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Ab-initio SCF Potential Energy Surfaces for the Nucleophilic Attack of Hydride on Coordinated Carbon Monoxide

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Ab-initio SCF calculations are reported for the nucleophilic addition of the hydride ion H^- on the iron pentacarbonyl $Fe(CO)_5$ complex. The stereochemistry of the attack has been established from the determination of two potential energy surfaces. The reaction is shown to be highly exothermic and with no activation barrier. This activation of CO towards the nucleophilic addition is rationalized in terms of molecular orbital interactions.

Key words: Nucleophilic addition – CO activation – *Ab-initio* SCF calculations.

1. Introduction

The reactions of suitable hydride sources with metal carbonyl complexes to yield formyl complexes have been recently evidenced [1–5]. Such formyl complexes are believed to occur as reactive intermediates in many catalytic or stoechiometric processes [1]. They can also be regarded as a first step in the activation of carbon monoxide towards reduction [1, 6]. Theoretical analyses of this type of reaction are still lacking however, despite their relevance to the mechanistic aspects of the activation of carbon monoxide. We present here the results of LCAO-MO-SCF *ab-initio* calculations for the nucleophilic addition of the hydride anion H^- on the iron pentacarbonyl complex $Fe(CO)_5$ **1** to give the formyl complex $(CO)_4Fe(CHO)^-$ **2** (where experimentally [2–4, 7] the hydride is released by appropriate hydride donors). Our conclusions are derived from two potential

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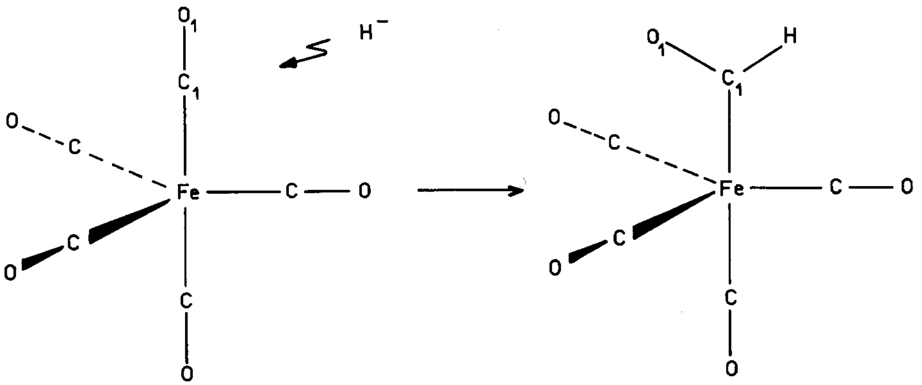

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Fig. 1. Schematic representation of the nucleophilic reaction $H^- + Fe(CO)_5 \rightarrow (CO)_4Fe(CHO)^-$

energy surfaces computed for this reaction, one keeping the geometry of the $Fe(CO)_5$ skeleton frozen and the other one allowing the $Fe—C_1—O_1$ angle (see Fig. 1) to relax during the nucleophile approach. The determination of these two surfaces is also a first – but necessary – step for subsequent studies like the influence of Lewis acids, the protonation of both reactants and products or the possibility for the formyl complexes to act themselves as hydride donors. We then compare our results with those obtained previously for the nucleophilic addition of H^- to the CO ligand alone [8] and to H_2CO [9–10].

2. The Calculations

The *ab-initio* calculations were carried out with the system of programs Asterix [11] using the following basis sets: (13, 8, 6) contracted to [5, 3, 3] for iron [12], (9, 5) contracted to [3, 2] for the first-row atoms [13] and (6) contracted to [3] for hydrogen [14]: the contracted basis set is a minimal set for the inner shells, a double-zeta for the valence shells and a triple-zeta for the 3*d* of iron and for the hydrogen atom. Our choice of a triple-zeta contracted basis set for the hydrogen atom was determined by the requisite of a fairly balanced description of the interacting hydride at long and short C—H distances [15].

