

Inversion versus Retention of Configuration for Nucleophilic Substitution at Vinylic Carbon

Robert D. Bach,[†] Anwar G. Baboul,[‡] and H. Bernhard Schlegel^{*,§}

Contribution from the Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, Division of Chemistry, Argonne National Laboratory, Argonne Illinois 60439, and Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received January 26, 2001

Abstract: A high-level computational study using CCSD, CCSD(T), and G2(+) levels of theory has shown that unactivated vinyl substrates such as vinyl chloride would afford gas phase, single-step halide exchange by a pure in-plane σ -approach of the nucleophile to the backside of the C–Cl σ bond. Geometry optimization by CCSD/6-31+G* and CCSD(T)/6-31+G* confirms the earlier findings of Glukhovtsev, Pross, and Radom that the S_N2 reaction of Cl^- with unactivated vinyl chloride in the gas phase occurs by a σ attack. Complexation of vinyl chloride with Na^+ does not alter this in-plane σ preference. However, moderately activated dihaloethylenes such as 1-chloro-1-fluoroethylene undergo gas-phase S_N2 attack by the accepted π -route where the nucleophile approaches perpendicular to the plane of the C=C. In the latter case a single-step π pathway is preferred for the $Cl^- + H_2C=CFCl$ reaction. This is the first definitive example at a high level of theory where a single-step π nucleophilic vinylic substitution is preferred over a multistep mechanism in the gas phase. The activation barriers for these gas-phase single-step σ - and π -processes involving both naked anions and Na^+ complexes are, however, prohibitively high. Solvation and the presence of a counterion must play a dominant role in nucleophilic vinylic substitution reactions that proceed so readily in the condensed phase. In solution, nucleophilic vinylic substitution reactions involving electron-withdrawing groups on the carbon–carbon double bond (e.g., $-CN$, $-CHO$, and $-NO_2$) would almost certainly proceed via a free discrete carbanionic intermediate in accord with experiment.

I. Introduction

Organic chemists prefer to classify reactions according to mechanistic types centered around descriptors such as electrophiles, nucleophiles, etc. Nucleophilic substitution at saturated carbon remains one of the most important reactions in both synthetic and mechanistic organic chemistry. It is generally assumed that bimolecular S_N2 nucleophilic substitution at saturated carbon (sp^3) proceeds with inversion of configuration¹ while S_N2 attack at vinylic carbon (sp^2) affords a substitution product with retention of configuration.^{2,3} Reactions of nucleophilic vinylic substitution, however, display a greater variety of mechanisms.^{4–11} Both the stepwise and the concerted processes normally lead to retention of configuration, although when the carbanion intermediate is long-lived, partial or

complete stereoconvergence may result.^{6–8} The most common reaction route is an addition–elimination mechanism (Ad_N-E) that is initiated by nucleophilic attack at the π -bond^{4–9} and portrays some features of aromatic nucleophilic substitution.¹¹ The generally accepted mechanism for nucleophilic attack on a vinyl halide involves approach of the nucleophile perpendicular to the plane of the carbon–carbon double bond. One of the remaining mechanistic questions is whether the overall nucleophilic substitution reaction proceeds by a multistep addition–elimination process or by a concerted addition–elimination process in the absence of a discrete carbanionic intermediate. An overwhelming number of experimental and computational studies support the occurrence of this multistep route.^{6,8} Poor leaving groups in most systems and good leaving groups in highly activated vinylic systems cause a multistep mechanism that involves the formation of one or more carbanion intermediates, such as that indicated in Scheme 1. While the variable-transition-state model developed for nucleophilic vinylic substitution by Rappoport^{2,6} leaves the possibility of a concerted single-step mechanism as an open question for very slightly

[†] University of Delaware.

[‡] Argonne National Laboratory.

[§] Wayne State University.

(1) Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry, the S_N2 Mechanism*; Wiley: New York, 1992.

(2) (a) Rappoport, Z. *Acc. Chem. Res.* **1992**, *25*, 474. (b) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (c) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (d) Rappoport, Z. *J. Org. Chem.* **1982**, *47*, 1397. (e) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73.

(3) (a) Shainyan, B. A. *Russ. Chem. Rev. (Engl. Transl.)* **1986**, *55*, 511.

