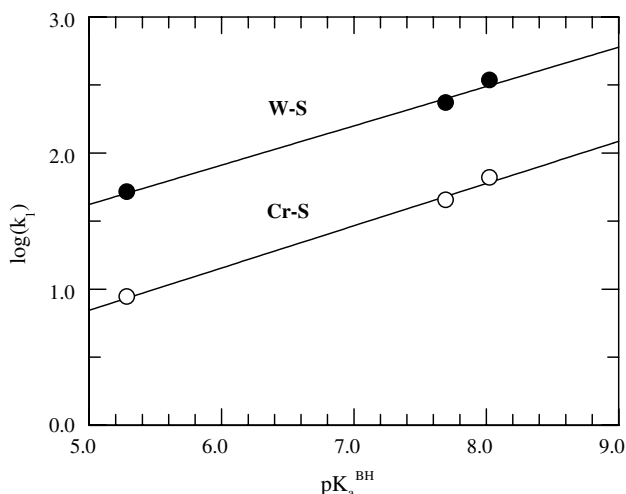


Fig. 5. Bronsted-type plots for $\log(k_1)$.

primary aliphatic amines with Cr–SR which is again 0.60 for Cr–OR–RNH₂ reactions. The comparable β_{nuc} for the reaction of M–S and Cr–SR and significantly lower than that for Cr–OR reflects a fact that in the latter reaction the C–N bond formation is more advanced in the transition state than those of former reactions and corresponds to a Hammond effect. The comparatively smaller degree of C–N bond formation is the consequence of large steric effect imposed by the S atom in M–S and Cr–SR in the transition state compared to the O atom in Cr–OR.

For leaving group departure steps Bronsted plots for k_3^B/k_{-1} path yield $\beta(k_3^B/k_{-1}) = 0.367 \pm 0.04$ and 0.360 ± 0.01 for Cr–S and W–S, respectively, which are slightly higher than that for Cr–OR with $\beta(k_3^B/k_{-1}) = 0.15 \pm 0.02$ [37] (Fig. 6). For (k_3^{OH}/k_{-1}) path $\beta(k_3^{\text{OH}}/k_{-1}) = -0.979 \pm 0.07$ and -1.07 ± 0.22 for Cr–S and W–S, respectively, which was found to be $\beta(k_3^{\text{OH}}/k_{-1}) = -0.77$ for Cr–OR–RNH₂ reactions [37]. Though, fortunately

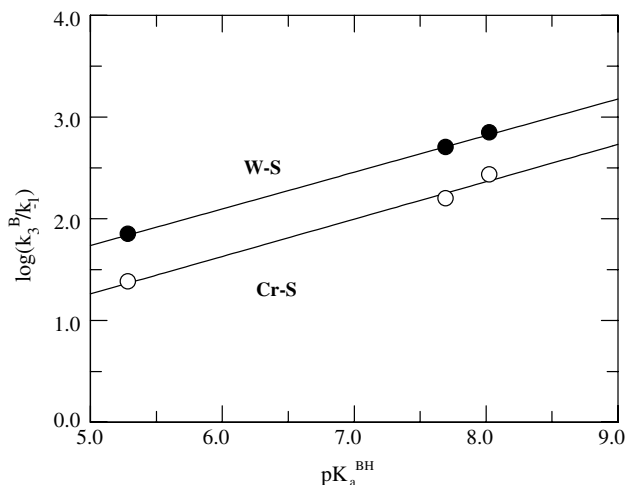


Fig. 6. Bronsted-type plots for $\log(k_3^B/k_{-1})$.

there is a good correlation for the plot of $\text{p}K_a^{\text{BH}}$ vs. $\log(k_3^{\text{OH}}/k_{-1})$ for Cr–S, there is a scattering of points for the similar plot for W–S–RNH₂ system and arises mainly due to the higher degree of uncertainties associated with the determination of the (k_3^{OH}/k_{-1}) from the dependence of k_A on [RNH₂]. From Eqs. (8) and (9) one can deduce Eqs. (10) and (11)

$$\beta(k_3^B/k_{-1}) = \beta(k_3^{\text{BH}}) + \beta(K_a^\pm) - \beta(K_a^{\text{BH}}) - \beta(k_{-1}), \quad (10)$$

$$\beta(k_3^{\text{OH}}/k_{-1}) = \beta(k_3^{\text{H}_2\text{O}}) + \beta(K_a^\pm) - \beta(k_{-1}). \quad (11)$$

