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Ion Pair S_N2 Reactions. Theoretical Study of Inversion and Retention Mechanisms

Sjoerd Harder,[†] Andrew Streitwieser,[*,†] Jeffrey T. Petty,[†] and Paul von Ragué Schleyer[*,‡]

*Contribution from the Department of Chemistry, University of California,
Berkeley, California 94720, and Computer Chemistry Center, Institüt für Organische Chemie,
Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42,
D-91054 Erlangen, Germany*

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Abstract: Transition state structures have been found in *ab initio* calculations of identity reactions of lithium fluoride and chloride and of sodium chloride with methyl fluoride and chloride. The retention transition state can be considered as an S_Ni type in which a methyl cation interacts with a metal halide triple ion, MX_2^-. The inversion transition states are highly bent from the linear $X \cdots C \cdots X$ bond angles found for the ionic analogs. The inversion TS can also be considered as an ionic assembly. These bond angles become more linear and the activation energies are reduced for reactions with ion pair aggregates; such transition states can be considered as a $(XCH_3X)^-$ triple ion interacting with a $(MXM)^+$ triple ion.

The direct displacement or S_N2 reaction is one of the most important reactions in chemistry. In the most common type of S_N2 reaction a nucleophilic anion reacts with an alkyl halide (or sulfonate or related ester) via an anionic transition state to give a neutral substitution product and an anionic nucleofuge. Such reactions have been the subject of many theoretical treatments at a variety of theory levels.[1] Most of the recent studies have made use of ab initio MO methods.[2–32] Some of the theoretical work has dealt with the effect of solvent on the S_N2 mechanism.[13,14,19,33–37] The typical anion gas-phase potential energy surface of the double-well type[2,3,5,7] converts to a unimodal surface when solvation is included;[34] that is, the initial complex formed between nucleophile and substrate becomes less well defined or important in solution. It is well-known that under many conditions the S_N2 reactions actually involve ion pairs as the nucleophiles. Early in this century, Acree[38] showed that the observed rate constant for an S_N2 reaction can be dissected into the rate constant for the free anion (k_i) and for the ion pair (k_{ip}), eq 1, in which α is the degree of dissociation of the ion pair.

$$k = k_i\alpha + k_{ip}(1 - \alpha) \tag{1}$$

The ion pair reactions have been much less studied even though ion pairing is known to change the order of reactivity of halide ions.[39] Especially significant is the recent report that the ϱ value for an S_N2 reaction of benzylic halides has a different sign for ions and ion pairs.[40] The ion pair displacement reaction is also

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[†] University of California, Berkeley.

[‡] University of Erlangen-Nürnberg.

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Table 1. Absolute Energies (Hartree), Zero-Point Energy (ZPE in kcal mol^{-1}), and Number of Imaginary Frequencies (NIMAG)

