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A Theoretical Study of Substituent Effects on Allylic Ion and Ion Pair S_N2 Reactions

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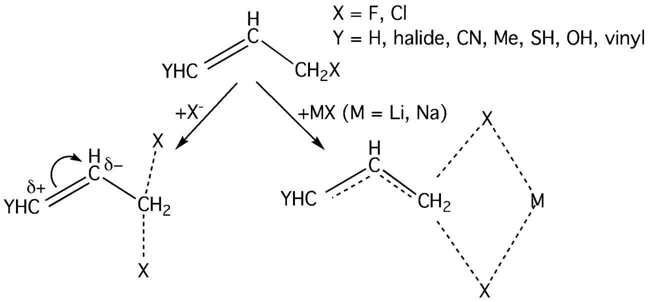

An ab initio study of ionic and ion pair displacement reactions involving allylic systems has been carried out at the RHF/6-31+G* level. The geometries and natural charges show the absence of conjugative stabilization in the ionic transition states, thus differing from traditional explanations. The high reactivity of allyl halides is explained by electrostatic polarization of the double bond. Substituent effects were also studied; in general, electron-withdrawing groups lower the barriers of the ionic S_N2 reactions but increase the barriers of the ion pair reactions. The allylic reactions are compared with related benzylic systems. Hammett correlations give ρ of opposite sign for the ionic and ion pair displacement reactions, in agreement with some experimental results.

Introduction

Many theoretical studies of S_N2 reactions are concerned with the effects of entering and leaving groups, especially in methyl transfer reactions.[1-3] Studies on the reactions of compounds higher than methyl and with substituents are far fewer. Substituents on the reactive center are found to be involved in a complex interplay of electronic and steric effects that affect the reactivities.[4-7] An unsaturated substituent has the additional potential of interaction of the π-system.[8-10]

A few groups have reported theoretical studies of S_N2 reactions with allylic compounds. Lee et al. have carried out computations at the HF and MP2 levels of reactions of allyl halides with various nucleophiles.[11,12] Kormos and Cramer focused on the reaction of allyl chloride with chloride ion and included solvation with a continuum model and some methyl substituents.[13] Zipse studied the same reaction without solvation for comparison with a radical system.[14] However, there are no studies to our knowledge on reactions of systematically substituted allylic systems. In this article, we present an ab initio study of ionic and ion pair S_N2 reactions on allylic systems with substituents at the γ-position sterically removed from the reactive center but conjugated to it. The results are compared with other types of substituents and with conventional models in physical organic chemistry.

Computational Methods

Ab initio calculations were carried out with various versions of the Gaussian program suite up to Gaussian 03.[15] Previous

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studies by Lee et al. pointed out that the calculated structures of reactants and transition structures with the 6-31+G* and 6-31++G** levels show only small differences at the Hartree−Fock level.[16] Zipse[14] and Kormos and Cramer[13] also found relatively small effects of basis set or theory level on the transition structure geometries. Moreover, we wished to emphasize the general effect of substituents rather than absolute energies. Thus, all structures were optimized at the restricted Hartree−Fock (RHF) level using the 6-31+G* basis set.[17,18] The nature of the stationary points was determined by carrying out vibrational frequency analyses. The variations in the electron density distribution during the reaction were analyzed by calculating the natural charges using the NPA method implemented in the Gaussian program.[19,20] The resulting charges are generally presented as "reduced charges" in which the charges of attached hydrogens are added to a carbon center. The reaction barriers are called "activation energies", ΔE^*, for convenience and are calculated from the transition structure and the separated reactants using the energies corrected for zero-point vibrational energies (ZPVE) scaled by a factor of 0.9153 as suggested by Scott and Radom.[21]

Geometries, energies, and zero-point energies for all computed structures are given in Table S1 in the Supporting Information. A portion of the significant results is summarized in Tables 1−4.

