Kinetics of Nucleophilic Attack upon Coordinated Organic Moieties. Part 22≠. Reaction of $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-dienyl}]^+$ Cations with Imidazole

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Received February 23, 1982

Synthetic and kinetic studies are reported for the reactions of the cations $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-dienyl})]^+$ (dienyl = C_6H_7 or 2-$MeOC_6H_6$) with imidazole. The results (e.g. Rate = k[complex][imidazole]) support direct addition of imidazole to the dienyl rings. For attack on the C_6H_7 cation, imidazole is about twice as reactive as pyridine, as expected from its greater basicity. However, this nucleophilic order is strongly reversed (i.e. pyridine > imidazole) for analogous attack on $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$. This surprising observation suggests some specific rate-retarding interaction between the latter cation and imidazole, such as H-bonding between the imidazole-NH and the oxygen of the 2-MeO substituent.

Introduction

The importance of steric and electronic factors in the addition of amines to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$ (Ia) and related cations was recently delineated using substituted anilines and pyridines as nucleophiles [1, 2]. As an extension of these studies and as part of a programme investigating the interaction of organometallic cations with biologically significant molecules, we now wish to report related studies of the reactions of (Ia) and $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ (Ib) with imidazole.

Experimental

Materials

The cations (Ia) and (Ib) were isolated as their BF_4^- salts and purified using published procedures [3]. Imidazole was purchased in pure form from BDH, and used without further purification. Acetonitrile (BDH) solvent was distilled in bulk and stored over molecular sieves (grade 3A) under a dinitrogen atmosphere.

Tricarbonyl (1-4-η-5-imidazoliocyclohexa-1,3-diene) Iron Tetrafluoroborate, (IIa)

$[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)][BF_4]$ (0.10 g, 0.327 mmol) and imidazole (0.022 g, 0.323 mmol) were shaken together in acetone (10 cm^3) for 5 min. under a dinitrogen atmosphere. Rotary evaporation of the resultant solution to dryness yielded a yellow-orange oil. Dissolution in acetone (0.5 cm^3) followed by addition of diethyl ether (40 cm^3) gave the product (IIa) as a pale yellow precipitate (0.050 g, 45% yield). (Found: C, 37.1; H, 3.2; N, 8.6. Calc. for $C_{12}H_{11}BF_4FeN_2O_3$: C, 38.5; H, 3.0; N, 7.5%). An acetone solution exhibited two intense IR carbonyl bands at 2060 and 1991 cm^{-1}. The presence of a band at ca. 1060 cm^{-1} (Nujol mull) confirmed the presence of the BF_4^- anion. ^1H NMR ($(CD_3COCD_3)\tau$ 0.99 (s, 1H, H^a of imidazole), 2.30 (overlapping doublets, 2H, H^b and H^c of imidazole), 4.10 (overlapping multiplets, 2H, H^2 and H^3), 4.80 (m, 1H, $H^{5'}$), 6.75 (overlapping multiplets, 2H, H^1 and H^4), 7.30 (m, 1H, $H^{6'}$), 8.20 (m, 1H, H^6). For the proton assignments see the numbering scheme in Fig. 1.

A sample of the PF_6^- salt, $[Fe(CO)_3(1\text{-}4\text{-}\eta\text{-}C_6H_7\cdot C_3H_4H_2)][PF_6]$, was isolated by a modified procedure. $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)][BF_4]$ (0.20 g, 0.654 mmol) and excess imidazole (0.088 g, 1.30 mmol) were shaken in acetone (25 cm^3) under dinitrogen for 2 hr. Addition of diethyl ether (40 cm^3) gave no precipitate. Rotary evaporation to dryness, followed by dissolution in water (10 cm^3) and addition of solid $[NH_4][PF_6]$ gave a waxy solid. Recrystallization from acetone/diethyl ether yielded the product as an off-white solid (Found: C, 34.5; H, 2.4; N, 4.6. Calc. for $C_{12}H_{11}PF_6FeN_2O_3$: C, 33.3; H, 2.6; N, 6.5%).

Tricarbonyl (1-4-η-2-methoxy-5-imidazoliocyclohexa-1,3-diene) Iron Tetrafluoroborate, (IIb)

This salt was quantitatively prepared *in situ* by mixing equimolar amounts of $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_4)][BF_4]$ (Ib) and imidazole in d^6-acetone solvent to give [Fe] = [imidazole] = 0.18 mol dm^{-3}. ^1H NMR ($(CD_3COCD_3)\tau$ 1.00 (s, 1H, H^a of imidazole), 2.30 (overlapping doublets, 2H, H^b and H^c of

≠Part 21. J. G. Atton and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, in press.

