

66/THEORETICAL STUDIES ON ION-PAIRS.
AN *AB INITIO* INVESTIGATION
ON THE Na-FORMALDEHYDE ION-PAIR

FERNANDO BERNARDI^(°) (*), GIANFRANCO PEDULLI (*),
MAURIZIO GUERRA (**), and H. BERNHARD SCHLEGEL (***)

(*) *Istituto di Chimica Organica dell'Università, Bologna*

(**) *Laboratorio CNR dei Composti del Carbonio, Ozzano Emilia (Bologna)*

(***) *Department of Chemistry, Queen's University, Kingston, Ont., Canada*

Summary. — The Na-formaldehyde ion-pair has been investigated using an *ab initio* MO SCF UHF procedure. The results of the calculations suggest the existence of only one stable species with the Na⁺ cation 1.90 Å above the oxygen atom. The bond with Na⁺ is found to be mostly ionic, whereas that with the corresponding first row cation, Li⁺, was found to be mostly covalent. The origin of this difference is traced to the different magnitude of the interactions between the occupied MO's of CH₂O⁻ and the vacant orbitals of the two cations. Since these interactions are larger with Li⁺ than with Na⁺, the electron transfer from the anion to the cation is greater with the smaller ion, this being responsible for the greater covalent character of the oxygen-metal bond.

Riassunto. — La coppia ionica Na-formaldeide è stata studiata con un trattamento *ab initio* MO SCF UHF. I risultati dei calcoli suggeriscono l'esistenza di una sola specie stabile con il catione Na⁺ ad 1,90 Å sopra l'atomo di ossigeno.

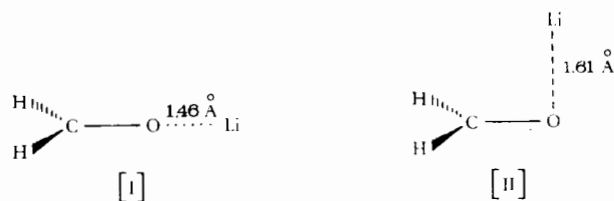
Si è trovato che il legame con Na⁺ è principalmente di carattere ionico, mentre il legame con il catione Li⁺ era stato trovato essere principalmente covalente. L'origine di questa differenza è dovuta alla diversità d'interazione tra gli MO occupati di CH₂O⁻ e gli orbitali vacanti dei due cationi. Poiché queste interazioni sono significativamente maggiori con Li⁺ che con Na⁺, il trasferimento elettronico dall'anione al catione è maggiore con lo ione più piccolo, causando in questo caso un maggior carattere covalente del legame ossigeno-metallo.

The structural properties of ion-pairs of ketyls have been the subject of increasing interest in the last few years, particularly from the experimental point of view⁽¹⁾. To obtain greater insight into the structure of these species and the strength of the interaction between anion and cation, we

^(°) Author to whom correspondence should be addressed; Istituto di Chimica Organica dell'Università, Viale Risorgimento 4, 40136 Bologna.

⁽¹⁾ K. S. Chen, S. W. Mao, K. Nakamura, N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6004 (1971); K. Nakamura, B. F. Wong, N. Hirota, *ibid.*, **95**, 6919 (1973) and references therein.

have recently investigated theoretically the Li-formaldehyde ion-pair⁽²⁾. A detailed analysis of that portion of the energy surface relevant to the discussion of the bond formation in the ion-pair, was carried out by an *ab initio* method. Our calculations showed two energy minima corresponding to the structures [I] and [II], the former being more stable by 19 kcal mol⁻¹.



Unfortunately, no detailed experimental studies have been made on such a simple alkali metal-ketyl complex. However, its properties are not expected to differ greatly from those of ketyls of larger dimensions, since in each case the main functional group responsible for the formation of the partial bond between anion and cation is the carbonyl group. Our previous calculations on the lithium ion-pair of formaldehyde are in qualitative agreement with the results of Hirota and his co-workers⁽¹⁾ on the ion-pairs of aromatic ketyls, as they postulated an equilibrium between just these two forms, [I] and [II], to explain the solvent and temperature dependence of the ¹³C and alkali metal splittings. The main discrepancies between the experimental and theoretical results are the following: i) the computed energy difference between the two stable species [I] and [II] is too large when compared to the experimental estimate of only a few kcal mol⁻¹, and ii) the covalent character of the oxygen-lithium bond seems too large for an ion-pair. These discrepancies can be attributed not only to the limitations of the computational method used (*i.e.* one-determinant wave function and small basis set) but also to the differences in the systems investigated theoretically and experimentally, and in particular to the neglect of solvation effects. In fact, it must be emphasized that our theoretical results refer to an isolated ion-pair in the gas phase. A detailed understanding of this situation is essential before the effects of solvation can be taken into account.

