Dissociative Electron Capture by Chloromethane in Condensed Phases

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Ab initio molecular orbital calculations with diffuse and Rydberg augmented basis sets indicate that the potential energy curve for $MeCl^{\bullet-}$ in condensed phases (simulated by curtailing the basis set) is purely dissociative, in contrast to the situation in the gas phase, where the barrier to dissociation is calculated to be 19 kcal mol^{-1} (1 kcal = 4.18 kJ).

Dissociative electron capture by alkyl halides is a fundamental process in many chemical reactions.[1] The nature of alkyl halide radical anions is, however, still unclear. Chloromethane, for instance, has a dipole moment of 1.87 Debye[2] and should therefore have a positive Born–Oppenheimer electron affinity,[3] although this may be too low to give a bound anion for anything other than the hypothetical motionless state.[4] Other alkyl chlorides and bromides have higher dipole moments[2] and should give more stable radical anions. It should be emphasised, however, that these anions are all dipole-bound species whose structure is practically identical to that of the neutral parent. Salem *et al.*[5] have investigated the dissociation of dipole-bound $MeCl^{\bullet-}$ to give $Me^{\bullet}$ + Cl^{-} and found a barrier of 25 kcal mol^{-1} (1 kcal = 4.18 kJ) using *ab initio* molecular orbital calculations with configuration interaction. The barrier, which arises from the crossing of the extra electron from an extremely diffuse orbital to the outermost valence orbital of Cl^{-}, was reduced to 16 kcal mol^{-1} by solvation with two water moelcules.[5] Recently, however, it has been shown that restricting the basis set in *ab initio* calculations on radical anions gives a good simulation of condensed phase behaviour.[6] This communication reports a reinvestigation of the potential energy surface for $MeCl^{\bullet-}$ using this technique. The results suggest that the potential energy curve for the methyl chloride radical anion is purely dissociative in condensed phases. This conclusion is in accord with the fact that alkyl halide radical anions can only be observed as loose, cavity bound complexes, even in low temperature matrices.[7—9]

The diffuse augmented 6-31 + G* basis set[10] was used for all calculations.† This basis gives an adequate description of valance-like anions, and should therefore be suitable for simulating $MeCl^{\bullet-}$ in condensed phases.[6] For a better description of the gas phase potential surface a single very diffuse (Rydberg) sp shell (exponent 0.005) was added to the carbon basis set. The geometries used were obtained by

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† All calculations used in the GAUSSIAN 82 (J. S. Binkley, R. A. Whiteside, K. Raghavachari, R. Seeger, D. J. DeFrees, H. B. Schlegel, M. J. Frisch, J. A. Pople, and L. R. Kahn, Carnegie-Mellon University, 1982) or GAUSSIAN 76 (J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. J. Newton, Quantum Chemistry Program Exchange, program No. 368, Indiana University, 1978) series of programs. Radicals were calculated using the unrestricted Hartree–Fock formalism and MP2 calculations did not include non-valence orbitals.

