

The Kinetics and Mechanism of the Substitution of Benzylideneacetone by Azadienes in the Irontricarbylbenzylideneacetone Complex

Fatima Squizani⁺, Edison Stein* and Eduardo J.S. Vichi

Instituto de Química, Universidade Estadual de Campinas, C.P. 6154,
13083-970 Campinas - SP, Brazil

Received: September 13, 1995; January 12, 1996

A cinética das reações de substituição da benzilidenoacetona (*bda*) pelos azadienos 2,2'-bipiridina (*bipy*), 2-acetilpiridinaanil (*apa*) e diacetildianil (*dad*), no complexo $\text{Fe}(\text{bda})(\text{CO})_3$ foi feita em tolueno, no intervalo de temperatura entre 40 e 55 °C. Os resultados mostraram que o mecanismo das reações com *bipy* e *dad* – ligantes simétricos, aromático e alifático, respectivamente – envolvem dois passos paralelos de reação, um dissociativo e o outro associativo. No caso do *apa* – ligante assimétrico –, somente o passo dissociativo é operante, levando a um intermediário semi-ligado. Na etapa seguinte, dois novos intermediários podem ser formados, dependendo de o átomo de nitrogênio do ligante que entra ser alifático ou aromático.

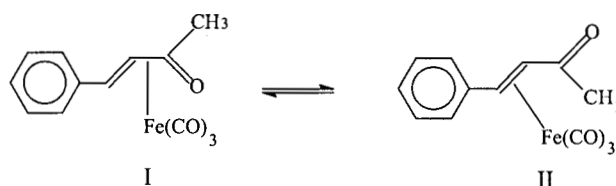
The kinetics of the substitution reactions of benzylideneacetone (*bda*) by the azadienes 2,2'-bipyridine (*bipy*), 2-acetylpyridineanil (*apa*), and diacetyldianil (*dad*), in the $\text{Fe}(\text{bda})(\text{CO})_3$ complex was performed in toluene in the temperature range between 40 and 55 °C. The results of this study showed that the mechanism of the reactions with *bipy* and *dad* – which are symmetric ligands, aromatic and aliphatic, respectively – involves two parallel reaction paths, one being dissociative and the other associative. In the case of *apa* – a asymmetric ligand – only the dissociative path is operative, leading to a half-bonded intermediate. The next step leads to the formation of two different new intermediates, depending on whether the incoming ligand nitrogen atom is aliphatic or aromatic.

Keywords: kinetics, mechanism, irontricarbylbenzylideneacetone, azadienes

Introduction

The benzylideneacetoneirontricarbyliron(0) complex, $\text{Fe}(\text{bda})(\text{CO})_3$ (I) reacts readily in mild conditions with phosphines, arsines and stibines¹, dienes² and azadienes³ giving products in which the *bda* ligand is substituted by the nucleophile. In preparing $\text{Fe}(\text{diene})(\text{CO})_3$ or $\text{Fe}(\text{azadiene})(\text{CO})_3$, the substitution reactions of $\text{Fe}(\text{bda})(\text{CO})_3$ by dienes and azadienes are preferred over the direct reaction of $\text{Fe}_2(\text{CO})_9$ with the ligands, because they are carried out under milder conditions and avoid dimeric iron dicarbonyl products.

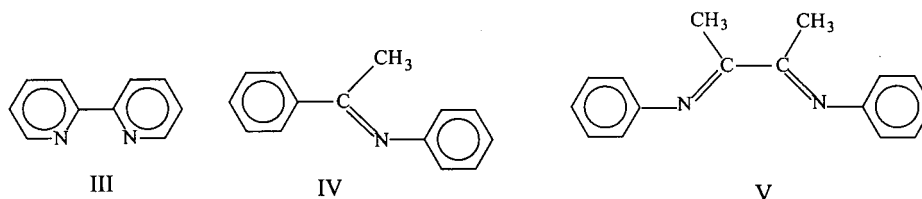
Kinetic studies of the reactions of (I) with dienes⁴ and phosphines⁵ showed that the mechanism involves both dissociative and associative reaction paths. The occurrence



of a dissociative path is attributed to the facile rupture of the Fe-ketonic CO bond leading to the 16-electron intermediate (II).

