Interaction between Iron(0) and Formaldehyde, Thioformaldehyde, and Acetone: "Ab Initio" Calculations on the Model Compounds Fe(CO)2(\(\eta^2\)-CH2O), Fe(CO)2(\(\eta^2\)-CH2S), Fe(PH3)4(\(\eta^2\)-CH2O), and Fe(PH3)4(\(\eta^2\)-CMe2O)

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"Ab initio" calculations have been performed on the model systems Fe(CO)2(\(\eta^2\)-CH2O), Fe(CO)2(\(\eta^2\)-CH2S), Fe(PH3)4(\(\eta^2\)-CH2O), and Fe(PH3)4(\(\eta^2\)-CMe2O) to investigate the nature and the energetics of the interaction between iron and formaldehyde, thioformaldehyde, and acetone. The results allow a complete description of the electronic structure of the model compounds: the coordinate bond between the iron fragment and the unsaturated molecule may essentially be described in terms of the \(\pi\)-back-donation from the transition metal to the \(\pi\)-acceptor ligand. Partial geometry optimizations obtained by gradient calculations show that the geometry of the coordinated ligand is greatly distorted and the deformation upon coordination is satisfactorily reproduced when a comparison with experimental data is available. Thioformaldehyde gives rise to a stronger bond with iron than formaldehyde, because it is found to be a better \(\pi\)-acceptor ligand and a better \(\sigma\)-donor ligand. The \(\pi\)-back-donations are comparable in Fe(PH3)4(\(\eta^2\)-CH2O) and Fe(PH3)4(\(\eta^2\)-CMe2O), but acetone exhibits a weaker bond with iron than formaldehyde since it requires a higher deformation energy.

Introduction

The interaction between transition-metal complexes and formaldehyde has been experimentally studied in the last few years since the presence of a metal–formaldehyde complex has been postulated to be a pivotal intermediate in the catalytic activation of carbon monoxide. An important contribution should be the understanding of the interaction of CH2O formed formally from a mixture of CO + H2 with a metal site. A structural model for such an event may be the interaction of a carbonyl group with a metal site.

The interaction of CH2O with a metal site has usually been described by two limiting schemes: either a metal–cyclopropane scheme or the olefin-type Chatt–Dewar–Duncanson model involving ligand to metal \(\sigma\)-donation and metal to ligand back-donation. Recent "ab initio" theoretical studies suggest, however, that neither of these models seems appropriate, since the metal uses essentially a single orbital in a back-donation interaction with CH2O. In addition, the driving force for the distortion of the formaldehyde resides in the enhanced back-donation stabilization thus obtained. The presence of electron-donor ligands coordinated to the transition metal increases the electron density at the metal center and, therefore, the \(\pi\)-back-donation and the strength of the M–CH2O bond.

In this paper we intend to investigate, via "ab initio" calculations, the interaction between iron, a metal that plays an important role as catalyst in the Fischer–Tropsch synthesis, and formaldehyde, thioformaldehyde, and acetone. The main objective of the present study is the evaluation of the critical factors affecting the M(C=X) interaction in terms of energetic balance, namely (a) the nature of the heteroatom (X), (b) the substituents at the carbon, which can affect both the electron-withdrawing properties and the changes in geometry required for enabling coordination to the metal, and (c) the critical ligand substitution at the metal.

For this purpose, we have studied the complexes Fe(CO)2(\(\eta^2\)-CH2O), Fe(CO)2(\(\eta^2\)-CH2S), Fe(PH3)4(\(\eta^2\)-CH2O), and Fe(PH3)4(\(\eta^2\)-CMe2O) (Me = CH3). The first one has an experimental counterpart, that is Fe(CO)2[P(OCH3)3]2(\(\eta^2\)-CH2O), a well-characterized species, while the other three are assumed to be model complexes, for the purpose of comparison of the coordinate bond of CH2O with those of CH2S and CMe2O. The more basic fragment Fe(PH3)4 has been considered for the interaction with acetone, since a bond weaker than those of CH2O and CH2S is expected for this molecule.

