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The Reduction of Chloroalkanes by Alkali Metals: a Model *Ab initio* Study

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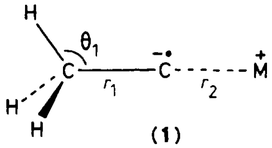
Model calculations using the 6-31+G* basis set suggest that, in contrast to the situation for the isolated chloromethane radical anion in condensed phases, there is a barrier to the dissociation of ion paired MeCl$^{-\bullet}$ into a methyl radical and a chloride ion.

The one-electron reduction of alkyl halides to give alkyl radicals and halide ions as the ultimate products is an important reaction that has been extensively investigated. Salem *et al.*[1] found a barrier of about 20 kcal mol^{-1} to dissociation of the dipole-bound[2] chloromethane radical anion in an *ab initio* study with configuration interaction, but also predicted a significant lowering of the barrier by solvation. Later work[3,4] confirmed the gas-phase prediction but suggested that the potential curve for MeCl$^{-\bullet}$ should be purely dissociative in condensed phases. This result is in accord with matrix e.s.r. studies,[5—7] which reveal no discrete alkyl halide radical anions. Reduction of alkyl halides with a dianion sodium salt, however, gives results which may indicate the existence of RX$^{-\bullet}$ M$^+$ ion pairs, at least for long enough to affect the course of the reaction, although another interpretation of these results has been proposed.[8] We now report model calculations on MeCl$^{-\bullet}$ M$^+$ ion pairs (M = Li, Na, K) which suggest that such species do indeed have modest barriers to dissociation.

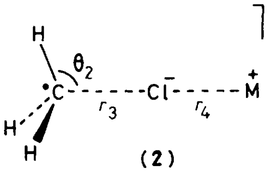
Because electron transfer from one neutral species to another is essentially a condensed phase phenomenon, the calculations must be forced to give the configuration corresponding to MeCl$^{-\bullet}$ M$^+$. This is easily achieved by removing the valence orbitals from the metal basis set so that the last metal electron must be transferred to the organic fragment. We have used this technique previously to simulate purely ionic allyl-lithium.[9]

All calculations[†] used the standard 6–31 + G* basis set[10,11] for the MeCl moiety with the core orbitals from 6–31G[10] for Li and Na. The core orbitals from the MINI4 basis set[12] were used for K. For each metal, optimisation within C_s symmetry led to the C_{3v} ion pair (**1**). This was found to dissociate *via* the C_{3v} transition states (**2**) to give the weak Me$^\bullet$ ClM complexes (**3**), which also have C_{3v} symmetry. The Me group is formally inverted during this process, but this is unlikely to have observable consequences because of the weakness of these complexes (**3**).

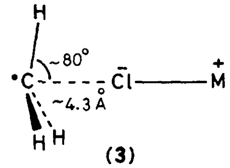
The MeCl$^{-\bullet}$ ion pairs (**1**) all show remarkably short carbon–chlorine bonds (for comparison, the C–Cl bond length in MeCl at 6–31 + G* is 1.786 Å). The Cl–C–H bond angles are all close to 108°, compared with 108.4° in neutral chloromethane. Dissociation is calculated to occur *via* the C_{3v} transition states (**2**), in which the C–Cl distance is close to 2.0 Å and the Cl–C–H angles approximately 105°. The barrier to dissociation increases from 2.8 kcal mol^{-1} for (**1**)–Li to a maximum of 3.4 kcal mol^{-1} for (**1**)–Na and then decreases to 1.5 kcal mol^{-1} for (**1**)–K (see Table 1). This, and the fact that the C–Cl bond lengths in (**1**) decrease on going from lithium to potassium, are surprising results because the metal ion can influence the MeCl$^{-\bullet}$ moiety only electrostatically. Lithium, the smallest of the three alkali metals investigated, might therefore be expected to cause the largest deviation from the purely dissociative potential energy curve found for isolated MeCl$^{-\bullet}$ with the same basis set.[3,4]



(**1**)



(**2**)



(**3**)

[†] 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) series of programs adapted for CDC computers by Dr. A. Sawaryn was used throughout. All calculations used the unrestricted Hartree–Fock formalism and all optimisations, which were constrained to C_s symmetry, led to the C_{3v} structures shown. Five real d-orbitals were used rather than the six Cartesian d-functions used in the original 6–31G* basis set.[10]

Table 1. Geometric parameters (Å and degrees) and activation energies (kcal mol^{-1})^a for the dissociation of MeCl$^{-\bullet}$ M$^+$, (**1**).

