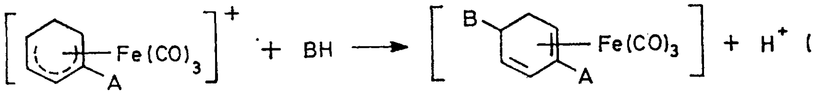
Kinetics of Nucleophilic Attack on Co-ordinated Organic Moeities. Part 3.† Effect of Solvent on Addition of Pentane-2,4-dione to Complexes of Cyclic Dienyls

By **C. A. Mansfield** and **L. A. P. Kane-Maguire,*** Department of Chemistry, University College Cardiff, Cardiff CF1 1XL

The kinetics of addition of pentane-2,4-dione (Hpd) to $[Fe(C_6H_7)(CO)_3][BF_4]$ and related dienyl salts have been studied in the solvents nitromethane, acetone, and dichloromethane. Comparison with previous data in acetonitrile shows that the reactions are not sensitive to solvent changes, and indicate the general rate law $-d[R]/dt = k[R][Hpd]$ (R = dienyl cation). These solvent effects, together with the effects of added acid, added base, and deuteriation of Hpd, are explained in terms of a common mechanism involving rapid pre-equilibrium dissociation of Hpd to give the pd^- carbanion which then adds directly to the dienyl rings. The analogous reaction of $[Ru(C_6H_7)(CO)_3][BF_4]$ with Hpd is considerably slower.

A PREVIOUS paper [1] in this series reported the kinetics of addition of β-diketones to cyclic dienyl iron cations in acetonitrile as solvent [equation (1); A = H or OMe]. The results supported earlier suggestions [2] that the reactions proceed *via* direct addition to the organic ring. We proposed a detailed mechanism involving a rapid pre-equilibrium in which the β-diketone dissociated to give a small concentration of reactive carbanion, which then attacked the dienyl ring in a rapid but rate-determining manner. The reactions of $[Fe(C_6H_7)(CO)_3][BF_4]$ (1), $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ (2), and some related cations with pentane-2,4-dione (Hpd) have now been examined in greater detail in order to throw further light on the mechanims of the additions. In particular, the effects of (*i*) variation in solvent, (*ii*) acid, (*iii*) base, and (*iv*) deuteriation have been examined.



(1)

EXPERIMENTAL

Preparation of Complexes.—The salts $[Fe(C_6H_7)(CO)_3][BF_4]$ (1), $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ (2), $[Fe(C_7H_9)(CO)_3][BF_4]$ (3), and $[Ru(C_6H_7)(CO)_3][BF_4]$ (4) were prepared by published methods [3-5] and their purity was checked by analysis (Found: C, 35.6; H, 2.5. Calc. for $C_9H_7BF_4FeO_3$: C, 35.1; H, 2.3. Found: C, 35.9; H, 2.5. Calc. for $C_{10}H_9BF_4FeO_4$: C, 35.8; H, 2.7. Found: C, 37.4; H, 2.9. Calc. for $C_{10}H_9BF_4FeO_3$: C, 37.5; H, 2.8. Found: C, 31.1; H, 2.4. Calc. for $C_9H_7BF_4O_3Ru$: C, 30.8; H, 2.6%).

Tricarbonyl(2-*methoxycyclohexadienyl*)*iron tetraphenylborate.* The complex $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ was dissolved in a minimum volume of water and an excess of sodium tetraphenylborate (also dissolved in water) was added. On cooling in ice a cream precipitate separated, which was filtered off and washed with water. The precipitate was dried in a vacuum desiccator (yield *ca.* 95%) (Found: C, 71.7; H, 5.3. Calc. for $C_{34}H_{29}BFeO_4$: C, 71.9; H, 5.3%).

All the solvents were distilled under nitrogen and stored over molecular sieves. Their water contents were determined by the Karl-Fischer method.[6] Typical values were MeCN (0.003), $MeNO_2$ (0.05), and CH_2Cl_2 (0.008% w/w). The solvents were deoxygenated by passage of a stream of nitrogen for 30 min immediately prior to use.