$\beta(k_{-1})$ can be estimated with the help of Eq. (12)

$$\beta(k_{-1}) = \beta(k_1) - \beta(K_1). \quad (12)$$

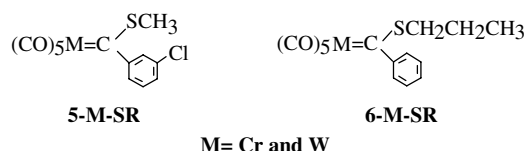
On the basis of numerous reactions of amines with electrophilic olefins PhCH=CXY, for which $\beta(K_1)$ values were found to fall in the range 0.70–0.90. [51,52]. We assume a value of $\beta(K_1) = 0.80$ for our system, which was also picked up by Bernasconi et al. for Cr–OR–RNH₂ reactions [37]. This yields a value $\beta(k_{-1}) = -0.483$ and -0.512 for Cr–S and W–S, respectively. The values of $\beta(K_a^\pm)$ and $\beta(K_a^{\text{BH}})$ can be set ≈ -1.0 [37]. Solving Eqs. (10) and (11) affords $\beta(k_3^{\text{BH}}) = -0.123$ and -0.152 and $\beta(k_3^{\text{H}_2\text{O}}) = -0.469$ and -0.582 . $\beta(k_3^{\text{BH}})$ corresponds to β_{push} which is negative and indicates that the push is negligible, suggesting a transition state in which leaving group departure has a very little progress. $\beta(k_3^{\text{H}_2\text{O}})$ is negative and even lower than $\beta(k_3^{\text{BH}})$, reflecting not only small push but also the opposing influence of the amine basicity due to acid catalysis by RNH₃⁺ to the departing MeS group, presumably because C–S bond breaking has made very little progress. Thus both small push and the weak sensitivity to the acidity of the catalyst give a consistent picture of a transition state that is very much intermediate-like (T_A^-). The relatively high $\beta(k_1)$ and low $\beta(k_{-1})$ suggest that the transition state of the first step is also close to the respective intermediate (T_A^\pm). It is to be mentioned here that all the parameters $\beta(k_1)$, $\beta(k_{-1})$, $\beta(k_3^{\text{H}_2\text{O}})$ and $\beta(k_3^{\text{BH}})$ are comparatively higher for Cr–OR–RNH₂ reactions than the Cr–S system. Though, it is not possible to make a direct comparison between the two systems, as they differ not only by XR group but also by alkyl/aryl group, it can be concluded that in the Cr–OR, MeO[−] being a better leaving group than MeS[−] the C–N bond formation and C–O bond breaking has better progress in Cr–OR than Cr–S in the transition state. A high degree of uncertainties associated with the determination of (k_3^{OH}/k_{-1}) , particularly for W–S–RNH₂ reaction, leads to significant uncertainties in $\beta(k_3^{\text{H}_2\text{O}})$.

CH₃ vs. Ph. With respect to nucleophilic attack Cr–S were found to be more reactive than Cr–SR. As for example, for AA as nucleophile, $k_1(\text{Cr–S})/k_1(\text{Cr–SR}) \sim 34$ while for leaving group departure, the reverse trend is prevailing: $(k_3^{\text{H}_2\text{O}}K_a^\pm/k_{-1}K_w)(\text{Cr–S})/(k_3^{\text{H}_2\text{O}}K_a^\pm/k_{-1}K_w)(\text{Cr–SR}) = 0.138$. The reaction of AA with Cr–SR showed no catalysis by amine like NMM or TEA

[39]. This implies that the formation of T_A^\pm with AA is thermodynamically more favorable for Cr–S than Cr–SR, though based on inductive effect it should show a reverse trend. This mainly arises due to 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. Similar reactivity trend was observed for the morpholine reactions towards M–S [42].

Cr vs. W. Nucleophilic addition to the tungsten carbene complexes is slightly favored over the addition to chromium complexes; though in some cases almost the similar reactivities were observed, particularly for the reaction of Cr–OR and W–OR with OH^- and water [30,53]. The higher reactivity of tungsten carbene complexes over the chromium ones is particularly true for thioalkyl carbene complexes, as is borne out by the results for the reaction of M–SR, 5–M–SR and 6–M–SR with OH^- and water [27,28,54]. The higher k_1 values ($k_1(W-S)/k_1(Cr-S) \sim 6.2-5.1$) are obtained for the reactions of AA, GEE and GA with W–S compared to Cr–S. Similar $k_1(W)/k_1(Cr)$ ratios have been reported for the reactions of MeO^- in MeOH and various thiolate ions in 50% MeCN–50% H_2O with M–XR–Z [27,28,35,36,42]. They show a consistent pattern of somewhat enhanced electrophilic reactivity of tungsten complexes. The k_3^{OH}/k_{-1} and (k_3^B/k_{-1}) are also slightly higher for tungsten than chromium complexes.