Results and Discussions

Allylic Ionic S_N2 Reactions. Studies on ionic S_N2 reactions of alkyl halides, and of allylic systems in particular, in the gas phase show that the potential energy profile of these reactions is generally described by a double well potential consisting of separated reactants, ion−dipole complex formed by the reactants, transition state, and the product ion−dipole complex and separated products. The transition structures were generally found to have trigonal bipyramidal reactive carbon centers with apical leaving and attacking groups. An exception was found in the case of the allyl fluoride−fluoride ion reaction system; the Lee group and our group both found a transition structure in which the fluorines are in the equatorial position. This is clearly an artifact of the unsolvated gas phase.

TABLE 1. Reaction Barriers (kcal mol^{-1}) Calculated for Ionic S_N2 Reactions of Chloride Ion with γ-(Y)Substituted Allyl Chlorides[a]

Y	ΔE^* kcal mol^{-1}	reaction angle	bond lengths, Å[b] C−X	$C_\alpha-C_\beta$	$C_\beta-C_\gamma$
H[c]	8.63	161.74	2.497	1.463	1.322
		trans			
F	5.33	160.75	2.506	1.452	1.313
Cl	5.37	163.19	2.470	1.463	1.315
CN	1.20	167.86	2.414	1.471	1.324
OH	5.09	157.47	2.594	1.429	1.330
Me	8.03	160.39	2.531	1.453	1.324
SiH_3	7.09	164.43	2.466, 2.462	1.470	1.328
		cis			
F	7.63	163.15	2.487	1.457	1.314
Cl	7.30	164.81	2.456	1.464	1.318
CN	3.97	167.99	2.412	1.472	1.326
OH	9.73	160.14	2.559	1.441	1.326
Me	7.24	160.90	2.518	1.457	1.326
SiH_3	6.50	164.41	2.473, 2.458	1.471	1.328

[a] $\Delta E^* = E(\text{transition structure}) - \sum E(\text{reactants})$. Some important geometry parameters are given, including the reaction angle (Cl−C−Cl). [b] Bond lengths calculated for allyl chloride: C−X = 1.804; $C_\alpha-C_\beta$ = 1.496; $C_\beta-C_\gamma$ = 1.321. Other theory levels, respectively: HF 6-31++G**, 1.805, 1.495, 1.321; MP2, 1.795, 1.489, 1.339 (ref 12). [c] Other theory levels, respectively: HF 6-31++G**, 8.30, 162.22, 2.499. 1.462, 1.321; MP2, 8.11, 167.90, 2.363, 1.460, 1.343 (ref 12).

TABLE 2. Reduced Natural Charges (Atom plus Attached Hydrogens) on Allylic Carbon Centers, Attacking and Leaving Chloride Groups, and Substituents Y, HF 6-31+G*

Y[a]	reduced charges C_α	C_β	C_γ	Cl	Y
H	0.506	−0.038	0.078	−0.773	
			trans		
F	0.519	−0.124	0.576	−0.781	−0.409
Cl	0.497	−0.018	0.084	−0.756	−0.052
CN	0.448	0.133	−0.081	−0.712	0.333, −0.409
OH	0.561	−0.217	0.561	−0.828	−0.247
Me	0.533	−0.070	0.116	−0.794	0.008
SiH_3	0.484	0.034	−0.426	−0.753	0.411
			cis		
F	0.512	−0.120	0.546	−0.767	−0.405
Cl	0.491	−0.014	0.052	−0.745	−0.039
CN	0.448	0.131	−0.096	−0.708	0.326, −0.393
OH	0.553	−0.163	0.474	−0.808	−0.248
Me	0.519	−0.067	0.103	−0.786	0.020
SiH_3	0.482	0.027	−0.427	−0.750	0.421

[a] Reduced charges calculated for allyl chloride: C_α, 0.078; C_β, −0.005; C_γ, 0.035; Cl, −0.107.

