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# Ab Initio Study of the $S_N2$ Reactions of $OH^-$ and $OOH^-$ with $CH_3Cl$

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**Abstract:** Ab initio molecular orbital calculations have been used to determine energy profiles for the $S_N2$ reactions of hydroxide and hydroperoxide anions with methyl chloride. Geometry optimizations were carried out at the Hartree–Fock level with the 6-31+G(d) basis set. These calculations were supplemented by computations of the correlation energy with second and third-order Møller–Plesset theory. Though the reactions are exothermic by 40–50 kcal/mol, both are found to have the double-well energy surfaces characteristic of gas-phase $S_N2$ reactions. At the Hartree–Fock level the central barrier heights are 2.9 and 4.1 kcal/mol for $OH^-$ and $OOH^-$, and the transition states are 12.4 and 9.7 kcal/mol lower in energy than the reactants. Electron correlation raises the barrier by 2.1 kcal/mol for $OH^-$, but it has much larger effects on the overall exothermicities. Vibrational energy changes are found to be less than 1.5 kcal/mol up to the transition state. The geometrical results for the ion–molecule complexes and transition states are discussed and show a somewhat later transition state for the reaction with hydroperoxide ion. The results are consistent with experimental observations including the lower reactivity of $OOH^-$ than $OH^-$ in the gas phase. Experimental and theoretical data are also combined to consider energy profiles for $S_N2$ reactions in aqueous solution.

In view of the importance of $S_N2$ reactions in organic chemistry, substitutions of alkyl halides by anions continue to be actively studied. However, the emphasis changed around 1970 from solution-phase kinetic studies to theoretical and experimental examination of the reactions in the gas phase. The gas-phase results are important for understanding intrinsic reactivity and have clearly demonstrated the profound role of solvation on the reaction kinetics.[1-6] Studies of the reactivity of anion–solvent clusters have also provided illuminating insights on the middle ground between isolation and condensed phases.[7,8]

The new era was much stimulated by the initial observations of Bohme et al., who demonstrated the occurrence and high reactivity for $S_N2$ processes in the gas phase.[1] The extensive kinetic investigations of Brauman and co-workers were also seminal and were nicely rationalized through the now familiar double-well potential model for the gas-phase reactions.[2] Such surfaces had been found previously in ab initio molecular orbital studies particularly for $F^- + CH_3F$.[9] The theoretical work was greatly expanded by Wolfe et al., who obtained energy surfaces for numerous $S_N2$ reactions with the 4-31G basis set.[10] They found good correlations between transition-state structure and overall exothermicities and between computed activation energies and predictions from Marcus theory.[10] The theoretical understanding of the simple exchange reaction of $Cl^- + CH_3Cl$ is now sufficiently complete that it has been possible to combine gas-phase results and statistical mechanical methodology to model the reaction in aqueous solution as well as in DMF.[11] Thus, the gas-phase studies have come full circle to allow better understanding of changes in solvation along reaction paths and of the origin of solvent-induced activation barriers.[11]

Nevertheless, the quantum mechanical problem of obtaining quantitatively reliable results for $S_N2$ reactions in the gas phase is still formidable, particularly when first-row anions are involved. Large basis sets including diffuse functions are required for such anions as well as computation of the correlation energy. The latter need arises due to the bonding changes that occur during the general reaction of $X^- + CH_3Y \rightarrow CH_3X + Y^-$. For example, the computed $\Delta E$ for reaction 1 is −121 kcal/mol with use of the

$$OH^- + CH_3Cl \rightarrow CH_3OH + Cl^- \qquad (1)$$

3-21G basis set and −89 kcal/mol at the 6-31G* level.[12] Since both values seriously overestimate the experimental exothermicity of −50 ± 5 kcal/mol,[13] such Hartree–Fock treatments may be anticipated to significantly distort the energy surfaces. In view of the computational demands, the requisite higher level calculations have largely been restricted to the reaction of $F^- + CH_3F$.[14a,b] Double-$\zeta$ basis sets augmented by polarization and diffuse functions (DZ+P+D) were used; however, the two methods for computing the correlation energy do not agree on the sign of the contribution to the barrier height.

