Journal of Organometallic Chemistry, 221 (1981) 291—299
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTION MECHANISM OF ALKYL HALIDES AND POLYHALIDES WITH MONO- AND DI-SUBSTITUTED DERIVATIVES OF IRON PENTACARBONYL

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(Received June 26th, 1981)

Summary

Mono- and di-substituted derivatives of iron pentacarbonyl react with alkyl halides and polyhalides through two parallel paths, one radical and the other molecular. Only in two cases could the two mechanisms be isolated and studied separately. The reaction between $Fe(CO)_3(AsPh_3)_2$ and CCl_4 to give $Fe(CO)_2(AsPh_3)_2Cl_2$ is radical and affected by light and duroquinone. The proposed mechanism is similar to that of the reaction between $Fe(CO)_3L_2$ and halogens. The reaction between $Fe(CO)_3(PMe_3)_2$ and MeI to form $Fe(CO)_2(PMe_3)_2(COMe)I$ is first order in both reactants, and free CO or $P(Me)_4I$ has no effect on the rate. The kinetics are interpreted in term of a concerted nucleophilic displacement involving formation of anionic intermediate.

Introduction

Oxidative addition, insertion and reductive elimination are important steps in all the processes involving homogeneous catalysis by transition metals [1]. The mechanisms of these reactions have been much studied [2].

It is difficult to find substrates which undergo all the three reactions under conditions in which they can be studied kinetically. If this were possible, the study would produce very interesting information on the catalytic processes. Suitable reactions seem to be the oxidative addition of alkyl halides to disubstituted complexes of the type $M(CO)_3L_2$ (M = Fe, Ru; L = Group V ligands), which gives complexes of the type $M(CO)_2L_2(Me)X$, the insertion of CO or other groups, and the reductive elimination in the presence of CO, which regenerates the original disubstituted complex.

Some information on oxidative addition and on carbon monoxide insertion is reported for the iron complexes [3]. There is no evidence for the elimination reaction, but it is reasonable to assume that it does occur. This paper is concerned

0022-328X/81/0000—0000/$02.50

with the mechanism of the reaction of mono- and di-substituted iron complexes with alkyl halides and polyhalides.

Experimental

General procedures and materials

All operations, including the purification of solvents, were carried out under dry nitrogen purified by passage through Fieser's solution [4]. Toluene, benzene, n-pentane and n-hexane were refluxed for 24 hours over sodium wire and distilled from it. Diethyl ether was dried by refluxing over $LiAlH_4$ and distilled. Methyl and ethyl alcohols were dried with magnesium [4].

CH_3I was shaken with $Na_2S_2O_3$ for 2 hours, distilled into a flask containing molecular sieves (Merck, 5 Å), then redistilled and stored in a flask containing mercury [5], with protection from light at all stages. CCl_4 was refluxed over NaOH pellets for 2 hours ($NaOH/CCl_4$ = 5/100) then distilled into a flask containing P_2O_5 and refluxed again for 2 hours before being distilled under dry nitrogen, all the procedures being carried out with exclusion of light [6]. CHI_3 was purified as described by Vogel [7]. The other halides (CBr_4, $CHBr_3$, CH_2Br_2) were commercial products, and were used without purification.

The ligands PPh_3, $AsPh_3$, $SbPh_3$ were commercial products and were recrystallized from EtOH. The ligand PMe_3 was prepared following the method described by Schmidbaur [8]. The complexes $Fe(CO)_4L$ (L = PPh_3, $AsPh_3$, $SbPh_3$, PMe_3) were made from $Fe_2(CO)_9$ [9], and purified by sublimation or recrystallization. The corresponding disubstituted complexes $Fe(CO)_3L_2$ were prepared from (η^4-$C_6H_5CH{=}CHCH{=}NC_6H_5)Fe(CO)_3$ [10] and recrystallized from a mixture of hexane and dichloromethane.

