Li$^+$ Ion Attachment to Chloromethyl and Chlorofluoromethyl Peroxyl Radicals: Structures and Properties of CH$_n$Cl$_{3-n}$O$_2$-Li$^+$ and CF$_n$Cl$_{3-n}$O$_2$-Li$^+$ (n=0−3) Complexes

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The structures and stabilities of these still experimentally unknown CH$_n$Cl$_{3-n}$O$_2$-Li$^+$ and CF$_n$Cl$_{3-n}$O$_2$-Li$^+$ ions have been theoretically investigated by *ab initio* molecular orbital theory and density functional theory (DFT) in conjunction with the 6-311G(d,p), 6-311＋G(d,p), 6-311＋G(2d,p) and 6-311＋G(2df,2p) basis sets. The optimized geometries, chemical bonding and NBO analysis indicate that these complexes of CH$_n$Cl$_{3-n}$O$_2$-Li$^+$ and CF$_n$Cl$_{3-n}$O$_2$-Li$^+$ exist as ion-dipole molecules. The calculated affinity energies of these species exceed 41.9 kJ/mol, which are large enough to suggest the possibility that these title complexes could be detected as stable species in gas phase by Li$^+$ ion attachment mass spectrometry.

Keywords　chloromethyl, chlorofluoromethyl peroxyl, ion attachment mass spectrometry

Introduction

Radicals are often extremely reactive and their character could only be determined at suitable and right experimental conditions. A large set of mass spectrometric methods have been employed for the generation and study of radicals from thermal reactions, pyrolysis, photolysis, flames, or electrically induced plasmas.[1-3] Among them, lithium ion attachment mass spectrometry (IAMS) has been introduced as a new method for detection and identification of radical species in the gas phase.[4] This method provides mass spectra of quasi-molecular ions formed by lithium-ion attachment to the radical species under high-pressure conditions in a similar way to that proposed for the detection of stable molecules.[5] Briefly, the alkali-metal ion association reaction is described by the termolecular process:

$$M^+ + R + N \rightarrow [M-R]^+ + N \qquad (1)$$
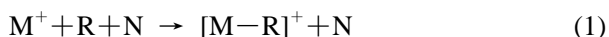
where M denotes a positively charged alkali metal ion, R is a radical species, and N acts as a third-body. The binding energy of the radical R to the alkali cation M$^+$ is defined by the enthalpy change for the preceding reaction. Deriving primarily from electrostatic forces, the binding energy of the reagent alkali metal ion M$^+$ to the radical must be high enough to permit a significant number of adducts to be formed at the partial pressure used in the experiments. Cationized adducts are generally stable and give a direct information on the molecular weights of the neutral counterpart of the [M＋R]$^+$ adduct. The relative binding energies of radicals have been estimate by theoretical calculations,[6,7] indicating that the binding energies of a wide range of such species with the alkali ion are high enough to be detectable at low concentrations. The advantages of this method for radical detection are a measure of mass as a guide for radical identification without fragmentations, adaptability to a large range of steady-state pressures, and direct continuous measurements of any species emerging from dynamic systems. In addition, the technique allows one to probe at the same time both the ionic and radical species flowing out from the investigated systems, which make possible to obtain correlations between them.[8]

Peroxyl radicals have received much attention because of the essential roles they play in atmospheric chemistry[9-12] as well as in biological systems.[13-17] Recently, we have presented a systematic investigation of structures and properties including geometries, NBO analysis, vibrational frequencies and cation affinity of NF$_3$—M$^+$,[18] CF$_3$—M$^+$ (M＝Li, Na, K)[19] and CH$_n$F$_{3-n}$O$_2$-Li$^+$ (n＝0—3). In the present work, we go on studying the structures and properties of these CH$_n$Cl$_{3-n}$O$_2$-Li$^+$ and CF$_n$Cl$_{3-n}$O$_2$-Li$^+$ (n＝0—3) complexes in a similar method. At the same time, we want to get some information on the possibility to detect CH$_n$Cl$_{3-n}$O$_2$ and CF$_n$Cl$_{3-n}$O$_2$ radicals by ion attachment mass spectrometry at different theoretical methods.