Computational Details

Basis Sets. Two Gaussian basis sets, hereafter denoted as I and II, have been employed throughout this work. In basis I, the functions for iron were derived from Huzinaga's MINI-4 basis by splitting the outermost s and d functions. The MINI-1 basis was used for the phosphorus atoms and the carbonyl groups, and a (2s) contraction of Van Duijneveldt's (4s) primitive set was adopted for the phosphine hydrogens. For the component atoms of formaldehyde, thioformaldehyde, and acetone, Dunning's basis set of double-\(\delta\) quality was employed. All geometry optimizations described herein were conducted by using this basis. Subsequent single-point SCF calculations at the optimized geometries were performed for the compounds Fe(CO)2(\(\eta^2\)-CH2O) and Fe(CO)2(\(\eta^2\)-CH2S), by using the extended basis II (but not for the largest system, Fe(PH3)4(\(\eta^2\)-CMe2O), due to the size of the problem). Here the s,p basis for iron was taken from the (12s6p4d) set of ref 24 with the addition of two basis functions to describe the 4p orbital, while the Fe d basis was the reoptimized (5d) set of ref 26, contracted (4f) to describe the 4p orbital. The Fe d basis was the reoptimized (5d) set of ref 26, contracted (4f) to describe the 4p orbital, while the Fe d basis was the reoptimized (5d) set of ref 26, contracted (4f) to describe the 4p orbital.

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2 Università de Lausanne.

References

(20) Van Duijneveldt, F. B. IBM J. Res. Dev. 1971, 945.
for iron, contracted (8s6p2d). A double-σ expansion was used for all ligand atoms, with a (4s2/2s) basis for hydrogen, a (9s5p/4s2p) contraction for carbon and oxygen, and an (11s7p/6s4p) contraction for phosphorus and sulfur.

The basis set superposition error has been calculated as proposed by Boys and Bernardi\(^\text{24}\) for the complex Fe(CO)\(_2\)(PH\(_3\))\(_2\)(q\(^2\)-CH\(_2\)O). Basis I and basis II values of 3.9 and 4.6 kcal/mole\(^\text{1,35}\), respectively, suggest that our results should not be unduly affected by superposition errors.

Ab initio spin-restricted Hartree-Fock calculations were performed on the complex Fe(CO)\(_2\)(PH\(_3\))\(_2\)(q\(^2\)-CH\(_2\)O) and in deriving estimates of the binding energies of all complexes with respect to the free unsaturated ligand and the fragment species. It is well known that correlation effects may affect substantially the description of systems with transition-metal atoms. Configuration interaction calculations, carried out on the complex Fe(CO)\(_2\)(CH\(_2\)O) and the separated fragments CH\(_2\)O and Fe(CO)\(_2\), have clarified, however, that the correlation effects do not markedly influence the energetics of bond formation between Fe and CH\(_2\)O, so that the interaction energies computed at the Hartree-Fock level appear to be satisfactorily reliable.

In the case of the formaldehyde complex, we have already addressed\(^\text{17}\) the question of whether dissociation would lead to singlet or triplet products. At the Hartree-Fock level of theory, the fragments Fe(CO)\(_2\)(PH\(_3\)) and Fe(PH\(_3\)) are predicted to have a triplet ground state, but as has been found in the case of iron-tetracarbonyl through configuration interaction calculations,\(^\text{17}\) the relative energy of the first singlet state is expected to decrease drastically upon inclusion of correlation effects and possibly become the true ground state. The high energy gap between the singlet ground state and the first excited state of CH\(_2\)O, CH\(_2\)S, and CMe\(_2\)O (71.9,\(^\text{19}\) 41.5,\(^\text{19}\) and \(?88\) kcal/mole\(^\text{1,35}\), respectively) should be attainable for them.

All computations were performed by using the GAMESS program package,\(^\text{33}\) implemented on the cluster of FPS-164 processors at the IBM European Center for Scientific and Engineering Computing (ECSEC, Rome, Italy).