Infrared spectra were recorded on Perkin-Elmer 257 or 521 spectrophotometers, which were calibrated with a polystyrene film. The dielectric constants of the toluene/CH_3I mixtures were measured with a WTW DMO1 dipolmeter.

Reaction of alkyl halides with $Fe(CO)_3L_2$.

(a) Reaction of $Fe(CO_3)(PMe_3)_2$ with MeI. The reaction between $Fe(CO)_3$-$(PMe_3)_2$ and MeI was carried out as previously described [3]. All the other alkyl halides produce dihalogenated complexes, $Fe(CO)_2L_2X_2$ (X = Cl, Br, I), some of which have been described previously [11], they were identified by their CO stretching frequencies; the CO stretching frequencies of the others are listed in Table 1. Some of these reactions are described in detail

(b) Reaction of $Fe(CO)_3(AsPh_3)_2$ with CCl_4 or CBr_4. The reaction was performed in CCl_4 at 25°C; initial formation of $Fe(CO)_3(AsPh_3)Cl_2$ was observed, and this was then transformed into the disubstituted complex $Fe(CO)_2$-$(AsPh_3)_2Cl_2$. Both complexes were of low stability, and decomposed to give a yellow precipitate containing chlorine; its spectra are identical to those of authentic $FeCl_2$. C_2Cl_6 was looked for in the solution, but was not found. The reaction with CBr_4 was similar.

(c) Reaction of $Fe(CO)_3(SbPh_3)_2$ with $CHBr_3$ or CBr_4. The reaction was followed spectrophotometrically and the spectra are reported in Fig. 1. The initial formation of a carbonyl complex (B) (ν(CO) = 1977 cm^{-1}) was followed by conversion into the complex $Fe(CO)_3(SbPh_3)Br_2$ (C). This reacted slowly with

TABLE 1

CO STRETCHING FREQUENCIES OF $Fe(CO)_3LX_2$ AND $Fe(CO)_2L_2X_2$ IN VARIOUS SOLVENTS

Complex	ν(CO) (cm^{-1})	Solvent
$Fe(CO)_3(AsPh_3)Br_2$	2102, 2057, 2032	Toluene
$Fe(CO)_3(AsPh_3)I_2$	2084, 2042, 2022	Toluene
$Fe(CO)_3(AsPh_3)Cl_2$	2115, 2064, 2037	CCl_4
$Fe(CO)_2(AsPh_3)_2Br_2$	2032, 1997	Toluene
$Fe(CO)_2(AsPh_3)_2Cl_2$	2037, 1992	CCl_4
$Fe(CO)_3(SbPh_3)Br_2$	2102, 2052, 2025	Toluene
$Fe(CO)_3(SbPh_3)I_2$	2085, 2040, 2015	Toluene
$Fe(CO)_3(SbPh_3)Cl_2$	2112, 2059, 2030	CCl_4
$Fe(CO)_2(SbPh_3)_2Br_2$	2022, 1972	$CHBr_3$
$Fe(CO)_2(SbPh_3)_2Cl_2$	2025, 1978	CCl_4
$Fe(CO)_2(PMe_3)_2I_2$	2020, 1965	THF
$Fe(CO)_2(PMe_3)_2Cl_2$	2030, 1974	CCl_4

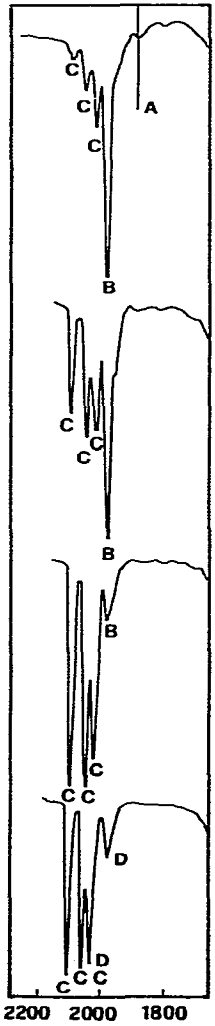

Fig. 1. IR spectra in the CO stretching region for the reaction between $Fe(CO)_3(SbPh_3)_2$ and $CHBr_3$ at various times (5, 10, 15 and 20 min). A: $Fe(CO)_3(SbPh_3)_2$; B: intermediate; C: $Fe(CO)_3(SbPh_3)Br_2$; D: $Fe(CO)_2(SbPh_3)_2Br_2$.