An analysis of an ion-pair involving an alkali metal larger than lithium is also necessary for understanding the effects of size, polarizability and electron affinity of the cation, on the properties of these complexes. With this purpose we report in the present paper the results of an *ab initio* theoretical investigation on the Na-formaldehyde ion pair and compare the results with the properties of the Li-formaldehyde ion-pair.

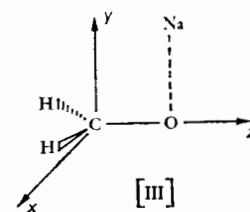
⁽²⁾ F. Bernardi, G. F. Pedulli, *J. Chem. Soc. Perkin II*, 194 (1975).

The Na-formaldehyde ion-pair was investigated by a computational method. The Na-formaldehyde ion-pair species.

The procedure employed⁽³⁾ with the computation, using the Gaussian method.

Since the wavefunction was used as an eigenfunction of the spin operator, the spin conformations investigated when compared with the results obtained by higher order perturbation theory.

We have first investigated the Na-CH₂O—Na complex and the Na-formaldehyde ketyl. The distance at various directions was determined, maintaining the formaldehyde molecule in the plane of the sodium atom, though the formaldehyde molecule was not investigated it was assumed to be in a situation of a cationic complex. The geometry was optimized in a previous investigation of the Li-formaldehyde ion-pair. The HCH = 113.72 degrees. The one minimum corresponds to the structure [III] and the other to the structure [I] and [II].



⁽³⁾ J. A. Pople, R. Krishnamoorti, and W. J. Hehre, *J. Chem. Phys.*, **57**, 1517 (1972).

⁽⁴⁾ W. J. Hehre, R. Krishnamoorti, and J. A. Pople, *J. Chem. Phys.*, **57**, 2229 (1972). "Quantum Chemistry Program Exchange," U.S.A.

⁽⁵⁾ W. J. Hehre, R. Krishnamoorti, and J. A. Pople, *J. Chem. Phys.*, **57**, 2229 (1972).

⁽⁶⁾ F. Bernardi, G. F. Pedulli, and J. A. Pople, *J. Chem. Phys.*, **61**, 1157 (1974).

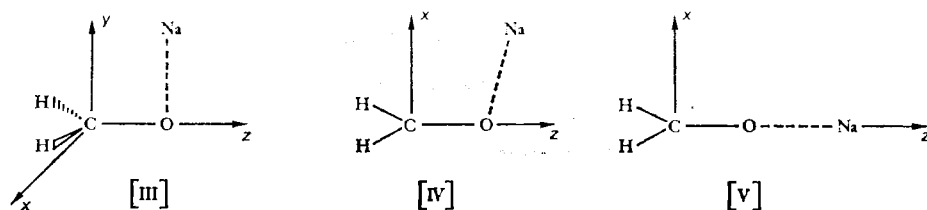
COMPUTATIONAL PROCEDURE

The Na-formaldehyde ion-pair has been investigated using the same computational method as used in the previous investigation for the Li-formaldehyde ion-pair⁽²⁾, in order to provide comparable data for the two species.

The procedure consists of an Unrestricted Hartree-Fock (UHF) treatment⁽³⁾ with the computations performed at two different levels of sophistication, using the Gaussian 70 series of programs⁽⁴⁾.

Since the wavefunction optimized with a UHF treatment is not an exact eigenfunction of the spin operator S^2 , it is informative to say that, for all the conformations investigated, the $\langle S^2 \rangle$ value is of the order of 0.76, which, when compared with the correct value of 0.75, demonstrates that the contamination by higher spin eigenfunctions is in the present case quite small.