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0020-1693/82/0000-0000/$02.75

imidazole), 4.30 (m, 1H, H^3), 4.95 (m, 1H, $H^{5'}$), 6.21 (s, 3H, MeO), 6.60 (m, 1H, H^1 or H^4), 7.10 (m, 1H, H^1 or H^4), 7.35 (m, 1H, $H^{6'}$), 8.25 (m, 1H, H^6).

This acetone solution upon dilution exhibited two intense ν(CO) bands at 2060 and 1989 cm^{-1}. No other carbonyl peaks were noted, confirming quantitative adduct formation at low concentrations ([Fe] = [imidazole] = 5×10^{-3} mol dm^{-3}) also.

Tricarbonyl (1-4-η-5-imidazoliocyclohexa-1,3-diene) Iron, (IIIa)

This neutral derivative was prepared by treating salt (I, 0.10 g, 0.327 mmol) with a large excess of imidazole (0.2 g, 2.94 mmol) in acetone (20 cm^3) under dinitrogen. Rotary evaporation yielded a yellow solid which was difficult to separate from excess imidazole. However, the presence of neutral (IIIa) was confirmed by the presence of two strong ν(CO) bands at 2055 and 1979 cm^{-1} in acetone, and from the ^{1}H NMR spectrum (CD_3COCD_3): τ 1.8–2.9 (imidazole), 4.22 (overlapping multiplets, 2H, H^2 and H^3), 5.17 (m, 1H, $H^{5'}$), 6.88 (overlapping multiplets, 2H, H^1 and H^4), 7.50 (m, 1H, $H^{6'}$), 8.40 (m, 1H, H^6).

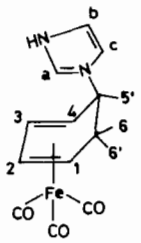


Fig. 1. Structure of adduct (IIa).

Spectroscopic Studies

Infrared spectra were recorded on a Pye Unicam SP3 200 spectrophotometer using matched 0.5 mm CaF_2 cells. ^{1}H NMR spectra (90 MHz) were measured on a Perkin Elmer R32 spectrophotometer.

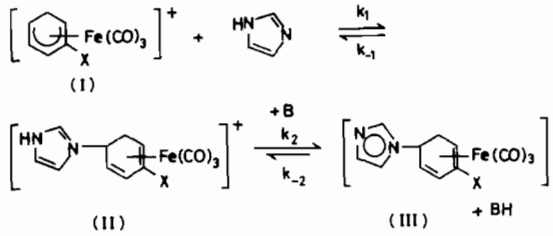
Kinetic Studies

The reactions of (Ia) and (Ib) with imidazole in CH_3CN were generally studied under pseudo-first-order conditions using a large excess of nucleophile ([Fe] = $1.2–1.5 \times 10^{-3}$ mol dm^{-3}, [imidazole] = $0.5–8.0 \times 10^{-2}$ mol dm^{-3}). All of the reactions were rapid and proceeded to completion under the kinetic conditions employed. They were conveniently monitored by following the decrease in absorbance at 390 nm using a thermostatted (±0.1 °C) stopped-flow spectrophotometer. Reaction traces were stored on a Tektronic 564B storage oscilloscope fitted with a log converter, thus giving a direct record of absorbance changes.

Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of log $(A_t - A_\infty)$ *vs.* time. Such plots were generally linear for more than two half-lives, except in the few cases where [imidazole]/[Fe] < 10. Each k_{obs} is the average of at least three separate runs, with an average reproducibility of ±5%. The second-order rate constants, k, were calculated from a least-squares analysis of the k_{obs} *vs.* [imidazole] plots (*e.g.* Fig. 2).

Results and Discussion

Spectroscopic studies show that the reactions of cations (Ia) and (Ib) with excess imidazole occur in two stages, as shown in Scheme 1 (X = H or OMe).



