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Preliminary communication

RELATIVE THERMODYNAMIC STABILITIES OF ACETYL AND FORMYL COMPLEXES: A THEORETICAL DETERMINATION

A. DEDIEU* and S. NAKAMURA

Université Louis Pasteur, E.R. No. 139 du CNRS, Laboratoire de Chimie Quantique, 4 rue Bl. Pascal, 67000 Strasbourg (France)

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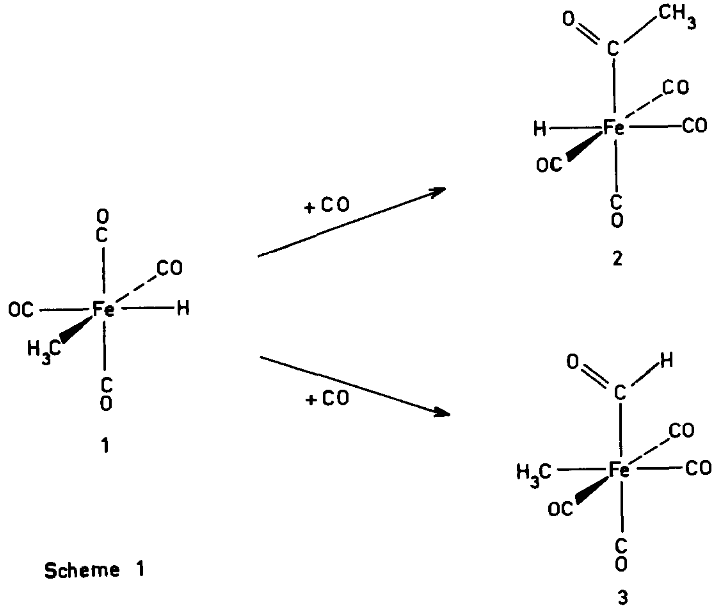
Summary

Ab initio LCAO-MO-SCF calculations have been used to calculate the relative thermodynamic stabilities of the complexes $[Fe(CO)_4(CH_3)(CHO)]$ and $[Fe(CO)_4(COCH_3)H]$; the results throw light on the relative ease of CO insertion into the Fe—H or Fe—CH_3 bond of $[Fe(CO)_4(CH_3)H]$.

There is much current interest in the insertion of the carbonyl ligand into the metal—hydrogen bond, which is thought to be as a possible step in catalytic hydrogenation of carbon monoxide. Yet, in contrast to the insertion of the CO ligand into a metal—alkyl bond, proof of the occurrence of the insertion into the metal—hydrogen bond has been rather elusive. This feature has generally been ascribed to the greater thermodynamic stability of the acyl complex compared to the formyl complex, the difference usually being traced to the difference between the strength of the M—H bond (estimated to 50—60 kcal/mol) and that of the M—CH_3 bond (20—30 kcal/mol) [1,2]. There is, however, only a limited amount of thermodynamic data available for these insertion reactions, especially with respect to the relative stability of the acyl and formyl complexes. A lower limit of 7.5 kcal/mol has been suggested by Casey et al. [1] on the basis of measured equilibrium constants for CO insertion into the Fe—H and Fe—CH_3 bonds of pentacoordinate d^8 iron complexes. In a recent review [2] the difference between the M—H and M—CH_3 bond energies (about 20 to 30 kcal/mol, i.e. a much higher value) was tentatively adopted by Gladysz as a measure of the relative stability of formyl and acyl complexes. The few available kinetic data (either experimental [3] or theoretical [4]) do not permit a thorough comparison to be made of the insertion into the metal—hydrogen bond with that into the metal—alkyl bond.



Scheme 1

In this connection, the $Fe(CO)_4(CH_3)(H)$ system 1, which has been recently been suggested to be an intermediate in a catalytic cycle for methanol homologation [5] is particularly interesting, since the two processes, the insertion into the $Fe{-}CH_3$ bond and the insertion into the Fe—H bond, are a priori conceivable (Scheme 1). Although this system is, in fact, believed to involve insertion into the $Fe{-}CH_3$ bond, it provides a unique opportunity to derive from a theoretical study an accurate comparison (vide infra) of these two insertion reactions, in both the thermodynamic and kinetic aspects.

The first part of this study, which we report here, has been devoted to the thermodynamic aspects of the two processes. More precisely, the relative thermodynamic stabilities of the resultant products have been derived from ab-initio LCAO-MO-SCF calculations [6] carried out on the hydridoacetyl complex $Fe(CO)_4(COCH_3)(H)$ (2) and the methylformyl complex $Fe(CO)_4(CHO)(CH_3)$ (3). For these systems the pseudo octahedral geometry shown in 2 and 3 was first chosen [11], and the Fe—H, $Fe{-}CH_3$, Fe—C(formyl) and Fe—C(acetyl) bond lengths were then optimized to 1.57, 2.12, 2.08 and 2.11 Å, respectively [17]. Other bond lengths were taken from previous calculations or from related structures [18]. Further refinements of the geometry indicated a slight bending (7° for 2 and 5° for 3) of the equatorial ligands [21] toward the axial hydride and methyl ligand and away from the axial carbonyl [22].