(b) Minkin, V. I.; Simkin, B. Y.; Minyaev, R. M. *Quantum Chemistry of Organic Compounds--Mechanisms of Reactions*; Springer-Verlag: Berlin, 1990.

(4) (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73.

(5) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211.

(6) (a) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (b) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (c) Rappoport, Z. *Acc. Chem. Res.* **1992**, *25*, 474.

(7) Shainyan, B. A. *Russ. Chem. Rev. (Engl. Transl.)* **1986**, *55*, 511.

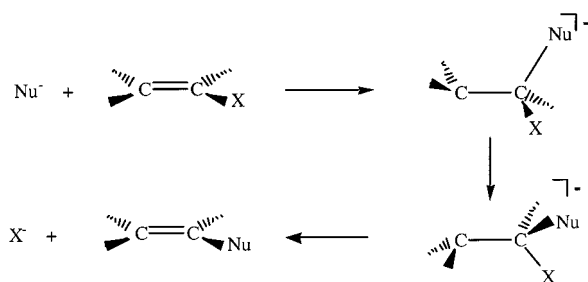
(8) Minkin, V. I.; Simkin, B. Y.; Minyaev, R. M. *Quantum Chemistry of Organic Compounds--Mechanisms of Reactions*; Springer-Verlag: Berlin, 1990.

(9) (a) Stang, P. J. *Prog. Phys. Org. Chem.* **1973**, *10*, 205. (b) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinylic Cations*; Academic Press: New York, 1979. (c) Nefedov, V. D.; Sinotova, E. N.; Lebedev, V. P. *Russ. Chem. Rev. (Engl. Transl.)* **1992**, *61*, 283.

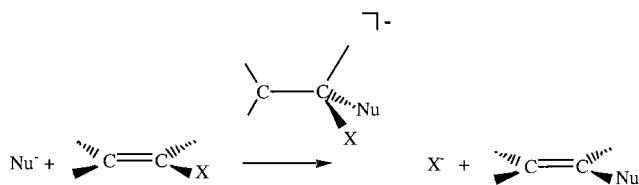
(10) (a) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107. (b) Hanack, M.; Subramanian, L. R. *J. Chem. Educ.* **1975**, *52*, 80.

(11) (a) Bunnet, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273. (b) Bunnet, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (c) Glukhovtsev, M. N.; Bach, R. D.; Laiter, S. J. *Org. Chem.* **1997**, *62*, 4036.

Scheme 1



Scheme 2



activated systems, other alternative mechanisms of the substitution appear to dominate in such cases. Furthermore, the existence of a very short-lived intermediate is anticipated even for a mechanism that is classified as a single-step process within this model.⁴

Early calculations of Stohrer,^{12a} using Extended Hückel Theory, suggested a concerted addition–elimination process in the absence of a discrete carbanionic intermediate (Scheme 2). Despite the computational results of Stohrer and the experimental studies on nucleophilic substitution in unactivated vinyl systems which led to the description of these reactions as bimolecular substitutions¹³ (for example, reactions of unactivated vinyl halides with alkyl and aryl selenide^{13e}), clear-cut evidence for a single-step mechanism was not yet available. Most of the mechanistic tools applied to study nucleophilic vinylic substitution were not yet capable of providing a definitive answer.^{6–8} As a consequence, concerted mechanisms of nucleophilic vinylic substitution are usually considered as unlikely processes.³ In 1984^{14a} we provided the first theoretical evidence supporting a concerted addition–elimination pathway for reactions of a series of nucleophiles with 1-chloro-1-fluoroethene. We chose this vinylic halide because dihaloethylenes are viable substrates in $\text{S}_{\text{N}}2$ reactions as a consequence of additional inductive stabilization of the developing carbanionic π -TS by the halogen substituent.