Computational details

All calculations were carried out with the Gausian 03 package[20] on a SGI 3900 supercomputer. The stable equilibriums of $CH_nCl_{3-n}O_2\text{-}Li^+$ and $CF_nCl_{3-n}O_2\text{-}Li^+$ were optimized using UMP2 (second order unrestricted Moler-Plesset) and B3LYP levels in conjunction with the 6-311G(d,p), 6-311+G(d,p), 6-311+G(2d,p), and 6-311+G(2df,2p) basis sets. All the optimized geometries corresponding to a local minimum point have real frequencies except for $CH_2ClO_2\text{-}Li^+$ adduct with no imaginary at B3LYP level. To improve the accuracy of energies, single-point calculations were performed by the DFT method with 6-311+G(2df,2p) basis set using the B3LYP/6-311G(d,p) optimized geometries.

Results and discussion

Geometries and chemical bond analysis

Figure 1 shows stationary points on the potential energy profiles of these complexes. Their detailed geometries, the results of chemical bonding analysis and the NBO charges are collected in Tables 1—4, respectively. For comparative purposes and to appreciate the performance of the various employed theoreticcal levels, we have investigated these complexes.
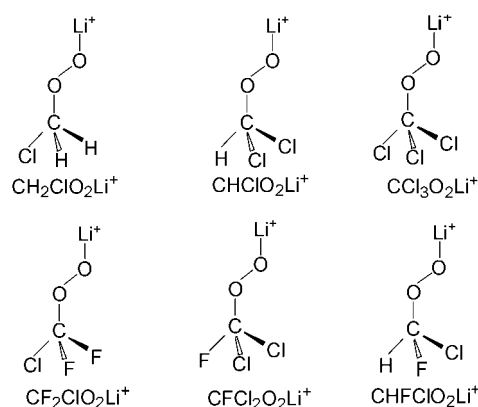

Figure 1 The optimized geometry of $CH_nCl_{3-n}O_2\text{-}Li^+$ and $CF_{3-n}\text{-}Cl_nO_2\text{-}Li^+$ ($n=0$—3) complexes.

Table 1 The geometry parameters of optimized complexes at MP2 and B3LYP level with different basis sets[a]

	Basis set	OLi	CO	OO	COO
$CH_3O_2Li^+$					
B3LYP	6-311G(d,p)	0.1875	0.1466	0.1312	112.1
	6-311+G(2d,p)	0.1875	0.1464	0.1315	111.8
	6-311+G(2df,2p)	0.1872	0.1461	0.1311	112.1
MP2	6-311G(d,p)	0.1863	0.1471	0.1275	112.0
	6-311+G(d,p)	0.1870	0.1473	0.1276	112.0
$CH_2ClO_2Li^+$					
B3LYP	6-311G(d,p)	0.1890	0.1495	0.1312	111.1
	6-311+G(2d,p)	0.1889	0.1491	0.1315	110.7
	6-311+G(2df,2p)	0.1885	0.1490	0.1311	111.0
MP2	6-311G(d,p)	0.1878	0.1500	0.1274	110.9
	6-311+G(d,p)	0.1883	0.1501	0.1275	111.0
$CHCl_2O_2Li^+$					
B3LYP	6-311G(d,p)	0.1889	0.1506	0.1305	113.4
	6-311+G(2d,p)	0.1885	0.1502	0.1308	113.0
	6-311+G(2df,2p)	0.1881	0.1502	0.1304	113.2
MP2	6-311G(d,p)	0.1894	0.1518	0.1268	113.0
	6-311+G(d,p)	0.1898	0.1519	0.1289	112.8
$CCl_3O_2Li^+$					
B3LYP	6-311G(d,p)	0.1893	0.1562	0.1300	113.2
	6-311+G(2d,p)	0.1891	0.1552	0.1304	112.8
	6-311+G(2df,2p)	0.1887	0.1554	0.1299	113.0
MP2	6-311G(d,p)	0.1892	0.1568	0.1264	112.9
	6-311+G(d,p)	0.1897	0.1570	0.1264	113.0