	symmetry	3-21G	6-31G*	6-31+G*	MP2/6-31+G*// 6-31+G*	MP3/6-31+G*// 6-31+G*	MP4/6-31+G*// 6-31+G*	ZPE (NIMAG)/ 6-31+G*//6-31+G*
$F^- + CH_3F$								
F^-	K_h		−99.350 48	−99.418 59	−99.623 85	−99.613 63	−99.629 75	
CH_3F	C_{3v}		−139.034 62	−139.044 23	−139.352 45	−139.362 41	−139.377 78	26.6(0)
complex	C_{3v}			−238.483 28	−238.998 41	−238.998 21	−239.030 14	26.9(0)
TS inv	D_{3h}			−238.453 74	−238.978 58	−238.973 16	−239.014 00	26.5(1)
TS ret	C_s	−237.013 57	−238.306 67	−238.360 33	−238.899 63	−238.890 13	−238.937 51	25.8(1)
$LiF + CH_{3F}$								
LiF	$C_{\infty v}$	−106.354 18	−106.934 23	−106.946 25	−107.144 43	−107.137 58	−107.150 28	1.3(0)
$CH_{3F\cdots LiF}$	C_s	−244.688 14	−245.999 67	−246.015 88	−246.524 19	−246.527 78	−246.555 93	29.3(0)
TS inv	C_{2v}	−244.561 00	−245.883 49	−245.909 00	−246.415 69	−246.415 72	−246.453 54	27.2(1)
TS ret	C_s	−244.602 36	−245.909 80	−245.929 84	−246.442 93	−246.441 51	−246.480 67	27.7(1)
$Cl^{-+} CH_3Cl$								
Cl^-	K_h			−459.539 66	−459.671 15	−459.682 38	−459.685 84	
CH_3Cl	C_{3v}		−499.093 15	−499.094 16	−499.357 21	−499.381 42	−499.391 63	25.5(0)
complex	C_{3v}			−958.647 96	−959.043 40	−959.078 87	−959.092 66	25.7(0)
TS inv	D_{3h}			−958.623 31	−959.014 83	−959.049 39	−959.067 15	25.2(1)
TS ret	C_s		−958.529 36	−958.541 74	−958.926 24	−958.961 47	−958.983 05	23.5(1)
$NaCl + CH_3Cl$								
NaCl	$C_{xb0\infty v}$		−621.399 62	−621.401 99	−621.538 82	−621.550 48	−621.553 87	0.5(0)
$CH_{3Cl\cdots NaCl}$	C_s	−1114.960 04	−1120.509 78	−1120.512 51	−1120.916 21	−1120.952 20	−1120.965 87	26.7(0)
TS inv	C_{2v}		−1120.437 06	−1120.439 97	−1120.836 59	−1120.872 07	−1120.891 62	25.8(1)
TS ret	C_s		−1120.429 88	−1120.433 19	−1120.821 06	−1120.858 15	−1120.875 77	24.6(1)
$(LiF)_2 + CH_3F$								
$(LiF)_2$	D_{2h}		−213.982 32	−213.995 13	−214.388 17	−214.377 60	−214.399 78	4.9(0)
complex	C_s	−351.175 16	−353.041 86	−353.059 11	−353.763 54	−353.763 17	−353.801 31	32.3(0)
TS inv	C_{2v}	−351.099 47	−352.968 15	−352.989 44	−353.704 20	−353.697 94	−353.724 84	31.7(1)
TS ret	C_s	−351.062 55	−352.928 69	−352.954 12	−353.659 78	−353.654 49	−353.682 44	29.7(1)
TS ret br	C_s	−351.071 81	−352.925 85	−352.944 49	−353.658 19	−353.651 87	−353.680 37	29.4(1)
$LiCl + CH_3Cl$:								
LiCl	$C_{\infty v}$	−464.790 63	−467.009 19	−467.011 38	−467.149 88	−467.161 76	−467.165 08	0.9(0)
$CH_{3Cl\cdots LiCl}$	C_s	−961.509 91	−966.122 45	−966.125 16	−966.531 61	−966.567 82	−966.581 48	27.3(0)
TS inv	C_{2v}	−961.444 27	−966.043 62	−966.046 73	−966.439 40	−966.476 43	−966.494 71	25.9(1)
TS ret	C_s	−961.447 83	−966.045 75	−966.048 68	−966.439 19	−966.476 56	−966.493 76	25.3(1)
$(LiCl{\cdot}LiH) + CH_3Cl$								
$LiCl{\cdot}LiH$	C_{2v}	−472.802 35	−475.068 36	−475.069 77	−475.227 74	−475.243 85	−475.248 34	5.5(0)
complex	C_s	−969.516 39	−974.176 09	−974.178 33	−974.604 96	−974.645 40	−974.660 33	31.8(0)
TS inv	C_{2v}	−969.478 32	−974.125 09	−974.127 38	−974.546 71	−974.586 31	−974.605 18	31.2(1)
TS ret	C_s		−974.085 22	−974.088 73	−974.492 31	−974.534 37	−974.551 61	29.4(1)

known to have different secondary isotope effects.[41-44] Theoretical treatments of the ion pair displacement reactions are sparce. Carbonell et al.[22] did examine various interactions of one and two lithium cations with methyl fluoride and its transition state with fluoride ion but did not examine the ion pair transition state. In their book on theoretical studies of the S_N2 reaction, Shaik et al.[45] do not mention ion pairs. Recent theoretical studies have dealt with the closely related ring openings of epoxides by organolithium reagents[46] and S_Ni reactions of chlorosulfites.[47,48] In this paper we present results of our study of the identity reactions of methyl fluoride and chloride with one and two molecules of lithium fluoride and chloride and with sodium chloride. We also compare inversion and retention mechanisms.

Calculational Methods

All geometries were fully optimized within the designated symmetry constraints at the restricted Hartree−Fock level by using gradient optimization techniques and standard basis sets (3-21G, 6-31G*, 6-31+G*) incorporated in the GAUSSIAN 90[49] and GAMESS[50] program systems. Stationary points were characterized by frequency analysis at different levels (minima with 0, transition states with 1 imaginary frequency). The absolute energies, number of imaginary frequencies, and zero-point energies of the structures involved in this study are summarized in Table 1. The zero-point vibrational energies (ZPE) were scaled by an empirical factor of 0.9.[51-53] The effect of electron correlation was studied by applying Møller−Plesset theory[54,55] at the fourth order (MP4SDTQ), keeping the core electrons frozen. Charges and bond orders have been calculated by use of the Natural Population Analysis[56] at the RHF/6-31+G*//6-31+G* level.