Pentane-2,4-dione (Hpd) was distilled under nitrogen immediately prior to use. Deuteriated pentane-2,4-dione ($MeCOCD_2COMe$) was prepared by shaking Hpd (10 cm³) with deuterium oxide (10 cm³) for 1 h, and extracting with sodium-dried diethyl ether. The extract was dried over anhydrous magnesium sulphate and the ether removed. The degree of deuteriation was determined by ^1H n.m.r. to be *ca.* 80%.

Kinetic Studies.—All the reactions were studied in the dark under nitrogen using the i.r. technique previously described.[1] In general, the disappearance of the longest-wavelength carbonyl band of the original dienyl salt at *ca.* 2 110 cm⁻¹ was monitored. A large excess of pentane-2,4-dione was always employed, and pseudo-first-order rate constants were calculated from the gradients of plots of log A_t against time, where A_t = absorbance at time t of the reaction solution at the chosen wavelength.

For the runs at constant pH, analytical grade sulphuric acid was added to the solvents acetonitrile, nitromethane, and acetone prior to mixing with (1) or (2). With dichloromethane, toluene-*p*-sulphonic acid was employed due to the immiscibility of H_2SO_4 with this solvent.

Conductivity Studies.—Solutions of fluoroboric acid (40%) of the appropriate concentrations were made up in freshly distilled nitromethane or acetonitrile. The amount of water introduced in this manner was never greater than 0.3%. Conductivities were measured at 25 ± 0.1 °C using a Pye-Unicam type E7566/3 conductivity bridge.

Keto–Enol Equilibrium Values.—The keto–enol equilibrium concentrations for Hpd in various (deuteriated) solvents were calculated from the relative intensities of their respective methyl peaks in the ^1H n.m.r. spectrum.

Reaction of Tricarbonyl[2-*methoxy*-5-(*pentane*-2′,4′-*dionyl*)-*cyclohexa*-1,3-*diene*]*iron with Acid.*—A small amount of the

---

† Part 2, K. M. Al-Kathumi and L. A. Kane-Maguire, *J. Organometallic Chem.*, 1975, **102**, C4.

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

[2] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.* (*C*), 1969, 2024.

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

[4] M. A. Hasmi, S. D. Munro, and P. L. Pauson, *J. Chem. Soc.* (*A*), 1967, 240.

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

[6] A. Vogel, 'Quantitative Inorganic Analysis,' 2nd edn., Longmans, 1951, p. 698.

complex[1] was dissolved in acetonitrile and exhibited i.r. bands at 2 040 and 1 980 cm^{-1}. Addition of one drop of concentrated H_2SO_4 to the solution resulted in immediate loss of these peaks and the appearance of bands due to $[Fe(C_6H_6OMe)(CO)_3]^+$, *i.e.* at 2 110 and 2 060 cm^{-1}.

RESULTS

Linear first-order kinetics were generally obtained for 40—50% completion of reaction in nitromethane and for at least 75% completion of reaction in dichloromethane. These deviations from linearity are analysed in the Discussion. Kinetic data for the addition of pentane-2,4-dione to cations (1) and (2) are summarised in Tables 1 and 2. All the rate constants are the average of at least duplicate determinations (reproducibility ± 5% in $MeNO_2$, and ± 10% in CH_2Cl_2). The poorer reproducibility in dichloromethane may arise from evaporation problems, since some of the runs were performed near the boiling point of the solvent (40 °C). The results with acetone are subject to considerable error since the first-order kinetic plots showed an unusual acceleration in rates after *ca.* 30—50% completion of reaction. This acceleration may be due to a concomitant acid-catalysed aldol condensation. The data in Table 2 indicate a linear dependence of $k_{obs.}$ on [Hpd] for its reaction with $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ in both nitromethane and dichloromethane as solvent.

