# Kinetics of Substitution Reactions of
# Cyclopentadienyl Metal Carbonyl Halides

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*The kinetics of the substitution reactions of the iron cyclopentadienyl carbonyl halides and iron methylcyclopentadienyl carbonyl halides are reported for a series of phosphite ligands. A dissociative mechanism is observed in all cases. Detailed solvent studies are presented and a rationalization of these is given in terms of conjugation effects.*

## Introduction

The substitution reactions of metal carbonyl complexes have been studied extensively.[1] A dissociative $S_N 1$ type mechanism has been found to be the most common process occurring in these reactions although quite a number, especially those of $\pi$-cyclopentadienyl metal complexes, occur by a bimolecular displacement reaction.[2] It has previously been observed[3] that the $\pi$-cyclopentadienyl iron dicarbonyl halides react with a variety of ligands, e.g. triphenylphosphine, in arene solvents to give a mixture of the covalent product $\pi CpFe(CO)LX$ and the ionic product $[\pi CpFe(CO)_2 L]^+ X^-$.

$$2\pi CpFe(CO)_2 X \rightarrow \pi CpFe(CO)LX + [\pi CpFe(CO)_2 L]^+ X^-$$
$$+ CO$$
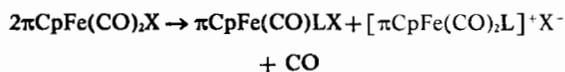
In view of the recent debate on possibly anomalous substitution reactions by $^{14}CO$ as compared with other ligands in the case of $Ni(CO)_4$[4] and $Co(CO)_3 NO$,[5] it seemed of interest to attempt kinetic studies of the above substitution reactions and to compare them with CO exchange data where available.* In the course of this work a systematic study of solvent effects was also commenced. The effect of methyl substitution in the cyclopentadienyl ring upon the kinetic parameters has also been measured.

## Experimental Section

*Solvent Purification.* (a) n-octane was purified by distillation under nitrogen through a 3 ft. electrically heated glass column packed with glass helices and the middle fraction was collected. Immediately before use it was distilled under nitrogen from lithium aluminium hydride. (b) di n-butyl ether was refluxed for several hours over calcium hydride and then distilled. Immediately before use it was distilled under nitrogen from lithium aluminium hydride.

*Ligand Purification.* $P(OC_6H_5)_3$ was distilled over sodium in a stream of nitrogen at reduced pressure. Triethyl phosphite and trihexyl phosphite were distilled.

*Preparative Reactions.* $\pi CpFe(CO)_2 I$[6] and $\pi CpFe(CO)_2 Br$[7] were prepared as described previously. $\pi MeC_5H_4 Fe(CO)_2 I$, $\pi MeC_5H_4 Fe(CO)_2 Br$, and $\pi MeC_5H_4 Fe(CO)_2 Cl$ were prepared similarly.

$\pi\text{-}CpFe(CO)P(OPh)_3 I$ was prepared by refluxing $\pi CpFe(CO)_2 I$ (2.5 g) and a slight excess of $P(OPh)_3$ in benzene (50 mls) under nitrogen for 24 hours. Filtration hot, addition of equal volume of n-octane and slow evaporation gave green crystals, recrystallized from chloroform-n-octane mixture.

$\pi\text{-}CpFe(CO)P(OPh)_3 Br$, $\pi\text{-}MeC_5H_4 Fe(CO)P(OPh)_3 I$, $\pi\text{-}MeC_5H_4 Fe(CO)P(OPh)_3 Br$ were obtained in a similar manner except that the last two compounds were recrystallized from n-heptane. In all cases, quantitative yields >90% of the covalent, monosubstituted products were obtained as observed by Treichel *et al.*[3] for the stronger nucleophile, $PPh_3$. The analytical and infrared data for the above compounds are given in Tables I and II.

*Kinetic Studies.* n-octane and di n-butyl ether were purified as above. The reaction vessel was maintained at a constant temperature ($\pm 0.1°C$) by means of an oil bath and under nitrogen at constant flow rate. The importance of efficient removal of CO during a substitution reaction has already been stressed;[1c] the observed rate constants were found to be independent of flow rate of the nitrogen.

