Quantum Chemical Investigations on the Structure of the Gas Phase Ion Solvates $M^+(DMF\text{-}CH_3^+)$

B. M. Rode

Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

and

and R. Ahlrichs

Abteilung für Theoretische Chemie, Institut für Physikalische Chemie und Elektrochemie der Universität Karlsruhe, Kaiserstraße 12, D-7500 Karlsruhe

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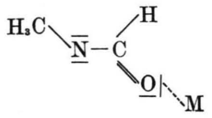
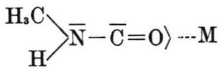
The structure of the dimethylformamide fragment ($DMF\text{-}CH_3^+$) and its complexes with Li^+ and Na^+ being observed in low pressure gas phase solvation has been investigated by means of ab initio SCF calculations with two different basis sets. Stabilization energies, charge transfer and polarization effects upon complex formation are discussed.

Introduction

Mass spectrometric investigations on gas phase solvation of metal ions by dimethylformamide (DMF) at pressures below 10^{-5} torr led to the detection of monosolvate complexes of the ($DMF\text{-}CH_3$) fragment with the alkali metals Li, Na and K [1]. These observations raised the question about the structure of such complexes, since the usual chemical considerations allow two possible tautomeric arrangements, the one being derived from the amide form (A), the second from the isocyanate structure (B).



(A)



(B)

An experimental answer to this question is – under the conditions of the observation of these compounds – almost impossible. On the other hand, these conditions (gas phase, absence of other ions than M^+ and other compounds than the solvent and its fragments, as well as the very low concentrations) correspond very well to the conditions involved in the usual quantum chemical model calculations, which treat the isolated complex systems.

For this reason, molecular orbital calculations seemed to represent a reliable way to decide, which of both structures should be realized in the experiment. The only difficulty remaining for the quantum chemical treatment was the question, whether the compounds are present in their ground states or in any excited states, due to the ionization process in the mass spectrometer. Considering, however, that the lowest possible ionization energy has been applied during the experiments [1], we believe the ground state to be the most prominent one realized. We therefore performed our calculations on the fragment ($DMF\text{-}CH_3^+$), which is known to be formed readily from DMF, and its reaction products with the metal ions, treating them all as closed shell systems.

Method of Calculation

Two different Gaussian lobe basis sets have been employed in our calculations:

a) a minimal basis set, 2 s/1 p for C, N, O, 1 s for H, 2 s for Li^+, 4 s/2 p for Na^+ [2];

b) a larger basis set, 8 s/4 p (5111/31) for C, N, O, 4 s (31) for H, 7 s (511) + polarization functions for Li^+ [3].

The calculations with the large basis have been performed at the UNIVAC 1108 computer of the University of Karlsruhe using a standard SCF program (essential parts of this program are described in Ref. 7), those with the small basis at the CDC 3300 computer of the University of Innsbruck.

For bond lengths and angles, we took the experimental values of dimethylformamide [4], except for the C/N/C angle in fragment (A) and the $M^+ \dots O$ distance in both types of fragments. These parameters were varied with respect to lowest total energy using the small basis set.

Results and Discussion

1. Geometrical parameters

The C/N/C angle in ($DMF\text{-}CH_3^+$) was calculated to be approximately 110°, the remaining CH_3 group occupying the trans position to carbonyl oxygen. The $Li^+ \dots O$ distance was found to be 1.80 Å in both complexes, the $Na^+ \dots O$ distance resulted at 2.10 Å.

2. Energies

The calculated total energies are collected in Table 1. In Table 2, the energy differences between the tautomeric fragments and their complexes with the metal ions are presented, together with the respective energies of complex formation. From these values it can be deduced, that within both basis sets, the amide form (A) should be highly favoured over the isocyanate form (B), although the complex

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Reprint requests to Dr. B. M. Rode, Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, *A-6020 Innsbruck*, Austria.

Table 1. Total energies in a. u., A . . . amide structure, B . . . isocyanate structure.