TABLE 1

Kinetic data for the addition of pentane-2,4-dione to $[Fe(C_6H_7)(CO)_3][BF_4]$ in nitromethane

θ_c/°C	$10^5k_{obs.}$/s^{-1}
35.1	5.40
35.2	5.62
40.1	8.50
50.2	17.1
54.9	23.0

TABLE 2

Kinetic data for addition of Hpd to $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ in various solvents

Solvent	[Hpd]/mol dm^{-3}	θ_c/°C	$10^5k_{obs.}$/s^{-1}
$MeNO_2$	1.00	40.1	0.79
	1.00	45.0	1.02
	1.00	50.6	1.68
	1.00	59.9	2.85
	0.80	59.9	2.10
	0.50	59.9	1.26
	0.20	59.9	0.675
CH_2Cl_2	1.00	24.5	0.53
	1.00	29.2	1.14
	1.00	34.8	2.05
	1.00	39.6	3.85
	0.60	34.8	0.96
Me_2CO	1.00	29.3	2.31
	1.00	40.1	4.16
	1.00	49.6	7.03

Activation enthalpies for each reaction were calculated from the gradients of plots of log $k_{obs.}$ against $1/T$, and are collected in Table 3. The gradients were estimated by least-squares analysis, the errors quoted being the standard errors of estimation. Entropies of activation were calculated by standard methods using $k_{obs.}$ data obtained with [Hpd] = 1.00 mol dm^{-3}.

The effect of added acid on $k_{obs.}$ for addition of Hpd to cations (1) and (2) is shown in Table 4 and Figure 1. In all four solvents (acetonitrile, nitromethane, acetone, and dichloromethane) this resulted in a significant decrease in rate. On the other hand, addition of the base 2,6-dimethylpyridine caused an instantaneous reaction in all solvents.

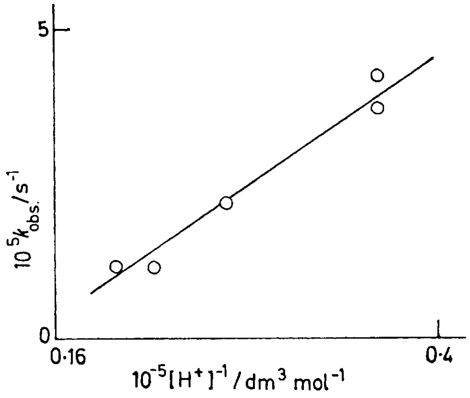


FIGURE 1 Dependence of $k_{obs.}$ on [H+] for the addition of Hpd to $[Fe(C_6H_7)(CO)_3][BF_4]$ in acetonitrile at 50.4 °C

TABLE 3

Comparison of rates and activation parameters (1 cal = 4.184 J) for addition of Hpd (1.00 mol dm^{-3}) to dienyl cations in various solvents

Complex	Solvent	$10^5k_{obs.}$ (40 °C)/s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}
(1)	MeCN [a]	5.6	16.3 ± 0.2	−26
	$MeNO_2$	8.5	14.0 ± 0.7	−33
(2)	MeCN [a]	0.62	17.1 ± 0.5	−28
	$MeNO_2$	0.79	13.5 ± 0.6	−41
	Me_2CO	4.2	10.9 ± 0.4	−52
	CH_2Cl_2	3.7	23.7 ± 0.9	−3
(3)	MeCN [a]	4.53 [b]	15.6 ± 0.3	−33
	$MeNO_2$	3.94 [b]		
(4)	$MeNO_2$	0.8 [c]		

[a] Ref. 1. [b] At 61.0 °C. [c] Upper limit.

TABLE 4

Effect of added H_2SO_4 on $k_{obs.}$ for addition of Hpd (1.00 mol dm^{-3}) to cyclic dienyl salts

Complex	Solvent	$[H_2SO_4]$/mol dm^{-3}	$10^5[H^+]$ [a]/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
(1)	MeCN [b]	0	0	15.0
		0.015	2.75	3.97
		0.027	3.72	2.18
		0.040	4.4	1.15
		0.050	5.00	1.17
	$MeNO_2$ [b]	0		17.1
		0.027		*c*
	Me_2CO [d]	0		4.16
		0.027		0.74
(2)	$MeNO_2$ [d]	0		0.79
		0.027		*c*
	CH_2Cl_2 [d,e]	0		4.00
		0.027		1.2

[a] Calculated using the relation $pH = \frac{1}{2}pK_a - \frac{1}{2}\log c$, and considering only dissociation of the first proton [pK_a 7.3 (ref. 9)]. [b] At 50.4 °C. [c] No reaction. [d] At 40.0 °C. [e] Toluene-*p*-sulphonic acid was added.

