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Kinetics of Nucleophilic Attack on Coordinated Organic Moieties. Part 16. Electrophilic Attack by $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]^+$ on Di- and Trimethoxy Benzenes

GLYN R. JOHN and LEON A. P. KANE-MAGUIRE
Chemistry Department, University College Cardiff, P.O. Box 78, Cardiff, CF1 1XL, U.K.

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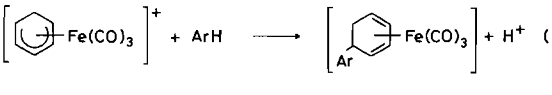
The cation $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]^+$ (I) has been shown to react with a variety of methoxy-benzenes to give novel diene-substituted aromatic species according to eqn. (1) (ArH = 1,3,5-trimethoxy-, 1,2,3-trimethoxy-, 1,2,4-trimethoxy-, 1,3-dimethoxy-, and 1,4-dimethoxybenzene). For each reaction in CH_3NO_2 solvent, the rate law Rate =

$$[(C_6H_7)Fe(CO)_3]^+ + ArH \rightarrow [(Ar{\cdot}C_6H_7)Fe(CO)_3] + H^+ \qquad (1)$$

$= k_2K_1$ [complex][ArH]/(1 + K_1[ArH]) is observed. This is interpreted in terms of an electrophilic substitution mechanism involving rapid pre-equilibrium formation (K_1) of a π-complex followed by rate-determining rearrangement (k_2) to a Wheland-type σ-complex intermediate. Rapid proton loss then leads to the observed products.

Introduction

Recent studies [1–9] have highlighted the synthetic potential of employing organometallic cations such as $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]^+$ (I) as electrophilic reagents towards aromatic substrates. For example, cation (I) reacts with a wide range of heterocyclic aromatic species [1, 5, 6] as well as a number of activated arenes [2, 8, 9] according to eqn. (1). Kinetic studies of some of these processes (*e.g.*, ArH = indoles [5], pyrrole [6], N,N-dimethylaniline [8, 9]) have shown that they are similar to electrophilic substitution with more conventional electrophiles.



(1)

(ArH = indoles, pyrrole, furan, thiophen, N,N-dimethylaniline, and 1,3,5-trimethoxybenzene)

Reactions (1; ArH = 1,3,5-trimethoxybenzene, 1,3-dimethoxybenzene) have been described briefly [2]. Synthetic details are reported here, and the range of methoxybenzene substrates extended. In addition, detailed kinetic studies have now been carried out in CH_3NO_2 solvent for ArH = 1,3,5-trimethoxy-, 1,2,3-trimethoxy-, 1,2,4-trimethoxy-, 1,3-dimethoxy-, and 1,4-dimethoxy-benzene in order to throw further light on the mechanisms of these novel processes.

Experimental

Materials

The salt $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]BF_4$ (I) was prepared and purified following published procedures [10]. The methoxy-benzene substrates were purchased in the purest grades available (Research Chemicals) and the solids used as supplied.

Nitromethane solvent (BDH) was distilled in bulk under an atmosphere of nitrogen and stored over molecular sieves (Grade 3A). The water content was shown to be 0.04% w/w using the Karl-Fischer method [11]. The nitromethane was deoxygenated by passing through a stream of nitrogen for about 30 min. immediately prior to use.

Tricarbonyl{5-(2,4,6-trimethoxyphenyl)cyclohexa-1,3-diene}iron, (IIa)

Complex (I, 0.20 g) was dissolved in CH_3NO_2 (25 cm^3) and 1,3,5-trimethoxybenzene (0.11 g) added. The reaction flask was sealed under nitrogen, wrapped in aluminium foil, and heated at 60 °C for 24 h. Rotary evaporation yielded an oily solid which on recrystallisation from methanol/water gave the product as an off-white powder (0.15 g, 60% yield), M.p. 109 °C. The IR spectrum of a solution in CH_3NO_2 exhibited two strong carbonyl bands at 2045 and 1965 cm^{-1}, while its field desorption (f.d.) mass spectrum showed a single strong parent peak at m/Z 386. *Anal.* Found: C, 56.1; H, 4.7. Calcd. for $C_{18}H_{18}FeO_6$: C, 56.0; H, 4.7%.

