

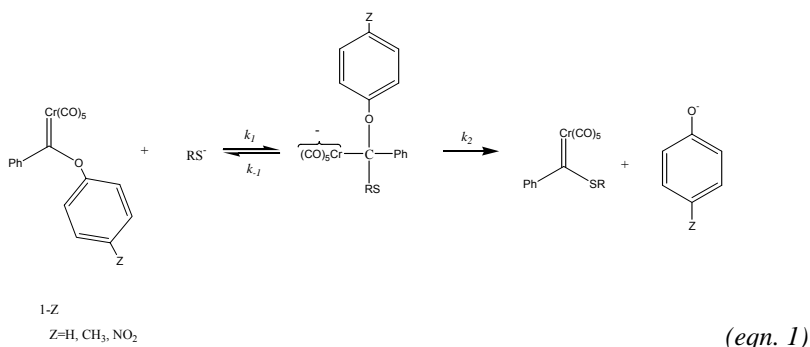
The Physical Organic Chemistry of a Transition Metal Carbene Complex: Kinetics of the Reactions of (Arylphenoxy)pentacarbonyl Chromium(0) with thiolate ions in 50/50 Water/Acetonitrile.

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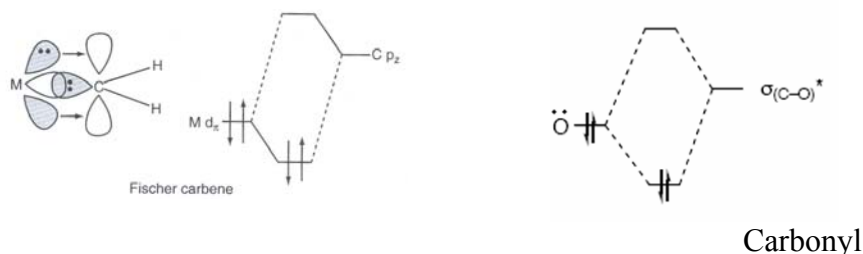
Abstract:

The kinetic study of the reaction (**eqn. 1**) of aryloxy Fischer carbene complexes **1-Z** with thiolate ions; propanethiolate, 2-mercaptoethanol, methyl 3-mecaptopropionate, methyl thioglycolate were preformed. Interest in the reactivity of Fischer carbenes is due to the similarity between the tetrahedral transition state of Fischer carbenes and that of organic esters. Evidence suggests that Fischer carbenes react via a reaction mechanism pathway analogous to saponification.¹ To examine the reaction represented in **equation 1**, stopped-flow method reaction kinetics were carried out in 50% acetonitrile-50% water 1:1 (v/v) mixture at 25°C. Reactions were run in an internal thiol/thiolate buffer. Pseudo-first order conditions were maintained by using the thiolate nucleophile concentration in large excess with respect to the Fischer carbene substrate to determine k_1 . The rate of appearance of the reaction leaving group, paranitrophenoxide, was monitored at 400nm for **1-NO₂**, however for substrates **1-CH₃** and **1-H**, the rate of disappearance of the respective Fischer carbene was monitored at 414nm. The reaction rate constant k_1 for various thiolate nucleophiles were determined for each substrate. Kinetic data from Brønsted β_{nuc} and Hammett ρ plots indicated both an effect from the nucleophile and leaving group para-director **Z** on the transition state.



The purpose of this project was to study the reaction depicted in **equation 1** and determine the effect of both thiolate nucleophiles and para-directing groups on the tetrahedral transition state of an aryloxy- Fischer carbenes (**1-Z**). Primary interest in Fischer carbene reaction kinetics is due to the likeness of Fischer carbene reactivity to carbonyl complexes, in particular isolobal carboxylic esters.² This can be understood by the comparison of the molecular orbitals in both compounds (**Figure 1**).³