The present calculations indicate that the hydrido acetyl complex 2 is more stable than the methyl formyl complex 3 by 12.6 kcal/mol [23]. This theoretical value for the relative thermodynamic stability of the two systems is probably reliable, since we are dealing with a comparison of the energies of two closely related systems (they are in fact structural isomers) rather than with calculations of separate reaction energies. Hence errors which are typically associated with the SCF computations of reaction energies, such as the basis set superposition error or the correlation energy error, should cancel out or at least be strongly minimized [24]. It is noteworthy that the computed value agrees rather well with the lower limit estimated by Casey et al. [1], but lies somewhat outside the range of 20 to 30 kcal/mol obtained as the difference between the M—H and the M—CH_3 bond strengths. Reaction enthalpies of —4.5 and —5.9 kcal/mol have been reported for the reaction $(C_5Me_5)_2Th(H)(OR) + CO \rightarrow (C_5Me_5)_2Th(CHO)(OR)$, depending on R [3]. On the other hand values of —12.7 and —11.7 kcal/mol have been found for the CO insertion into the Hf—R bond (R = CH_3 or $CH_2C_6H_5$, respectively) during the reaction $Cp_2HfR_2 + CO \rightarrow Cp_2Hf(R)(COR)$ [26]. Although the comparison is not strictly valid, since different metals are involved, but both having a d^0 electron count and an η^2 geometry of the formyl and acyl ligands, it is relevant to note that the difference between the two reactions is also much lower than the above mentioned value of 20 to 30 kcal/mol. Hence additional factors probably influence the relative thermochemistry of the insertion of CO into the M—H and M—CH_3 bond. In Gladysz's estimation [2] the metal—formyl and metal—acetyl bond strengths were implicitly assumed to be rather similar. From calculations carried out for the nucleophilic addition of H^- and CH_3^- to both $Fe(CO)_5$ and CO systems [16] the metal—formyl bond strength seems to be about 7.5 kcal/mol greater than the metal—acetyl bond strength (for this d^8 pentacoordinate system) [27]. If account were taken of this feature, then there would be better agreement with the present theoretical value [28].

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Hydrido formyl and hydrido acetyl complexes of iridium(III) have also been found to be *cis* [15]. The orientations of the acetyl and formyl ligands were defined so as to retain a C_s symmetry for 2 and 3, respectively. This restriction should not affect our results, since π back donation to the π^* acceptor orbital appears to be rather unimportant [16], and hence the rotational barrier in these systems must be rather small. Moreover, whatever the conformation of the acyl ligand, it would probably be the same for the acetyl and the formyl ligands in both systems 2 and 3, and the energy difference between these two systems would not be essentially modified.
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18 The C—O bond length was kept to 1.22 Å [19] in the formyl and acetyl ligand. The C—H and $C—CH_3$ bond lengths of the formyl and acetyl ligands were fixed at 1.15 and 1.57 Å, respectively, as optimized previously for the $Fe(CO)_4(CHO)^-$ [20] and $Fe(CO)_4(COCH_3)^-$ [16] systems. The previously optimized Fe—C—O and Fe—C—H angle values (128 and 117°, respectively) of the formyl ligand [20] were also taken for the Fe—C—O and Fe—C—C angles of the acetyl ligand.

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21 We define the plane of the three carbonyls and of either the acetyl carbon or formyl carbon atoms as the equatorial plane.

22 The effect of the bending was a stabilization of 8.8 kcal/mol for 2 and of 4.1 kcal/mol for 3.

23 The corresponding total energies are −1862.9082 a.u. for 2 and −1862.8881 a.u. for 3 (1 a.u. = 627.7 kcal/mol).

24 The computed energy for the insertion into the $Fe—CH_3$ bond (1 → 2) is 19.3 kcal/mol. This should be compared for instance with the average value of 8.4 kcal/mol determined for the formation of the solvated acyl complex from $Cp(CO)_2FeR$ in DMSO [25].

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27 This feature may be rationalized on the basis of the greater electronegativity of $COCH_3^-$ than of HCO^- i.e. the lone pair of $COCH_3^-$ is lower in energy than the lone pair of HCO^-. The interaction of this lone pair with the empty d_{z^2} orbital of the $Fe(CO)_4$ fragment is therefore greater in the case of HCO^-. The same rationale would apply equally well to the interaction with a d^6 $M(CO)_5$ C_{4v} fragment, as is the case here.

28 Note however that a recent experimental estimation of these bond strengths [29] points to the metal-formyl bond strength being slightly smaller than the metal-acetyl bond strength (by about 3±3 kcal/mole) for the $Mn(CO)_5(CO)$ system ($R = H, CH_3$).

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