To pursue this problem further, we have undertaken an extensive study of the energy surface for reaction 1. Ab initio theory with a large basis set and correlation energy calculations with second- and third-order Møller–Plesset theory have been utilized. The reaction is particularly intriguing because the high exothermicity could possibly lower the product side of the energy surface enough to remove the central barrier and yield a single-well profile. This would not be inconsistent with the experimental results of Olmstead and Brauman; the observed reaction efficiency of 0.68 places the putative barrier top at the same energy as the ion–dipole precursor in their RRKM treatment.[2a] Application of Marcus theory with available data on the intrinsic barriers and exothermicities also predicts a negligible barrier height.[10,13] Furthermore, exploratory calculations in our laboratory several years ago for reaction 1 with the 3-21G basis set found no barrier; however, the gross error for the exothermicity could swamp a small barrier

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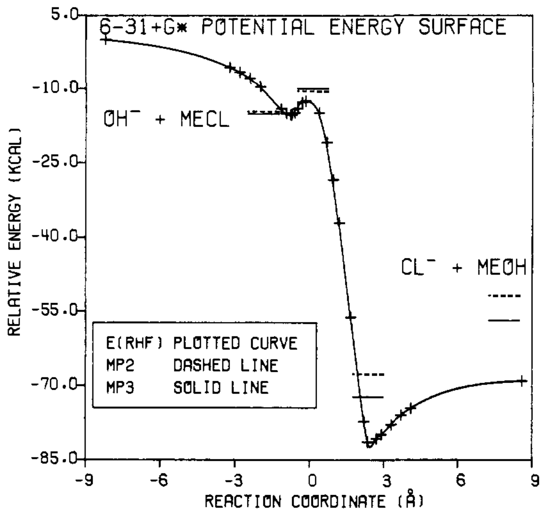

**Figure 1.** Computed energy profile for the reaction $OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$. The reaction coordinate is defined as $r$(C–Cl) – $r$(C–O) in angstroms.

so further study was postponed until improved computational facilities became available. In the meantime, Ohta and Morokuma have reported ab initio results for reaction 1 and its mono- and dihydrated versions.[12] Though a large basis set was used, the correlation energy was not treated and the reaction surface was only considered up to the transition state. They did find the transition state to be 2.8 kcal/mol above a $HO^-\cdots CH_3Cl$ complex.[12] The barrier is increased considerably by hydration as found experimentally by Bohme and Mackay.[7a] Recently, Cernusak et al. have expanded their ab initio studies to the $HO^- + CH_3F$ reaction.[14c] Using the 4-31G geometries obtained by Wolfe et al.[10] they have examined correlation effects with a DZ+P+D basis set. Since $F^-$ is a poorer leaving group than $Cl^-$ and has a larger intrinsic barrier for self-exchange, the overall reaction is less exothermic ($\Delta H$ = ca. −19 kcal/mol) and a large central barrier is expected and was found (10.1 kcal/mol).[14c]

Besides computing a complete energy profile for reaction 1, we have also studied the analogous reaction 2 with hydroperoxide as the nucleophile. The same basis set was employed as for

$$HOO^- + CH_3Cl \rightarrow CH_3OOH + Cl^- \qquad (2)$$

reaction 1, though the correlation energy calculations were confined to the reactants and products. As discussed below, the results provide insight into the question of an $\alpha$ effect for gas-phase substitution reactions.[6,10]

## Computational Methods

The ab initio molecular orbital calculations for reactions 1 and 2 were carried out with the GAUSSIAN/80 program on a Harris H-800 computer and GAUSSIAN/82 on a Gould 32/8750.[15,16] Geometries for all structures were optimized with use of analytical energy gradients and the 6-31+G(d) basis set.[17] The basis set (formerly denoted 6-31+G*) is of the split-valence type with d-type polarization functions and diffuse s and p orbitals on all atoms except hydrogen. Diffuse functions are well-known to be important for describing the electronic structure of anions containing first-row elements.[17,18] The electronic correlation energy was computed by means of Møller–Plesset perturbation theory up to the third order which is comparable to configuration interaction with full double excitations. In view of the magnitude of the calculations, the post-Hartree–Fock computations were carried out only for the stationary points in reaction 1 and for the reactions and products in reaction 2. Thus, the standard notation for these calculations is MP3/MP2/6-31+G(d)//6-31+G(d).[18] Only valence shell orbitals have been included in the correlation calculations. Zero-point vibrational energies and their thermal corrections were also computed for the stationary points in reaction 1 with use of vibrational frequencies obtained with the 6-31+G(d) basis set and analytical second derivatives. Vibrations with frequencies below 500 cm⁻¹ were treated as rotations ($E_v = RT/2$). For reaction 2, the calculations of the vibrational energy were restricted to reactants and products. The 3-21G basis set[19] was used in this case on 3-21G optimized geometries. Consistent with earlier work,[18] little difference is found in using 3-21G or 6-31+G(d) frequencies for reaction 1.

