Kinetics of Nucleophilic Attack on Co-ordinated Organic Moieties. Part 5.† Mechanisms of Addition of Heterocyclic Aromatic Species to Tricarbonyl(1–5-η-cyclohexadienyl)-iron and -ruthenium Cations

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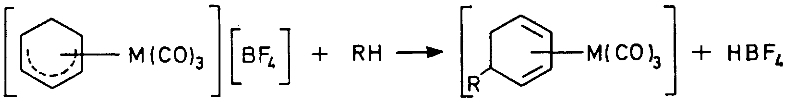
A kinetic investigation has been made of the addition of heterocyclic aromatic molecules to the cations $[M(C_6H_7)(CO)_3][BF_4]$ (1; M = Fe or Ru). For RH = pyrrole and M = Fe or Ru, the equation Rate = k[complex][RH] is observed, while a similar second-order law holds for RH = furan and M = Fe. These results are consistent with

$$[M(C_6H_7)(CO)_3][BF_4] + RH \longrightarrow [M(C_6H_7R)(CO)_3] + HBF_4 \qquad \text{(i)}$$

electrophilic attack by the dienyl cations on the heterocyclic aromatics. The absence of primary kinetic-isotope effects for RH = pyrrole and M = Fe or Ru shows that the final proton loss is rapid, and suggests that either π- or σ-complex intermediate formation is rate determining. The relative susceptibility of a wide range of heterocyclic aromatic substrates towards the electrophile $[Fe(C_6H_7)(CO)_3]^+$ has been established in both nitromethane and acetonitrile as solvents, showing a difference of 10^6 between pyrrole and thiophen.

RECENT studies [1,2] have demonstrated the synthetic utility of reaction (1; M = Fe or Ru) as a route to diene-substituted aromatic species. Addition occurs with a wide range of heterocyclic aromatic species (RH) together with a number of activated arenes. Kinetic studies [3] of reaction (1) with RH = indole and substituted indoles showed that this reaction may be regarded as involving electrophilic substitution on indole by the cations $[M(C_6H_7)(CO)_3]^+$ [M = Fe (1a) or Ru (1b)].



(1)

Kinetic investigation of reaction (1) has now been extended to include the heterocyclic substrates pyrrole, furan, 2-methylfuran, thiophen, and 2-methylthiophen. Data are reported for both nitromethane and acetonitrile as solvents.

EXPERIMENTAL

Materials.—The cations (1a) and (1b) were isolated as their tetrafluoroborate salts and purified by published procedures.[4,5] The salt $[Fe(C_6H_7)(CO)_3][BPh_4]$ was prepared from the analogous tetrafluoroborate as previously described.[3]

The substituted diene product from the addition of 2-methylfuran to (1a) has been isolated and characterised by its mass (m/e 300) and i.r. spectra (carbonyl bands at 2 045 and 1965 cm^{-1}).[6] Other workers have isolated the product from the reaction of pyrrole with (1a) in tetrahydrofuran (thf).[7] Repeated attempts by us to isolate this product from reaction in nitromethane or acetonitrile solvents resulted in intractable oils. Although product isolation was not attempted with the less reactive heterocyclic aromatic

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† Part 4, C. A. Mansfield and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1976, 2193.

[1] L. A. P. Kane-Maguire and C. A. Mansfield, *J.C.S. Chem. Comm.*, 1973, 540.

[2] C. A. Mansfield, K. M. Al-Kathumi, and L. A. P. Kane-Maguire, *J. Organometallic Chem.*, 1974, **71**, C11.

[3] L. A. P. Kane-Maguire and C. A. Mansfield, *J.C.S. Dalton*, 1976, 2192.

[4] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

[5] R. G. Cowles, Ph.D. Thesis, University College, London, 1969.

[6] G. R. John, R. Davis, and L. A. P. Kane-Maguire, unpublished work.

[7] A. Burrows, B. F. G. Johnson, and J. Lewis, personal communication.

substrates reported here, in each case two new strong carbonyl bands appeared at *ca.* 2 045 and 1970 cm^{-1} as expected for neutral tricarbonyl(diene)-iron or -ruthenium complexes.

