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Temperature and pressure dependence of the addition of 4-cyanopyridine to tricarbonyl(1-5- η -dienyl)iron(II) complexes (dienyl = C₆H₇ or C₇H₉)

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Abstract

The kinetics of the addition of 4-cyanopyridine to the coordinated dienyl ligand in tricarbonyl(1-5- η -dienyl)iron(II) complexes have been studied as a function of temperature and pressure in acetonitrile for dienyl = C₆H₇ and C₇H₉ by stopped-flow techniques. The reported activation parameters (ΔH^\ddagger , ΔS^\ddagger and ΔV^\ddagger) for both the forward addition and reverse dissociation reactions support the concept of the previously suggested "ordered transition state" in which bond formation and bond breaking on the coordinated dienyl ligand occur simultaneously, and which can be described as an interchange process. The results are discussed by comparison with those for similar systems investigated previously as well as those for related substitution, insertion and addition reactions.

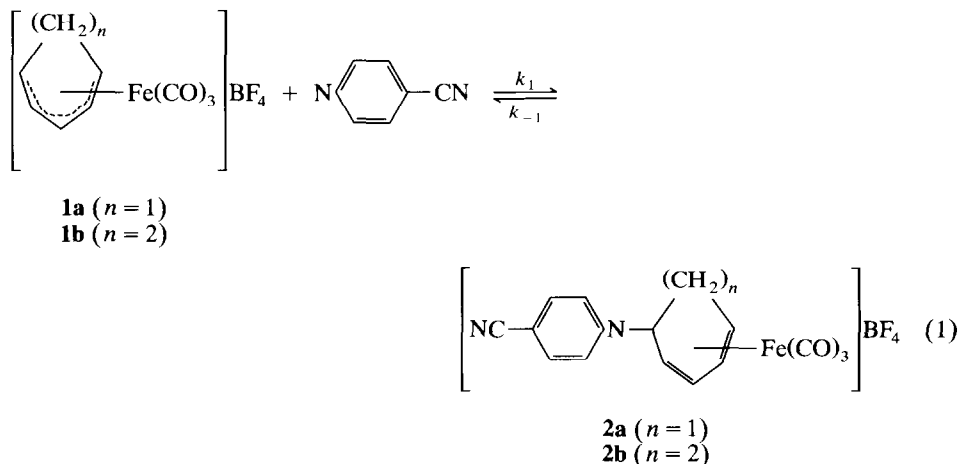
Introduction

Additions of a wide variety of anilines and pyridines to complexes of the type [Fe(CO)₃(1-5- η -dienyl)]BF₄ to form novel 1,3-diene products have been studied in detail [1–12]. The influence of nucleophile basicity, steric effects, and the electronic nature of the dienyl fragment on the kinetics of the addition and reverse dissociation reactions were studied systematically and it was shown that the degree of accumulation of positive charge in the transition state of these reactions depends largely on the nature of the coordinated organic group [9]. The addition reactions are generally characterized by relatively low ΔH^\ddagger and significantly negative ΔS^\ddagger values, whereas bond cleavage is usually accompanied by significantly higher ΔH^\ddagger and positive ΔS^\ddagger values. These features are in keeping with direct addition of the nucleophile to the dienyl rings of the complexes during bond formation, and *vice versa* during bond breaking. However, there are cases in which

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bond breaking is characterized by significantly negative ΔS^\ddagger values and for which an "ordered transition state mechanism" was suggested [10].

Information about details of bond formation and bond breaking processes in inorganic, organometallic and bioinorganic chemistry can be obtained from the pressure dependence of such processes [13–15], and high pressure kinetic studies have become an important tool in mechanistic investigations [16]. Recent work in our laboratory has clearly demonstrated the applicability of this technique to organometallic reactions [17–25]. We have now investigated the temperature and pressure dependence of a typical addition/dissociation system (reaction 1) in an effort to increase understanding of the underlying reaction mechanism. We have also obtained thermodynamic data for the overall equilibrium (1), and so can compare these with data estimated from kinetic parameters for related systems reported in the literature.



Experimental

Materials

The complexes **1a** and **1b** were synthesized and purified as described before [26,27]. Chemical and spectroscopic analyses confirmed their purity. 4-Cyanopyridine (4-CNpy) was purchased in the purest grade available (Aldrich) and used as supplied. Acetonitrile (MeCN) was distilled and then stored over molecular sieves (3 Å) under dinitrogen. The reaction products **2a** and **2b** were fully characterized [28,29] and shown to be similar to those obtained previously [4,11]. Bonding of 4-CNpy is through the amine N to the C(5) carbon atom of the diene fragment.

