Mechanistic Information from the Effect of Temperature and Pressure on the Addition of a Series of Para-Substituted Anilines to an α,β-Acetylenic Pentacarbonylchromium Carbene Complex

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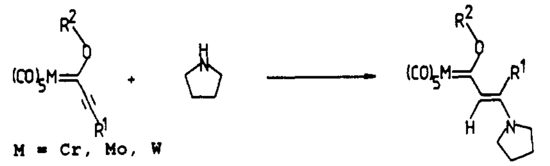
The temperature and pressure dependence of the addition of para-substituted anilines to the carbene complex $(CO)_5CrC(OC_2H_5)(C_2C_6H_5)$ was studied for a series of anilines, and the corresponding activation parameters are reported. These data are used to gain insight into the intimate nature of the addition mechanism and reveal in combination with kinetic isotope measurements that these reactions occur according to a two-step process. A Brönsted plot of log k versus pK_a of the aniline conjugated acids has a slope of 0.75 ± 0.04, indicating a strong dependence of the addition rate constant k on the amine basicity. The ΔV^* values become more negative for the slower addition reactions and reveal information regarding the position of the transition state along the reaction coordinate. These values along with a Hammett plot slope of −2.95 ± 0.14 indicate significant bond formation in the polar transition state.

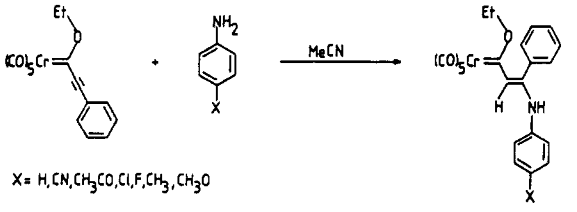
Introduction

The Michael-type addition reactions of amines to α,β-unsaturated Fischer carbene complexes to form β-aminovinyl-substituted products are well-known,[1-7] since they are interesting intermediates in organic synthesis reactions via organometallics. We recently investigated the effects of the central metal atom, temperature, pressure, and solvent on the addition reaction of pyrrolidine to a series of such carbene complexes as shown in reaction 1.[8] This study indicated that the reactions are characterized by low ΔH^* and significantly negative ΔS^* and ΔV^* values. In addition, the ΔV^* values for the reactions in acetonitrile are all -16 ± 1 cm^3 mol^{-1}, independent of M, but become significantly more negative (up to -22 cm^3 mol^{-1}) on decreasing the polarity of the solvent. These results along with a negligible kinetic isotope effect were interpreted in terms of a two-step mechanism involving a polar transition state and a zwitterionic intermediate.[8]



(1)

We have now extended this work to the addition of a series of para-substituted anilines to the chromium complex as indicated in reaction 2, since variation of the substituent X has a remarkable influence on the rate of the addition reaction. The results enable a correlation with the basicity of the amine and allow us to comment on the location of the transition state in terms of "early" or "late", depending on the rate of the addition process. Finally, the data are in good agreement with the conclusions drawn from our study on the addition of pyrrolidine to this and related complexes.[8]



(2)

Experimental Section

Materials. The chromium carbene complex was synthesized and purified as described before.[1,9] Chemical and spectroscopic analyses confirmed its purity. Aniline and 4-substituted anilines were purchased in the purest grade available (Merck or Fluka). The liquids were freshly distilled prior to use and the solids recrystallized from water/ethanol (1:1) and dried over P_2O_5. Acetonitrile and toluene were dried (molecular sieves or CaH_2) and distilled in the usual way.

Instrumentation. Infrared spectra: Nicolet FT-IR 5SX. ^{1}H-NMR spectra: Bruker AM 400 WB (internal reference $CDCl_3$). Elemental analyses were carried out by Mikroanalytisches Laboratorium Beller, Göttingen.