the $SbPh_3$ which released in the previous step, producing the complex $Fe(CO)_2(SbPh_3)_2Br_2$ (D). The reaction was complete in 20 minutes. Attempts to isolate the intermediate (B) were unsuccessful even at —70°C. The reaction with CBr_4 in toluene took a similar course.

(d) Reaction of $Fe(CO)_3(AsPh_3)_2$ with CHI_3. This reaction was performed at room temperature in toluene with both commercial and purified CHI_3. In the first case, the reaction was complete in 80 minutes and produced $Fe(CO)_3(AsPh_3)I_2$ in low yield (30%). In the second case, the reaction was slower and proceeded via two parallel paths, one giving the monohalogenated derivative and the other an unstable intermediate which was difficult to characterize. These unstable intermediates were also formed with commercial CHI_3, but in lower yields. In both cases the complex $Fe(CO)_2(AsPh_3)_2I_2$ was obtained finally.

Reaction of alkyl halides with $Fe(CO)_4L$

$Fe(CO)_4L$ reacted with alkyl halides ($CHCl_3$, CCl_4, $CHBr_3$, CBr_4, CHI_3, CH_3I) at room temperature to give the dihalogenated monosubstituted derivatives $Fe(CO)_3LX_2$. For a given L the monosubstituted reacted more slowly than the disubstituted complexes. They were identified by their CO stretching frequencies [11].

