Enhanced Hyperconjugation and Facile 1,2-Halogen Shifts in Metal Cation Complexes of 2-Halogenoalkyl Radicals: an *Ab initio* Study

Andreas von Onciul and Timothy Clark*

Institut für Organische Chemie der Friedrich-Alexander-Universität, Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany

UMP4/6-31G*//6-31G* calculations suggest that complexation of Li^+ to either the β-fluoro- or β-chloro-ethyl radicals results in a significant reduction in the 1,2-shift barrier, as found previously for the protonated radicals, and an overall stabilisation of the radicals by enhanced odd-electron hyperconjugation.

1,2-Halogen shifts in β-halogenoalkyl radicals are examples of the type of radical reaction in which an odd-electron bond is found in and around the transition state, but not in the product or starting material. In contrast to 1,2-hydrogen shifts in alkyl radicals, the electronic configuration in the transition state for 1,2-halogen shifts can be described as having a three-electron, three centre bond between the migrating halogen atom and the two carbon atoms involved ($^2A_1$ in C_{2v} symmetry for a β-halogenoethyl radical).[1] In this situation, introduction of charge into the reacting system can be expected to lower the activation energy significantly because odd-electron bonds are only favourable in charged systems.[2] This has been shown for 1,2-shifts in protonated β-halogeno-[3,4] and β-hydroxy-ethyl radicals.[5] Similarly, addition of the methyl radical to an ethylene–Li^+ complex has been calculated to be easier than to ethylene itself.[6] This type of metal cation catalysis of radical reactions should be quite general and overcomes the major problem encountered in our work on protonated β-halogenoethyl radicals; their tendency to dissociate to the hydrogen halide and ethylene$^{+\cdot}$.[3,4] We have therefore investigated the effect of complexation with Li^+ on the activation energies for 1,2-halogen shifts in the title radicals.

The structures of the Li^+ complexes of $FCH_2CH_2^\cdot$ and $ClCH_2CH_2^\cdot$ were optimised at UHF/6-31G*[7] using the Convex

Table 1. Total (Hartrees) and relative (kcal mol^{-1}, in parentheses) energies of (**1**)—(**6**) and their possible dissociation products.[a]

Species	HF[a]	MP2	MP3	MP4sdtq
$C_2H_4^{+\cdot}$ + LiF	−184.64609 (58.9)	−185.04256 (64.9)	−185.07361 (58.0)	−185.08231 (59.2)
$FCH_2CH_2^{\cdot}$ + Li^+	−184.67869 (38.5)	−185.08126 (40.6)	−185.10286 (39.7)	−185.12064 (40.9)
$CH_3CHF^{\cdot}$ + Li^+	−184.68342 (35.5)	−185.08995 (35.4)	−185.10979 (35.4)	−185.12885 (35.7)
(**1**) (minimum)	−184.74002 (0.0)	−185.14594 (0.0)	−185.16618 (0.0)	−185.18580 (0.0)
(**3**) (saddle point)	−184.70880 (19.6)	−185.11738 (17.9)	−185.13641 (18.7)	−185.15914 (16.7)
(**7**) (minimum)	−184.73567 (2.7)	−185.14337 (1.6)	−185.16304 (2.0)	−185.18286 (1.8)
$C_2H_4^{+\cdot}$ + LiCl	−544.72147 (34.6)	−545.06307 (49.5)	−545.10090 (47.0)	−545.11256 (49.6)
$ClCH_2CH_2^{\cdot}$ + Li^+	−544.73526 (27.6)	−545.09947 (26.7)	−545.13305 (26.8)	−545.14808 (27.3)
$CH_3CHCl^{\cdot}$ + Li^+	−544.73891 (23.7)	−545.10590 (22.6)	−545.13915 (23.0)	−545.15461 (23.2)
(**2**) (minimum)	−544.77663 (0.0)	−545.14198 (0.0)	−545.17584 (0.0)	−545.19163 (0.0)
(**4**) (saddle point)	−544.77097 (3.6)	−545.12605 (10.0)	−545.16176 (8.8)	−545.17699 (9.2)
(**8**) (minimum)	−544.77355 (1.9)	−545.14355 (−1.0)	−545.17701 (−0.7)	−545.19242 (−0.5)
C_2H_5F + Li^+	−185.31276 (0.0)	−185.74340 (0.0)	−185.76486 (0.0)	−185.77466 (0.0)
(**5**) (minimum)	−185.37254 (−37.5)	−185.80570 (−39.1)	−185.82623 (−38.5)	−185.83707 (−39.2)
C_2H_5Cl + Li^+	−545.36706 (0.0)	−545.75919 (0.0)	−545.79260 (0.0)	−545.79925 (0.0)
(**6**) (minimum)	−545.40635 (−24.7)	−545.80021 (−25.7)	−545.83391 (−25.9)	−545.84801 (−26.1)