(*) $C^{18}O$ exchange studies are at present in progress by Dr. J. P. Day, University of Manchester.
(1) For reviews see: (a) R. J. Angelici, *Organometal. Chem. Rev.,* 3, 173 (1968); (b) F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reactions», 2nd ed., J. Wiley & Sons, Inc., New York, N.Y., 1967; (c) D. A. Brown, *Inorg. Chim. Acta Rev.,* 1, 35 (1967).
(2) H. G. Schuster-Woldan and F. Basolo, *J. Amer. Chem. Soc.,* 88, 1657 (1966).
(3) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.,* 5, 1177 (1966).
(4) J. P. Day, F. Basolo, R. G. Pearson, L. F. Kangas, and P. M. Henry, *J. Amer. Chem. Soc.,* 90, 1925 (1968).
(5) G. Reichenbach, G. Innorta, and A. Foffani, *Inorg. Chim. Acta,* 3, 139 (1969).
(6) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.,* 2, 38 (1956).
(7) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.,* 3030 (1956).

**Table I.**

| Compound | % Found | | | | % Required | | | |
| | C | H | X | P | C | H | X | P |
|---|---|---|---|---|---|---|---|---|
| πCH₃C₅H₄Fe(CO)₂Cl | 42.4 | 3.1 | 15.6 | — | 42.9 | 3.2 | 15.9 | — |
| πCH₃C₅H₄Fe(CO)₂I | 30.1 | 2.1 | 39.6 | — | 30.5 | 2.2 | 39.9 | — |
| πC₅H₅FeCO P(OC₆H₅)₃ I | 49.4 | 3.4 | — | 5.4 | 49.2 | 3.4 | — | 5.3 |
| πC₅H₅FeCO P(OC₆H₅)₃ Br | 52.1 | 3.6 | — | — | 52.0 | 3.6 | — | — |
| πCH₃C₅H₄FeCO P(OC₆H₅)₃ I | 50.0 | 3.8 | 21.4 | — | 50.0 | 3.7 | 21.2 | — |
| πCH₃C₅H₄FeCO P(OC₆H₅)₃ Br | 54.3 | 4.1 | 14.7 | — | 53.8 | 4.0 | 14.4 | — |

**Table II.** CO Stretching Frequencies (cm⁻¹) of RC₅H₄Fe(CO)₂X and its Derivatives. Solvent n-heptane

| Compound | $\nu$(C—O) cm⁻¹ | |
|---|---|---|
| πC₅H₅Fe(CO)₂I | 2043 | 2004 |
| πC₅H₅Fe(CO)₂Br | 2050 | 2010 |
| πC₅H₅Fe(CO)₂Cl | 2055 | 2016 |
| πCH₃C₅H₄Fe(CO)₂I | 2038 | 1998 |
| πCH₃C₅H₄Fe(CO)₂Br | 2047 | 2005 |
| πCH₃C₅H₄Fe(CO)₂Cl | 2050 | 2008 |
| πC₅H₅FeCO P(OC₆H₅)₃ I | | 1988 |
| πC₅H₅FeCO P(OC₆H₅)₃ Br | | 1990 |
| πCH₃C₅H₄FeCO P(OC₆H₅)₃ I | | 1983 |
| πCH₃C₅H₄FeCO P(OC₆H₅)₃ Br | | 1986 |
| πCH₃C₅H₄FeCO P(OC₆H₅)₃ Cl | | 1987 |

In a sample run, the ligand was added at time zero to a thermostatted solution of substrate in the reaction vessel; aliquots were subsequently withdrawn through a self-sealing sampling device and transferred to a 1 mm KBr I.R. cell. The reaction was monitored by following the rate of disappearance of the high frequency carbonyl band (~2050 cm⁻¹) of the substrate using a Perkin-Elmer 337 infrared spectrophotometer. Comparison of the I.R. spectrum of a run after several half-lives with that of the pure product obtained in the above preparative experiments confirmed that all kinetic runs involving P(OPh)₃ went to completion to the covalent product only (90%). Good linear plots of $\log_{10}$ (A-A$_\infty$) versus time, where A is absorbance at time t, were obtained. In all cases the kinetic experiments were carried out under pseudo first-order conditions with at least 10-fold excess of ligand. For the normal iodide and the methyl-substituted iodide and chloride, investigation of the effect of ligand concentrations up to 500-fold excess was made in n-octane and recorded in Tables III and IV.

Rate constants were reproducible to 5% (except in the case of the chloride where some decomposition occurred and the error was up to 10%). Errors in activation parameters are estimated as ±1 kcal Mole⁻¹ for $E_a$ and ±2 e.u. for $\Delta S^*$.

