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An experimental study of the mechanism for the combined C–O and C–H bond activation of dimethylether by bare Fe^+ ions

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Dedicated to Diethard K. Böhme — a great friend and scientist

Abstract

By means of mass spectrometric experiments, a semi-quantitative potential-energy surface for the coupled C–O and C–H bond activation of dimethylether by gaseous Fe^+ is proposed, which can account for all experimental observations made for this system. Thus, the insertion of the metal cation into the C–O bond to afford the insertion species $[CH_3\text{–}Fe\text{–}OCH_3]^+$ is rate determining, followed by β-hydrogen transfer to first afford the bisligated complex $(CH_4)Fe(CH_2O)^+$ and then the final products $Fe(CH_2O)^+ + CH_4$.

Keywords: Bond activation; Dimethylether; Iron; Isotope effects; Reaction mechanisms

1. Introduction

Gas-phase ion chemistry has substantially contributed to the understanding of fundamental organometallic reaction mechanisms and the principles of transition-metal-mediated catalysis [1]. Several cornerstones of this research were related with the chemistry of iron, in part due to experimental advantages associated with the availability of iron pentacarbonyl as an easily handable, volatile precursor, and in part due to the particular chemistry of iron. The pioneering studies of Allison and Ridge on the gas-phase ion chemistry of transition metals, for example, dealt with the unprecedented formation of iron–carbon bonds [2]. Likewise, the concept of two-state reactivity [3,4], which is nowadays widely accepted to play a role in the reactions of transition-metal fragments, has been developed starting from ion/molecule reactions of the iron-oxide cation FeO^+ [5].

Here, we report unimolecular and collision-induced reactions of dimethylether complexed to bare Fe^+ cations. Already in 1981, Freiser and coworkers [6] noted that bare Fe^+ can activate dimethylether to afford the formaldehyde/Fe^+ complex as ionic and methane as neutral product (reaction (1)) [7,8]:

$$Fe^+ + CH_3OCH_3 \rightarrow Fe(CH_2O)^+ + CH_4 \quad (1)$$

Quite obviously, reaction (1) must comprise both C–H as well as C–O bond activations and is expected to proceed in several steps (Scheme 1) [9]. At first, the metal cation and the neutral reagent form the ion/neutral complex **1**. Subsequent C–H bond activation can then lead to the insertion species **2**, from which C–O bond activation via β-CH_3 migration [10,11] leads to the bisligated complex **4** which finally affords the ionic product $Fe(CH_2O)^+$ concomitant with neutral CH_4. Alternatively, however, initial C–O bond activation of **1** could lead to the insertion species **3** from which the bisligated complex **4** is accessible via β-H migration, a process well-known to occur in transition-metal alkoxides [12–17].

In the present work, we attempt to approach the relevant parts of the potential-energy surface of the dimethylether/Fe^+ sys-

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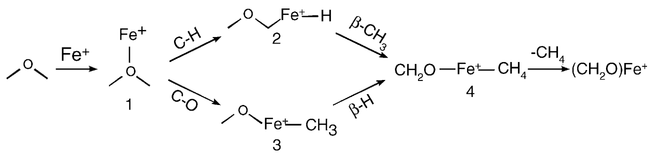

Scheme 1.

tem by mass spectrometric means in conjunction with isotope labeling.

2. Experimental methods

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) described previously [18]. The Fe^+ complexes of interest were generated by chemical ionization (CI) of a mixture of $Fe(CO)_5$ and the appropriate substrates with a large excess of carbon monoxide [19]. After acceleration to 8 keV kinetic energy, the ions of interest were mass-selected using B(1) and E(1) and characterized by metastable ion (MI) and collisional activation (CA) spectra; in CA, helium (80% transmission) was used as a collision gas. To this end, the either unimolecularly or collision-induced fragment ions formed in the field-free region between E(1) and B(2) were monitored by scanning the latter sector. The spectra were recorded and on-line processed with the AMD/Intectra data system; up to 50 scans were accumulated in order to improve the signal-to-noise ratio.

Except the labeled compounds, all reagents were used as purchased. CD_3OCH_3 was prepared by acid-catalyzed transetherification of 2-methoxy-2-butene with CD_3OD and afterwards purified by trap-to-trap distillation. The labeled methyl acetates CD_3COOCH_3 and CH_3COOCD_3 were made in 10 mmol scales by reacting acetyl chloride with methanol (both either blank or accordingly labeled) in quinoline. Likewise, $CH_3COOCHD_2$ was made from CHD_2OH in 2 mmol scale.

3. Results and discussion

As mentioned at the outset, bare Fe^+ leads to a demethanation of dimethylether according to reaction (1). In full accordance with the ion–cyclotron–resonance studies of Freiser and coworkers [6], loss of CH_4 largely prevails in the metastable ion spectrum of the complex **1** generated by chemical ionization of $Fe(CO)_5$ with dimethylether. Upon collisional activation, several other fragments are formed, among which loss of the entire ligand to form bare Fe^+ is most prominent; nevertheless, elimination of methane does still give rise to the base peak in the CA spectrum.