Computational methods are now sufficiently reliable to be a useful alternative to explore the possibility of a concerted vinylic nucleophilic substitution. Theoretical studies^{15–19} have, in

general, supported the stepwise π -route whereas a concerted in-plane $\text{S}_{\text{N}}2$ pathway involving backside attack at carbon has long been excluded as a viable pathway on the basis of both theoretical and historical grounds.^{3,15} However, this in-plane single-step $\text{S}_{\text{N}}2$ process involving backside attack at the vinylic carbon has recently received considerable attention. High-level ab initio calculations have questioned the accepted mechanism and predicted the occurrence of an in-plane $\text{S}_{\text{N}}2$ approach of the nucleophile to the σ bond (σ -attack) that is preferred over π -attack in an unactivated substrate such as vinyl chloride.^{20a} Glukhovtsev, Pross, and Radom reported two discrete pathways for the reaction of Cl^- with $\text{CH}_2=\text{CHCl}$. The calculations using modified G2 theory²¹ (denoted as G2(+))^{20a} demonstrated that the barrier height for a σ -approach (σ -TS-3, Figure 1) was lower in energy than the traditional π -approach (π -TS-4). The corresponding β,β -dichloroethyl anion, the putative intermediate required for a two-step process, was found to be unstable, collapsing to a loose ion–molecule complex. A σ -pathway is by definition a single-step process while a π -approach can be either a single-step process or involve a carbanionic intermediate in a multistep addition–elimination reaction. In the case of Cl^- with $\text{CH}_2=\text{CHCl}$, since the σ -TS is lower in energy than the π -pathway, a multistep path can be ruled out. It was concluded that nucleophilic substitution at the unactivated vinyl carbon of vinyl chloride is a single-step process initiated by either σ - or π -attack, rather than a multistep reaction involving a carbanionic intermediate.^{20a} Lucchini, Modena, and Pasquato^{20b} have provided an interesting rationale for the $\text{S}_{\text{N}}\text{-}\sigma$ versus the $\text{S}_{\text{N}}\text{-}\pi$ mechanism based upon the relevance of the symmetry of the LUMO orbital of the alkene. Their arguments were based upon the energy level diagram of the antibonding combination of the four-electron HOMO–HOMO orbital interaction that we discussed in several earlier studies.¹⁴ A more recent theoretical study at the G2(+) level by Lee et al.^{20c} also demonstrated that weaker bases (nucleophiles) such as Cl^- and Br^- react with vinyl chloride by the novel in-plane σ -approach with inversion of configuration, but that stronger nucleophiles (OH^- , SH^-) substitute by the usual out-of-plane $\text{S}_{\text{N}}\text{-}\pi$ path but with retention of configuration. This was an important observation since we now have a situation where the unactivated vinyl carbon of vinyl chloride can operate with either the $\text{S}_{\text{N}}\text{-}\sigma$ or the $\text{S}_{\text{N}}\text{-}\pi$ mechanism depending upon the electrostatic HOMO–HOMO interactions experienced by the incoming nucleophile.

Since the only substrate to date that has shown theoretical evidence for the $\text{S}_{\text{N}}\text{-}\sigma$ -path is unactivated vinyl chloride, where both $\text{S}_{\text{N}}\text{-}\sigma$ and $\text{S}_{\text{N}}\text{-}\pi$ mechanisms are observed for different nucleophiles, we seek to resolve the question as to whether this novel pathway is in fact exclusive to this simple unactivated vinyl halide. A question that also remains is whether a concerted pathway is preferred over a multistep process when the latter is not ruled out by instability of the carbanionic intermediate. It is usually assumed that the existence of an intermediate in nucleophilic vinylic substitution implies that the multistep pathway via this intermediate has a lower activation energy than a concerted single-step mechanism. We now report the results of high-level ab initio calculations that corroborate our earlier findings^{14a} and indicate the preference of the gas-phase concerted

(12) (a) Stohrer, W.-D. *Tetrahedron Lett.* **1975**, 3, 207. (b) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, 101, 5095. (c) Rappoport, Z.; Avramovitch, B.; Karni, M.; Apeloig, Y. *Isr. J. Chem.* **1989**, 29, 267.

(13) (a) Klein, J.; Levene, R. *J. Am. Chem. Soc.* **1972**, 94, 2520. (b) Rajaram, J.; Pearson, R. G.; Ibers, J. I. *J. Am. Chem. Soc.* **1974**, 96, 2103. (c) Chalchat, J. C.; Theron, F.; Vessiere, R. *Bull. Soc. Chim. Fr.* **1973**, 2501. (d) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Montanucci, M. *J. Org. Chem.* **1983**, 48, 4795. (e) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Tetrahedron Lett.* **1984**, 25, 4975.