Tricarbonyl{5-(2,3,4-trimethoxyphenyl)cyclohexa-1,3-diene}iron, (IIb)

A similar mixture of (I, 0.15 g) and 1,2,3-trimethoxybenzene (0.08 g) in CH_3NO_2 (25 cm^3) was allowed to react at 45 °C until a large amount of product had formed (as evidenced by the IR spectrum). Rotary evaporation gave an oil which was then dissolved in acetone and passed through an alumina H column. Evaporation again yielded a colorless oil, which was crystallised from acetone/water as the off-white product (0.105 g, 56% yield), M.p. 104–105 ^{3}C. A nitromethane solution showed two strong ν(CO) bands at 2045 and 1965 cm^{-1}. Its f.d. mass spectrum showed a single strong parent ion at m/Z 386. *Anal.* Found: C, 56.3; H, 4.5. Calcd. for $C_{18}H_{18}FeO_6$: C, 56.0; H, 4.7%.

Tricarbonyl{5-(2,4,5-trimethoxyphenyl)cyclohexa-1,3-diene}iron, (IIc)

A similar procedure using 0.15 g of (I) and 0.08 g of 1,2,4-trimethoxybenzene gave 0.14 g (74% yield) of product (IIc) as a clear oil. A liquid film exhibited two strong ν(CO) bands at 2045 and 1965 cm^{-1}. *Anal.* Found: C, 55.8; H, 4.5. Calcd. for $C_{18}H_{18}FeO_6$: C, 56.0; H, 4.7%.

Tricarbonyl{5-(2,4-dimethoxyphenyl)cyclohexa-1,3-diene}iron, (IId)

This compound (IId) was obtained as a clear oil in 78% yield using a similar procedure to those above. A liquid film showed two strong ν(CO) bands at 2045 and 1965 cm^{-1}. *Anal.* Found: C, 57.1; H, 4.8. Calcd. for $C_{17}H_{16}FeO_5$: C, 57.3; H, 4.5%.

Spectroscopic Studies

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. ^{1}H NMR (90 MHz) spectra of the products (IIa–IId) in $(CD_3)_2CO$ were obtained on a Perkin-Elmer R32 spectrophotometer. Field desorption (f.d.) mass spectra were recorded using a Varian combined FD/FI/EI source on a CH5D mass spectrometer linked to a Varian 620 i data system. Acetone was employed as solvent, and low emitter currents were used to desorb the samples.

Kinetic Studies

The overall reactions (1) with each of the methoxy-benzenes employed were slow enough to follow by IR spectroscopy. Kinetic runs were carried out in the dark under nitrogen using sampling techniques previously described [12]. The disappearance of the longest-wavelength carbonyl band of the original dienyl cation at 2110 cm^{-1} was monitored.

All reactions were studied employing a large excess of the particular methoxy-benzene, and pseudo-first order rate constants, k_{obs}, calculated from the slopes of plots of log A_t *versus* time. Such plots were generally linear for at least 70% completion of reaction.

TABLE I. Hydrogen-1 NMR Spectra of Neutral Diene Products in $(CD_3)_2CO$.