Nitromethane and acetonitrile solvents were distilled under nitrogen and stored over molecular sieves. All the aromatic substrates were distilled under nitrogen immediately prior to use. [$^2H_5$]Pyrrole was prepared by the published method.[8]

Kinetic Studies.—Except for RH = pyrrole (M = Fe), all the reactions (1) investigated were slow enough to be followed by i.r. spectroscopy. The reactions were studied in the dark under nitrogen using sampling techniques previously described.[9] The disappearance of the original tricarbonyl-(dienyl)metal cation band at *ca.* 2110 cm^{-1} was followed using a Perkin-Elmer 257 spectrophotometer. Most runs were carried out employing a large excess of the aromatic species, and pseudo-first-order rate constants were calculated from the gradients of plots of log A_t against time (A_t = absorbance of reaction solution at 2110 cm^{-1} at time t).

TABLE 1

Kinetic data for the reaction of $[M(C_6H_7)(CO)_3]^+$ with pyrrole in nitromethane.* [Fe] = 3 × 10^{-3}, [Ru] = 5 × 10^{-3} mol dm^{-3}

Complex	$\frac{\theta_c}{°C}$	$\frac{[\text{pyrrole}]}{\text{mol dm}^{-3}}$	$\frac{k_{obs.}}{\text{s}^{-1}}$	$\frac{k_2}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$
$[Fe(C_6H_7)(CO)_3][BF_4]$	20.0	1.00	0.162	
	27.5	1.00	0.293	
	36.0	1.00	0.592	
	45.0	1.00	0.898	
	55.0	1.00	1.43	
	45.0	0.20	0.132	0.660
	45.0	0.50	0.470	0.940
	45.0	0.75	0.634	0.845
	45.0	1.00	0.898 (1.34)	0.898 (1.34)
	45.0	2.00	1.76	0.880
$[Fe(C_6H_7)(CO)_3][BPh_4]$	22.3	0.40	0.109	0.272
	22.3	0.70	0.171	0.244
	22.3	1.00	0.216	0.216
	22.3	2.00	0.442	0.221
$[Ru(C_6H_7)(CO)_3][BF_4]$	28.0	0.60	0.535 × 10^{-4}	
	35.0	0.60	0.792	
	45.0	0.60	1.23	
	55.0	0.60	2.18	
	60.0	0.60	2.87	
	45.0	0.08	0.158	1.98 × 10^{-4}
	45.0	0.20	0.464	2.32
	45.0	0.40	0.844	2.11
	45.0	0.60	1.23	2.05
	45.0	1.00	2.10	2.10

* Values in parentheses are for acetonitrile as solvent.

The reaction of pyrrole (≥0.20 mol dm^{-3}) with (1a) in both nitromethane and acetonitrile solvents was too rapid to follow by conventional methods. A thermostatted (±0.1 °C) stopped-flow apparatus was employed using techniques previously described.[3] The progress of the reaction was monitored at 390 nm where a large decrease in absorbance occurs. Pseudo-first-order rate constants were estimated from the gradients of plots of log A_t against time.

RESULTS

All the reactions were studied under pseudo-first-order conditions, and gave linear kinetic plots for at least 75% completion of reaction. The only exception was the reaction of thiophen with (1a) which, because of its extremely slow rate, was only monitored for 30% completion of reaction.

Kinetic data for the reaction of $[Fe(C_6H_7)(CO)_3][BF_4]$ (1a) with pyrrole in nitromethane solvent at various temperatures and pyrrole concentrations are collected in Table 1, and compared with results for the corresponding tetraphenylborate salt. Each $k_{obs.}$ value is the average of four separate stopped-flow runs (average reproducibility ±4%). The linear dependence of $k_{obs.}$ on pyrrole concentration indicates the rate equation (2; RH = pyrrole). From the gradient of the plot of $k_{obs.}$ against [pyrrole] we estimated a k_2 value

$$\text{Rate} = k_2[\text{complex}][\text{RH}] \qquad (2)$$

of 0.890 dm^3 mol^{-1} s^{-1} for reaction of (1a) with pyrrole at 45.0 °C. Similarly, a k_2 value of 0.227 dm^3 mol^{-1} s^{-1} was calculated for the analogous reaction of $[Fe(C_6H_7)(CO)_3]$-$[BPh_4]$ at 22.3 °C. Corresponding rate constants for the reaction of $[Ru(C_6H_7)(CO)_3][BF_4]$ (1b) with pyrrole are also summarised in Table 1. Again, close adherence to the rate equation (2) was observed over the range [pyrrole] = 0.08—1.00 mol dm^{-3}. From the gradient of the plot of $k_{obs.}$ against [pyrrole] a k_2 value of 2.08 × 10^{-4} dm^3 mol^{-1} s^{-1} was estimated at 45.0 °C.