Synthesis of *N*-Deuterioaniline. In a flask containing a stirring bar and equipped with a condenser was mixed 5 mL (54 mmol) of aniline with 10 mL (556 mmol) of deuterium oxide and a drop of D_2SO_4. The solution was refluxed and stirred for 48 h. The organic layer was collected, dried over $MgSO_4$, and then distilled. The extent of deuteration was checked by NMR spectroscopy.

Characterization of the Products. For the isolation of the aniline adduct, a red solid, the previously described procedure was adopted.[8] The compound could be characterized as pentacarbonyl[(2E)-3-anilino-3-phenyl-1-ethoxypropen-1-ylidene)-

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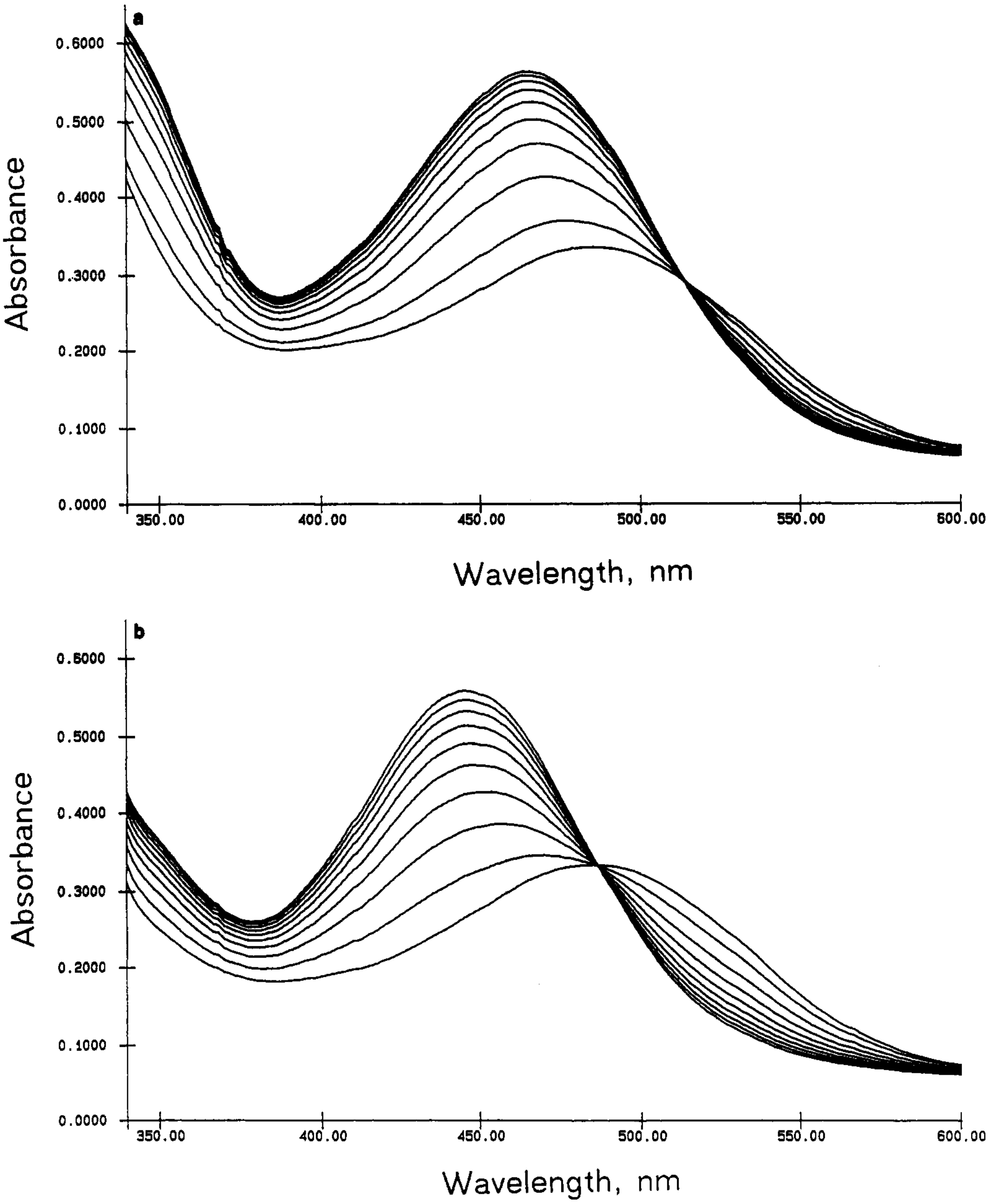