Instrumentation

Reaction 1 is characterized by significant UV-VIS spectral changes, in particular an absorbance increase at 400 nm, which were monitored with a Shimadzu UV 250 spectrophotometer. The spectral data could be used to estimate the equilibrium constant for reaction 1. UV-VIS spectra under pressures up to 150 MPa were recorded on a Zeiss DMR 10 spectrophotometer equipped with a thermostatted high pressure cell [30]. The kinetics of reaction 1 was studied under pseudo-first-

order conditions involving use of a large excess of 4-CNpy. The addition reactions are fast and were monitored by use of a thermostatted ($\pm 0.1^\circ\text{C}$) Durrum D110 stopped-flow instrument coupled to an on-line data acquisition and analysis system [31]. Kinetic experiments at pressures up to 100 MPa were performed on a home-made high pressure stopped-flow instrument [32]. Excellent first-order behaviour was observed under all experimental conditions, and the first-order rate constants, k_{obs} , were calculated from plots of $\ln(A_\infty - A_t)$ versus t in the usual way. Such plots were linear for at least 2–3 half-lives of the reaction. Reported rate constants are the mean values of 4 and 5 determinations. All rate and activation parameters were calculated by linear least squares analysis.

Results and discussion

The products formed in the addition of pyridines to dienyl complexes, as in reaction 1, have been characterized by the isolation of the products and *in situ* IR and ^1H NMR studies [4,11,12]. The products **2a** and **2b** are yellow solids [28,29] that exhibit two strong carbonyl bands at ~ 2055 and 1980 cm^{-1} , characteristic of cationic 1,3-diene-substituted iron complexes [4,11,12,33], and a broad band at $\sim 1060\text{ cm}^{-1}$ due to the counterion BF_4^- . IR spectra recorded for equimolar mixtures of complexes **1** with 4-CNpy in MeCN [28,29] contained carbonyl bands at 2120 and 2065 cm^{-1} in addition to those due to the products **2**, which indicates that reaction 1 is an equilibrium and requires an excess of nucleophile to go to completion.

The observed pseudo-first-order rate constant for reaction 1 depends linearly on the nucleophile concentration, as demonstrated by the data summarized in Table 1 and Fig. 1. Plots of k_{obs} versus [4-CNpy] have non-zero intercepts, which is characteristic of an equilibrium process, and can be expressed as in eq. 2, where k_1 is the forward and k_{-1} the reverse rate constant for reaction 1.

$$k_{\text{obs}} = k_{-1} + k_1[4\text{-CNpy}] \quad (2)$$

The values of k_1 and k_{-1} at various temperatures are listed in Table 1, and the corresponding activation parameters are summarized in Table 2.

The characteristic spectral changes observed for reaction 1 can be employed to determine the overall equilibrium constant K_1 . A plot of the absorbance at 400 nm versus [4-CNpy] is curved, and reaches a limiting value at high [4-CNpy]. K_1 can be expressed by eq. 3,

$$K_1 = (A - A_0)/(A_\infty - A) \times [4\text{-CNpy}] \quad (3)$$

where A_0 , A and A_∞ are the absorbances in the absence and in the presence of small to large concentrations of 4-CNpy, respectively. A plot of $(A - A_0)/[4\text{-CNpy}]$ versus A should be linear with a slope of K_1 , and this was found to be the case for reaction 1 (see Fig. 2), which gave values of K_1 of 12.1 ± 0.6 and $7.3 \pm 0.3\text{ M}^{-1}$ at 20.2°C for dienyl = C_6H_7 and C_7H_9 , respectively. These values are in fair agreement with those calculated from the kinetic data for these conditions in Table 1, namely $K_1 = k_1/k_{-1} = 27$ and 12 M^{-1} , respectively. It should be kept in mind that such equilibrium constants determined from spectroscopic data are usually subject to significantly larger errors than those obtained from the ratio of two rate constants.

Table 1

k_{obs} as a function of nucleophile concentration and temperature for the addition of 4-CNpy to **1a** and **1b** in MeCN ^a