## Results and Discussion

The values of the observed first-order rate constants, $k_{obs}$ 10⁴ sec⁻¹ are given in Tables III-V for a variety of substrates and ligands which react in both n-octane and di n-butyl ether according to the above equation. In all cases good first-order plots were obtained and, where studied, it can be seen that variation not only of ligand concentration but of the nature of the ligand itself produced no change in observed rate constant greater than experimental error. In the case of the trialkylphosphites the rate of disappearance of the

**Table III.** RC₅H₄Fe(CO)₂I + L = RC₅H₄Fe(CO)LI + CO. Solvent n—octane

| Substrate | Temp. (°C) | Ligand | Ligand moles litre⁻¹ | 10⁴$k_{obs}$ (sec⁻¹) |
|---|---|---|---|---|
| C₅H₅Fe(CO)₂I | 89.30 | P(OPh)₃ | 4 ×10⁻² | 1.47 |
| C₅H₅Fe(CO)₂I | 89.30 | P(OPh)₃ | 1.6 ×10⁻² | 1.49 |
| C₅H₅Fe(CO)₂I | 89.30 | P(OC₂H₅)₃ | 5.7 ×10⁻² | 1.55 |
| C₅H₅Fe(CO)₂I | 89.30 | P(OC₂H₅)₃ | 2.3 ×10⁻² | 1.50 |
| C₅H₅Fe(CO)₂I | 89.30 | P(OC₆H₁₃)₃ | 2.8 ×10⁻² | 1.57 |
| CH₃C₅H₄Fe(CO)₂I | 89.65 | P(OPh)₃ | 4 ×10⁻² | 1.02 |
| C₅H₅Fe(CO)₂I | 93.85 | P(OPh)₃ | 4 ×10⁻² | 2.07 |
| C₅H₅Fe(CO)₂I | 93.85 | P(OPh)₃ | 1.6 ×10⁻² | 2.08 |
| C₅H₅Fe(CO)₂I | 93.85 | P(OC₂H₅)₃ | 5.7 ×10⁻² | 2.10 |
| C₅H₅Fe(CO)₂I | 93.85 | P(OC₂H₅)₃ | 2.3 ×10⁻² | 2.18 |
| C₅H₅Fe(CO)₂I | 93.85 | P(OC₆H₁₃)₃ | 2.75×10⁻² | 2.26 |
| C₅H₅Fe(CO)₂I | 93.85 | P(OC₆H₁₃)₃ | 1.1 ×10⁻² | 2.28 |
| CH₃C₅H₄Fe(CO)₂I | 93.85 | P(OPh)₃ | 4 ×10⁻² | 1.45 |
| CH₃C₅H₄Fe(CO)₂I | 98.60 | P(OPh)₃ | 1 ×10⁻² | 2.46 |
| CH₃C₅H₄Fe(CO)₂I | 98.60 | P(OPh)₃ | 5 ×10⁻² | 2.45 |
| CH₃C₅H₄Fe(CO)₂I | 98.60 | P(OPh)₃ | 10 ×10⁻² | 2.53 |
| CH₃C₅H₄Fe(CO)₂I | 98.60 | P(OPh)₃ | 20 ×10⁻² | 2.42 |
| CH₃C₅H₄Fe(CO)₂I | 98.60 | P(OPh)₃ | 50 ×10⁻² | 2.53 |
| C₅H₅Fe(CO)₂I | 98.85 | P(OPh)₃ | 4 ×10⁻² | 3.82 |
| C₅H₅Fe(CO)₂I | 98.85 | P(OPh)₃ | 1.6 ×10⁻² | 3.83 |
| C₅H₅Fe(CO)₂I | 98.85 | P(OC₂H₅)₃ | 5.7 ×10⁻² | 3.79 |
| C₅H₅Fe(CO)₂I | 98.85 | P(OC₆H₁₃)₃ | 2.75×10⁻² | 4.03 |