The allyl chloride−chloride ion system, however, behaves normally, and some comments on this prototypical system are appropriate at this point. S_N2 reactions at allyl halides are of comparable rate to methyl and substantially faster than ethyl. This increased reactivity has traditionally been attributed to the conjugation of the reactive center with the double bond. This conjugation has been expressed symbolically as in A in Figure 1,[22] or more explicitly in terms of orbital interactions as in B in Figure 1.[6,7] A perturbation molecular orbital analysis has concluded that a low-lying empty π^*-orbital interacting with the reactive center serves as an electron

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TABLE 3. **Energy Barriers (kcal mol^{-1}) for Some Identity Ion Pair S_N2 Reactions of LiCl with γ-Substituted (Y) Allyl Chlorides**[a]

		reaction angle	bond lengths, Å			
Y	ΔE*	deg	Li−Cl	C−Cl	C_α−C_β	C_β−C_γ
H	12.49	82.75	2.214	2.988	1.407	1.347
		trans				
F	9.62	81.56	2.213	3.019	1.390	1.352
Cl	12.62	81.98	2.212	3.008	1.397	1.353
CN	22.37	84.94	2.228	2.900	1.420	1.343
Me	5.59	80.65	2.206	3.072	1.390	1.361
OH	12.24	79.78	2.200	3.125	1.374	1.378
vinyl(a)[b]	3.76	78.76	2.199	3.153	1.379	1.374
vinyl(s)[c]	4.39	79.40	2.200	3.131	1.379	1.374
		cis				
F	13.21	82.89	2.215	2.985	1.398	1.350
Cl	15.68	82.96	2.215	2.984	1.401	1.354
CN	24.84	86.07	2.232	2.875	1.425	1.343
Me	5.89	79.70	2.205	3.098	1.389	1.366
SH	6.76	79.62	2.202	3.115	1.377	1.379
OH	1.61	79.78	2.200	3.125	1.374	1.377

[a] The reaction angle (Cl−C−X) and some important bond lengths are also given. Additional results are given in Table S2 (Supporting Information). [b] anti. [c] syn.

TABLE 4. **Reduced Natural Charges on Allylic Carbon Centers, Attacking and Leaving Chlorides, and on the Substituents, Y, for Ion Pair S_N2 Reactions of LiCl with γ-Substituted Allyl Chlorides**

	reduced charges					
Y	C_α	C_β	C_γ	Li	Cl	Y
H	0.688	−0.199	0.404	0.897	−0.895	.....
			trans			
F	0.658	−0.252	0.845	0.897	−0.902	−0.345
Cl	0.671	−0.191	0.315	0.897	−0.899	0.105
CN	0.696	−0.097	0.241	0.901	−0.874	0.227, −0.220
Me	0.659	−0.219	0.413	0.895	−0.908	0.069
OH	0.632	−0.240	0.724	0.893	−0.912	−0.183
vinyl(a)[a]	0.615	−0.205	0.376	0.893	−0.916	−0.108, 0.262
vinyl(s)[b]	0.615	−0.209	0.387	0.893	−0.915	−0.118, 0.263
			cis			
F	0.687	−0.278	0.831	0.897	−0.895	−0.348
Cl	0.689	−0.213	0.306	0.897	−0.893	0.106
CN	0.703	−0.102	0.235	0.902	−0.866	0.213, −0.214
Me	0.655	−0.232	0.424	0.910	−0.895	0.078
SH	0.617	−0.231	0.162	0.894	−0.912	0.383
OH	0.630	−0.285	0.744	0.893	−0.915	−0.151

[a] anti. [b] syn.

acceptor that stabilizes the transition structure.[9] All of these approaches imply double bond character in the C_α−C_β single bond and some single bond character in the allylic double bond. A comparison of bond distances in the allyl chloride−Cl^- transition structure (Table 1a) with that of the starting allyl chloride shows that the changes are actually rather small; the C_β−C_γ double bond increases by only 0.001 Å and the C_α−C_β single bond shortens by only 0.033 Å. These values change comparatively little at other basis set and theory levels.[12,13] The rotation barrier for the C_α−C_β bond in the transition state is 5.01 kcal mol^{-1} for the allyl chloride identity reaction system, only a little greater than that for allyl chloride itself, 1.30 kcal mol^{-1}. The small changes in C−C bond lengths together with low values of the rotation barrier imply the absence of any important conjugative stabilization in the transition structures.

