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Successive reactions of iron carbonyl cations with methanol

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Abstract

The reactivity of $Fe(CO)_n^+$ cations with methanol has been investigated using a triple-cell Fourier transform ion cyclotron resonance apparatus. Successive substitutions of the CO ligands by methanol occur rapidly with similar rates. For $n = 3–5$ the last CO ligand is not replaced, and the terminal substitution products are $FeCO(CH_3OH)_{n-1}^+$. A second reaction pathway is observed for $n = 3–5$, in which two CO ligands are replaced by one methanol molecule. This pathway occurs even if the $Fe(CO)_n^+$ ions have been radiatively relaxed before reaction, providing information on the bond energies in the product ions. Strong internal energy effects are observed on the reaction rates and branching ratios for further substitution of the intermediate products. The substitution product $Fe(CH_3OH)^+$ from $FeCO^+$ reacts further, with C–O bond cleavage followed by substitution. The resulting $Fe[C_2, H_7, O_2]^+$ ion undergoes either isomerization or collisional deactivation, then slow association with methanol. The reaction of Fe^+, due to excited states only, begins with formation of $FeOH^+$ and involves the same final steps as in the preceding case. (Int J Mass Spectrom 199 (2000) 267–285) © 2000 Elsevier Science B.V.

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1. Introduction

The reactivity of metallic complexes in the gas phase is strongly influenced by the nature and number of ligands born by the metal ion. Detailed knowledge of the dependence of the gas-phase reactivity with ligation, for a given metal ion and neutral reactant, may contribute to a better understanding of the respective role of ligands, solvent, and counterion in the reactivity of organometallic species, and finally of its relationship with solution reactivity [1,2]. An important point determining the reactivity is related to the binding energies of the different ligands to the metal ion. The successive binding energies of the L ligands in complexes such as ML_n^+ have been recently determined for several types of metals and ligands [3]. However relatively little is known about the mutual stabilization or destabilization effects of the ligands in complexes bearing two or more ligands different from each other.

The present study is focused on the reactivity of methanol with the different iron carbonyl cations $Fe(CO)_n^+$ $(n = 0–5)$. The nature of the successive

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Dedicated to Henri Eduoard Audier on the occasion of his 60th birthday.

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substitution reactions observed allows one to gain thermodynamic information on the mutual interaction of the methanol and CO ligands. A second point worth studying in these systems consists in further reactions of the resulting methanol complexes, leading to C–O bond activation. Reactions of $Fe(CO)_n^+$ with methanol in an ion cyclotron resonance (ICR) cell have first been reported in 1976 by Allison and Ridge [4,5]. In these early experiments the reaction schemes were deduced from the dependence of product distribution with reaction pressure, since the reaction time could not be varied. In the present study, time dependences of ion product distribution have been measured, allowing determination of complete reaction schemes and of rate constants for the involved reactions, in particular for processes occurring at long reaction times.

In the ICR cell the primary reactions take place at thermal kinetic energy. Internal energy effects can be possible if excited states of the reactant ions are involved. These effects can be partly monitored by providing a variable relaxation delay before the reaction. In this way, ions with nearly thermal energy are brought to reaction, and valid thermodynamic conclusions can be drawn from the reactions observed.

2. Experimental

The triple cell Fourier transform ICR (FTICR) spectrometer used in the present study has been described previously [6]. The three ion traps of the tricyclotron are differentially pumped. The first is used as an ion source; the second, maintained at low residual pressure, is alternately used for radiative relaxation of ions before reaction, and as a detection cell; the third is the reaction zone. The ions can be stored successively in each trap for a well controlled time and transferred from one cell to the next by drifting them perpendicularly to the magnetic field. Their drift kinetic energy remains negligible compared to the thermal kinetic energy. Indeed lifetime studies using this experimental setup have shown its ability to perform ion–molecule reactions at thermal kinetic energy [7,8]. The time needed to transfer the ions from one cell to the next is in the millisecond range. The $Fe(CO)_n^+$ ions are generated in the first cell by electron impact ionization of $Fe(CO)_5$ at a pressure of $\sim 10^{-5}$ Torr. The energy of the electron beam is adjusted to get a satisfying amount of the desired reactant ion. The typical energy used was 23 eV except for Fe^+ which was produced with a 70 eV electron beam. Ejection of all the ions except the desired $Fe(CO)_n^+$ reactant ion is performed in the first cell. The reactant ions are drifted into the central cell maintained at a low pressure of $\sim 10^{-8}$ Torr, where they can be stored for a variable relaxation time, then to the third cell containing methanol as a reactant gas. The methanol pressure in the third cell was adjusted to $2–4 \times 10^{-6}$ Torr. The reaction time could be varied between 1 ms and several seconds. The ions are then drifted back to the central cell for FTICR detection.

The intensity of each ion signal, normalized to the total ion signal (sum of the ions with significant intensity) is plotted as a function of the reaction time. To check the reaction schemes and get the rate constants of the different processes, data analysis was performed using a homemade program allowing a global optimization of the parameters. All abundance curves of an experiment were treated simultaneously with a global analysis method based on the transfer matrix for a set of pseudo-unimolecular reactions [9]. Reaction schemes were tested using nonlinear optimization of the reaction rates and initial concentrations (minimizing the least square residual between the model and the unweighted data). Error analyses were performed with a Monte Carlo method [10]. In most cases the reaction scheme initially introduced into the program for rate constant optimisation included all the reasonable pathways between the different species, so that it could be checked that the reactions which were not retained in the final scheme were found to have null rate constants. However, for complicated systems opening all the conceivable pathways in the same scheme may be inefficient because of an increasing number of parameters, and it is preferable to test different schemes individually.

The uncertainty on the rate constant fits is in the 1%–5% range unless otherwise specified, corresponding to ~10% uncertainty on the relative values of rate constants within a given experiment. Due to slight

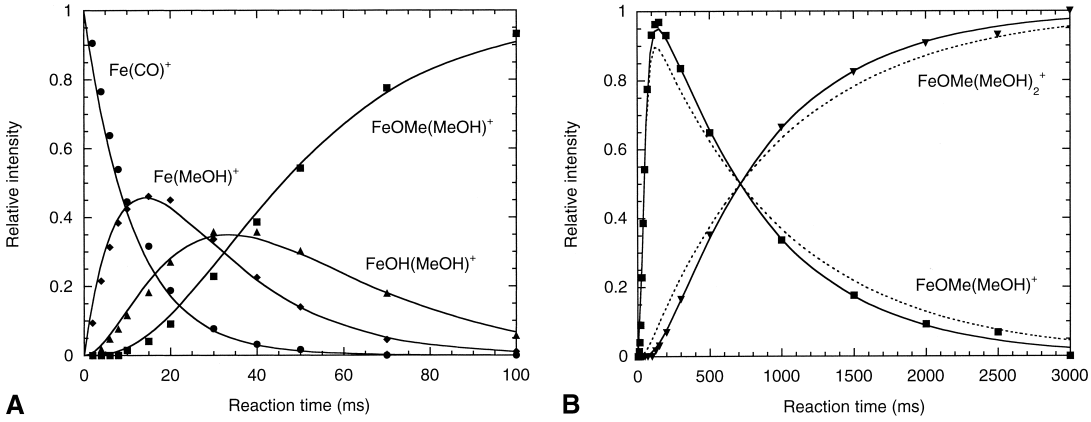


Fig. 1. Dependence of ion distribution with reaction time for the reaction of $Fe(CO)^+$ with methanol (relaxation time 200 ms; reaction pressure: 2.3×10^{-6} Torr): *m/z* 84, $Fe(CO)^+$ (circle); *m/z* 88, $Fe(CH_3OH)^+$ (diamond); *m/z* 105, $FeOH(CH_3OH)^+$ (triangle); *m/z* 119, $FeOCH_3(CH_3OH)^+$ (square); *m/z* 151, $FeOCH_3(CH_3OH)_2^+$ (inverted triangle). Solid lines are fits corresponding to the reaction schemes and rate constants reported in text. Dotted lines in (b) are fits obtained without introducing the isomerization or deactivation step of *m/z* 119 ion. (a) Short reaction times and (b) long reaction times. For clarity, only the *m/z* 119 ion is shown at both time scales.

pressure fluctuations and to uncertainty on pressure measurement, the uncertainty on absolute rate constants is significantly higher, in the order of 20%–25%.

3. Results

In this section we use the term “rate constant” for the apparent rate constants directly obtained from fitting the abundance curves of the different ions. As will be shown later, some of these “rate constants” depend strongly on the internal energy of the reactant ions. The real “thermal” values of the rate constants can be determined only for some of the reactions involved (see sec. 4). Pseudo-first-order rate constants are referred to as k, pseudo-second-order rate constants corresponding to termolecular association reactions are referred to as k_a.

3.1. Reactivity of $FeCO^+$ with methanol

As reported by Allison and Ridge [4,5], substitution of the CO ligand leading to $Fe(CH_3OH)^+$ is followed by an unexpected reaction involving C–O bond cleavage in the complexed methanol by an incoming methanol ligand. Further reaction consists in water elimination.

The time dependence of the relative abundances of products from reaction of $FeCO^+$ with methanol is reported in Fig. 1. The abundance curves up to 100 ms [Fig. 1(a)] are nicely fitted using the following succession of reactions and rate constants:

$$FeCO^+ + CH_3OH \rightarrow Fe(CH_3OH)^+\ (m/z\ 88) + CO$$

$$k = 1.2 \times 10^{-9}\ cm^3\ s^{-1}$$

$$Fe(CH_3OH)^+ + CH_3OH$$

$$\rightarrow (CH_3OH)FeOH^+\ (m/z\ 105) + CH_3^{\bullet}$$

$$k = 6.7 \times 10^{-10}\ cm^3\ s^{-1}$$

$$(CH_3OH)FeOH^+ + CH_3OH$$

$$\rightarrow (CH_3OH)FeOCH_3^+\ (m/z\ 119) + H_2O$$

$$k = 5.7 \times 10^{-10}\ cm^3\ s^{-1}$$

In the absence of relaxation delay in the second cell, the general pattern of the abundance curves remain practically the same, with the same rate constants for formation of $Fe(CH_3OH)^+$ and subsequent reactions. A slight distortion appears in the initial part of the $FeCO^+$ and $Fe(CH_3OH)^+$ curves, corresponding to slower formation of $Fe(CH_3OH)^+$. This distortion is close to experimental uncertainty but reproducible.