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Continued

	Basis set	OLi	CO	OO	COO
CFCl$_2$O$_2$Li$^+$					
B3LYP	6-311G(d,p)	0.1901	0.1544	0.1300	113.5
	6-311+G(2d,p)	0.1899	0.1538	0.1303	113.0
	6-311+G(2df,2p)	0.1896	0.1538	0.1298	113.3
MP2	6-311G(d,p)	0.1902	0.1545	0.1266	113.0
	6-311+G(d,p)	0.1910	0.1546	0.1267	112.9
CF$_2$ClO$_2$Li$^+$					
B3LYP	6-311G(d,p)	0.1906	0.1526	0.1308	110.5
	6-311+G(2d,p)	0.1907	0.1521	0.1311	110.0
	6-311+G(2df,2p)	0.1902	0.1522	0.1306	110.3
MP2	6-311G(d,p)	0.1920	0.1520	0.1274	110.4
	6-311+G(d,p)	0.1928	0.1519	0.1275	110.5
CF$_3$O$_2$Li$^+$					
B3LYP	6-311G(d,p)	0.1917	0.1509	0.1307	110.7
	6-311+G(2d,p)	0.1920	0.1505	0.1309	110.3
	6-311+G(2df,2p)	0.1918	0.1506	0.1305	110.6
MP2	6-311G(d,p)	0.1935	0.1499	0.1276	110.5
	6-311+G(d,p)	0.1948	0.1498	0.1278	110.6
CHFClO$_2$Li$^+$					
B3LYP	6-311G(d,p)	0.1892	0.1504	0.1307	111.9
	6-311+G(2d,p)	0.1892	0.1499	0.1310	111.6
	6-311+G(2df,2p)	0.1888	0.1500	0.1306	111.8
MP2	6-311G(d,p)	0.1901	0.1508	0.1272	111.6
	6-311+G(d,p)	0.1910	0.1507	0.1273	111.5

[a] bond distance in nm; angle in (°).

Table 2 The NPA charge distribution of complexes

		B3LYP/6-311G(d,p)			B3LYP/6-311G(d,p)
CH$_2$ClO$_2$Li$^+$	C	−0.0696	CFCl$_2$O$_2$Li$^+$	C	0.5105
	O	−0.0808		O	−0.1124
	O	−0.3310		O	−0.2984
	H	0.2167		F	−0.2996
	Cl	0.0693		Cl	0.1097
	Li	0.9788		Li	0.9804
CHCl$_2$O$_2$Li$^+$	C	0.0149	CF$_2$ClO$_2$Li$^+$	C	0.9394
	O	−0.0935		O	−0.1320
	O	−0.3065		O	−0.2820
	H	0.2190		F	−0.3017
	Cl	0.0929		Cl	0.0971
	Li	0.9803		Li	0.9808
CCl$_3$O$_2$Li$^+$	C	0.0181	CHFClO$_2$Li$^+$	C	0.4761
	O	−0.1127		O	−0.1071
	O	−0.3025		O	−0.3021
	Cl	0.1494		F	−0.3036
	Cl	0.1339		Cl	0.0591
	Li	0.9800		Li	0.9802

Table 3 The second interaction energies of these attached reactions[a]

Complex	Donor → acceptor	ΔE_{ij}^2
$CH_2ClO_2Li^+$	$CR(Li^+) \to BD^*(O—O)$	0.46
	$LP(Cl) \to BD^*(C—O)$	27.0
$CHCl_2O_2Li^+$	$CR(Li^+) \to BD^*(O—O)$	0.67
	$LP(Cl) \to BD^*(C—O)$	29.9
$CCl_3O_2Li^+$	$CR(Li^+) \to BD^*(O—O)$	0.59
	$LP(Cl) \to BD^*(C—O)$	33.2
$CFCl_2O_2Li^+$	$CR(Li^+) \to BD^*(O—O)$	0.50
	$LP(Cl) \to BD^*(C—O)$	31.0
$CF_2ClO_2Li^+$	$CR(Li^+) \to BD^*(O—O)$	0.54
	$LP(Cl) \to BD^*(C—O)$	25.7
$CHFClO_2Li^+$	$CR(Li^+) \to BD^*(O—O)$	0.67
	$LP(Cl) \to BD^*(C—O)$	17.2

[a] ΔE_{ij}^2 in kJ/mol; CR: center core pair; BD*: antibond; LP: lone pair.

