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Ab Initio MO Studies on the Potential Energy Surface of the Methyl Chloride Radical Anion

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Abstract: The potential energy surface of the methyl chloride radical anion has been studied by ab initio molecular orbital theory. The following calculated results are obtained, different from the reported C–Cl dissociation potential curves: (1) A shallow least energy point (stationary point) is found within C_{3v} symmetry in cases where dynamical correlation effects are taken into consideration. (2) The well-known C_{3v} dissociation path is not the minimum energy one, and a planar C_{2v} minimum geometry is found on the potential energy surface of methyl chloride radical anion. On the C–Cl dissociation minimum energy path, the initial C_{3v} structure is changed to the planar C_{2v} one by a CH_3 rocking deformation. The calculated results also provide a possibility that the experimentally observed methyl radical–chloride ion adduct has the planar C_{2v} structure instead of the C_{3v} one.

1. Introduction

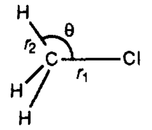
Methyl chloride is known to undergo dissociative electron capture to generate the methyl radical and chloride ion. Experimental studies on the dissociative electron attachment process and its temporary anion state have been extensively carried out.[1-5] The C–Cl dissociation potential curve of the methyl chloride radical anion has also been theoretically studied by using ab initio MO theory.[6-8] In these theoretical studies, the potential curve has always been calculated on the assumption that the CH_3 group keeps C_{3v} symmetry throughout the C–Cl dissociation (C_{3v} path). In other words, the C_{3v} path has been believed to be the sole C–Cl dissociation path and probably the minimum energy one on the potential energy surface of the methyl chloride radical anion. According to the reported calculated results, the C–Cl dissociation potential curve monotonically decreases with no potential minimum except for the case of dipole-bound anions.[7]

In this paper, we present more accurate calculated results which provide a new understanding on the potential energy surface of the methyl chloride radical anion. In the first half of this paper, our calculated potential energy surface, which is different from the reported C–Cl dissociation potential curves, is described. A C_{3v} stationary point and a planar C_{2v} minimum energy point are found on the potential energy surface of the methyl chloride radical anion. In the latter half, possible C–Cl dissociation paths and a relationship between the calculated metastable methyl chloride radical anion and the methyl radical–chloride ion adduct, which was reported to be experimentally observed,[9] are discussed.

2. Method of Calculation

Ab initio MO calculations were performed using the GAUSSIAN 82,[10] GAUSSIAN 86,[11] and HONDO 7[12] programs. Geometry optimizations of the methyl chloride radical anion were carried out using analytical gradient techniques[13] at both the UHF and the second-order Møller–Plesset perturbation (MP2)[14,15] (with all electrons correlated) levels. Vibrational frequencies were calculated to ensure a true minimum geometry. To confirm the least energy point of the methyl chloride radical anion within C_{3v} symmetry, UHF SDCI and coupled-cluster with double substitutions[16] (CCD) calculations were carried out. In these post-Hartree–Fock calculations, all valence and virtual canonical orbitals were included in the active space. In our RHF SDCI calculations on the methyl chloride radical anion, the Hartree–Fock determinant was found to dominate the wave function along the C–Cl dissociation paths for both C_{3v} and planar C_{2v} symmetries, indicating that the UHF and the single-reference UMP2 wave functions are fairly good approximations to the exact wave function. The calculated $\langle S^2 \rangle$ values on the potential energy surface are in the range of 0.76–0.77. This indicates that there exists no serious spin contamination in our UHF and UMP2 calculations. The 6-31+G*[17] basis set which contains sp-diffuse functions was employed throughout this work.