For the $Fe(CO)_5$ system the experimental geometry [18] was chosen. The corresponding trigonal bipyramid symmetry was kept for the formyl complex as indicated from a preliminary X-ray crystal structure of the phosphite substituted homolog $(CO)_3\,[P(ArO)_3]\,Fe(CHO)^-$ [19, 20]. On the basis of this structure the hydride approach was restricted to the plane containing the two axial and one equatorial ligands, as schematically sketched in the Fig. 1 [21]. The $Fe(CO)_5$ bond distances and bond angles were retained for the $Fe(CO)_4$ moiety and for the $Fe—C_1$ and $C_1—O_1$ bond lengths during the approach (unless otherwise specified).

3. Results and Discussion

We first consider the nucleophilic attack of H^- on a rigid $Fe(CO)_5$ system. The corresponding surface, shown on the Fig. 2, displays some interesting features from both energetical and stereochemical points of view. The direction of attack is approximately equidistant from the equatorial and the axial carbonyl ligands which seem therefore to play roughly the same role. A slight preference for the

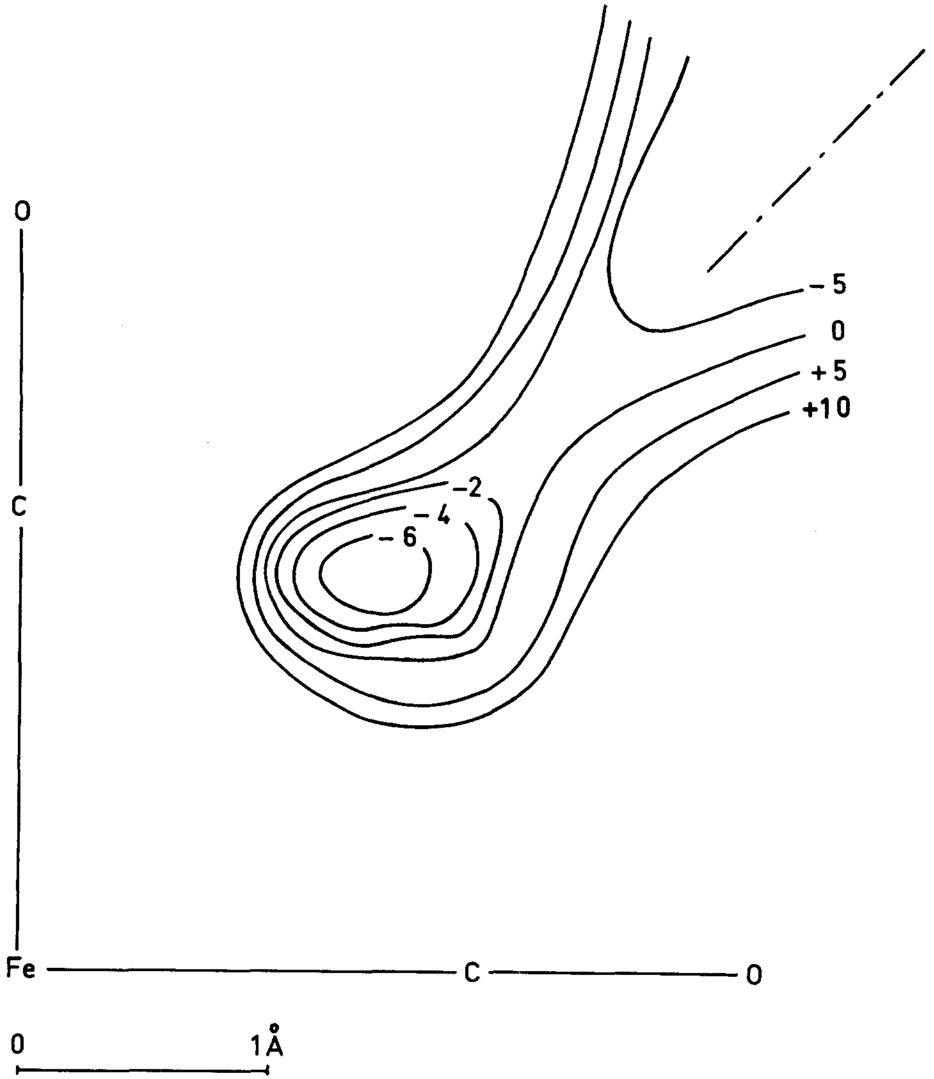
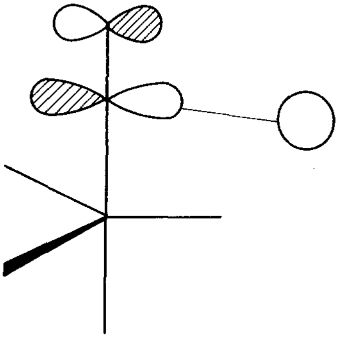