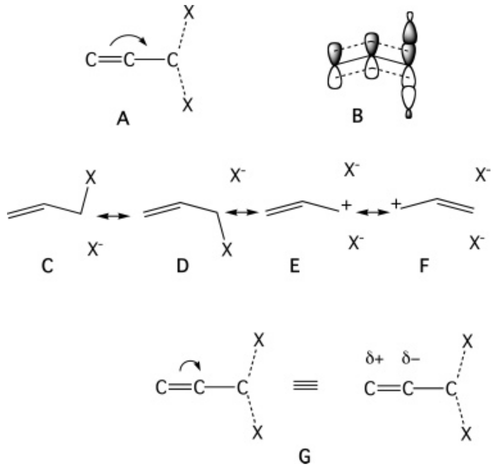

FIGURE 1. Conjugation anticipated in the S_N2 transition states of allyl systems based on molecular orbital (B) and valence bond (resonance) theory (C, D, E, F, and G).

S_N2 reactions have been treated in valence bond theory in terms of structures C and D shown in Figure 1.[23] The reaction of methyl chloride with chloride ion develops substantial positive charge on the central carbon at the transition state as measured by Bader's integrated atoms-in-molecule method.[24−26] The computed positive charge is greater at the HF level than at MP2 but even at MP2 it amounts to +0.40 units.[24] Consequently, Shi and Boyd considered that charge polarized structures such as E should be included in a valence bond treatment.[24,26] For allyl, this implies that the conjugation structure F should also be considered. As shown in Table 2, the charge at the central $C_\alpha H_2$ group in the allyl chloride−chloride ion transition state is +0.51 units by NPA and indicates that the polarized structure E in Figure 1 plays a significant role; however, unlike allyl cation in which the terminal positions have the same charge, the amount of charge delocalized in the transition structure to the γ-position is only +0.08, indicating that the structure F in Figure 1 plays only a minor role. This result parallels that based on bond distance changes and undoubtedly has a simple electrostatic basis: with two negative ions, the incoming and leaving groups, so close to the positive charge in the allyl moiety this positive charge is effectively localized at the α-position.

If conjugation is ineffective in the allyl S_N2 transition state, why are allyl halides then so reactive? We suggest a significant role for structure G in Figure 1, in which polarization of the double bond is emphasized. Such electrostatic polarization has a high distance dependence and is affected much more by the positive charge on the reactive carbon than by the negative charges on the nucleophiles farther away. Natural charges in the transition structure of the allyl chloride−chloride system show the charge on C_β to be increased by 0.034 units and on C_γ reduced by 0.045 units compared to the parent allyl chloride in complete agreement with this polarization

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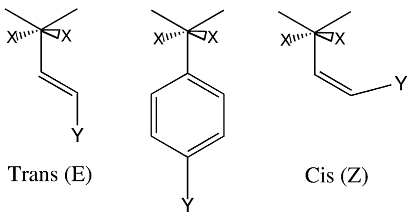

FIGURE 2. Vinylogous relationship of allyl and benzyl substituents.

mechanism. Note that a somewhat different analysis of the transition structure is given by Lee et al.[12]

We turn next to allyl substituent effects. Lee et al.[12] have pointed out the relationship of allyl S_N2 reactions to benzyl. We also find it convenient to compare γ-substituted (E) allyl with p-substituted benzyl; as illustrated in Figure 2, they have a vinylogous relationship. For comparison, we have included the corresponding cis (Z) allyl substituents for the reactions of allylic chloride with chloride ion, although now the substituent is sufficiently close to the reaction center that proximity effects could intrude.