**Geometries and Geometry Optimization.** In all the calculations described herein we have confined our attention to geometries involving end-on coordination of formaldehyde, thioformaldehyde, and acetone, an approach consistent with the experimental structure of the transition-metal complexes involving formaldehyde or thioformaldehyde.\(^\text{10,11}\) End-on coordination has been observed for the acetone molecule in [CP\(_5\)(CH\(_2\)O)]\(^+(\text{BPh}_4)\).\(^\text{14}\) The high positive charge on the vanadium atom favors the electrostatic interaction over the σ-back-donation. The Fe(0) unsaturated fragments Fe(CO)\(_2\)(PH\(_3\))\(_2\) and Fe(PH\(_3\))\(_2\) have a strong Lewis basicity, and therefore, only side-on coordination should be attainable for them. In the partial geometry optimization calculations we have optimized the geometrical parameters involving the iron atom and the atoms of the formaldehyde and formaldehyde-derived ligands. The geometries of the Fe(CO)\(_2\)(PH\(_3\))\(_2\) and Fe(PH\(_3\))\(_2\) groups have been kept fixed at the values appropriate to the formaldehyde complexes, as described in ref 17. No geometry optimization has been performed for the dissociated species: the geometries of the Fe(CO)\(_2\)(PH\(_3\))\(_2\) and Fe(PH\(_3\))\(_2\) fragments have been taken equal to those in the complexes, while the experimental geometries\(^\text{35}\) have been used for CH\(_2\)O, CH\(_2\)S, and CMe\(_2\)O.\(^\text{35}\)

**Figure 1.** Optimized geometry of the model system Fe(CO)\(_2\)(PH\(_3\))\(_2\)(q\(^2\)-CH\(_2\)O). Bond lengths and angles are reported in Table I.

**Table I.** Optimized Geometries of the Systems under Investigation\(^a\)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C</td>
<td>1.952 (2.03)(^\text{11})</td>
<td>Fe-C 1.957</td>
</tr>
<tr>
<td>Fe-O</td>
<td>1.971 (2.00)(^\text{11})</td>
<td>Fe-S 2.325</td>
</tr>
<tr>
<td>C-O</td>
<td>1.311 (1.32)(^\text{11})</td>
<td>Fe-S 1.815</td>
</tr>
<tr>
<td>C-H</td>
<td>1.082</td>
<td>C-H 1.078</td>
</tr>
<tr>
<td>C=O</td>
<td>1.108 (108.5)(^\text{11})</td>
<td>C-C=O 1.077</td>
</tr>
<tr>
<td>C=Fe-CO</td>
<td>1.124</td>
<td>ZH-C=O 1.070</td>
</tr>
<tr>
<td>C=H-C</td>
<td>29.1</td>
<td>ZH-C 1.070</td>
</tr>
</tbody>
</table>

\(^{11}\) Bond lengths are in angstroms and bond angles in degrees. \(^{11}\) a is the distortion angle, defined as the angle between the CH\(_2\) plane and the C-O bond in the formaldehyde compound. \(^{11}\) Experimental values relative to Fe(CO)\(_2\)(PO(CH\(_3\))\(_3\))(q\(^2\)-CH\(_2\)O).

### References

interaction between Fe(0) and CH₂O, CH₂S, and CMe₂O complexes under investigation are shown in Table I. For the sake of clarity, the structure of the complex Fe(CO)_2(PH₃)_2(q₂-CH₂O) in its optimized geometry, including the coordinate system, has been reported in Figure 1. Each compound can be viewed as either a distorted trigonal bipyramid, with a five-coordinated iron atom, or a distorted octahedron, with a six-coordinated iron atom, depending on whether one considers the unsaturated ligand CH₂O, CH₂S, or CMe₂O to be monodentate or bidentate. The iron atom is bound to two mutually trans phosphines in the axial sites and to two carbonyls (or two phosphines) and the unsaturated molecule in the equatorial sites. A comparison with experimental data is possible only for Fe(CO)_2(PH₃)_2(q₂-CH₂O), which is a model system for the well-characterized compound Fe(CO)_2[P(OCH₃)₂]q₂-CH₂O. The distortion of the formaldehyde molecule upon coordination is satisfactorily reproduced. In particular, the experimentally observed elongation of the C-O distance in bonding, from 1.21 to 1.31 Å, is accurately predicted (1.31 Å in the optimized structure), while the distortion angle, defined as the angle between the CH₂ plane and the C-O bond, is calculated to be 29.1°. This value is in line with the experimental angle of 26.6° found in the nickel complex Ni(PEt₃)₂(q₂-CH₂O). The iron-CH₂O bond length is now noticeably shorter (by 0.12 Å) than the Fe-C distance.