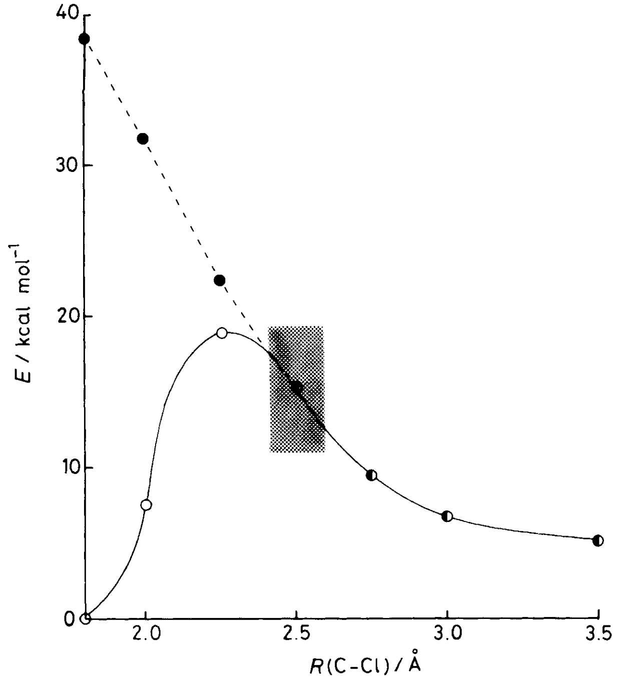

Figure 1. Calculated energy profiles for the dissociation of $MeCl^{\cdot -}$ within C_{3v} symmetry. The open circles are calculated with the Rydberg augmented basis set (see text) and represent the gas phase. The closed circles are points obtained with the 6-31+G* basis set (appropriate to condensed phases). The shaded area indicates the complex which fits best the experimental data.

optimizing $MeCl^{\cdot -}$ at 6-31 + G* within C_{3v} symmetry at fixed C–Cl distances. Energy calculations with the two above basis sets included a second order Moller–Plesset (MP2) correction for electron correlation.[11] The calculated (MP2) electron affinity of MeCl with the Rydberg augmented basis set is −0.17 eV, compared with what must be a slightly positive value within the Born–Oppenheimer approximation.[3,4] The energy for the reaction $MeCl^{\cdot -} \longrightarrow Me^{\cdot} + Cl^{-}$ is calculated to be +4.9 kcal mol^{-1}, compared with a value of 1.1 ± 0.5 kcal mol^{-1} obtained from experimental data[12] and assuming an electron affinity for MeCl close to zero.

The energy curves obtained for the dissociation of $MeCl^{\cdot -}$ are shown in Figure 1. The Rydberg-augmented basis set (solid line) gives results similar to those reported by Salem *et al.*,[5] but with a slightly lower (19 kcal mol^{-1}) barrier to dissociation and an earlier transition state (at 2.28 Å, compared with 2.65 Å found earlier[5]). These differences are probably due to the inclusion of d-orbitals in the basis set in this study. The conclusions reached by Salem *et al.* are, however, confirmed for the gas phase.

The 6-31 + G* energy profile (dashed line) deviates drastically from that obtained with the larger basis set at short C–Cl distances. In contrast to the results obtained for $MeCN^{\cdot -}$ using an 'anion' basis set[6] there is no minimum at a geometry related to the dipole bound structure. The calculated curve indicates no minimum for a methyl chloride anion, the energy profile being purely dissociative. As found earlier,[6] however, these results are in good agreement with experimental data obtained in a frozen matrix.[7] The radical-anion complex observed is trapped in a matrix cavity and has a planar methyl moiety with about 5% of the spin delocalised on chlorine.[7] These data are reproduced closely (90.1° Cl–C–H angle, 6% spin on chlorine) by a point on the dissociation curve at a C–Cl distance of 2.5 Å, as indicated by the shaded area of Figure 1. This distance is close to that expected on the basis of geometry relaxation arguments similar to those used recently by Symons.[13] Relaxation of the methyl fragment to a planar geometry without moving the hydrogen atoms gives a C–Cl distance of 2.13 Å, so that a further bond lengthening of 0.37 Å would give the geometry suggested by the calculations. If this were the case, however, and the gas phase energy profile were applicable to the matrix, the cavity trapped complex would undergo recombination with an activation energy of about 4 kcal mol^{-1}, as observed for $MeCN^{\cdot -}$.[14] Such a process has not, however, been observed, suggesting that the 'condensed phase' 6-31 + G* curve shown in Figure 1 is a good representation of the situation in the matrix. The energy profile should be similar in solution, although Infelta and Schuler[15] have reported results which indicate ready capture of electrons in alkane solution by methyl chloride to give a radical anion with a lifetime of about 3 × 10^{-8} s. The nature of this anionic species was, however, not established and the possibility that it is an electron solvated by MeCl and the alkane solvent[16] cannot be ruled out.

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