**Table I.** Calculated Total Energies (au)[a]

| species | 6-31+G(d) | MP2 | MP3 |
|---|---|---|---|
| $Cl^-$ | −459.539 66 | −459.671 15 | −459.682 38 |
| $OH^-$ | −75.376 42 | −75.587 79 | −75.581 42 |
| $OOH^-$ | −150.158 35 | −150.543 82 | −150.540 89 |
| $CH_3Cl$ | −499.094 16 | −499.357 22 | −499.381 42 |
| $CH_3OH$ | −115.040 97 | −115.356 49 | −115.371 03 |
| $CH_3O_2H$ | −189.802 50 | −190.300 78 | −190.314 80 |
| $HO^-\cdots CH_3Cl$ | −574.494 90 | −574.968 71 | −574.986 85 |
| $(HO\cdot\cdot CH_3\cdot\cdot Cl)^-$ | −574.490 42 | −574.961 54 | −574.978 89 |
| $CH_3OH\cdots Cl^-$ | −574.600 28 | −575.052 71 | −575.077 99 |
| $HOO^-\cdots CH_3Cl$ | −649.274 50 | | |
| $(HOO\cdot\cdot CH_3\cdot\cdot Cl)^-$ | −649.267 90 | | |
| $CH_3O_2H\cdots Cl^-$ | −649.360 95 | | |

[a] Results for geometries optimized with the 6-31+G(d) basis set in $C_s$ symmetry.

**Table II.** Calculated Relative Energies (kcal/mol) for $OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$ and Computed Vibrational Energies (kcal/mol) with the 6-31+G(d) Basis Set

| species | 6-31+G(d) | MP2[a] | MP3[a] |
|---|---|---|---|
| reactants | 0.0 | 0.0 | 0.0 |
| $HO^-\cdots CH_3Cl$ | −15.3 | −14.9 | −15.1 |
| transition state | −12.4 | −10.4 | −10.1 |
| $CH_3OH\cdots Cl^-$ | −81.4 | −67.6 | −72.3 |
| products | −69.1 | −51.8 | −56.8 |

| species | $E_v^\circ$ | $\Delta E_v^{298}$ | $E_v^{298}$ | $\Delta H^{298}$ |
|---|---|---|---|---|
| reactants | 31.2 | 0.1 | 31.3 | 0.0 |
| $HO^-\cdots CH_3Cl$ | 31.0 | 1.6 | 32.6 | −15.9 |
| transition state[b] | 30.2 | 1.5 | 31.8 | −11.7 |
| $CH_3OH\cdots Cl^-$ | 35.0 | 1.0 | 35.9 | −69.7 |
| products | 34.2 | 0.3 | 34.5 | −54.2 |

[a] Using 6-31+G(d) optimized geometries. [b] The one imaginary frequency has been ignored.

It should be noted that the geometries obtained with basis sets as large as 6-31+G(d) are generally in excellent agreement with experimental data for neutral molecules, hydrogen-bonded complexes, and anions. Rotational barriers are also well reproduced at this level, while vibrational frequencies are systematically 5–10% too high. Thorough discussion of these points is provided in Chapter 6 of ref 18.

## Results and Discussion

**$OH^- + CH_3Cl$.** Geometry optimizations were carried out for 25 fixed values of the reaction coordinate which is defined in Figure 1 as the difference in the C–Cl and C–O distances. All remaining variables were optimized with the one constraint of $C_s$ symmetry. Gradient calculations were also used to locate the stationary points which were shown by the subsequent vibrational frequency calculations to be true local minima and a transition state. The resultant energy profile is shown in Figure 1, while the total and relative energies for the stationary points are recorded in Tables I and II. Key points on the reaction surface are illustrated in Figure 2. Full details on the optimized geometries for the stationary points are provided as supplementary material. Table II also contains the results for the vibrational energies including the zero-point energy ($E_v^\circ$), the vibrational energy change between 0 and 298 K ($\Delta E_v^{298}$), and the enthalpy at 298