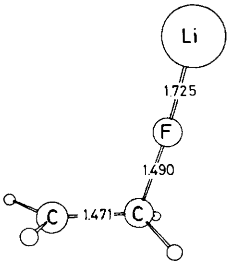
[a] Restricted Hartree–Fock (RHF) for closed-shell systems and unrestricted Hartree–Fock (UHF) for radicals (cal = 4.184 J).

version of the Gaussian 82 suite of programs.[8] The nature of the stationary points found was determined by diagonalisation of the Hessian matrix at this level and the UHF/6-31G* geometries were used for single point energy calculations using the 6-31G* basis set with a fourth order Møller-Plesset correction[9] for electron correlation including single, double, triple, and quadruple excitations (MP4SDTQ/6-31G*//6-31G*). Non-valence orbitals were not included in the MP4 correction calculations. The geometries obtained are shown in Scheme 1. Table 1 shows the absolute and relative energies of the species calculated and their energetic relationship to some possible dissociation products.

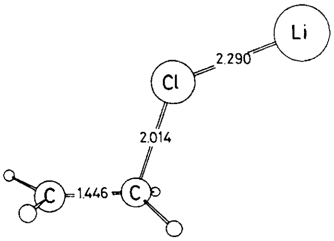
The Li^+ complex of the β-fluoroethyl radical (**1**) shows enhanced hyperconjugation between the CF bond and the radical centre compared with the uncomplexed radical.[3] The preferred conformation is analogous to that found in the β-chloroethyl radical[3,10] and the CC bond length is significantly shorter than that found in the free radical. The CCF angle is slightly smaller (108.7° *vs.* 110.0°) than in the uncomplexed radical. These changes are all expected on the basis of the simple theory of odd-electron bonds,[2] which suggests that odd-electron hyperconjugation should be weak in neutral radicals but stronger in radical ions. The Li^+ complex of $ClCH_2CH_2^{\cdot}$ (**2**) shows even more evidence of enhanced hyperconjugation relative to the free radical. The CC bond length is only 1.446 Å and the CCCl angle is 107.2°, (the corresponding values in $ClCH_2CH_2^{\cdot}$ are 1.481 Å and 111.4°).[3] The transition states for the 1,2-LiF- (**3**) and 1,2-LiCl-shifts (**4**) have C=C bond lengths (1.384 and 1.387 Å, respectively) that are intermediate between those of the uncomplexed radicals and their protonated forms.[3,4,10] The CF and CCl distances (2.259 and 2.765 Å) are, however, very much shorter than in the free and protonated bridged forms. These geometrical features suggest that the lithium complexes are more strongly bound relative to dissociation into $C_2H_4^{+\cdot}$ and LiX than the protonated forms and that the 1,2-shift barriers should be lower than in the free radicals.

The energies shown in Table 1 confirm this conclusion. Dissociation to the alkene radical cation and a lithium halide is even less favourable than halogen atom dissociation from the corresponding uncomplexed radicals[3] and the lithium cation affinities of the radicals are around 40 kcal mol^{-1} for the fluorethyl radical and 30 kcal mol^{-1} for its chlorine counterpart. As expected, the 1,2-LiX-shift barriers in (**1**) and (**2**) are lower than those for the free radicals. More importantly, the 1,2-shift transition states, (**3**) and (**4**), lie significantly lower in energy than the possible dissociation products, so that a true concerted 1,2-shift pathway exists.

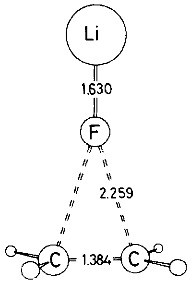
The effect of lithium complexation on the reactivity of alkyl halides should, however, also be measurable. In order to test this hypothesis, the C_2H_5F–Li^+ and C_2H_5Cl–Li^+ complexes (**5**) and (**6**) were also investigated. The lithium cation affinities



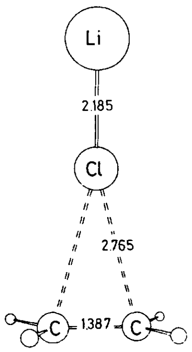
(1)



(2)



(3)



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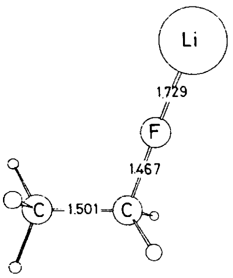
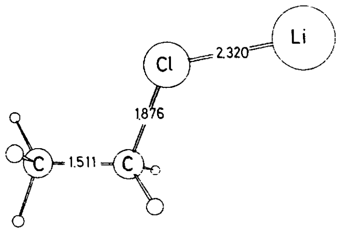


(5)



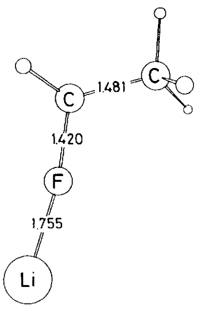
(6)

of the ethyl halides are slightly lower than those of the corresponding β-halogeno radicals. The lithium complexed radicals therefore enjoy some extra stabilisation because of the enhanced hyperconjugation relative to the free radicals. This is shown by the calculated energies for reaction (1).