This paper reports the first kinetic study of the reactions of $\text{Fe}(\text{bda})(\text{CO})_3$ with the azadiene 2,2'-bipyridine (III, type a), 2-acetylpyridineanil (IV, type b) and diacetyldianil (V, type c).

⁺ Present address: Universidade Federal de Santa Maria, Instituto de Química, Santa Maria, R.S.



Experimental

Synthesis

Literature³ methods were used to prepare the complex $\text{Fe}(\text{bda})(\text{CO})_3$ (ν_{CO} : 2065, 2005, 1985 cm^{-1} ; cyclohexane). Diacetyldianil (*dad*) and 2-acetylpyridineanil (*apa*) were prepared according to the reported methods⁴; 2,2'-bipyridine (*bipy*) (Fluka) was used as received; toluene was dried with sodium wires, distilled and degassed prior to use. All reactions were carried out under argon. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrometer, using a 0.5 mm path length NaCl cell. A blank composed of solvent-azadiene in appropriate concentrations was used for the kinetic experiments.

The syntheses of the reaction products were carried out under argon in Schlenk flasks. Equimolar quantities of $\text{Fe}(\text{bda})(\text{CO})_3$ and azadiene dissolved in previously deaerated benzene, were left to react for 5 h at a convenient temperature (*ca.* 50 °C). After this time, the IR spectrum of the reaction mixture showed that the starting complex reacted completely and violet (*bipy*), deep red (*dad*) and deep blue (*apa*) solutions were obtained following filtration. The solvent was removed under vacuum and the residue was washed three times with cooled cyclohexane, dissolved in warm cyclohexane, and left to crystallize in an ice bath. The products were identified by their infrared absorption spectra, showing good agreement with the literature^{5, 6}: $\text{Fe}(\text{bipy})(\text{CO})_3$, violet solid, ν_{CO} 1994 (s), 1930 (s) cm^{-1} , in n-hexane; $\text{Fe}(\text{dad})(\text{CO})_3$, red solid, ν_{CO} 2028 (s), 1967 (s), 1957 (s) cm^{-1} , in n-hexane. The new complex, $\text{Fe}(\text{apa})(\text{CO})_3$, a deep blue solid, shows infrared absorption at ν_{CO} 2018 (s), 1958 (s) and 1942 (s) cm^{-1} in n-hexane. Due to the high instability of this compound the microanalysis results were not reproducible.

Kinetic experiments

The reactions were carried out in toluene solutions in glass ampoules sealed under argon. Ampoules were taken at appropriate time intervals from a thermostated bath controlled to 0.1 °C and cooled in an ice bath. Aliquots were transferred under argon to an IR liquid cell using a syringe. The reactions were followed for at least three half-lives under pseudo-first order conditions. Rate constants, k_{obs} , were obtained from a normal least-square analysis of plots

(a) $\ln A$ vs. time, for the disappearance of the absorption band at 2065 cm^{-1} of the starting complex ($A_{\infty} = 0$), or (b) $-\ln(A_{\infty} - A_t)$ vs. time for the product. As the small amount of decomposition observed even under strict exclusion of air prevented the accurate determination of A values for the product, no agreement between the values obtained from both methods was observed. The more precise k_{obs} values obtained by method (a) were considered. Duplicate runs carried out under the same conditions showed that the k_{obs} values are reproducible to better than 5%.

Results and Discussion

Reaction 1 was followed kinetically in toluene at various temperatures and concentrations. The results are shown in Table 1 (*bipy*) and Table 2 (*apa* and *dad*). Plots of k_{obs} vs. [azadiene] are linear for all ligands studied, as shown in Figures 1-3.