TABLE 2

Kinetic data for the reaction of $[Fe(C_6H_7)(CO)_3][BF_4]$ with furan in acetonitrile.* [Fe] = 6.5 × 10^{-3} mol dm^{-3}, 45 °C

$\frac{[\text{furan}]}{\text{mol dm}^{-3}}$	$\frac{10^5 k_{obs.}}{\text{s}^{-1}}$	$\frac{10^5 k_2}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$
0.50	1.49	2.98
1.00	2.28	2.28
2.00	4.88	2.44
4.00	9.65	2.41
	(2.49)	(0.622)
6.00	14.2	2.37

* Values in parentheses are for nitromethane solvent.

Tables 2 and 3 summarise the kinetic data for reaction

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[8] B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, 1956, **24**, 720.

[9] L. A. P. Kane-Maguire, *J. Chem. Soc.* (*A*), 1971, 1602.

(1; M = Fe or Ru) with a range of other heterocyclic molecules in both nitromethane and acetonitrile solvents. With M = Fe and RH = furan, equation (2) was obeyed for furan concentrations as high as 6.0 mol dm^{-3} (Table 2). A k_2 value of 2.35 × 10^{-5} dm^3 mol^{-1} s^{-1} at 45.0 °C was calculated from the plot of $k_{obs.}$ against [furan]. Second-order rate constants, k_2, quoted for the other aromatic substrates in Table 3 were calculated assuming equation (2). The relative reactivity of the cation [Fe(C$_6$H$_7$)(CO)$_3$]$^+$ towards each of the heterocyclic aromatic substrates in both nitromethane and acetonitrile solvents at 45.0 °C is shown in Table 4. This reactivity order was calculated using the thiophen reaction as a basis and from the primary kinetic data in Tables 1—3.

TABLE 3

Kinetic data for reaction of [M(C$_6$H$_7$)(CO)$_3$][BF$_4$] with other heterocyclic aromatics in nitromethane at 45.0 °C

M	RH	[RH] mol dm^{-3}	$10^6k_{obs.}$ * s^{-1}	10^5k_2 * dm^3 mol^{-1} s^{-1}
Fe	2-Methylfuran	0.100	39.0	39.0
			(95.3)	(95.3)
	2-Methylthiophen	1.00	9.34	0.934
			(26.1)	(2.61)
	Thiophen	1.00	0.280	0.028
			(1.98)	(0.198)
Ru	2-Methylfuran	2.00	44.7	2.23

* Values in parentheses are for acetonitrile as solvent.

TABLE 4

Relative reactivity of [Fe(C$_6$H$_7$)(CO)$_3$][BF$_4$] towards various heterocyclic aromatic substrates at 45.0 °C

	Relative k_2	
RH	MeCN	MeNO$_2$
Pyrrole	6.7 × 10^5	3.2 × 10^6
Indole *		2 × 10^6
2-Methylfuran	4.8 × 10^2	1.4 × 10^3
2-Methylthiophen	13	33
Furan	11	23
Thiophen	1	1

* From ref. 3.

Activation parameters for reaction (1; RH = pyrrole) in nitromethane are collected in Table 5, and compared with known [3] values for the analogous reactions with indole. Activation enthalpies were obtained from the gradients of Arrhenius plots calculated by a least-squares method. The errors quoted are the standard errors of estimation derived from the least-squares analyses. Entropies of activation were calculated using the second-order rate constants, k_2.

TABLE 5

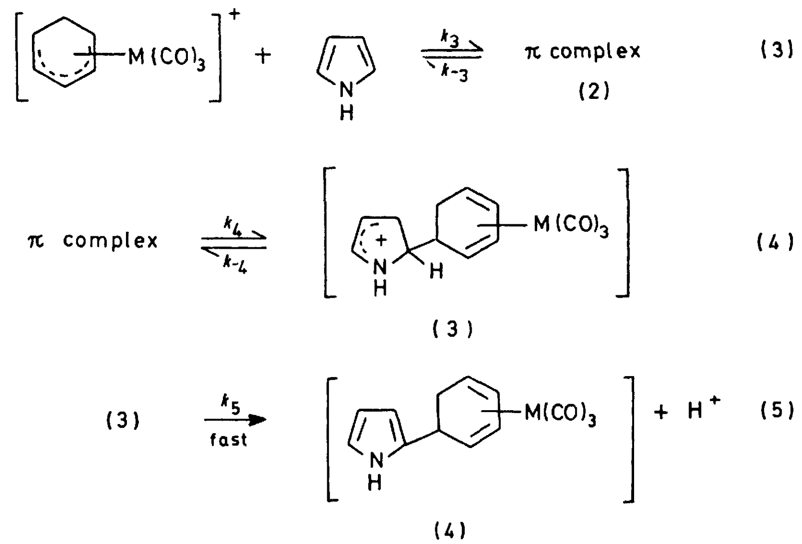
Activation parameters [a] for reaction of [M(C$_6$H$_7$)(CO)$_3$][BF$_4$] (M = Fe or Ru) with pyrrole and indole in nitromethane