(14) (a) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, 106, 1401. (b) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, 106, 1410. (c) Bach, R. D.; Wolber, G. J.; Klux, R.; Kost, D.; Pross, A. *Nouv. J. Chim.* **1984**, 8, 711. (d) Bach, R. D.; Coddens, B. A.; Wolber, G. J. *J. Org. Chem.* **1986**, 51, 1030.

(15) Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, 93, 1953.

(16) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, 101.

(17) Liotta, C. L.; Burgess, E. M.; Eberhardt, W. H. *J. Am. Chem. Soc.* **1984**, 106, 4849.

(18) (a) Shainyan, B. A.; Sidorkin, V. F. *Zh. Org. Khim. (USSR)* **1980**, 16, 3. (b) Shainyan, B. A. *Zh. Org. Khim. (USSR)* **1980**, 16, 1113.

(19) Cohen, D.; Bar, R.; Shaik, S. S. *J. Am. Chem. Soc.* **1986**, 108, 231.

(20) (a) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, 116, 5961. (b) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1995**, 117, 2297. (c) Kim, C. K.; Hyun, K. H.; Kim, C. K.; Lee, I. J. *J. Am. Chem. Soc.* **2000**, 122, 2294.

(21) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, 94, 7221.

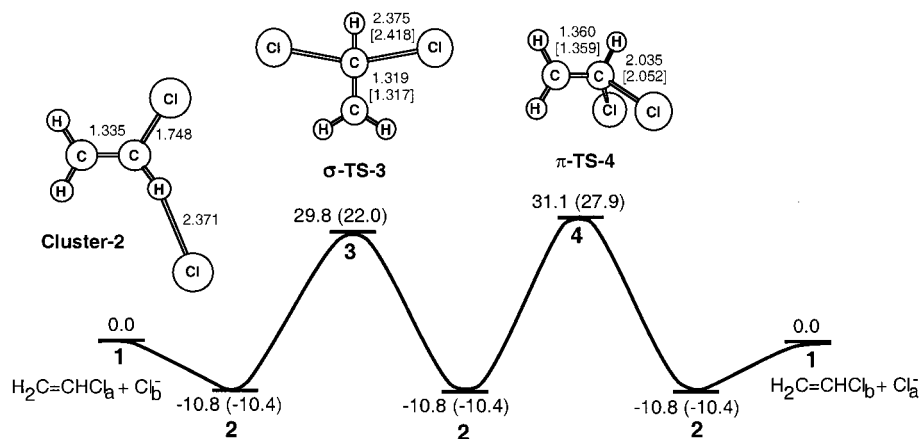


Figure 1. MP2(Full)/6-31+G* geometries and relative energies of reactant **Cluster-2**, π transition state π -**TS-4**, and σ transition state σ -**TS-3** for the reaction of Cl^- with 1-chloroethene. G2(+) energies are given in parentheses. Energies are in kcal/mol relative to isolated reactants, bond lengths are in Å, and angles are in deg.

route over a multistep pathway proceeding via a carbanionic intermediate.

II. Computational Methods

Ab initio molecular orbital calculations were performed with the GAUSSIAN 98 system of programs.^{22a} Geometries were optimized at the MP2(full)/6-31+G* level of theory. Cartesian coordinates and total energies are available in the Supporting Information. The 6-31+G* basis set includes diffuse functions, since most of the structures are carbanions. The stationary points on the potential energy surfaces were characterized by calculations of vibrational frequencies at the MP2(full)/6-31+G* level. To obtain heats of reaction and barrier heights to chemical accuracy, selected reactions were computed at the G2(+) level of theory where geometries are optimized at MP2(full)/6-31+G* and thermal corrections are based upon a HF/6-31+G* frequency calculation.^{20a} For the chloride + vinyl chloride reaction, structures were also optimized at the CCSD(T)/6-31+G* level using the ACES II program system.^{22b}