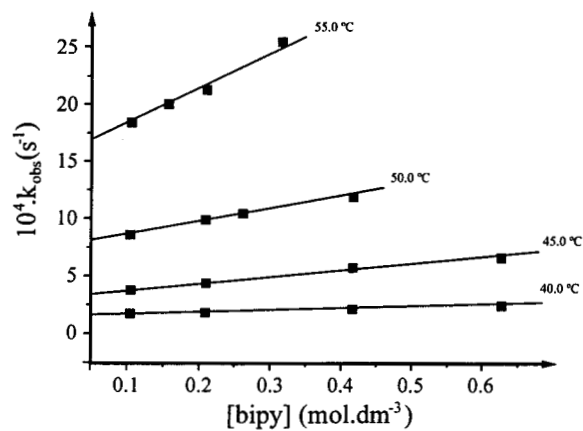
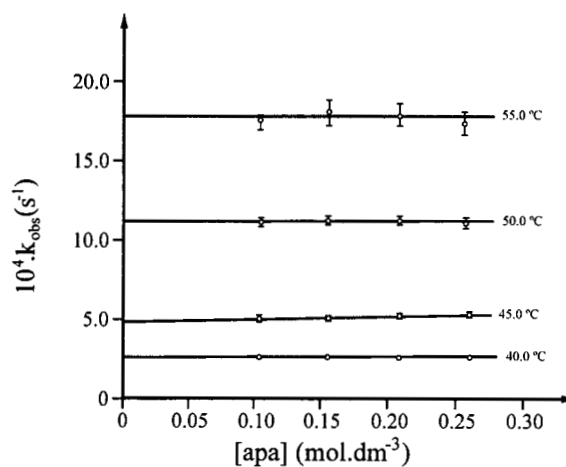


Table 1. Observed rate constants for reactions of the $\text{Fe}(\text{bda})(\text{CO})_3$ complex with bipyridine.

Temperature (°C)	[<i>bipy</i>] ($\text{mol} \cdot \text{dm}^{-3}$)	$10^4 \cdot k_{\text{obs}}$ (s^{-1})
40.0	0.105	1.69 (0.04)
	0.210	1.83 (0.03)
	0.419	2.16 (0.04)
	0.629	2.57 (0.03)
45.0	0.105	3.78 (0.05)
	0.210	4.38 (0.06)
	0.419	5.78 (0.05)
	0.629	6.70 (0.53)
50.0	0.105	8.64 (0.13)
	0.210	9.94 (0.16)
	0.262	10.5 (0.40)
	0.419	12.0 (0.20)
55.0	0.105	18.4 (0.50)
	0.157	20.1 (0.90)
	0.210	21.2 (0.30)
	0.315	25.5 (0.40)

Table 2. Observed rate constants for reactions of the $\text{Fe}(\text{bda})(\text{CO})_3$ complex with diimines.

Temperatures ($^{\circ}\text{C}$)	Diimine	[Diimine] ($\text{mol}\cdot\text{dm}^{-3}$)	$10^{-4}\cdot k_{\text{obs}} (\text{s}^{-1})$	$10^{-4}\cdot k_{\text{obs}} (\text{s}^{-1})$
40.0	apa	0.105	2.62 (0.04)	
		0.157	2.66 (0.06)	
		0.210	2.63 (0.05)	
		0.262	2.63 (0.08)	
45.0	apa	0.105	5.06 (0.16) ^a	3.28 (0.07) ^b
		0.157	5.06 (0.10)	3.39 (0.21)
		0.210	5.28 (0.12)	3.52 (0.27)
		0.262	5.31 (0.16)	3.48 (0.06)
50.0	apa	0.105	11.1 (0.20)	6.63 (0.27)
		0.157	11.2 (0.20)	6.46 (0.15)
		0.210	11.2 (0.20)	6.73 (0.28)
		0.262	11.0 (0.30)	6.44 (0.30)
	dad	0.105	0.84 (0.02)	
		0.157	0.88 (0.01)	
		0.210	0.81 (0.03)	
		0.262	0.87 (0.02)	
55.0	apa	0.105	17.4 (0.40)	10.9 (0.20)
		0.157	18.0 (0.80)	10.8 (0.20)
		0.210	17.5 (0.60)	11.1 (0.50)
		0.262	17.3 (0.70)	11.0 (0.50)
	dad	0.105	1.27 (0.06)	
		0.157	1.37 (0.07)	
		0.210	1.44 (0.03)	
		0.262	1.56 (0.10)	

^a Part A: for ligand *apa* in Fig. 4.^b Part B: for ligand *apa* in Fig. 4.**Figure 1.** Plots of k_{obs} vs. $[\text{bipy}]$ for the reaction of $\text{Fe}(\text{bda})(\text{CO})_3$ with *bipy*.**Figure 2.** Plots of k_{obs} (A) vs. $[\text{apa}]$ for the reaction of $\text{Fe}(\text{bda})(\text{CO})_3$ with *apa*.