Fig. 2. Potential energy surface for the approach of the hydride ion, the geometry of the $Fe(CO)_5$ substrate being kept frozen. The axes are the equatorial and axial iron-carbonyl bonds and the metal is at the origin. The dot-dashed line corresponds to an approach that would be exactly equidistant from both carbonyl ligands. The zero of energy is for the separated reactants, and relative energies are in kcal/mol

attack of the axial carbonyl ligand is found however. This may be traced to the empty π^*_{CO} orbital being lower in energy for the axial carbonyl ligand, therefore inducing a greater stabilization when interacting with the doubly occupied S_{H^-} orbital [22]. This is also true for the lowest energy point which corresponds roughly to a C_{ax}—H distance of 1.4 Å and a $\angle O_{ax}$—C_{ax}—H angle of $\simeq 100°$ (whereas the C_{eq}—H distance and the $\angle O_{eq}$—C_{eq}—H angle amount to 1.63 Å and 106° respectively). The obtuse O—C—H angles result – as already shown by Anh and Eisenstein [10] – from a compromise to maximize the two-electron stabilizing interaction between S_{H^-} and π^*_{CO} (see **3** for the interaction with the axial ligand) and to minimize the four-electron destabilizing interaction between S_{H^-} and π_{CO} (see **4** for the interaction with the axial ligand), these two interactions occurring simultaneously (*vide infra*).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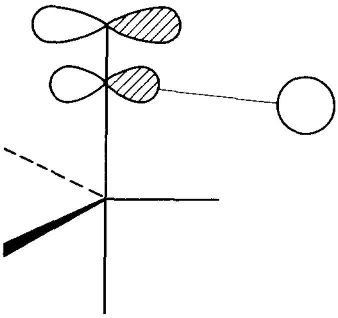
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The surface is characterized by two energy minima separated by a saddle point. The first one which corresponds to a stabilization of about 7 kcal/mol (compared to the energy of the separated reactants $Fe(CO)_5$ and H^-) occurs at about 3 Å from the carbon atoms and may be traced in part to an induced dipole–charge interaction between $Fe(CO)_5$ and H^- [23]. The energy along the reaction path then raises. This destabilization corresponds to a region of the space where one finds some repulsion between the oxygen ends of both the axial and equatorial ligands (see **3** and **4**) which is not compensated by the attractive interaction from the carbon component of the π^*_{CO} (see **3**). When the latter interaction dominates, the energy again decreases down to the second minimum (which is found to be about 7.7 kcal/mol lower in energy than the reactants). If the C—H distance is shortened further a strong repulsive interaction between π_{CO} and S_{H^-} develops (see **4**), thus leading to an overall destabilization of the whole system.