II. Results and Discussion

II.1. Single-Step $\text{S}_{\text{N}}2$ σ -Pathway. As noted above,^{20a} the in-plane σ -approach of chloride ion to vinyl chloride is favored over the more classical π -approach by 5.9 kcal/mol at the G2-(+) level of theory (Figure 1). This observation was sufficiently novel that we felt further investigation was warranted. However, the overall classical activation barrier (ΔE^\ddagger) for $\text{S}_{\text{N}}2$ substitution measured relative to gas-phase **Cluster-2** is very high at 32.4 kcal/mol. Since the MP2 level of theory is sometimes inadequate when more than one bond is being broken, geometry optimization at a higher level of correlation would be prudent. At the CCSD/6-31+G* level^{22b} the transition state for the σ -approach, σ -**TS-3** in Figure 1, remains 7.6 kcal/mol lower in energy than the π -approach, π -**TS-4**. The energy difference between these

two discrete pathways is only 1.3 kcal/mol at the MP2(Full)/6-31+G* level, but 5.9 kcal/mol at G2(+). Geometry optimization at CCSD(T)/6-31+G* also placed the π -approach, π -**TS-4**, 6.3 kcal/mol above the σ -transition state. Significantly, the geometries changed very little at the CCSD level (with and without the triples)^{22b} relative to the MP2 geometry. All of the key bond lengths elongated only slightly with the exception of C–Cl bond distance in σ -**TS-3** changing from 2.375 to 2.418 Å and in π -**TS-4** from 2.035 to 2.052 Å. Our calculations corroborate the findings of Glukhovtsev et al.^{20a} that the existence of a σ pathway for unactivated vinyl chloride is based upon a firm theoretical basis.

The hypothesis was also advanced by Glukhovtsev et al. that σ -**TS-3** could potentially be more highly solvated than π -**TS-4** and that their unusual findings could also be maintained in solution. Although σ -**TS-3** maintains C_{2v} symmetry in the gas phase, that may well be less likely in the condensed phase or in the presence of a counterion. This prompted us to examine the effect of a sodium ion on the relative energies of these contrasting reaction pathways. We located a loose reactant **Cluster-6** between NaCl and $\text{H}_2\text{C}=\text{CHCl}$ that was 12.2 kcal/mol lower in energy than isolated reactants (Figure 2). The corresponding β,β -dichloroethyl carbanion complexed to a sodium cation at carbon exists only as a very shallow minimum (**Min-7** shown in Figure 2) at the MP2(Full)/6-31+G* level of theory. A C–Na⁺ bond distance of 2.382 Å was found when the Na⁺ is complexed cis to the two chlorines as in **Min-7** (C_s). The trans isomer **TS-8** (C_s) is a transition state for rotation about the C–C bond and is 11.7 kcal/mol higher in energy reflecting the loss of Na⁺–Cl bonding.

We located both σ - and π -transition states, σ -**TS-9** and π -**TS-10**, for elimination of NaCl affording vinyl chloride·NaCl, **Cluster-6**. The nonplanar ($\angle\text{C}-\text{C}-\text{H} = 148.5^\circ$) C_s σ -**TS-9** remains 0.6 kcal/mol (MP2(Full)/6-31+G*) lower in energy than the corresponding π transition state. Presumably at the G2-(+) level the energy difference between σ - and π -approaches in Figure 2 would increase as noted above for σ -**TS-3** and π -**TS-4** in Figure 1 and make σ the dominant pathway. Although the gas-phase addition of NaCl to $\text{H}_2\text{C}=\text{CHCl}$ affords an intermediate **Min-7** that is 35.3 kcal/mol above isolated reactants, the classical barrier height for the σ transition state eliminating NaCl (σ -**TS-9**) is 2.5 kcal/mol below the cis minimum **Min-7**. Since **Min-7** is higher in energy than the σ pathway for chloride ion attack at vinyl carbon (σ -**TS-9**) a concerted pathway is indicated. Significantly, at the MP2/6-

(22) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zalewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, Ö.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Peterson, G. A.; Ayala, P. Y.; Rabuck, A. D.; Raghavachari, K.; Cui, Q.; Morokuma, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Barone, V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Nanayakkara, A.; Peng, C. Y.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Pople, J. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998, and earlier versions. (b) ACES II (Advanced Concepts in Electronic Structure Program System): Bartlett, R. J.; Purvis, G. D., III; Fitzgerald, G. B.; Harrison, R. J.; Rittby, M.; Sosa, C.; Lee, Y. S.; Trucks, G. W.; Cole, S. J.; Salter, E. A.; Pal, S.; Watts, J.; Laidg, W. D.; Magers, D. H.; Stanton, J. F.; Bernholdt, D.