The computed ΔE^* values at the RHF/6-31+G* level are presented in Table 1 together with some structural parameters. Among the trans (E) substituents, electron-attracting groups reduce the barrier with the highly electron-attracting CN group being an extreme example. An electron-withdrawing γ-chloro group also gives a lower reaction barrier than the parent. Experimentally, S_N2 reactions in solution are faster for such substituents.[27,28] The agreement is less good for methyl. The *trans*-γ-methyl substituent produces a slightly higher barrier than cis; experimentally, both are more reactive than allyl chloride itself, with cis being faster than trans.[29,30] The general effect of the *cis*-allyl substituents is less than trans. This difference is readily understandable considering the effect of the substituent as an electrostatic interaction of the substituent dipole with the net charge of the reaction center. For γ-trans substituents this dipole is directed almost toward the reaction center, whereas for cis groups the angle is closer to perpendicular. In addition, the cis groups are now sufficiently close to the reaction center that steric effects might also play a role.

The OH group, normally electron-donating in benzenoid systems, appears anomalous. The electronegative oxygen is inductively electron-attracting, and this property appears to be dominating in the present case. Among all of the substituents treated in our study, the OH group is the only unsymmetrical group. With all of the other substituents, the substituent dipole is coincident with the bond axis. As shown for the computed structure in Figure 3, however, the OH group dipole is less effectively oriented with respect to the reaction center than the bond axis; that is, its inductive effect is reduced. For the *cis*-OH group, on the other hand, the group dipole is oriented in the opposite direction and the inductive effect is now effectively electron-donating. The *cis*-OH substituent accordingly has a higher barrier. In a real system, of course, several conformations would be involved and the actual inductive effect would be more complex compared to these models, but this difference suggests that unsymmetric groups should generally be compared to axially symmetric substituents only with due circumspection.

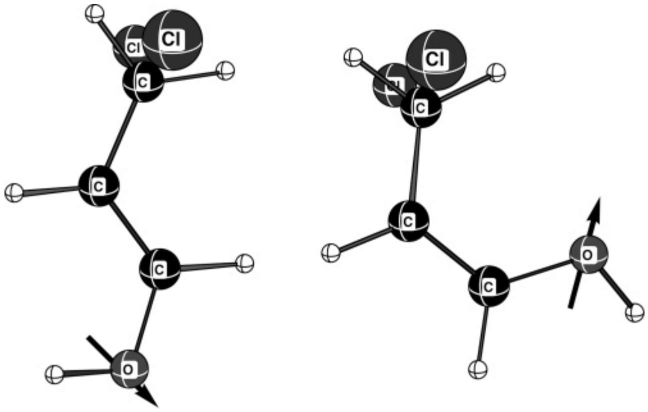

FIGURE 3. Transition structures for *trans*- and *cis*-γ-hydroxyallyl chloride plus chloride ion showing the approximate orientation of the OH group dipoles (shown as arrows) with respect to the reaction center.

The electropositive and polarizable SiH_3 group has a reduced barrier (trans = 7.09, cis = 6.50 kcal mol^{-1}) compared to the parent allyl chloride$-Cl^-$ system (8.63 kcal mol^{-1}). This electronic effect is consistent with the effective charges of the attacking and leaving groups and of the carbon atoms in the transition structures. The reduced natural charges (charge including attached hydrogens) at the important atomic centers are given in Table 2. In all cases the reactive carbon, C_α, is highly positive whereas the charge on C_γ is consistent with the effective electronegativity of the attached substituent.

An alternative approach is to invoke the vinylogous relationship of allyl and benzyl and to compare the computed barriers with the corresponding substituent constants. From the preceding discussion, however, to avoid complications from different conformational interactions compared to benzenoid systems, only substituents that are effectively axially symmetric are considered; that is, Me, SiH_3, halo, and CN. The computed reaction barriers are plotted against σ_p in Figure 4. The points give a reasonable correlation with $\rho = -8.3$ (trans) and -4.6 (cis). Approximate barriers for gas-phase reactions of benzylic chlorides with chloride ion are in the same direction with lower reaction barriers for electron-attracting groups and with methyl less reactive than hydrogen.[31] The same direction for substituent effects is found for reactions in solution such as the reaction of benzylic chlorides with potassium iodide in acetone.[32] If interaction with a carbocation center were important, as in structure F, Figure 1, a correlation with σ^+ constants would be more appropriate. Such a correlation is poorer for our computed barriers; for example, such an at-