The system Fe(PH₃)₄(q₂-CH₂O) is computed to have shorter Fe-C and Fe-O bond lengths compared with those exhibited by Fe(CO)_2(PH₃)_2(q₂-CH₂O) (Fe-C, 1.900 Å; Fe-O, 1.917 Å), and this suggests the presence of a stronger interaction. The distorted molecule is more pronounced in the tetrakis(phosphine) compound. Considering now the thioformaldehyde complex, we see that in the optimized structure the Fe-C distance (1.957 Å) is very close to the value found in the corresponding formaldehyde compound. How ever, thioformaldehyde itself undergoes a stronger geometry change than CH₂O upon coordination: the deviation from planarity is 40.9°, and the elongation of the C-S distance relative to that in free C-S is about 0.2 Å. It is interesting to note that the resulting C-S distance of 1.85 Å is typical of a C-S single bond (1.81–1.82 Å) and substantially longer than that observed in other CH₂S complexes (1.74Å and 1.76 Å in [CH₃CH₂Re(NO)(PPh₃)₂(q₂-CH₂S)]PF₆ and C₅H₅N(q₂-CH₂S), respectively). The C-S bond length has been experimentally observed in the u₅-selenoformaldehyde complex (q₅-C₅H₅R₇Mₗ₆(CO)₄(C₅H₅Se)); in this compound, however, selenoformaldehyde functions as a bridging ligand. Finally, we may comment briefly on the optimized structure of Fe(PH₃)₄(q₅-C₂Me₂O). In this case the presence of the two methyl groups causes an increase of ~0.09 Å in the Fe-C bond length and a decrease of 0.05 Å in the Fe-O distance, with respect to those in the corresponding CH₂O complex. As a result, the Fe-O distance is now noticeably shorter (by 0.12 Å) than the Fe-C distance. Furthermore, the acetone distortion angle is expectedly larger than that in CH₂O. A comparable C-O bond elongation is instead observed in the two complexes (the C-O distance in free acetone is 1.222 Å), which results in a C-O bond length somewhat intermediate between that of the free ligand and that of a C-O single bond (1.41–1.43 Å).

Results and Discussion

The total SCF energies of the four complexes investigated and of their related free fragments are reported in Table II, together with the estimated binding energies. The binding energies have been computed as the differences between the energies of the complexes and the energies of the separated fragments. Since in computing these energies we have used partially optimized geometries for the complexes and nonoptimized geometries for the free iron fragments, we expect our data to somewhat overestimate (in absolute value) the true fragmentation energies of the complexes. However, this should not affect the main qualitative conclusions of our comparative analysis.

In our model the binding energy (BE) can be thought of as the sum of a positive deformation energy (DEF) arising from the distortion of the unsaturated ligand and a negative interaction energy (INT) resulting from the interaction between the iron fragment and the distorted ligand. The deformation and interaction energies are also reported in Table II.