Compound	Basis	A	B
$(DMF\text{-}CH_3^+)$	2/1	−175.9076	−175.7192
	8/4	−207.1735	−206.9805
$(DMF\text{-}CH_3^+)\,Li^+$	2/1	−182.5365	−182.3501
	8/4	−214.6624	−214.4882
$(DMF\text{-}CH_3^+)\,Na^+$	2/1	−325.2289	−325.0432

Table 2. Relative stabilization of fragments and complexes ($E_A - E_B$) and solvation energies (E_S) in kcal/mole.

Compound	Basis	$E_A - E_B$	E_S (A)	E_S (B)
$(DMF\text{-}CH_3^+)$	2/1	118.2	—	—
$(DMF\text{-}CH_3^+)\,Li^+$	8/4	121.1	—	—
	2/1	109.3	137.4	138.6
	8/4	117.0	159.1	170.9
$(DMF\text{-}CH_3^+)\,Na^+$	2/1	116.5	121.5	123.2

formation energies in the latter are somewhat greater than in the first one. We therefore conclude, that the amide form is also being dominant under the experimental conditions mentioned above.

This conclusion is confirmed also by the calculated one particle energies, since the highest eigenvalue resulting for $(DMF\text{-}CH_3^+)$ in the isocyanate structure turns out to be positive, even in the larger basis set.

3. Charge distribution

The minimal basis seems to reflect correctly the relative stabilization of the compounds. We cannot expect, however, to obtain detailed information about the electronic structure and the charge distribution within such a rough approximation to the wave function. Comparing the Mulliken [5] population values resulting from the two basis sets for the fragments and the corresponding Li^+ complexes (cf. Table 3), it can be seen that discrepancies do not exist only for the absolute values, but – for type (A) compounds – even for the relative change in charge distribution upon ion bonding, i.e. the polarization effects due to ion influence.

Table 3. Mulliken charge densities (q) for $(DMF\text{-}CH_3^+)$ and relative changes (Δq^M) due to the influence of the ion M^+.

a) amide structure

	q (a)	q (b)	Δq^{Li} (a)	Δq^{Li} (b)	Δq^{Na} (a)
$H(CH_3)$	0.941	0.978	+0.039	+0.065	+0.034
$C(CH_3)$	6.268	6.079	−0.012	+0.074	−0.008
N	7.690	7.685	+0.061	+0.023	+0.048
C	5.753	5.677	+0.092	−0.176	+0.070
H	1.060	1.000	+0.047	+0.241	+0.039
O	8.408	8.623	−0.291	−0.159	−0.213
M	—	—	−0.015	−0.199	−0.035

b) isocyanate structure

	q (a)	q (b)	Δq^{Li} (a)	Δq^{Li} (b)	Δq^{Na} (a)
$H(CH_3)$	0.927	0.980	+0.042	+0.067	+0.037
$C(CH_3)$	6.100	5.935	−0.011	−0.070	−0.009
N	7.738	7.684	+0.028	+0.022	+0.022
C	6.108	5.981	+0.111	+0.128	+0.087
H	0.892	0.880	+0.082	+0.121	+0.073
O	8.381	8.581	−0.332	−0.201	−0.249
M	—	—	−0.006	−0.199	−0.037

(a) . . . small basis (b) . . . large basis

The reason for this is probably, that the minimal basis is not sufficiently flexible to describe correctly polarization and charge transfer occuring simultaneously along more than one or two bonds, since in the case of smaller and more simple ion-solvent complexes [6], such discrepancies did not occur. In the isocyanate structure, the strong polarization effects are localized almost at the $C=0$ group. In this case, the small basis set should account better for these effects, as can be demonstrated also by the calculated values (cf. Table 3).

With regard to the stabilization of the metal complexes, it can be assumed, that the remarkable rearrangement of electronic charge and the charge transfer to the cation should contribute to a good part to the high complex formation energy, which is about three times larger than the corresponding values for the formation of the $M^+(DMF)$ complexes [2].

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