TABLE 5

Effect of deuteriation on $k_{obs.}$ for addition of Hpd (2.00 mol dm^{-3}) to $[Fe(C_6H_7)(CO)_3][BF_4]$ at 25 °C

	$10^5k_{obs.}$/s^{-1}		
Solvent	Me_2CO	$MeCOCD_2COMe$	k_H/k_D
MeCN	3.92	4.60	0.85
CH_2Cl_2	1.70	1.87	0.96

Deuteriation of the Hpd nucleophile had little effect on $k_{obs.}$ for addition to $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ in either acetonitrile or dichloromethane as solvent (Table 5).

Figure 2 shows the variation in equivalent conductance (Λ) of fluoroboric acid with concentration (c) in the solvents acetonitrile and nitromethane. The proportions of keto- and enol tautomers of Hpd present at equilibrium in various solvents are summarised in Table 6.

Attempts to extend the range of solvents were hampered by solubility problems or reaction of the iron substrates with the solvent (methanol, ethanol, or dimethyl sulphoxide). The complex $[Ru(C_6H_7)(CO)_3][BF_4]$ (4) could not be studied in acetonitrile or nitromethane because slow decomposition occurred to give an unidentified product(s). However, since addition of 1.00 mol dm^{-3} Hpd caused no significant increase in the rate of disappearance of (4), an upper rate limit could be estimated for the reaction of (4) with Hpd (Table 3).

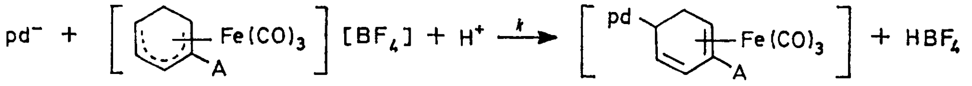
DISCUSSION

In our previous investigation[1] of the addition [equation (1)] of pentane-2,4-dione to cyclic dienyl salts ($R[BF_4]$) in acetonitrile solvent the mechanism in equations (2) and (3) was proposed. This mechanism envisages rapid pre-equilibrium dissociation of Hpd to generate the reactive pd$^-$ carbanion, which then adds to the dienyl complexes in a rapid but rate-determining fashion. The rate equation for such a scheme is given in (4), and was supported[1] by the decrease in $k_{obs.}$ observed on addition of acid. However, in less-polar solvents such as dichloromethane $K_a(= k_d/k_r)$ for the

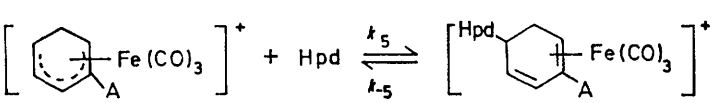
$$\text{Rate} = \frac{k_r k}{k_d[\text{H}^+]}\cdot[\text{Hpd}][\text{Fe}] \qquad (4)$$
$$= k_{obs.}[\text{Fe}]$$

acid-dissociation step (2) is expected to be very small.[7] In such solvents an alternative mechanism [equations (5) and (6)] involving direct addition of undissociated Hpd to the dienyl cations might be anticipated. It is interesting therefore that the present results confirm the operation of the mechanism in (2) and (3) in each of the solvents investigated (acetonitrile, nitromethane, acetone, and dichloromethane). After considering the general influence of solvent on reaction (1), the specific effects of added acid, added base, and deuteriation will be discussed in turn.