We have first made a detailed search of the energy surface of the $\cdot\text{CH}_2\text{O}-\text{Na}$ complex at the STO-3G level⁽⁵⁾, keeping the geometry of the formaldehyde ketyl fixed and optimizing only the Na-formaldehyde bond distance at various directions of attack of the cation, both in the plane containing the formaldehyde ketyl and in a plane perpendicular to it. Even though the formaldehyde ketyl is probably pyramidal⁽⁶⁾, in the present investigation it was assumed to be planar in an attempt to reproduce the situation of a cationic attack on the carbonyl group of a planar aromatic ketyl. The geometrical parameters used for the CH_2O^- anion are those optimized in a previous *ab initio* investigation⁽⁶⁾ and used in the study of the Li-formaldehyde ion-pair (*i.e.*, $r(\text{C}-\text{O}) = 1.3173 \text{ \AA}$, $r(\text{C}-\text{H}) = 1.0909 \text{ \AA}$, $\widehat{\text{HCH}} = 113.72$ degrees). At this computational level, we have found only one minimum corresponding to structure [III]. We then reinvestigated this minimum [III] and the transition states to rotation around the C—O bond,



⁽³⁾ J. A. Pople, R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1974).

⁽⁴⁾ W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, J. A. Pople, "Quantum Chemistry Program Exchange", Indiana University, Bloomington, Ind., U.S.A.

⁽⁵⁾ W. J. Hehre, R. F. Stewart, J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

⁽⁶⁾ F. Bernardi, M. Guerra, G. F. Pedulli, *J. Phys. Chem.*, **78**, 2144 (1974).

[IV], and to linear inversion, [V], with an STO-6G basis set⁽⁵⁾, by minimizing the energy with respect to the C—O and Na—O bond lengths.

The preparation of energy surfaces such as shown in figures 2 and 3 has been described in detail in previous papers⁽⁷⁾. An expression with several linear parameters is fitted to the calculated energies by a "least-squares" procedure. The resulting equation is used to calculate the energy of the molecule at the mesh points. These energies are then plotted as a perspective view of the surfaces.

RESULTS AND DISCUSSION

The results of the investigation on the Na-formaldehyde ion-pair at the STO-3G level are summarized in figure 1, where curve 2 refers to a cationic attack in the plane of the anion (horizontal attack) and curve 1 to a cationic attack in the plane bisecting the HCH angle (perpendicular attack). These two curves show the variation of the total energy of the

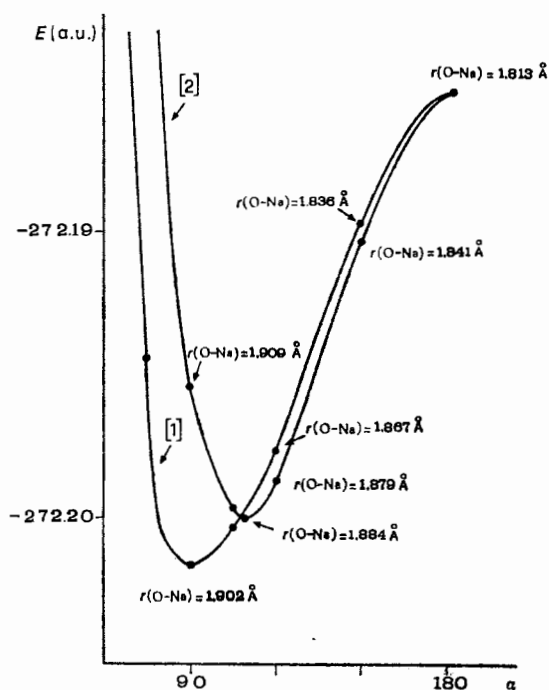


Fig. 1. - Optimum total energy values vs the angle α for a horizontal (curve 2) and a perpendicular (curve 1) cationic attack. Each $r(\text{O-Na})$ (Å) value refers to the optimum O—Na bond distance at the given α value.

(7) F. Bernardi, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M. Whangbo, S. Wolfe, *J. Amer. Chem. Soc.*, **97**, 2209 (1975).

sodium complex of the formaldehyde ion-pair. The C—O and O—Na bond system was minimized.

In figure 1 we also show that the energy values are almost the same for any value of α and

Both curves of figure 1 (curve 1) the minimum

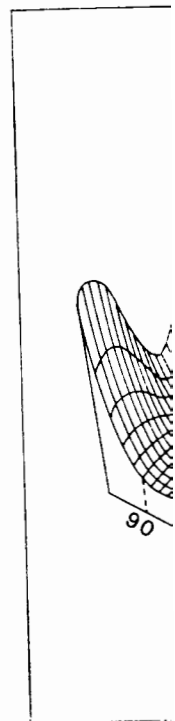


Fig. 2. - Rotation

located on the symmetric conformer is, at the Na-formaldehyde ion-pair occurs at $\alpha = 108.9^\circ$ but, rather, is the transition is better illustrated in about the C—O bond

(*) The α values are: 60, 75, 90, 105, 1

sodium complex of the formaldehyde ketyl with α being the angle between the C—O and O—Na bonds. For each value of α (*), the total energy of the system was minimized with respect to the O—Na bond distance.