Figure 1

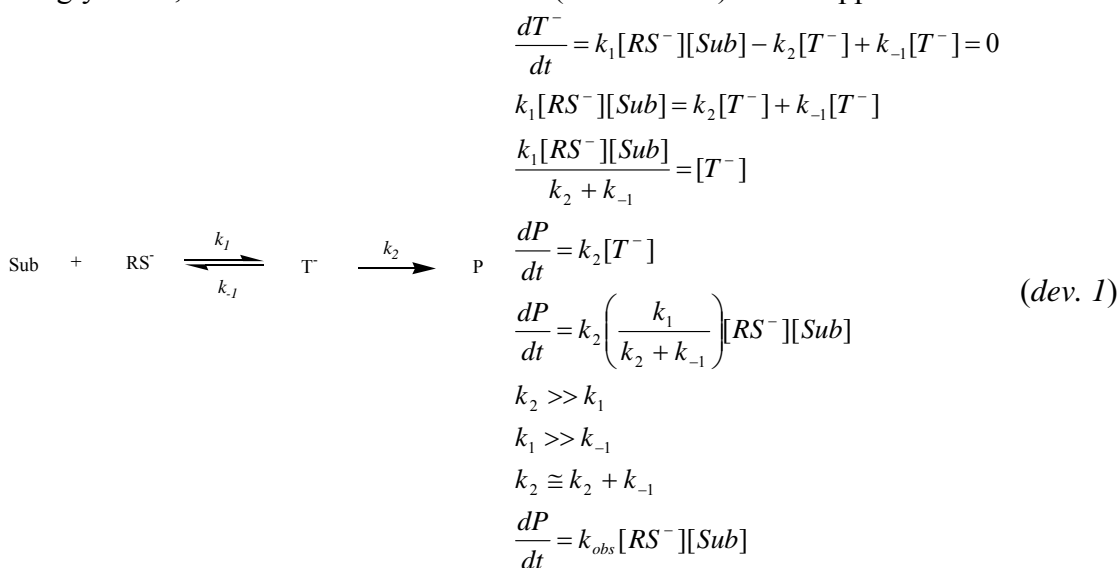


Two-step mechanism reactivity analogous to saponification (**eqn 1**) has been observed for Fischer carbenes with various nucleophiles,^{4,5} in particular interest here, thiolates, have been studied in available literature.^{1,4}

The reaction (**eqn 1**) has some fundamental limitations under the reaction conditions which were employed for the kinetic experiments as k_1 cannot be adequately measured as $k_{hydrolysis}$ was much faster in the 50% water 50% acetonitrile solvent used for our reaction conditions.⁶ Hence, no intrinsic rate constant could be determined, however the reaction rate constant to k_1 can allude to both the effect of the nucleophile and leaving group para-director **Z** on the transition state.

Pseudo-first order kinetic reaction conditions where-in the concentration of substrate **1-Z** was on the order of 10^{-5} M and the concentration of nucleophile was, at minimum, ten times this amount, allowed for the examination of the reaction in equation 1 without appreciable build up of the tetrahedral intermediate due to a quite large k_2 . Also, the thermodynamically unfavorable reverse reaction was much slower than hydrolysis of the substrate, corresponding to rate constant k_{-1} , was indeed quite small, within k_1 error. The measurement of k_{obs} was adequate for the determination of k_1 .

Thus, this led to the determination of k_1 for the family of nucleophiles; propanethiolate, 2-mercaptoethanolate, methyl 3-mecaptoethanolate, methyl thioglycolate, and the three substrates **1-Z** (derivation 1) with stopped flow methods.