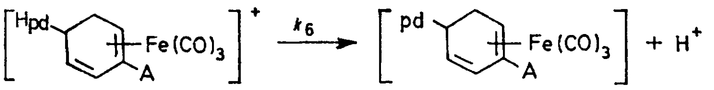
$$\mathrm{Hpd} \underset{k_r}{\overset{k_d}{\rightleftharpoons}} \mathrm{pd}^- + \mathrm{H}^+ \qquad (2)$$



(3)



(5)



(6)

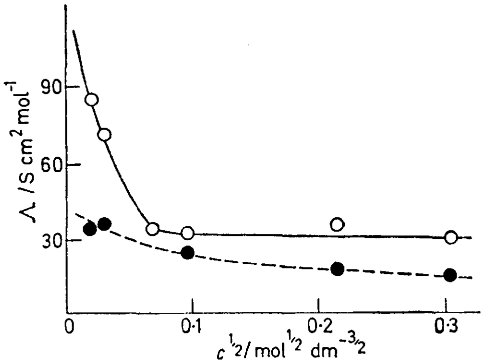


FIGURE 2 Variation of equivalent conductance of HBF_4 with concentration in the aprotic solvents MeCN (○) and $MeNO_2$ (●)

Influence of Solvent on Reaction (1).—Variation in solvent is seen (Table 3) to have little effect on the size of $k_{obs.}$ for reaction (1). There is only a six-fold increase on changing from acetonitrile to dichloromethane. While this small solvent dependence might be thought to lend support to the mechanism in (5) and (6) in which the rate-determining step involves a neutral reactant, it is not inconsistent with processes (2) and (3). The smaller K_a value anticipated for step (2) in dichloromethane

TABLE 6

Keto–enol equilibrium concentrations of Hpd in various solvents

Solvent	Keto (%)	Enol (%)
Hpd	16.0	84.0
CD_3CN	38	62
CD_3CN (+H^+)	38	62
CD_3COCD_3	26	74
CD_3Cl	17	83

---

[7] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, ch. 7.

compared to acetonitrile is expected to be counterbalanced by a more rapid k for step (3).[7]

Solvation of anions is generally poor in the aprotic solvents employed here.[8,9] This lack of anion stabilisation by solvation leads many neutral acids to dissociation in acetonitrile as shown in equation (7).[9] The

$$\mathrm{HA} + \text{solvent} \rightleftharpoons (\text{solvent})\mathrm{H}^+ + \mathrm{AH}\ldots\mathrm{A}^- \quad (7)$$

anion A^- achieves stabilisation *via* hydrogen bonding (homoconjugation) to the parent acid. Unfortunately, the extent of homoconjugation has not been measured for Hpd in any of the solvents employed here. If it were complete, the nucleophile in step (3) of the mechanism in (2) and (3) would be the homoconjugate species Hpd . . . pd⁻. This would lead to the modified rate equation (8). However, the first-order dependence of

$$\text{Rate} = K_a k[\mathrm{Hpd}]^2[\mathrm{Fe}]/[\mathrm{H}^+] \quad (8)$$

$k_{obs.}$ on [Hpd] for the solvents acetonitrile,[1] nitromethane (Table 2), and dichloromethane (Table 2) argues against significant homoconjugation in reaction (1).

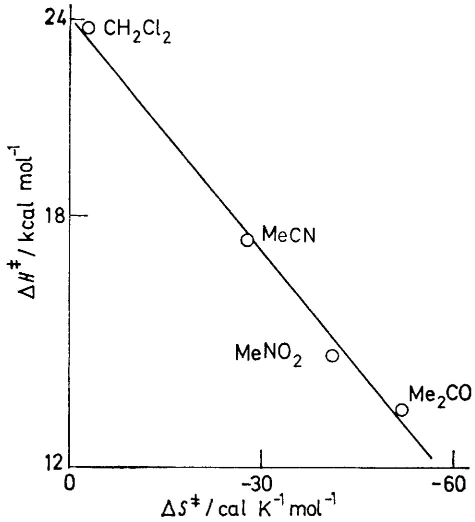


FIGURE 3 Correlation of $\Delta H^‡$ with $\Delta S^‡$ for the reaction of pentane-2,4-dione with $[\mathrm{Fe(C_6H_6OMe)(CO)_3}][\mathrm{BF_4}]$

Hydrogen-1 n.m.r. measurements show that Hpd exists largely in the enol form in each of the solvents acetonitrile, acetone, and chloroform (Table 6). The enol : keto ratio in dichloromethane is expected to be similar to that in chloroform (*ca.* 83%). These results are in keeping with earlier observations[10] that enol : keto ratios generally increase with decreasing hydrogen bonding capacity of the solvent. The presence of acid has no significant effect on the position of the tautomeric equilibrium (Table 6).