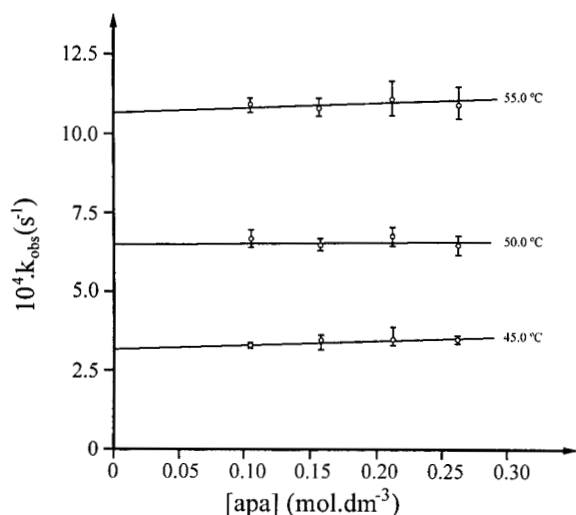


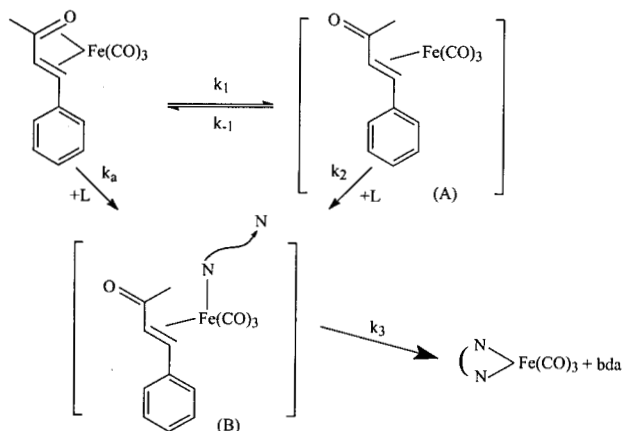
Figure 3. Plots of $k_{\text{obs}}(\text{B})$ vs. $[\text{apa}]$ for the reaction of $\text{Fe}(\text{bda})(\text{CO})_3$ with *apa*.

The kinetics of the reactions with *bipy* and *dad* can be interpreted in terms of the proposed mechanism for the reactions of $\text{Fe}(\text{bda})(\text{CO})_3$ with other mono and bidentate ligands⁷⁻¹¹. The mechanism involving two parallel reaction paths is shown in Scheme 1. In one path the process is dissociative and independent of the concentration of the incoming ligand, and the rate is controlled by the rupture of the bond between the iron atom and the ketonic carbonyl of *bda*. The other path is associative, and as such is dependent on the incoming ligand concentration.

Applying the steady-state approximation to intermediates A and B the kinetic law shown in Eq. 2 is obtained.

$$k_{\text{obs}} = \frac{k_1 \cdot k_2[\text{L}]}{(k_{-1} + k_2)} + k_a [\text{L}] \quad (2)$$

In the limit, $k_2[\text{L}] > k_{-1}$, and $k_{\text{obs}} = k_1 + k_a[\text{L}]$ (intercept = k_1 , slope = k_a).



Scheme 1.

The values for the rate constants derived for both dissociative and associative paths are shown in Table 3. In the reaction with *dad* at 50.0 °C, the overall reaction rate is independent of *dad* concentration. The associative path starts to contribute when the temperature is raised to 55.0 °C. When the temperature increases above 55.0 °C the plots of $-\ln A$ vs. time become non-linear. For temperatures below 50.0 °C the reaction is too slow to be followed.