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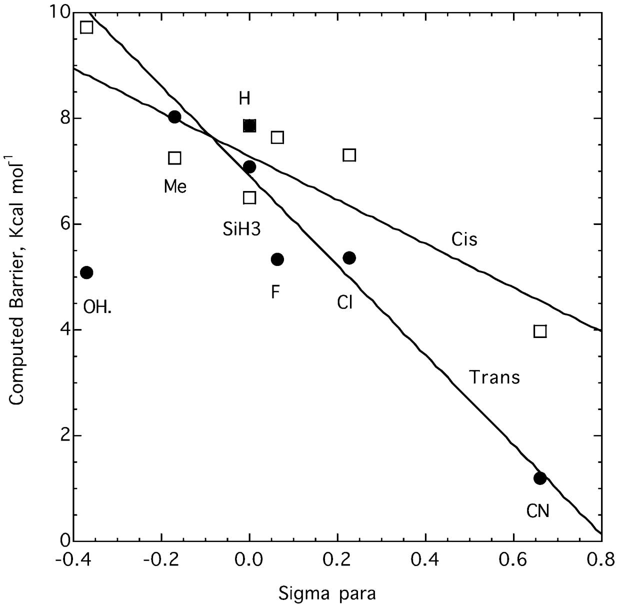

FIGURE 4. Hammett plots for computed reaction barriers vs σ_p constants. The lines shown (except OH) are trans (●): 6.91 ± 0.34 − (8.48 ± 1.17) σ_p ($R^2 = 0.929$); cis (□): 7.29 ± 0.40 − (4.15 ± 1.36) σ_p ($R^2 = 0.699$). The σ_p values were taken from McDaniel and Brown[33] except for SiH_3. The σ_p of $SiMe_3$ was used and taken to be approximately 0.00.[34]

tempted correlation with the trans-substituents gives larger uncertainties in the linear parameters and a smaller R^2 of 0.83.

A propos the discussion above, the *trans*-γ-OH group is clearly anomalous. The *cis*-γ-OH group fits its correlation somewhat better, but we regard this result as fortuitous.

Allylic Ion Pair S_N2 Reactions. Many important reactions in organic chemistry take place in nonpolar solvents and generally involve ion pairs instead of free ions. These ion pair reactions have substrates and transition states with no net charge and for which solvation effects are much smaller than for ions. Accordingly, we studied some ion pair displacement reactions of allyl halides. The complete results are summarized in Table S2 (Supporting Information) with a sample of the results given in Table 3. Earlier studies on ion pair S_N2 reactions of LiCl with methyl chloride showed that the lithium, nucleophiles, and the central carbon form a four-membered ring transition structure with a narrow X−C−X bond angle and a high reaction barrier, 36.9 kcal mol^{-1} at 6-31+G* from the separated reactants,[35] with correlation and basis set having only relatively small effects.[3,36] The reaction of LiCl with ethyl chloride has a somewhat smaller barrier,[35] 23.2 kcal mol^{-1}, but the barrier with allyl chloride is much lower, 12.5 kcal mol^{-1}. The role of allylic conjugation is clearly enhanced in the ion pair reaction. Consistent with this inference are the bond lengths in the allyl transition structure; the single bond is 0.05 Å shorter and the double bond is 0.03 Å longer than in the transition structure for reaction with chloride ion. The transition structure for the LiCl−allyl chloride reaction is shown in Figure 5.

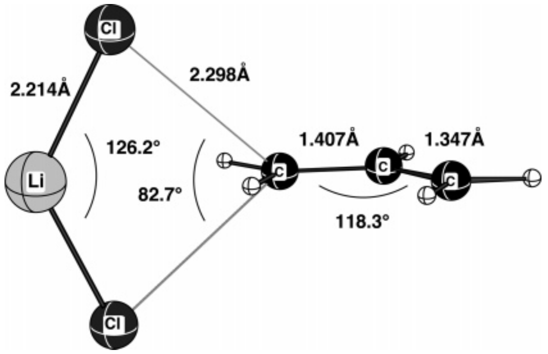

FIGURE 5. Transition structure for LiCl−allyl chloride at 6-31+G*. The transition structures for reactions of allyl fluoride with LiF and NaF are similar to those of M−F = 1.692, 2.070 Å; F−M−F = 122.7°, 104.6°; F−C−F = 73.25°, 87.5°; C_α−C_β = 1.414, 1.424 Å; C_β−C_γ = 1.344, 1.339 Å, respectively.