Our experimental approach to the dimethylether/Fe^+ system is based on isotopic labeling in conjunction with the directed gas-phase synthesis of isomeric ions [20,21]. Specifically, we have prepared three isomeric $FeC_2H_3D_3O^+$ ions by chemical ionization of $Fe(CO)_5$ with adequate precursors.

At first, CI of $Fe(CO)_5$ with CH_3OCD_3 should afford the encounter complex CH_3OCD_3/Fe^+ (**1a**) with one fully deuterated methyl group. As expected, prevailing losses of methane, leading to the corresponding formaldehyde complexes, are observed in the MI spectrum of **1a**, along with a small amount of ligand detachment leading to bare Fe^+. Surprisingly, however, formation of the heavier isotopologue $Fe(CD_2O)^+$ concomitant with loss of CH_3D is clearly preferred over that of $Fe(CH_2O)^+$ concomitant with elimination of CHD_3 in a ca. 100:60 ratio (Table 1). With regard to the mechanistic routes shown in Scheme 1, this result implies that C–H(D) bond activation is not rate-determining, because formation of $Fe(CH_2O)^+$ should be favored otherwise. Instead, a significant, formally inverse kinetic isotope effect (KIE) is operative for the migrating H(D) atom, in that more $Fe(CD_2O)^+$ is formed via migration of deuterium followed by loss of CH_3D than $Fe(CH_2O)^+$ via hydrogen migration and elimination of CHD_3. Thus, a notable secondary KIE appears to be involved. The abundances of the eliminations of CH_3D and CHD_3 in the CA spectrum of **1a** (100:64) further confirms this conclusion with a small change of the apparent KIE towards unity, as expected.

Independent evidence for the operation of secondary KIEs arises from the direct C–O cleavage (loss of methyl) in the CA spectrum of **1a**, as significantly more CH_3 than CD_3 is expelled as a neutral entity (ratio 20:15). To a first approximation, this implies a secondary KIE of $k(CH_3)/k(CD_3) = 1.3$ associated with C–O bond activation. Note that this value must be regarded as a lower limit for the metastable ions, because the KIEs upon CA are attenuated due to the higher internal energy of the dissociating ions. While not strictly conclusive, these results indicate that either the C–O bond activation ($\mathbf{1} \rightarrow \mathbf{3}$) or, less likely, the ß-methyl migration (step $\mathbf{2} \rightarrow \mathbf{4}$) [11] constitutes the rate-determining step of reaction (1).

In order to substantiate this conjecture, we attempted to prepare isomers of **1a** in the ion source of the mass spectrometer. In this respect, advantage can be taken from the fact that many transition-metal cations promote loss of carbon monoxide from carbonyl compounds, such as aldehydes, ketones, or esters

Table 1
Major fragments[a] (given as mass differences Δm) in the MI and CA mass spectra of mass-selected $[FeC_2H_{6-n}D_nO]^+$ isotopologues generated by CI of $Fe(CO)_5$ with the indicated neutral reagents

	CH_3OCD_3		CH_3COOCD_3		CD_3COOCH_3		CH_2O/CD_4	
	MI	CA	MI	CA	MI	CA	MI	CA
−14				4				
−15		20		17				
−16						4		
−17	100	100	100	100				
−18		15				18		8
−19	60	64			100	100		
−20							100	100
−30								4
−32								2
−33						20		
−35				19				
FeD^+		7		2				
FeH^+		5				1		5
Fe^+	8	43		6		10	5	30

[a] Normalized to the base peak (1 0 0).