MeO vs. MeS as leaving group. As there is no report on the reaction of M–O with amine as nucleophile, a direct comparison of reactivity M–O and M–S is not possible. Based on the reactivity of water, OH^- and thiolate ions toward M–OR and M–SR complexes [27,28,35,36,51] an indirect comparison can be drawn for the reactivity of M–O and M–S towards AA. Very similar reactivity of M–OR and M–SR towards water to form tetrahedral intermediate was observed: $k_1^{H_2O}(2-Cr(S))/k_1^{H_2O}(2-Cr(O)) = 0.355$ while the ratio $k_1^{H_2O}(2-W(S))/k_1^{H_2O}(2-W(O)) = 1.16$. This is in contrast with the reactions of OH^- and thiolate ion, where M–SR is substantially more reactive than M–OR, which apparently violate the reactivity–selectivity principle [55] or Hammond [56]–Leffler postulate [57].



4. Conclusions

- (i) The reaction of M–S with three primary aliphatic amines (AA, GEE and GA) leads to the nucleophilic substitution of the thiomethyl group by a

three step mechanism of Scheme 1. The general base catalysis was observed which is in the same line for reaction of AA with Cr–SR.

- (ii) The intermediates T_A^\pm and T_A^- remain undetectable even at high amine concentration and high pH as $k_1[RNH_2]/(k_3^{H_2O} + k_3^{BH}[RNH_3^+]) < (\ll) 1$.
- (iii) With respect to nucleophilic attack Cr–S was found to be more reactive than Cr–SR, while for leaving group departure the reverse trend is prevailing. This implies that the formation of T_A^\pm with AA is thermodynamically more favorable for Cr–S than Cr–SR.
- (iv) The tungsten carbene complex is slightly more reactive than its chromium counterpart with $k_1(W-S)/k_1(Cr-S) \sim 6.2-5.1$ for AA, GEE and GA reactions indicating a slightly enhanced electrophilic behavior of tungsten carbene complexes and the corresponding chromium counter part.
- (v) At high pH, the assignment of rate-limiting MeS^- expulsion from T_A^- is based on the values of k_3^{OH}/k_3^B ratio which are significantly enhanced with the decrease in pK_a^{BH} of the amine acids.
- (vi) The comparable β_{nuc} for the reaction of M–S and Cr–SR and significantly lower than that for Cr–OR reflects a fact that in the latter reaction the C–N bond formation is well advanced in the transition state than those of former reactions and corresponds to a Hammond effect. The comparatively smaller degree of C–N bond formation is the consequence of large steric effect imposed by the larger S atom over the O atom in the transition state in Cr–XR.

5. Experimental section

5.1. Material

[Methyl(thiomethyl)carbene]pentacarbonylchromium(0), $(CO)_5Cr=C(CH_3)(SCH_3)$ (Cr–S) and [Methyl(thiomethyl)carbene]pentacarbonyl tungsten(0), $(CO)_5W=C(CH_3)(SCH_3)$ (W–S) were obtained from the previous studies [41,42]. Reagent grade amines were from Aldrich chemicals and were either recrystallized from water–ethanol solution (for solid amines) or distilled over CaH_2 (for liquid amines) before use.

5.2. pH measurements

The pH in 50% MeCN–50% H_2O (v/v) at an ionic strength $0.10 \text{ mol dm}^{-3} \text{ mo}^{-1}$ (KCl) at $25^\circ C$ (maintained by using water jacketed container and flowing water through it from a thermostatic water bath) was determined by following Eq. (13) according to Allen and Tidwell [59] 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.

$$\text{pH}_{\text{actual}} = \text{pH}_{\text{measured}} + 0.18. \quad (13)$$

5.3. Kinetic runs and spectra

Stock solutions of the carbenes 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. Faster reactions were carried out in an Applied Photo-physics DX.17MV Stopped-flow apparatus. All kinetic experiments were conducted in 50% CH₃CN–50% H₂O (v/v) under pseudo-first-order conditions with the carbene as the minor component and monitored by the disappearance of the substrate at 448 nm for Cr–S, and at 432 nm for W–S for more than four half-lives of the reaction. Typical substrate concentrations were (5.0–9.0) × 10^{−5} M. The pseudo-first-order rate constants (k_{obsd} , s^{−1}) as a function of free amine concentration at a constant pH were obtained by fitting the kinetic traces with suitable computer-fit program and the results were found to fall within the error limit ±5%. The study of reactions at two different wave lengths (say 432 and 335 nm for W–S) do not show any visible wavelength dependency of rates.

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