Complex	Temperature (°C)	$10^2 \times [4\text{-CNpy}]$ (M)	k_{obs}^b (s ⁻¹)	k_1 (M ⁻¹ s ⁻¹)	k_{-1} (s ⁻¹)
1a	5.2	1.0–8.0	– ^c	344 ± 7	5.0 ± 0.3
	10.1			457 ± 7	9.8 ± 0.3
	15.1			669 ± 11	22.1 ± 0.5
	20.1			937 ± 10	34.8 ± 0.5
	25.0			1172 ± 22	52.8 ± 1.1
1b	15.3	1.0	1.47 ± 0.02	18.0 ± 0.4	1.27 ± 0.02
		2.0	1.65 ± 0.04		
		4.0	1.95 ± 0.02		
		6.0	2.34 ± 0.02		
		8.0	2.70 ± 0.02		
	20.2	10.0	3.10 ± 0.03	24.6 ± 0.3	2.11 ± 0.02
		1.0	2.35 ± 0.05		
		2.0	2.58 ± 0.02		
		4.0	3.12 ± 0.02		
		6.0	3.60 ± 0.02		
	25.0	8.0	4.10 ± 0.02	30.0 ± 0.02	3.42 ± 0.01
		10.0	4.54 ± 0.03		
		1.0	3.73 ± 0.02		
		2.0	4.04 ± 0.02		
		4.0	4.60 ± 0.02		
	30.3	6.0	5.20 ± 0.05	41.9 ± 0.5	4.92 ± 0.03
		8.0	5.83 ± 0.02		
		10.0	6.43 ± 0.02		
		1.0	5.30 ± 0.02		
		2.0	5.81 ± 0.03		
35.0	4.0	6.60 ± 0.02	53.6 ± 0.7	8.08 ± 0.04	
	6.0	7.40 ± 0.03			
	8.0	8.30 ± 0.03			
	10.0	9.10 ± 0.03			
	1.0	8.60 ± 0.03			
	2.0	9.21 ± 0.03			
	4.0	10.20 ± 0.04			
	6.0	11.3 ± 0.1			
	8.0	12.3 ± 0.1			
	10.0	13.5 ± 0.1			

^a Experimental conditions: [Fe] = 1.5×10^{-3} M. ^b Mean value of 4 to 5 kinetic experiments. ^c Rate data are reported in Fig. 1.

The effect of pressure on k_{obs} for the addition reactions was studied at low and high 4-CNpy concentrations in order to obtain the pressure dependence of mainly the intercept (k_{-1}) or the slope (k_1) in Fig. 1, respectively. The results, summarized in Table 3, demonstrate that within the limits of experimental error, k_{obs} (and also k_1 and k_{-1}) does not show any significant pressure dependence and $\Delta V^\ddagger \approx 0$. This was rather surprising, and calls for a more detailed discussion in which the results of the present study are compared with those previously presented [1–12]. The pressure independence of k_1 and k_{-1} suggests that the overall equilibrium constant for reaction 1 must also be pressure independent, *i.e.*

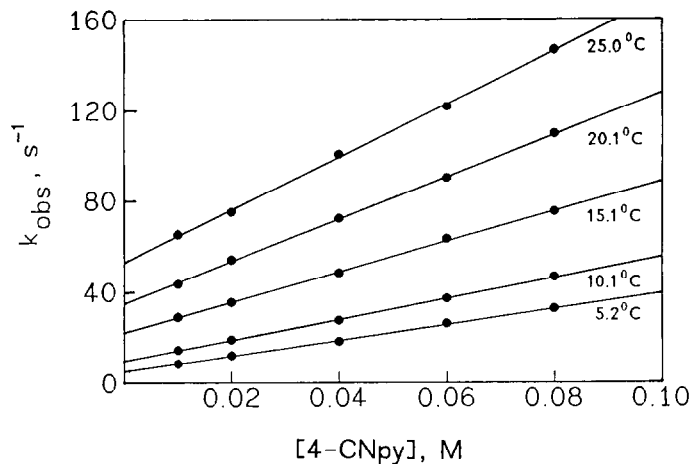


Fig. 1. Plots of k_{obs} versus $[4\text{-CNpy}]$ for the reaction of **1a** with 4-CNpy in MeCN as a function of temperature.

Table 2

Rate and activation parameters for the forward and reverse reactions in (1)^a

Dienyl	k_1 at 25°C ($M^{-1} s^{-1}$)	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	k_{-1} at 25°C (s^{-1})	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)
C_6H_7	1172	42 ± 2	-46 ± 6	53	81 ± 6	$+60 \pm 20$
C_7H_6	30	38 ± 1	-89 ± 5	3.4	65 ± 2	-16 ± 8

^a Activation parameters calculated from the data in Table 1.

