Theoretical Studies on Ion Pairs. An *ab-initio* Investigation of the Lithium–Formaldehyde Ion Pair

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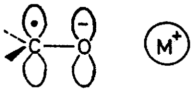
The lithium–formaldehyde ion pair has been investigated by an *ab-initio* MO–SCF–UHF treatment. The computations have been carried out at two different levels of sophistication. A detailed search of the energy surface of this system has been made at the STO-3G level, by optimizing the Li–O bond lengths at various directions of cationic attack. At this computational level two minima were found; we then reinvestigated the two minima with an STO-6G basis set. In the more stable species (A) the Li^+ is 1·46 Å from the oxygen atom on the C–O bond axis, while in the other stable species (B) Li^+ is 1·61 Å above the oxygen atom. In species (A) the bond between the cation and the anion has a dominant π character, while in species (B) the bond has mainly σ character.

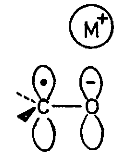
SINCE the importance of ion pairs in organic processes has been recognized, an increasing number of papers describing the structure and properties of this kind of complex has appeared.[1] Most of this work has been done by employing magnetic resonance techniques, the more widely used being e.s.r. However only a few theoretical investigations have been reported on this subject, most of them dealing with the calculation of spin densities at the metal atom and at the organic anion.[1] The only example of *ab-initio* MO calculations was recently reported by Hinchliffe *et al.* on the lithium–pyrazine system.[2] The lowest energy conformation of this complex was predicted to be that in which the lithium atom is located in the plane of the pyrazine ring on the axis passing through the nitrogen atoms. This result is of some interest as previous calculations performed on the same ion pair by the CNDO/2 and extended Hückel methods failed to predict the correct geometry,[3] the favoured structure being calculated as that with the lithium counterion above the centre of the pyrazine ring, in complete disagreement with the experimental evidence.[4]

Because of our interest in ion pairs involving organic anions containing carbonyl groups, we have undertaken a similar study on the lithium–formaldehyde system. Although no experimental results are available for alkali metal complexes of this simple ketyl, its properties are expected not to differ much from those of ketyls of larger dimensions, since it is the carbonyl group that the cation attacks forming the cation–anion partial bond. Furthermore the limited complexity of this system allows a detailed analysis of the energy surface at the *ab-initio* level.

Contact ion pairs of aromatic ketyls have been extensively investigated and useful information has been obtained on their structure. The most detailed studies have been made by Hirota and his co-workers on fluorenone ketyl by following, by e.s.r., the process of cation solvation by polar solvents [5] and anion solvation by various alcohols.[6] The observed changes of the alkali metal splittings and carbonyl ^{13}C splittings were explained in terms of the following model. The ion pair may exist in two stable conformations, one (A) with the cation in the molecular plane of the ketyl, and the other (B) with the cation above that plane approximately on the $2p_z$ orbital of the carbonyl oxygen.



(A)



(B)

The 'in plane' position is favoured with smaller cations while larger cations prefer the 'above the plane' position. The above conclusion has been reached mainly on the assumption that these two positions are characterized by different splitting constants at the alkali metal, since in the case of (A) the more important spin transfer mechanism from the anion to the cation should be indirect polarization due to σ–π exchange implying a negative alkali splitting. For position (B), on the other hand, direct electron transfer occurring through mixing of the aromatic MO containing the unpaired electron and the valence orbital of the alkali atom gives rise to a positive splitting. On this basis the temperature dependence of the lithium splitting in the lithium–fluorenone ion pair has been interpreted as indicating that form (A) is favoured at low temperature, while the importance of form (B) increases when the temperature is raised. Also the dependence of line broadening on the nuclear quantum number of the alkali metal has been explained in terms of exchange between positions (A) and (B) and the relative rate constants have been determined.[5]

METHOD

The lithium–formaldehyde complex can be considered the simplest ion pair involving an alkali cation and an organic anion containing the carbonyl group. A detailed investigation of the bond formation between the two ions has been carried out at the *ab-initio* level.

The resulting system is a radical species, *i.e.* an open-

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[1] 'Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley, New York, vol. 1, 1972.

[2] A. Hinchliffe, J. C. Cobb, and A. J. Duke, *Theor. Chim. Acta*, 1974, **32**, 341.