M	r_1	r_2	θ_1	r_3	r_4	θ_2	$\Delta E^{\ddagger}$
Li	1.812	2.493	107.7	1.999	2.405	104.5	2.8
Na	1.805	2.707	108.0	2.006	2.636	104.7	3.4
K	1.802	3.165	108.3	1.942	3.162	106.2	1.5

^{a} 1 cal = 4.184 J.

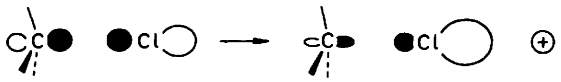


Figure 1

The effect of the metal counter-ion is two-fold: to stabilise the entire radical anion electrostatically and to redistribute the electron density in the occupied molecular orbitals of the organic moiety (the electrostatic orbital localisation discussed previously[9]). The general electrostatic stabilization of MeCl$^{-\bullet}$ also involves rehybridisation of the chlorine contribution to the σ^*_{C-Cl} and n (chlorine σ lone pair) orbitals. The chlorine p-orbital colinear with the bond is stabilized more by the positive charge than the other chlorine valence orbitals and therefore becomes more easily available for mixing with the chlorine 3s orbital. This leads to significant changes in the constitution of the σ^*_{C-Cl} and n orbitals, but not to the low-lying σ_{C-Cl}, which is predominantly composed of chlorine 3s and carbon 2s contributions. This electrostatic stabilization and chlorine rehybridisation give the stable minima (**1**).

The second effect, the localization of high-lying orbitals by the positive charge, leads to the low barrier to dissociation of (**1**)-Li. Although the σ_{C-Cl} orbital is little affected, the bonding component of the n orbital is weakened if the positive charge is allowed to approach chlorine too closely (Figure 1).

This results in the curious maximum in the activation energy to dissociation observed for the sodium counter-ion. Potassium gives behaviour approaching that of the unpaired radical anion,[3,4] sodium provides adequate electrostatic stabilisation to give a moderate barrier, and lithium once more weakens the bond by electrostatic orbital localisation.

The other possible mode of attack of a lithium atom on chloromethane, from the backside of the Me group, leads to dissociation into methyl-lithium and a chlorine atom without activation energy. These products are obtained because of the electrostatic attraction between the Li$^+$ ion and the extra electron.

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References

1 E. Canadell, P. Karafiloglou, and L. Salem, *J. Am. Chem. Soc.*, 1980, **102**, 855.
2 See, for example, W. R. Garrett, *Chem. Phys. Lett.*, 1979, **62**, 325; O. H. Crawford, *Mol. Phys.*, 1971, **20**, 585; O. H. Crawford and W. R. Garrett, *J. Chem. Phys.*, 1977, **66**, 4968.
3 T. Clark, *J. Chem. Soc., Chem. Commun.*, 1984, 93.
4 T. Clark, *Faraday Discuss. Chem. Soc.*, 1984, **78**, 203.
5 E. D. Sprague and F. Williams, *J. Chem. Phys.*, 1971, **54**, 5425; E. D. Sprague, Ph.D. Thesis, University of Tennessee, 1971, pp. 99—102.
6 S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1973, 391; M. C. R. Symons and I. G. Smith, *ibid.*, 1979, 1362.
7 T. Doba, K. U. Ingold, W. Siebrand, and T. A. Wildman, *Faraday Discuss. Chem. Soc.*, 1984, **78**, 175.
8 J. F. Garst, R. D. Roberts, and J. A. Pacifici, *J. Am. Chem. Soc.*, 1977, **99**, 3528; M. C. R. Symons, *J. Chem. Res. (S)*, 1978, 360.
9 T. Clark, C. Rohde, and P. v. R. Schleyer, *Organometallics*, 1983, **2**, 1344.
10 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.
11 T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.
12 Y. Sakai, H. Tatewaki, and S. Huzinaga, *J. Comput. Chem.*, 1981, **2**, 100.