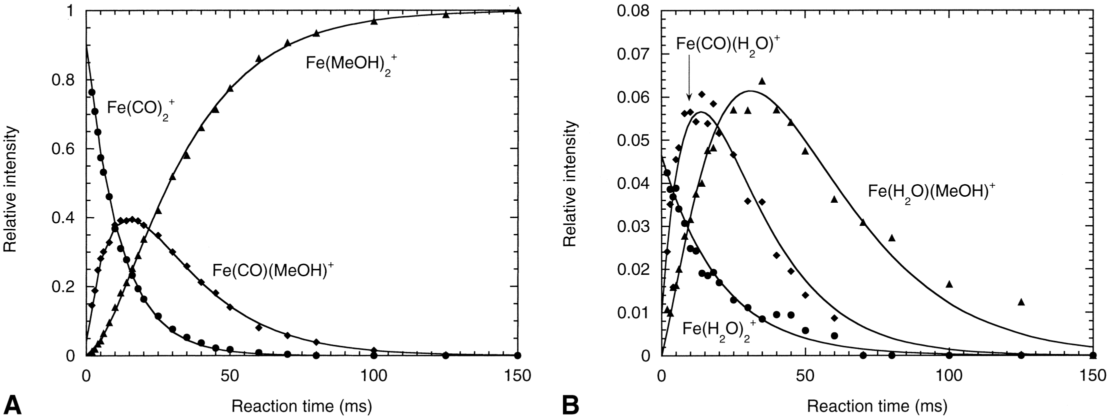


Fig. 2. Dependence of ion distribution with reaction time for the reaction of $Fe(CO)_2^+$ with methanol (relaxation time 300 ms; reaction pressure: 1.9×10^{-6} Torr). (a) Major ions: *m/z* 112, $Fe(CO)_2^+$ (circle); *m/z* 116, $Fe(CO)(CH_3OH)^+$ (diamond); *m/z* 120, $Fe(CH_3OH)_2^+$ (triangle). (b) Minor ions arising from residual water: *m/z* 92, $Fe(H_2O)_2^+$ (circle); *m/z* 102, $Fe(CO)(H_2O)^+$ (diamond); *m/z* 106, $Fe(H_2O)(CH_3OH)^+$ (triangle). Solid lines are fits corresponding to the reaction schemes and rate constants reported in text. Experimental points between 150 and 600 ms are not shown (*m/z* 120 only).

For long reaction times, a new reaction is observed, corresponding to net association of a methanol molecule to the last product

$$(CH_3OH)FeOCH_3^+ + CH_3OH$$
$$\rightarrow (CH_3OH)_2FeOCH_3^+ \ (m/z\ 151)$$

Interestingly, the abundance curves cannot be satisfactorily fitted by using this reaction directly on the *m/z* 119 ion issued from reaction of *m/z* 105 ion. The kinetic data indicate an intermediate step involving transformation of the *m/z* 119 ion according to the following scheme:

$$Fe[C_2, H_7, O_2](1)^+ \rightarrow Fe[C_2, H_7, O_2](2)^+$$
$$k = 1.8 \times 10^{-11}\ cm^3\ s^{-1}$$
$$Fe[C_2, H_7, O_2](2)^+ + CH_3OH$$
$$\rightarrow (CH_3OH)_2FeOCH_3^+$$
$$k_a = 1.3 \times 10^{-21}\ cm^6\ s^{-1}$$

This intermediate step may be either a chemical or an energetic transformation, i.e. either isomerization or collisional deactivation (see sec. 4).

3.2. Reactivity of $Fe(CO)_2^+$ with methanol

The abundance curves corresponding to the reaction of $Fe(CO)_2^+$ with methanol are reported in Fig. 2. The only reactions observed are successive substitutions of the two CO ligands:

$$Fe(CO)_2^+ + CH_3OH$$
$$\rightarrow FeCO(CH_3OH)^+ \ (m/z\ 116) + CO$$
$$k = 1.2 \times 10^{-9}\ cm^3\ s^{-1}$$
$$FeCO(CH_3OH)^+ + CH_3OH$$
$$\rightarrow Fe(CH_3OH)_2^+ \ (m/z\ 120) + CO$$
$$k = 7.7 \times 10^{-10}\ cm^3\ s^{-1}$$

The $Fe(CH_3OH)_2^+$ ion is stable in the presence of methanol, no other reaction product being detected up to 600 ms reaction time. In particular C–O cleavage in a methanol ligand is not observed.

The rate constants reported above are obtained from curve fits in the case of $Fe(CO)_2^+$ ions relaxed for 300 ms. If the relaxation time is short (10 ms), the curves are slightly distorted compared to those of relaxed $Fe(CO)_2^+$, and the data fit using the same reaction scheme is much less satisfying. Further study

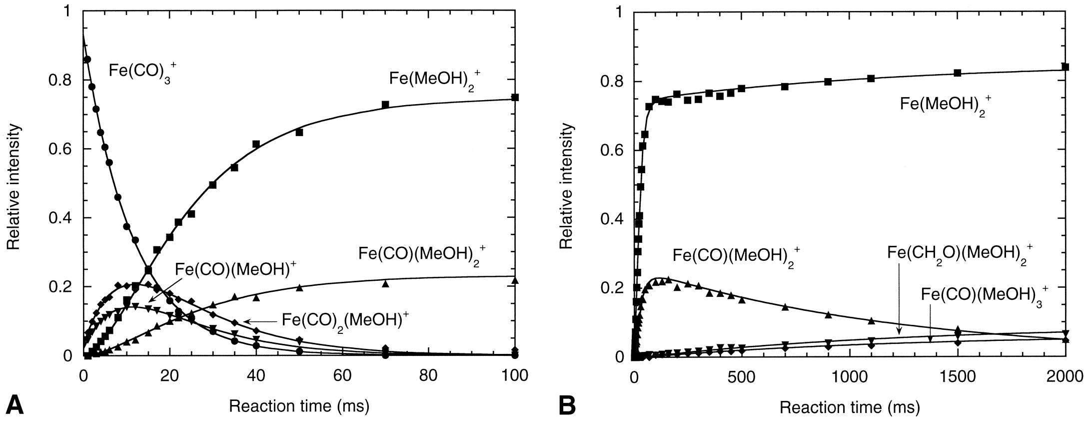


Fig. 3. Dependence of ion distribution with reaction time for the reaction of $Fe(CO)_3^+$ with methanol (reaction pressure: 2.2×10^{-6} Torr): *m/z* 140, $Fe(CO)_3^+$ (circle); *m/z* 144, $Fe(CO)_2(CH_3OH)^+$ (diamond); *m/z* 148, $Fe(CO)(CH_3OH)_2^+$ (triangle); *m/z* 116, $FeCO(CH_3OH)^+$ (inverted triangle); *m/z* 120, $Fe(CH_3OH)_2^+$ (square); *m/z* 150, $Fe(CH_2O)(CH_3OH)_2^+$ (inverted triangle); *m/z* 180, $Fe(CO)(CH_3OH)_3^+$ (ν). Solid lines are fits corresponding to the reaction schemes and rate constants reported in text. (a) Short reaction times and (b) long reaction times. For clarity, only the *m/z* 120 and 148 ions are shown at both time scales.

of such effects is outside the scope of the present work and will be reported separately.

At relatively short reaction times, side products arising from residual water also appear. Water substitution on $Fe(CO)_2^+$ in the second cell gives low amounts of $Fe(CO)(H_2O)^+$ (*m/z* 102) and/or $Fe(H_2O)_2^+$ (*m/z* 92), which are present in the third cell at the beginning of the reaction, and react further with methanol. For 10 ms relaxation time only $Fe(CO)(H_2O)^+$ (4%) is detected at the beginning of the reaction, while for 300 ms relaxation time both $Fe(CO)(H_2O)^+$ (1%) and $Fe(H_2O)_2^+$ (4%) are present.

In both experiments the product distributions are consistent with the following scheme:

$$Fe(H_2O)_2^+ + CH_3OH$$
$$\rightarrow Fe(H_2O)(CH_3OH)^+ \ (m/z\ 106) + H_2O$$
$$k = 8 \times 10^{-10}\ cm^3\ s^{-1}$$

$$Fe(CO)(H_2O)^+ + CH_3OH$$
$$\rightarrow Fe(H_2O)(CH_3OH)^+ + CO$$
$$k = 7 \times 10^{-10}\ cm^3\ s^{-1}$$

$$Fe(H_2O)(CH_3OH)^+ + CH_3OH$$
$$\rightarrow Fe(CH_3OH)_2^+ + H_2O$$
$$k = 7 \times 10^{-10}\ cm^3\ s^{-1}$$

$$Fe(CO)_2^+ + H_2O$$
$$\rightarrow Fe(CO)(H_2O)^+ \ (m/z\ 102) + CO$$
$$k \approx 1\text{–}2 \times 10^{-9}\ cm^3\ s^{-1}$$

The last rate constant is roughly evaluated supposing a H_2O pressure equal to the residual pressure (1–2 10^{-7} Torr) measured in the third cell in the absence of methanol.

Concerning the $Fe(CO)(H_2O)^+/CH_3OH$ reactivity, it can be noticed that substitution of the H_2O ligand is conceivable as well as substitution of the CO ligand. Opening the H_2O substitution pathway in the data fit leads to a null value for the corresponding rate constant. Therefore substitution of the CO ligand is actually preferred to substitution of the H_2O ligand.