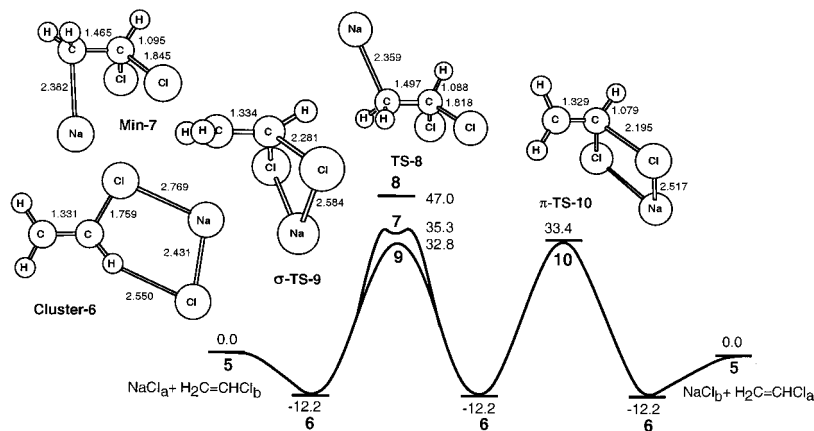


Figure 2. MP2(Full)/6-31+G* geometries and relative energies for reactant cluster **Cluster-6**, carbanion minimum **Min-6**, rotational transition state **TS-8**, σ transition state **σ -TS-9**, and π transition state **π -TS-10** for the reaction of NaCl with 1-chloroethene. Energies are in kcal/mol relative to isolated reactants, bond lengths are in Å, and angles are in deg.

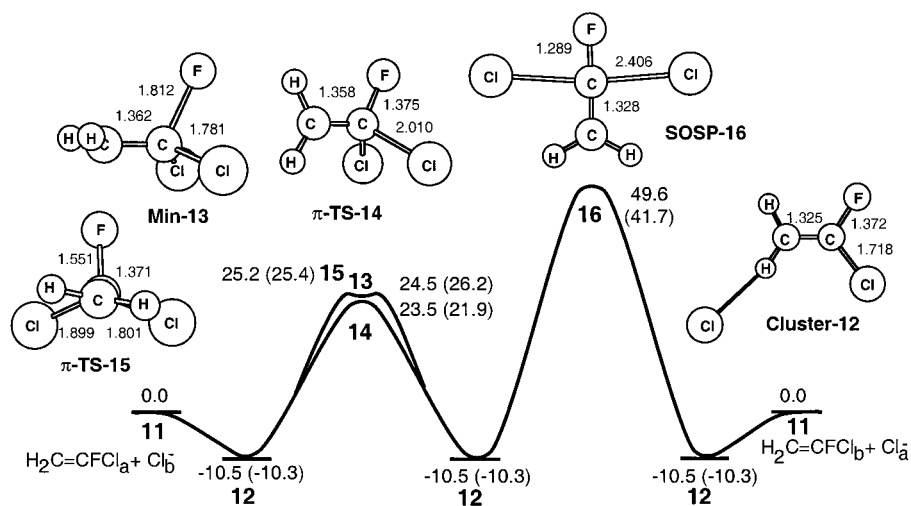


Figure 3. MP2(Full)/6-31+G* geometries and relative energies for reactant cluster **Cluster-12**, carbanion minimum **Min-13**, π transition state **π -TS-14**, twisted transition state **π -TS-15**, and second-order saddle point **SOSP-16** for the reaction of Cl⁻ with 1-chloro-1-fluoroethene. G2(+) energies are given in parentheses. Energies are in kcal/mol relative to isolated reactants, bond lengths are in Å, and angles are in deg.

