Solvent Effect on the Isotopomerization of $Fe(^{13}CO)(CO)(PMe_3)_2MeI$: Implication on the Mechanism of CO Insertion

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Received October 30, 1991

The isotopomerization of the $Fe(^{13}CO_a)(CO_b)(PMe_3)_2MeI$ complex was studied in various solvents. The kinetic and thermodynamic parameters suggest that the isotopomerization proceeds via ionization of the Fe-I bond, rearrangement of the formed ion-pair, and reentry of the iodide ligand. This behavior supports a CO insertion mechanism proceeding via direct substitution of the iodide with CO and formation of an ionic intermediate.

Introduction

The properties of the solvents affect the rate of the CO insertion in the metal-carbon bond;[1] nucleophilic and polar solvents usually increase[2] the insertion rate and this effect was attributed to the stabilization of the unsaturated intermediate.[3] This explanation was confirmed by Bergman's work on the CO insertion in $CpMo(CO)_3Me$,[4] but it is not completely satisfactory.[5] In fact, Halpern[6] showed, at least in one case, that the role of nucleophilic solvents is not to stabilize the coordinatively unsaturated acyl intermediates but rather to catalyze their formation. Furthermore, when strong solvent effects are observed, there is the possibility of a different mechanism in which the migratory insertion is not the rate-determining step.[7]

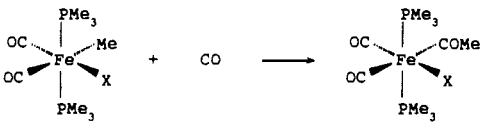
Recently a strong solvent effect was observed[8,9] in the CO insertion of Scheme I. On going from *n*-hexane to CH_2Cl_2 a variation of, at least, 10^4 was observed. Baird suggested an ionic mechanism.[8] Since a kinetic study of this reaction is difficult because of the high rate and the heterogeneous system, we approached the problem by studying the behavior of $Fe(CO)_2(PMe_3)_2MeI$ in various solvents in order to prove the presence of an ionization process. The test reaction studied was the isotopomerization of $Fe(^{13}CO_a)(CO_b)(PMe_3)_2MeI$ (**2**) to $Fe(CO_a)(^{13}CO_b)(PMe_3)_2MeI$ (**3**) (the a and b indices correspond to carbon monoxide trans or cis to the Me group).

Experimental Section

$Fe(CO)_2(PMe_3)_2MeI$ (**1**) and $Fe(^{13}CO)_2(PMe_3)_2MeI$ (**4**) were prepared as described in refs 10 and 9, respectively; the solvents (*n*-hexane, toluene, $CHCl_3$, CH_2Cl_2, nitromethane, CH_3OH, CH_3CN) were dehydrated by conventional methods.[11]

The IR spectra were obtained with a 1725 X FTIR Perkin-Elmer spectrophotometer. The ^1H, ^{13}C (^1H not decoupled), and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrophotometer. The ^1H and ^{13}C NMR shifts are relative to tetramethylsilane as internal reference and the $^{31}P\{^1H\}$ NMR shifts are relative to 85% H_3PO_4 in D_2O with a positive sign indicating a shift to lower field.

Scheme I



The stereochemical structure of the complexes studied is given in Figure 1 (for the ionic compounds the anion is BPh_4^-); their NMR and IR characterizations are given in Table I. The structural assignments are based on the arguments presented in refs 8, 9, 12, and 13.

Preparation of $Fe(^{13}CO_a)(CO_b)(PMe_3)_2MeI$ (2). Complex **1** (70 mg) was reacted in *n*-hexane at 30 °C with ^{13}CO (99%, 40 mL) for 6 h (P_{CO} = 1 atm). No labeling of the acetyl substituent was observed by IR. Decarbonylation of the acetyl in *n*-hexane at 30 °C for 2 h gave complex **2** (75%), complex **1** (20%), complex **3** (3%), and complex **4** (2%).