[6,19,22–24]. Specifically with respect to iron, bare Fe^+ decarbonylates acetone as well as acetic acid to yield the corresponding insertion compounds $(CH_3)Fe(CH_3)^+$ and $(CH_3)Fe(OH)^+$ [20,25,26]. By analogy, CI of $Fe(CO)_5$ with methyl acetate inter alia yields a $[FeC_2H_6O]^+$ cation; the major product channel leads to the products $CH_3COOFe^+ + CH_3^{\bullet}$ [27]. The metastable ion spectrum of mass-selected $[FeC_2H_6O]^+$ is very similar to that of **1**, but now elimination of methane occurs exclusively. The absence of a signal due to bare Fe^+ in the MI spectrum as such is not structurally significant because it might be attributed to a different internal energy content of the ion formed in this way. A definitive structural insight arises from consideration of the labeled species, however. Thus, CI of $Fe(CO)_5$ with CH_3COOCD_3 yields a $[FeC_2H_3D_3O]^+$ ion which shows exclusive loss of CH_3D ($\Delta m = -17$), thus clearly demonstrating that the two methyl groups are distinct in the $[FeC_2H_3D_3O]^+$ species in that neither H/D exchange nor equilibration of the intact CH_3/CD_3 units occur. This result is clear evidence for the formation of the insertion species $(CH_3)Fe(OCD_3)^+$ from this precursor mixture. Complementary proof is provided by an inverse labeling experiment, as the MI spectrum of the $[FeC_2H_3D_3O]^+$ ion generated upon CI of $Fe(CO)_5$ with CD_3COOCH_3 shows exclusive elimination of CHD_3 ($\Delta m = -19$) which is consistent with the formation of $(CD_3)Fe(OCH_3)^+$. The CA experiments further support the formation of isotopomeric insertion species: Thus, the ion generated upon CI of $Fe(CO)_5$ with CH_3COOCD_3 shows a loss of CH_3 ($\Delta m = -15$) but not of CD_3 ($\Delta m = -18$), while precisely the opposite holds true when CD_3COOCH_3 is used as a precursor. The same structural distinction of the two methyl groups can also be deduced from the fragments formally corresponding to eliminations of neutral methanol ($\Delta m = -33$ and -35, respectively). Accordingly, the labeling studies provide unambiguous experimental evidence that the insertion species **3** exists as a genuine minimum. Furthermore, the bisligated complex $(CH_2O)Fe(CD_4)^+$ was generated by chemical ionization of $Fe(CO)_5$ in the presence of formaldehyde using CD_4 as reagent gas. The corresponding spectra are clearly consistent with the proposed connectivity and further demonstrate that the reverse reaction cannot compete with simple ligand losses, as has already previously been demonstrated by Freiser and coworkers [7]. Thus, also structure **4** is a minimum of the potential-energy surface of $[FeC_2H_6O]^+$.

In addition, yet another experiment was performed in order to further investigate the possibly hidden contribution of the C–H(D) bond-activation step to the overall KIE observed for CH_3OCD_3/Fe^+. To this end, the insertion intermediate $CH_3FeOCHD_2^+$ was generated via chemical ionization of $Fe(CO)_5$ in the presence of selectively labeled $CH_3COOCHD_2$. In the MI spectrum, this ion undergoes exclusive losses of CH_4 and CH_3D in a ratio of (1.8 ± 0.2):1. If further acknowledging the statistical propensity for H versus D transfer from a CHD_2 moiety, this result implies a KIE of about 3.6 for the hydrogen-atom transfer step ($\mathbf{3} \rightarrow \mathbf{4}$). Note that the pronounced primary KIE sampled in this particular experiment compared to the inverse KIE in the case of CD_3OCH_3/Fe^+ (see above) is a rather remarkable demonstration for the seminal statement of Derrick and Donchi that "indeed the intermolecular kinetic isotope effects can be effectively independent of transition state characteristics" [28]. In the present case, this refers to the situation that in the case of CD_3OCH_3/Fe^+ the overall reaction is probed, whereas the fragmentation of the intermediate **3** samples only part of the potential-energy surface; for a similar example of different KIEs in metal-mediated reactions of methoxy compounds, see Ref. [29].

From the experimental findings reported above, an internally consistent qualitative potential-energy surface of the dimethylether/Fe^+ system can be deduced (Fig. 1). At first, dimethylether and bare Fe^+ coordinate to the adduct complex **1** of which the bond dissociation energy (BDE) is unknown. By analogy to structurally related systems, the ligand-binding energies may, however, be estimated as $\mathrm{BDE}(Fe^+{-}CH_3OCH_3) \approx \mathrm{BDE}(Fe^+{-}CH_3OH) = 1.49 \pm 0.1$ eV [30]. Likewise, the overall exothermicity of reaction (1) can be derived as $\Delta_r H = (-1.34 \pm 0.08)$ eV from the heats of formation $\Delta_f H(CH_3OCH_3) = (-1.91 \pm 0.005)$ eV, $\Delta_f H(CH_4) = (-0.78 \pm 0.003)$ eV, and $\Delta_f H(CH_2O) = (-1.13 \pm 0.004)$ eV combined with $\mathrm{BDE}(Fe^+{-}OCH_2) = 1.43 \pm 0.07$ eV [31,32]. The energy of the product complex **4** can be estimated to lie ca. 1.9 eV below the entrance channel using a simple additivity approach, i.e., assuming $\mathrm{BDE}((CH_2O)Fe^+{-}CH_4) \approx \mathrm{BDE}(Fe^+{-}CH_4) = 0.59 \pm 0.03$ eV [33]. For the intermediates **2** and **3** as well as the associated transition structures TS **1/2**, TS **1/3**, TS **2/4**, and TS **3/4**, however, no quantitative conclusions can be drawn from experiment alone. Nevertheless, several semi-quantitative deductions can obviously be made based on the labeling data.