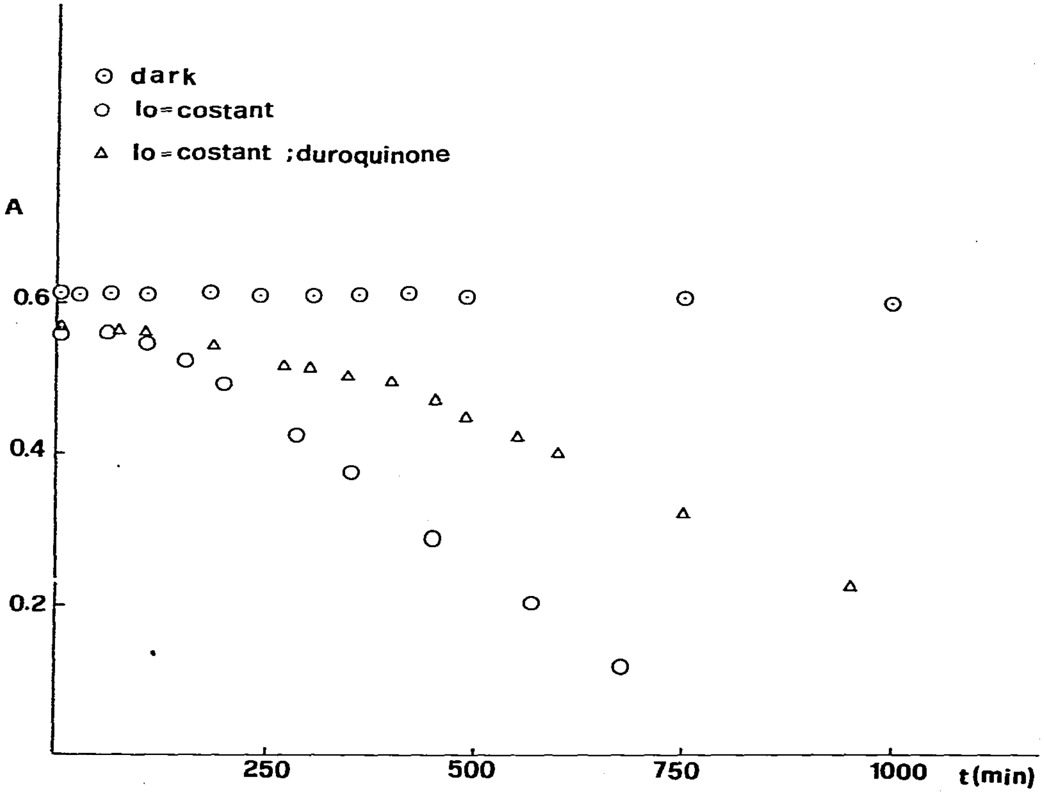

Fig. 2. Absorbance (A) of the CO stretching band of $Fe(CO)_3(AsPh_3)_2$ at various times t for the reaction with CCl_4; I_0 = light intensity.

Kinetic measurements

(a) Reaction of $Fe(CO)_3(AsPh_3)_2$ with CCl_4. The reaction was performed at 25°C in toluene with initial concentrations of the complex and CCl_4 of $\sim 6 \times 10^{-3}$ *M* and $\sim 1 \times 10^{-2}$ *M*, respectively. The reaction was monitored by observing the disappearance of the CO stretching band of the disubstituted complex with time. The results are shown in Fig. 2.

In complete darkness no significant reaction took place even in 15 hours. In the presence of light an induction period was observed, which decreased with the light intensity. Under the same conditions the presence of duroquinone (6.3×10^{-2} *M*) slowed down the reaction and increased the induction period.

(b) Reaction of $Fe(CO)_3(PMe_3)_2$ with MeI. If MeI is not freshly purified the formation of $Fe(CO)_2(PMe_3)_2I_2$ and $Fe(CO)_2(PMe_3)_2(COMe)I$ is observed. When MeI was freshly purified the reaction was stoichiometric in terms of the following equation up to 95% reaction:

$$Fe(CO)_3(PMe_3)_2 + MeI \rightarrow Fe(CO)_2(PMe_3)_2(COMe)I$$

The reaction was studied between —9.5°C and 19.9°C. Higher temperatures could not be used because of the volatility of CH_3I and because some of the dihalogenated complex was formed. Since the reaction is fairly slow, it was studied either in pure MeI or in a very concentrated solution of MeI in toluene (Table 2). The reactions were performed with exclusion of light in an apparatus previously described [12]. The reaction was monitored by observing the disappearance of the 1870 cm^{-1} CO stretching band of the disubstituted complex and the appearance of the band, of higher intensity, of the acetyl complex ($\nu(CO) = 1960\ cm^{-1}$).

TABLE 2

SECOND ORDER RATE CONSTANTS (k_2) AT VARIOUS TEMPERATURES AND AT VARIOUS DIELECTRIC CONSTANTS (D) FOR THE REACTION $Fe(CO)_3(PMe_3)_2 + MeI \rightarrow Fe(CO)_2(PMe_3)_2(COMe)I$

T (K)	X_{MeI} (molar fraction)	P_{CO} (atm)	$10^7 \times k_2$ [a] ($M^{-1}\ sec^{-1}$)	D(20°C)	$\frac{D-1}{2D+1}$
263.7	1	0	1.27 ± 0.05	7.000	0.400
273.3	1	1	2.95 ± 0.10	7.000	0.400
273.3	1	0	3.14 ± 0.10	7.000	0.400
293.1	1	0	19.8 ± 0.5	7.000	0.400
293.1	1	1	19.0 ± 0.5	7.000	0.400
293.1	1	0.1	19.1 ± 0.8	7.000	0.400
293.1	1	1 [b]	19.8 ± 0.6	7.000	0.400
293.1	1	1 [c]	18.9 ± 0.5	7.000	0.400
293.1	0.710	0	9.55	4.823	0.359
293.1	0.406	0	4.62	3.521	0.313
293.1	0.290	0	3.55	3.162	0.295
293.1	0.280	0	4.10	3.101	0.270
293.1	0.152	0	2.54	2.756	0.255
293.1	0.078	0	2.50 ± 0.15	2.560	0.254