Figure 1. Repetitive scan spectra for reaction 2 in acetonitrile at 25 °C. Experimental conditions: [complex] = 5.5×10^{-5} M; (a) [4-CN] = 0.1 M, Δt = 10 min; (b) [4-OCH$_3$] = 6.25×10^{-4} M, Δt = 60 s.

chromium(0). Spectral data. ^{1}H-NMR δ: 1.67 (t, 3H), 4.98 (q, 2H), 6.63 (s, 1H), 6.7–7.5 (m, 10H). IR (hexane, cm^{-1}): 1925 vs, 1946 s, 1982 w, 2042 m. Anal. Found (calcd): C, 59.6 (59.5); H, 4.01 (4.05); N, 3.12 (3.15).

For a variety of substituted anilines, the characterization was done by in situ ^{1}H-NMR spectroscopy and the products were similar to the obtained aniline adduct.

Kinetic Measurements. The overall addition reaction could be studied using a UV–vis spectrophotometer (Shimadzu UV-250 or Varian Cary 1). The progress of the reaction was normally followed by the appearance of the product MLCT band which depends on the nature of the para substituent, viz. 466 (X = CN), 463 (X = CH$_3$CO), 455 (X = Cl), 451 (X = H), 448 (X = F), 448 (X = CH$_3$), and 447 nm (X = CH$_3$O). Depending on the rapidity of the reaction, high-pressure kinetic measurements where either performed on a homemade high-pressure stopped-flow unit[10] or on a Zeiss DMR 10 spectrophotometer equipped with a high-pressure cell.[11] In the latter case solutions were placed in a quartz pillbox cell[12] using a special filling technique.[13] All spectroscopic instruments were thermostated at ±0.1 °C, and all reactions were carried out under pseudo-first-order conditions by using a large excess of the amine. Reactions were followed for at least 4 half-lives, and an infinity absorbance program was employed to calculate the rate constants. High-pressure stopped-flow data acquisition and handling were performed on an on-line computer system.[14] The corresponding plots were linear over the studied time range, and the estimated rate constants were reproducible to within 5%.

Results and Discussion

The addition reactions outlined in (2) in general produce products of the type pentacarbonyl[(2*E*)-3-*N*-anilino-3-phenyl-1-ethoxypropen-1-ylidine]chromium(0) and are accompanied by characteristic changes in the MLCT (π–π^*) bands[15,16] depending on the nature of the nucleophile as indicated for two different anilines in Figure 1. The

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Table I. Kinetic Data for the Reaction of Pentacarbonyl[ethoxy(phenylethynyl)carbene]chromium(0) with Anilines in Acetonitrile