Preparation of $[Fe(^{13}CO_b)(CO_b)(CO_a)(PMe_3)_2Me]BPh_4$ (5). In a reactor containing 46 mL of ^{13}CO at -33 °C (P_{CO} = 1 atm), 3 mL of a methanol solution of $NaBPh_4$ (1 g) and 7 mL of a methanol solution of complex **1** (100 mg) were added. The mixture was stirred for 5 min; an instantaneous precipitation was observed; the solution was bubbled with nitrogen and filtered. Complex **5** (120 mg, 78% yield) was obtained.

Preparation of $[Fe(^{13}CO_b)(CO_b)(^{13}CO_a)(PMe_3)_2Me]BPh_4$ (7). The mixture obtained in the preparation of complex **2** was used for a further reaction with ^{13}CO in order to obtain complex **7**. Ten milliliters of a solution in methanol of this mixture (60 mg) was added to 3 mL of a solution in methanol of $NaBPh_4$ (1 g), contained in a reactor filled with ^{13}CO (46 mL, P_{CO} = 1 atm) and thermostated at -33 °C. The solution was stirred for 5 min and filtered after bubbling with nitrogen. The solid was dried and analyzed by $^{31}P\{^1H\}$ NMR and IR. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 gives the following composition: complex **7**, 73%; complex **8**, 3%; complex **5**, 20%; complex **9**, ≈4%. At room temperature this solution scrambled all the CO groups and after 2 h the statistical distribution of the CO and ^{13}CO groups was observed. The scrambling rate was higher in acetone in which the equilibrium was obtained after 30 min.

Scrambling of CO in Complexes 1 and 4. Equimolar quantities of **1** and **4** complexes were dissolved in CH_2Cl_2 and allowed to react for 3 h at 30 °C. No scrambling of CO and ^{13}CO was observed.

Preparation of $[Fe(CO)_2(PMe_3)_2(NCCH_3)Me]BPh_4$ (11). This complex was prepared in a manner different from that given in ref 14. Complex **1** (100 mg) was dissolved in CH_3OH (16 mL) containing $NaBPh_4$ (1 g) at -20 °C. To the stirred solution, CH_3CN (0.5 mL) was added. After a few minutes, a white solid precipitated, which was filtered, washed with CH_3OH, and dried (60 mg, ≈40% yield).

Preparation of $[Fe(^{13}CO_a)(CO_b)(PMe_3)_2(NCCH_3)Me]BPh_4$ (12). The mixture obtained in the preparation of complex **2** (50 mg) was dissolved in CH_3OH (8 mL) containing $NaBPh_4$ (0.5 g) at -20 °C. To the stirred solution CH_3CN (0.25 mL) was added. After a few minutes, a white

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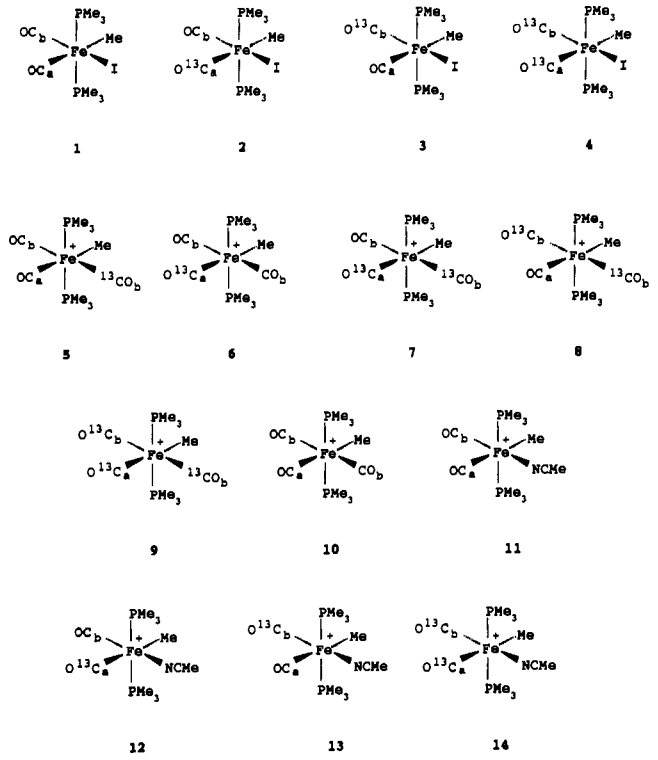

Figure 1. Structures of the complexes.

solid precipitated, which was filtered, washed with CH_3OH, and dried (30 mg, ≈40% yield). The $^{31}P\{^1H\}$ NMR analysis indicates the presence of complex **12** (75%), complex **11** (20%), complex **13** (3%), and complex **14** (2%). This composition corresponds to that of the starting mixture (see the preparation of complex **2**).

