Further work is under way to delineate the mechanism of the intermolecular coupling reaction and to more fully investigate nickel-promoted cyclization reactions.

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Studies of Cation Hydration

Sir:

Cation–water interactions have been of interest to chemists for many years but only relatively recently have accurate experimental data[1] been available on the energetics of such processes. There has been considerable interest in predicting the structure of ion hydrates using theoretical molecular orbital techniques, and a large number of semiempirical[2] and *ab initio*[3] calculations have been reported in the literature.

We have been carrying out high-accuracy *ab initio* molecular orbital studies on cation hydrates and now have a number of results which may be of general interest.

In Table I, we have calculated the energy of complex

Table I. Cation–Water Interactions

M	$-\Delta E_{\text{exptl}}$, kcal/mol	$-\Delta E_{\text{calcd}}$, kcal/mol	R, Å
Li$^+$	34	37	1.85
Be^{2+}		140	1.50
Na$^+$	24	27	2.20
Mg^{2+}		80	1.95
Al^{3+}		180	1.75
K$^+$	18	18	2.65
Ca^{2+}		53	2.40

formation and minimum energy M–O distance for Li$^+$, Be^{2+}, Na$^+$, Mg^{2+}, Al^{3+}, K$^+$, and Ca^{2+} monohydrate.[4] These complexes have a C_{2v} structure, with the metal along the line bisecting the oxygen lone pairs. A simple classical ion–dipole model would predict this geometry but would not give any information about the minimum

(1) I. Dzidic and P. Kebarle, *J. Phys. Chem.*, **74**, 1466 (1970), and references cited therein; J. D. Payzant, R. Yamdagni, and P. Kebarle, *Can. J. Chem.*, **49**, 3308 (1971).

(2) J. Daly and R. E. Burton, *Trans. Faraday Soc.*, **66**, 1281, 2408 (1970); **67**, 1219 (1971); H. Lischka, Th. Plesser, and P. Schuster, *Chem. Phys. Lett.*, **6**, 263 (1970), and references cited therein; K. G. Breitschwerdt and H. Kistenmacher, *ibid.*, **14**, 288 (1972).

(3) (a) G. H. F. Diercksen and W. P. Kraemers, *Theor. Chim. Acta*, **23**, 387, 393 (1972), and references cited therein; (b) P. Schuster and H. Preuss, *Chem. Phys. Lett.*, **11**, 35 (1971).

(4) The basis sets used in these calculations were as follows: for water, Dunning's optimum contraction [*J. Chem. Phys.*, **53**, 2833 (1970)] of Huzinaga's 9s/5p → 4s/2p augmented by a set of d polarization functions on oxygen and a set of p functions on hydrogens (see ref 5 for the exponents); for Li and Be, a 9s/3p set contracted to 4s/2p (see P. A. Kollman, *et al.*, *J. Amer. Chem. Soc.*, in press, for details); for Na, Mg, and Al, Huzinaga's [*J. Chem. Phys.*, **50**, 1371 (1969)] 11s/7p contracted to 6s/4p was used; and for K$^+$ and Ca^{2+} Wachter's 14s/9p → 8s/6p [*ibid.*, **52**, 1033 (1970)] basis was used.

energy M–O distance or the ΔE of complex formation. Our calculations on Li$^+$, Na$^+$, and K$^+$ hydrate are in very good agreement with experiment and with similar SCF studies,[3a] so we have some confidence in our prediction of the energetics and structure for the other cations.

Our long-term interests are in larger ion–water clusters which might approximate ions in liquid water. The many-body interaction ideas discussed by Hankins, *et al.*,[5] in their studies of water dimer and trimer are very useful in this regard. These ideas are summarized in eq 1. In a collection of n particles at positions x_1,

$$E(x_1, x_2, \ldots, x_n) = \sum_{i=1}^{n} E(x_i) +$$
$$\sum_{i>j=1}^{n} E^{(2)}(x_i, x_j) + \sum_{i>j>k=1}^{n} E^{(3)}(x_i, x_j, x_k) +$$
$$\sum_{i>j>k>l} E^{(4)}(x_i, x_j, x_k, x_l) + \ldots \quad (1)$$