Table 4 B3LYP/6-311+G(2df,2p) charge densities ρ (e/a.u.^{3}) and Laplacian of the charge densities [a]

Species	Bcp	ρ	$\nabla^2\rho$
$CCl_3O_2Li^+$	C—Cl	0.20738	−0.2506
	O—Li	0.03493	0.2406
$CF_2ClO_2Li^+$	C—F	0.31487	−0.4460
	C—Cl	0.22084	−0.3024
	O—Li	0.03326	0.2273
$CFCl_2O_2Li^+$	C—F	0.30857	−0.3809
	C—Cl	0.21257	−0.2712
	O—Li	0.03426	0.2338
$CH_2ClO_2Li^+$	C—Cl	0.20727	−0.2820
	O—Li	0.03573	0.2441
$CHCl_2O_2Li^+$	C—Cl	0.20545	−0.2595
	O—Li	0.03534	0.2450
$CHFClO_2Li^+$	C—F	0.29815	−0.2856
	C—Cl	0.21037	−0.2811
	O—Li	0.03453	0.2385

[a] $\nabla^2\rho$ (e/a.u.^{5}), evaluated at the bond critical points (bcp) located on the attractor interaction lines of the $CH_nCl_{3-n}O_2$-Li^+ and $CF_nCl_{3-n}O_2$-Li^+ complexes.

The attachments of Li^+ to the outer O atom of $CH_nCl_{3-n}O_2$-Li^+ and $CF_nCl_{3-n}O_2$-Li^+ lead to the formations of C_s symmetry, which were characterized as local minimum points on their respective energy surfaces of the various theoretical levels. The values of O—Li^+ bond length in CH_3O_2-Li^+ and CF_3O_2-Li^+ decrease with the size of basis set increasing from 6-311G(d,p), 6-311+G(2d,p) to 6-311+G(2df,2p) at B3LYP level, but increase going from 6-311G(d,p) to 6-311+G(d,p) at MP2 level. And the values investi-

gated at MP2 level are lower than these at B3LYP level. These indicate that the bond length of O—Li^+ is sensitive to size of basis set, diffusion function and theoretical method. However, we first note that, irrespective of the employed computational level and basis set, the values of the Li^+—O bond lengths are invariably predicted to be larger than 0.18 nm, which are structurally-telling of ion-dipole adducts between Li^+ and $CH_nCl_{3-n}O_2$-Li^+ and $CF_nCl_{3-n}O_2$—Li^+.[18,19] Accordingly, from Table 4, the bond critical points (bcps) on the attractor interaction lines corresponding to the Li^+—O bonds are associated with charge densities ρ as small as 0.035 (CCl_3O_2-Li^+), 0.033 (CF_2ClO_2-Li^+), 0.034 ($CFCl_2O_2$-Li^+), 0.036 (CH_2ClO_2-Li^+), 0.035 ($CHCl_2O_2$-Li^+) and 0.035 e/a.u.^{3} ($CHFClO_2$-Li^+), respectively, and with positive values of the Laplacian of ρ, 0.24 (CCl_3O_2-Li^+), 0.22 (CF_2ClO_2-Li^+), 0.23 ($CFCl_2O_2$-Li^+), 0.24 (CH_2Cl-O_2-Li^+), 0.24 ($CHCl_2O_2$-Li^+) and 0.24 e/a.u.^{5} ($CHFCl$-O_2-Li^+), which are typical of closed-shell-type electrostatic interactions.[19]