Isotopomerization of Complex 2. Complex **2** isotopomerizes in all solvents giving an equimolar mixture of **2** and **3** complexes. The kinetics of isotopomerization were followed in various solvents: *n*-hexane, toluene, $CHCl_3$, CH_2Cl_2, nitromethane, CH_3OH, CH_3CN. The experimental procedure was essentially the same. The analytical measurements were carried out in *n*-hexane, since the CO stretching bands of the different isotopomers are resolved in this solvent only (see Table I). An example of the procedure is described for a generic solvent S. A 10–15-mg portion of complex **2** was dissolved in solvent S (2–3 mL), previously deaerated and thermostated at the prefixed temperature (±0.1 °C). Portions of the solution (≈0.25 mL) were withdrawn at prefixed time and quickly dried with nitrogen. The residue was dissolved in *n*-hexane (≈0.25 mL) and the IR spectrum was recorded in the range 2100–1900 cm^{-1}. An overall pattern of the spectra obtained at various times is given in Figure 2. The concentrations of complexes **1** and **4**, present as impurity, remained unchanged during the kinetic runs.

Behavior of Complex 1 in CH_3CN. Complex **1** dissolved in CH_3CN shows an equilibrium with the ionic complex $[Fe(CO)_2(PMe_3)_2(NCCH_3)Me]I$. The structure of this complex is assigned on the basis of the CO stretching bands and of the ^1H and $^{31}P\{^1H\}$ NMR spectra.[14] The equilibrium is shifted toward complex **1** by adding tetra-*n*-butylammonium iodide (NBu_4I). The equilibrium constant was not calculated because it is not possible to measure the concentration of the free iodide anion; the spectroscopic information gives the total cation concentration, both as ion pair or as free cation. The rate of the equilibrium process was high and the ^1H NMR bands were fluxional. An approximate evaluation of the rate constant was obtained on the basis of the coalescence temperature (T = 300 K) of the methyl ^1H NMR band of the phosphine ligand:[15] k = 0.5 min^{-1}.

Isotopomerization of Complex 2 in CH_3CN. When complex **2** was dissolved in CH_3CN, the ionization equilibrium indicated in Scheme II was immediately reached. The structure of the cation was assigned by comparison with the IR and NMR bands of analogous labeled complexes (vide infra). The ionic complex isotopomerized slowly with respect to the rate of ionization. The rate of isotopomerization was measured as described for the other solvents, since, on drying the solution, only the neutral complexes were obtained. Some reactions were carried out in the presence of NBu_4I in order to observe the effect of the concentration of I^- on the reaction rate. The results are given in Table II.

Isotopomerization of Complex 12 in CH_3CN. Complex **12** was dissolved in CH_3CN and the isotopomerization to complex **13** was followed. Owing to the overlap between the IR stretching CO bands of the two complexes in CH_3CN, it was difficult to obtain quantitative values of the rate constants for this reaction. Qualitative information indicates that the rate of isotopomerization is very slow with respect to the same reaction with the iodide anion.

Results

(1) Stereochemistry of the Reaction with Nucleophiles (CO, CH_3CN). The reaction of complex **1** with ^{13}CO in CH_3OH in the presence of $NaBPh_4$ gives complex **5**; the reaction of complex **2** with ^{13}CO in CH_3OH in the presence of $NaBPh_4$ gives complex **7**. Successively, both of the stereospecifically formed complexes give all the other isotopomers in quantities that are in agreement with a statistical distribution of the CO and ^{13}CO ligands. This process was attributed to the scrambling of CO via a dissociative mechanism.[14,16] The reaction of complex **2** with CH_3CN, in CH_3OH in the presence of $NaBPh_4$, gives complex $[Fe(^{13}CO_a)(CO_b)(PMe_3)_2(NCCH_3)Me]BPh_4$ (**12**). The structure of complex **12** was assigned on the basis of the $^2J_{P-CO}$ coupling constant, which is a very reliable method, as previously demonstrated.[8,9,12,13]