[3] T. A. Claxton and D. McWilliams, *Trans. Faraday Soc.*, 1969, **55**, 3129.

[4] N. M. Atherton and A. E. Goggins, *Trans. Faraday Soc.*, 1966, **62**, 1702.

[5] K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, 1971, **93**, 6004.

[6] K. Nakamura, B. F. Wong, and N. Hirota, *J. Amer. Chem Soc.*, 1973, **95**, 6919.

shell system, and in principle two *ab-initio* approaches, the Restricted Hartree–Fock (RHF) [7a] and the Unrestricted Hartree–Fock (UHF) [7b] could be used. The main disadvantage of the UHF method is that the resulting optimized wavefunction is not an eigenfunction of the spin operator S^2, but it is contaminated by higher spin eigenfunctions. Despite this limitation, the UHF treatment has been chosen here on account of a desire to obtain spin density values, that cannot be obtained by the RHF method. However it must be emphasized that in the present case the contamination from higher spin eigenfunctions is quite small. For instance the $\langle S^2 \rangle$ values for the two conformations denoted by (A) and (B) (see later) computed at the STO-6G [8] level are 0·7647 and 0·7585 instead of the correct 0·75.

The computations were performed with the Gaussian 70 series of programs [9] at two different levels of sophistication. We first made a detailed search of the energy surface of this system with an STO-30 [8] basis set, keeping fixed the geometry of the formaldehyde ketyl and optimizing only the lithium–formaldehyde bond length at various directions of attack of the cation.* The geometrical parameters used for the formaldehyde ketyl are those optimized in a previous *ab-initio* investigation,[10] *i.e.* r(C–O) 1·3173 Å, r(C–H) 1·0909 Å, $\widehat{\mathrm{HCH}}$ 113·72°.

At this computational level we found two minima in the surface and reinvestigated these two points with an STO-6G [8] basis set, by minimizing the energy with respect to the C–O and O–Li bond lengths.

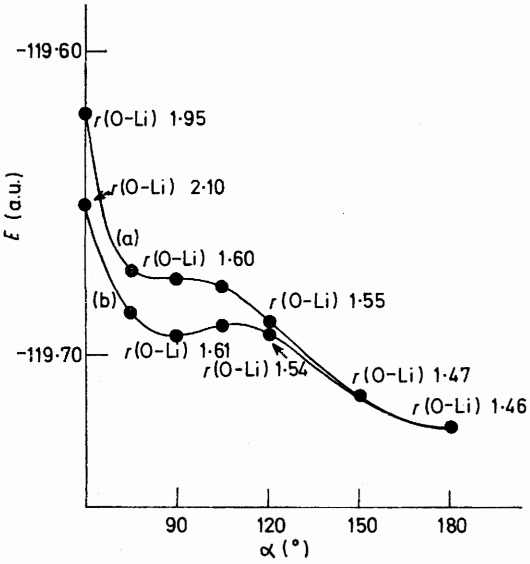

FIGURE 1 Optimum total energy values *versus* the angle α for horizontal [curve(a)] and perpendicular [curve (b)] cationic attack. The r(O–Li) (Å) values refer to the optimum O–Li bond distances at the various α values

RESULTS AND DISCUSSION

We first investigated the potential energy surface in order to determine the structure of each local minimum, *i.e.* each stable species, and their relative stabilities.

To this purpose we examined the lithium–formaldehyde ion pair with the cation approaching the anion in its molecular plane and in a plane perpendicular to it. In each case we minimized the total energy of the system with respect to the O–Li bond length at α = 60, 75, 90, 105, 150 and 180°, α being the angle between the C–O and O–Li bonds. The results of such calculations are shown in Figure 1 where we have plotted the optimum energies computed at the STO-3G level against the α values. Curve (a) refers to cationic attack in the molecular plane of the anion (horizontal attack). This curve shows only one minimum at α = 180°. Curve (b) refers to cationic attack in the plane perpendicular to the molecular plane of the anion and containing the C–O bond axis (perpendicular attack). In this case there are two minima, the lowest again at α = 180° and the other at α = 90°. This means that only two stable species exist, the more stable (A) with Li$^+$ 1·46 Å from the oxygen atom on the C–O bond axis, and the second (B) with Li$^+$ 1·61 Å above the oxygen atom.