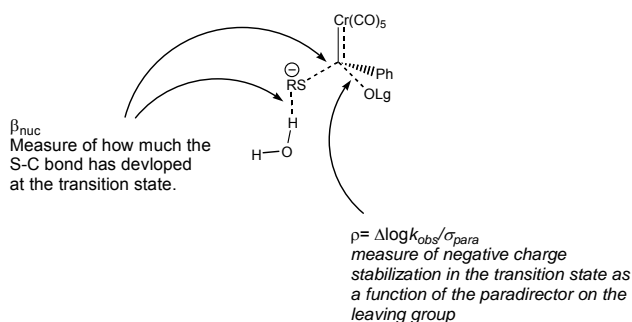
A wavelength at which the stopped-flow reaction (**eqn 1**) was monitored was dependent on the presence of a chromophor in the reaction mixture with sufficient optical

density. These wavelengths were determined via UV-Vis where in reactions synonymous with equation 1 were carried out in a quartz cuvette. In the case of **1-NO₂**, exponential increase in concentration of the paranitrophenoxide leaving group was monitored due to each buffer maintaining a pH higher than that of the pK_a of paranitrophenol. For reactions with substrates **1-H**, **1-CH₃** the primary chromophore with sufficient optical density was the Fischer carbene and the exponential decrease in concentration of **1-H**, **1-CH₃** was monitored. The relationship between concentration and reaction rate constant can be derived from the Beer's law relationship and the first order integrated rate law shown in equations 2,3.

$$A = \epsilon bc$$

$$[A] = [A_0]e^{-k_{obs}t} \quad (eqn 2,3)$$

Primary interest in examination of the structure of the transition state can be quantitatively determined by Brønsted β_{nuc} and Hammett ρ values and their relationship to the tetrahedral intermediate is depicted in figure 2.



(figure 2)

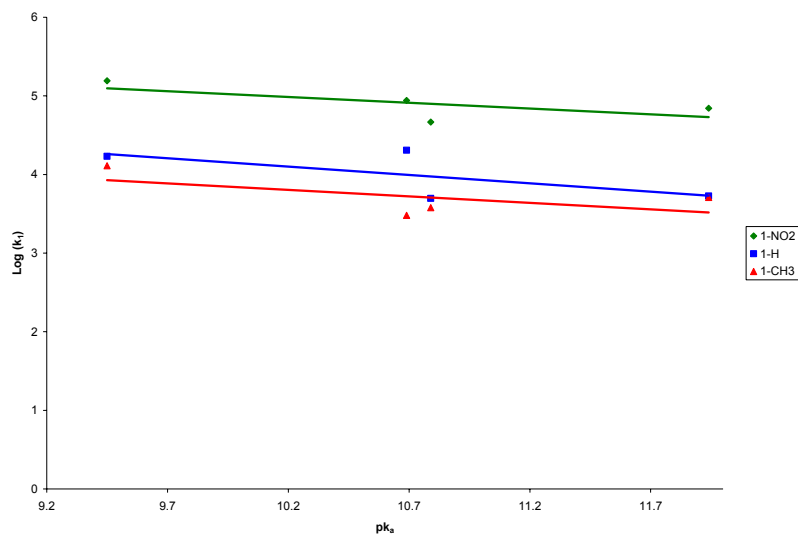
Determination of k_1 , β_{nuc} , ρ from kinetic results are tabulated in **Table 1, 2, 3** respectively and β_{nuc} , ρ are graphically represented in **Chart 1, 2**.