(2) Kinetic Measurements. The isotopomerization process (Scheme III) is a first-order reversible reaction and was studied by using the following kinetic law[17]

$$\ln \frac{C_o - C_e}{C - C_e} = (k_1 + k_{-1})t \qquad (1)$$

in which C_o, C_e, and C represent the concentrations of the complex **2** at t = 0, at equilibrium, and at the time t, respectively. k_1 and k_{-1} are the first-order rate constants of the direct and reverse reactions, respectively. Since complexes **3** and **2** are isotopomers $k_1 = k_{-1}$ and the kinetic law becomes

$$\ln \frac{C_o - C_e}{C - C_e} = 2k_1 t \qquad (2)$$

By use of the ratio F of the concentration of complexes **3** and **2**, eq 2 becomes

$$\ln \frac{1 + F}{1 - F} = 2k_1 t \qquad (3)$$

Equation 3 is independent of the absolute concentration of complexes **2** and **3** and gives a strong experimental advantage; in fact, it is unnecessary to withdraw identical volumes of solution and dissolve the residue in an identical volume of *n*-hexane.

Since the extinction coefficients of the corresponding CO stretching bands of complexes **2** and **3** are not identical, it is not possible to calculate F by the adsorbance ratio. We observed that the sum of the areas of the CO stretching bands of **3** (1987, 1905 cm^{-1}) was equal to the sum of the areas of the CO stretching bands of **2** (1977, 1915 cm^{-1}) at equal concentrations. The areas were measured by the computer options of the FTIR, using the base line method. Then the F values are measured as

$$F = \frac{[3]}{[2]} = \frac{\text{area}(1987) + \text{area}(1905)}{\text{area}(1977) + \text{area}(1915)} \qquad (4)$$

For each solvent the measures were performed at three temperatures in order to calculate the activation parameters. The kinetic runs in nitromethane, methanol, and acetonitrile were only measured at 20 and 30 °C because at T > 30 °C the reaction

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Table I. NMR (CD_2Cl_2) and IR (CH_2Cl_2) Relevant Data