3.3. Reactivity of $Fe(CO)_3^+$ with methanol

The abundance curves corresponding to reaction of $Fe(CO)_3^+$ with methanol are reported in Fig. 3. In contrast with the cases of $Fe(CO)^+$ and $Fe(CO)_2^+$, substitution of a CO ligand by methanol is not the only primary reaction. The other reaction of $Fe(CO)_3^+$

is substitution of two CO ligands by one methanol molecule

$$\mathrm{Fe(CO)_3^+ + CH_3OH \rightarrow Fe(CO)_2(CH_3OH)^+}\ (m/z\ 144) + \mathrm{CO}$$

$$k = 6.4 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)_3^+ + CH_3OH \rightarrow Fe(CO)(CH_3OH)^+}\ (m/z\ 116) + 2\ \mathrm{CO}$$

$$k = 4.6 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

The corresponding branching ratio is not modified by the presence or absence of a relaxation delay in the second cell. More generally, the $Fe(CO)_3^+/CH_3OH$ system did not show any relaxation effect. Further substitutions occur similarly, and $Fe(CO)_2(CH_3OH)^+$ reacts with methanol through loss of either one or two CO ligands:

$$\mathrm{Fe(CO)_2(CH_3OH)^+ + CH_3OH \rightarrow Fe(CO)(CH_3OH)_2^+}\ (m/z\ 148) + \mathrm{CO}$$

$$k = 3.8 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)_2(CH_3OH)^+ + CH_3OH \rightarrow Fe(CH_3OH)_2^+}\ (m/z\ 120) + 2\ \mathrm{CO}$$

$$k = 6.5 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{FeCO(CH_3OH)^+ + CH_3OH \rightarrow Fe(CH_3OH)_2^+ + CO}$$

$$k=1.1 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}$$

Surprisingly, $Fe(CO)(CH_3OH)_2^+$ (m/z 148) did not undergo substitution of the last CO ligand, since $Fe(CH_3OH)_3^+$ (m/z 152) was not detected.

For very long reaction times, slow decay of $Fe(CO)(CH_3OH)_2^+$ (m/z 148) was observed, along with increase of $Fe(CH_3OH)_2^+$ (m/z 120) and appearance of low amounts of m/z 150 and m/z 180 ions

$$\mathrm{Fe(CO)(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CH_3OH)_2^+}\ (m/z\ 120) + [\mathrm{HCOOCH_3}]$$

$$k = 4.9 \times 10^{-12}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CH_2O)(CH_3OH)_2^+}\ (m/z\ 150) + \mathrm{CH_2O}$$

$$k = 4.1 \times 10^{-12}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CO)(CH_3OH)_3^+}\ (m/z\ 180)$$

$$k_a = 4.3 \times 10^{-23}\ \mathrm{cm^6\ s^{-1}}$$

The structures written for ions and neutrals involved in these reactions seem the most likely but other possibilities can be considered (see sec. 4).

Like in the $Fe(CO)_2^+$ system, side reactions involving residual water are detected: $Fe(CO)_2(H_2O)^+$ is present in low amount (1.4%) at the beginning of the reaction, and reacts further with methanol

$$\mathrm{Fe(CO)_3^+ + H_2O \rightarrow Fe(CO)_2(H_2O)^+}\ (m/z\ 130) + \mathrm{CO}$$

$$k \approx 1\text{–}2 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)_2(H_2O)^+ + CH_3OH \rightarrow Fe(CO)(H_2O)(CH_3OH)^+}\ (m/z\ 134) + \mathrm{CO}$$

$$k = 8 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)_2(H_2O)^+ + CH_3OH \rightarrow Fe(H_2O)(CH_3OH)^+}\ (m/z\ 106) + 2\ \mathrm{CO}$$

$$k = 8 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)(H_2O)(CH_3OH)^+ + CH_3OH \rightarrow Fe(CO)(CH_3OH)_2^+ + H_2O}$$

$$k = 3 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(H_2O)(CH_3OH)^+ + CH_3OH \rightarrow Fe(CH_3OH)_2^+ + H_2O}$$

$$k = 4 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

Like $Fe(CO)(H_2O)^+$, $Fe(CO)_2(H_2O)^+$ ion reacts with methanol by substitution of a CO ligand rather than H_2O, since a null rate constant is found for H_2O

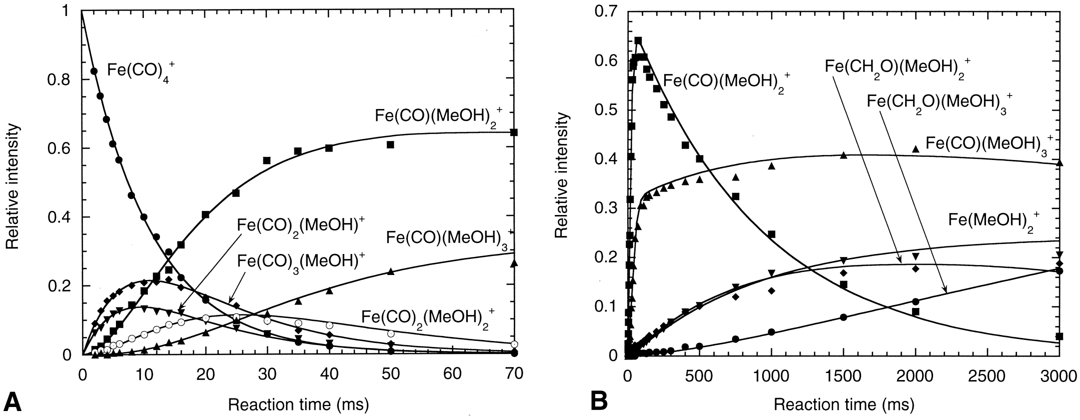


Fig. 4. Dependence of ion distribution with reaction time for the reaction of $Fe(CO)_4^+$ with methanol (reaction pressure: 2.6×10^{-6} Torr): *m/z* 168, $Fe(CO)_4^+$ (circle); *m/z* 172, $Fe(CO)_3(CH_3OH)^+$ (diamond); *m/z* 176, $Fe(CO)_2(CH_3OH)_2^+$ (circle); *m/z* 180, $Fe(CO)(CH_3OH)_3^+$ (triangle); *m/z* 144, $Fe(CO)_2(CH_3OH)^+$ (inverted triangle); *m/z* 148, $Fe(CO)(CH_3OH)_2^+$ (square); *m/z* 120, $Fe(CH_3OH)_2^+$ (inverted triangle); *m/z* 150, $Fe(CH_2O)(CH_3OH)_2^+$ (diamond); *m/z* 182, $Fe(CH_2O)(CH_3OH)_3^+$ (circle). Solid lines are fits corresponding to the reaction schemes and rate constants reported in text. (a) Short reaction times and (b) long reaction times. For clarity, only the *m/z* 148 and 180 ions are shown at both time scales.

substitution. This ion also undergoes substitution of two CO ligands by one methanol molecule, similarly to $Fe(CO)_3^+$.

3.4. Reactivity of $Fe(CO)_4^+$ with methanol

The abundance curves corresponding to reaction of $Fe(CO)_4^+$ with methanol are reported in Fig. 4. The major trends of the reactivity are the same as in the $Fe(CO)_3^+/CH_3OH$ system. Introduction of a relaxation delay in the second cell does not modify the branching ratios or any of the curve features. The following reactions are observed for relatively short reaction times:

$$Fe(CO)_4^+ + CH_3OH$$

$$\rightarrow Fe(CO)_3(CH_3OH)^+ \ (m/z\ 172) + CO$$

$$k = 6.3 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_4^+ + CH_3OH$$

$$\rightarrow Fe(CO)_2(CH_3OH)^+ \ (m/z\ 144) + 2\ CO$$

$$k = 4.6 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_3(CH_3OH)^+ + CH_3OH$$

$$\rightarrow Fe(CO)_2(CH_3OH)_2^+ \ (m/z\ 176) + CO$$

$$k = 5.8 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_3(CH_3OH)^+ + CH_3OH$$

$$\rightarrow Fe(CO)(CH_3OH)_2^+ \ (m/z\ 148) + 2\ CO$$

$$k = 4.8 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_2(CH_3OH)_2^+ + CH_3OH$$

$$\rightarrow Fe(CO)(CH_3OH)_3^+ (m/z\ 180) + CO$$

$$k = 6.7 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_2(CH_3OH)^+ + CH_3OH$$

$$\rightarrow Fe(CO)(CH_3OH)_2^+ + CO$$

$$k = 1.40 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}$$

Similarly to the $Fe(CO)_3^+/CH_3OH$ system, the last CO ligand of $Fe(CO)(CH_3OH)_3^+$ is not substituted by methanol since $Fe(CH_3OH)_4^+$ is not detected. After a few hundreds of milliseconds, the evolution of product distribution confirms the reactivity of $Fe(CO)(CH_3OH)_2^+$ observed in the $Fe(CO)_3^+/CH_3OH$ system: decrease of *m/z* 148 ion, slow increase of *m/z*

120 and 180, and formation of *m/z* 150 ion. A new ion of *m/z* 182 appears later. The relative intensities of these ions are fitted using the following reaction scheme:

$$\mathrm{Fe(CO)(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CH_3OH)_2^+}\ (m/z\ 120) + \mathrm{[HCOOCH_3]}$$

$$k = 4.6 \times 10^{-12}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CH_2O)\ (CH_3OH)_2^+}\ (m/z\ 150) + \mathrm{CH_2O}$$

$$k = 5.1 \times 10^{-12}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CO)(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CO)(CH_3OH)_3^+}\ (m/z\ 180)$$

$$k_a = 3.7 \times 10^{-23}\ \mathrm{cm^6\ s^{-1}}$$

$$\mathrm{Fe(CO)(CH_3OH)_3^+ + CH_3OH \rightarrow Fe(CH_2O)(CH_3OH)_3^+}\ (m/z\ 182) + \mathrm{CH_2O}$$

$$k = 8.9 \times 10^{-13}\ \mathrm{cm^3\ s^{-1}}$$

$$\mathrm{Fe(CH_2O)(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CH_2O)(CH_3OH)_3^+}\ (m/z\ 182)$$

$$k_a = 2.8 \times 10^{-23}\ \mathrm{cm^6\ s^{-1}}$$

Substitution of two CO ligands on $\mathrm{Fe(CO)_2(CH_3OH)^+}$, leading to $\mathrm{Fe(CH_3OH)_2^+}$ (*m/z* = 120), could be expected since this reaction is observed in the $\mathrm{Fe(CO)_3^+/CH_3OH}$ system. The raw intensity of *m/z* 120 ion is actually well fitted at short reaction time if this reaction is introduced (the corresponding rate constant being ~10 times smaller than for simple substitution). However, several very minor ions which cannot be completely eliminated from the initial reaction mixture lead to $\mathrm{Fe(CH_3OH)_2^+}$ as major terminal product (the relative intensity of each of these ions for a very short reaction time of 4 ms is indicated as % in parentheses): $\mathrm{Fe(CO)(CH_3OH)^+}$ (*m/z* 116, 0.5%), $\mathrm{Fe(CO)_2(H_2O)^+}$ (*m/z* 130, 0.5%), $\mathrm{Fe(CO)_3^+}$ and ^{13}C isotope (*m/z* 140, 1.2% and *m/z* 141, 0.5%).