Results and Discussion

In all cases the effects of basis set changes are relatively small. Addition of diffuse functions (6-31G* to 6-31+G*) changed

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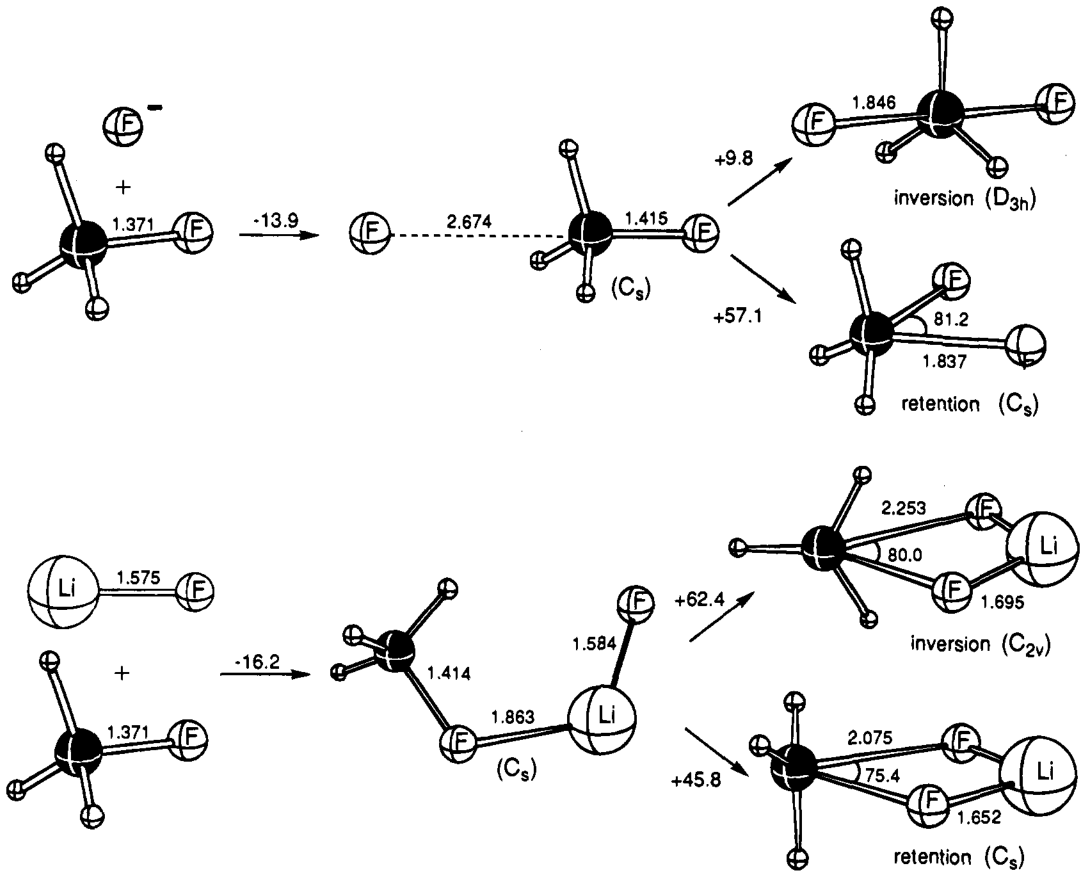
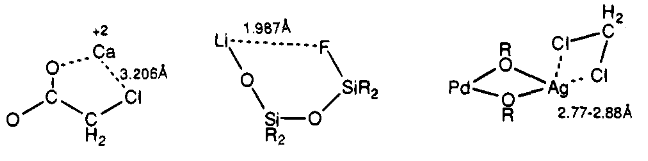


Figure 1. Calculated reaction mechanisms for the F-identity exchange reactions $F^- + CH_3F$ and $LiF + CH_3F$ at the (MP4SDTQ/6-31+G*//6-31+G*+ZPE) level. Relative energies in kcal mol^{-1}, bond lengths in Å, and angles in deg.

the energies of complex formation and inversion generally by only a few tenths of a kilocalorie per mole, but the effects with the LiF reactions were generally larger. The addition of some correlation gave somewhat larger changes, but even here MP4 changed the reaction energies as given by 6-31+G* by only about 1−4 kcal mol^{-1}. The effects on the retention reactions are somewhat greater.

F^- + CH_3F and LiF + CH_3F. The results for these reactions are summarized in Figure 1. The initial step in the fluoride identity exchange reaction is the formation of a $F^- \cdots CH_3F$ complex. Such complexation was found first by calculation[2,3] and has been confirmed experimentally by ion cyclotron resonance spectroscopy.[57] We confirmed this finding in order to put the ionic and ion pair results on the same level of theory. Transition states were found for both the inversion and retention displacements. The complexation energy is calculated to be 13.9 kcal mol^{-1}, and energies of the inversion and retention transition structures (TS's) are 9.8 and 57.1 kcal mol^{-1} above the complex, respectively. A comparably large difference was found earlier by Schlegel et al.[6] with a smaller basis set. The large energy gap between retention and inversion TS's ($E_{ret} - E_{inv} = +47.3$ kcal mol^{-1}) probably originates in large part from electrostatic repulsion between the two fluorines in the retention TS which are highly anionic (−0.745 by NPA).