Using equimolar amounts of (Ia) {or (Ib)} and imidazole, the monocationic adducts (IIa,b) are prepared and characterised (see Experimental). *In situ* IR and ^{1}H NMR studies show that these additions proceed to completion. The ^{1}H NMR spectra of (IIa) and (IIb) are characteristic of substituted 1,3-diene complexes of iron tricarbonyl, and are similar to that previously reported [2] for the analogous pyridinium adduct with (Ia). Interestingly, comparison with the ^{1}H NMR spectrum of free imidazole in d^6-acetone shows that the H^a proton is shifted downfield by 1.13 τ upon attachment of the $Fe(CO)_3(C_6H_7)^+$-residue to the tertiary nitrogen. This downfield shift is even larger than that (0.8 τ) experienced by H^a upon protonation at the tertiary nitrogen. The H^b and H^c protons, which show only a single averaged

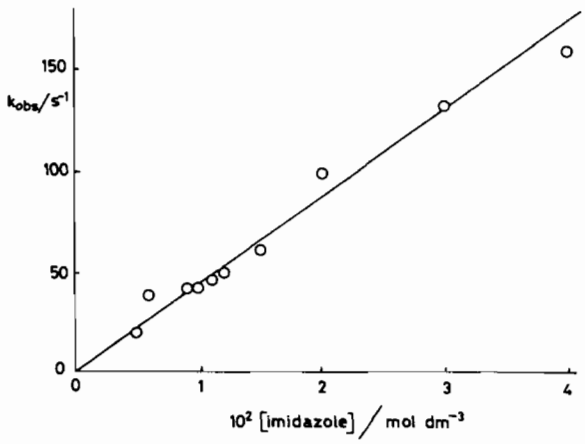


Fig. 2. Plot of k_{obs} *vs.* [imidazole] for addition of imidazole to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)]$ I in CH_3CN at 0 °C.

peak in free imidazole due to rapid proton-exchange between the nitrogen centres, become inequivalent as expected in adducts (IIa) and (IIb), and experience somewhat smaller downfield shifts (*ca.* 0.6 τ). However, rapid exchange of the imidazole -NH proton is still evident in adducts (IIa,b), as shown by the failure to detect an appropriate ^{1}H NMR resonance and the absence of coupling between H^a, H^b and NH. Finally, the ^{1}H NMR spectrum of the Fe(CO)$_3$(diene)-fragment of (IIb) confirms exclusive addition of imidazole at the 5-position of the dienyl ring, as has been found with a range of other nucleophiles [3, 4].

The ν(CO) bands of (IIa) and (IIb) in acetone at *ca.* 2060 and 1990 cm^{-1} are also very similar to those (2055 and 1980 cm^{-1}) found [2] for the pyridinium adduct. Further confirmation of the cationic nature of (IIa) comes from the presence of $\nu(BF_4^-)$ and ν(NH) bands in its Nujol mull IR spectrum at *ca.* 1060 and 3350 cm^{-1}, respectively.

On the other hand, treatment of (Ia) with a large excess of imidazole in acetone produced the neutral complex (IIIa), presumably via deprotonation of (IIa) as shown in Scheme 1 (B = imidazole). *In situ* ^{1}H NMR experiments showed that (IIa) could also be deprotonated with triethylamine in d^6-acetone to produce (IIIa) quantitatively. As expected, the diene ring protons in neutral (IIIa) exhibit an upfield chemical shift compared with those in cation (IIa). The maximum shift of 0.37 τ is experienced by the $H^{5'}$ proton, due to its proximity to the site of protonation/deprotonation. The ν(CO) bands for (IIIa) in acetone at 2055 and 1979 cm^{-1} are also, as anticipated, at slightly lower frequency than those for cation (IIa). A similar difference of *ca.* 10 cm^{-1} has been previously observed [1] between the ν(CO) bands of the related cationic and neutral anilino-derivatives [Fe(CO)$_3$(1-4-η-5-C$_6$H$_5$NH$_2$·C$_6$H$_7$)]$^+$ and [Fe(CO)$_3$(1-4-η-5-C$_6$H$_5$NH·C$_6$H$_7$)].

The reverse protonation of (IIIa) by trifluoroacetic acid (TFA) in d^6-acetone has also been examined. Addition of 5 drops of TFA causes rapid and quantitative conversion to cation (IIa), as evidence by ^{1}H NMR and IR spectra. In contrast, addition of only a single drop of TFA produces an ^{1}H NMR spectrum intermediate between those of (IIa) and (IIIa). This sharp spectrum is believed to represent the equilibrium mixture of (IIa) and (IIIa) under these conditions, the proton-exchange equilibrium K_2 (Scheme 1) being established rapidly on the NMR time scale. Cooling to −50 °C causes some line broadening, but considerably lower temperatures will apparently be required to slow the exchange sufficiently to freeze out the individual spectra.