One has to worry throughout this study about the basis set superposition error and the neglect of electron correlation. One may reasonably think that the choice of a triple-zeta contracted basis set for the hydrogen atom would account for the basis set superposition error effects. To test this hypothesis, calculations using the counterpoise method [24, 25] have been carried out on several points of the reaction path of the surface shown on the Fig. 2. As expected the computed intermolecular energies are not profoundly altered, being reduced by at most 4.3 kcal/mol [26]. The electron correlation should also not change the computed intermolecular energy by more than a few kcal/mol since the two interacting species are closed-shell species. This is supported by the calculations of Schleyer et al. on the reactions $H^- + CO \rightarrow HCO^-$ [8] and by calculations performed for *SN*2 reactions involving the hydride ion [27–28].

A more realistic pathway of the reaction is of course obtained when the attacked carbonyl ligand is allowed to bend. This CO bending motion is accounted for in the potential energy surface shown on the Fig. 3, where for each calculated point the $\angle Fe—C_1—O_1$ angle is optimized [29]. The lowest energy point on the surface – i.e. the formyl complex – corresponds to a C—H bond length of 1.15 Å

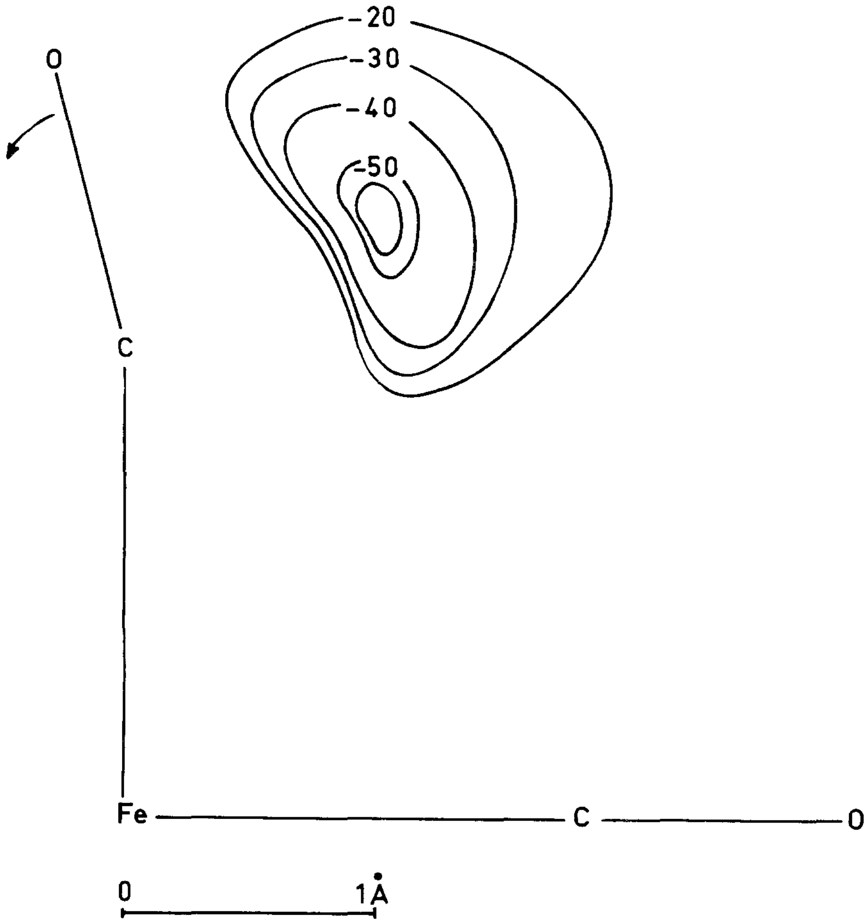


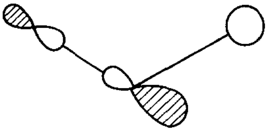
Fig. 3. Potential energy surface for the approach of the hydride ion, the axial carbonyl ligand being allowed to relax at each point. The axes are the equatorial and axial Fe—C bonds and the metal is at the origin. The zero of energy is for the separated reactants and relative energies are in kcal/mol. The inner contour corresponds to a relative energy of −52 kcal/mol