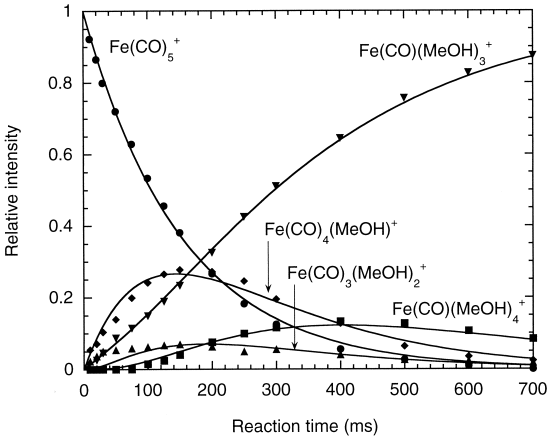


Fig. 5. Dependence of ion distribution with reaction time for the reaction of $\mathrm{Fe(CO)_5^+}$ with methanol (reaction pressure: 3.5×10^{-6} Torr): *m/z* 196, $\mathrm{Fe(CO)_5^+}$ (circle); *m/z* 200, $\mathrm{Fe(CO)_4(CH_3OH)^+}$ (diamond); *m/z* 204, $\mathrm{Fe(CO)_3(CH_3OH)_2^+}$ (triangle); *m/z* 212, $\mathrm{Fe(CO)(CH_3OH)_4^+}$ (square); *m/z* 180, $\mathrm{Fe(CO)(CH_3OH)_3^+}$ (inverted triangle). Solid lines are fits corresponding to the reaction schemes and rate constants reported in text.

Therefore the *m/z* 120 intensity has to be corrected by subtracting the part resulting from reaction of these minor ions. If this is done, the reaction of formation of $\mathrm{Fe(CH_3OH)_2^+}$ from $\mathrm{Fe(CO)_2(CH_3OH)^+}$ is unnecessary, and the data are best fitted by assuming that $\mathrm{Fe(CH_3OH)_2^+}$ is formed by slow reaction of $\mathrm{Fe(CO)(CH_3OH)_2^+}$ (*m/z* 148) exclusively. If $\mathrm{Fe(CH_3OH)_2^+}$ is formed from $\mathrm{Fe(CO)_2(CH_3OH)^+}$, the corresponding rate constant is less than $5 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$, which is too small to be measurable in the presence of the other reaction channels.

3.5. Reactivity of $\mathrm{Fe(CO)_5^+}$ with methanol

The abundance curves corresponding to reaction of $\mathrm{Fe(CO)_5^+}$ with methanol are reported in Fig. 5. Reactivity studies on $\mathrm{Fe(CO)_5^+}$ are experimentally much more difficult than those on other $\mathrm{Fe(CO)_n^+}$ ions, since electron impact ionization always yields very low amounts of $\mathrm{Fe(CO)_5^+}$ ions: at electron energies larger than ~20 eV $\mathrm{Fe(CO)_5^+}$ is a very minor product due to fragmentation, while lower electron energies lead to inefficient ionization.

Because of this low amount of reactant ions the signal-to-noise ratio is poor. Consequently there is a large uncertainty on minor ion intensities: only relative intensities larger than ~3% could be reliably measured, while in all the other experiments abundances less than 1% are easily determined. The imperfect matching of data fits with experimental points for low relative intensities is probably due to this experimental uncertainty. The low signal-to-noise ratio also precluded the use of a relaxation delay in the second cell, since a loss in ion transmission results from each additional step included in the pulse sequence. However, involvement of excited $Fe(CO)_5^+$ in the reactions is unlikely since $Fe(CO)_5^+$ reacts very slowly, so that collisional deactivation of potentially excited states should be faster than their reactions.

The reactivity of $Fe(CO)_5^+$ follows the same trends as that of $Fe(CO)_4^+$, but the former is much less reactive. Therefore some of the intermediate product ions are not detected, since they are consumed more rapidly than they are generated. For the successive substitutions involving pentacoordinated complexes, the detectable steps are the following:

$$Fe(CO)_5^+ + CH_3OH \rightarrow Fe(CO)_4(CH_3OH)^+ \ (m/z\ 200) + CO$$

$$k = (4.4\text{–}4.5) \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_4(CH_3OH)^+ + CH_3OH \rightarrow Fe(CO)_3(CH_3OH)_2^+ \ (m/z\ 204) + CO$$

$$k = (3.7\text{–}6.5) \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_3(CH_3OH)_2^+ + 2CH_3OH \rightarrow\rightarrow Fe(CO)(CH_3OH)_4^+ \ (m/z\ 212) + 2\ CO$$

$$k = (9.4\text{–}13.5) \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

The last reaction implies two successive substitutions, rather than an unlikely termolecular reaction. The first substitution step leads to the intermediate $Fe(CO)_2(CH_3OH)_3^+$ (*m/z* 208) which is not detected since it reacts further to $Fe(CO)(CH_3OH)_4^+$ as soon as formed. Therefore the measured rate constant refers to the first, rate-limiting step of the global process, corresponding to formation of the undetected $Fe(CO)_2(CH_3OH)_3^+$ intermediate.

As in the $Fe(CO)_3^+$ and $Fe(CO)_4^+$ cases, the last CO ligand is not substituted by methanol. For each reaction two extreme values are given for the rate constants because the data are consistent with a whole range of different rate constant sets relative to the general reaction schemes, as explained in the following.

Substitutions leading to tetracoordinated complexes give only $Fe(CO)(CH_3OH)_3^+$ (*m/z* 180) in measurable amount. Traces of $Fe(CO)_2(CH_3OH)_2^+$ (*m/z* 176) were also detected. Several reaction pathways may contribute to the formation of $Fe(CO)(CH_3OH)_3^+$, since the "5-to-4-ligand step" corresponding to substitution of two CO by one methanol may take place at different stages. Due to the missing reaction intermediates, these pathways cannot be distinguished from each other, so that many different sets of rate constants lead to an acceptable fit of the data. In particular, the rate constant for the formation of $Fe(CO)(CH_3OH)_3^+$ from $Fe(CO)_3(CH_3OH)_2^+$ (*m/z* 200), corresponding to the 5-to-4-ligand step occurring on this ion, may be varied from zero to 1.4×10^{-10} cm^3 s^{-1}, associated to rate constants varying from 3.0×10^{-11} to 0 cm^3 s^{-1} for the formation of $Fe(CO)(CH_3OH)_3^+$ from $Fe(CO)_4(CH_3OH)^+$ (*m/z* 204). The range of rate constants which is given for each reaction of the $Fe(CO)_5^+/CH_3OH$ system corresponds to these two extreme cases. The different global processes leading to $Fe(CO)(CH_3OH)_3^+$ are

$$Fe(CO)_5^+ + 3\ CH_3OH \rightarrow\rightarrow\rightarrow Fe(CO)(CH_3OH)_3^+ + 4CO$$

$$k = (1.2\text{–}1.4) \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_4(CH_3OH)^+ + 2\ CH_3OH \rightarrow\rightarrow Fe(CO)(CH_3OH)_3^+ + 3\ CO$$

$$k = (0\text{–}3.0) \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

$$Fe(CO)_3(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CO)(CH_3OH)_3^+ + 2\ CO$$

$$k = (0\text{–}1.4) \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

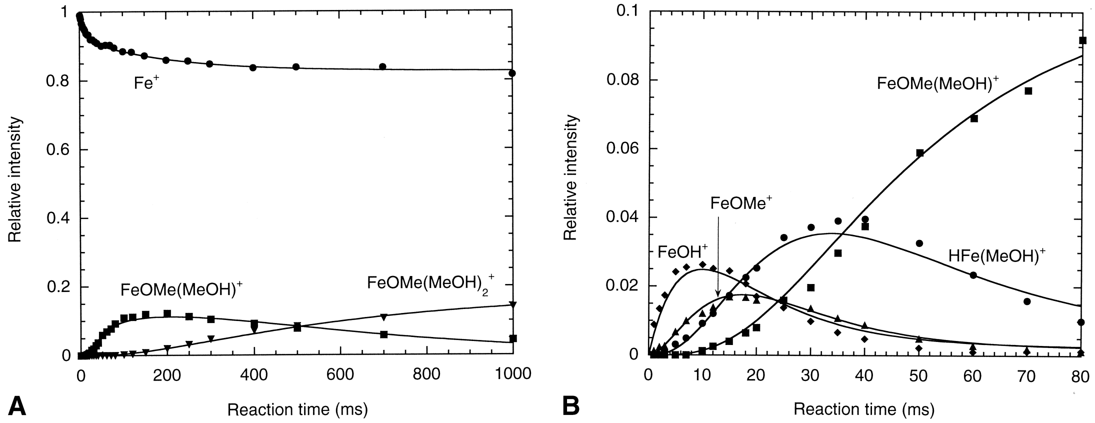


Fig. 6. Dependence of ion distribution with reaction time for the reaction of Fe^+ with methanol (reaction pressure: 3.5×10^{-6} Torr): *m/z* 56, Fe^+ (circle); *m/z* 73, $FeOH^+$ (diamond); *m/z* 87, $FeOCH_3^+$ (triangle); *m/z* 89, $HFe(CH_3OH)^+$ (λ); *m/z* 119, $FeOCH_3(CH_3OH)^+$ (square); *m/z* 151, $FeOCH_3(CH_3OH)_2^+$ (inverted triangle). Solid lines are fits corresponding to the reaction schemes and rate constants reported in text. (a) Major ions and (b) low intensity products detected at short reaction times. For clarity, only the *m/z* 119 ion is shown at both time scales.