The activation parameters for the reaction with *bipy* are also shown in Table 3. For the dissociative path the highly positive values of ΔH_1^\ddagger and ΔS_1^\ddagger are compatible with the rupture of the iron-*bda* bond in the rate determining step. However, the values of ΔH_a^\ddagger and ΔS_a^\ddagger are even higher and would not be expected for a conventional associative pathway. However, these values are compatible with a process in which a ring-opening mechanism is operative⁶. An X-ray study evidenced that in $\text{Fe}(\text{bda})(\text{CO})_2\text{L}$ complexes ($\text{L} = \text{PEt}_3$ and PPhMe_2)¹² the iron atom adopts a distorted octahedral geometry in which three facial sites are occupied by the *bda* ligand. A ¹³C-NMR study suggests that this is also true for the $\text{Fe}(\text{bda})(\text{CO})_3$ complex¹³. As such, the ring-opening mechanism also involves a rearrangement from a rigid distorted octahedron to a pentagonal intermediate in which both *bda* and *bipy* have more freedom, and a positive activation entropy is expected. The highly positive value of ΔH_a may be accounted for if bond breaking is more important than bond making in the formation of the activated complex^{14, 15}.

The substitution of *bda* by *apa* (Table 4) shows a kinetics profile completely different from that observed for the reactions in which *bda* is substituted by *bipy* or *dad*. Plots of $-\ln A$ vs. time at 40.0 °C are linear in almost all of the extension of the reaction (up to 3 half-lives). At higher temperatures (45.0, 50.0 and 55.0 °C), two straight lines emerge from the obtained data (Fig. 4). The rate constants obtained for parts A and B of the reactions are shown in Table 4. Figures 2 and 3 show that both k_3 and k_3' are

Table 3. Rate constants for the reaction between $\text{Fe}(\text{bda})(\text{CO})_3$ and Diimines.

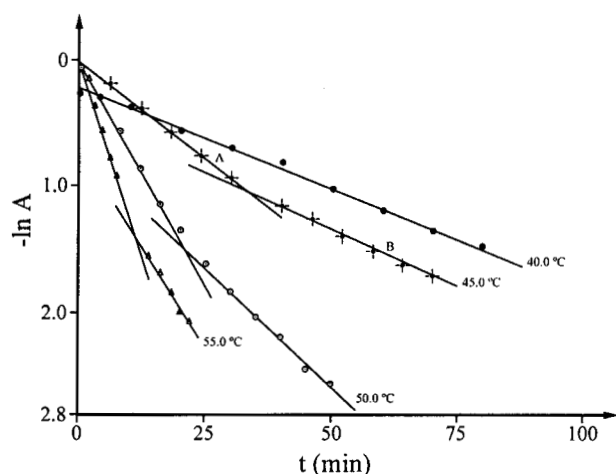
T	°C	Diimine	$10^4 \cdot k_1$
40.0	<i>bipy</i> ^a	1.48 (0.04)	1.69 (0.10)
45.0	<i>bipy</i>	3.21 (0.17)	5.70 (0.44)
50.0	<i>bipy</i>	7.68 (0.12)	10.4 (0.40)
50.0	<i>dad</i>	0.86 (0.09)	-
55.0	<i>bipy</i>	14.6 (0.90)	33.3 (4.40)
55.0	<i>dad</i>	1.07 (0.05)	1.82 (0.23)

^aThe activation parameters of the dissociative step are $\Delta H_1^\ddagger = 134 \pm 3$ kJ.mol⁻¹, and $\Delta S_1^\ddagger = 110 \pm 11$ J.mol⁻¹.K⁻¹, and those of the associative step are $\Delta H_a^\ddagger = 177 \pm 1$ kJ.mol⁻¹, and $\Delta S_a^\ddagger = 227 \pm 42$ J.mol⁻¹.K⁻¹.

Table 4. Rate Constants for the Reaction between $\text{Fe}(\text{bda})(\text{CO})_3$ and *apa*.