In figure 1 we also report the computed optimum $r(\text{O—Na})$ values which are almost the same for the horizontal and perpendicular cationic attacks for any value of α and decrease slightly with increasing α .

Both curves of figure 1 show a minimum. For the perpendicular attack (curve 1) the minimum occurs at $\alpha = 90$ degrees, with the sodium atom

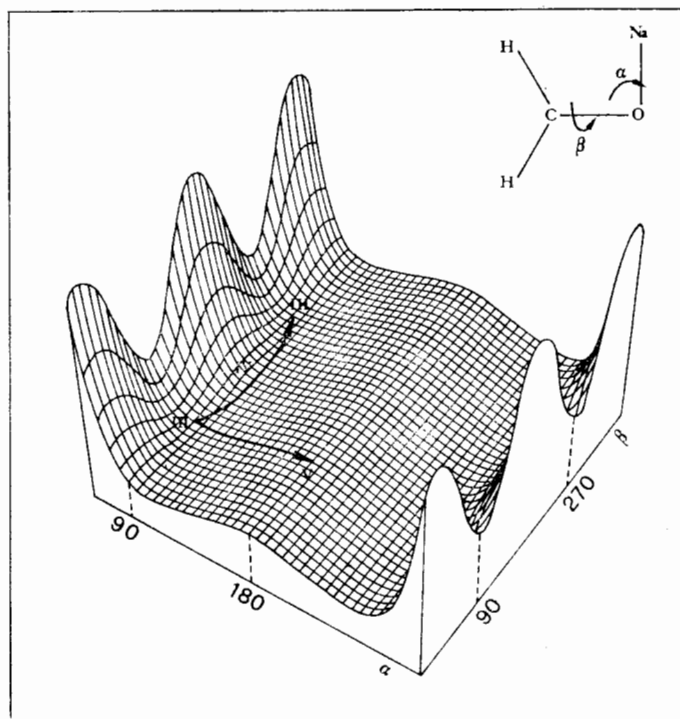


Fig. 2. - Rotation-inversion surface for the Na-formaldehyde ion-pair.

located on the symmetry axis of the $2p_y$ orbital of oxygen. The corresponding conformer is, at this computational level, the only stable species for the Na-formaldehyde ion-pair. For the horizontal attack (curve 2) the minimum occurs at $\alpha = 108.9^\circ$; this conformer, however, is not a stable species, but, rather, is the transition state to rotation about the C—O bond. This is better illustrated in figure 2 which shows the surface for the rotation about the C—O bond and linear inversion at the oxygen centre.

(*) The α values (in degrees), at which the computations were carried out, are: 60, 75, 90, 105, 120, 150 and 180°.

In this surface there is only one minimum corresponding to structure [III], while structures [IV] and [V] are the transition states to rotation and linear inversion, respectively. These three structures have been reinvestigated at the STO-6G level by optimizing $r(\text{C—O})$ and $r(\text{O—Na})$. The computed optimum values are listed in table 1. The $r(\text{O—Na})$ distances are in very good agreement with those computed at the STO-3G level. Furthermore, the energy differences, computed at the two levels of sophistication, between structure [III] and structures [IV] and [V] are practically identical. These values, which are the energy barriers to rotation and inversion, are 1.22 and 10.4 kcal mol⁻¹, respectively, at the STO-6G level and 1.41 and 10.23 kcal mol⁻¹ at the STO-3G level. These are all indications that the STO-3G data shown in figure 1 are quite reliable.