The Natural Bond Orbital (NBO) analysis is used for better understanding the nature of the corresponding intermolecular interactions. There is a considerably small charge transfer in these complexes from Li^+ to these chloromethyl and chlorofluoromethyl peroxyl radicals because of the electropositive nature of the alkali metal. Li^+ ion is shown to retain 0.9788, 0.9803, 0.9800, 0.9804 and 0.9802 electronic units (e) positive charge in these adducts. This result indicates that bonding is due mostly to electrostatic interaction, and the main contribution of which is ion-dipole attraction.[21,22] The optimized structures of these complexes and the corresponding bonding analysis reveal also that the formal additions of Li^+ to the outer O atom of $CH_nCl_{3-n}O_2$ and $CF_nCl_{3-n}O_2$ radicals enhance back-donation from the surrounding chlorines.

Analysis of the NBO second-order interaction energies ΔE_{ij}^2 of these interactions leads to a further interpretation. Li^+ ion can be considered as Lewis acid, so the analysis of ΔE_{ij}^2 is carried out to examine the possible interactions between donor (Lewis-type) and acceptor (non-Lewis). Inspection of Table 3, it can be seen that second-order interaction energies ΔE_{ij}^2 between the center core pair of Li^+ and the antibond of O(2)—O(3) are 0.46 kJ/mol (CH_2ClO_2-Li^+), 0.67 kJ/mol ($CHCl_2O_2$-Li^+), 0.59 kJ/mol (CCl_3O_2-Li^+), 0.50 kJ/mol ($CFCl_2O_2$-Li^+), 0.54 kJ/mol (CF_2ClO_2-Li^+) and 0.67 kJ/mol ($CHFClO_2$-Li^+), respectively. In comparison with the interaction energies (ΔE_{ij}^2) between lone pair of Cl atom and the antibond of C—O, these values are so small, which supports our assumption that the interactions between Li^+ ion and $CH_nCl_{3-n}O_2$ ($CF_nCl_{3-n}O_2$) radicals mostly attribute to the electrostatic and $CH_nCl_{3-n}O_2$-Li^+ ($CF_nCl_{3-n}O_2$-Li^+) exist as ion-dipole type complexes.

Energies

Understanding of the affinity energy of Li^+ cation

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(LCA) investigated in this study provides a significant insight into the possibility that $CH_nCl_{3-n}O_2$ and CF_n-$Cl_{3-n}O_2$ radicals could be detected by Li^+ ion attachment mass spectrometry. In order to observe any stable complexes between Li^+ ion and a molecule using mass spectrometric technique, it has been noted that the gas-phase Li^+ ion affinity should be at least 41.9 kJ/mol at room temperature.[22] In general, only the inclusion of electron correlation effects and the use of sufficiently large and flexible polarized diffuse split-valence basis sets[23] can provide the quantitative theoretical reproduction of the experimentally measured lithium cation affinity. In our latest work, we investigated the LCA of $CH_nF_{3-n}O_2$ radicals systematically with CCSD(T)/6-311 +G(2df,2p) theoretical method. But we found that the values investigated with this method are only lower by 7.9 kJ/mol than those with B3LYP/6-311+G(2df,2p) method which costs less time than the former. In present work, considering that the chlorine atom is large in comparison with small fluorine atom, we adopt MP2 and B3LYP levels in conjunction with the 6-311G(d,p), 6-311+G(d,p), 6-311+G(2d,p) and 6-311+G(2df,2p) basis sets to investigate the affinity energies of lithium ion, which are shown in Figures 2 and 3. At B3LYP/6-311+G(2df,2p) level, we obtained the LCA values which are 128.6 kJ/mol (CH_2ClO_2-Li^+), 120.3 kJ/mol ($CHCl_2O_2$-Li^+) and 104.3 kJ/mol (CCl_3O_2-Li^+). And these values are not too large in comparison with those at other levels. Whereas, the values investigated at MP2 and B3LYP level using 6-311G(d,p) basis set, we think that, may be larger than the presently unknown experimental values. Figures 2 and 3 show the variation of the LCA with the degree of chlorine substitution. It is worth noting that the substitution of either H or F by Cl shows a good liner relationship. It can be also seen from Figure 3 that the LCA in CCl_3O_2 point suddenly decreases in comparison with one in $CFCl_2O_2$ point at B3LYP/6-311+G(2df,2p) level when going from CF_3O_2-Li^+, CF_2Cl-O_2-Li^+ and $CFCl_2O_2$-Li^+ to CCl_3O_2-Li^+. This may be due to the steric hindrance introduced by the three bulky