[a] The errors in k_2 are the deviations from the mean for at least three runs. The activation parameters in MeI as solvent are: $\Delta H^{\neq} = 13$ kcal/mol and $\Delta S^{\neq}_{293.1K} = -33$ e.u. [b] Saturated solution of PMe_4I. [c] Duroquinone = $(5-10) \times 10^{-3}$ *M*.

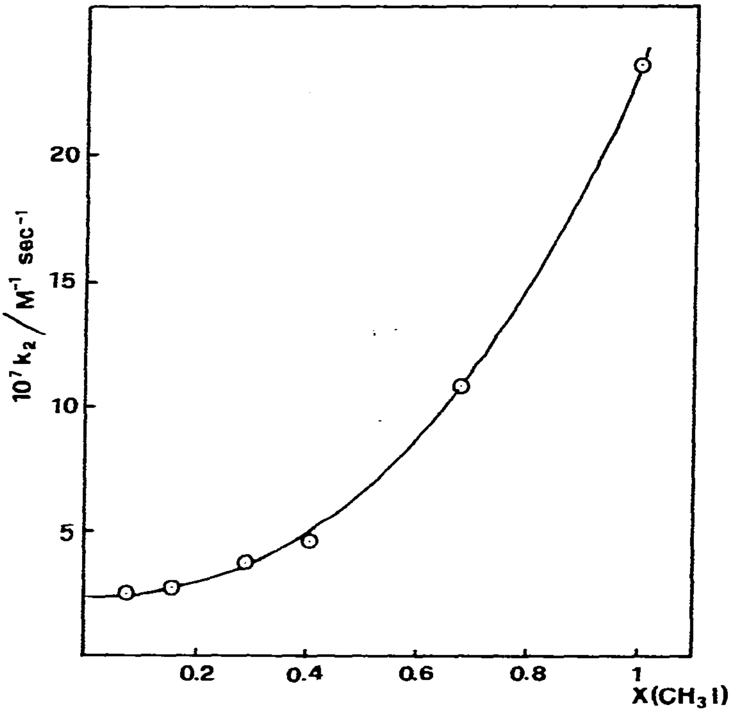

Fig. 3. Second order rate constants (k_2) vs X_{MeI} for the reaction between $Fe(CO)_3(PMe_3)_2$ and MeI in toluene at 19.9°C.

The pseudo-first-order rate constants were obtained by plotting ln A_0/A vs. t for the disappearance of the band at 1870 cm^{-1} (where A_0 is the initial absorbance and A the absorbance at time t) and by plotting ln $A_\infty/(A_\infty - A)$ vs t for the appearance of the band at 1960 cm^{-1} (where A_∞ is the absorbance at the end of the reaction and A is that at time t). The rate constants obtained by the two methods for the same kinetic run agreed within 5%. The reproducibility of the rate constants for different kinetic runs was within 10% the variations may be due in part to traces of oxygen, which induce radical reactions. Some kinetic studies were performed with a CO atmosphere and others in the presence of duroquinone or PMe_4I.

The reaction is first order in the disubstituted complex; it was difficult to determine the order in MeI because it was not possible to obtain kinetic data for diluted solutions of MeI in toluene (see above). Furthermore, it is not valid to compare the second order constants obtained by dividing the pseudo-first-order constant by the MeI concentration, because the nature of the solvent varied too greatly from one solution to an other. The reaction order was obtained by plotting such second order rate constants vs. the molar fraction of MeI(X(MeI)) (see Fig. 3). The plot of k_2 vs. X(MeI) tends to a constant value when $X_{MeI} \rightarrow 0$, indicating that k_2 remains constant on varying the MeI concentrations for dilute solutions. Thus the reaction is first order in MeI.