Interestingly, addition of a large excess (10 drops) of TFA to (IIIa) in d^6-acetone causes not only protonation, but also release of imidazole and regeneration of the dienyl cation (Ia). Thus the ^{1}H NMR spectrum a few minutes after acid addition shows a mixture of (IIa) and (Ia). After a further 3 h at room temperature, imidazole release is complete and the only iron species present is (Ia). Similar acid-catalysed release of methoxy [5], anilinio [1], and pyridinio [2] substituents from (substituted diene) iron tricarbonyl complexes has been previously noted.

Kinetic results for the reactions of cations (Ia) and (Ib) with imidazole in acetonitrile are collected in Table I. Under the kinetic conditions employed both processes proceed rapidly to completion, yielding (IIIa) and (IIIb), and obey expression (1). These results may be rationalised in terms of the two-step mechanisms in Scheme 1. Assuming a steady-state concentration for the intermediate cationic adduct (II), Scheme 1 leads to the general expression (2).

$$k_{obs} = k[\text{imidazole}] \quad (1)$$

Since the deprotonation step, k_2, is believed from the above ^{1}H NMR evidence

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

to be much faster than k_{-1}, eqn. (2) can be simplified to expression (3). This is consistent with the observed relationship (1). Thus, the k values

$$k_{obs} = k_1[\text{imidazole}] \quad (3)$$

in Table I are considered to refer to the second-order rate constants, k_1, for the addition of imidazole to the dienyl rings of (Ia,b).

Consistent with direct attack, k_1, at the dienyl rings is the rate trend $C_6H_7 \gg$ 2-MeOC$_6$H$_6$ (relative rates *ca.* 85:1, Table I). The electronic and possible

TABLE I. Kinetic Results for Addition of Imidazole to [Fe(CO)$_3$(1-5-η-dienyl)]$^+$ Cations in CH$_3$CN at 0 °C.

Cation	10^2[imidazole]/mol dm^{-3}	k_{obs}/s^{-1}	k/mol^{-1} dm^3 s^{-1}
Ia	0.50	19.30	
	0.60	41.4	
	0.90	43.1	
	1.00	42.2	
	1.10	46.7	4390 (130)[a]
	1.20	48.9	
	1.50	60.5	
	2.00	103	
	3.00	132	
	4.00	157	
Ib	1.00	0.370	
	2.00	0.900	51.4 (0.5)[a]
	4.00	2.00	
	8.00	3.97	

[a]Values in brackets are the standard errors of estimate from the least squares analyses.

steric influence of the 2-methoxy substituent is expected to retard nucleophilic addition at the dienyl ring, as has been found in the analogous additions by pyridine [2] and triphenylphosphine [4]. However, the retardation was much less marked with these latter nucleophiles (only a factor of five).

One interesting result of the above differences is that although imidazole is *ca.* twice as reactive as pyridine towards cation (Ia) {k_1 values of 4390 and 2170 mol^{-1} dm^3 s^{-1}, respectively}, the rate order pyridine > imidazole (relative rates 8:1) is observed for analogous attack on (Ib). As far as we are aware, this is the first time that a reversal of nucleophilicity order has been reported for additions to different $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ cations. These results contrast with Ritchie's [6] observation of a common nucleophilicity order towards a wide range of metal-free stabilized carbonium ions.

The unexpectedly slow reaction of imidazole with (Ib) compared to (Ia) may reflect a specific interaction, such as H-bonding between the imidazole-NH and the oxygen of the 2-methoxy substituent. This could sterically retard subsequent ring addition by imidazole at C(5). The importance of H-bonding interactions in the reactions of imidazole with biological substrates such as metalloporphyrins has recently been emphasised [7].

We observed no reaction between pyrazine and (Ia) at room temperature. Thus, for this parent cation, the nucleophilicity order of the tertiary amines (imidazole > pyridine ≫ pyrazine) is seen to parallel their basicities (pK_a's of 6.95, 5.25, and 0.65, respectively).

Finally, the above results are relevant to our studies [5] of the interactions between amino acids and organometallic cations such as (Ia,b). The high nucleophilicity of imidazole suggests that in histidine this group may be able to compete with the NH_2 and COO^- donors for the π-hydrocarbon substrates. The possible synthetic and mechanistic implications are currently being explored.

Acknowledgement

We thank the SRC for a Studentship (to D.J.E.) and for financial support.

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