The significance of the observed activation parameters for reaction (1) in various solvents (Table 3) is difficult to assess in terms of the mechanism in (2) and (3) since they are composite values, *i.e.* $\Delta H_{obs.}^‡ = \Delta H_2^{\ominus} + \Delta H_3^‡$ and $\Delta S_{obs.}^‡ = \Delta S_2^{\ominus} + \Delta S_3^‡$. Nevertheless, it is interesting that a plot of $\Delta H_{obs.}^‡$ against $\Delta S_{obs.}^‡$ for reaction of Hpd with cation (2) in the various solvents is linear (Figure 3), indicating an isokinetic relation. This observation is consistent with a common mechanism with similar roles for the solvent in each case. Fortuitous linearity seems unlikely in view of the wide range of activation parameters observed. (However, it should be noted that there are literature examples[11] of irregular plots of $\Delta H^‡$ against $\Delta S^‡$ despite constancy of mechanism in a range of solvents.) The similar $k_{obs.}$ values in each solvent are seen to arise from the compensating influences of the enthalpy and entropy contributions, *e.g.* the lower activation enthalpies for cations (1) and (2) in nitromethane compared to acetonitrile are almost exactly balanced by more negative entropies of activation.

Influence of Added Acid.—A sharp decrease in $k_{obs.}$ is observed in all solvents on addition of acid (Table 4). This behaviour provides strong support for the mechanism in (2) and (3), and eliminates processes (5) and (6) which should be acid independent. Quantitative support for the mechanism in (2) and (3) comes from the approximate linearity of a plot of $k_{obs.}$ against $1/[\mathrm{H}^+]$ for the reaction of $[\mathrm{Fe(C_6H_7)(CO)_3}][\mathrm{BF_4}]$ with Hpd in H⁺–MeCN (Table 4, Figure 1). A further alternative mechanism [equations (5) and (6a)] in which step (6) is considered to be reversible (with equilibrium constant K') is also inconsistent with acid retardation, since this would lead to the rate equation (9).

$$k_{obs.} = k_5[\mathrm{Hpd}] + \frac{k_{-5}[\mathrm{H}^+]}{K' + [\mathrm{H}^+]} \quad (9)$$

The effect of added acid is most dramatic with nitromethane as solvent, where reaction (1) is effectively stopped. Conductivity studies suggest that this result may arise from the more extensive dissociation of acids in nitromethane compared with acetonitrile or dichloromethane, leading to a higher effective free [H⁺]. The shapes of the curves of Λ against $c^{\frac{1}{2}}$ for fluoroboric acid (Figure 2) show that $\mathrm{HBF_4}$ is a much stronger acid in the nitromethane employed than in acetonitrile.* The present data are consistent with the Λ_0 value of 196.8 previously found[12] for $\mathrm{HPF_6}$ in acetonitrile. Although conductivity values for $\mathrm{HBF_4}$ in dichloromethane were not measured, it seems reasonable to assume that the acid will be almost completely undissociated in this solvent. This would account for the fact that pseudo-first-order rate plots are linear for at least 75% completion of reaction (1) in dichloromethane. The earlier curvature generally observed in the more polar solvents (*ca.* 40% completion of reaction) is expected since $\mathrm{HBF_4}$ is produced during reaction (1).

The possibility that the effect of added acid arises from the presence of added electrolytes is eliminated by the

---

* Since small amounts of water are reported to greatly increase conductivity values in nitromethane, it is not known whether these observations represent an intrinsic property of the solvent.

[8] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

[9] S. F. Coetzee, *Progr. Phys. Org. Chem.*, 1967, **4**, 45.

[10] R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, 1970, **9**, 39.

[11] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2207.