Results and discussion

Reaction mechanism of $Fe(CO)_3L_2$ and alkyl halides

The disubstituted complexes react by two parallel paths. One of them is affected by light and radicals, and gives dihalogenated mono- or di-substituted compounds. The other is not influenced by light or radicals and produces unstable compounds which quickly decompose. Only in the case of MeI is a stable acetyl complex obtained [3]. It is difficult to make a quantitative study if both paths are present, but in two cases we succeded in isolating the two reaction paths. In fact, the reaction between $Fe(CO)_3(AsPh_3)_2$ and CCl_4 follows the first route, and the reaction of $Fe(CO)_3(PMe_3)$ with CH_3I in the dark the second route.

Mechanism of the radical reactions.

The results of Fig. 1 for the reaction of $Fe(CO)_3(AsPh_3)_2$ with CCl_4 indicate that (a) there is no reaction in the dark; (b) there is an induction period which decreases on increasing the light intensity; (c) duroquinone (a radical scavenger) increases the induction period and decreases the reaction rate.

These results are typical of a radical reaction [13] initiated by light, which produces $Cl^\cdot$ radicals from CCl_4. The radical reaction is observed also with other alkyl halides, some of which give radicals thermally [14]. The fact that the reaction is a radical process explains the increase of the reaction rate with decrease in the C—X bond energy [14] which follows the order

$$C{-}Cl > C{-}Br > C{-}I$$

With the same alkyl halide but varying L the rate for $Fe(CO)_3L_2$ decreases in the following order

$$SbPh_3 > AsPh_3 > PPh_3 > PMe_3$$

This is the order of increasing basicity of L [15].

The first stable product of the reaction is the di-halogenated monosubstituted complex $Fe(CO)_3LX_2$. Thus the reaction proceeds via initial substitution of the ligand L; afterwards L reacts with $Fe(CO)_3LX_2$ producing $Fe(CO)_2L_2X_2$ in a previously described reaction [16]. Previous studies have shown that this reaction involves an initial step in which halogen radicals are formed photochemically or thermally from alkyl halides. These radicals react with $Fe(CO)_3L_2$ via one-electron oxidation to give the radical cation $[Fe(CO)_3L_2]^{+\cdot}$, as recently shown for the reaction of halogens with $Fe(CO)_3L_2$ [17]. This mechanism is further supported by the observation of intermediate (B) (Fig. 1) during the reaction of $Fe(CO)_3(SbPh_3)_2$ with $CHBr_3$; this has the same infrared characteristics as the ion $[Fe(CO)_3L_2]^+$ described in ref. 17. The effect of the basicity of L on the rate indicates that the replacement of L is a rate determining step in the previously proposed scheme [17]. The monosubstituted complexes $Fe(CO)_4L$ react with alkyl halides by the same mechanism as $Fe(CO)_3L_2$, giving the monosubstituted dihalogenated complexes $Fe(CO)_3LX_2$ with expulsion of a carbon monoxide ligand.

Mechanism of the reaction between $Fe(CO)_3(PMe_3)_2$ and MeI [18]

This reaction was studied in pure MeI and in concentrated solutions of MeI in toluene. The reaction is second order (see Experimental section) and the fall in the rate constant on lowering the molar fraction of MeI is attributable to the decrease in the dielectric constant of the medium. The second order rate constants are listed in Table 2. The activation parameters in pure MeI are $\Delta H^{\neq} = 13$ kcal/mol and $\Delta S^{\neq} = -33$ e.u., and are consistent with an S_N2 mechanism. It was conceivable that the reaction might proceed via a predissociation of CO or PMe_3 from the starting complex, freeing a coordination position for the attack of MeI, as found with other complexes [19], but this is not the case, for the following reasons: (i) an atmosphere of CO does not alter the rate; (ii) the reaction is quantitative; since PMe_3 reacts with MeI to form PMe_4I the reaction would not be quantitative if PMe_3 dissociated from $Fe(CO)_3(PMe_3)_2$. If, on the other hand, the formation of PMe_4I is a reversible process [20], the addition of PMe_4I would influence the rate; (iii) if predissociation of phosphine were a rate determining step, $Fe(CO)_3(PEt_3)_2$ would react more rapidly with MeI; whereas it did not react at all.