The natural charges summarized in Table 4 (a complete table is given as Table S3, Supporting Information) reflect further the role of conjugation. Compared to the reaction of allyl chloride with chloride ion, the LiCl reaction produces more positive charge at the α-carbon. The increased positive charge at the γ-carbon comes in equal measures from delocalization from C_α and polarization with C_β. The structure analogous to F in Figure 1 is now more important because the presence of the lithium cation electrostatically compensates for the chloride ions and permits greater delocalization from C_α to C_γ. These conclusions apply as well to the other ion pair reactions studied, the reactions of allyl fluorides with LiF and with NaF (Table S3, Supporting Information). The reaction barriers with the fluorides are much larger than those for LiCl with allyl chlorides but the substituent patterns are comparable.

An electron-donating methyl substituent at the γ-position increases the reactivity in all three LiF, LiCl, and NaF ion pair reaction systems. The stabilization is about the same, 6−8 kcal mol^{-1}, regardless of cis or trans orientation. The halogens have relatively small effects. *trans*-Fluoro is slightly stabilizing, and cis is slightly destabilizing. *trans*-Chloro is slightly destabilizing, and cis has a greater destabilizing effect. The strongly electron-withdrawing cyano group has much higher reaction barriers in all cases.

The vinyl group has only a small inductive effect, but it has a powerful effect in lowering the barriers of all of the ion pair reactions, a clear indication of the role of extended conjugation. Natural charges show that substantial net positive charge (0.10−0.15 units) is delocalized to the terminal vinyl group. Note that four conformations of γ-vinylallyl (pentadienyl) were computed: trans−anti with an extended W-configuration, trans−syn and cis−anti having sickle-shaped configurations, and cis−syn with a U-shape. The most stable is the trans−anti structure with its extended chain. The cis−syn structure is by far the least stable; the terminal position is now quite close to the reacting center which has a high positive charge (0.801 with LiF and 0.806 with NaF). The

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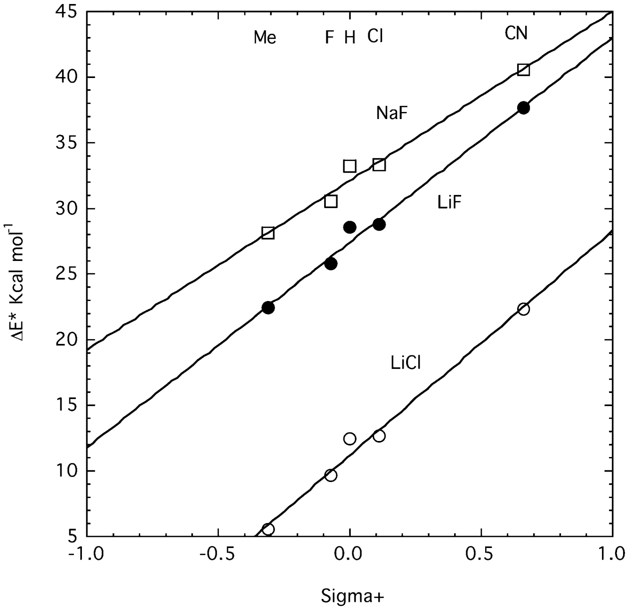

FIGURE 6. Ion pair S_N2 reactions of NaF and LiF with allyl fluoride and of LiCl with allyl chloride vs σ^+ constants. Lines shown are: NaF, 32.14 ± 0.34 + (12.88 ± 1.03) σ^+, $R^2 = 0.981$; LiF, 27.42 ± 0.35 + (15.62 ± 1.06) σ^+, $R^2 = 0.986$; LiCl, 11.21 ± 0.39 + (17.09 ± 1.17) σ^+, $R^2 = 0.986$.

calculated transition structure has more of the MX_2^- R^+ ion pair character of an S_N1 reaction.