**Table IV.** $RCpFe(CO)_2Br + P(OPh)_3 = RCpFe(CO)LBr + CO$. Solvent n—octane

| Substrate | Temp. (°C) | Ligand | Ligand Moles litre⁻¹ | $10^4 k_{obs}$ (sec⁻¹) |
|---|---|---|---|---|
| $C_5H_5Fe(CO)_2Br$ | 69.90 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 2.78 |
| $C_5H_5Fe(CO)_2Br$ | 69.90 | $P(OPh)_3$ | $1.6 \times 10^{-2}$ | 2.74 |
| $CH_3C_5H_4Fe(CO)_2Br$ | 69.90 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 1.81 |
| $C_5H_5Fe(CO)_2Br$ | 74.75 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 5.26 |
| $C_5H_5Fe(CO)_2Br$ | 74.75 | $P(OPh)_3$ | $1.6 \times 10^{-2}$ | 5.27 |
| $CH_3C_5H_4Fe(CO)_2Br$ | 74.75 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 3.58 |
| $C_5H_5Fe(CO)_2Br$ | 79.75 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 9.80 |
| $CH_3C_5H_4Fe(CO)_2Br$ | 79.95 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 6.40 |
| $CH_3C_5H_4Fe(CO)_2Cl$ | 50.6 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 1.51 |
| $CH_3C_5H_4Fe(CO)_2Cl$ | 55.4 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 2.68 |
| $CH_3C_5H_4Fe(CO)_2Cl$ | 55.4 | $P(OPh)_3$ | $10 \times 10^{-2}$ | 2.61 |
| $CH_3C_5H_4Fe(CO)_2Cl$ | 55.4 | $P(OPh)_3$ | $20 \times 10^{-2}$ | 2.57 |
| $CH_3C_5H_4Fe(CO)_2Cl$ | 60.5 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 5.03 |

**Table V.** Solvent di n—butyl ether

| Substrate | Temp. (°C) | Ligand | Ligand Moles litre⁻¹ | $10^4 k_{obs}$ (sec⁻¹) |
|---|---|---|---|---|
| $C_5H_5Fe(CO)_2I$ | 95.05 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 2.31 |
| $C_5H_5Fe(CO)_2I$ | 95.05 | $P(OPh)_3$ | $1.6 \times 10^{-2}$ | 2.29 |
| $CH_3C_5H_4Fe(CO)_2I$ | 95.40 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 1.64 |
| $C_5H_5Fe(CO)_2I$ | 98.85 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 3.59 |
| $C_5H_5Fe(CO)_2I$ | 98.85 | $P(OPh)_3$ | $1.6 \times 10^{-2}$ | 3.55 |
| $CH_3C_5H_4Fe(CO)_2I$ | 98.85 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 2.62 |
| $CH_3C_5H_4Fe(CO)_2I$ | 104.85 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 4.21 |
| $C_5H_5Fe(CO)_2I$ | 104.95 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 5.39 |
| $C_5H_5Fe(CO)_2I$ | 104.95 | $P(OPh)_3$ | $1.6 \times 10^{-2}$ | 5.42 |
| $C_5H_5Fe(CO)_2Br$ | 70.55 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 2.34 |
| $C_5H_5Fe(CO)_2Br$ | 70.55 | $P(OPh)_3$ | $1.6 \times 10^{-2}$ | 2.35 |
| $CH_3C_5H_4Fe(CO)_2Br$ | 70.55 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 1.42 |
| $C_5H_5Fe(CO)_2Br$ | 75.15 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 3.82 |
| $C_5H_5Fe(CO)_2Br$ | 75.15 | $P(OPh)_3$ | $1.6 \times 10^{-2}$ | 3.75 |
| $CH_3C_5H_4Fe(CO)_2Br$ | 75.15 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 2.56 |
| $C_5H_5Fe(CO)_2Br$ | 76.20 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 4.17 |
| $C_5H_5Fe(CO)_2Br$ | 79.20 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 6.65 |
| $C_5H_5Fe(CO)_2Br$ | 79.20 | $P(OPh)_3$ | $1.6 \times 10^{-2}$ | 6.72 |
| $CH_3C_5H_4Fe(CO)_2Br$ | 79.20 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 4.82 |
| $CH_3C_5H_4Fe(CO)_2Cl$ | 50.50 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 1.41 |
| $CH_3C_5H_4Fe(CO)_2Cl$ | 55.70 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 3.07 |
| $CH_3C_5H_4Fe(CO)_2Cl$ | 60.50 | $P(OPh)_3$ | $4 \times 10^{-2}$ | 5.39 |

**Table VI.** Activation Parameters for the Reaction
$RC_5H_4Fe(CO)_2X + L = RC_5H_4FeCOLX + CO$
$R = H, CH_3; \quad L = P(OC_6H_5)_3; \quad X = I, Br$
Solvent n—octane

| Complex | $E_a$ Kcal/mole | $\Delta S^*$, e.u. |
|---|---|---|
| $C_5H_5Fe(CO)_2I$ | 26.84 | −4.22 |
| $C_5H_5Fe(CO)_2Br$ | 31.22 | +14.13 |
| $CH_3C_5H_4Fe(CO)_2I$ | 28.35 | −0.83 |
| $CH_3C_5H_4Fe(CO)_2Br$ | 30.79 | +12.09 |

