115. A Theoretical Study of Complex Formation between Formaldehyde and Lithium

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Summary

Ab initio SCF and CI calculations on the cationic and neutral complexes of formaldehyde and lithium are reported. For the cationic complex CH_2O/Li^+, the stabilization energy of 41.7 kcal/mol obtained from the SCF calculation increases to 51.6 kcal/mol if a configuration interaction is introduced. For the neutral complex CH_2O^-/Li^+, the C_{2v}-conformer of the $^2A_1$-state with the equilibrium bond distances of $d(C-O) = 1.23$ Å and $d(O-Li) = 1.90$ Å is calculated to be more stable than the $^2B_1$-state with $d(C-O) = 1.34$ Å, and $d(O-Li) = 1.65$ Å. Charge transfer and polarization effects upon complex formation are discussed.

1. Introduction. – Complex formation of cations with ligands containing the carbonyl group has received a considerable attention during the past few years. An enormous wealth of experimental results on the coordination chemistry of organic compounds, in which the carbonyl group acts as the binding site, has been accumulated [1]. Recently it has been demonstrated that the carbonyl groups are essential for complexing in most of the neutral carrier molecules which are responsible for the alkali cation transport through biological membranes [2]. For the interpretation and classification of the experimental results, theoretical information on the interaction energy between a metal ion and the carbonyl group, and on the equilibrium geometry of this fragment of a complex, can be of great help.

Formaldehyde is the simplest representative in the family of carbonyl-containing ligands, and, for obvious reasons, lithium is chosen from the group of alkali metals.

Several authors have studied the direction from which the metal ion attacks the ligand molecule. The closed-shell system H_2CO/Li^+ has been studied by *Russeger & Schuster* [3] in the SCF-LCGO-MO approximation. They found that in the most stable geometry the metal ion is situated on the C–O bond axis, at a distance of 1.77 Å from the oxygen atom, but did not give the total SCF energy of the complex necessary for comparing the quality of the wavefunctions.

In the open-shell system H_2CO^-/Li^+ *Bernardi & Pedulli* [4] varied the oxygen-lithium distance for various directions of cationic attack. They concluded that the most stable conformation has again the C_{2v}-symmetry, with an astonishingly short O−Li bond distance of 1.46 Å. Only the $^2B_1$-state was considered. A second minimum with C−O−Li bond angle of 90° was found to be much less stable than the linear conformer, with a considerably larger O−Li distance.

In the present study both closed and open-shell systems are reinvestigated employing a basis set larger than those used in [3] [4]. For the closed-shell system the binding energy at the r_e-structure is calculated at three levels of sophistications:

(a) as a difference of the SCF energies at the equilibrium geometry and at infinite separation of metal ion and ligand;

(b) by comparing the SCF minimum with the result of a 'ghost orbital' calculation [5] at the same geometry, and

(c) by refining the SCF energies by means of a configuration interaction (CI) scheme.

For the equilibrium geometry, the wavefunction is analysed by electron populations, difference density plot and the quadrupole coupling constants.

2. Calculation. – The approximate *Hartree-Fock* SCF orbitals for C, O and Li employed in this work were the *Gaussian* lobe function representation [6]. To ensure a near double-zeta quality for the molecular calculation we additionally split the long-range s-group into two contractions of 2 and 1 primitive *Gaussians* and likewise the p-groups of C and O were split into two contractions of 3 and 2 *Gaussian* lobe functions. The two contracted s-functions on the hydrogenatoms were built from 4 short and intermediate *Gaussians* and 1 long-range *Gaussian*. The exponent of the hydrogen functions [7] were scaled by a factor of $2^{1/2}$ for the molecular calculation. The size of basis set which contains a total of 28 contracted *Gaussian* functions give approximately the same accuracy as the molecular double-zeta basis set.

In dealing with weak interactions such as this within a truncated basis set, it is worthwhile to study the basis set extension effect to the interaction energy, since a fictitious energy stabilization due to a mutual basis set improvement might take place when two constituents approach each other. In the ghost orbital approach [5] by which the basis set effect may be eliminated in the SCF calculation the binding energy between CH_2O and Li^+ is calculated by comparing the SCF energy of the CH_2O/Li^+ system in its equilibrium with the SCF energies of CH_2O and Li^+ fragments. In each fragment calculation the full set of basis functions of the CH_2O/Li^+ system is employed.