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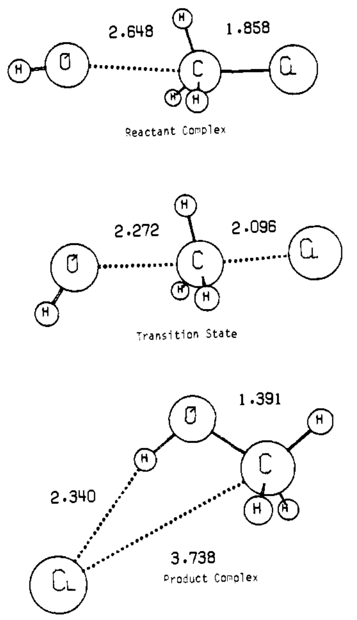

**Figure 2.** Optimized structures of the reactant complex, transition state, and product complex for reaction 1 obtained with the 6-31+G(d) basis set. Bond lengths in angstroms. Full structural details are provided in the supplementary material.

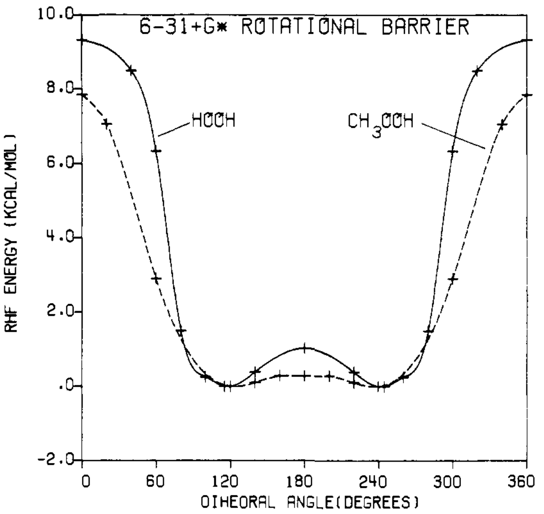

**Figure 3.** Torsional energy surfaces computed for hydrogen peroxide and methyl hydroperoxide as a function of the dihedral angle about the O–O bond.

K relative to the reactants ($\Delta H^{298}$). The latter is computed from eq 3 where $\Delta E_e°$ is the electronic energy change including correlation corrections and the final terms are for changes in the number of rotational and translational degrees of freedom and the work term.

$$\Delta H^{298} = \Delta E_e° + \Delta E_v° + \Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298} + \Delta(PV) \quad (3)$$

In spite of the exothermicity, a small central barrier is found at all computational levels. The initial ion–dipole complex occurs at a C–O separation of 2.65 Å (Figure 2) and is 15 kcal/mol lower in energy than the reactants. This well depth is essentially unaffected by the correlation energy. However, the barrier to the transition state at $r$(CO) = 2.27 Å increases from 2.9 kcal/mol at the Hartree–Fock level to 5.0 kcal/mol with the MP3 correction. The size and sign of the correction are the same as found previously for $Cl^-$ + $CH_3Cl$,[12] though the 16-kcal/mol barrier for $OH^-$ + $CH_3F$ is reduced to 10 kcal/mol with fourth-order many-body perturbation theory.[14c] For reaction 1, the barrier top still remains ca. 10 kcal/mol lower in energy than the reactants which is consistent with the observed efficiency for the reaction.[2a] The geometry of the transition state (Figure 2) shows extension of the C–Cl bond length to 2.10 Å from 1.79 Å in methyl chloride. The O–C–Cl angle is 175.8° and the C–O–H angle of 122.6° is approaching the value of 110.4° in methanol.

The vibrational energy changes up to the transition state are modest. The vibrational energies for the initial ion–dipole complex and transition state are 1.3 and 0.5 kcal/mol higher than those for the reactants at 298 K. Quantitatively similar results have been obtained previously for $F^-$ + $CH_3F$ and $OH^-$ + $CH_3F$ with use of 4-31G derived frequencies.[14b,c] The net effect of the vibrational energy change is to lower the central barrier for reaction 1 by 0.8 kcal/mol which yields a final computed barrier height of 4.2 kcal/mol. Furthermore, the final results predict the enthalpies for the reactant complex and transition state to be 15.9 and 11.7 kcal/mol lower than those for the reactants (Table II).