The rate constants measured for the first and second reactions refer to their first, rate-limiting step corresponding to substitution of two CO by one methanol, forming the intermediates $Fe(CO)_3(CH_3OH)^+$ (*m/z* 172, undetected) and $Fe(CO)_2(CH_3OH)_2^+$ (*m/z* 176, detected as traces), respectively. Further substitutions on these tetracoordinated intermediates were expected to be fast compared to their formation, since the substitution rate constants measured in the $Fe(CO)_4^+/CH_3OH$ system are in the 10^{-10}–10^{-9} $cm^3\ s^{-1}$ range.

It can be noticed that no ions bearing three or two ligands are detected in the reaction products, in contrast to the $Fe(CO)_4^+/CH_3OH$ system. For reaction times longer than ~600 ms, a slight decrease of $Fe(CO)(CH_3OH)_4^+$ ion is observed, which can be attributed to the following reaction:

$$Fe(CO)(CH_3OH)_4^+ \rightarrow Fe(CO)(CH_3OH)_3^+ + CH_3OH$$

$$k = (3.1\text{–}5.1) \times 10^{-11}\ cm^3\ s^{-1}$$

3.6. Reactivity of Fe^+ with methanol

The abundance curves corresponding to reaction of Fe^+ with methanol are reported in Fig. 6. The reactivity of Fe^+ with methanol is only due to excited states, as shown by the decay curve of Fe^+: after a fast decay down to ~88% in the first 100 ms, Fe^+ relative intensity decreases much more slowly, being still larger than 80% after one second reaction time. The reactivity observed for Fe^+ remains the same in the absence of ejection of the undesired ions. This shows that this reactivity is not due to Fe^+ ions with excess kinetic energy gained during ejection of other ions (a process which may happen if the ejection conditions are not fully appropriate), but to electronically excited $(Fe^+)^*$. Introduction of a 300 ms radiative relaxation delay in the second cell before reaction brings little change in product amount and distribution.

The primary reaction product of excited Fe^+ is $FeOH^+$. The shape of the Fe^+ intensity curve indicates that at least two excited states of Fe^+, both leading to $FeOH^+$ but with different rates, are required to account for the data. Successive formation of $FeOCH_3^+$, $HFe(CH_3OH)^+$, and $(CH_3OH)FeOCH_3^+$ is then observed. Even if we assume that only two excited states $(Fe^+)^{**}$ and $(Fe^+)^*$ are involved, it is difficult to estimate separately their initial populations, the rate constants for their collisional relaxation, and the rate constants of their reactions with methanol since both of these excited states give the same product $FeOH^+$. Many different sets of values attributed to those parameters actually lead to an acceptable fit of the data, whereas each of the rate constants found for the subsequent reactions must remain in a narrow range of values in order to fit the data. Therefore in the scheme used for data fit we introduce the initial populations reported in literature [11]: $(Fe^+)^{**}$ 0.40, $(Fe^+)^*$ 0.25, Fe^+ 0.35. The species $(Fe^+)^*$ and $(Fe^+)^{**}$ mentioned in the reaction scheme refer respectively to $^4F\ Fe^+$ (0.25 eV above ground state), and to all the higher energy states considered together (see sec. 4)

$$(Fe^+)^{**} + CH_3OH \rightarrow (Fe^+)^* + CH_3OH$$

$$k = 5.8 \times 10^{-10}\ cm^3\ s^{-1}$$

$$(Fe^+)^* + CH_3OH \rightarrow Fe^+ + CH_3OH$$

$$k = 3.7 \times 10^{-11}\ cm^3\ s^{-1}$$

$$(Fe^+)^{**} + CH_3OH$$

$$\rightarrow FeOH^+\ (m/z\ 73) + CH_3^{\cdot}$$

$$k = 1.5 \times 10^{-10}\ cm^3\ s^{-1}$$

$$(Fe^+)^* + CH_3OH$$

$$\rightarrow FeOH^+ + CH_3^{\cdot}$$

$$k = 7.2 \times 10^{-12}\ cm^3\ s^{-1}$$

$$FeOH^+ + CH_3OH$$

$$\rightarrow FeOCH_3^+\ (m/z\ 87) + H_2O$$

$$k = 1.2 \times 10^{-9}\ cm^3\ s^{-1}$$

$$FeOCH_3^+ + CH_3OH$$

$$\rightarrow HFe(CH_3OH)^+\ (m/z\ 89) + CH_2O$$

$$k = 1.4 \times 10^{-9}\ cm^3\ s^{-1}$$

$$HFe(CH_3OH)^+ + CH_3OH$$

$$\rightarrow (CH_3OH)FeOCH_3^+\ (m/z\ 119) + H_2$$

$$k = 4.3 \times 10^{-10}\ cm^3\ s^{-1}$$

$$Fe[C_2, H_7, O_2](1)^+$$

$$\rightarrow Fe[C_2, H_7, O_2](2)^+$$

$$k = 2.0 \times 10^{-11}\ cm^3\ s^{-1}$$

$$Fe[C_2, H_7, O_2](2)^+ + CH_3OH$$

$$\rightarrow (CH_3OH)_2FeOCH_3^+\ (m/z\ 151)$$

$$k_a = 1.2 \times 10^{-21}\ cm^6\ s^{-1}$$

The two final steps are the same as those observed in the $Fe(CO)^+/CH_3OH$ system.

4. Discussion

4.1. Major trends of the substitution reactions

Unless otherwise indicated, the thermodynamic data used in the discussion are taken from [3] for iron ionic complexes, from [12] and [13] for other neutral or ionic species.

The $Fe(CO)_n^+/CH_3OH$ system displays different types of reactivities depending on n. For $n = 1$ and 2, substitutions of one CO ligand by one methanol molecule occur until no CO ligand is present on the metal, leading to $Fe(CH_3OH)^+$ and $Fe(CH_3OH)_2^+$, respectively. The case $n = 1$ is due to further reactions of the monoligated species $Fe(CH_3OH)^+$ with methanol, which will be discussed separately. On the contrary, for $n = 3$, 4, and 5 the last CO ligand is not substituted by methanol: ions $FeCO(CH_3OH)_2^+$, $FeCO(CH_3OH)_3^+$, and $FeCO(CH_3OH)_4^+$ were respectively obtained, but in none of the experiments the species $Fe(CH_3OH)_n^+$ ($n = 3$, 4, or 5) were detected. These trends are similar to those observed for substitution reactions in the $Fe(CO)_n^+/H_2O$ system [14].

Except for $Fe(CO)_5^+$ which is much less reactive than the other iron carbonyl ions, the rate constants of all the observed substitution reactions are of the same order of magnitude, remaining in a range of $3–12 \times 10^{-10}\ cm^3\ s^{-1}$ whatever the number of ligands. It can be noticed that $Fe(CO)_2(CH_3OH)_2^+$ is easily converted into $Fe(CO)(CH_3OH)_3^+$ while the less hindered $Fe(CO)(CH_3OH)_2^+$ does not react. This means that steric hindrance is not a likely explanation for the absence of substitution of the last CO ligand for $n = 3–5$. If thermodynamically allowed, these substitutions would occur at similar rates as all the other ones. Therefore it seems likely that substitution of the last

Table 1
Summary of the rate constants for the CO substitution reactions; the results concerning undoubtedly thermalized reactant ions are underlined; those concerning probably "hot" reactant ions are written in parentheses

Reactant ion	Total rate constant (10^{-10} cm^3 s^{-1})	Product	Rate constant[a] (10^{-10} cm^3 s^{-1})
$FeCO^+$	11.7	$Fe(CH_3OH)^+$	11.7
$Fe(CO)_2^+$	12.0	$Fe(CO)(CH_3OH)^+$	12.0
$Fe(CO)(CH_3OH)^+$	11.1	$Fe(CH_3OH)_2^+$	11.1
$Fe(CO)_3^+$	11.0	$Fe(CO)_2(CH_3OH)^+$	6.4
		$Fe(CO)(CH_3OH)^+$	4.6
$Fe(CO)_2(CH_3OH)^+$	14.0	$Fe(CO)(CH_3OH)_2^+$	14.0
		$Fe(CH_3OH)_2^+$	≈0
$Fe(CO)_4^+$	10.9	$Fe(CO)_3(CH_3OH)^+$	6.3
		$Fe(CO)_2(CH_3OH)^+$	4.6
$Fe(CO)_3(CH_3OH)^+$	10.6	$Fe(CO)_2(CH_3OH)_2^+$	(5.8)[a]
		$Fe(CO)(CH_3OH)_2^+$	≈0[b]
$Fe(CO)_2(CH_3OH)_2^+$	(6.7)[a]	$Fe(CO)(CH_3OH)_3^+$	(6.7)
$Fe(CO)_5^+$	0.6	$Fe(CO)_4(CH_3OH)^+$	0.45
		$Fe(CO)_3(CH_3OH)^+$	0.13
$Fe(CO)_4(CH_3OH)^+$	0.7[c]	$Fe(CO)_3(CH_3OH)_2^+ + Fe(CO)_2(CH_3OH)_2^+$?	

[a] In analogy with the trends observed for simple substitution reactions occurring in two systems, the thermal rate constant should be larger than this value, which is measured for hot ions (see text).

[b] Due to the absence of this reaction in the $Fe(CO)_5^+$ system (see text).

[c] Reactant ions considered as nearly thermalized because the reaction is slow.

CO is not thermodynamically allowed for $n = 3–5$. Although no detailed theoretical study on $Fe(CO)_x(ROH)_y^+$ ions is available, a particular stability of $Fe(CO)(CH_3OH)_n^+$ ions would not be surprising since electron donation by several methanol ligands increases the metal ability to backdonation, therefore strengthening the remaining Fe—CO bond.

Another feature of the reactivity of ions bearing at least three ligands is the possibility of substituting two CO ligands by one methanol molecule, as already mentioned by Allison and Ridge [5]. For the $Fe(CO)_3^+$ and $Fe(CO)_4^+$ systems we checked that the intensity of the corresponding products is not modified if a relaxation delay in the 10–300 ms range is provided before the reaction. Since it is very unlikely that electronically and/or vibrationally excited states of $Fe(CO)_n^+$ have such long lifetimes, we can conclude that this reaction pathway is actually due to thermal $Fe(CO)_n^+$ ions, so that valid thermodynamic implications can be drawn from these reactions.