Complex	Proton	Chemical shift, τ^a
IIa	H^1, H^4	6.70 (2, overlapping multiplets)
	H^2, H^3	4.40 (2, overlapping multiplets)
	$H^{5'}$	7.00 (1, m)
	$H^6, H^{6'}$	7.96 (2, overlapping multiplets)
	aromatic	3.80 (2, s)
	$O–CH_3$	6.16 (9, s)
IIb	H^1, H^4	6.80 (2, overlapping multiplets)
	H^2, H^3	4.36 (2, overlapping multiplets)
	$H^{5'}$	7.10 (1, m)
	$H^6, H^{6'}$	*ca.* 8.5 (2, overlapping multiplets)
	aromatic	3.48 (1, d)
		3.70 (1, d)
	OCH_3	6.29 (9, s)
IIc	H^1, H^4	6.80 (2, overlapping multiplets)
	H^2, H^3	4.32 (2, overlapping multiplets)
	$H^{5'}$	7.11 (1, m)
	H^6	8.39 (1, m)
	$H^{6'}$	8.58 (1, m)
	aromatic	3.55 (1, s)
		3.65 (1, s)
	OCH_3	6.25 (9, s)
IId	H^1, H^4	6.70 (2, overlapping multiplets)
	H^2, H^3	4.53 (2, overlapping multiplets)
	$H^{5'}$	7.08 (1, m)
	$H^6, H^{6'}$	8.36 (2, m)
	aromatic	2.84 (1, d)
		3.44 (1, d)
		3.54 (1, s)
	OCH_3	6.26 (6, s)

^{a}Intensities and multiplicities are given in parentheses.

However, because of their extremely slow rates at 60 °C, the reactions (1) with 1,2,3-trimethoxybenzene and 1,4-dimethoxybenzene were only monitored for *ca.* 40% completion of reaction.

An initial rapid process was also noted in the reaction of 1,3,5-trimethoxybenzene with (I), being observed initially on a Multiplex 610 rapid-scanning (640–340 nm) stopped-flow spectrophotometer. A large decrease in absorbance occurred at 470 nm, and a preliminary kinetic run was carried out at this wavelength using a thermostatted (±0.1 °C) stopped-flow spectrophotometer that has been previously described [5]. A pseudo-first-order rate constant, k_{obs}, was calculated from the gradient of a plot of

TABLE II. Kinetic Results for Reaction of $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)\text{-}Fe(CO)_3]BF_4$ with Various Methoxy Benzenes in CH_3NO_2 at 60.0 °C, [Fe] = 6.54×10^{-3} mol dm^{-3}.

Arene	[ArH] /mol dm^{-3}	10^6 k_{obs}/s^{-1}
1,3,5-trimethoxy benzene	0.10	196
	0.20	283
	0.40	415
	0.60	442
	0.80	466
	1.00	486
	1.50	518
1,2,4-trimethoxy benzene	0.10	2.49
	0.20	4.33
	0.40	7.45
	0.60	8.79
	0.80	11.0
	1.00	12.1
1,3-dimethoxy benzene	0.20	1.57
	0.40	2.52
	0.60	3.27
	0.80	3.84
	1.00	4.33
1,2-3-trimethoxy benzene	0.20	0.498
	0.40	0.568
	0.60	0.640
	1.00	0.648
1,4-dimethoxy benzene	0.20	0.273
	0.40	0.371
	0.60	0.421
	1.00	0.481

log $(A_t - A_\infty)$ *versus* time. This plot was linear for two half-lives.

Results and Discussion

Nature of the reactions

During each of the reactions (1) with various di- and tri-methoxybenzenes in CH_3NO_2 the disappearance of the original dienyl cation ν(CO) bands at 2110 and 2065 cm^{-1} was accompanied by the growth of two product peaks at 2045 and 1965 cm^{-1}. These product bands are characteristic of neutral tricarbonyl(diene) iron complexes. No other carbonyl bands were observed, and each of the reactions proceeded to completion.