Continuing toward the products, an ion–molecule complex of the form $HOCH_3\cdots Cl^-$ was not found. Rather, the system rearranges to the global minimum with chloride ion hydrogen bonded to methanol (Figure 2). The strength of the hydrogen bond increases from 12.3 to 15.5 kcal/mol when the correlation corrections are included. As for anion–water complexes,[20] the further corrections including the zero-point energy change needed to convert the interaction energy to an enthalpy difference at 298 K are small and in the present case exactly cancel. The resultant hydrogen bond enthalpy of 15.5 kcal/mol compares favorably with reported experimental values of 14.1 and 16.8 kcal/mol for $Cl^-\cdots HOCH_3$ in the gas phase.[21]

The major effect of the correlation corrections is on the energy of the global minimum and products relative to the reactants. The overall energy release of 69.1 kcal/mol at the 6-31+G(d) level is reduced to 56.8 kcal/mol, including the MP2 and MP3 modifications. Conversion to an enthalpy change at 298 K via eq 3 yields −54.2 kcal/mol which is in accord with the experimental value of −50 ± 5 kcal/mol for reaction 1.[13]

Finally, it may be noted that the central barrier height obtained here at the 6-31+G(d) level is nearly identical with Ohta and Morokuma's result of 2.8 kcal/mol.[12] Their computed stabilization of 14.4 kcal/mol for the initial ion–dipole complex is 0.9 kcal/mol less than our results, though the geometries for the reactant complex and transition state are very similar from the two studies. As they surmised,[12] the effect of electron correlation on the forward half of the reaction is not large in an absolute sense. However, the height of the central barrier is increased by 70% and the calculated heat of reaction is substantially improved.

**$OOH^-$ + $CH_3Cl$.** The energy profile for reaction 2 was also determined in $C_s$ symmetry. This could be problematic in view of the anticipated preference of methyl hydroperoxide for a skew conformation as for hydrogen peroxide.[22,23] The issue was pursued by computing torsional energy surfaces for HOOH and $CH_3OOH$ with the 6-31+G(d) basis set. For each value of the dihedral angle about the OO bonds, all remaining geometrical variables were optimized. The skew minimum was also located with gradient methods. The results are presented in Figure 3.

For hydrogen peroxide, the energy minimum occurs at a dihedral angle of 115.4° which is intermediate between experimental results of 111.5° (IR) and 120° (microwave).[22] The computed cis and trans barrier heights of 9.33 and 1.03 kcal/mol may also be compared with the IR results of 7.0 and 1.1 kcal/mol.[22a] The torsional surface for the methyl derivative is found to be flatter with a trans barrier of only 0.28 kcal/mol and a cis maximum of 7.85 kcal/mol. The rotamer with lowest energy now occurs at 120.3°. The results for both molecules in Figure 3 are similar to those obtained by Radom et al. using the much smaller 4-31G basis set.[23] However, as those authors note, when full optimization

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**Table III.** Calculated Relative Energies (kcal/mol) for $OOH^- + CH_3Cl \rightarrow CH_3OOH + Cl^-$

| species | 6-31+G(d) | MP2[a] | MP3[a] |
|---|---|---|---|
| reactants | 0.0 | 0.0 | 0.0 |
| $HOO^- \cdots CH_3Cl$ | −13.8 | | |
| transition state | −9.7 | | |
| $CH_3OOH \cdots Cl^-$ | −68.0 | | |
| products | −56.3 | −44.5 | −47.0 |

[a] Using 6-31+G(d) optimized geometries.

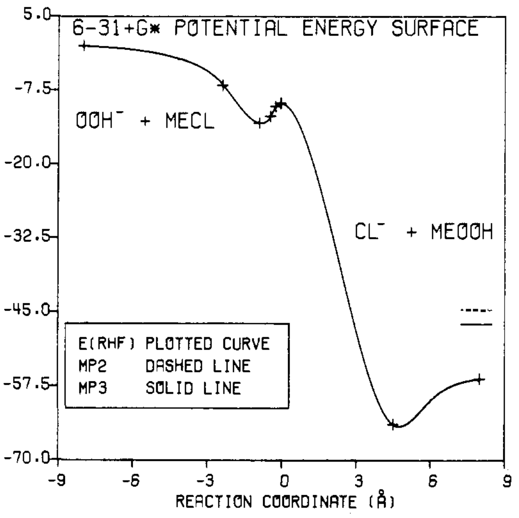

**Figure 4.** Computed energy profile for the reaction $HOO^- + CH_3Cl \rightarrow CH_3OOH + Cl^-$. The reaction coordinate is defined as $r$(C–Cl) − $r$(C–O) in angstroms.