It is interesting to notice that net CO loss was never observed in the reaction schemes [except for the slow conversion of $Fe(CO)(CH_3OH)_2^+$ into $Fe(CH_3OH)_2^+$, which will be discussed later]. For instance no Fe^+ is detected in the reaction products of $Fe(CO)^+$, showing that the following reaction does not occur:

$$FeCO^+ + CH_3OH \xrightarrow{\;-x\;} Fe^+ + CH_3COOH$$

Since this reaction would be exothermic by 68 kJ mol^{-1}, this indicates a barrier to the rearrangement of the intermediate complex $Fe(CO)(CH_3OH)^{+*}$ to $Fe(CH_3COOH)^{+*}$ by CO insertion within this complex.

4.2. Values of the rate constants, energy effects

The upper limit of the rate constant for reactions of methanol with a positive ion is given by the collision rate k_{ADO} $(CH_3OH) = 1.7 \times 10^{-9}$ cm^3 s^{-1} [15,16]. For $n = 1–4$, nearly all the ligand substitution reactions observed have a rate constant larger than 0.2 k_{ADO}. As shown in Table 1, the total reaction rate constants of the different species all have remarkably similar values, corresponding to 0.7 k_{ADO}. For $\mathrm{Fe(CO)_5^+}$ the total rate constant drops to 0.04 k_{ADO}, consistently with the general lack of reactivity of $\mathrm{Fe(CO)_5^+}$ compared to the other iron carbonyl cations. This lack of reactivity may be due either to steric hindrance or to a particularly short lifetime of the intermediate complex $[\mathrm{Fe(CO)_5(CH_3OH)^+}]^*$, which is a 19-electron species.

It can be noticed that in several cases the apparent rate constants for the same reaction appear clearly different in two different systems. The most striking example is the reactions of $\mathrm{Fe(CO)_2(CH_3OH)^+}$ (*m/z* 144), which are observed both in the $\mathrm{Fe(CO)_3^+}$/$\mathrm{CH_3OH}$ and in the $\mathrm{Fe(CO)_4^+}$/$\mathrm{CH_3OH}$ systems. Two products are formed in the $\mathrm{Fe(CO)_3^+}$/$\mathrm{CH_3OH}$ system, $\mathrm{Fe(CO)(CH_3OH)_2^+}$ (*m/z* 148, rate constant k_{148}) and $\mathrm{Fe(CH_3OH)_2^+}$ (*m/z* 120, rate constant k_{120}) whereas in the second system only $\mathrm{Fe(CO)(CH_3OH)_2^+}$ is formed at a measurable rate. The rate constants measured in the two systems are compared as follows:

	$\mathrm{Fe(CO)_3^+}$ system	$\mathrm{Fe(CO)_4^+}$ system
k_{148} (10^{-10} cm^3 s^{-1})	3.8	14.0
k_{120} (10^{-10} cm^3 s^{-1})	6.5	$<$0.5
Total reaction rate constant ($k_{148} + k_{120}$) (10^{-10} cm^3 s^{-1})	10.3	14.0
Branching ratio k_{148}/k_{120}	0.6	$>$30

From the $\mathrm{Fe(CO)_3^+}$ to the $\mathrm{Fe(CO)_4^+}$ system, k_{148} is multiplied by nearly 4 while k_{120} drops to 0 or nearly 0, so that the branching ratio is multiplied by a large factor, at least 45. The values of the apparent rate constants obtained from curve fits have been checked to be reproducible within 20% from one experiment to another, which is much less than the differences observed. These apparent discrepancies can be due to a difference in the internal energies of the ions, resulting from different formation mechanisms. Since replacement of two CO by one methanol is necessarily less exothermic than replacement of one CO by one methanol, $\mathrm{Fe(CO)_2(CH_3OH)^+}$ formed from $\mathrm{Fe(CO)_4^+}$ should have been internal and/or kinetic energy than $\mathrm{Fe(CO)_2(CH_3OH)^+}$ formed from $\mathrm{Fe(CO)_3^+}$. If we assume that ions possessing less kinetic and/or internal energy react preferentially through the most exothermic pathway, whereas the less exothermic or slightly endothermic pathways are easier for ions having more energy, the differences observed between the measured rate constants appear fully consistent: k_{148}, corresponding to the most exothermic pathway, is larger for low energy $\mathrm{Fe(CO)_2(CH_3OH)^+}$ ions formed from $\mathrm{Fe(CO)_4^+}$ than for higher energy ions formed from $\mathrm{Fe(CO)_3^+}$, while the reverse is true for k_{120}. Since k_{120} is very small in the $\mathrm{Fe(CO)_4^+}$ system, the corresponding reaction of $\mathrm{Fe(CO)_2(CH_3OH)^+}$ giving $\mathrm{Fe(CH_3OH)_2^+}$ may be endothermic. The total reaction rate constant is much less dependent on the production pathway of the reactant ions than the branching ratio, since it changes by a factor less than 1.4 from one system to the other. The larger value, corresponding to the less energetic reactant ions, is close to k_{ADO}.

This interpretation is confirmed by considering the rate constants of other reactions involved in two different systems. Only one of these reactions is fast: methanol substitution on $\mathrm{Fe(CO)(CH_3OH)^+}$ (*m/z* 116) leading to $\mathrm{Fe(CH_3OH)_2^+}$ (*m/z* 120), occurring either with $\mathrm{Fe(CO)(CH_3OH)^+}$ formed by simple substitution on $\mathrm{Fe(CO)_2^+}$ or with $\mathrm{Fe(CO)(CH_3OH)^+}$ formed by substitution of two CO ligands on $\mathrm{Fe(CO)_3^+}$. In this case again there is a significant difference between the two measured rate constants, 7.7 and 11.1 × 10^{-10} cm^3 s^{-1}, respectively. As shown in Sec. 4.3 the reaction is probably exothermic by several tens of kJ mol^{-1}, therefore it is not surprising to observe a larger rate constant for the ion formed with less energy. This trend is similar to that of the substitution reaction rate constant k_{148} relative to the $\mathrm{Fe(CO)_2(CH_3OH)^+}$ reaction.

If we now look at the slow reactions found in two systems, as reactions of $\mathrm{FeOCH_3(CH_3OH)^+}$ and $\mathrm{Fe(CO)(CH_3OH)_2^+}$ ions, we observe that the measured rate constants are close to each other within experimental uncertainties. In these cases $k \ll k_{\mathrm{ADO}}$, so that collisional deactivation allows thermalization of most reactant ions. Therefore the formation pathway of reactant ions no longer influences the reaction rate, and reliable thermal rate constants are obtained.

Table 1 summarizes the thermal or nearly thermal

Table 2
Summary of the rate constants concerning rapid reactions involving methanol and methoxy complexes; these values are indicative since they concern probably unthermalized ions

Reactant ion	Rate constant (10^{-10} cm^3 s^{-1})	Product
$Fe(CH_3OH)^+$	6.7	$FeOH(CH_3OH)^+$
$FeOH(CH_3OH)^+$	5.7	$FeOCH_3(CH_3OH)^+$
$FeOH^+$	11.7	$FeOCH_3^+$
$FeOCH_3^+$	14.0	$HFe(CH_3OH)^+$
$HFe(CH_3OH)^+$	4.3	$FeOCH_3(CH_3OH)^+$

rate constants for the substitution processes observed. For reactions occurring in two different systems, the rate constant measured for the reactant ions formed through the less exothermic pathway is retained in Table 1, since it can be considered as the closest to the thermal rate constant according to the discussion above. As indicated in Table 1, the thermal rate constants of simple substitution reactions are probably higher than the experimental rate constants measured on “hot” reactant ions, in analogy with the trends observed for the reactions involved in two different systems. Substitution of two CO ligands on $Fe(CO)_3(CH_3OH)^+$ ion is observed in the $Fe(CO)_4^+$ system, where the reactant ion is formed by an exothermic simple substitution. On the other hand, that reaction does not occur significantly on the nearly thermal $Fe(CO)_3(CH_3OH)^+$ ions formed in the $Fe(CO)_5^+$ system since neither its product $Fe(CO)(CH_3OH)_2^+$ nor products from further reactions are detected. Therefore a zero value is assigned to the corresponding rate constant.

Table 2 summarizes the rate constants found for other fast reactions concerning $Fe(CH_3OH)^+/CH_3OH$ and Fe^+/CH_3OH systems. Since in these cases we have no indication on the internal energies of the reactant ions, nor on their influence on the reaction rates, these values are only indicative of the thermal rate constants. The rate constants for slow processes are summarized in Table 3.

4.3. Thermodynamic implications

All the reaction sequences observed from thermalized $Fe(CO)_n^+$ ions and methanol are necessarily thermodynamically allowed. In particular, sequences involving the replacement of two CO ligands by one methanol molecule enable one to assign minimum values to the bond energies of the methanol ligand, using the successive bond energies of $Fe(CO)_n^+$: 129, 148, 70, 104, and 104, kJ mol^{-1} [17].