TABLE 1. - OPTIMUM VALUES OF $r(\text{C—O})$ AND $r(\text{O—Na})$ (Å) COMPUTED AT THE STO-6G LEVEL FOR STRUCTURES [III], [IV] AND [V]

| Distance | [III] | [IV] | [V] |
|------------------|--------|--------|--------|
| $r(\text{C—O})$ | 1.3414 | 1.3311 | 1.3107 |
| $r(\text{O—Na})$ | 1.8946 | 1.8843 | 1.8214 |

It is interesting to observe that the C—O bond lengths follow the same trend as the C—O overlap populations listed in table 2. With respect to the unperturbed situation of the formaldehyde ketyl, in structure [III] the charge transfer to the cation causes a decrease both in the σ and π overlap populations of the C—O bond and, correspondingly, there is a lengthening

TABLE 2. - OVERLAP POPULATIONS OF THE C—O BOND COMPUTED AT THE STO-6G LEVEL FOR STRUCTURES [III], [IV], [V] AND CH_2O^-

| | [III] | [IV] | [V] | CH_2O^- |
|------------------------------|--------|--------|--------|-------------------------|
| σ -overlap population | 0.2437 | 0.2518 | 0.2737 | 0.2526 |
| π -overlap population | 0.0516 | 0.0583 | 0.0654 | 0.0739 |
| Total overlap population | 0.2953 | 0.3101 | 0.3391 | 0.3265 |

of the C—O distance. In structure [IV] the decrease in the overlap population is smaller and accordingly the lengthening of the C—O bond is also smaller. In structure [V] there is an increase in the σ overlap population due to a reduction of the antibonding character of the interaction between the 2s orbitals of C and O as a consequence of the charge transfer to Na^+ .

Although the π overlap becomes slightly greater length becomes slightly

It is instructive to with the corresponding visualize better the difference in figure 3 and has been a previous paper (2). It corresponding to the transition to rotation around the higher (11.6 kcal mol⁻¹)

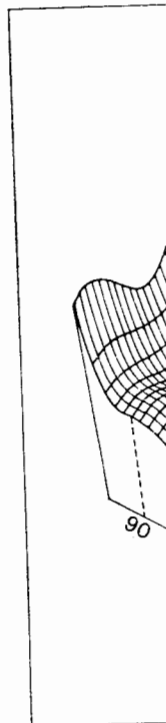


Fig. 3. - Rotation

In order to rotate these ion-pairs when it seems appropriate conformation, *i.e.* str

An important part of electron transfer from electron transfer cou

Although the π overlap population decreases, the total overlap population becomes slightly greater than in CH_2O^- and correspondingly the C—O bond length becomes slightly shorter.

It is instructive to compare the potential energy surface just discussed with the corresponding one for the Li-formaldehyde ion-pair, in order to visualize better the differences in the two cases. The latter surface is shown in figure 3 and has been obtained from the STO-3G results reported in a previous paper (²). It is evident that in this surface there are two minima corresponding to the two stable species [I] and [II]. In this case the barrier to rotation around the C—O bond for the Li analogue of [III] is much higher ($11.6 \text{ kcal mol}^{-1}$) than in the Na complex.

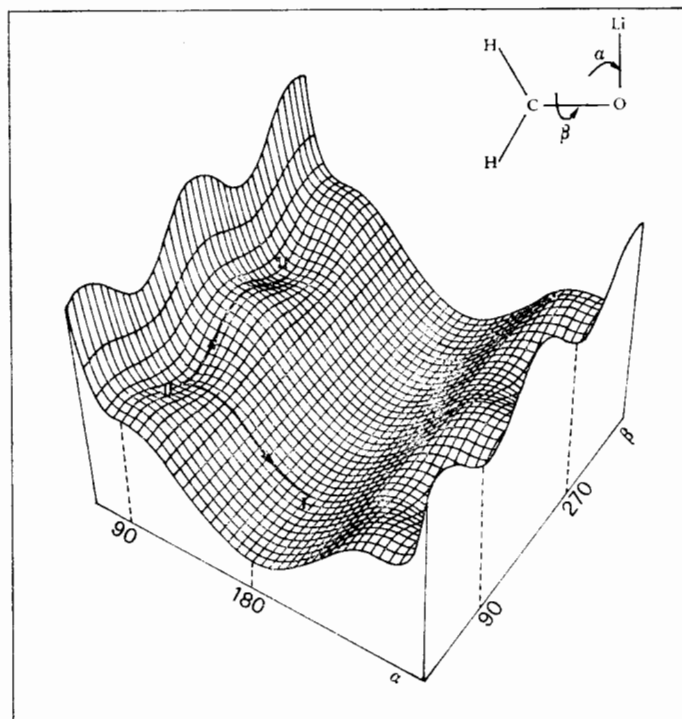


Fig. 3. - Rotation-inversion surface for the Li-formaldehyde ion-pair.