$x_2, \ldots, x_n$, the total energy can be represented in terms of the energies of the individual particles, $E^{(1)}$, interacting pairs of particles $E^{(2)}$, triplets $E^{(3)}$, etc. If we can show by our *ab initio* calculations that terms such as $E^{(4)}$ are small for geometries of interest, we can determine the energies of essentially infinite clusters of molecules using the results of three-body potential surface studies which determine the various $E^{(1)}$, $E^{(2)}$, and $E^{(3)}$ terms. We have carried out SCF calculations on Be^{2+} and three water molecules, using a slightly smaller basis set[6] than in the cation–single water studies, to determine the magnitude of the $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ terms for a typical configuration.[7] All Be–O distances were 1.5 Å (that found in the single Be–H$_2$O complex); two waters were placed along the x and $-x$ axes, with hydrogens in the xy plane, the third was along the z axis, with hydrogens in the xz plane. The results of carrying out SCF calculations on one, two, three, and four molecule combinations are presented in Table II. As one can see, the size of the three water interaction and four-body interaction is quite small compared to the other terms and gives one confidence that large ion hydrate clusters can be studied by only carrying out computations on one, two, and three molecule clusters. For example, the relative energy of tetrahedral and octahedral coordination of an ion hydrate can be determined by calculating the following potential surfaces as a function of $R(\text{M–O})$: (1) the ion–single water surface; (2) the ion, one water along the x axis, the other along the $-x$; (3) the ion, one water along the x axis, the other along the y axis; and finally (4) the ion, one water along the x axis and the other approaching at a tetrahedral angle from the x axis. Such studies are now under way in our laboratory.

A final subject of interest is the effect of an ion on the hydrogen bonding ability of a water molecule nearby. We have begun this study using Li$^+$ as our representative cation, placing one water in the optimum geometry for

(5) D. Hankins, J. W. Moscowitz, and F. Stillinger, *ibid.*, **53**, 4544 (1970).

(6) No d functions on oxygen or p on hydrogens were included in the Be–3H$_2$O calculations.

(7) Obviously, the two-, three-, and four-body energies are geometry dependent. Our Be–O distance is shorter than the one expected for the higher hydrates, so the three- and four-body terms are larger in magnitude than they would be at the minimum energy configuration. Thus, our calculations give "upper bounds" for the magnitude of these higher order energy terms.

Table II. Many-Body Interaction Energies[a]

$$Be^{2+}-3H_2O, \ R(Be^{2+}-O) = 1.50 \ A$$
$E^{(1)}(Be^{2+}) = -13.610806 \ au$
$E^{(1)}(H_2O) = -76.009255 \ au$
$E^{(2)}(Be^{2+}-OH_2)^b = -150.6 \ kcal/mol$
$E^{(2)}(2H_2O, \ parallel)^c = 6.8 \ kcal/mol$
$E^{(2)}(2H_2O, \ perpendicular)^d = 24.3 \ kcal/mol$
$E^{(3)}(3H_2O) = -3.5 \ kcal/mol$
$E^{(3)}(Be^{2+}-2H_2O, \ parallel) = 1.50 \ kcal/mol$
$E^{(3)}(Be^{2+}-2H_2O, \ perpendicular) = 36.4 \ kcal/mol$
$E^{(4)}(Be^{2+}-3H_2O) = -4.0 \ kcal/mol$

$$Li^+\cdots(OH_2)_a\cdots(OH_2)_b, \ R(O_1-O_2) = 2.7 \ \text{Å}, \ R(Li^+-O_1) = 1.85 \ \text{Å}$$
$E^{(1)}(Li^+) = -7.235987 \ au$
$E^{(1)}(H_2O) = -76.046536 \ au$
$E^{(2)}(Li^+\cdots(O_2H_2)_a) = -37.2 \ kcal/mol$
$E^{(2)}(Li^+\cdots(O_2H_2))_b = -6.6 \ kcal/mol$
$E^{(2)}(H_2O)\cdots(H_2O)_b) = -4.1 \ kcal/mol$
$E^{(3)}(Li^+\cdots(OH_2)_a\cdots(OH_2)_b = -4.5 \ kcal/mol$

[a] Terms calculated using eq 1; for example, $E^{(3)}(3H_2O)$ was determined by carrying out SCF calculations on (a) the three waters, (b) two waters parallel = $E^{(2)}(2H_2O, \ parallel)$, (c) two waters perpendicular = $E^{(2)}(2H_2O, \ perpendicular)$, and (d) the energy of an isolated water. Then $E^{(3)} = E(\text{SCF for 3 waters}) - E^{(2)}(2H_2O, \ parallel) - 2E^{(2)}(2H_2O, \ perpendicular) - 3E^{(1)}(H_2O)$. [b] A negative $E^{(2)}$ means the two bodies are at a lower energy than the sum of $E^{(1)}$. [c] Parallel means one water along the x axis and the other along the $-x$ axis. [d] Perpendicular means one water along the x axis and the other along the y.

Li^+-H_2O complex formation and placing the second water in a position to form a hydrogen bond with the first water. The results of SCF calculations[8] on the three molecules and the three two-body combinations, at the minimum O–O distance between water molecules, are presented in Table II. There are two points of special interest: (1) the minimum energy O–O distance has been shortened from the 3.0 Å found in the water dimer to 2.7 Å; (2) the three-body interaction energy $E^{(3)}$ for this configuration is −4.5 kcal/mol, indicating that the hydrogen bond is 8.6 kcal/mol,[9] in comparison to the 5.0 kcal/mol found for the optimum H bond in the water dimer.[10] These results are of considerable interest, because they demonstrate the magnitude of the effect that monoatomic cations can have on the energetics and geometries of H bonding between water molecules and the electrostriction that these cations might bring about.