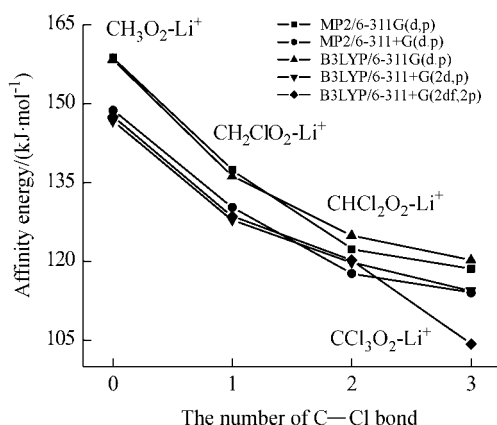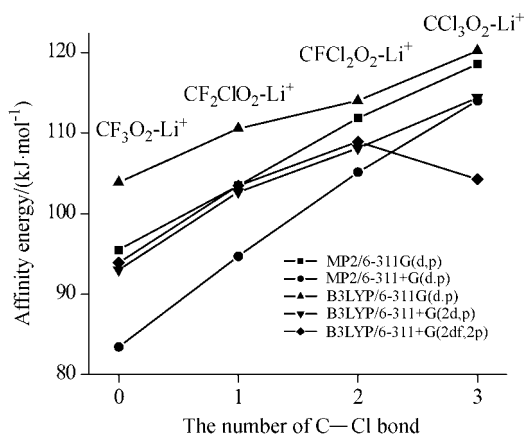**Figure 3** The relationship between Li^+ cation affinity energy of $CF_nCl_{3-n}O_2$-Li^+ (in kJ/mol) and the number of C—Cl bond at different level.

Cl atoms and the favorable geminal interactions of Cl—Cl and Cl—F.[24] In general, irrespective of the employed computation level, these values are large enough to support that $CH_nCl_{3-n}O_2$ and $CF_nCl_{3-n}O_2$ radicals could be possibly detected by lithium cation attachment mass spectrometry.

Conclusion

We have used *ab intio* and DFT theoretical methods in conjunction with different basis sets from small to large to investigate the geometries and the affinity energies of $CH_nCl_{3-n}O_2$-Li^+ and $CF_nCl_{3-n}O_2$-Li^+ ($n=0$—3) complexes. From our calculation, we can draw some preliminary conclusions: (1) the substitute Cl atoms in these chloromethyl and chlorofluoromethyl peroxyl radicals have an effect on the lithium cation affinity at different levels. The LCA decreases when going from CH_3O_2-Li^+, CH_2ClO_2-Li^+ and $CHCl_2O_2$-Li^+ to CCl_3-O_2-Li^+, which may be due to the increase of the electron-withdrawing ability of the chlorine-substituted methyl group. On the other hand, the steric hindrance and geminal interactions of Cl—Cl and Cl—F may contribute to the increase of the LCA from CF_3O_2-Li^+, CF_2ClO_2-Li^+ and $CFCl_2O_2$-Li^+ to CCl_3O_2-Li^+. (2) $CH_nCl_{3-n}O_2$ and $CF_nCl_{3-n}O_2$ could be possibly detected by Li^+ ion attachment mass spectrometry.

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Figure 2 The relationship between Li^+ cation affinity energy of $CH_nCl_{3-n}O_2$-Li^+ (in kJ/mol) and the number of C—Cl bond at different level.

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