Reaction of CH_3F with LiF starts with the formation of a complex[22] releasing 16.2 kcal mol^{-1} of complexation energy. The $CH_3F \cdots LiF$ complex is more stable than the alternative $LiF \cdots CH_3F$ complex which was found to be a second order saddle point at 6-31G* on the potential surface (two imaginary frequencies). The corresponding minimum is a C_s structure with a slightly bent Li−F−C bond only 0.14 kcal mol^{-1} lower in energy than the saddle point and 14.69 kcal mol^{-1} higher than the alternative complex. At 6-31+G* this minimum has the linear C_{3v} structure.[58] The bent structure of the more stable $CH_3F \cdots LiF$ complex optimizes the dipole−dipole interactions between both participating species (Figure 1). The effect of $Li \cdots F$ complexation is 2-fold: (i) it lowers the C−F bond order from 0.53 in CH_3F to 0.47 in the complex with a concomitant increase in the C−F bond distance from 1.371 to 1.414 Å and (ii) it increases the effective positive charge on the CH_3 group from +0.45 in CH_3F to +0.51 in the complex. Several examples of alkyl halogenide/metal interactions have been found in X-ray structures: an intramolecular $Ca \cdots Cl$ bond in the structure of calcium chloroacetate, **1**,[59] an intramolecular $Li \cdots F$ bond in a fluorinated disiloxanolate, **2**,[60] and a nice example of methylene chloride functioning as a bidentate ligand chelating a Ag^I metal nucleus, **3**.[61]



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(Partial Structures)

The inversion TS with inclusion of the Li cation shows a remarkable deformation from the linear geometry found in S_N2 reactions with anions. The bridging action of the Li cation causes a large decrease of the F−C−F angle from 180° to 80.0°

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and an increase in the C−F bond distance from 1.846 to 2.253 Å. Smaller changes are observed for the introduction of the Li cation in the retention TS in which the already existing acute angle of 81.2° decreases to 75.4° and the C−F bond distance increases from 1.837 to 2.075 Å (Figure 1).

A similar effect of ion pairing on transition states has been found for proton transfer reactions. The typical linear transition state for transfer of a proton between ions is bent by the presence of a cation.[62−64] Introducing the Li cation in the anion S_N2 mechanism clearly affects the ionicity of the reaction. NPA charges on the CH_3 group increase from +0.58 to +0.89 and +0.49 to +0.79 for inversion and retention TS's, respectively. The high ionic character of the S_N2 reactions has been noted before. Duke and Bader[2] found F charges of −0.86 by integration of the electron density in the fluorine basins[65] in the $(FCH_3F)^-$ transition state. Such high charges were found for many S_N2 transition states by Shi and Boyd[24] although they also found that these charges were somewhat reduced with inclusion of electron correlation.[25,28] The bending of the entering and leaving fluorine by a lithium cation in the ion pair transition state is readily rationalized by such an ion multiplet model. That is, although there is no doubt that covalency plays a significant role in bonding to the entering and leaving groups in the S_N2 transition state,[45] such bonds are relatively long and weak and ionic character plays a dominant role; these transition states are more readily modeled as triple ions than as covalent complexes. In the same manner, the ion pair S_N2 transition state can be modeled as a triple ion, LiF_2^-, interacting with a methyl cation.

This character is also clearly shown in the retention TS by the near planarity of the methyl group. Planarity of the CH_3 group in the inversion TS is imposed by C_{2v}-symmetry restrictions but planarity in the retention TS (the average HCH′/HCH″ dihedral angle is 157.6°—for a planar CH_3 this angle is 180°) indicates a high degree of carbocation character. The reaction is clearly an S_Ni type of carbocation reaction.[47,48] The fluoride exchange reaction can be considered as a CH_3 cation transfer between two F anions. TS's with inclusion of Li may be regarded as LiF_2 triple anions interacting with CH_3 cations. The CH_3^+ bridging mode in the retention TS is favored; the energy gap between retention and inversion TS's ($E_{ret} - E_{inv}$) is −16.6 kcal mol^{-1}. Thus, including Li in the anion S_N2 model lowers the energy of the retention TS by stabilizing the electrostatic $F^- \cdots F^-$ repulsion but increases the barrier for the inversion reaction by strongly deforming its ideally linear geometry. It is also instructive to examine the ion pairing behavior of the different ionic systems. Ion association of Li^+ with F^- is clearly much stronger than to the triple ion charges of the inversion transition state even when the two fluoride ions are pulled toward the cation, but ion association is stronger with the more angular $(CH_3F_2)^-$ retention TS and is actually greater than that of Li^+ with F^-.