A configuration interaction (CI) treatment [8] has been carried out employing the occupied molecular orbitals and the SCF virtual orbitals. In the CI calculation, the three doubly occupied MO's of the lowest energies which represent the 1s orbitals of C, O and Li were treated as a frozen core. We included all 6 valence shell orbitals and the lower lying 10 transformed virtual orbitals as orbitals of variable occupancy. The transformed virtual orbitals were obtained by an exchange maximization [9] between the variable set of 6 occupied orbitals

and the SCF virtual orbitals. The SCF ground state was augmented by all configurations which were doubly excited and which fulfilled an energy interaction threshold of 10^{-3} a.u. The *Hamiltonian* matrix was diagonalized and the energy and the wavefunction were obtained. In the final run the wavefunction obtained by the above procedure was considered to form a new parent set of the ground state. Again, this set was augmented by all doubly excited configurations with respect to each member of the parent set which had an interaction threshold greater than 10^{-5} a.u.

The open-shell system, H_2CO^-/Li^+ has been treated in the frame of spin-restricted open-shell *Hartree-Fock* method [10].

3. Results and discussion. – 3.1. *The closed-shell CH_2O/Li^+ system.* The geometry of formaldehyde molecule was first optimized in a separate calculation. Fixing the C–H bond length and the HCH bond angle at the experimental values of 1.10 Å and 120°, respectively, the C–O bond length was varied. At $d(C–O) =$ 1.225 Å a minimum with a total energy of -113.7932 a.u. was obtained.

The total SCF energy for the closed-shell CH_2O/Li^+ system was calculated as a function of the C–O bond length and the O–Li distance. The energy *vs.* distance curve at the optimized C–O distance shows a clear minimum at $d(O–Li) =$ 1.80 Å *(Fig. 1)* in fair agreement with the result given in [3]. The optimized C–O bond length of 1.23 Å is nearly identical to the equilibrium structure of the isolated CH_2O, indicating that structural relaxation of the ligand is not important in the present example. The minimum SCF energy of -121.0947 a.u. was obtained.

The difference in the SCF energies between the complex and its isolated constituents is calculated as 0.0665 a.u., or 41.7 kcal/mol. Within the frame of the ghost orbital method [5] this difference amounts to 40.9 kcal/mol, indicating that the basis set effect is negligibly small. Finally the SCF energies were refined by means of a CI calculation at the SCF minimum geometry and at infinite separation to -121.2126 a.u., and -121.1304 a.u., respectively. A binding energy of 51.6 kcal/ mol is computed at the CI level.

A comparison with the results of *Russeger & Schuster* [3] is interesting at this moment. From a semi-empirical CNDO/2 calculation they obtained a binding energy of 51.5 kcal/mol; a first *ab initio* SCF calculation yielded a value of 44.9 kcal/mol, while enlargement of the basis set reduced this value to 43.2 kcal/ mol. This trend seems to continue in the SCF calculation of the present work, leading to a value of 41.7 kcal/mol by traditional way and a value of 40.9 kcal/mol using the ghost orbital method as mentioned above. However, the configuration interaction results in a marked increase in the binding energy to 51.6 kcal/mol.

The influence of complex formation on the electron density distribution is illustrated by *Mulliken* population-analysis and the difference density plot. From *Table 1* and *Figure 2* it is evident that almost no net charge flow occurs between formaldehyde and lithium cation. However, pronounced polarization of the formaldehyde electron density is observed. In the binding π orbital, 0.173 e.u. are shifted from the carbon to the oxygen atom, while the σ-electrons are redistributed only to a smaller extent. The hydrogen atoms are deshielded by 0.074 e.u. each, while

Table 1. *Gross atomic charges for the* $^1A_1$*-states*[a])

		H_2CO/Li^+	H_2CO[b])
C	σ	5.332	5.250
	π	0.585	0.758
	Total	5.917	6.009
O	σ	7.287	7.242
	π	1.415	1.242
	Total	8.702	8.484
H	σ	0.680	0.754
Li	σ	2.020	–

[a]) C_{2v}-equilibrium geometry. [b]) Ref. [11].

Table 2. *Electric field gradient tensors and the quadrupole splitting parameter for the* $^1A_1$*-state*

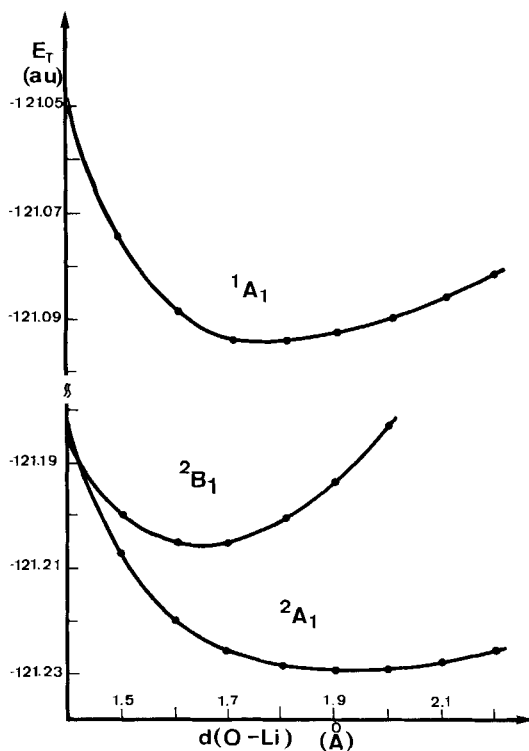|	^{17}O	^7Li	^2D
q_{xx}(a.u.)	1.0400	0.0084	– 0.1546
q_{yy}(a.u.)	1.4979	0.0111	– 0.1664
q_{zz}(a.u.)	– 2.5379	– 0.0195	0.3209
η(%)	18.04	13.85	3.68
eQq_{zz}(kHz)	15,706	193	211