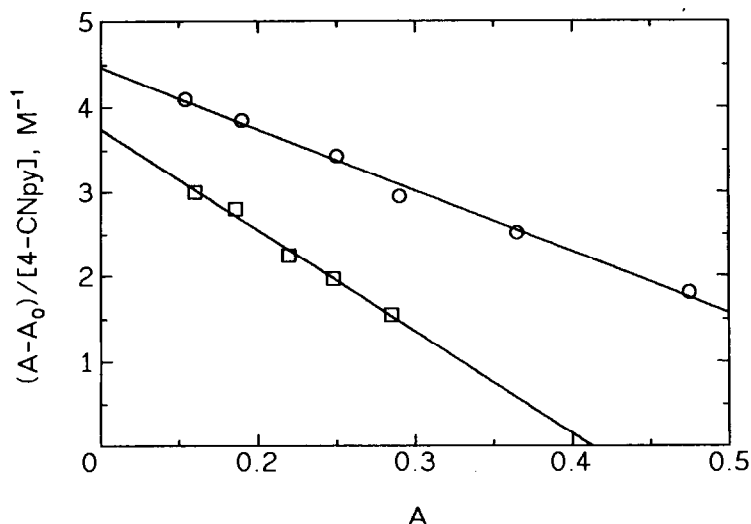


Fig. 2. Plots of $(A - A_0)/[4\text{-CNpy}]$ versus A for reaction 1. \square , dienyl = C_6H_7 ; \circ , dienyl = C_7H_9 .

Table 3

Effect of pressure on the addition of 4-CNpy to **1a** and **1b** in MeCN ^a

Complex	Temperature (°C)	10 ² × [4-CNpy] (M)	Pressure (MPa)	k _{obs} ^b (s ⁻¹)
1a	15.1	1.0	0.1	29.0 ± 0.4
			10	28.5 ± 0.5
			50	29.2 ± 0.4
			100	29.5 ± 0.5
		8.0	0.1	74.4 ± 0.5
			10	74.8 ± 0.5
			50	75.3 ± 0.4
			100	75.5 ± 0.6
1b	20.2	1.0	0.1	2.35 ± 0.02
			10	2.25 ± 0.02
			50	2.28 ± 0.02
			100	2.31 ± 0.01
		8.0	0.1	4.54 ± 0.02
			10	4.49 ± 0.03
			50	4.52 ± 0.02
			100	4.51 ± 0.02

^a Experimental conditions: [Fe] = 1.5 × 10⁻³ M. ^b Mean value of 4 to 5 kinetic experiments.

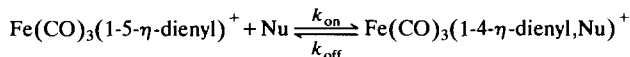
$\Delta\bar{V}(K) = \Delta V^\ddagger(k_1) - \Delta V^\ddagger(k_{-1}) \approx 0$. This was investigated experimentally by recording UV-VIS spectra of a mixture of **1a** (and **1b**) and 4-CNpy as a function of pressure. The observed spectral changes could be related to the pressure dependence of **1a** and **1b** in MeCN, *i.e.* due to piezochromic effects, and revealed that equilibrium 1 shows no dependence on pressure; thus $\Delta\bar{V}(K) \approx 0$.

The k_1 value for the addition of 4-CNpy to **1a** is significantly larger than that for the addition to **1b**, which mainly shows up in the larger ΔS^\ddagger value. The same is true for the reverse step (k_{-1}), and again it is the entropy term that accounts for the difference. The overall equilibrium constant is only slightly larger for **1a** than for **1b** (see Table 4). These effects are ascribed to steric hindrance caused by the additional CH₂ group in **1b** when 4-CNpy approaches from above the diene rings, since this could account for the more positive ΔS^\ddagger values. A comparison of the k_1 and k_{-1} values for reaction 1 with different nucleophiles based on data in Table 4 reveals that the differences can be related to the basicity of the nucleophiles and the effect of the diene ring size. The overall equilibrium constants suggest that 4-CNpy behaves very like 4-Clani in reaction with **1a**, but like 2,6-Me₂ani in that with **1b**. Furthermore, it is mainly the large difference in k_{off} for 2-Etpy and 4-CNpy that accounts for the significant decrease in K for **1b**. This effect is not significant in the case of **1a**, which points to an important role of the additional CH₂ group in **1b**.