aniline	10^3[aniline], M	T, °C	P, MPa	10^3k_{obs}, s^{-1}	aniline	10^3[aniline], M	T, °C	P, MPa	10^3k_{obs}, s^{-1}
$C_6H_5NH_2$	2.5	25.3	0.1	1.62 ± 0.04	$4\text{-}CNC_6H_4NH_2$	50	25.5	0.1	0.221 ± 0.006
	5.0			3.48 ± 0.18		100			0.537 ± 0.018
	10.0			6.72 ± 0.15		200			1.22 ± 0.08
	20.0			14.5 ± 1.0		400			2.63 ± 0.07
	5.0	15.0		2.43 ± 0.02		200	15.0		0.663 ± 0.006
		25.3		3.48 ± 0.18			25.5		1.22 ± 0.08
		35.1		5.25 ± 0.06			35.0		1.64 ± 0.07
		45.1		6.74 ± 0.23			45.0		2.38 ± 0.09
	20.0	25.0	10	18.2 ± 0.7		50	15.3	5	0.129 ± 0.009
			40	24.7 ± 0.5				40	0.199 ± 0.005
			70	32.1 ± 0.5				70	0.281 ± 0.009
			100	40.8 ± 1.1				100	0.390 ± 0.010
$4\text{-}ClC_6H_4NH_2$	5.0	25.3	0.1	1.06 ± 0.07	$4\text{-}CH_3COC_6H_4NH_2$	25	25.5	0.1	0.507 ± 0.006
	10.0			2.21 ± 0.07		50			1.28 ± 0.06
	20.0			4.50 ± 0.06		100			2.60 ± 0.01
	40.0			8.37 ± 0.22		200			5.45 ± 0.14
	20.0	15.0		2.96 ± 0.02		100	15.5		1.47 ± 0.05
		25.3		4.50 ± 0.06			25.5		2.60 ± 0.01
		35.0		6.95 ± 0.04			35.1		3.39 ± 0.03
		45.1		9.06 ± 0.21			45.1		5.28 ± 0.02
	40.0	34.0	10	13.4 ± 0.8		100	43.6	10	5.28 ± 0.05
			40	17.4 ± 0.3				40	7.29 ± 0.09
			70	23.8 ± 0.5				70	9.64 ± 0.07
			100	31.5 ± 0.8				100	13.2 ± 0.2
$4\text{-}FC_6H_4NH_2$	2.5	25.3	0.1	1.48 ± 0.09	$4\text{-}CH_3OC_6H_4NH_2$	0.625	25.5	0.1	3.14 ± 0.04
	5.0			3.04 ± 0.13		1.25			6.24 ± 0.05
	10.0			6.08 ± 0.24		2.50			12.4 ± 0.8
	20.0			12.9 ± 0.3		5.00			24.9 ± 0.6
	10.0	15.0		4.54 ± 0.07		0.625	15.0		2.32 ± 0.04
		25.0		6.48 ± 0.26			25.5		3.14 ± 0.04
		35.1		8.64 ± 0.14			35.0		4.09 ± 0.04
		45.1		12.5 ± 0.5		5.00	25.0	10	34.7 ± 0.9
	20.0	25.0	10	12.5 ± 0.1				40	46.7 ± 0.4
			50	17.2 ± 0.8				70	59.9 ± 1.0
			100	23.4 ± 0.1				100	74.7 ± 0.5
			150	30.2 ± 0.9					
$4\text{-}CH_3C_6H_4NH_2$	2.5	25.3	0.1	4.32 ± 0.15					
	5.0			8.66 ± 0.33					
	10.0			17.7 ± 1.4					
	20.0			33.6 ± 1.7					
	2.5	15.0		3.37 ± 0.12					
		25.2		4.32 ± 0.15					
		35.1		6.60 ± 0.24					
		45.1		9.50 ± 0.43					
	20.0	25.0	10	53.5 ± 1.2					
		40		71.7 ± 1.8					
		70		92.6 ± 1.5					
		100		115 ± 2					

Table II. Rate and Activation Parameters for the Addition of 4-Substituted Anilines to $(CO)_5CrC(OC_2H_5)(C_2C_6H_5)$ in Acetonitrile As Outlined in Reaction 2