Fig. 1. *Total SCF energies for the complex* H_2CO/Li^+ ($^1A_1$*-state) and* H_2CO^-/Li^+ ($^2A_1$*- and* $^2B_1$*-states) with* C_{2v} *symmetry, as a function of the oxygen and lithium distance*
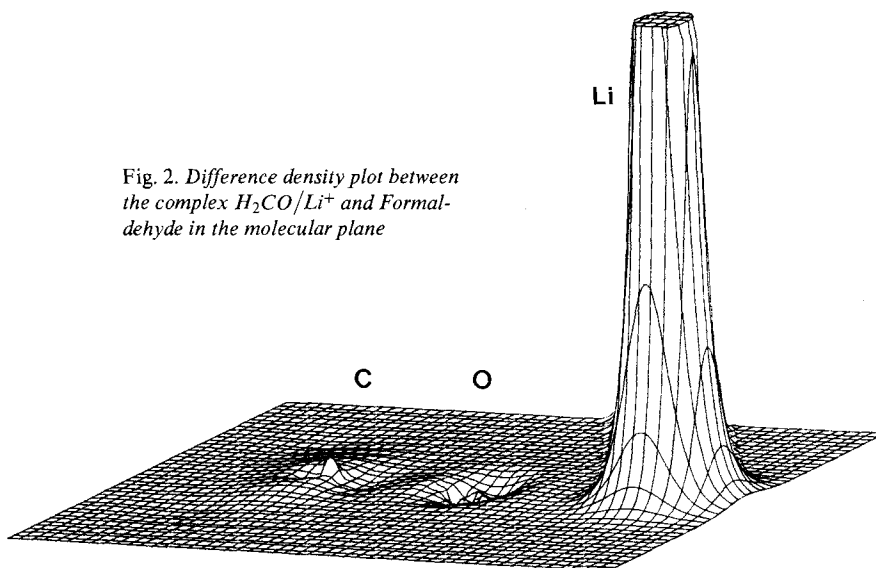
Fig. 2. *Difference density plot between the complex H_2CO/Li^+ and Formaldehyde in the molecular plane*

Table 3. ^2D-*quadrupole splitting parameters*

	$H_2CO/Li^{+a})$	$H_2CO^{b})$	$HDCO^{c})$
$eQq_{zz}(kHz)$	211	200	170 ± 2.5
$\eta(\%)$	3.68	1.3	0.09

[a]) This work. [b]) S.[11]. [c]) Experimental value, s. [12].

0.082 e.u. of density accumulates at carbon atom and 0.045 e.u. at oxygen atom, the rest of 0.020 shifting towards the lithium atom.

Electric field gradient tensors have been calculated at the sites of lithium, oxygen and hydrogen. ^7Li has a quadrupole moment, while the field gradients at the other two sites could be proved by ^{17}O and ^2D substitution. In *Table 2* the principal axis values q_{xx}, q_{yy} and q_{zz} of the *efg*-tensors are given. Asymmetry parameter η and the quadrupole splitting frequencies eQq_{zz} are calculated using nuclear quadrupole moments given in [12]. Perhaps more interesting than the absolute values is a comparison with an *ab initio* calculation on formaldehyde [11] and with experimental data for HDCO [13]. From *Table 3* it does not seem impossible that a change in the quadrupole splitting parameter on complex formation could be detected experimentally.

3.2. The open-shell CH_2O^-/Li^+ system. The total SCF energy for the open-shell CH_2O^-/Li^+ system was calculated as a function of the O–Li distance with $d(C-O) = 1.23$ Å, and the result is shown in the lower part of the *Figure 1*.

In the open-shell system, the unpaired electron may occupy either an orbital of a_1-symmetry (σ-type) or an orbital of b_1-symmetry (π-type). The calculation shows that the $^2A_1$-state is considerably more stable. The energy rises steeply for short O–Li distances, but only vary slowly for large separations of the metal ion. The broad minimum is centered around at $d(O-Li) = 1.90$ Å, with a total SCF energy of -121.2295 a.u. For the $^2B_1$-state, the energy minimum of -121.2060

a.u. is reached at $d(O-Li) = 1.65$ Å, the stretching force constant being much larger than for the $^2A_1$-state. An additional energy optimization with respect to $d(C-O)$ shows, however, that the $^2B_1$-state has appreciably longer C-O bond length of 1.34 Å than the $^2A_1$-state of $d(C-O) = 1.23$ Å.