It is interesting to compare with some chemistry of bridgehead halides that cannot undergo backside displacement. 1,3,5,7-Tetrabromoadamantane is unreactive under typical solvolysis conditions but exchanges halogen readily with AlX_3 and other Lewis acids. A model calculation of $CH_3F + AlF_3$ gave a transition state that can be regarded essentially as a $CH_3^+\ AlF_4^-$ ion pair.[66]

$Cl^- + CH_3Cl$, $LiCl + CH_3Cl$, and $NaCl + CH_3Cl$. Results for these systems are summarized in Figure 2. The complexation energy of 9.4 kcal mol^{-1} for Cl^- with CH_3Cl is smaller than that calculated for the fluoride analogue, probably because of the longer anion$\cdots CH_3X$ distance resulting in smaller dipole induction. The energies calculated for the inversion and retention TS's of the chloride ion identity reactions are 15.6 and 66.8 kcal mol^{-1} above the complex, respectively.

Whereas the C$\cdots$F bond distances in the F anion exchange TS's are similar (1.846 and 1.837 Å for inversion and retention, respectively), the C$\cdots$Cl bond distance in the retention TS (2.790 Å) is significantly longer than in the inversion TS (2.393 Å). In addition, with the large Cl−C−Cl angle of 98.6° observed in the retention TS, it seems likely that the larger Cl^- radius is responsible for this effect. The large C$\cdots$Cl bond distances in the retention TS give rise to a pronounced ionicity of the reaction mechanism as deduced from the NPA charges (charge on CH_3 is +0.725 compared +0.49 for the inversion TS) and the near planarity of the CH_3 group (the average dihedral HCH′/HCH″ angle is 169.0°). Here also the retention mechanism is that of a carbocation S_Ni type.

The reaction of LiCl with CH_3Cl starts with formation of a $CH_3Cl\cdots LiCl$ complex. The alternative $LiCl\cdots CH_3Cl$ was found to be stable at the 3-21G level but dissociated at higher levels. The CH_3Cl + LiCl complexation energy of 14.7 kcal mol^{-1} is slightly smaller than that calculated for the F analogue, most likely because of weaker dipole−dipole interactions. Retention and inversion TS's are both 53.2 kcal mol^{-1} higher in energy than the complex.

Similarly, the reaction of NaCl with CH_3Cl starts with formation of a $CH_3Cl\cdots NaCl$ complex followed by substitution routes with inversion and retention TS's 45.8 and 54.6 kcal mol^{-1} higher in energy, respectively. Exchanging Li for Na results in larger metal−Cl bond distances and therefore weaker ionic bonds between metal and chlorines. This effect is also reflected in the shorter C$\cdots$Cl distances and larger Cl$\cdots$C$\cdots$Cl angles in the TS's. Although the stereoselectivity deduced from the calculated energy barriers is in favor of the inversion pathway, the activation energy of 45.8 kcal mol^{-1} for this mechanism is still rather high.

Including the cation (Li^+ or Na^+) in the chloride identity exchange reaction has a small stabilizing effect on the TS's for the retention mechanism, but the energy barrier for the inversion pathway increases considerably. In all cases, the ion attraction of the metal cation is stronger with the $(CH_3X_2)^-$ retention TS than with the free X^-, but the effect is smaller for the larger chloride ion compared to fluoride and also smaller for the large sodium cation compared to lithium. Ion association of the cation with the more obtuse $(CH_3X_2)^-$ inversion TS is in all cases much less than for the free halide ions, but the changes again reflect relative ionic sizes. Moreover, for the larger ions a smaller distortion is involved of the preferred linear "nucleophile−C−leaving group" angle. The Cl$\cdots$C$\cdots$Cl angle in the inversion LiCl/CH_3Cl TS is 92.5° compared to 80.0° for F$\cdots$C$\cdots$F in the analogous F model. Distortion from the linear Cl−C−Cl geometry in the NaCl/CH_3Cl inversion TS is even less (Cl−C−Cl = 119.1°) and so is the increase in activation energy. Thus, the inversion TS aims for a high linearity along the "nucleophile−C−leaving group" reaction coordinate.

$(LiF)_2 + CH_3F$. Much of the increased activation energy for the inversion ion pair S_N2 reactions compared to the ionic analogs is associated with the reduced ion association energy of the TS ion dipole compared to the metal halide ion pair. A model in which a LiX dimer instead of LiX monomer is the