Table I. Geometry of Methyl Chloride Radical Anion Optimized within C_{3v} Symmetry by Various Post-Hartree–Fock Level Calculations



method	r_1 (Å)	r_2 (Å)	θ (deg)
UMP2	3.923	1.080	82.3
UHF-SDCI	4.042	1.081	82.5
CCD	3.967	1.084	82.6

3. Results and Discussion

The C_{3v} potential energy curves calculated by the UHF and UMP2 methods are shown in Figures 1 and 2, respectively. In the UHF/6-31+G*//UHF/6-31+G* level calculations, no least energy point is found within C_{3v} symmetry, as in the reported potential energy curves determined from the UMP2/6-31+G*//UHF/6-31+G*[7] and MCSCF/6-31+G*[8] calculations. On the contrary, a shallow least energy point (stationary point) is found in the case of the UMP2/6-31+G*//UMP2/6-31+G*

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(1) Wentworth, W. E.; George, R.; Keith, H. *J. Chem. Phys.* **1969**, *51*, 1791.

(2) Burrow, P. D.; Modelli, A.; Chiu, N. S.; Jordan, K. D. *J. Chem. Phys.* **1982**, *77*, 2699.

(3) Wan, H.; Moore, J. H.; Tossell, J. A. *J. Chem. Phys.* **1991**, *94*, 1868.

(4) Chu, S. C.; Burrow, P. D. *Chem. Phys. Lett.* **1990**, *172*, 17.

(5) Scheuneman, H. U.; Illenberger, E.; Baumgaertel, H. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 580.

(6) Canadell, E.; Karafiloglou, P.; Salem, L. *J. Am. Chem. Soc.* **1980**, *102*, 855.

(7) Clark, T. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 203.

(8) Benassi, R.; Bernardi, F.; Bottoni, A.; Robb, M. A.; Taddei, F. *Chem. Phys. Lett.* **1989**, *161*, 79.

(9) Sprague, E. D.; Williams, F. *J. Chem. Phys.* **1971**, *54*, 5425.

(10) Binkley, J. S.; Frisch, M. J.; Defrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, 1982.

(11) Frish, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowcz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. GAUSSIAN 86, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, 1988.

(12) Dupuis, M.; Watts, J. D.; Villar, H. O.; Hurst, G. J. B. HONDO 7, QCPE 544, Indiana University, 1987.

(13) Pulay, P. *Ab Initio Methods in Quantum Chemistry*; Lawley, K. P., Ed.; Wiley: New York, 1987; p 241.

(14) Pople, J. A.; Krishnan, R. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(15) Krishnan, R.; Frish, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(16) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545.

(17) Hehre, W. J.; Radom, L.; Schleyer, P. von R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

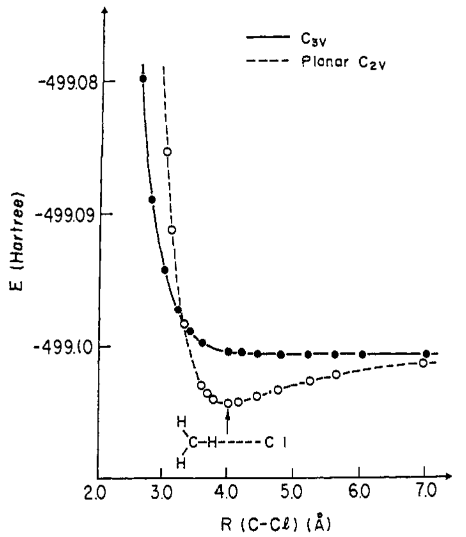

Figure 1. C–Cl dissociation potential energy curve of the methyl chloride radical anion within C_{3v} and planar C_{2v} symmetry estimated by UHF/6-31+G* level calculations.

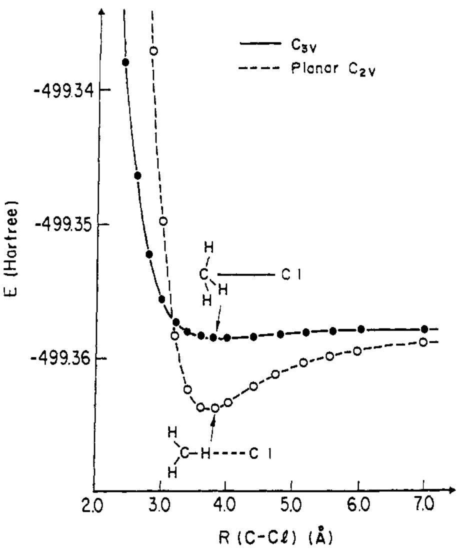

Figure 2. C–Cl dissociation potential energy curve of the methyl chloride radical anion within C_{3v} and planar C_{2v} symmetry estimated by UMP2/6-31+G* level calculations.