In order to rationalize the differences in the electronic properties of these ion-pairs when a first-row cation is replaced by a second-row cation, it seems appropriate to compare the two species which have the same conformation, *i.e.* structures [II] and [III].

An important property in this kind of molecular system is the extent of electron transfer from the anion to the cation. A suitable measure of the electron transfer could be given by $Q = 1 - q$, where q is the net atomic

| MO Type | CH_2O^- | $\text{CH}_2\text{O}-\text{Li}^+$ | $\text{CH}_2\text{O}-\text{Na}^+$ |
|---------|--|--|--|
| | <p>0.0000 0.7041 0.0000 0.2960</p> | <p>Li 0.2974 0.0001 0.4803 0.0001 0.2221</p> | <p>Na 0.0228 0.0002 0.5959 0.0002 0.3810</p> |
| | <p>0.1645 0.0196 0.1645 1.6512</p> | <p>Li 0.1078 0.1403 0.0903 0.1908 1.4203</p> | <p>Na 0.0129 0.1527 0.0305 0.1527 1.0512</p> |
| | <p>0.0000 0.8997 0.0000 1.1003</p> | <p>Li 0.1901 0.0282 0.6198 0.0282 1.1337</p> | <p>Na 0.1756 0.0012 0.7183 0.0012 1.1036</p> |
| | <p>0.0786 0.5431 0.0786 1.2097</p> | <p>Li 0.0945 0.0553 0.5180 0.0553 1.2769</p> | <p>Na 0.0343 0.0777 0.5900 0.0777 1.2296</p> |
| | <p>0.4567 0.8088 0.4567 0.2788</p> | <p>Li 0.0447 0.3434 0.6868 0.3434 0.3697</p> | <p>Na 0.0047 0.4239 0.8774 0.4239 0.2701</p> |

Fig. 4. - Partial gross atomic charges in the MO's of CH_2O^- , $\text{CH}_2\text{O}-\text{Li}^+$ and $\text{CH}_2\text{O}-\text{Na}^+$.

charge of the cation. With the transfer of the anion from the Na-formaldehyde ion-pairing stable species of the anion to the cation, it is second-row cations. It is more ionic than that involving the five occupied molecular orbitals of the two ion-pairs, and have made the assumption and in the two ion-pair corresponds to that of the occupancy of the LUMO framework of a UHF method the energy and symmetry occupied molecular orbitals "doubly-occupied MO" theory allows independent since this ordering is following arguments:

These results can be described in terms of the orbital description of the formaldehyde ketyl anion shows the ordering of the orbitals of Li^- and of the vacant orbitals at the level. From the magnitude of the singly-occupied HOMO of the vacant orbitals of CH_2O^- have, of course, the energy of CH_2O^- and Ψ_B the energy of Φ_A mixes with Ψ_B in the process of electron transfer from Φ_A to

where E_{Φ_A} and E_{Ψ_B} are the energies of Φ_A and Ψ_B , and n the number of electrons transferred from Φ_A to Ψ_B .

(8) N. D. Epiotis

charge of the cation. With this definition, Q measures the number of electrons transferred from the anion to the cation. In [III], the stable species of the Na-formaldehyde ion-pair, $Q = 0.26$ electrons, while in [II], the corresponding stable species of the Li-formaldehyde ion pair, $Q = 0.75$ electrons⁽²⁾. Although in both cases Q is positive, implying an electron transfer from the anion to the cation, its magnitude is significantly different with first and second-row cations. It follows that the Na-formaldehyde bond is much more ionic than that involving the lithium atom. The details of the electron transfer are given in figure 4 where we report the partial gross atomic charges in the five occupied molecular orbitals (MO) of highest energy of CH_2O^- and of the two ion-pairs, as obtained from a Mulliken population analysis. We have made the assumption here that the ordering of the MO's in CH_2O^- and in the two ion-pairs remains the same, and, further, that this ordering corresponds to that of the closed shell system CH_2O with the further single occupancy of the LUMO (lowest unoccupied molecular orbital). Within the framework of a UHF calculation, it is possible to determine with certainty the energy and symmetry of only the singly-occupied HOMO (highest occupied molecular orbital). The correct energy ordering of the other "doubly-occupied MO's" cannot be determined unambiguously since the theory allows independent ordering of the α and β spin orbitals. However, since this ordering is used only to provide a qualitative explanation, the following arguments still hold even if the ordering is not correct.