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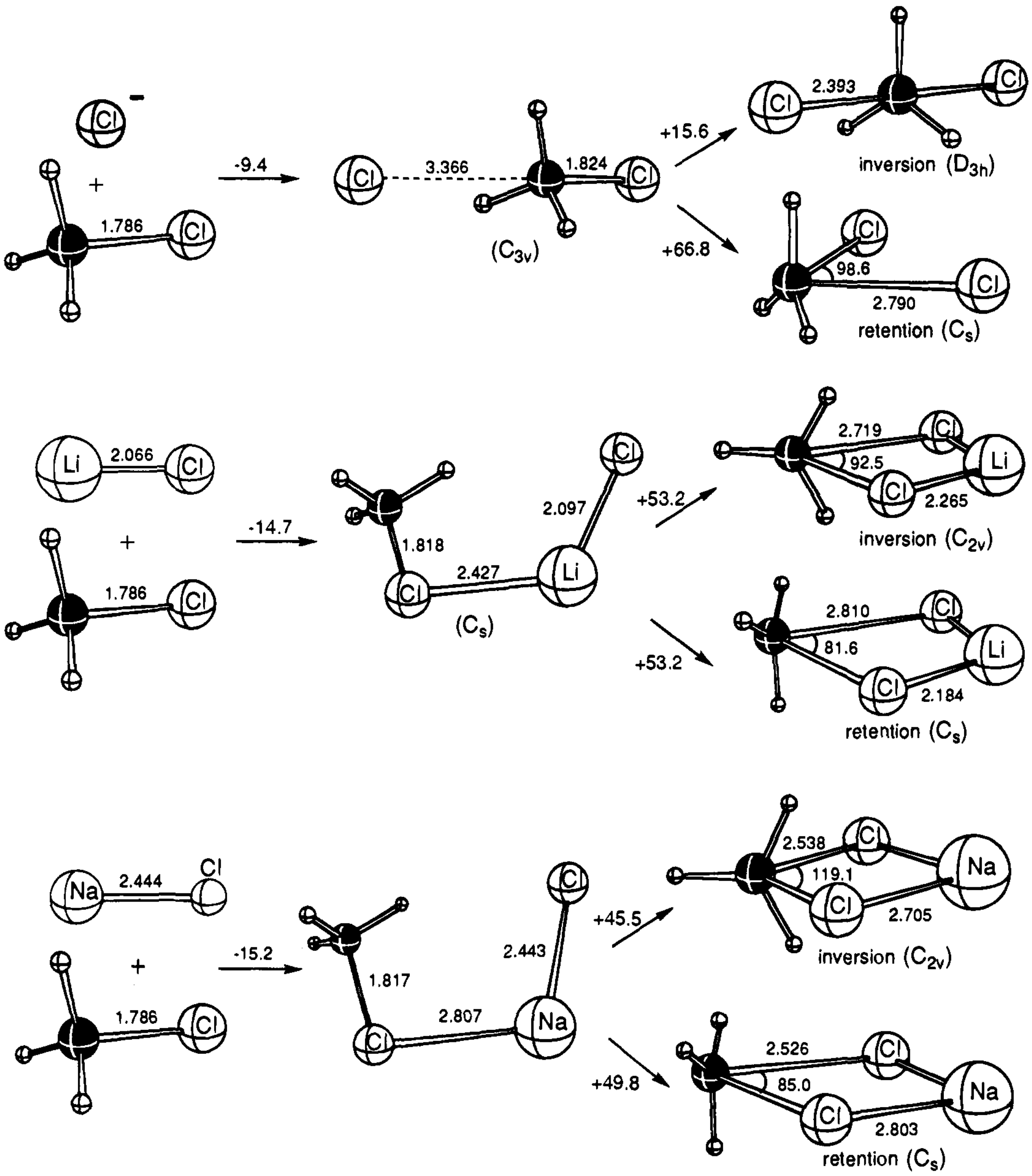
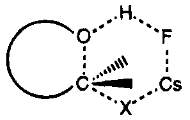


Figure 2. Calculated reaction mechanisms for the Cl-identity exchange reactions Cl^- + CH_3Cl, LiCl + CH_3Cl, and NaCl + CH_3Cl at the (MP4SDTQ/6-31+G*//6-31+G*+ZPE) level as in Figure 1.

attacking species should reduce this effect and should also give rise to a larger flexibility in the angle of attack. Nucleophile and leaving group can be bridged by the larger Li−X−Li moiety which enables higher linearity along the reaction coordinate. The results computed for the $(LiF)_2$ + CH_3F reaction are summarized in Figure 3.

The first step is again the formation of a complex. The complexation energy of 14.2 kcal mol^{-1}, as well as the structure of the optimized complex are similar to that with CH_3F/LiF, but the TS's show some remarkable differences. The inversion TS exhibits a F−C−F angle with only a small distortion from linearity (F−C−F = 158.3°). The C···F bond length of 1.908 Å and bond order of 0.165 differ substantially from those obtained for the monomeric model, LiF/CH_3F (C···F = 2.253 Å, bond order = 0.05), and are more similar to those obtained for the anion model, F^-/CH_3F (C···F = 1.846 Å, bond order = 0.22). The NPA charges in the TS on the inversion pathway for $(LiF)_2/CH_3F$ also show a similarity to those calculated for F^-/CH_3F. The TS can be considered as a $(F\cdots CH_3\cdots F)^-$ TS interacting with the triple cation: $(LiFLi)^+$. A similar mechanism has been suggested for the ring closure of large macrocycles promoted by the addition of cesium fluoride; the proposed TS **4** resembles that of our model.[67]



4

The TS for the retention pathway is nearly identical to that calculated for the LiF/CH_3F model (C···F bond lengths and F−C−F bond angles are in similar ranges). The NPA charges are also similar, and a largely ionic TS is observed with a charge of +0.83 on the CH_3 group. Thus, the retention TS can be considered as a CH_3 cation interacting with the Li_2F_3 anion. An alternative TS in which both Li atoms bridge the exchanging F atoms was found but is of comparable energy.