**Table VII.** Activation Parameters for the Reaction
$RC_5H_4Fe(CO)_2X + L = RC_5H_4Fe(CO)LX + CO$
$R = H, CH_3; \quad L = P(OC_6H_5)_3; \quad X = Br, I$
Solvent di—n—butyl ether

| Complex | $E_a$ Kcal/mole | $\Delta S^*$, e.u. |
|---|---|---|
| $C_5H_5Fe(CO)_2I$ | 23.85 | −12.47 |
| $C_5H_5Fe(CO)_2Br$ | 26.36 | −0.49 |
| $CH_3C_5H_4Fe(CO)_2I$ | 26.73 | −5.44 |
| $CH_3C_5H_4Fe(CO)_2Br$ | 29.30 | +7.03 |

substrate was the same as for $P(OPh)_3$ in n-octane at a given temperature; however the product I.R. spectrum invariably showed two carbonyl peaks and we believe that this is due to isomerism. This problem is being investigated further. The evidence points strongly to a simple dissociative mechanism operating in all the cases studied here. In other words, in the case of the π-cyclopentadienyl metal carbonyl halides the cyclopentadienyl ring does not promote an $S_N2$ type mechanism as previously suggested for πCpM-$(CO)_2$ (M = Co, Rh, Ir).[2] The activation parameters calculated in normal way are given in Table VI and VII for the two solvents employed.

In view of the problems associated with a comparison between the ¹⁴CO exchange reactions and direct ligand substitution reactions of $Ni(CO)_4$,[4] it is of interest to compare the above rate constants for the substitution of $CpFe(CO)_2Br$ and $CpFe(CO)_2I$ by $P(OPh)_3$, a relatively weak nucleophile, with those reported previously for ¹⁴CO exchange.[8]

(8) F. Basolo and F. Wojcicki, *J. Amer. Chem. Soc.*, **83**, 525 (1961).

Comparison with the data in Table I, reference 8, reveals an alarming difference but private correspondence with Professor Basolo has shown, quote « the values of $k_{appar}$ in Table I of reference 8 were recorded incorrectly and should be changed to read, from top to bottom:

| | | | |
|---|---|---|---|
| $1.3 \times 10^{-3}$, | $3.6 \times 10^{-5}$, | $4.8 \times 10^{-5}$, | $2.8 \times 10^{-4}$, |
| $5.2 \times 10^{-6}$, | $1.6 \times 10^{-5}$, | $4.1 \times 10^{-5}$, | $3.3 \times 10^{-5}$, |
| $2.3 \times 10^{-5}$, | $1.0 \times 10^{-4}$, | $5.0 \times 10^{-6}$, | $2.0 \times 10^{-3}$, |
| $1.0 \times 10^{-2}$ | | | |

Comparison between these corrected values allowing for the lower temperature and different solvent employed in [14]CO exchange work and our own values is reasonable. Nevertheless, in view of the recent reinvestigation of the [14]CO exchange of Ni(CO)$_4$ and comparison with C[18]O exchange and the conclusion that previous studies of [14]CO exchange of volatile substrates are in doubt it is obviously important to obtain new values for CO exchange on the cyclopentadienyl iron carbonyl halides; as mentioned earlier, these are in progress and eagerly awaited.

*Activation Parameters and Solvent Effects.* In both solvents and for both cyclopentadienyl and methyl substituted cyclopentadienyl compounds the rate constants fall in the sequence:

$$Cl > Br > I$$

This is the same sequence as observed in analogous studies of the manganese pentacarbonyl halides which also undergo substitution by a dissociative process.[7] In this case it was argued that the increasing polarizability (and decreasing electronegativity) of the above sequence is paralleled by an increasing M-CO bond strength as a consequence of increased $d\pi$–$p\pi$ bonding; this argument was supported by the $\nu$(C—O) stretching frequencies of these compounds. However, in contrast to the above group for which the rate sequence was paralleled by an increase in activation energy $E_a$ in the sequence $Cl < Br < I$, our results (Tables VI and VII) show that, in contrast to the rate constants, the activation parameters are solvent dependent and for n-octane lie in the sequence $I < Br > Cl$ ($E_a$) and for di n-butyl ether $I < Br < Cl$.