complex	^1H δ, ppm (J, Hz)	$^{31}P\{^1H\}$ δ, ppm (J, Hz)	^{13}C δ, ppm (J, Hz)	IR, cm^{-1}
1[a]	δ_{CH_3} = 0.37 t ($^3J_{CH_3-P}$, 9.4) δ_{PMe_3} = 1.56 m ($\lvert^2J_{H-P} = {}^4J_{H-P}\rvert$, 8.1)	δ_P = 13.4 s		1998 (s) 1937 (s)
2[a]	δ_{CH_3} = 0.37 t ($^3J_{CH_3-P}$, 9.4)	δ_P = 13.4 d ($^2J_{P-CO_a}$, 16.0)	δ_{CO_a} = 208.6 t ($^2J_{CO_a-P}$, 15.9)	1977 (s) 1915 (s)
3[a]	δ_{CH_3} = 0.37 td ($^3J_{CH_3-P}$, 9.4; $^3J_{CH_3-CO_b}$, 1.7)	δ_P = 13.4 d ($^2J_{P-CO_b}$, 25.6)	δ_{CO_b} = 220.1 tq ($^2J_{CO_b-P}$, 25.5; $^3J_{CO_b-CH_3}$, 1, 7)	1987 (s) 1905 (s)
4[a]	δ_{CH_3} = 0.37 td ($^3J_{CH_3-P}$, 9.4; $^3J_{CH_3-CO_b}$, 1.7)	δ_P = 13.4 dd ($^2J_{P-CO_a}$, 16.0; $^2J_{P-CO_b}$, 25.6)	δ_{CO_a} = 208.6 td ($^2J_{CO_a-P}$, 15.9; $^2J_{CO_a-CO_b}$, 5.9) δ_{CO_b} = 220.1 tdq ($^2J_{CO_b-P}$, 25.5; $^2J_{CO_b-CO_a}$, 5.8; $^3J_{CO_b-CH_3}$, 1, 7)	1982 (s) 1895 (S)
5	δ_{CH_3} = 0.04 td ($^3J_{CH_3-P}$, 7.2; $^3J_{CH_3-CO_b}$, 2.2) δ_{PMe_3} = 1.56 m ($\lvert^2J_{H-P}\rvert$, 6.5; $\lvert^4J_{H-P}\rvert$, 2.5)	δ_P = 17.1 d ($^2J_{P-CO_b}$, 24.8)	δ_{CO_b} = 208.5 td ($^2J_{CO_b-P}$, 24.8; $^3J_{CO_b-CH_3}$, 2.2)	2070 (w) 2020 (s) 1988 (s)
6	δ_{CH_3} = 0.04 t ($^3J_{CH_3-P}$, 7.2)	δ_P = 17.1 d ($^2J_{P-CO_a}$, 15.1)	δ_{CO_a} = 203.6 t ($^2J_{CO_a-P}$, 15.1)	
7	δ_{CH_3} = 0.04 td ($^3J_{CH_3-P}$, 7.2; $^3J_{CH_3-CO_b}$, 2.2)	δ_P = 17.1 dd ($^2J_{P-CO_b}$), 24.8; $^2J_{P-CO_a}$, 15.1)	δ_{CO_a} = 203.6 t ($^2J_{CO_a-P}$, 15.1) δ_{CO_b} = 208.5 td ($^2J_{CO_b-P}$, 24.8; $^3J_{CO_b-CH_3}$, 2.2)	2065 (w) 1994 (s) 1976 (s)
8	δ_{CH_3} = 0.04 tt ($^3J_{CH_3-P}$, 7.2; $^3J_{CH_3-CO_b}$, 2.2)	δ_P = 17.1 t ($^2J_{P-CO_b}$, 24.8)	δ_{CO_b} = 208.5 m[b]	
9	δ_{CH_3} = 0.05 tt ($^3J_{CH_3-P}$, 7.2; $^3J_{CH_3-CO_b}$, 2.2)	δ_P = 17.1 td ($^2J_{P-CO_b}$, 24.8; $^2J_{P-CO_a}$, 15.1)	δ_{CO_a} = 203.6 tt ($^2J_{CO_a-P}$, 15.1; $^2J_{CO_a-CO_b}$, 5.6) δ_{CO_b} = 208.5 tdq ($^2J_{CO_b-P}$, 24.8; $^2J_{CO_b-CO_a}$, 5.6; $^3J_{CO_b-CH_3}$, 2.2)	2034 (vw) 1973 (vs)
10	δ_{CH_3} = 0.04 t ($^3J_{CH_3-P}$, 7.2)	δ_P = 17.1 s		2082 (vw) 2018 (vs)
11[c]	δ_{CH_3} = 0.19 t ($^3J_{CH_3-P}$, 8.4) δ_{PMe_3} = 1.47 m ($\lvert^2J_{H-P} = {}^4J_{H-P}\rvert$, 8.4) δ_{NCCH_3} = 1.66 s	δ_P = 20.3 s		2255 (w) 2022 (s) 1969 (s)
12[c]	δ_{CH_3} = 0.19 t ($^3J_{CH_3-P}$, 8.4)	δ_P = 20.3 d ($^2J_{P-CO_a}$, 14.8)	δ_{CO_a} = 204.9 t ($^2J_{CO_a-P}$, 15.1)	2005 (s) 1941 (s)
13[c]	δ_{CH_3} = 0.19 t ($^3J_{CH_3-P}$, 8.4)	δ_P = 20.3 d ($^2J_{P-CO_b}$, 28.7)	δ_{CO_b} = 213.8 t ($^2J_{CO_b-P}$, 28.7)	1993 (s) ≈1953 (s)
14[c]	δ_{CH_3} = 0.19 t ($^3J_{CH_3-P}$, 8.4)	δ_P = 20.3 dd ($^2J_{P-CO_a}$, 14.7; $^2J_{P-CO_b}$, 28.7)	δ_{CO_a} = 204.9 td ($^2J_{CO_a-P}$, 15.1; $^2J_{CO_a-CO_b}$, 5.9) δ_{CO_b} = 213.8 td ($^2J_{CO_b-P}$, 28.7; $^2J_{CO_b-CO_a}$, 5.9)	1935 (s) ≈1966 (s)

[a] IR spectra in *n*-hexane. [b] Pattern not resolved owing to the overlap with the bands of the other isotopomers. [c] IR spectra in CH_3CN.