The radical mechanism can also be excluded because duroquinone does not affect the rate, and because a radical mechanism produces only the dihalogenated compound, as shown in experiments performed in daylight.

The proposed mechanism is a concerted nucleophilic displacement (2-center S_N2) [21]:

$$Fe(CO)_3(PMe_3)_2 + MeI \overset{k_2}{\rightarrow} [Fe(CO)_3(PMe_3)_2(Me)^+ I^-]$$

$$[Fe(CO)_3(PMe_3)_2(Me)^+ I^-] \xrightarrow[\text{insertion of CO}]{\text{fast}} Fe(CO)_2(PMe_3)_2(COMe)I$$

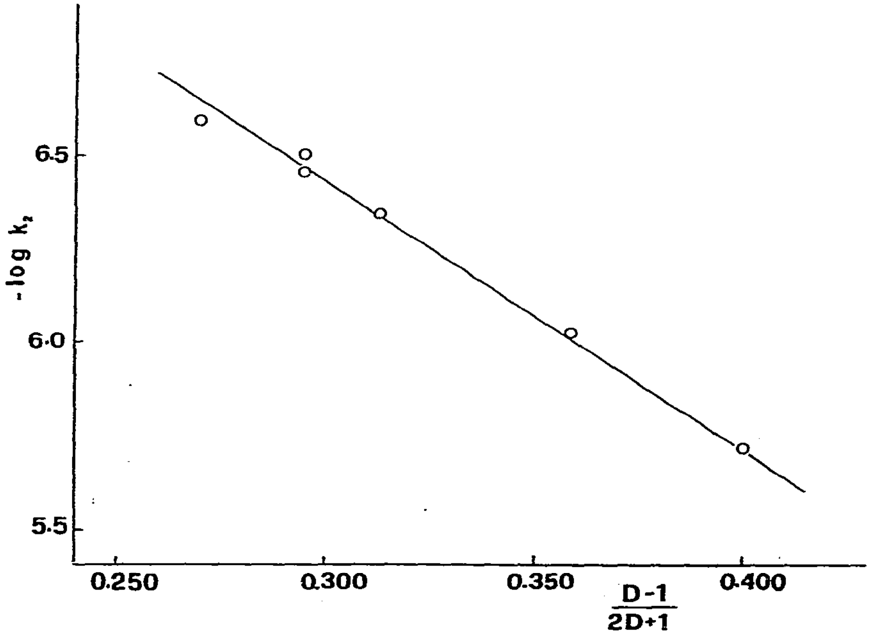

Fig. 4: —log k_2 vs. $\frac{D-1}{2D+1}$ for the reaction between $Fe(CO)_3(PMe_3)_2$ and MeI at 19.9°C in mixtures of toluene and MeI.

Since it involves the formation of ionic species as intermediates this mechanism is consistent with the observed sensitivity of the reaction rate to the dielectric constant of the medium. The mechanism corresponds with those found for the reactions of iron carbonyls with halogens, which involve the formation of the ionic intermediates $[Fe(CO)_3L_2X^+X^-]$ [17,22]. The presence of a polar activated complex is confirmed by the correlation between lg k_2 and $(D - 1)/(2D + 1)$, (where D is the dielectric constant of the solution) shown in Fig. 4 and Table 2. Such a linear correlation is a characteristic of Mentschukin reactions, which occur via ionic intermediates [23].

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