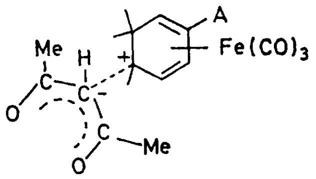
[12] C. J. Janz and S. S. Danyluk, *Chem. Rev.*, 1960, **60**, 209.

observation that added sodium tetraphenylborate (0.027 mol dm^{-3}) makes no measurable difference to the rate at which Hpd reacts with $[Fe(C_6H_6OMe)(CO)_3][BPh_4]$.

Effect of Added Base.—General base catalysis is anticipated for a mechanism of the type in (2) and (3). As expected, the addition of 2,6-dimethylpyridine (0.4 mol dm^{-3}) to a solution of Hpd (1.0 mol dm^{-3}) and cation (2) in acetonitrile resulted in extremely rapid formation of a diene product. This reaction is not due to addition by 2,6-dimethylpyridine, since only a slow reaction is observed between this base and (2) in the absence of Hpd. A similar acceleration in rate by added base was observed for reaction (1) in dichloromethane solvent. Interestingly, in nitromethane as solvent there is an instantaneous reaction between (2) and 2,6-dimethylpyridine (in the absence of Hpd). This is thought to arise *via* proton abstraction from the solvent generating $CH_2NO_2^-$ which then adds to (2). Such a process is only feasible in nitromethane ($K_a = 6 \times 10^{-11}$ mol dm^{-3} in water[13]), since acetonitrile and dichloromethane are extremely weak acids (K_a *ca.* 10^{-25} mol dm^{-3} in water).

Effect of Deuteriated Pentane-2,4-*dione.*—Experiments with $MeCOCD_2COMe$ in both acetonitrile and dichloromethane as solvent indicate that there is no primary kinetic-isotope effect for addition to $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ (Table 5). This might at first sight be regarded as evidence against the mechanism in (2) and (3) since step (2) involves cleavage of a C–H bond. Replacement of the two methylene hydrogens in Hpd by deuterium should decrease K_a. For example, in enolisation of the keto-form of 3-methylpentane-2,4-dione the primary isotope effect in water solvent is $k_H/k_D = 3.5$.[14] However, a smaller K_a value will be exactly balanced in $k_{obs.}$ by the smaller resulting $[H^+]$ [equation (4)]. This result is therefore fully consistent with the mechanism in (2) and (3), although it is also anticipated for the alternative in (5) and (6) in which rapid proton loss follows the rate-determining step.

Conclusions.—All the kinetic data presented here are consistent with a common mechanism [equations (2) and (3)] for reaction (1) in each of the solvents acetonitrile, nitromethane, acetone, and dichloromethane. While most of the observations are also consistent with an alternative path [equations (5) and (6)] involving rate-determining addition of neutral pentane-2,4-dione, this latter mechanism is eliminated by the general observation of acid retardation. A possible transition state is given below which assumes direct addition of the pd$^-$ carbanion to the dienyl ring, without prior attachment to the metal or other sites. Direct addition is supported by stereochemical evidence[15,16] showing *exo*-addition of pd$^-$ to cation (2).



It is interesting that $[Ru(C_6H_7)(CO)_3][BF_4]$ (4) reacts at least 10 times slower with Hpd than does its iron analogue (1) (Table 3). Even larger rate differences have recently been observed[17] for addition of aromatic nucleophiles to (1) and (4). While these differences may indicate a change in mechanism on varying the metal, they may be simply related to changes in electron density or free valency at the dienyl rings. INDO molecular-orbital calculations are currently being made to determine whether relative rates can be correlated with such parameters.

We thank the S.R.C. for the award of a studentship (to C. A. M.), and Dr. D. A. Sweigart for many helpful discussions.

[5/2494 *Received, 22nd December*, 1975]

---

[13] D. J. Cram and G. S. Hammond, ' Organic Chemistry,' 2nd edn., McGraw–Hill, 1964, p. 214.

[14] F. A. Long and D. Watson, *J. Chem. Soc.*, 1958, 2019.

[15] C. A. Mansfield, R. Davis, and L. A. P. Kane-Maguire, unpublished work.

[16] A. J. Birch, K. B. Chamberlain, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1900.

[17] L. A. P. Kane-Maguire and C. A. Mansfield, following paper.