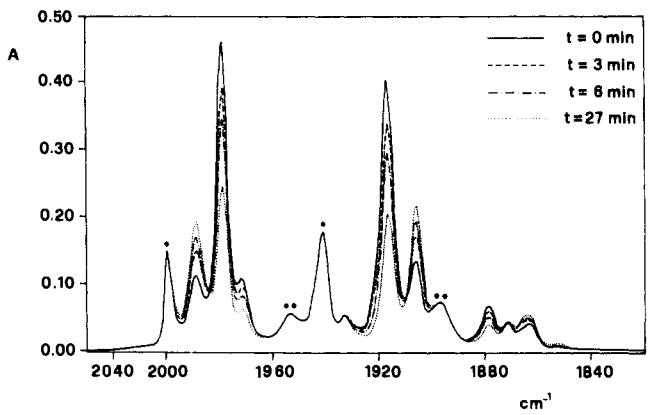


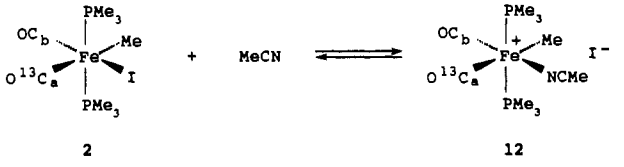
Figure 2. Absorbances (A) of the CO stretching bands (in *n*-hexane) at various times during a kinetic run of reaction 1 carried out in CH_3OH at 30 °C (* and ** indicate impurities of the complexes **1** and **4**, respectively).

was too fast to be followed, while at $T < 20$ °C, during the time necessary for drying, the reaction proceeds further and modifies the relative concentrations.

Some reactions in CH_3CN were followed in the presence of an excess of NBu_4I. In all these cases no appreciable effect on the rate constants was observed (Table II).

The values of k_1, ΔH^*, and ΔS^* are given in Table II. The values of ΔH^* decrease with increasing dielectric constant of the solvents, indicating that the solvent polarity stabilizes the activated complex. The values of ΔS^* become more negative on increasing the dielectric constant of the solvent, indicating a strong solvation of the activated complex.

Scheme II



At the same dielectric constant, the coordinating power of the solvent[18,7a] does not influence k_1, ΔH^*, and ΔS^* in the limits of the experimental error (compare the values for nitromethane, methanol, and acetonitrile in Table II).

Discussion

The absence of scrambling of CO and ^{13}CO between complexes **1** and **4** excludes an isotopomerization which occurs via CO dissociation.[19] It also excludes an isotopomerization which occurs via migratory insertion because according to this mechanism,

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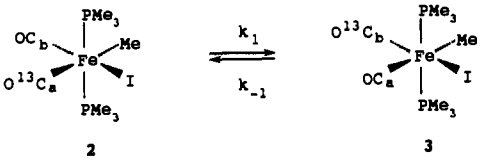
Table II. Kinetic Data and Activation Parameters for the Reaction of Scheme III[a]

solvent	T, °C	10^3k_1, min^{-1}	ΔH^*, kJ·mol^{-1}	ΔS^*, J·mol^{-1}·K^{-1}	$D_{30\,°C}$	donor no.[b]
n-hexane	30	0.369 ± 0.002				
	40	1.70 ± 0.05	104 ± 3	0 ± 12	1.87	
	50	5.10 ± 0.02				
toluene	30	1.2 ± 0.01				
	40	4.9 ± 0.1	97 ± 3	−8 ± 8	2.37	0.1
	50	14.1 ± 0.8				
chloroform	20	1.48 ± 0.01				
	30	5.1 ± 0.1	85 ± 1	−42 ± 4	4.77	
	40	14.7 ± 1				
CH_2Cl_2	20	2.4 ± 0.1				
	30	6.0 ± 0.3	77 ± 2	−67 ± 4	8.71	2
	35	11.9 ± 0.2				
nitromethane[c]	20	9.7 ± 0.3	75 ± 4	−54 ± 13	35.87	2.7
	30	28.7 ± 0.1				
methanol[c]	20	11.1 ± 0.4	67 ± 4	−84 ± 13	31.67	19.0
	30	28.8 ± 0.6				
acetonitrile[c]	20	9.65 ± 0.06	75 ± 4	−67 ± 4	36.73	14.1
	30	28.7 ± 0.6				
	20[d]	9.5 ± 0.1				
	20[e]	9.2 ± 0.2				