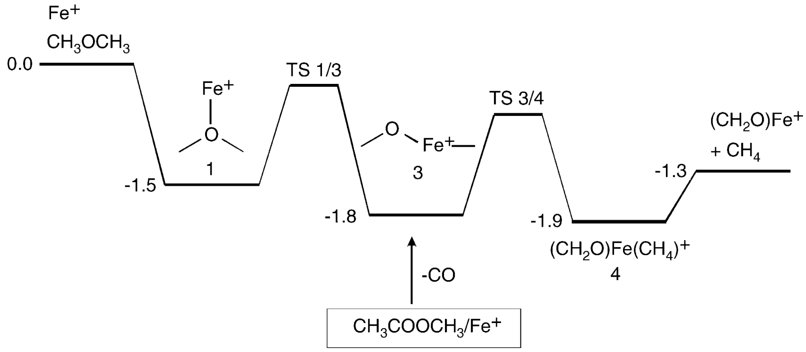

Fig. 1. Semi-quantitative potential-energy surface (relative energies in eV) for the coupled C—H and C—O bond activation of dimethylether by bare Fe^+.

At first, the independent access to intermediate **3** via decarbonylation of CH_3COOCH_3/Fe^+ unambiguously demonstrates that the insertion species **3** corresponds to a minimum, which is separated by reasonably large barriers from the reactant and product complexes **1** and **4**, respectively. Further, the notable inverse, secondary KIE associated with reaction (1) in the case of CD_3OCH_3 strongly suggests that C–H bond activation is not involved in the rate-determining step of the overall reaction. In terms of Scheme 1, we can accordingly conclude that either C–O bond activation via TS **1/3** or β-CH_3 migration via TS **2/4** constitutes the rate-determining step of reaction (1). If the latter were the case, however, no explanation for the large intramolecular KIE in the case of the insertion intermediate $CH_3–Fe^+–OCHD_2$ can be provided. In addition, the specific losses of CH_3D from $CH_3FeOCD_3{}^+$ and of CHD_3 from $CD_3FeOCH_3{}^+$ demonstrate that TS **1/3** must be located above TS **3/4**. Furthermore, the fact that a small, but yet significant amount of ligand loss is observed for metastable **1** implies that the barrier associated with the rate-determining step in the dimethylether/Fe^+ system is energetically situated below, but yet relatively close to the energy of the entrance channel $Fe^+ + CH_3OCH_3$. In addition, the relative energy of the intermediate **3** may be estimated reasonably well by means of an additivity approach using literature thermochemistry in conjunction with ab initio data. Thus, for the closely related insertion intermediate CH_3FeOH^+, Shioto and Yoshizawa computed $BDE(CH_3–FeOH^+) = 1.77\,eV$ using density functional theory [34]. Assuming a similar Fe–C bond strength for **3**, we may thus combine $\Delta_f H(FeOCH_3{}^+) = 9.37\,eV$ [15] and $\Delta_f H(CH_3) = 1.51\,eV$ with $\Delta_f H(Fe^+) = 12.19\,eV$ and $\Delta_f H(CH_3OCH_3) = -1.91\,eV$ [35], thereby concluding that **3** is situated ca. 1.8 eV below the entrance channel corresponding to $Fe^+ + CH_3OCH_3$. Resuming these data leads to a semi-quantitative potential-energy surface for the bond activation of dimethylether by bare Fe^+ (Fig. 1).

The surface depicted in Fig. 1 accounts for all experimental findings. C–O bond activation via TS **1/3** constitutes the rate-determining step and is apparently associated with a notable secondary KIE. For the so-formed insertion intermediate **3**, the subsequent TS **3/4** is sufficiently lower in energy than TS **1/3**, because C–O cleavage is found to be irreversible in the experiment. Nevertheless, TS **3/4** is situated above the exit channel to afford $(CH_2O)Fe^+ + CH_4$ because otherwise partial or even complete H/D equilibration via reverse passage of TS **3/4** is to be expected, which is not observed experimentally.

4. Conclusions

The present study demonstrates that even by mere virtue of mass spectrometric experiments quite profound insight into the qualitative nature of the potential-energy surface of an organometallic gas-phase reaction can be achieved, provided that sufficient and adequate labeling experiments can be made. Specifically, the present, admittedly somewhat fortuitous results can be used to establish a mechanistic scenario for the coupled C–O and C–H bond activation in the reaction of bare Fe^+ ions with dimethylether, which can account for all experimental observations. Thus, C–O bond activation is rate-determining followed by β-hydrogen transfer from the insertion intermediate $[CH_3–Fe–OCH_3]^+$ to the product complex $[(CH_4)Fe(CH_2O)]^+$ from which then methane is released to form the $Fe(CH_2O)^+$ cation.

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