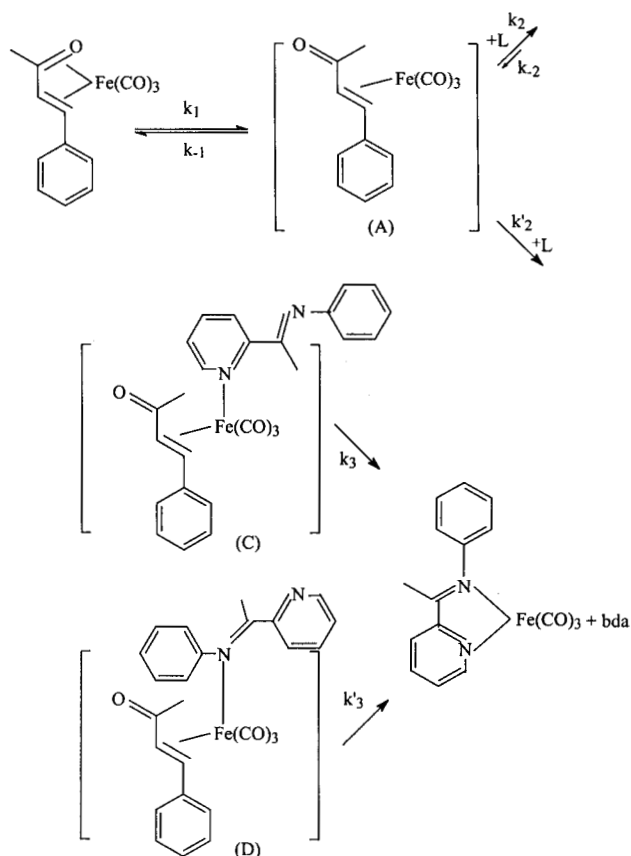
T, °C	$10^4 \cdot (k_3 \pm k_3'), \text{s}^{-1}$ ^a	$10^4 \cdot k_3', \text{s}^{-1}$ ^b
	Part A	Part B
40.0	2.63 (0.15)	-
45.0	4.83 (0.62)	3.16 (0.44)
50.0	11.3 (0.80)	6.65 (1.38)
55.0	17.8 (3.00)	10.7 (1.20)

^aActivation parameters: $\Delta H^\ddagger_{(3+3')} = 115 \pm 1 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger_{(3+3')} = 53 \pm 5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. ^bActivation parameters: $\Delta H^\ddagger_3 = 103 \pm 9 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger_3 = 12 \pm 27 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

**Figure 4.** Plots of $-\ln A$ vs. time for the reaction of $\text{Fe}(\text{bda})(\text{CO})_3$ with *apa*.

independent of the concentration of *apa*. A mechanism which accounts for these facts is presented in Scheme 2.

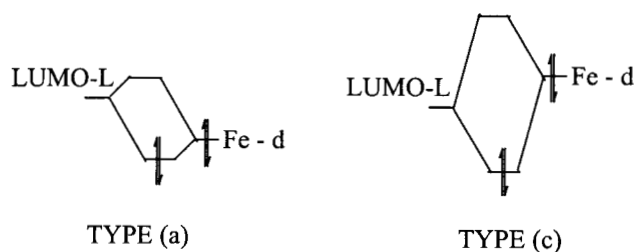
A reasonable explanation for all data obtained is that both steric and electronic effects of the ligand *apa* will be among the effects of the ligands *bipy* and *dad*, because it can be considered as having one half of the ligand *bipy* and the other half of the ligand *dad*. Hence, k_2 and k_3' should be bigger than k_2' and k_3 , as can be expected for the rate constants of the reactions of $\text{Fe}(\text{bda})(\text{CO})_3$ with *bipy* and *dad*, respectively. At temperatures below 40.0 °C, the reaction is too slow to be followed. At 40.0 °C, the reaction of $\text{Fe}(\text{bda})(\text{CO})_3$ with *apa* occurs, forming the intermediates C and D at almost the same rate as they are consumed; therefore the plot of $-\ln A$ vs. time is a straight line. When the temperature increases, k_{obs} is equal to $k_3 + k_3'$ in the first part (A), and to k_3' in the second part (B) of the curve $-\ln A$ vs. time (Fig. 4). The formation of intermediates C and D must be fast, but the product formation controlled by k_3 is slower than that controlled by k_3' . As a consequence, there is an accumulation of the intermediate C, and when it reaches the proper concentration it equilibrates with A. All

**Scheme 2.**

these effects must be reflected on the rate of the disappearance of the reactant.

Another argument in favor of these statements is that the π -acceptor capacities of azadiene ligands increase in the order aromatic < mixed < aliphatic^{16, 17}. This increasing order of (a) to (c) azadienes is consistent with the increase of the HOMO-LUMO interaction of metal and ligand, respectively¹⁸.