Table 1: k_1 for each 1-Z

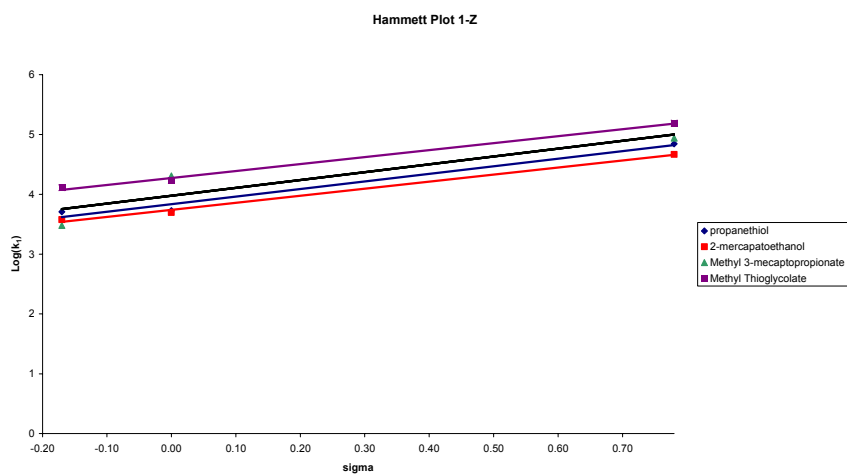
Nucleophile	pK _a (Acn/water)	1-NO ₂		1-H		1-CH ₃	
		k_1	Error in k_1	k_1	Error in k_1	k_1	Error in k_1
propanethiol	11.9	6.80E+04	9.31E+03	5.33E+03	5.28E+02	5.11E+03	1.21E+02
2-mercaptoethanol	10.8	4.65E+04	1.28E+03	3.44E+03	9.22E+02	2.47E+03	5.34E+02
Methyl 3-mecatpropionate	10.7	8.75E+04	4.88E+03	2.04E+04	1.17E+03	1.55E+04	1.13E+02
Methyl thioglycolate	9.45	1.55E+05	1.07E+03	1.11E+04	1.07E+03	1.30E+04	9.74E+02

Table 2: β_{nuc} Brønsted values for each 1-Z

Substrate	β_{nuc}	error
1-NO ₂	-1.51E-01	1.08E-01
1-H	-1.36E-01	2.16E-01
1-CH ₃	-1.74E-01	2.27E-01

Chart 1: β_{nuc} Brønsted Plot for each 1-Z**Table 3: Hammett ρ values**

Nucleophile	pK_a (Acn/water)	ρ	error ρ
propanethiol	11.94	1.256	0.1956
mercaptoethanol	10.79	1.375	0.08976
Methyl 3- mecatpropionate	10.69	0.7978	0.0691
Methyl thioglycolate	9.45	1.238	0.02807

Chart 2: Hammett ρ plot

Solvation effects explain the negative β_{nuc} values¹ and instances wherein thiolate nucleophiles have had a negative such value have been observed for other Fischer carbene nucleophilic substitution reactions.^{1,8} The deviation⁸ of said effect allows for a fundamental representation of the solvation effects on the nucleophile. Regardless of the large error associated with the determined β_{nuc} values, they overall, are negative.

Hammett Sigma Values⁹ for the corresponding para directors are, p-NO₂=0.78, p-H=0, p-CH₃=0.17. The sigma values are not in 50% acetonitrile-50% water and the corresponding Hammett ρ values as defined by the $\Delta\log(K_a)/\sigma$ thus are only an indirect measure of charge stabilization in the transition state as illustrated in **Figure 2**.

Hammett ρ values for the nucleophilic addition to **1-Z** are positive and consistent with nucleophilic addition reaction. They are relatively small, approximately 1.5. A number of factors may contribute to the Hammett ρ values and they are the result not only of the build up of negative charge on the (CO)₅Cr moiety of the transition state but also of the π -donor effect of the phenoxy leaving group.¹ The net result is an increase in reactivity with electron withdrawing substituent.

Conclusions:

1. The reaction of equation 1 can be described by nucleophilic substitution. In a buffered solution at the pK_a of the nucleophile, the reaction can be described by $S \leftrightarrow T \leftrightarrow P^-$ under pseudo-first order conditions, wherein the limiting step is k_1 .
2. The β_{nuc} values for thiolate ion attachment to **1-Z** are negative. This implies that desolvation of the nucleophile is an important part of the activation process and that C-S bond formation has made very little progress at the transition state. This appears to be characteristic for the reactions of thiolate ions with Fischer carbenes.¹
3. The substituent dependence of k_1 is relatively small as expressed by Hammett ρ values. Possible reasons include the π -donor effect of the phenoxy leaving group in the transition state as well as the **Z** para-director ability to stabilize the charge formation at carbene carbon. The net result is an increase in reactivity with electron withdrawing substituent.

Future Work

Further kinetic experiments could be to decrease error in the current data.

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