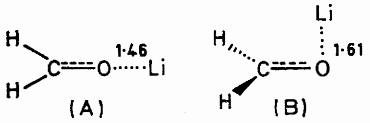

Figure 1 also reports, for the various α values at which the computations have been carried out, the optimized O–Li distances. It can be seen that they are almost the same for horizontal [curve (a)] or perpendicular [curve (b)] cationic attack at a given value of α and they gradually decrease with increasing α. The distance of 2·1 Å at α = 60° (curve b) is only estimated because satisfactory convergence in the SCF procedure could not be obtained for such large values of r(O–Li).

From the energies reported in Figure 1, species (A) is seen to be more stable than (B) by *ca.* 19 kcal mol^{-1} while the barrier to the interconversion of (B) and (A) is only 2·2 kcal mol^{-1}.

In order to determine a more accurate estimate of the relative stability of the two species (A) and (B), and also to assess the reliability of the STO-3G results, in both cases we carried out a geometrical optimization with respect to the C–O and the O–Li bond lengths with the more accurate STO-6G basis set.

The optimum values for r(C–O) and r(O–Li) are 1·3454 and 1·459 Å at α = 180° and 1·3127 and 1·605 Å at α 90°. These results show that the approximation of keeping constant the C–O bond length in the previous STO-3G computations was reasonable and also that the computed r(O–Li) values are practically the same at the two different computational levels. Furthermore, from comparison of energy values listed in

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* It has already been shown that in the optimum conformation of CH$_2$O$^{\bullet-}$ the methylene group is pyramidal.[10] However in the present investigation we have taken the formaldehyde ketyl to be planar with the intention of reproducing the situation of a cationic attack on the carbonyl group of planar organic anions.

[7] (*a*) C. C. J. Roothaan, *Rev. Mod. Phys.*, 1960, **32**, 179; (*b*) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 1954, **22**, 571;

[8] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.

[9] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, 'Quantum Chemistry Program Exchange,' Indiana University, Bloomington, Indiana.

[10] F. Bernardi, M. Guerra, and G. F. Pedulli, *J. Phys. Chem.*, 1974, **78**, 2144.

Table 1 it can be seen that, while the energies of the two species (A) and (B) differ significantly at the two computational levels, their difference is almost insensitive to the change in the basis set.

TABLE 1

Energy values (a.u.) of the two species (A) and (B) computed with STO-3G (a) and STO-6G (b) basis sets

	(a)	(b)
Species (A)	−119·7239	−120·8982
Species (B)	−119·6937	−120·8668
ΔE	0·0302	0·0314

Let us now discuss the orbital interactions which are responsible for bond formation in the two species (A) and (B). The principal orbital interactions involve the higher energy occupied MOs of the formaldehyde ketyl and the vacant 2*s* and 2*p* orbitals of Li^+. Figure 2 shows the ordering and approximate shape of some of the highest occupied MOs of the formaldehyde radical anion, which should be mostly responsible for the interaction with Li^+. It should be pointed out that from the results of an UHF calculation it is possible to determine with certainty the singly occupied HOMO (highest occupied molecular orbital), but it is not so easy to establish the correct ordering of the other doubly occupied orbitals, since the theory allows independent ordering of α and β spin orbitals. We have made the assumption here that the ordering in the radical, in this case $CH_2O^{\cdot -}$, should reflect the ordering of the corresponding closed shell system CH_2O, with the further single occupancy of the LUMO (lowest unoccupied molecular orbital). Since this ordering is used only to provide a qualitative explanation, the following rationalization still holds if the ordering of the doubly occupied orbitals is not correct. The effect of such orbital interactions is an electron transfer from the highest occupied orbitals of $CH_2O^{\cdot -}$ to the vacant orbitals 2*s* and 2*p* of Li^+. Only interactions between orbitals of the same symmetry are allowed, and since these interactions are one or two electron, they are all stabilizing in nature. In the formation of species (A) (α 180°), by symmetry, orbitals ψ_1 and ψ_3 can interact only with $2p_y$, ψ_2 with $2p_x$, and ψ_4 with 2*s* and $2p_z$ (see Figure 2). While the last interaction is of σ type, the others are all of π type. Therefore, we should expect that the bond between the cation and the anion has significant π character. This result is confirmed by the overlap population values listed in Table 2 and by the gross orbital charges listed in Table 3. The total overlap population between Li^+ and $CH_2O^{\cdot -}$ is 0·2709, of which the π component is 0·1914 and the σ component only 0·0795. The same information is provided by the values of the gross orbital charges from which it is evident that the greatest charge transfer is to the $2p_y$ and $2p_x$ orbitals of Li^+.