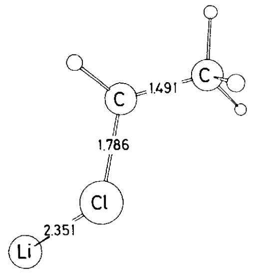
$$XCH_2CH_2^{\cdot} + C_2H_5X\text{–}Li^+ \rightarrow C_2H_5X + Li^+\text{–}XCH_2CH_2^{\cdot} \quad (1)$$

$$\Delta E = -1.5 \text{ kcal mol}^{-1} (X = F)$$
$$\Delta E = -1.2 \text{ kcal mol}^{-1} (X = Cl)$$

Because, however, Li$^+$-complexation of an α-halogenoalkyl radical should not lead to enhanced hyperconjugation, but rather to reduced inductive stabilisation, the relative stabilities of the α- and β-isomers should be changed by such complexation. The $CH_3CHF^{\cdot}$–Li^+ and $CH_3CHCCl^{\cdot}$–Li^+ complexes (**7**) and (**8**) were therefore also investigated. The calculated isomerisation energies for reactions (2) and (3) demonstrate this trend and even suggest that the regioselectivity for hydrogen atom abstraction from alkyl fluorides can be changed by complexation with Li$^+$. These effects should be experimentally verifiable as long as a solvent system can be found in which Li$^+$ complexes to the alkyl halide. Lithium cation complexation should, in any case, strongly favour



(7)



(8)

1,2-halogen shifts in β-fluoro- and β-chloroalkyl radicals. Note that Li$^+$-complexation is not expected to affect 1,2-H-shift barriers because hydrogen shifts involve a different orbital occupation ($^2B_2$ in the C_{2v} ethyl radical) to their halogen counterparts.

$$CH_3CHX^{\cdot} \rightarrow XCH_2CH_2^{\cdot}$$

$$\Delta E = 5.2 \text{ kcal mol}^{-1} (X = F)$$
$$\Delta E = 3.9 \text{ kcal mol}^{-1} (X = Cl)$$

$$CH_3CHX^{\cdot} : LI^+ \rightarrow Li^+ : XCH_2CH_2^{\cdot}$$

$$\Delta E = -1.8 \text{ kcal mol}^{-1} (X = F)$$
$$\Delta E = 0.5 \text{ kcal mol}^{-1} (X = Cl)$$

This work was supported by the Fonds der Chemischen Industrie, the Stiftung Volkswagenwerk, and the Convex Computer GmbH.

Received, 31st January 1989; Com. 9/00515C

References

1 T. Clark in NATO ASI Series C, 'Substituent Effects in Radical Chemistry,' eds. H. G. Viehe, R. Merenyi, and Z. Janousek, Reidel, Amsterdam, 1986; ACS Petroleum Division Preprints, 1986, **31**, 864.
2 T. Clark, *J. Am. Chem. Soc.*, 1988, **110**, 1672.
3 T. Clark and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1986, 96.
4 J. C. Morrow and T. Baer, *J. Phys. Chem.*, 1988, **92**, 6567.
5 B. T. Golding and L. Radom, *J. Chem. Soc., Chem. Commun.*, 1973, 939.
6 T. Clark, *J. Chem. Soc., Chem. Commun.*, 1986, 1774.
7 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; M. Francl, M. Pietro, W. J. Hehre, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.
8 J. S. Binkley, R. A. Whiteside, K. Raghavachari, R. Seeger, D. J. DeFrees, H. B. Schlegel, M. J. Frisch, J. A. Pople, and L. Kahn, 'Gaussian 82,' Carnegie-Mellon University, 1982.
9 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618; J. S. Binkley and J. A. Pople, *Int. J. Quant. Chem.*, 1975, **9**, 229 and references cited therein; J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quant. Chem. Suppl.*, 1976, **10**, 1 and references cited therein; M. J. Frisch, R. Krishnan, and J. A. Pople, *Chem. Phys. Lett.*, 1980, **75**, 66.
10 A. C. Hopkinson, M. H. Lien, and I. G. Csizmadia, *Chem. Phys. Lett.*, 1980, **71**, 557, and references cited therein.