rather than rigid rotation is used at the 4-31G level, the trans conformers erroneously become the global minima.[23] For the present purposes, the key finding is the trivial energy difference between the trans and skew rotamers for methyl hydroperoxide. Thus, the use of $C_s$ symmetry for reaction 2 is not anticipated to displace the energetics by more than a few tenths of a kcal/mol from optimal values.

Structures for reaction 2 were fully optimized in $C_s$ symmetry for eight values of the reaction coordinate including the stationary points. The total and relative energies are reported in Tables I and III, while the computed energy profile and key structures are in Figures 4 and 5. The reaction profile is qualitatively similar to that for hydroxide ion; a double well is found with a small central barrier. Since hydroperoxide ion is a weaker Brønsted base than hydroxide ion by 16 kcal/mol in the gas phase,[13b,24] it is not surprising that the interaction energy for the initial ion–molecule complex is less for $OOH^-$ than $OH^-$, cf., 13.8 vs. 15.3 kcal/mol with the 6-31+G(d) basis set. The central barrier at the Hartree–Fock level is also higher for the $\alpha$-nucleophile, 4.1 vs. 2.9 kcal/mol, and the overall exothermicity is less, −56.3 vs. −69.1 kcal/mol. The MP3, zero-point, and other corrections, as made for reaction 1 above, yield a final computed enthalpy change for reaction 2 of −45.1 kcal/mol at 298 K. This agrees with the experimental value of −42 ± 7 kcal/mol.[13] The actual vibrational energy change in preceeding from reactants to products is +2.8 kcal/mol at 298 K with use of 3-21G frequencies. This is lower than the values of 3.2 and 4.4 kcal/mol for reaction 1 obtained from 6-31+G(d) and 3-21G frequencies, respectively. The difference may be attributed to the relatively low frequency of 2923 $cm^{-1}$ for $OH^-$ in comparison to 3613, 3868, and 3824 $cm^{-1}$ for the O–H stretches in $OOH^-$, $CH_3OH$, and $CH_3OOH$ at the 3-21G level.

The global minimum is again a hydrogen-bonded structure, $CH_3OOH \cdots Cl^-$ (Figure 5). However, the possible occurrence of other minima has not been ruled out by the present limited search of the product side of the energy surface. The hydrogen bond energy is 11.7 kcal/mol which may be compared with the value of 14.3 kcal/mol for $CH_3OH \cdots Cl^-$ also obtained at the 6-31+G(d)//6-31+G(d) level (Table II) and of 12.6 kcal/mol for $Cl^- \cdots H_2O$ with use of 6-31+G(d)//6-31G(d).[20] The order does not parallel the gas-phase acidities for the hydrogen bond donors which should be $CH_3OOH > CH_3OH > H_2O$ assuming $CH_3OOH$ is at least as acidic as $H_2O_2$.[13b] The deviation of methyl hydroperoxide from the expected pattern[21a] may be ascribed to unfavorable electrostatic interactions between the chloride ion and the far oxygen in the hydrogen-bonded complex. This is reflected in Figures 2 and 5 where the hydrogen bond is seen to be bent toward the carbon for $CH_3OH \cdots Cl^-$ but away from the far oxygen in $CH_3OOH \cdots Cl^-$. For $Cl^- \cdots H_2O$, the hydrogen bond is also bent toward the far hydrogen.[20]

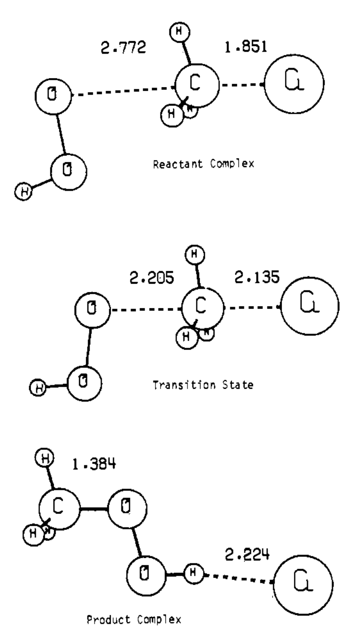

**Figure 5.** Optimized structures of the reactant complex, transition state, and product complex for reaction 2. Other details as in Figure 2.