In general it is reasonable to expect negative ΔS^\ddagger values for bond formation (*i.e.* addition) reactions in contrast to the positive values for bond breaking (*i.e.* dissociation) reactions. The data in Table 2 confirm the former, but not necessarily the latter. In earlier studies [10,12] significantly negative ΔS^\ddagger values were reported for the reverse dissociation reactions summarized in Table 4, and were interpreted in terms of an "ordered transition state" mechanism [5,10]. This mechanism

Table 4

Summary of rate and equilibrium constants for a series of addition reactions by various nucleophiles to **1a** and **1b** in MeCN at 25°C according to the overall reaction



Dienyl	Nu ^a	k_{on}^b ($M^{-1} s^{-1}$)	k_{off}^b (s^{-1})	$K = k_{\text{on}}/k_{\text{off}}$ (M^{-1})
C ₆ H ₇ (1a)	2-Etpy	593	23	25.8
	4-CNpy	1054 ^c	53 ^c	19.9
	ani	3278	72	45.5
	2-Meani	2928	53	55.2
	4-Clani	1793	73	24.6
C ₇ H ₉ (1b)	2-Etpy	29	0.20	145
	4-CNpy	30 ^c	3.6 ^c	8.3
	ani	508	3.1	164
	2-Meani	141	4.1	34.4
	4-Clani	166	5.8	28.6
	2,6-Me ₂ ani	51	12	4.3

^a Abbreviations: py = pyridine; ani = aniline. ^b Extrapolated from the activation parameters reported in [10,12] unless otherwise indicated. ^c This work.

involves simultaneous bond making and bond breaking, which in terms of the dissociation reaction (reverse of reaction 1) means that Fe–C(diene) bond formation in **2** (1-4- η to 1-5- η) and C(diene)–N(4-CNpy) bond breaking occur simultaneously. This would mean that dissociation involves an interchange type mechanism on the coordinated diene in which a C–N bond is interchanged for a Fe–C bond.

The concept of an interchange mechanism for the dissociation of the ligand bound nucleophile to account for the “ordered transition state” is supported by the absence of any significant pressure effect, i.e. a zero volume of activation. This would suggest that the volume collapse associated with Fe–C(diene) bond formation (i.e. the diene moiety moving further into the coordination sphere) is cancelled out by the volume increase associated with C(diene)–N(4-CNpy) bond breaking. On the basis of microscopic reversibility, this suggestion would also require the addition process to follow a similar interchange type of mechanism, which is also in agreement with the pressure independence of k_1 . Again the transition state seems to be highly ordered (negative ΔS^\ddagger), although the volume changes associated with bond formation {C(diene)–N(4-CNpy)} and bond breakage (η^5 - to η^4 -Fe–C) seem to cancel out in the transition state. This interpretation is based solely on intrinsic volume arguments, and it remains an open question as to what extent solvational contributions resulting from changes in electrostriction during the addition/dissociation process contribute towards the overall effect. In order to resolve this question it will be necessary to investigate the effect of solvent polarity on such processes, especially on the values of ΔS^\ddagger and ΔV^\ddagger [15,16]. Solvational contributions could, for instance, also partly account for the significantly more negative ΔS^\ddagger values than the zero ΔV^\ddagger values found in this study. However, solvational changes do not seem to be very important in the reaction of amines with [(dienyl)Fe(CO)₃]⁺ complexes as seen from the k_1 values of $6470 \pm$

260, 1010 ± 5 , 386 ± 5 (MeCN) and 11000 ± 443 , 3130 ± 20 , 560 ± 49 (MeNO₂) $M^{-1} s^{-1}$ reported for the addition of 4-methylaniline to dienyl = C₆H₇, 2-MeOC₆H₆ and C₇H₉, respectively [11].

The concept of an interchange mechanism for the addition of a nucleophile to a coordinated ligand is, as far as we know, new, but provides the only possibility of accounting for all the available activation parameters. Such interchange could occur at a single carbon atom, that exchanges its binding to Fe with that to N(4-CNpy) and *vice versa*. The interchange mechanism for ligand substitution on octahedral metal centers is a well accepted concept [15,16], and has recently been suggested to account for such processes in the case of metal carbonyl complexes [34–36]. In the latter case the reactions are also accompanied by small absolute values of ΔV^\ddagger , in line with the concept of a simultaneous exchange of the entering and leaving ligands. On the other hand, processes that are accompanied by significant bond formation at the metal center, even if the coordinated dienyl ligand undergoes ring-slippage (η^5 to η^3), are characterized by significantly negative volumes of activation [24]. Similarly, recent studies on insertion reactions on metal-carbene complexes [37], and [2 + 2] cycloaddition reactions on the coordinated ligand of metal-carbene complexes [38], indicated that such processes are significantly accelerated by pressure, *i.e.* show negative ΔV^\ddagger values. Thus bond formation on a metal center or a coordinated ligand results in a negative ΔV^\ddagger and a pressure accelerated process. The rather unusual pressure independence observed for such bond formation and bond breaking processes on the coordinated dienyl ligand in this study must be due to the associated change in bonding mode of the ligand to the metal center as suggested above. Similar processes will be studied in more detail in our laboratories in order to improve the understanding of the suggested interchange/“ordered transition state” concept.

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