The increased cationic charge at C_γ in the reactions with ion pairs suggests a difference in inductive effect interactions with γ-substituents. In their study of the reaction of benzylic chlorides with sodium ethoxide, Cayzergues et al. dissected the rates into those for ethoxide ion and for sodium ethoxide ion pairs.[37] Hammett $\sigma\rho$ correlations give $\rho = 2.2$ for the ionic reaction and $\rho = -0.6$ for the reaction with ion pairs. Our results follow this same general pattern; electron-attracting groups now raise the barrier and electron-donating groups lower it, exactly the reverse of the reaction with chloride ion. A Hammett plot using σ_p values gives a correlation with $\rho = +18.8$, the opposite sign from the chloride ion reaction. The effect of γ-F is especially revealing. This group lowers the barrier. We note in this connection that the σ^+ constant for p-F, −0.07, is opposite in sign from σ_p, 0.06; that is, the fluoro substituent is net electron-donating toward benzylic cations. This result suggests that a correlation with $\sigma+$ constants would be more appropriate. Such a correlation shown in Figure 6 for five substituents is indeed excellent. Comparable results were found for the reactions of allyl fluorides with LiF and with NaF and are included in Figure 6.

The cis substituents also give satisfactory correlations with the same σ^+ constants (Figure S1, Supporting Information), but in these cases the correlations are just as good with σ constants. Substituents that are nonaxially symmetric such as OH show anomalous behavior as in the ionic reactions. The thiol group is normally quite stabilizing toward carbocations, and the SH group is stabilizing in the ion pair S_N2 transition states but the degree is quite variable with different MX groups and cis−trans orientation.

Some structures were also investigated with a fluoro or methyl substituent at the C_β position, with results included in Tables 3 and 4. β-F-Substitution increases the reaction barrier substantially; it withdraws charge from the β- and γ-carbons but has little effect on C_α. A β-methyl group has a slight stabilizing effect apparently because opposing effects of σ-stabilization and steric effects appear to balance.

The bending of incoming and attacking nucleophiles toward the metal is proportional to the energy barrier. Thus, the bending angle (X−C−X) is small with substituents characterized by low energy barriers (Table 3). Similarly, greater delocalization is found in the transition states with lower energy barriers and is evident from the C−C bond lengths in the transition states (Table 3).

In general, ion pair reactions are less favorable than the corresponding ionic reactions, although this comparison depends on solvation effects. Some of the computed ion pair reaction barriers in the present study, however, are so low that such reactions should be observable in solution−and probably have been. For example, kinetic studies of sodium phenoxide with allyl chloride in the butyl alcohols probably involved the reactions of sodium phenoxide ion pairs.[38]

Conclusions

A theoretical investigation of some ionic and ion pair S_N2 reactions of allyl halides has shown that the transition structures of the ionic substitution reactions do not exhibit stabilization by conjugation, as shown by the calculated bond lengths and natural charges. Polarization of the double bond observed in the ionic transition structures provide a rationalization of the high reactivity of allyl halides. However, more delocalization is observed in the ion pair transition structures. The calculations of reactions involving allyl halides with substituents at the γ-position show that electron-withdrawing groups favor the ionic reactions, whereas electron-donating groups favor the delocalized cyclic ion pair transition states. cis-Substitution has less effect on the reactivity than trans-substitution because of unfavorable dipole interactions and steric effects. Anomalous behavior is exhibited by nonaxially symmetric substituents such as the hydroxyl group in both ionic and ion pair reactions. The existence of a vinylogous relationship between allyl and benzyl systems is used to compare the computational results. Calculated Hammett $\sigma\rho$ correlations parallel the experimental observations on benzylic systems that ionic and ion pair reactions give ρ values of opposite signs.

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Supporting Information Available: Tables of computation results and additional figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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