These results can be qualitatively rationalised in terms of a perturbational description of the interactions between the occupied MO's of the formaldehyde ketyl and the vacant atomic orbitals of Li^+ and Na^+ . Figure 5 shows the ordering of the energy levels of the vacant $2s$ and $2p$ orbitals of Li^+ and of the vacant $3s$ and $3p$ orbitals of Na^+ computed at the STO-6G level. From the magnitude of the MO coefficients it appears that the singly-occupied HOMO of CH_2O^- should have an energy slightly lower than those of the vacant orbitals of Li^+ , and the remaining doubly-occupied MO's of CH_2O^- have, of course, even lower energies. If Φ_A denotes the filled MO of CH_2O^- and Ψ_B the unfilled atomic orbital of the cation, in the interaction Φ_A mixes with Ψ_B in a bonding combination and this amounts to an electron transfer from Φ_A to Ψ_B , given by the expression⁽⁸⁾:

$$Q_{AB} = n [\langle \Phi_A | \hat{H} | \Psi_B \rangle / (E_{\Phi_A} - E_{\Psi_B})]^2$$

where E_{Φ_A} and E_{Ψ_B} denote the energy levels of the unperturbed orbitals Φ_A and Ψ_B , and n the occupation number of the resulting MO. Therefore, the electron transfer from Φ_A to Ψ_B is inversely proportional to the square of

(8) N. D. Epiotis, *J. Amer. Chem. Soc.*, 95, 3087 (1973).

their energy difference (the energy factor) and directly proportional to the square of their interaction matrix element.

Using this equation we can now trace the terms dominating the electron transfer occurring in the two ion-pairs. An interesting result arises from a comparison of the partial gross atomic charges in the MO.s of the ion-pairs: it is evident that the electron transfer from a given MO of CH_2O^- is always larger with Li^+ , and this result suggests that the electron transfer to different cations is dominated by the energy factor. It is also interesting

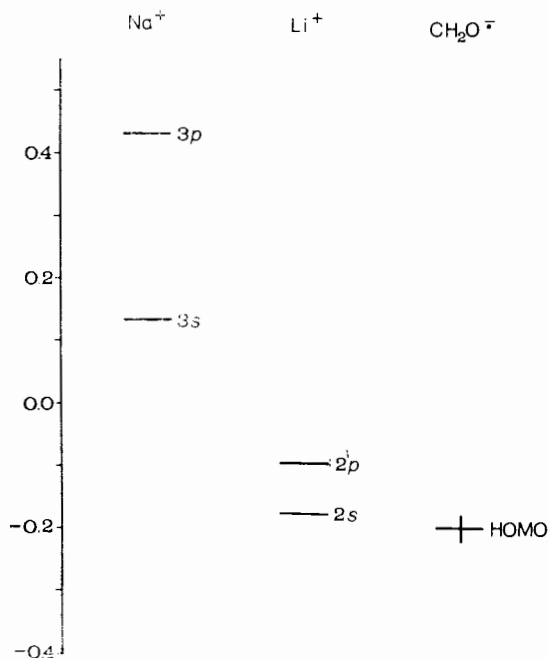


Fig. 5. - Relative ordering of the energy levels of the vacant orbitals of Li^+ and Na^+ with respect to the singly occupied HOMO of CH_2O^- .

to observe that while the largest electron transfer in $\text{CH}_2\text{O}-\text{Li}$ occurs from the HOMO of CH_2O^- , the largest electron transfer in $\text{CH}_2\text{O}-\text{Na}$ comes from the inner doubly-occupied π MO of CH_2O^- , suggesting that the importance of the matrix element increases going from Li^+ to Na^+ .

A quantitative comparison of the bond strengths in the ion-pairs can be made on the basis of the data listed in table 3.

Within the limits that the bond overlap population can be assumed to be a measure of the strength of covalent bonding between two atoms, it is evident that the bond with Li^+ has a higher covalent character than that with Na^+ . Furthermore, with Na^+ the bond is almost completely a σ bond, while with Li^+ the π component is quite significant (*ca.* 35%)⁽²⁾.