calculations, as shown in Figure 2. The least energy point within C_{3v} symmetry is also found in our UHF SDCI and CCD level calculations using the Fletcher–Powell optimization procedure.[18] The calculated optimized geometries of the methyl chloride radical anion with C_{3v} symmetry at the UMP2, UHF SDCI, and CCD levels of theory are summarized in Table I. These calculated results indicate that the shallow least energy point within C_{3v} symmetry is found in cases where dynamical correlation effects are taken into consideration. We suggest that the MCSCF level calculations could also give the least energy point if dynamical correlation effects are fully taken into consideration.

This stationary point, however, has doubly degenerate imaginary frequencies (140i cm^{-1}) on the UMP2 potential energy surface, indicating that this point is not a minimum. As these imaginary frequencies are along the CH_3 rocking vibrations as shown in Figure 3a, this C_{3v} structure is unstable for CH_3 rocking deformations. Another stationary point of a planar C_{2v} structure is found on a path along this rocking vibration. The planar C_{2v} stationary point is also found in the UHF level calculations, as shown in Figure 1. For this stationary point, both the UHF and the UMP2 level calculations give qualitatively the same result.

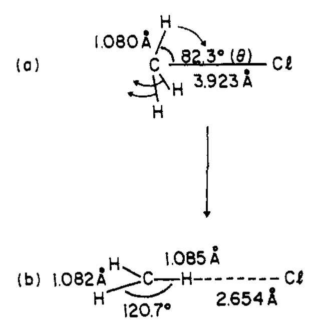

Figure 3. (a) Geometry at the C_{3v} stationary point of the methyl chloride radical anion (UMP2/6-31+G*). (b) Planar C_{2v} minimum geometry of the methyl chloride radical anion (UMP2/6-31+G*).

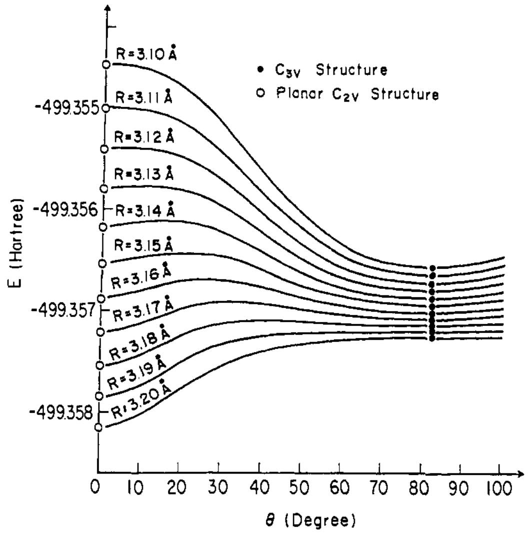

Figure 4. Potential energy curves of the methyl chloride radical anion at various C–Cl bond distances where the C_{3v} structure is changed to the planar C_{2v} one (UMP2/6-31+G*).