RH	M	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}
Pyrrole	Fe	11.3 ± 0.7	−23 ± 2
	Ru	9.8 ± 0.4	−45 ± 2
Indole [b]	Fe	10.4 ± 0.1	−27 ± 1
	Ru	14.4 ± 0.2	−24 ± 1

[a] 1 cal = 4.18 J. [b] From ref. 3.

DISCUSSION

Reaction with Pyrrole.—The kinetic data in Table 1 are consistent with electrophilic attack on pyrrole by the cations [M(C$_6$H$_7$)(CO)$_3$]$^+$ (M = Fe or Ru) in nitromethane solvent. The linear dependence of $k_{obs.}$ on [pyrrole] for both M = Fe and Ru [equation (2)] and the absence of primary kinetic-isotope effects [k_H/k_D = 0.97 (Fe) and 1.41(Ru)] can be accommodated by the general mechanism in equations (3)—(5). From the kinetic evidence it is not possible to distinguish between rate-determining formation of a π complex, (2) (*i.e.* $k_{obs.} = k_3$[pyrrole]), and rate-determining formation of the Wheland-type σ complex (3) with no significant contribution from π complex intermediates. Rapid proton loss in step (5) is probably facilitated by the electron-withdrawing character of the Fe(C$_6$H$_7$)(CO)$_3$ moiety.[10] Also consistent with this latter observation is the failure of the product (4) to undergo further reaction with excess of [Fe(C$_6$H$_7$)(CO)$_3$]$^+$, *i.e.* only monosubstitution on pyrrole occurs.



Hydrogen-1 n.m.r. and i.r. spectral studies [7] on the product (4; M = Fe) established attachment of the diene substituent at the 2-position of pyrrole, as shown in

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[10] J. M. Landesberg and L. Katz, *J. Organometallic Chem.*, 1971, **33**, C15.

equations (3)—(5). This result is consistent with molecular-orbital calculations [11] showing the highest π-electron density at the 2(and 5)-position of the pyrrole ring (considering only the highest-occupied energy levels), while examination of possible Wheland-intermediate resonance structures also predicts preferential attack by electrophiles at the 2-position. In practice, ratios of substitution at the 2- and 3-positions of 6 and 2.4 : 1 have been observed for acetylation and protodedeuteriation of pyrrole, respectively.[12] The isolation of only a 2-substituted product using (1a) indicates a high degree of positional selectivity. This is in keeping with the ' reactivity–selectivity principle ',[13] since (1a) is a relatively weak electrophile.

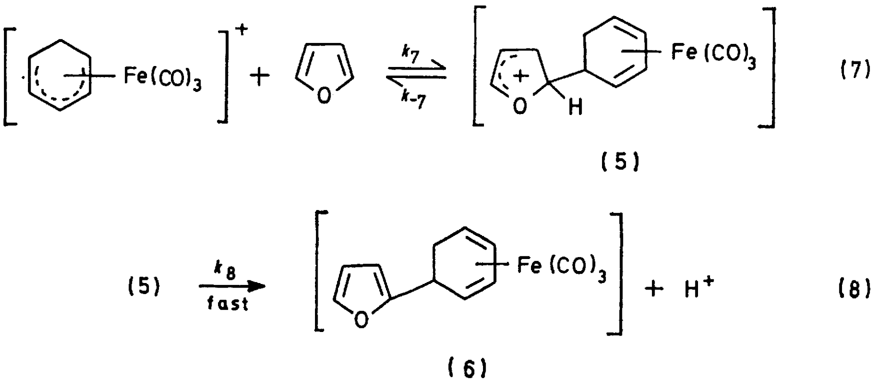
The observation of the second-order rate equation (2) for reaction (1; RH = pyrrole) with both iron and ruthenium cations is in marked contrast to their related reactions with indole.[3] With the latter substrate, while (1a) obeyed equation (2), the ruthenium reaction followed a complex rate equation of the general form (6), indicating formation of an intermediate prior to the rate-determining step.