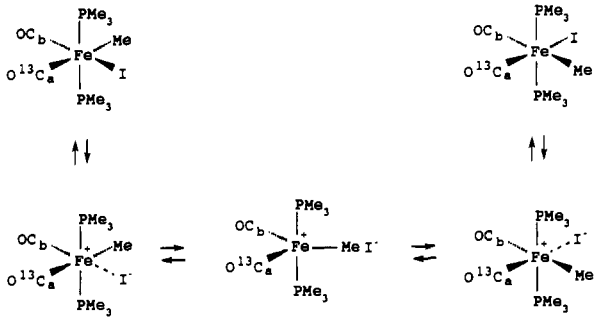
[a] ±standard deviation. [b] See ref 18. [c] The errors in ΔH^* and ΔS^* are evaluated on the basis of the variation of k_1 values at every single temperature. [d] Kinetic measurement carried out in the presence of a 3-fold excess of NBu_4I with respect to complex **2**. [e] Kinetic measurement carried out in the presence of a 6-fold excess of NBu_4I with respect to complex **2**.

Scheme III



2 **3**

Scheme IV



complex **2** should not isotopomerize. The effect of the dielectric constant on the rate constants and on the activation parameters suggests a mechanism which proceeds via ionization of the Fe–I bond in complex **2**, formation of an ion pair, rearrangement of the ion pair, and neutralization to obtain the isotopomer **3** (Scheme IV).

A theory of the influence of the dielectric constant (D) of the medium on the rate constant of ionization reactions has been developed by Kirkwood.[20] On the basis of this theory the following relation has been obtained

$$\ln k_1 = \ln k_{1o} + B\frac{D-1}{2D+1} \qquad (5)$$

where k_1 is the rate constant in a medium of D dielectric constant, k_{1o} is the rate constant in a medium of dielectric constant unity.

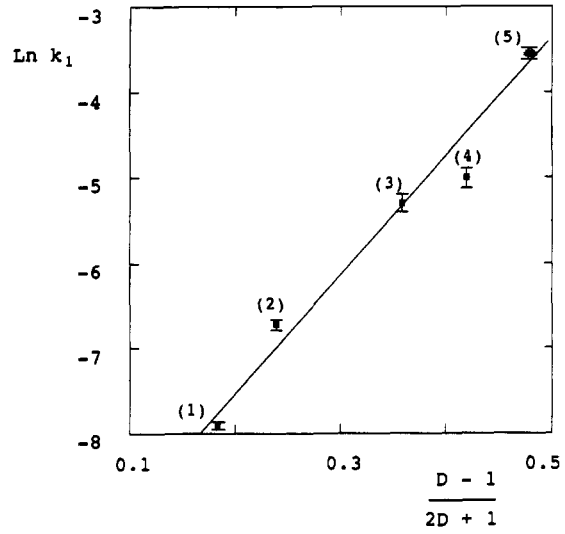


Figure 3. ln k_1 vs $(D-1)/(2D+1)$ for reaction 1 at 30 °C in various solvents (1, *n*-hexane; 2, toluene; 3, chloroform; 4, methylene chloride; 5, methanol, nitromethane, and acetonitrile).

B is a constant which is correlated to the electrostatic interaction in the activated and the starting complexes.[21] The trend of ln k_1 vs $(D-1)/(2D+1)$ is given in Figure 3. The linear trend observed strongly supports the ionization mechanism.