This planar C_{2v} geometry optimized by the UMP2 level calculations is shown in Figure 3b. In this planar C_{2v} anion, an unpaired electron is mostly localized on the $2p_z$ orbital of the carbon atom. This anion has a positive total overlap population value of 0.011 between the chlorine atom and the nearest hydrogen atom, indicating that there exists weak bonding between the negatively charged chlorine atom and the hydrogen atom. This planar anion, therefore, can be regarded as a weak complex between the methyl radical and chloride ion. The calculated total overlap population values also indicate that the C–H bond in the C–H–Cl part is somewhat weaker than the remaining two equivalent C–H bonds. Vibrational frequency analyses show that this planar C_{2v} structure is a true minimum geometry of the methyl chloride radical anion. This means that the C_{3v} path is not a minimum energy one on the potential energy surface of the methyl chloride radical anion. The C–Cl dissociation curves within the planar C_{2v} symmetry, estimated by UHF and UMP2 level calculations, are also shown in Figures 1 and 2 as dashed lines, respectively. Although the energy of the planar C_{2v} structure is higher than that of the C_{3v} one at a relatively short C–Cl bond distance, the planar C_{2v} potential energy curve crosses the C_{3v} curve. After this intersection point, the planar C_{2v} structure becomes more energetically stable than is the C_{3v} structure. The minimum energy geometry is found in this C–Cl distance region. At large C–Cl distances, the planar C_{2v} curve approaches the C_{3v} curve with an increase in the C–Cl distance. This indicates that the initial C_{3v} structure is changed to the planar C_{2v} one by a CH_3 rocking deformation on the minimum energy path of the potential energy surface, as shown in Figure 3.

The energy variation from the C_{3v} to the planar C_{2v} structure can be expressed as a function of the angle ∠HCCl (θ) defined in Figure 3a. Figure 4 shows the UMP2 energy variations of the

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[18] Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163.

methyl chloride radical anion at various C–Cl bond distances around the intersection in cases where the C_{3v} structure (θ = 81.7–81.9) is changed to the planar C_{2v} one (θ = 0). For a C–Cl bond distance of 3.10 Å, for example, the energy of the methyl chloride radical anion monotonically increases as the C_{3v} structure is changed to the planar C_{2v} one. Although the planar C_{2v} energy becomes lower than the C_{3v} energy for a C–Cl distance of 3.17 Å, an energy barrier exists between the planar C_{2v} and the C_{3v} structures. Around this narrow C–Cl distance region, both the C_{3v} and the planar C_{2v} minimum energy paths coexist on the potential energy surface. At a C–Cl distance region of more than 3.19 Å, the energy monotonically decreases with a decrease in θ and the planar C_{2v} path becomes solely a C–Cl dissociation minimum energy path. The potential energy curves in Figure 4 indicate that the minimum energy path rather discontinuously changes from the C_{3v} path to the planar C_{2v} one around the intersection.

It has recently been pointed out that MO calculations on temporary anions with negative first vertical ionization potentials (1st VIP) must be viewed with caution.[19,20] If one considers a temporary anion having a negative 1st VIP in any molecular structure, its ground state would be a neutral molecule plus a free electron state. The temporary anion state often observed by the electron transmission spectroscopy (ETS) is not a ground state of the anion in the above-mentioned sense. Therefore, caution is needed in cases where the MO theory based on the variational principle is applied to such a temporary anion state. If infinitely flexible basis sets are employed in calculations on such temporary anions, the singly occupied molecular orbitals (SOMO) would approach free-electron-like wave functions. MO calculations using the moderate-size basis sets containing diffuse functions, such as the 6-31+G* basis set, might give an intermediate result between the temporary anion state and the ground state of a neutral molecule plus a free electron. Considering that the 6-31G* rather than the 6-31+G* basis set gives more accurate negative electron affinity values for a methyl chloride temporary anion observed by ETS,[19] it may be necessary to put some spatial restrictions on the basis functions in order to more correctly describe the temporary anion state with a negative 1st VIP value within the framework of MO theory.

However, in an anion state whose unpaired electron is bound, it is feasible to apply the variational principle to such a system to obtain the ground-state wave function. From this point of view, the 1st VIP values on the C–Cl dissociation potential curves have been estimated by UMP4SDTQ(frozen core)/6-31+G*//UMP2/6-31+G* level calculations. According to the calculated results, the methyl chloride radical anion has positive 1st VIP values for C–Cl bond distances greater than 2.27 Å. The radical anion in its planar C_{2v} minimum geometry, for example, has a positive 1st VIP value of 3.27 eV. The MP2 potential curves of methyl chloride and its anion (C_{3v}) are found to intersect at a C–Cl distance of 2.24 Å. These results indicate that MO calculations with basis sets containing diffuse functions provide reliable results at least for C–Cl distances of more than 2.3 Å. Although the temporary anion state observed by ETS is outside this bond distance region, it should be stressed that the potential energy surface discussed in this paper lies mainly in this C–Cl distance region.