If one concentrates attention simply on the rate constant, in all cases other than for the methyl substituted chloride, there is a decrease in rate for the more polar solvent, di n-butyl ether. However, the effects are small and much greater changes occur in both $E_a$ and $\Delta S^*$. It is difficult to give a complete explanation of all these changes and especially in view of the marked change in reaction type (see below) in arene solvents we feel it unwise to offer anything but a tentative explanation of the pattern.

One conclusion is definite. The generally high $E_a$ and large positive $\Delta S^*$ values are consistent[1a] with a purely dissociative mechanism and support the data obtained from ligand variation studies given in Tables III-V. It is interesting to note, however, that for the case of the iodides (in n-octane) a small negative $\Delta S^*$ is recorded; nevertheless, ligand concentration studies

(Tables III-V) show clearly that for these compounds the bimolecular mechanism makes no contribution within experimental error.

We rationalise the variations in $E_a$ and $\Delta S^*$ for n-octane as follows. There is ample evidence, both experimental and theoretical[10] that $\pi$-complexes can be regarded as analogous to conjugated systems with accompanying transmission of electronic effects. In this case the halogen atom will exert both an inductive (—I) and mesomeric effect (+M) and the methyl an inductive (+I). The —I effect increases and +M effect decreases in the order $Cl > Br > I$, thus $E_a$ should increase in this order as observed for the Mn(CO)$_5$X sequence; however, both the C$_5$H$_5$ ring and especially the MeC$_5$H$_4$ group can act as electron sinks and so exert +I (or +M) effects. In the case of the bromides the —I effect of the bromine is in opposition to its +M effect and so in the transition state the +I effect of the ring system is called into play and counteracts the —I effect of the Br to such an extent as to lead to an actual increase in $E_a$ over that of the iodide. In contrast the more electronegative Cl exerts such a powerful —I effect that the ring system is insufficient to overcome this and so the activation energy drops again. It must be stressed that we are postulating that these effects occur in the transition state and that consequently reasonably large charge separations may occur in the transition state. This assumption is supported by a decrease in $E_a$ for both iodides in di n-butyl ether compared to n-octane and a concomitant decrease in $\Delta S^*$; both observations are consistent with greater solvation of the transition state in the polar solvent which implies a more polar transition state than ground state and that this difference in polarity is greater for the bromide than for the corresponding iodide.

This conclusion is the exact opposite of that for the Mn(CO)$_5$X system. In the case of methyl substituted chloride there is an increase in $E_a$ for the more polar solvent; we are not able to explain this fact. We suggest then that the above observations are consistent with a dissociative mechanism involving a more polar transition state than normally accepted for metal carbonyl substitution reactions due to the fact that the cyclopentadienyl $\pi$-electron system is called into play in a transition state of the schematic form:
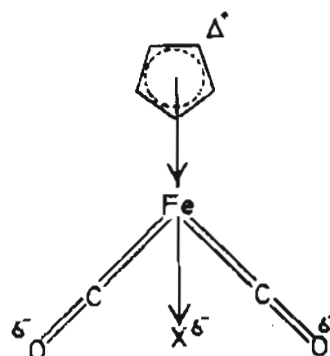


In view of these solvent effects it is interesting to recall Treichel's observations that in arene solvents

(9) R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc., 84*, 2495 (1962).

(10) D. A. Brown, Transition Metal Chemistry, Marcel Dekker, New York, 1966, p. 1.

stronger nucleophiles, *e.g.* PPh$_3$, lead to a different reaction product, [πCpFe(CO)$_2$L]$^+$X$^-$. We have found that even with the weaker nucleophile, P(OPh)$_3$, it is still possible to obtain the ionic product but its formation is favoured by higher temperatures and, of course, by an increase in the ionic character of the Fe–X bond. However, for the methyl substituted iodide in both benzene and toluene,* it is possible to obtain the covalent product only suggesting that the nucleophilicity of the attacking ligand is of prime importance. Further studies of the effect of both aromatic and polar solvents would be of interest in obtaining more details of the nature of the transition state in these systems.

(*) R. T. Sane, Unpublished observations.

Finally, it is of general interest to compare the reactivities of analogous compounds of elements of the three transition series in view of the suggestion that those of the second row may be most reactive.[1] Studies in these laboratories show that πCpRu(CO)$_2$I undergoes substitution with ligands such as P(OPh)$_3$ in exactly the same manner as described for the iron compounds;** however, kinetic studies of this reaction in n-octane as solvent gave a rate constant some 100 times slower than that for the iron compounds suggesting that for this class of compound the above generalization was incorrect. Further studies of these systems are in progress.

(**) H. J. Lyons, Unpublished observations.