Extending the LiF monomer in our model to a dimer gives rise to a decrease in the energy barrier for the inversion pathway

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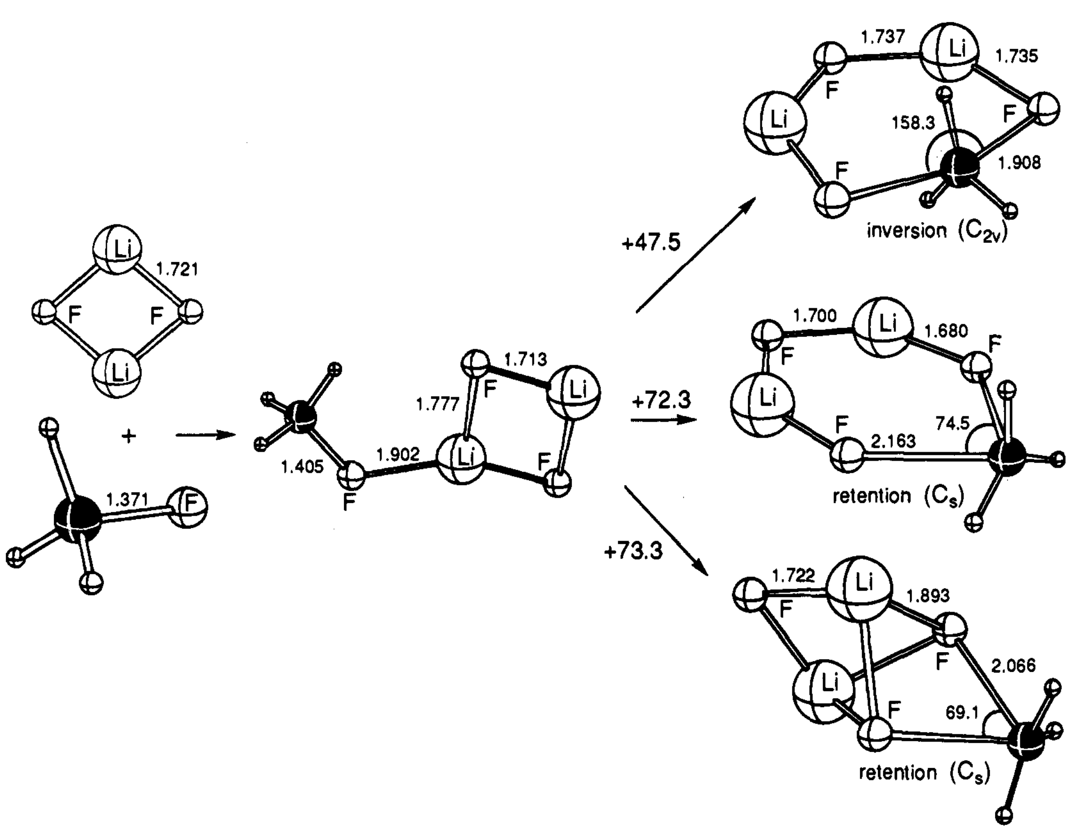

Figure 3. Calculated reaction mechanisms for the fluoride-identity exchange reaction $(LiF)_2 + CH_3F$ at the (MP4SDTQ/6-31+G*//6-31+G*+ZPE) level as in Figure 1.