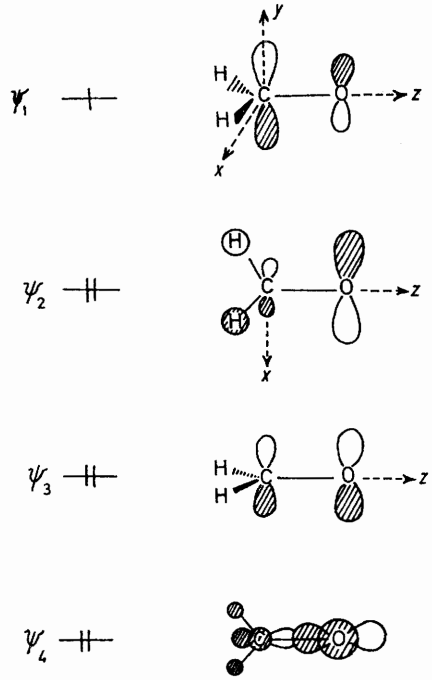

FIGURE 2 Shape and ordering of the first four higher occupied MOs of $CH_2O^{\cdot -}$

TABLE 2

Overlap populations between Li^+ and $H_2CO^{\cdot -}$ for the two stable species (A) and (B) computed with the STO-6G basis set

	(A)		(B)	
	C–Li	O–Li	C–Li	O–Li
σ component	−0·0707	0·1502	0·0093	0·1198
π component	−0·0069	0·1983	0·0015	0·0665
Total σ	0·0795		0·1291	
Total π	0·1914		0·0679	
Total (σ + π)	0·2709		0·1972	

TABLE 3

Net atomic charges (ρ) and gross orbital populations of the valence orbitals for species (A) and (B) computed with the STO-6G basis set

(A)

	ρ	*s*	p_x	p_y	p_z
C	−0·013	1·15	0·98	1·09	0·79
O	−0·305	1·79	1·71	1·60	1·21
H	+0·036	0·96			
Li	+0·248	0·09	0·25	0·30	0·11

(B)

	ρ	*s*	p_x	p_y	p_z
C	−0·049	1·17	0·99	1·07	0·83
O	−0·284	1·83	1·79	1·46	1·19
H	+0·040	0·96			
Li	+0·255	0·21	0·15	0·14	0·24

In the formation of species (B) (α 90°), only the interaction between orbital ψ_2 and $2p_x$ is of π type, while the other interactions between ψ_1, ψ_3, and ψ_4 and 2*s* and $2p_y$ are of σ type. Therefore, in the latter case, we should expect a bond with greater σ character and this result is confirmed again by the values of the overlap populations and of the gross orbital charges (see Table 3).

Additional interesting information can be obtained from the data listed in Table 3. The overall charge transfer from the anion to the cation is 0·75 and 0·74 e for species (A) and (B) respectively. The net atomic charges (see again Table 3) are not too dissimilar in the two species, with a carbon atom slightly negative, the two hydrogens slightly positive, and the oxygen atom significantly negative with an almost equivalent positive charge on Li.

The above results give a satisfactory explanation of the experimental observations as they actually predict that the more stable structure of the lithium–formaldehyde ion pair should be that with the metal atom on the molecular plane of the organic anion. It is also gratifying that the 'above the plane' position corresponds to an energy minimum. The calculated energy difference between these two structures is however too large with respect to the value estimated in ion pairs of aromatic ketyls. This discrepancy could be due to either the kind of basis sets used in the present computations (minimal basis sets), or the intrinsic differences between the model system investigated here and those experimentally studied. However we feel that the major reason for this failure lies in the neglect of solvation effects around the lithium atom.

When introducing explicit interaction with the solvent molecules we should also expect a reduction of the covalent character in the bond between anion and cation which, from the present calculations, seems to be exceedingly large for an ion pair.

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