Experimental determination of the bond energy of methanol to bare Fe^+, based on methanol substitution reaction on $Fe(C_2H_4)^+$, gave $Fe^+–(CH_3OH) = 144 \pm 9$ kJ mol^{-1} [18]. Another experimental evaluation based on measurement of methanol substitution efficiency on $Fe(CS_2)^+$ led to a value of 170 ± 7 kJ mol^{-1} [19,20], while calculations give at least 192 kJ mol^{-1} [21]. Formation of $Fe(CH_3OH)^+$ from $Fe(CO)^+$ but not from $Fe(CO)_2^+$ gives

Table 3
Summary of the rate constants concerning slow processes

Reactant ion	Product	First-order rate constant (10^{-12} cm^3 s^{-1})	Second-order rate constant[a] (10^{-23} cm^6 s^{-1})
$FeOCH_3(CH_3OH)^+$	$FeOCH_3(CH_3OH)_2^+$		130
$Fe(CO)(CH_3OH)_2^{+a}$	$Fe(CH_3OH)_2^+$	4.6	
	$Fe(CH_2O)(CH_3OH)_2^+$	5.1	
	$Fe(CO)(CH_3OH)_3^+$		3.7
$Fe(CH_2O)(CH_3OH)_2^+$	$Fe(CH_2O)(CH_3OH)_3^+$		2.8
$Fe(CO)(CH_3OH)_3^+$	$Fe(CH_2O)(CH_3OH)_3^+$	0.9	
$Fe(CO)(CH_3OH)_4^+$	$Fe(CO)(CH_3OH)_3^+$	4	

[a] Experimental values obtained from the $Fe(CO)_4^+/CH_3OH$ system. These values, which differ by less than 20% from those obtained from the $Fe(CO)_3^+/CH_3OH$ system, seem the most reliable since the reactant ions are both less energetic and more abundant than in the $Fe(CO)_3^+$ system.

$129\ \mathrm{kJ\ mol^{-1}} \leq \mathrm{Fe^+–(CH_3OH)} \leq 277\ \mathrm{kJ\ mol^{-1}}$, which is consistent with the reported values but does not give any more information.

The following minimum values can be assigned to the $\mathrm{Fe(CO)}_n^+$–$\mathrm{CH_3OH}$ bond energies, on the basis of the formation reactions of $\mathrm{Fe(CO)}_n\mathrm{(CH_3OH)^+}$ ions:

$\mathrm{Fe(CO)_3^+} \rightarrow \mathrm{Fe(CO)(CH_3OH)^+}$ leads to

$$\mathrm{Fe(CO)^+–(CH_3OH)} \geq 218\ \mathrm{kJ\ mol^{-1}}$$

$\mathrm{Fe(CO)_4^+} \rightarrow \mathrm{Fe(CO)_2(CH_3OH)^+}$ leads to

$$\mathrm{Fe(CO)_2^+–(CH_3OH)} \geq 174\ \mathrm{kJ\ mol^{-1}}$$

$\mathrm{Fe(CO)_5^+} \rightarrow \mathrm{Fe(CO)_3(CH_3OH)^+}$ leads to

$$\mathrm{Fe(CO)_3^+–(CH_3OH)} \geq 208\ \mathrm{kJ\ mol^{-1}}$$

Assuming $\mathrm{Fe^+–(CH_3OH)} = 144–170\ \mathrm{kJ\ mol^{-1}}$, we observe that the presence of CO ligands results in an increased bond strength between iron and methanol. Conversely, we also show that the presence of a methanol ligand increases the $\mathrm{Fe^+–(CO)}$ bond strength:

$\mathrm{Fe(CO)_3^+} \rightarrow \mathrm{Fe(CO)(CH_3OH)^+}$ leads to

Fe(CH3OH)+–(CO) ≥ 177 kJ mol−1

with $\mathrm{Fe^+–(CH_3OH)} = 170\ \mathrm{kJ\ mol^{-1}}$

Fe(CH3OH)+–(CO) ≥ 203 kJ mol−1

with $\mathrm{Fe^+–(CH_3OH)} = 144\ \mathrm{kJ\ mol^{-1}}$

Formation of $\mathrm{Fe(CH_3OH)_2^+}$ from $\mathrm{Fe(CO)_3^+}$ through two substitution steps gives information on the bond energy of the second methanol ligand:

$\mathrm{Fe(CO)_3^+} \rightarrow \rightarrow \mathrm{Fe(CH_3OH)_2^+}$ leads to

Fe(CH3OH)+–(CH3OH) ≥ 177 kJ mol−1

for $\mathrm{Fe^+–(CH_3OH)} = 170\ \mathrm{kJ\ mol^{-1}}$

Fe(CH3OH)+–(CH3OH) ≥ 203 kJ mol−1

for $\mathrm{Fe^+–(CH_3OH)} = 144\ \mathrm{kJ\ mol^{-1}}$

The second methanol ligand is more strongly bound than the first one, a trend often observed in $\mathrm{LnFe^+}$ complexes [3,22].

4.4. C–O cleavage and subsequent reactions

The particular reactivity of $\mathrm{Fe(CH_3OH)^+}$ with methanol has been mentioned by Allison and Ridge, who showed that C–O cleavage occurs in the complexed methanol molecule rather than in the incoming one. This reaction is thermodynamically allowed provided that the bond energy $\mathrm{FeOH^+–(CH_3OH)}$ is larger than $20\ \mathrm{kJ\ mol^{-1}}$, which is easily fulfilled since this bond energy is expected to be close to $\mathrm{Fe^+–(CH_3OH)} = 170\ \mathrm{kJ\ mol^{-1}}$. Similarly, C–O cleavage in complexed methanol has been observed in the reaction of $\mathrm{Fe(CH_3OH)^+}$ with water [2,23]. It can be noticed that the C–O cleavage observed in $\mathrm{Fe(CH_3OH)^+}$ does not occur if other ligands, either CO or MeOH, are present.

The reaction of $\mathrm{FeOH(CH_3OH)^+}$ with $\mathrm{CH_3OH}$ leading to $\mathrm{FeOCH_3(CH_3OH)^+}$ and $\mathrm{H_2O}$ implies H transfer from the $\mathrm{CH_3OH}$ to the OH ligand. This atom transfer may take place either as a rapid equilibrium within the $\mathrm{FeOH(CH_3OH)^+}$ reactant ion or upon collisional activation by the incoming methanol molecule. Anyway the corresponding barrier is not very high since the reaction is fairly rapid ($k \approx 0.3\ k_{\mathrm{ADO}}$).

The kinetic scheme involving transformation of $\mathrm{FeOCH_3(CH_3OH)^+}$ followed by an association reaction is found both in the $\mathrm{Fe^+/CH_3OH}$ and in the $\mathrm{Fe(CO)^+/CH_3OH}$ systems. For each step the rate constants, respectively, first-order and second-order, differ by less than 10% between the two systems. Differences could have been expected since the $\mathrm{FeOCH_3(CH_3OH)^+}$ ions have different precursors in the two systems. The data suggest that they have however the same structure.

The intermediate step observed before the association reaction of $\mathrm{Fe[C_2, H_7, O_2]^+}$ may correspond to simple collisional deactivation of *m/z* 119 ion which would be formed with excess kinetic and/or internal energy. Since the efficiency of an association reaction sharply decreases with increasing reactant energy, many collisions may be necessary for an ion to get close enough to thermal energy to undergo association efficiently. If the required energy decrease is $100\ \mathrm{kJ\ mol^{-1}}$ and if we assume that each collision with methanol reduces the energy excess of the reactant ion by 25% (a rough estimation based on energy partition on the available degrees of freedom of the $FeOCH_3(CH_3OH)^+/CH_3OH$ system), we find that collisional deactivation is completed after ~20 collisions, corresponding to a rate constant $0.05\ k_{ADO} \approx 8 \times 10^{-11}$ cm^3 s^{-1}. The experimental value 1.9×10^{-11} cm^3 s^{-1} $\approx 0.01\ k_{ADO}$ is significantly lower but in the same order of magnitude, and remains possible as a collisional relaxation rate constant if the energy transfer is not very efficient. This would be the case if a spin conversion has to occur, as it is usual for iron complexes which may be either sextets or quartets in their fundamental state, depending on the nature of the ligands.

Another possibility is isomerization of the *m/z* 119 ion, which may exist either as a methoxy or hydride–formaldehyde complex. The related ion $Fe[O, C, H_3]^+$ has been characterized as a mixture of these two structures separated by a relatively high activation barrier, $FeOCH_3^+$ ion being more stable than $HFe(CH_2O)^+$ [24]. Supposing that the $FeOH(CH_3OH)^+$ or $HFe(CH_3OH)^+$ precursors lead to the formaldehyde rather than methoxy complex, the following isomerization may occur:

$$HFe(O=CH_2)(CH_3OH)^+ \rightarrow FeOCH_3(CH_3OH)^+$$

Further experiments are planned to get more information about the nature of the transformation of *m/z* 119 ion, for instance investigation of CD_3OH reactivity.

It can be noticed that the association reaction for the Fe(II) complex $FeOCH_3(CH_3OH)^+$ is much faster than the association reactions occurring with Fe(I) complexes (Table 3). This may be due to the stronger positive charge on the metal in Fe(II) complex, resulting in stronger ion–dipole interaction. Particularly easy association reactions of Fe(II) compared to Fe(I) ions have been observed in other cases [23].

4.5. Reactivity of bare Fe^+

The reaction of Fe^+ with methanol forming $FeOH^+$ and a methyl radical has been observed by Allison and Ridge [4,5]. This reaction, endothermic by 20 kJ mol^{-1}, is only due to Fe^+ excited states, in consistency with the observation that most of the Fe^+ ions remain unreactive even for long reaction times. The value reported for the apparent rate constant of this reaction, relative to the total amount of Fe^+ produced by electron ionization of $Fe(CO)_5$ at 70 or 280 eV, is 0.8×10^{-10} cm^3 s^{-1} [25]. Considering two populations of excited ions, $(Fe^+)^*$ and $(Fe^+)^{**}$, our results give two rate constants for this reaction: 1.5×10^{-10} cm^3 s^{-1} for $(Fe^+)^{**}$ (40%) and 7.2×10^{-12} cm^3 s^{-1} for $(Fe^+)^*$ (25%), corresponding respectively to 0.6×10^{-10} cm^3 s^{-1} and 1.8×10^{-12} cm^3 s^{-1} relative to total Fe^+. The first value, corresponding to the fast reaction detected at short reaction times, is quite consistent with the earlier report.

Many excited states of Fe^+ have radiative lifetimes of hundreds or thousands seconds [26], therefore it is not surprising that a 300 ms relaxation delay has little effect on the reactivity. Collisional relaxation of metastable excited Fe^+ by various collision gases is much more efficient, and has been investigated by using their reactivity with $Fe(CO)_5$ as an energy probe [27]. According to this study, collisional relaxation by methanol is reported to be very efficient so that it is undisturbed by the reaction leading to $FeOH^+$, but only for a fraction of the $(Fe^+)^*$ population. Our results confirm the latter point since the decay curve of Fe^+ ions show that they still react on a long time scale, as confirmed by the low rate constant of $(Fe^+)^*$ collisional deactivation. Either for $(Fe^+)^{**}$ or $(Fe^+)^*$, the reaction leading to $FeOH^+$ is not negligible against collisional deactivation.