### Table II. Total SCF Energies (hartree) and Interaction (INT), Deformation (DEF), and Binding (BE) Energies (kcal-mol⁻¹) of the Analyzed Systems

<table>
<thead>
<tr>
<th>Complex</th>
<th>Basis I</th>
<th>Basis II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CO)₂(PH₃)₂(q₂-CH₂O)</td>
<td>-2276.7033</td>
<td>-2285.9449</td>
</tr>
<tr>
<td>Fe(CO)₂(PH₃)₂(q₂-CH₂S)</td>
<td>-2593.6666</td>
<td>-2608.6252</td>
</tr>
<tr>
<td>Fe(PH₃)₄(q₂-CH₂O)</td>
<td>-2734.3141</td>
<td></td>
</tr>
<tr>
<td>Fe(PH₃)₄(q₂-C₂Me₂O)</td>
<td>-2812.3495</td>
<td></td>
</tr>
</tbody>
</table>

*See text.*

To understand qualitatively the nature of the coordination bond between the iron substrate and the CH₂X ligand (X = O, S), it is useful to analyze the correlation between the molecular orbitals of the complex and those of the free fragments. Figure 2 shows such a correlation diagram for the orbitals of Fe(CO)₄(PH₃)₂(q₂-CH₂O) and those of the singlet fragments, where only the main correlations are reported. The orbitals mainly involved in the iron–formaldehyde bonding are 33a', 35a', and 36a'. The 33a', 35a', and 35a' molecular orbitals originate from the interaction of the filled orbitals 19a, from Fe(CO)₂(PH₃)₂, and 1b, from CH₂O. This
the strength of the back-donative interaction. The distortion of
between this orbital and the filled d, iron orbital, and this enhances
The resulting localized molecular orbitals reveal that effective
bonding between iron and formaldehyde is concentrated in a single
CHzX ligand.

context, since the deformation causes an energy lowering of the
the CH,X ligands upon coordination can also be viewed in this
approach: the main bonding orbital is 39a', which can be viewed as the overlap
metal to the ligand, while the CH20 → Fe σ-donation is almost
absent. This picture is substantiated on performing a localization
of the molecular orbitals by using the Foster–Boys algorithm.42
The resulting localized molecular orbitals reveal that effective
bonding between iron and formaldehyde is concentrated in a single
localized molecular orbital, featuring overlap of the metal 3d, and
the formaldehyde σ* orbitals.

Fe(CO)2(PH3)2 (η2-CH2S) shows the same bonding picture: the
main bonding orbital is 39a', which can be viewed as the overlap
between the fragment d, orbital and the virtual orbital of CH2S
3b, (π*). Therefore, we can conclude that the main bonding
interaction in both systems is the π-back-donation from the
transition metal to the unsaturated molecule. We note, however, that the net negative
charge on CH2S is computed to be appreciably smaller (by 0.35
electron) by use of basis

Table III. Mulliken Population Analysis of the Investigated Systems and π- and π*-Orbital Energies (hartree) of the Deformed Ligands

<table>
<thead>
<tr>
<th></th>
<th>Fe(CO)2(PH3)2</th>
<th>Fe(CO)2(PH3)2</th>
<th>Fe(CO)2(PH3)2</th>
<th>Fe(PH3)4</th>
<th>Fe(PH3)4</th>
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<tbody>
<tr>
<td></td>
<td>(η2-CH2O)</td>
<td>(η2-CH2S)</td>
<td>(η2-CH2S)</td>
<td>(η2-CH2O)</td>
<td>(η2-CMe2O)</td>
</tr>
<tr>
<td>Fe s</td>
<td>5.94</td>
<td>6.26</td>
<td>5.87</td>
<td>6.35</td>
<td>5.91</td>
</tr>
<tr>
<td>p</td>
<td>11.99</td>
<td>12.64</td>
<td>12.00</td>
<td>12.65</td>
<td>12.00</td>
</tr>
<tr>
<td>d</td>
<td>7.47</td>
<td>7.23</td>
<td>7.30</td>
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<td>7.14</td>
</tr>
<tr>
<td>ax ligands</td>
<td>26.00</td>
<td>35.61</td>
<td>35.96</td>
<td>35.48</td>
<td>35.86</td>
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<tr>
<td>eq ligands</td>
<td>28.60</td>
<td>28.26</td>
<td>28.34</td>
<td>27.88</td>
<td>28.24</td>
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<tr>
<td>π energy</td>
<td>-0.4980</td>
<td>-0.3855</td>
<td>-0.4856</td>
<td>-0.4392</td>
<td>-0.4392</td>
</tr>
<tr>
<td>π* energy</td>
<td>0.0677</td>
<td>-0.0019</td>
<td>0.0507</td>
<td>0.0582</td>
<td></td>
</tr>
</tbody>
</table>

* L is the unsaturated ligand: formaldehyde, thioformaldehyde, or acetone.