The minimum SCF energy for the $^2B_1$-state is calculated as -121.2250 a.u., which lies 2.82 kcal/mol above the $^2A_1$-state. Further optimization with respect to $< COH$ and the out-of-plane angle of the CH_2 group brought about no improvement in energy.

Interestingly, *Bernardi & Pedulli* [4] have not considered the possibility of a $^2A_1$-state at all. For the $^2B_1$-state, they found an energy minimum of -120.8982 a.u. at an O-Li separation of 1.46 Å.

Starting from the closed-shell system and adding an electron into an unoccupied a_1-orbital lengthens the O-Li bond due to stronger repulsive interactions between the σ-electrons, while inserting the electron into an orbital of $b_1(\pi)$-symmetry leads to a shorter bond distance, as the *Coulombic* attraction between the cation and anion seems to prevail in this case.

It is also of interest to compare the open-shell result of CH_2OLi with that of previous *ab initio* SCF study for CH_2OH [14]. It was previously shown that the hydroxymethyl radical (CH_2OH) is nonplanar with the out-of-plane angle of the CH_2 group of 25° and the θ $(< COH) = 115°$. It was concluded that the CH_2OH radical is a π-radical since the open-shell consists mainly of the CO π^*-character. Thus, the non-planarity of the CH_2OH radical is closely related to the non-planar structure of the electronically excited $n\pi^*$-state of CH_2O. On the other hand, the result of the open-shell calculation for CH_2OLi as a function of θ $(< COH)$ shows that the lower-lying $^2A_1$-state is a σ-radical, meaning that the open-shell consists mainly of the Li 2s orbital rather than the CO π^*-orbital. The qualitative difference in the geometrical structure between the CH_2OLi and CH_2OH radicals may thus be related to the energetics and diffuseness of the lithium 2s orbital which play significant roles in determining the open-shell nature of the CH_2OLi radical.

4. Conclusion. – *Ab initio* calculations have been carried out on the cationic and neutral complexes of formaldehyde and lithium. Some important results are summarized in *Table 4*.

For the closed-shell system H_2CO/Li^+, the earlier conclusion [3] was confirmed that the most stable conformer has C_{2v}-symmetry, with the lithium cation on the C,O-bond axis. The complex is stabilized mainly by electrostatic ion-dipole interactions, favoured by polarization of the π-electrons in the C=O double bond.

Table 4. *Summary of the equilibrium geometries and the total energies*

State	$d(C-O)$ [Å]	$d(O-Li)$ [Å]	Total energy [a.u.]	Method of calculation
$^1A_1$	1.23	1.80	-121.0947	SCF
			-121.2126	CI
$^2A_1$	1.23	1.90	-121.2295	SCF
$^2B_1$	1.34	1.65	-121.2250	SCF

An analysis of the wavefunction shows little covalent character of the bond between oxygen and lithium-atom, and the geometrical parameters of the formaldehyde molecule do not change appreciably on complex formation. The results are consistent with recent calculation on similar systems reported in the literature. *Rode & Ahlrichs* [15] have discussed complexes of alkali metal ions with dimethyl formamide occurring in mass spectroscopy. For Li$^+$, they found minimum energy when the metal ion is situated 1.80 Å apart from the oxygen atom on the bond axis. Complexation of Li$^+$ by formic acid has been investigated by *Rode et al.* [16]. The direction of attack of the metal ion is the same in the r_e-structure and the bond distance is determined as 1.75 Å. It seems, therefore, legitimate to claim that the results of this work are not confined to the specific example considered, but are representative for a wide class of lithium complexes with carbonyl ligands.

From a methodological point of view, it is interesting to note that the binding energies from SCF (41.7 kcal/mol) and CI calculations (51.6 kcal/mol) differ by about 20%. Both values are astonishingly large and indicate a rather stable bond. Results from the ghost orbital method indicate that the basis set effect to the binding energy is rather small, employing the present double-zeta basis set in the SCF calculation.

In the open-shell system H_2CO^-/Li^+, too, the linear geometry is more favoured with respect to the total energy. The $^2A_1$-state, not discussed in [4], was found to be more stable than the $^2B_1$-state by 2.82 kcal/mol. The equilibrium bond lengths of O−Li for both states (1.90 Å and 1.65 Å, respectively, *cf. Table 4*) are considerably longer than the value of 1.46 Å obtained by *Bernardi & Pedulli* [4].

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