The extension of these studies to other cations and ions, an analysis of ir properties of cation hydrates, and a decomposition of the energy of complex formation into electrostatic, charge-transfer, and polarization terms will be reported separately.

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Reactions of $[(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OEt)CH_3\}]BF_4$ with Nucleophiles. Evidence for Carboxonium Rather than Carbenoid Behavior

Sir:

Electrophilic alkylations of $M'\{C(OLi)R\}$, where $M' = M(CO)_5^1$ or $M(CO)_4PPh_3^2$ (M = Cr, Mo, or W), $(h^5\text{-}C_5H_5)M(CO)_2$ (M = Mn[1] or Re[3]), or $M''COR$, where $M'' = (h^5\text{-}C_5H_5)M(CO)_xPPh_3^4$ (M = Fe or Ru, $x = 1$ and M = Mo, $x = 2$), are generally regarded as giving rise to "metal–carbene" complexes. However, it seems appropriate, in view of their reactivity patterns, to consider them as metal-stabilized carboxonium rather than carbenoid compounds.

Our results on the reaction of $[(h^5\text{-}C_5H_5)Fe(CO)-(PPh_3)\{C(OEt)CH_3\}]BF_4^4$ (1) with a variety of nucleophiles show the characteristic modes[5] of behavior of purely organic carboxonium salts which has led to the description of the latter as ambient cations.[5,6]

The salt 1 undergoes dealkylation when treated with NaI in THF. Ethyl iodide is eliminated by rupture of the carbon to oxygen single bond to give $(h^5\text{-}C_5H_5)Fe-(CO)(PPh_3)(COCH_3)$ (2) and is in essence the reverse of the alkylation which produces 1.

Proton abstraction from the carbon atom β to the oxonium center occurs when 1 is treated with ethoxide ion in ethanol. The resulting vinyl ether $(h^5\text{-}C_5H_5)-Fe(CO)(PPh_3)\{C(OEt)CH_2\}$ (3), the conjugate base of 1, can be protonated by HBF$_4$–propionic anhydride mixtures to re-form 1. Reduction of 3 with either H_2/PtO or B_2H_6 in EtOH gives the σ-α-ethoxyethyl derivative $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{CH(OEt)CH_3\}$ (4). This reaction introduces a second chiral center at the carbon α to the chiral metal center. The pairs of enantiomers (RR,SS and RS,SR) have clearly different nmr spectra in the methyl region and are readily separable by fractionation from hexane. Nmr spectra methyl region (δ in acetone-d_6): less soluble enantiomeric pair (mp 130.5–131°) 1.08 (3, triplet, $J = 6.8$ Hz, CH$_2$Me), 1.55 (3, doublet, $J = 6.2$ Hz, CHMe); more soluble enantiomeric pair (mp 114–115°) 0.94 (3, triplet, $J = 6.8$ Hz, CH$_2$Me), 1.52 (3, doublet, $J = 6.2$ Hz, CHMe). Careful monitoring of the reaction shows that both pairs are produced in approximately equal amounts which indicates no significant asymmetric induction occurred on reduction. Treatment of 3 with methoxide ion in methanol gives rise to the methoxy vinyl derivative $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OMe)CH_2\}$ (5).

The treatment of 1 with an equimolar amount of

(1) E. O. Fischer and A. Maasböl, *Chem. Ber.*, 100, 2445 (1967).
(2) E. O. Fischer and R. Aumann, *ibid.*, 102, 1495 (1969).
(3) E. O. Fischer and A. Reidel, *ibid.*, 101, 156 (1968).
(4) M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc. A*, 794 (1971).
(5) H. Perst, "Oxonium Ions in Organic Chemistry," Academic Press, New York, N. Y., 1971.
(6) S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 3, 548 (1964).

(8) The same basis set as in the monohydrate calculations was used here.
(9) We estimate our H-bond strength by combining $E^{(2)}[(H_2O)_a\cdots(H_2O)_b]$ with $E^{(3)}(Li^+\cdots OH_a\cdots OH_b)$, since the main effect of the lithium is to increase the positive charge on the water hydrogens [(H$_2$O)$_a$] and to increase its ability to function as a proton donor. These calculations are similar to those carried out by Diercksen and Kraemers,[3a] who interpreted their calculations in terms of an H-bond strength of 16.1 kcal/mol. These authors have, we feel, incorrectly included the attraction of the lithium for the more distant water [$E^{(2)}(Li^+\cdots(OH)_2)_b$] as part of the H-bond strength. Thus, the increase in H-bond strength due to the presence of Li$^+$ is significant but not nearly as "drastic" as suggested.[3a]
(10) The optimum H bond for the water dimer with this basis set had an O–O separation of 3.0 Å with an H-bond strength of 5.0 kcal/mol. The other geometrical parameters were kept at the optimum values found in ref 5.