X in $NH_2C_6H_4X$	10^2k (25 °C), $M^{-1}\ s^{-1}$	$\Delta G^{\ddagger}_{298}$, kJ mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J $mol^{-1}\ K^{-1}$	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$
CN	0.69 ± 0.008	86	29.3 ± 2.6	−190 ± 9	-27.9 ± 0.6^{b}
CH_3CO	2.81 ± 0.03	82	28.9 ± 2.5	−179 ± 8	$-26.6 \pm 0.5^{a,d}$
Cl	20.8 ± 0.7	77	26.5 ± 1.7	−169 ± 6	$-24.5 \pm 0.4^{a,c}$
F	65.3 ± 1.3	74	22.7 ± 1.1	−172 ± 4	-24.6 ± 0.9^{a}
H	73.4 ± 1.9	74	24.0 ± 1.4	−167 ± 5	-22.2 ± 0.8^{a}
CH_3	167 ± 4	72	24.2 ± 2.3	−159 ± 8	-21.1 ± 1.0^{a}
CH_3O	497 ± 1	69	18.4 ± 0.2	−170 ± 1	-21.1 ± 1.0^{a}

[a] High-pressure stopped-flow method. [b] Zeiss DMR 10 method, T = 15.3 °C. [c] T = 34.0 °C. [d] T = 43.6 °C.

reactions exhibit clean isosbestic points for at least four half-lives of the reaction, and kinetic measurements were performed at wavelengths where maximum absorbance changes occur (see Experimental Section). Reaction 2 was studied for seven different anilines, and in all cases the pseudo-first-order rate constant varied linearly with the aniline concentration. This is demonstrated by the data in Table I, and typical plots of k_{obs} versus [aniline] exhibit no meaningful intercepts, such that k_{obs} can be expressed as indicated in (3). The temperature and pressure dependence of k_{obs} is also included in Table I, and the rate of activation parameters for the series of investigated anilines are summarized in Table II. Plots of ln k_{obs} versus pressure were linear within the experimental error limits involved over the investigated pressure range, and $\Delta V^{\ddagger}$ was calculated from the slope of such plots in the usual way.[17-19]

$$k_{obs} = k[NH_2C_6H_4X] \qquad (3)$$

The data in Table II clearly indicate the strong dependence of the second-order rate constant k on the

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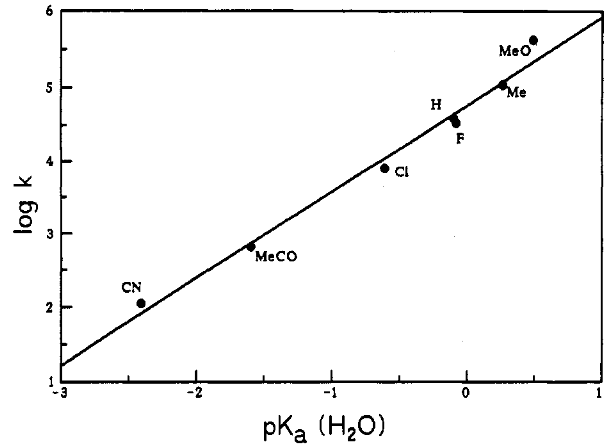

Figure 2. Brönsted plot for the reaction of para-substituted anilines with $(CO)_5CrC(OC_2H_5)(C_2C_6H_5)$ in MeCN at 25 °C; slope = 0.75 ± 0.04; the para substituent is indicated in the figure.

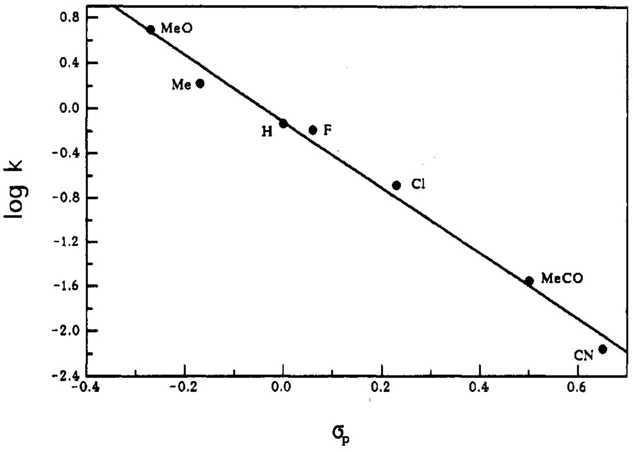

Figure 3. Hammett plot for the reaction of para-substituted anilines with $(CO)_5CrC(OC_2H_5)(C_2C_6H_5)$ in MeCN at 25 °C; slope = −2.95 ± 0.14; the para substituent is indicated in the figure.