Scheme 3 shows the HOMO-LUMO orbitals for metal-complexes with ligands type (a) and type (c). The interaction is stronger for ligands of type (a), making the Fe-N_{aliphatic} bond more effective and providing a greater metal to ligand back-bonding¹⁹. As such, in forming the

**Scheme 3.**

intermediates C and D, the former is less stable and equilibrates with intermediate A, while intermediate D, in spite of being more difficult to form than C, reacts more readily, giving the product. Accordingly, we suppose that in increasing the temperature, the equilibrium C/A is reached more quickly because k_2 and k_2' rise more than k_3 ($k_3' > k_3$), as shown in Scheme 2. The values of the activation parameters, *i.e.*, high ΔH^\ddagger and positive ΔS^\ddagger , shown in Table 4, support the proposed mechanism.

Conclusion

The first kinetic results obtained from the system *bda*/diimine ligands suggest that the mechanism of the substitution of *bda* by the ligands *bipy* and *dad* involves two parallel reaction paths. In one path the process is dissociative and the rate is controlled by the rupture of the iron-carbonyl bond of *bda*. The other path is associative, *i.e.*, dependent on the incoming ligand concentration.

The mechanism of the substitution of *bda* by the mixed ligand *apa* is more complex. Two intermediates, C and D, are formed by the attacking ligand before the rupture of the iron-carbonyl bond of *bda*. The relative concentration of these intermediates depend on the temperature. The rate of the formation of the product is controlled by the rupture of the iron-olephine bond in the intermediates C and D, being slower in the intermediate C.

The final conclusion is that both electronic and steric effects are operative in determining the kinetics of the reaction with *bipy* and *dad*. In the reaction with *apa* whose mechanism is dissociative only, the more important feature is the stabilization of the intermediate C compared with the intermediate D, even though the rate of the formation of C is slower than that of D.

References

1. Rubezhov, A.Z.; Gudin, S.P.; *Adv. Organomet. Chem.* **1972**, *10*, 347 and references therein.

2. Fruhauf, H.W.; Sanders, A.; Goddard, R.; Kruger, C.K.; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 64.
3. Howell, J.A.S.; Johnson, B.F.G.; Josty P.L.; Lewis, J.; *J. Organomet. Chem.* **1972**, *39*, 329.
4. Von Peckman, H.; *Ber. Dtsch. Chem. Gesellschaft* **1988**, *2111*, 1411.
5. Otsuka, S.; Yoshida T.; Nakamura, A.; *Inorg. Chem.* **1967**, *6*, 20.
6. Tom Dieck, H.; Orlopp, A.; *Angew. Chem. Int. Ed. Engl.* **1977**, *14*, 251.
7. Cardacci, G.; Bellachioma, G.; *Inorg. Chem.* **1977**, *16*, 3099.
8. Bellachioma, G.; Cardacci, G.; *J. Chem. Soc., Dalton Trans.* **1977**, 2181.
9. Howell, J.A.S.; Burkinshaw, P.M.; *J. Organomet. Chem.* **1978**, *152*, C5.
10. Burkinshaw, P.M.; Dixon, D.T.; Howell, J.A.S.; *J. Chem. Soc., Dalton Trans.* **1980**, 999.
11. Howell, J.A.S.; Kola, J.C.; Dixon, D.T.; Burkinshaw, P.M.; Thomas, M.J.; *J. Organomet. Chem.* **1984**, *266*, 83.
12. Vichi, E.J.S.; Raithby, P.R.; McPartlin, M.; *J. Organomet. Chem.* **1983**, *256*, 111.
13. Vichi, E.J.S.; Fujiwara, F.Y.; Stein, E.; *Inorg. Chem.* **1985**, *24*, 287.
14. Dobson, G.R.; *Acc. Chem. Res.* **1976**, *9*, 300.
15. Shi, Q.Z.; Richmond, T.G.; Trogler, W.C.; Basolo, F.; *Organometallics* **1982**, *1*, 1033.
16. Van Koten, G.; Vrieze, K.; *Adv. Organomet. Chem.* **1982**, *21*, 151.
17. Reinhold, J.; Benedix, R.; Birner, P.P.; Henning, H.; *Inorg. Chim. Acta* **1979**, *33*, 209.
18. Fukui, H.; *Theory of Orientation and Stereoselection*; Springer-Verlag; Berlin, Germany, 1975; p 8.
19. Fruhauf, H.W.; *J. Chem. Res. (M)* **1983**, *9*, 2035.