The data show that the rate of formation of $FeOH^+$ is strongly dependent on the Fe^+ electronic state, since at least two types of excited Fe^+ ions can be distinguished: $(Fe^+)^{**}$ reacting in the first 100 ms, and $(Fe^+)^*$ reacting over several hundred milliseconds. The choice of the initial populations $(Fe^+)^{**}$ and $(Fe^+)^*$ is of course somewhat arbitrary: although the state distribution of Fe^+ produced by $Fe(CO)_5$ electron ionization is relatively well known [11], we do not know which states react faster with methanol. The energy of the ^4F state is close to the endothermicity of the reaction, and it seems likely that a barrier to C–O bond cleavage results in slower reaction of the ^4F state taken as $(Fe^+)^*$. It is also possible that the slowly reacting $(Fe^+)^*$ includes higher states. The scheme using only two types of excited Fe^+ ions is certainly oversimplified, but it would be meaningless to consider a more detailed scheme since the data would not provide enough information.

Further reaction of $FeOH^+$ with methanol leads to $FeOCH_3^+$. This could be expected since water elimination is the usual reactivity of $FeOH^+$ with slightly acidic molecules as ammonia [28], acetone [29], or element hydrides [30]. Further reaction of $FeOCH_3^+$ with methanol leading to $HFe(CH_3OH)^+$ has been described [16] and accounted for by the structure equilibrium of $FeOCH_3^+$ mentioned previously, followed by substitution of formaldehyde by methanol. The $HFe(CH_3OH)^+$ ion is an isomer of the known ion $(H_2O)FeCH_3^+$ [31]. Reaction of methanol with $(H_2O)FeCH_3^+$ would be expected to yield $(CH_3OH)FeCH_3^+$, which is not detected. This suggests that structure interconversion of $HFe(CH_3OH)^+$ to $(H_2O)FeCH_3^+$ does not take place in the Fe^+/CH_3OH system.

The observed reaction of $HFe(CH_3OH)^+$ to $(CH_3OH)FeOCH_3^+$ is likely, since the main reaction of FeH^+ with methanol is H_2 elimination [32]. The subsequent reactions are the same as those occurring in the $FeCO^+$ system.

4.6. Evolution of m/z 148 ion

Simultaneous slow formation of *m/z* 120, 150, and 180 ions from $Fe(CO)(CH_3OH)_2^+$ (*m/z* 148) ion has been observed in the $Fe(CO)_3^+$ and $Fe(CO)_4^+$ systems. Although formation of $Fe(CO)(CH_3OH)_3^+$ (*m/z* 180) can be interpreted as a simple association reaction, the two other reactions are necessarily more complex: (1) the structure of *m/z* 150 ion needs to be elucidated since it cannot contain simply CO and methanol ligands, (2) for the formation of *m/z* 120 ion, a simple fragmentation reaction is unlikely since it is significantly endothermic, and this reaction is not fast enough to involve nonthermalized reactant ions. Therefore this process is probably a chemical reaction involving CO activation.

Complementary experiments are obviously required to get a nonambiguous elucidation of the corresponding processes. A tentative interpretation of the data, based on hydrogen transfer reactions within the iron complex, is given.

Formation of *m/z* 150 ion corresponds to net hydrogenation of *m/z* 148 ion, with no other possibility than methanol as hydrogen donor. The neutral product of the reaction would thus be formaldehyde.

$$Fe(CO)(CH_3OH)_2^+ + CH_3OH \rightarrow Fe(CH_2O)(CH_3OH)_2^+ + CH_2O$$

Since this reaction is very slow it may be endothermic by ~20 kJ mol^{-1} if the rate of the reverse reaction is close to the collision rate. Observation of this reaction still implies that the $(CH_3OH)_2Fe^+$–(OCH_2) bond in the product ion is ~60 kJ mol^{-1} more stable than the $(CH_3OH)_2Fe^+$–(CO) bond in the reactant ion, which is significantly larger than the corresponding difference (34 kJ mol^{-1}) between $(CH_2O)_2Fe^+$–(OCH_2) and $(CO)_2Fe^+$–(CO) [17]. Alternatively, other structures involving bond formation between ligands are possible for the product ion. A Fe(III) structure $(CH_3OH)Fe(OCH_3)_2^+$ is also possible, by analogy with the known corresponding Sc(III) complex [33]. However fragmentation of metastable $(CH_3OOCH_3)Fe^+$ ions has shown that $Fe(OCH_3)_2^+$ ion rearranges to the methanol–formaldehyde complex $Fe(CH_2O)(CH_3OH)^+$ [34].

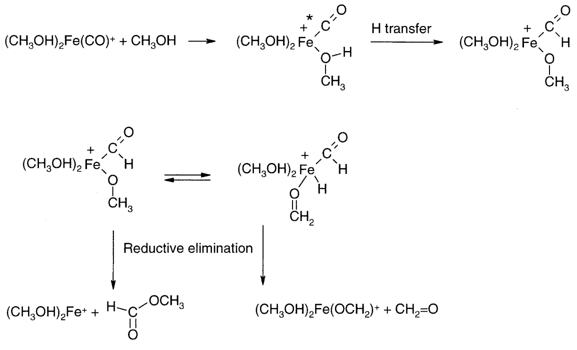
This suggests that the transition state of the reaction would correspond to hydrogen transfer to the CO ligand

$$Fe(CO)(CH_3OH)_2^+ + CH_3OH \rightarrow [Fe(CO)(CH_3OH)_3^+]^*$$

$$[Fe(CO)(CH_3OH)_3^+]^* \rightarrow [Fe(CH_2O)_2(CH_3OH)_2^+]^*$$

$$[Fe(CH_2O)_2(CH_3OH)_2^+]^* \rightarrow Fe(CH_2O)(CH_3OH)_2^+ \ (m/z\ 150) + CH_2O$$

Formation of $Fe(CH_3OH)_2^+$ (*m/z* 120) from $Fe(CO)(CH_3OH)_2^+$ and methanol cannot be explained by the ejection of two CH_2O molecules as the formation of 2 CH_2O from CO and CH_3OH is endothermic by 79 kJ mol^{-1}. Two neutral products are conceivable: CH_3COOH or $HCOOCH_3$, the formation of which from CO and CH_3OH is exothermic by 120 and 50 kJ mol^{-1}, respectively. The mechanism depicted in Scheme 1, leading to neutral $HCOOCH_3$, may account for simultaneous formation of *m/z* 150 and *m/z* 120 ions. Hydrogen transfer from an alkoxide to a ketone ligand has been observed within iron (I) complexes [35].



Scheme 1.

Formation of *m/z* 182 ion, observed in the $Fe(CO)_4^+/CH_3OH$ system, is also consistent with hydrogen transfer within the iron complex. The kinetic data suggest that $Fe(CH_2O)(CH_3OH)_3^+$ (*m/z* 182) is formed both through methanol association to $Fe(CH_2O)(CH_3OH)_2^+$ (*m/z* 150) and through reaction of $Fe(CO)(CH_3OH)_3^+$ (*m/z* 180). The latter reaction would be quite similar to the formation of $Fe(CH_2O)(CH_3OH)_2^+$ from $Fe(CO)(CH_3OH)_2^+$.

It cannot be excluded that CH_2O ligands are already present in the *m/z* 148 and/or 180 ions, the structure of which would thus be $Fe(CH_2O)_2(CH_3OH)^+$ and $Fe(CH_2O)_2(CH_3OH)_2^+$ respectively. Presence of ligands containing two carbon atoms may also be considered. Similarly, apparent simple methanol loss occurring in the transformation of $Fe(CO)(CH_3OH)_4^+$ (*m/z* 212) to *m/z* 180 ion may also be accompanied with structure rearrangement within the ligands.

5. Conclusions

The $Fe(CO)_n^+/CH_3OH$ systems exhibit well-differentiated reactivities according to the number of CO ligands. Substitution of two CO ligands by one methanol molecule has been shown to occur on thermalized $Fe(CO)_n^+$ reactant ions for $n \geq 3$, which implies a mutual stabilization of the CO and CH_3OH ligands, and stabilization of the second methanol ligand in $Fe(CH_3OH)_2^+$. When three ligands or more are present, the mutual stabilization effect between CO and CH_3OH is confirmed by the fact that the last CO ligand is not substituted, suggesting that for $n \geq 3$ $FeCO(CH_3OH)_{n-1}^+$ is more stable than $Fe(CH_3OH)_n^+$.

Apart from the less reactive pentacoordinated species, the global reaction rates of the different complexes are fast and remarkably independent of the number of ligands.

The $Fe(CH_3OH)^+$ ion has a unique reactivity with methanol, consisting in C–O cleavage of the complexed molecule with elimination of a methyl radical, a reaction which does not occur in the presence of other ligands. The resulting product $FeOCH_3(CH_3OH)^+$ undergoes relatively easy association with another methanol molecule, but only after an isomerization or collisional deactivation step which remains to be elucidated. Other slow processes met in the $Fe(CO)_3^+$ and $Fe(CO)_4^+$ systems deserve further studies, particularly concerning the formation and structure of *m/z* 150 ion which likely involves formaldehyde formation and chemical activation of a CO ligand, a type of reaction well known in solution but very unusual in the gas phase. Notice that these processes are observed only when at least three ligands are present on the metal ion.

In a multistep mechanism, the energy of the ionic product from a given step remains available for the next one and may influence its course. In the present case, the apparent rate constants and branching ratios for fast reactions are strongly influenced by the kinetic and/or internal energy of the reactant ions when these ions result from another reaction, more or less exothermic. The efficiency of simple substitutions of CO by methanol significantly increases with decreasing reactant ion energy, whereas it is the reverse for substitutions of two CO. It seems interesting to continue these investigations and extend them to other energy-dependent processes: submitting the product of a given process to a known energy-dependent fast reaction may constitute a way of getting information on the energy release of that process.

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