nature of the substituent on aniline. In total k increases ca. 700-fold on going from 4-cyano- to 4-methoxyaniline, which is accompanied by a significant decrease in ΔH^*, a significant increase in ΔV^*, and almost no change in ΔS^*. These trends can be explained in terms of the electron donator and acceptor properties of the substituent X. The significantly negative ΔS^* and ΔV^* values indicate that the reaction must involve significant bond formation in the transition state. In order to quantify the treatment of the kinetic data, k was found to correlate very well with the pK_a value of the conjugated acids of aniline,[20] i.e., with the basicity of the anilines as shown in Figure 2. The data give a good Brönsted relationship[21-23] (4), with a slope α

$$\log k = \alpha(pK_A) + \text{constant} \qquad (4)$$

of 0.75 ± 0.04. At this point it is interesting to note that this slope is very similar to the value of ca. 0.60 found for the rate-determining attack of amines on esters,[24,25] indicating a strong dependence of the rate constant on the amine basicity. In general, this trend fits in well with our earlier data for the addition of pyrrolidine to this complex ($k = 2.9 \times 10^4\ M^{-1}\ s^{-1}$, $pK_a = 11.3$)[8] since the data in Figure 2 predict a k value of $3.6 \times 10^4\ M^{-1}\ s^{-1}$ for pyrrolidine.

A Hammett plot for reaction 2 is linear and fits eq 5[23,26,27]

$$\log k = \vartheta\sigma_p + \text{constant} \qquad (5)$$

for which $\vartheta = -2.95 \pm 0.14$. This large negative slope reflects the sensitivity of the reaction against electronic effects and accounts for remarkable bond formation in the transition state. This is in line with the values of ΔS^* and ΔV^*. Furthermore, the trend in the ΔV^* data, taking into account that ΔV^* for the more basic pyrrolidine is $-15\ cm^3\ mol^{-1}$,[8] can be discussed in terms of an "early" and "late" transition state.[17-19] The most basic amine (pyrrolidine) reacts the fastest, has the lowest ΔH^* value, and therefore an early transition state and a moderate ΔV^* value of $-15\ cm^3\ mol^{-1}$. The less basic amine (4-cyanoaniline) reacts the slowest, has the highest ΔH^* value, and therefore a late transition state and a significantly more negative ΔV^* value of $-28\ cm^3\ mol^{-1}$. This trend seems to apply for all the addition reactions studied so far (Table II and ref 8).

We conclude that addition reactions of amines to α,β-unsaturated Fischer carbene complexes in general occur according to a two-step process as suggested before.[8] Significant bond formation occurs in the polar transition state which leads to the formation of an unstable zwitterionic intermediate. This mechanism is further supported by the absence of a significant isotope effect in the case of deuterioaniline, viz. $k_H:k_D = 1.2:1.0$. The observed effect is of secondary nature and indicates the operation of a two-step mechanism in which nitrogen–carbon bond formation is followed by a rapid intramolecular proton transfer from the aniline nitrogen to the C2 carbon atom of the carbene complex to produce the final product. Changing the solvent influences the rate, $k(\text{toluene}, \epsilon = 2.40):k(\text{MeCN}, \epsilon = 35.9)^{28} = 1:43$, in an expected way for amine addition reactions of such an α,β-unsaturated complex[8] and underlines the operation of a two-step mechanism. In the case of organometallics that react in one-step processes and pass through nearly isopolar transition states, no remarkable solvent effect can be observed.[29,30] Thus, amine basicity controls the rate of the bond-formation process and determines the location of the transition state in terms of "early" or "late" along the reaction coordinate.

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