TABLE 3. - OVERLAP P
BETWEEN THE TWO C.A.
IN

| Population | |
|------------------------|--|
| σ -Overlap | |
| π -Overlap | |
| ($\sigma+\pi$) | |
| Total σ | |
| Total π | |
| Total ($\sigma+\pi$) | |
| (a) Values for Li-f | |

The greater ioni
again from a compari
see that there is a l
by a significant nega
while the two hydro
in the Li-formaldeh
negative charge on ox

TABLE 4. - NET AT
OF THE VALENCE

| Atom | |
|------|--|
| C | |
| O | |
| H | |
| Na | |

This investigat
of isolated ion-pair
on the nature of t
stable species of t

TABLE 3. - OVERLAP POPULATIONS (PARTIAL AND TOTAL) FOR THE BONDS BETWEEN THE TWO CATIONS Na^+ AND Li^+ AND THE FORMALDEHYDE KETYL IN THE CORRESPONDING ION-PAIRS

| Population | Na-formaldehyde | | Li-formaldehyde ^(a) | |
|--------------------------|-----------------|--------|--------------------------------|--------|
| | C—Na | O—Na | C—Li | O—Li |
| σ -Overlap | 0.0151 | 0.0878 | 0.0093 | 0.1198 |
| π -Overlap | 0.0007 | 0.0090 | 0.0015 | 0.0665 |
| ($\sigma + \pi$) | 0.0158 | 0.0968 | 0.0108 | 0.1863 |
| Total σ | 0.1029 | | 0.1291 | |
| Total π | 0.0097 | | 0.0679 | |
| Total ($\sigma + \pi$) | 0.1126 | | 0.1972 | |

^(a) Values for Li-formaldehyde taken from ref. (2).

The greater ionic character of the Na-formaldehyde ion-pair emerges again from a comparison of the data listed in table 4, from which one can see that there is a large positive charge on the Na atom counterbalanced by a significant negative charge on oxygen and a smaller one on carbon, while the two hydrogens are only slightly negative. On the other hand, in the Li-formaldehyde ion-pair both the positive charge on Li and the negative charge on oxygen are much smaller (+0.25 and -0.31, respectively).

TABLE 4. - NET ATOMIC CHARGES (ρ) AND GROSS ORBITAL POPULATIONS OF THE VALENCE ORBITALS FOR THE STABLE SPECIES [III] COMPUTED WITH THE STO-6G BASIS SET

| Atom | ρ | s | p_x | p_y | p_z |
|------|--------|------|-------|-------|-------|
| C | -0.20 | 1.14 | 0.91 | 1.31 | 0.84 |
| O | -0.46 | 1.87 | 1.92 | 1.48 | 1.19 |
| H | -0.04 | 1.04 | — | — | — |
| Na | +0.74 | 0.19 | 0.22 | 0.25 | 0.23 |

CONCLUSIONS

This investigation has shown that the static and dynamic properties of isolated ion-pairs of ketyls in the gas phase are significantly dependent on the nature of the cation involved. With a first-row cation (Li^+) two stable species of the ion-pair exist, corresponding to the conformers [I]

and [II], and the bond between cation and anion is mostly covalent. However, with a second-row cation (Na^+) only one stable species exists corresponding to the conformer [III], where the bond between the two ions is mainly ionic. The different bond character in the complexes involving the two ions is rationalised in terms of the different magnitude of the interaction between the occupied orbitals of the anion and the vacant orbitals of the cations.

The theoretical results obtained for the Li-formaldehyde ion-pair agree, in a qualitative way, with the experimental evidence, whilst for the Na-formaldehyde complex the agreement is poorer. In fact, also in the case of sodium ion-ketals ion-pairs of the existence of two stable species ("in plane" and "above the plane") has been postulated to explain the observed trend of ^{13}C and alkali metal splittings with changes in the temperature and the solvent (1). On the other hand, the theoretical results show only one stable species, the "above the plane" conformer [III]. This latter result has been obtained in the absence of solvation effects. It must also be pointed out that the energy differences between the conformers [III], [IV] and [V] are not very large (*ca.* 1 kcal mol $^{-1}$ between [III] and [IV] and *ca.* 10 kcal mol $^{-1}$ between [III] and [V]) and therefore it is possible that solvation could affect these structures sufficiently to render [V] the most stable conformer.

The results presented here are a starting point for investigations aimed at elucidating the effects of solvation on these ion-pairs. Work in this direction is in progress.

Received on December 20th 1974.