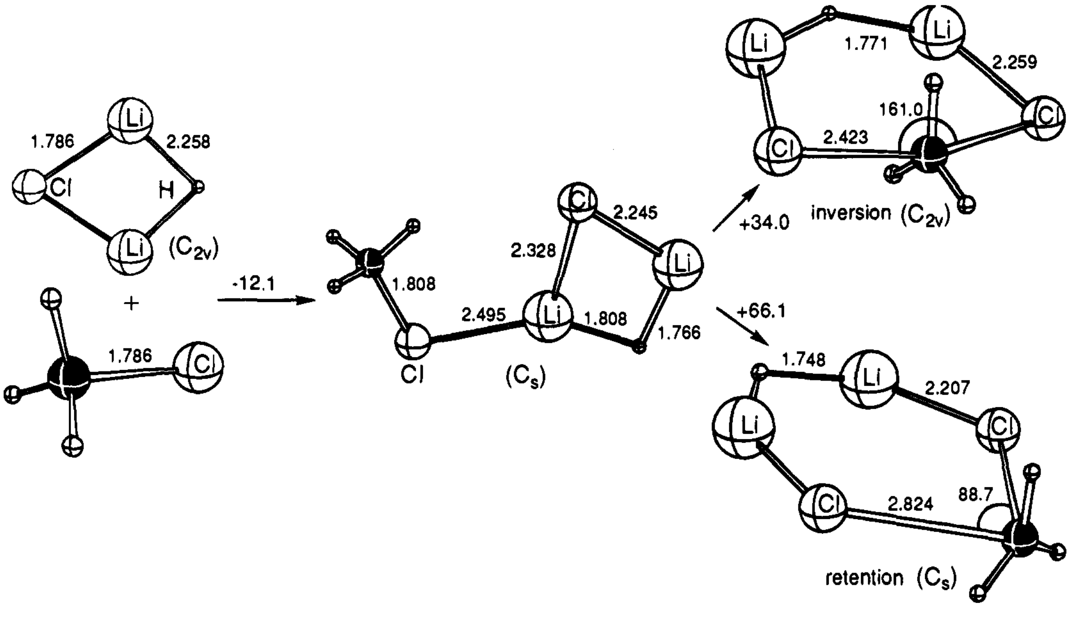

Figure 4. Calculated reaction mechanisms for the Cl-identity exchange reactions and LiCl/LiH + CH_3Cl at the (MP4SDTQ/6-31+G*//6-31+G*+ZPE) level as in Figure 1.

from 63.4 to 47.5 kcal mol^{-1} and an increase for the retention energy barrier from 45.8 to 72.3 kcal mol^{-1}. This result suggests that S_N2 reactions with ion aggregates may be facilitated but that aggregates provide no advantage with S_Ni reactions.

LiClLiH + CH_3Cl. In order to save computer time, calculations were done with the mixed dimer, LiCl/LiH, instead of $(LiCl)_2$. Results are summarized in Figure 4. The energy release for complexing LiCl/LiH with CH_3Cl is 12.1 kcal mol^{-1}. The TS for inversion exhibits a nearly linear Cl ··· C ··· Cl angle of 161.0°. The C−Cl bond of 2.423 Å and bond order of 0.21 largely differ from those in the LiCl/CH_3Cl inversion TS (2.719 Å, bond order = 0.11) and are more similar to those in the Cl^-/CH_3Cl inversion TS (C−Cl bond distance = 2.393 Å, bond order = 0.23). The NBA charges in the inversion LiClLiH/CH_3Cl TS are also more similar to the ionic analog. Thus, extending the monomeric ion pair attacking species to a dimer facilitates the inversion reaction, with a transition state that can be considered as a $(Cl \cdots CH_3 \cdots Cl)^-$ TS interacting with the triple cation: $LiHLi^+$.

The LiClLiH/CH_3Cl retention TS is nearly identical to that calculated for the LiCl/CH_3Cl model. The C−Cl bond distances and Cl−C−Cl bond angles are in approximately similar ranges. The character of this TS is largely ionic. The CH_3 group with a charge of +0.82 is almost planar (average HCH′/HCH″ dihedral angle is 170.4°). Thus, the retention TS can be considered as a CH_3 cation interacting with the Cl−Li−H−Li−Cl anion. The alternative TS for the retention pathway with both lithiums bridging both chlorines is calculated to be 7.7 kcal mol^{-1} (RHF/6-31+G*) higher in energy than the retention TS depicted in Figure 4 and has not been considered in further calculations.

The activation energies for the inversion and retention pathways are 34.0 and 66.1 kcal mol^{-1}, respectively. The large energy gap of +32.1 kcal mol^{-1} between retention and inversion TS ($E_{ret} - E_{inv}$) demonstrates a clear preference for the inversion pathway. This model might be a useful one for reactions of organolithium compounds with alkyl halides in solvents of low polarity (alkanes, Et_2O, or aromatic solvents).

Conclusions

Both retention and inversion TS's of ion pair S_N2 reactions behave as assemblies of ions. In the retention TS the coordination of the metal cation is on the same side of carbon to both entering and leaving halide ions and the central carbon is essentially a methyl cation. The inversion TS involves strong distortion of the halides from a conventional S_N2 linear arrangement in order for the metal cation to coordinate with both halides. For small cations (Li^+) and anions (F^-) distortion is so severe that TS energies are high; the retention mechanism, essentially a carbocation S_Ni reaction, is energetically easier. Only for the larger ions, Na^+ and Cl^-, is the inversion mechanism competitive. Carbon charges are high in all of these cases.

The association energies of Li^+ and Na^+ with F^- and Cl^- are substantially higher than with the $(XCH_3X)^-$ inversion TS; that is, an important part of the activation process is the necessity to separate the cation and anion in the ion pair to form the TS. This energy is substantially reduced in the retention TS. This energy is also reduced in reaction of the methyl halide with an ion pair aggregate. Moreover, the association of $(XCH_3X)^-$ with M_2X^+ allows a more linear coordination at the reacting carbon. These principles may well apply to alkylation reactions of organometallic aggregates with alkyl halides. The energy changes calculated in this paper apply to isolated gas-phase systems. The energies required for these ion pair processes in solution would undoubtedly be lower but, because the reaction species remain overall neutral throughout the reaction, solvation energies will be much lower than for corresponding ionic reactions; accordingly, the transition state structures calculated are probably reasonable models for the corresponding solution systems.

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