Comparisons of the results for reactions 1 and 2 are completely in line with Hammond's postulate. The reaction for hydroperoxide ion is less exothermic both overall and between the two ion–molecule complexes. Therefore, it should have a later transition state which is apparent in Figures 2 and 5; the C–O and C–Cl distances are shorter and longer, respectively, in the transition state for $OOH^-$ attack than for $OH^-$ substitution. The central barrier is also higher for reaction 2, a result which seems unlikely to change qualitatively at higher levels of theory. Overall, reactions 1 and 2 are sufficiently similar that differential correlation and zero-point effects should be small. It may be noted from Tables II and III that $\Delta E$ for both reactions is modified by 16–18% between the 6-31+G(d) and MP3 levels.

**The $\alpha$ Effect.** Since the interaction energy is less for the reactant complex with $OOH^-$ and the central barrier is higher, the transition state is closer in energy to the reactants. Specifically, at the 6-31+G(d) level the transition states for reactions 1 and 2 are 12.4 and 9.7 kcal/mol below the reactants. This leads to the expectation that the reaction efficiency should be less in the gas phase for hydroperoxide ion as the nucleophile than hydroxide ion.[2a] The predicted lower reactivity for hydroperoxide contrasts well-known behavior in solution where the nucleophilicity of anions with $\alpha$-heteroatoms is enhanced. For example, $OOH^-$ has been found to undergo various addition reactions $10^2$–$10^4$ times faster than $OH^-$ and is up to 35 times more reactive in alkylations than $OH^-$ or $CH_3O^-$.[25,26]

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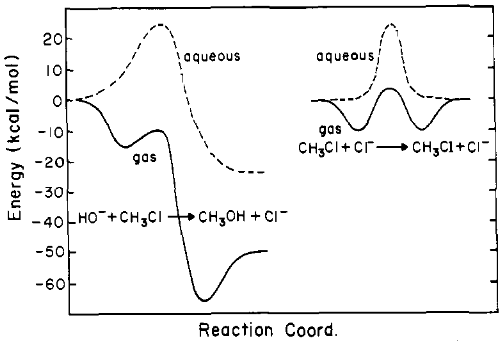

**Figure 6.** Summary of computed energy profiles for the gas-phase and semiquantitative energy profiles in aqueous solution for reactions 1 and 4.

Nevertheless, the present results are consistent with the observations of DePuy et al. that $OOH^-$ is less reactive with methyl fluoride than $OH^-$ in the gase phase.[6] Additional studies by these workers of the product ratios for $OOH^-$ and $OH^-$ reacting with methyl formate also showed no enhanced nucleophilicity for $OOH^-$.[6] Furthermore, the extensive ab initio studies of Wolfe et al. revealed no unusual geometrical or energetic effects for the transition states in gas-phase $S_N2$ reactions with the $\alpha$-nucleophiles $OOH^-$ and $OF^-$.[10a–c] Thus, the evidence is now substantial that $OOH^-$ is not intrinsically more nucleophilic than $OH^-$. The enhanced reactivity of the $\alpha$-nucleophile in solution is consequently due to solvent effects.[6] This is reasonable since the charge is much more delocalized in $OOH^-$ than $OH^-$, as noted previously.[10d,20] Therefore, the $\alpha$-nucleophile is less well solvated particularly in protic solvents.[27] Then, the increased reactivity for the $\alpha$-nucleophiles follows because differential solvation should be greater for the more charge-concentrated nucleophiles than for the transition states. As discussed elsewhere,[10] alternative explanations based on properties of the isolated nucleophiles such as HOMO energies must be erroneous.