and to the ∠Fe—C—O and ∠Fe—C—H angles amounting to 128° and 117° respectively. The computed angle values are in fairly good agreement with the experimental ones [19, 30]. The agreement seems less satisfactory for the C—H bond length since the experimental value in $(C_5H_5)Re(PPh_3)(NO)(CHO)$ amounts to 1.08 Å [30]. One should notice however that this value of 1.08 Å may be slightly too short since it results from a X-ray diffraction study and not from a neutron diffraction study. Moreover the corresponding estimated standard deviation is large, 0.9 Å [30]. On the other hand, our present theoretical value compares rather well with the theoretical values of the equilibrium C—H bond length in HCO^- - 1.166 Å [8, 31] - and in CH_3O^- - 1.12 Å - [9].

The reaction is found to be highly exothermic: the computed exothermicity for the lowest energy point on the surface amounts to 53.0 kcal/mol. It is even higher (73.1 kcal/mol) when one takes the experimental values for the $Fe—C_1$ and $C_1—O_1$ bond lengths - i.e. 1.95 Å and 1.22 Å respectively. We have previously mentioned that this value might be somewhat overestimated (between 5 and 10 kcal/mol) as a result of some basis set superposition error effects and of a slight unbalanced description for the reactants (especially H^-, see [15]) and the products [32, 33].

The high exothermicity of the $H^- + Fe(CO)_5 \rightarrow (CO)_4Fe(CHO)^-$ reaction is also a characteristic of the reaction $H^- + H_2CO \rightarrow CH_3O^-$ as found theoretically [9] and experimentally [34]. But these results are in sharp contrast with the theoretical and experimental findings for the nucleophilic addition of H^- on CO [8] which is exothermic by only a few kcal/mol. The question then arises as to rationalize these changes in the energetics of the H^- nucleophilic addition as a function of the substrate.

In these three reactions, the stabilization of the $XCOH^-$ ($X = Fe(CO)_4$, H_2, none) system is achieved through the attractive two electron interaction between π^*_{CO} and S_{H^-} (**3**) which is somewhat lessened however by the four electron repulsive interaction between π_{CO} and S_{H^-} (**4**). But for the $H^- + CO \rightarrow HCO^-$ reaction there is an additional and rather dominant interaction **5** between the $5\sigma_{CO}$ orbital



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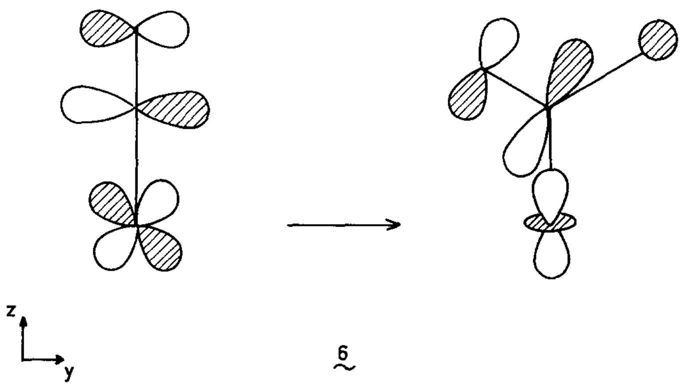
(mainly localized on the carbon atom) and the S_{H^-} orbital [35]. This four electron repulsive interaction is much less pronounced however in the two other reactions since the $5\sigma_{CO}$ orbital is already interacting with either the two hydrogen orbitals (when $X = H_2$) or with the d_{z^2} orbital of the iron atom (when $X = Fe(CO)_4$) [37]. In fact during the course of the $H^- + Fe(CO)_5 \rightarrow (CO)_4Fe(CHO)^-$ reaction the π^*_{CO} and $5\sigma_{CO}$ mix each other (due to the lowering of the symmetry from

D_{3h} to C_s) and exchange their role with respect to the d metal orbitals, as a consequence of the bending of the axial CO ligand: π^*_{CO} originally π antibonding with d_{yz} mixes in S_{H^-} and becomes σ bonding with the empty d_{z^2} (see **6**) and $5\sigma_{CO}$ (originally σ bonding with d_{z^2}) becomes π bonding with d_{yz} (see **7**) [38].