The trend of the activation parameters (ΔH^* and ΔS^*) in noncoordinating solvents is easily explainable on the basis of the stabilization of the more polar activated complex (ΔH^*) and on the basis of the stronger polarization of the solvent in the activated complex (ΔS^*). The isotopomerization is due to the shift of the methyl group to the vacant site in the activated complex.

The behavior of CH_3CN clarifies the reaction pathway with coordinating solvents. The isotopomerization of cation **12** with noncoordinating anion (BPh_4^-) is very slow with respect to the coordinating anion I^-. The concentration of NBu_4I has no appreciable effect on the reaction rate (Table II). On the other hand, the concentration of I^- affects the ionization equilibrium (Scheme II). These results show that the effect of I^- is in the form of an ion pair;[22] I^- plays an active role in isotopomerization, but its concentration has no effect because it depresses the

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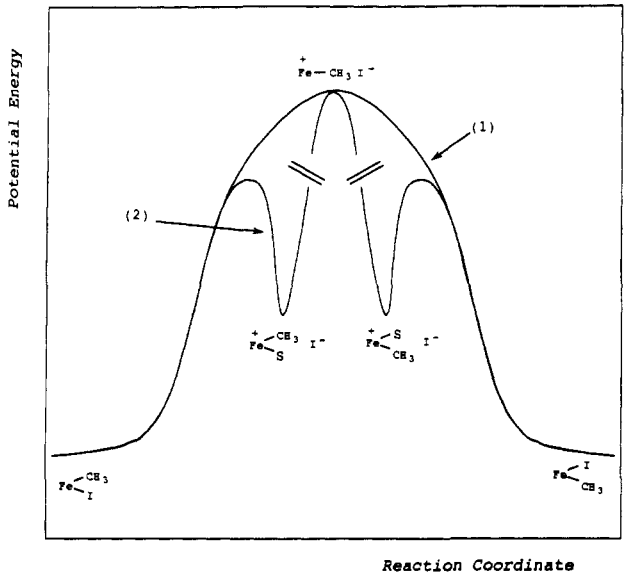

Figure 4. Reaction coordinate in solvents with the same dielectric constant and with different coordinating power (1, noncoordinating solvent; 2, coordinating solvent).

ionization equilibrium but increases the rate of formation of ion pairs, which are responsible for the isotopomerization.

The energy profiles obtained upon varying the properties of the solvent are given in Figure 4. With a noncoordinating solvent the charge separation in the bond Fe–I is the only step for the isotopomerization; with a coordinating solvent[18,7a] the ionic intermediates are stabilized and the rate constant to obtain them is strongly influenced by the coordinating power of the solvent. In the ionic intermediate, the nucleophiles (CH_3CN, CO) occupy the position of the iodide ligand. To obtain isotopomerization, the anion is very important and its presence in the activated complex is necessary as in noncoordinating solvents.

On the other hand, the stereospecific formation of the ionic intermediate **5** from complex **1** with ^{13}CO, of the ionic complex **7** from complex **2** with ^{13}CO and of the ionic complex **12** from complex **2** with CH_3CN strongly supports an insertion mechanism, for the reaction of Scheme I, which proceeds via ionization of the Fe–I bond,[8] formation of the ionic intermediate, and migratory insertion in the ionic intermediate to give the acetyl complex when the nucleophile is CO.

The ionization of the Fe–I bond should explain the strong solvent effect observed in the insertion reaction. The high rate of the migratory insertion in the ionic intermediate is supported by the strong catalytic effect of anions in the insertion reactions, due to ion-pair formation.[13,22,23]

Acknowledgment. This work was supported by grants from the Consiglio Nazionale delle Ricerche (CNR, Rome, Italy) and the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST, Rome, Italy).

Registry No. **1**, 33542-07-3; **2**, 89144-35-4; **3**, 91176-79-3; **4**, 88003-85-4; **5**, 141413-54-9; **6**, 141661-46-3; **7**, 141613-55-0; **8**, 141661-47-4; **9**, 89144-40-1; **10**, 82660-90-0; **11**, 89616-73-9; **12**, 141613-56-1; **13**, 141723-97-9; **14**, 141613-57-2.

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