**Reaction Profiles in Aqueous Solution.** In the prior combined quantum and statistical mechanical study of the chloride exchange reaction 4, energy profiles were computed for the gas phase,

$$Cl^- + CH_3Cl^* \rightarrow CH_3Cl + Cl^{-*} \qquad (4)$$

aqueous solution, and solution in DMF.[11] Though the condensed-phase simulations have not been attempted for reactions 1 or 2, enough theoretical and experimental data are now available for at least reaction 1 that some insights are accessible for the energy profile in aqueous solution. In particular, the heat of reaction in the gas phase (−50 ± 5 kcal/mol)[13] is known as are the heats of hydration for the reactants and products from the gas phase: $OH^-$ (−115 ± 10),[28,29] $CH_3Cl$ (−5.6),[30] $Cl^-$ (−82 ± 5),[29] and $CH_3OH$ (−10.8).[31] Combination yields an enthalpy change of −22 ± 12 kcal/mol for reaction 1 in aqueous solution at 25 °C, and the activation energy is known to be 24.3 kcal/mol.[32] This information along with the gas-phase results obtained here can be used to construct the energy profiles in Figure 6. The corresponding results for reaction 4 are shown for comparison; in this case the activation energy in water is ca. 23 kcal/mol[11,32] and the computed well depth and intrinsic barrier for the gas phase are −10.3 and 13.9 kcal/mol.[11]

For reaction 4, we found that the *free energy* profile in water is nearly flat to the position of the ion–dipole complex and then the central barrier ensues, though in DMF the ion–dipole complexes are still free energy minima.[11] Assuming similar shape for the energy curve suggests the aqueous profile in Figure 6. For this system, the reactants are better hydrated than the transition state by ca. 19 kcal/mol which added to the intrinsic energy difference of 3.6 kcal/mol yields the activation energy of 23 kcal/mol in water. It may be noted, however, that from the point of the ion–dipole complex, the activation barrier in water consists of the 14 kcal/mol intrinsic barrier plus 9 kcal/mol weaker solvation for the transition state.

The solvent effects on reaction 1 are far greater and remarkably result in nearly identical activation energies for the two reactions in water. First, it should be noted that through further simulation work we have shown that hydration has virtually no effect on the geometry of the transition state for reaction 4 since it is a covalently well-bound structure.[33,34] To a first approximation the same should be true for reaction 1, though the reduced exothermicity in water suggests some shift toward a later transition state. Assuming there is no shift, then the heats of hydration for the reactants, transition state, and products are −121 ± 10, −87 ± 10, and −93 ± 5 kcal/mol. Due to the strong hydration of the charge-concentrated hydroxide ion, the reactants are now better solvated than the transition state by 30–40 kcal/mol and the overall exothermicity is also reduced by ca. 30 kcal/mol. In view of the greater energetic effect of desolvation of the nucleophile for reaction 1 than reaction 4, it may be anticipated that the energy profile for reaction 1 in water is unimodal and begins to rise earlier than that for reaction 4. For the ion–substrate complexes to remain as minima in solution, it is necessary for the ion–substrate interaction to be comparable in strength or stronger than the ion–solvent interactions. This is achieved for reaction 4 in DMF and is a close call in water;[11] however, hydroxide–water interactions can be as strong as 25 kcal/mol[20,28] while the optimal $HO^- \cdots CH_3Cl$ interaction is 15 kcal/mol (Table II). On the basis of our prior findings for reaction 4 and the addition of $OH^-$ to $H_2C{=}O$ in water,[11,35] the hydration-induced activation barrier for reaction 1 is expected to result primarily from hydrogen bond weakening rather than losses in numbers of hydrogen bonds.

In closing, it should be noted that the extremes for reactions of anions with methyl chloride are well covered by reactions 1 and 4 in view of their differences in exothermicities and gas-phase efficiencies (0.68 vs. 0.003).[2a] Thus, the energy profiles in Figure 6 are representative of the range of possibilities and support the general occurrence of double-well and unimodal energy profiles in the gas phase and in aqueous solution, respectively, for $S_N2$ reactions with methyl chloride. Single-well surfaces in the gas phase are still possible for even stronger nucleophiles and/or better leaving groups on carbon. Though hydration effects were not considered in detail for reaction 2, this case should conform qualitatively to the trends for reaction 1. However, as noted above, it is expected that the difference in heats of hydration for the hydroxide and hydroperoxide ions should be somewhat greater than that for their transition states to account for the $\alpha$-effect.

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**Supplementary Material Available:** Full geometrical details for the reactants, products, ion–molecule complexes, and transition states in Z-matrix format (6 pages). Ordering information is given on any current masthead page.

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