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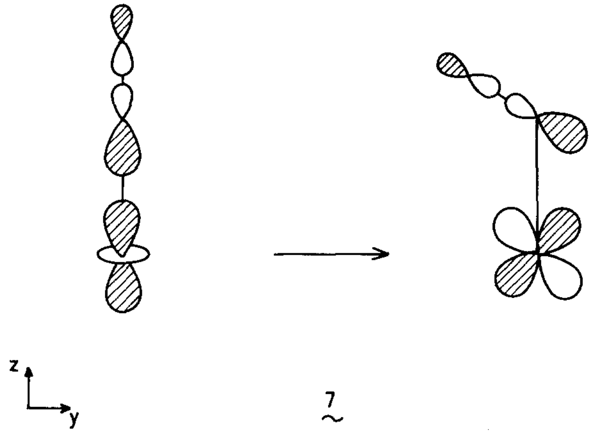

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This situation is reminiscent of what Hoffmann, Chen and Thorn [39] have analyzed for the bending of CO at the apex of a square pyramid. In our case the in-phase mixing of the formally empty d_{z^2} orbital into the bonding combination $\pi^*_{CO}+S_{H^-}$ provides some additional driving force for the reaction and explains its high exothermicity. Most of the transition metal carbonyl complexes which have been shown to undergo nucleophilic additions on the carbonyl ligand [1] have indeed such an empty metal d orbital which can mix into the $\pi^*_{CO}+S_{H^-}$ bonding combination during the reaction [40]. This in-phase mixing of d_{z^2} in the $Fe(CO)_5$ case may also explain the preference of the nucleophilic addition for the axial site rather than for the equatorial one: there is no empty metal d orbital pointing towards the equatorial ligand in $Fe(CO)_5$. In other words the formyl ligand which is a better σ donor than the carbonyl ligand prefers the axial site over the equatorial one in a d^8 trigonal-bipyramidal system [41].

A theoretical analysis of the reactivity of the formyl complex $(CO)_4Fe(CHO)^-$ lies beyond the scope of the present paper. We may simply note that the preferential nucleophilic attack on a carbonyl carbon atom rather than on a formyl carbon atom [19] seems to be charge and frontier controlled [42]: the carbonyl carbon atom has a greater positive charge than the formyl carbon atom (as indicated from the Mulliken population analysis [45]) and the π^* orbitals of the carbonyl ligands are lower in energy than the π orbital of the formyl ligand. Formyl complexes are also known to be donating hydride reagents [1]. This might appear rather puzzling given the high exothermicity found for the nucleophilic addition of H^- on $Fe(CO)_5$. One should keep in mind however, that in the actual reaction where the hydride is released from a borohydride ion, the heterolytic dissociation energy of the B—H bond should be subtracted from the present computed exothermicity value. On the other hand, one should also take into account a possible stabilization of the formyl complex by the remaining boron Lewis acid or by the cation of the borohydride salt [4]. Finally the reaction of formyl complexes with protonating agents is also of interest. Work along these lines is now in progress [40].

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32. Our computed exothermicity for the $CO + H^- \rightarrow HCO^-$ reaction is 14.9 kcal/mol to be compared with the experimental range of 1 to 6 kcal/mol quoted in Reference [8]. This value is reduced to 12.6 kcal/mol when using the counterpoise method and to 8.1 kcal/mol when using a (6)/⟨3⟩ basis set optimized for H^-
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