The natue of the products was further confirmed by isolation of (IIa–IId) in good yield (see Experimental), and from their mass and ^{1}H NMR spectra. At low emitter currents the f.d. mass spectra of (IIa) and (IIb) give base peaks corresponding to the parent molecular ions $[P]^+$. In common with other f.d. mass-spectral studies of neutral tricarbonyl (π-hydrocarbon) metal complexes, the only other significant peaks can be assigned to $[P + 1]^+$ ions and isotopic species. No stepwise loss of carbonyl ligands is observed. This contrasts with the electron-impact (e.i.) mass spectrum of (IIa), which shows [13] only a weak parent $[P]^+$ ion and extensive fragmentation. By analogy with related complexes [14, 15], the presence of weak fragment ions $[P - CO]^+$, $[P - 2CO]^+$, and $[P - 3CO]^+$, but an intense base peak at m/Z 300 corresponding to $[P - 3CO - H_2]^+$, supports the assignment of an *exo*-configuration to the trimethoxy-substituent on the diene ring of (IIa).

The ^{1}H NMR spectra of products (IIa–IId) are consistent with the formulations shown in Table I. As with a variety of related tricarbonyl (substituted-1,3-diene)iron species [10, 15, 16], overlapping multiplets characteristic of the outer diene protons (H^1 and H^4) occur at relatively high field (τ 6.7–6.8), while the inner diene protons (H^2 and H^3) resonate in the region τ 4.3–4.5. The H^6, $H^{6'}$ methylene protons appear at τ 7.9 and 8.6, respectively, while the $H^{5'}$ protons adjacent to the arene substituents are shifted slightly downfield to τ 7.0–7.1.

The ^{1}H NMR spectra in the aromatic region also allow unequivocal assignments of the positions of attachment of the (diene) $Fe(CO)_3$ moiety to the arene rings in (IIa–IId). These positions generally agree with those expected. For example, only the predicted product (IId) arising from electrophilic attack by cation (I) at the arene C(4) site was obtained in the reaction with 1,3-dimethoxybenzene. For 1,2,3-trimethoxy- and 1,2,4-trimethoxy-benzenes it is difficult to assess the overall electronic and steric directive effects, but attack by (I) at C(4) and C(5), respectively, seems reasonable. It is significant that only one product isomer has been isolated in all cases, suggesting that reactions (1) are regioselective. However, it is possible that minor amounts of other isomer(s) arising from attack at other arene sites were lost in product work-up.

Kinetics and Mechanism

Kinetic results for the reactions of (I) with a variety of di- and tri-methoxybenzenes in CH_3NO_2 at 60 °C are collected in Table II. Interestingly, in each case plots of k_{obs} *versus* [arene] are distinctly curved, and k_{obs} appears to approach limiting values at [arene] $\geqslant$ 1 mol dm^{-3} (*e.g.* Fig. 1a). This behaviour suggests the formation of an intermediate prior to the rate determining step in these reactions. A general mechanism consistent with all of the spectroscopic and kinetic evidence is shown in Scheme 1.

In this mechanism rapid pre-equilibrium formation of a π-complex intermediate (III) is followed by rate limiting rearrangement (k_2) to the Wheland-type

TABLE III. Derived K_1 and k_2 Values for Reactions of $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]^+$ with Various Methoxy-Benzenes in CH_3NO_2 at 60 °C.

Arene	$K_1/dm^3\ mol^{-1}$	$10^6\ k_2/s^{-1}$	Relative k_2
1,3,5-trimethoxybenzene	5.2	58	98
1,2,4-trimethoxybenzene	1.5	19	32
1,3-dimethoxybenzene	1.4	7.1	12
1,2,3-trimethoxybenzene	12	0.70	1.2
1,4-dimethoxybenzene	4.3	0.59	1