From the calculated potential energy surface, the following two possible C–Cl dissociation paths can be considered. One is a nearly C_{3v} path in which the C_{3v} symmetry is kept up to the large C–Cl bond distance region. In this case, the methyl chloride radical anion does not pass through the planar C_{2v} metastable state. Another is a path where the C_{3v} structure is changed to the planar C_{2v} one by a CH_3 rocking deformation over a relatively short C–Cl distance region. Considering that a large CH_3 deformation is required for such a structual change from the C_{3v} to the planar C_{2v} structure, it is rather difficult to estimate the real dissociation path. The released potential energy of the methyl chloride radical anion during the dissociation would be a large factor which determines the real C–Cl dissociation path on the potential energy surface. Classical trajectory calculations on the potential energy surface must be carried out for correct estimation of the C–Cl dissociation path.

However, even if the methyl chloride radical anion would dissociate on the nearly C_{3v} path, there is a high possibility that the planar C_{2v} metastable anion is formed by a recombination between the methyl radical and chloride ion. As previously described, this metastable anion is a weak complex between the methyl radical and chloride ion, with an unpaired electron mostly occupying a 2p orbital of the methyl radical. Nearly equivalent negative spin densities (0.028–0.030) are found on the three hydrogen nuclei in this anion. The spin density on the hydrogen atom in the C–H–Cl part is somewhat higher than the remaining two equivalent hydrogen atoms. Our calculated result that the metastable methyl chloride radical anion with planar C_{2v} symmetry has been found on the potential energy surface strongly suggests that the same series of methyl halide anions, such as methyl bromide and methyl iodide radical anions, also have the same kind of planar C_{2v} metastable state. It was reported that methyl radical–chloride ion pairs were observed by ESR spectroscopy although the hyperfine coupling constants were not reported.[9] The geometry of this weak complex was discussed[7] as a C_{3v} geometry in spite of the fact that the minimum energy point was not reported to be found on the C_{3v} potential curve. On the contrary, our calculated results provide a possibility that the experimentally observed methyl radical–chloride ion adduct has the planar C_{2v} structure instead of the C_{3v} one.[7] We also suggest the possibility that the experimentally observed methyl radical–bromide ion[9,21] and methyl radical–iodide ion[21] adducts have planar C_{2v} structure.

4. Concluding Remarks

The following principal conclusions are derived from the present work.

1. On the C–Cl dissociation potential curve of the methyl chloride radical anion, a shallow least energy point (stationary point) is found within C_{3v} symmetry in cases where dynamical correlation effects are taken into consideration.
2. The well-known C_{3v} dissociation path is not the minimum energy one, and a planar C_{2v} minimum geometry is found on the potential energy surface of the methyl chloride radical anion. On the minimum energy path, the initial C_{3v} structure is changed to the planar C_{2v} one by a large CH_3 rocking deformation.
3. Two possible C–Cl dissociation paths can be considered. One is a nearly C_{3v} path, and another is a path where the C_{3v} structure is changed to the planar C_{2v} one over a relatively short C–Cl distance region.
4. Even if the methyl chloride radical anion would dissociate on the nearly C_{3v} path, there remains the possibility that the planar C_{2v} metastable anion is formed by a recombination between a dissociated methyl radical and chloride ion. We suggest that the experimentally observed methyl radical–chloride ion adduct has the planar C_{2v} structure instead of the C_{3v} one.

Registry No. CH_3Cl, 69685-01-4; Cl^-, 16887-00-6; $\cdot CH_3$, 2229-07-4.

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(19) Guerra, M. *Chem. Phys. Lett.* **1990**, *167*, 315.

(20) Falcetta, M. F.; Jordan, K. D. *J. Phys. Chem.* **1990**, *94*, 5666.

(21) Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 391.