$$\text{Rate} = \frac{a[\text{indole}]}{1 + b[\text{indole}]} \qquad (6)$$

The nature of this intermediate is uncertain, although a π complex is an attractive suggestion [3] in view of the documented ability of indole to form charge-transfer (stacked) adducts.[14]

From Table 1, (1a) is seen to react *ca.* 4.5×10^3 times faster with pyrrole than does the analogous ruthenium cation. This is not reflected in the activation enthalpies (Table 5) since Fe has a somewhat higher value, but resides in the considerably more favourable entropy of activation for Fe. Both reactions involve large negative $\Delta S^\ddagger$ values as expected for equations (3)—(5). These activation parameters also contrast with earlier data (Table 5) for reaction of $[M(C_6H_7)(CO)_3]^+$ (M = Fe or Ru) with indole, where the faster process with Fe arises from a lower $\Delta H^\ddagger$ compared with Ru.[3]

Reaction (1) *with Other Heterocyclic Aromatic Substrates.*—The second-order rate equation (2) was also obeyed for the reaction of (1a) with furan in acetonitrile solvent (Table 2). This behaviour is again consistent with a general mechanism of the type in equation (3)—(5) in which formation of a π complex is rate determining. Alternatively, rate-determining formation of the σ complex (5) may be involved as in equations (7) and (8). The 2-methylfuran product analogous to (6) has been isolated,[6] but the position of the $Fe(C_6H_7)(CO)_3$ substituent has not as yet been established. It is assumed to be at the 5-position of the furan ring since this is the sole site of attack in all the reported electrophilic substitutions at 2-methylfuran.[15]



Reaction (1) provides an unusually broad and uniform series for quantitative comparative studies of the reactivity of aromatic systems towards electrophiles. Such studies have often been tedious or impossible in the past because of the complex nature of the reactions employed or in the changes in solvent involved.

Table 4 shows the relative susceptibilities of various heterocyclic aromatic substrates towards attack by the common electrophile (1a) in both acetonitrile and nitromethane as solvents. Quantitative differences between the data in Table 5 and a previous report [2] arise from the different temperature employed and a redetermination of the rates for thiophen and furan. The reactivity order for the fundamental five-membered rings is similar to that previously established [12] for other electrophiles, *i.e.* pyrrole > indole ≫ furan > thiophen. The present data provide one of the few quantitative comparisons between pyrrole and indole. However, Jackson *et al.* [16] have made a detailed study of the relative reactivities of pyrroles and indoles towards the *p*-nitrobenzenediazonium cation and have observed considerably larger differences in rates with this less reactive electrophile.

The range of reactivity of *ca.* 10^6 between pyrrole and thiophen towards (1a) is also similar to that previously reported for trifluoroacetylation [17] and bromination [18]

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[12] G. Marino, *Adv. Heterocyclic Chem.*, 1971, **13**, 235.

[13] H. C. Brown and K. L. Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.

[14] H. Sigel and C. F. Naumann, *J. Amer. Chem. Soc.*, 1976, **98**, 730 and refs. therein.

[15] C. H. Eugster and D. P. Bosshard, *Adv. Heterocyclic Chem.*, 1966, **7**, 377.

[16] A. H. Jackson, P. V. R. Shannon, and A. C. Tinker, *J.C.S. Perkin II*, in preparation.

[17] S. Clementi and G. Marino, *Tetrahedron*, 1969, **25**, 4599.

[18] P. Linda and G. Marino, *J. Chem. Soc.* (*B*), 1968, 392.

(5×10^7 and 6×10^8, respectively). The reason for the somewhat smaller substrate selectivity exhibited by (1a) is uncertain. The choice of solvent is apparently significant since the range of reactivities is five times greater in nitromethane than in acetonitrile (Table 5). This is consistent with the 'reactivity–selectivity principle'[13] since reaction (1) is faster for all the substrates in acetonitrile (Tables 1—4).

We thank the S.R.C. for support (to G. R. J. and C. A. M.), and for the award of a grant for a stopped-flow spectrophotometer.

[6/1524 *Received, 4th August,* 1976]