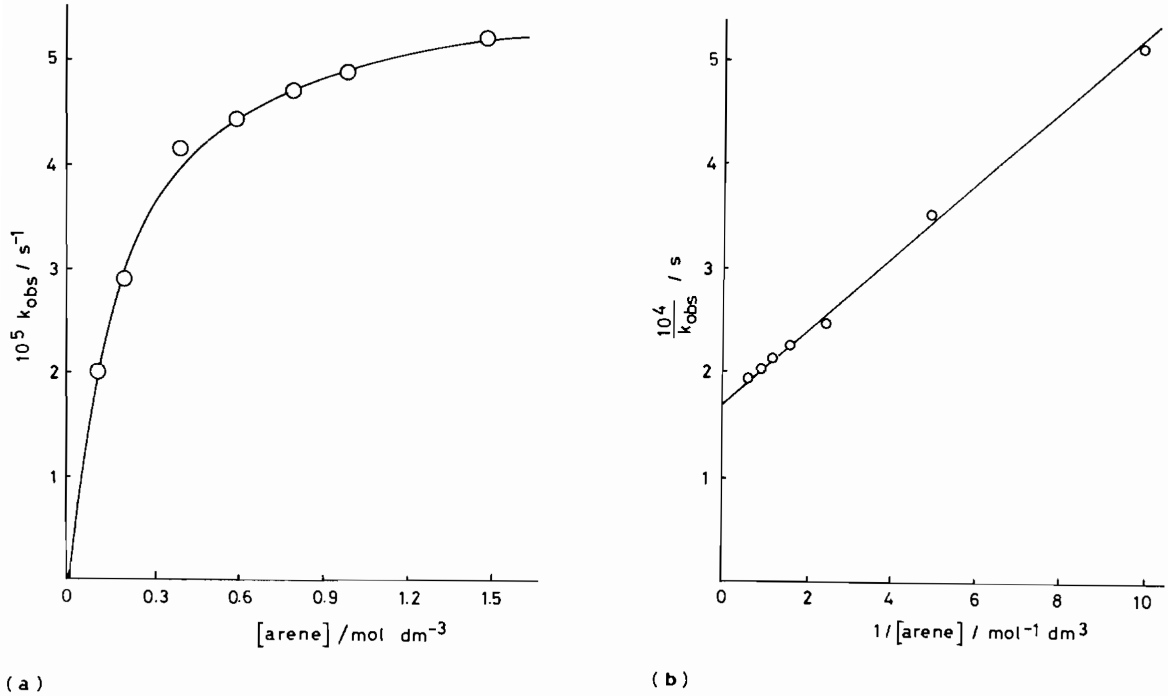
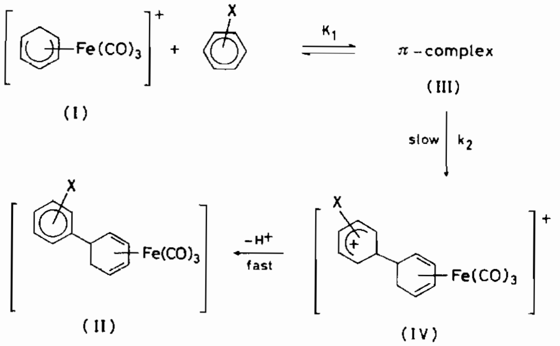


Fig. 1. Reaction of $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]BF_4$ with 1,3,5-trimethoxybenzene in CH_3CN at 60 °C: (a) Dependence of k_{obs} on [arene], (b) Dependence of $1/k_{obs}$ on 1/[arene].



Scheme 1

σ-complex intermediate (IV). Rapid proton loss in the last step would be facilitated by the known [17] electron-withdrawing character of the (diene)Fe(CO)$_3$ moiety. or such a mechanism the general expression (2) is derived for k_{obs}, which predicts the behaviour illustrated in Fig. 1a. If $K_1[\text{arene}] \gg 1$,

$$k_{obs} = \frac{k_2K_1[\text{arene}]}{1 + K_1[\text{arene}]} \tag{2}$$

expression (2) simplifies to eqn. (3), which explains the observation that k_{obs} tends towards limiting values at high [arene].