Figure 2. Molecular orbital correlation diagram of Fe(CO)2(PH3)2(η2-CH2O). For clarity's sake, only the main correlations are reported.

is a four-electron destabilizing interaction. Effective bonding, therefore, is concentrated in the 36a' orbital, which is the bonding combination of 11b1 of Fe(CO)2(PH3)2 (hereafter denoted as d,), which is predominantly Fe d, in character (the Fe–π*-C,0 moiety lies in the xz plane), and the virtual orbital 2b1 of CH2O (hereafter denoted as π*). Clearly the main bonding interaction between iron and formaldehyde is the π-back-donation from the transition metal to the ligand, while the CH20 → Fe σ-donation is almost absent. This picture is substantiated on performing a localization of the molecular orbitals by using the Foster–Boys algorithm.42 The resulting localized molecular orbitals reveal that effective bonding between iron and formaldehyde is concentrated in a single localized molecular orbital, featuring overlap of the metal 3d, and the formaldehyde π* orbitals.

Fe(CO)2(PH3)2(η2-CH2S) shows the same bonding picture: the main bonding orbital is 39a', which can be viewed as the overlap between the fragment d, orbital and the virtual orbital of CH2S 3b,(π*). Therefore, we can conclude that the main bonding interaction in both systems is the π-back-donation from the transition metal to the unsaturated molecule. The strength of the π-back-donation can be related to the π* orbital energy of the CH2X ligand. A lower π* energy implies a smaller energy gap between this orbital and the filled d, iron orbital, and this enhances the strength of the back-donative interaction. The distortion of the CH2X ligands upon coordination can also be viewed in this context, since the deformation causes an energy lowering of the π* orbital. The π energy is computed to be 0.1094 and 0.0433 au for free (undistorted) CH2O and CH2S, respectively, and decreases to 0.0677 au and ~0.0019 au, respectively, upon distortion. The lower π* orbital energy of CH2S is thus an indication that the π*-back-donative interaction is more effective in Fe(CO)2(PH3)2(η2-CH2S) than in Fe(CO)2(PH3)2(η2-CH2O). This is in agreement with the measured ν(CO) bands of the adducts of Os(CO)3(PPh3),1 which also suggest that CH2S is a stronger π-acceptor ligand than CH2O.

The conclusion that the π-back-donation is the main channel of interaction between iron and the CH2X molecules in the complexes investigated is also confirmed by the results of the Mulliken population analysis reported in Table III, which assigns a negative charge to the coordinated CH2X species. The Mulliken population analysis allows us to assign an oxidation state significantly different from the formal one, which foresees either +2 and -2 for iron and CH2X, respectively, or zero for both. The results of Table III show that coordination of CH2X implies a flow of electron density from the CO and PH3 ligands toward iron and then to the unsaturated molecule. We note, however, that the net negative charge on CH2S is computed to be appreciably smaller (by 0.35 electron) by use of basis II than by use of basis I, whereas the basis set change has a minor effect on the computed negative charge on coordinated CH2O (0.17 electron decrease). This suggests the presence of a nonnegligible ligand-to-metal σ-donative contribution to the interaction between thioformaldehyde and iron, which is better described by basis II than by basis I and is almost absent in the case of CH2O coordination. The π-orbital energy of CH2S, shown in Table III, is about 0.1 au higher than that of CH2O. This finding provides further evidence for the above conclusion. It seems clear that the σ-donative interaction should

strongly involve the empty iron 4p orbital, which is satisfactorily described by basis II but not by basis I. As can be seen from Table III, the iron p-orbital populations are almost identical in the fragment and in the two complexes (basis I), whereas the population is larger in the CH₂S complex (basis II).