$$k_{obs} = k_2 \tag{3}$$

Quantitative support for the general eqn. (2) comes from the excellent linearity and non-zero intercepts obtained on plotting $1/k_{obs}$ *versus* 1/[arene]

for each of the methoxy-benzenes (*e.g.* Fig. 1b). This behaviour is predicted from eqn. (4), obtained by inverting eqn. (2). Values of k_2, estimated from the intercepts ($1/k_2$) of such plots, are collected

$$1/k_{obs} = \frac{1}{k_2K_1[\text{arene}]} + \frac{1}{k_2} \qquad (4)$$

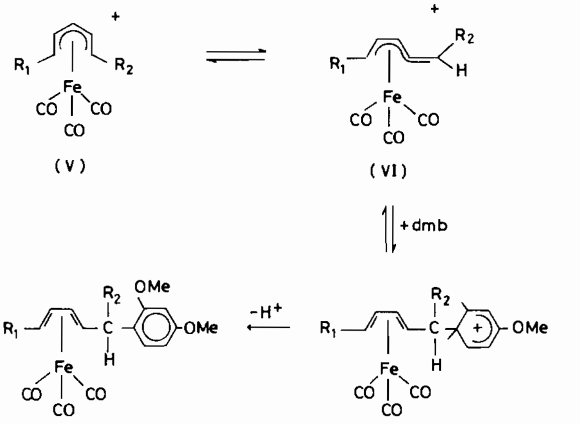
in Table III. From these k_2 values and the slopes ($1/k_2K_1$), values for the pre-equilibrium constant, K_1, can also be calculated (Table III).

The K_1 values listed in Table III indicate that under the conditions employed significant concentrations of the intermediates (III) should be present at the commencement of the IR kinetic runs. For example, with [1,3,5-trimethoxybenzene] = 1.0 mol dm^{-3}, *ca.* 83% of the iron species should be present as intermediate (III). However, during each of the reactions studied here no carbonyl bands other than those assignable to the original cation (I) and products (II) were observed. For this reason a loose π-complex formulation has been proposed for intermediate (III). It is not unreasonable that such a π-complex would exhibit carbonyl bands very similar to the original cation (I), since even substituents on the dienyl ring in $[(1\text{-}5\text{-}\eta\text{-}XC_6H_6)Fe(CO)_3]^+$ complexes have little effect on ν(CO) [10]. Other possible formulations for (III) involving attachment of the arenes to the iron, a carbonyl ligand, or σ-bonded to the ring as in a Wheland-type species (IV), would cause large changes in the ν(CO) bands.

Further support for a rapid initial process in these reactions comes from a preliminary stopped-flow study of the reaction with 1,3,5-trimethoxybenzene in CH_3NO_2. With [arene] = 1.0 mol dm^{-3}, a rapid decrease in absorbance was observed at 470 nm, giving a k_{obs} value of 1.83×10^{-2} s^{-1} at 3.4 °C. This initial process is thus confirmed to be at least several orders of magnitude faster than the overall reaction monitored by IR spectroscopy.

From Table III, the first rate-order constants (k_2) for rearrangement of the initial π-complexes to the Wheland-type intermediates (IV) are seen to decrease markedly in the order 1,3,5-trimethoxy- > 1,2,4-trimethoxy- > 1,3-dimethoxy- > 1,2,3-trimethoxy > 1,4-dimethoxy-benzene (98:32:12:1.2:1). This trend is as expected from the electronic properties of the arenes, since significant σ-bond formation is involved in this second step.

Finally, it is interesting that a rate law of the form (2) has also recently been reported by Powell *et al.* [7] for the much faster analogous reactions of $[(1\text{-}5\text{-}\eta\text{-}acyclicdienyl)Fe(CO)_3]^+$ (V) cations with methoxy-benzenes, again implying the presence of an intermediate. For such acyclic dienyl cations there is the possibility of a *trans*-intermediate (VI), as suggested [7] in Scheme 2 with 1,3-dimethoxybenzene. Clearly, such *trans*-intermediates are not feasible for the cyclic dienyl cation (I) studied here, with nevertheless gives the same kinetic features. Thus, a possible alternative explanation for the behaviour of acyclic dienyl cations is again the intermediacy of π-complexes.



Scheme 2

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