Comparative Study of the Iron–Formaldehyde and Iron–Acetone Bonds. Fe(PH₃)₄(η²-CH₂O) and Fe(PH₃)₄(η²-CMe₂O) show a bonding structure entirely comparable to the one described for Fe(CO)₅(PH₃)(η²-CH₂O) and Fe(CO)₅(PH₃)(η²-C₂H₄S). The molecular orbital analysis again shows that in both the iron-tetraphosphine formaldehyde and acetone complexes there is essentially one bonding orbital, i.e. the highest occupied molecular orbital (HOMO), which describes a σ-back-donative interaction between the iron d orbital and the π* orbital of formaldehyde and acetone. The fact that bonding is dominated by a net electron charge flow from the iron substrate to the unsaturated ligand is again confirmed by the net negative charge residing on the coordinated ligand (see Table III). From Table II we notice, however, that the formaldehyde adduct of iron-tetraphosphine is found to have a binding energy remarkably higher than that of Fe(CO)₅(PH₃)(η²-CH₂O). This larger binding energy results from the nearly doubled iron-formaldehyde interaction energy, which overcompensates the increased deformation energy of CH₂O itself. As has previously been discussed, an increase in interaction energy is to be expected upon replacement of carbonyl ligands with the stronger electron donor phosphine ligands, leading to an increased σ-back-donative capability of the iron atom toward CH₂O. Indeed, the presence of electron-donor ligands, such as the phosphine, increases the electron density at the iron atom and hence the σ-back-donation and the strength of the interaction between Fe and CH₂O. We see from Table III that the increase in Mulliken population (basis I) on formaldehyde upon coordination is 0.645 kcal-mol⁻¹ for Fe(CO)₅(PH₃)(η²-CH₂O) and 0.83 kcal-mol⁻¹ for Fe(PH₃)₄(η²-CH₂O). This increase of σ-back-donation implies an increase of the strength of the iron–formaldehyde bond, as suggested by the interaction energy, which is −45.9 and −86.7 kcal-mol⁻¹ for the iron–dicarbonyl–diphosphine and iron–tetraphosphine compounds, respectively (see Table II). The ligand influence can be explained in a different way by considering the energy of the fragment d orbital, which lies at −0.2657 au in Fe(CO)₅(PH₃) and at −0.1647 au in Fe(PH₃)₄. The replacement of CO by PH₃, therefore, decreases the gap between the CH₂O π* and the fragment d orbitals: hence, the overlap increases. As shown in Table II, the acetone adduct of Fe(PH₃)₄ is computed to have a binding energy (−36.8 kcal-mol⁻¹) substantially smaller than that of the corresponding complex of CH₂O (−59.2 kcal-mol⁻¹).

Identification and Characterization of Lithium Polysulfides in Solution in Liquid Ammonia

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This study uses Raman spectroscopy and UV-visible spectrophotometry for the identification and the characterization of lithium polysulfides in liquid ammonia solutions. It is shown that S₇²⁻ is the least reduced polysulfide, S₅²⁻ is in equilibrium with the radical S₅−. This equilibrium is strongly temperature dependent, and the equilibrium constant is 4.3 × 10²³ M⁻¹ at 293 K. A weak disproportionation of S₅²⁻ is shown, through the observation of S₃N⁻. The existence of S₃²⁻ in solution is proved. This species was found to disproportionate as demonstrated by the observation of S₇²⁻. The equilibrium constant for the disproportionation of S₅²⁻ is about 10⁻³ M, estimated from the absorbance of S₅⁻. The disulfide S₇²⁻ exists in solution and has low solubility. The possibility of S₅²⁻ in solution is also discussed.

Introduction

The aim of the present work is to contribute to the identification and the characterization of the lithium polysulfides in liquid ammonia solutions. Bergström,1 Zintl et al.,2 Watt and Otto,3 and Nelson4 have already contributed to the identification of the alkali polysulfides in solution in liquid ammonia. Nelson1 was

1 Bergström, F. W. J. Am. Chem. Soc. 1926, 48, 146.