31+G* level of theory, the gas-phase classical barriers for chloride ion exchange with vinyl chloride (45.0 and 40.6 kcal/mol, respectively) in the presence and absence of Na⁺ complexation are quite comparable when computed relative to their gas-phase clusters. The G2(+) barrier for the latter reaction is 32.4 kcal/mol relative to the **Cluster-2**.^{20a} These data are consistent with the gas-phase findings of Glukhovtsev et al. and lend further support to the suggestion that a σ -pathway is preferred for *unactivated* substrates such as vinyl chloride. However, it is well established that vinyl chloride^{2e} and vinyl bromide²³ are very unreactive in solution even when good nucleophiles (e.g. RS⁻) are employed at elevated temperature (e.g. 130 °C). This prompted us to examine the feasibility of such σ S_N2 pathways with more highly substituted alkenes.

II.2. Single-Step S_N2 π -Pathway. In an earlier study we^{14a} provided theoretical evidence supporting a concerted addition–elimination pathway for addition of a series of nucleophiles to 1-chloro-1-fluoroethene. This vinylic halide was chosen because dihaloethylenes are viable substrates in S_N2 reactions as a consequence of additional inductive stabilization of the developing carbanionic π transition state by the halogen substituent. We now provide higher level ab initio calculations that corroborate those earlier findings and provide evidence for a concerted π -approach in the current reaction series.

We found a dramatically different potential energy surface for the addition of Cl⁻ to the dihalo-substituted alkene H₂C=CFCl as shown in Figure 3. The reactant cluster between Cl⁻ and H₂C=CFCl, **Cluster-12**, has a stabilization energy of 10.5 kcal/mol at the MP2/6-31+G* level of theory while Cl⁻ addition to the C=C affording carbanionic energy minimum **Min-13** is 24.5 kcal/mol above isolated reactants. The long C–F bond distance in **Min-13** (1.812 Å) is a reflection of the strong negative hyperconjugation of the adjacent electron pair with the C–F bond. The estimated activation barrier for this carbanionic intermediate **Min-13** to eliminate Cl⁻ is <1 kcal/mol. A rotation about the C–C bond in **Min-13** of about 14° results in expulsion of Cl⁻ via transition state **π -TS-15**.

A first-order saddle point **π -TS-14** arises from Cl⁻-attack at C_α of the alkene π -bond and the classical activation barrier for this concerted addition–elimination Cl⁻ exchange process is predicted to be 21.9 kcal/mol relative to reactants at the G2(+) level of theory. We could not locate a σ transition state for this Cl⁻ exchange reaction but a second-order saddle point **SOSP-16** does lie 19.8 kcal/mol above **π -TS-14**. The first imaginary frequency (713i cm⁻¹, b₂) for **SOSP-16** corresponds to the motion along the reaction path for Cl⁻ exchange. The second imaginary frequency (68i cm⁻¹, b₁) is the out-of-plane bending mode that leads from **SOSP-16** toward **Min-13**. At the G2(+) level the concerted pathway **π -TS-14** is 4.3 kcal/mol lower in

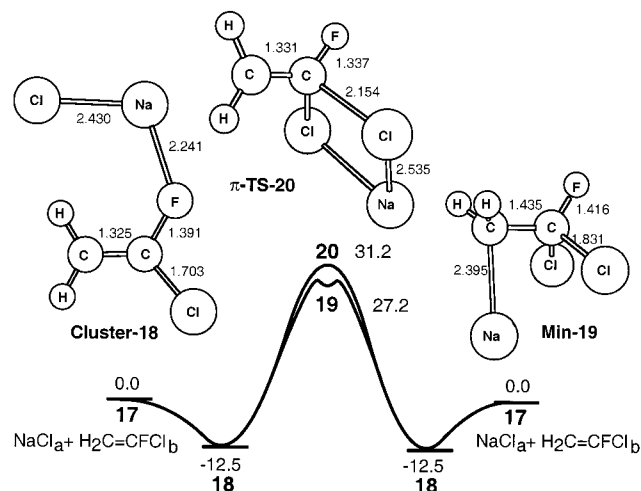


Figure 4. MP2(Full)/6-31+G* geometries and relative energies for reactant cluster **Cluster-18**, carbanionic minimum **Min-19**, and π transition state π -**TS-20** for the reaction of NaCl with 1-chloro-1-fluoroethene. Energies are in kcal/mol relative to isolated reactants, bond lengths are in Å, and angles are in deg.

energy than the carbanionic intermediate **Min-13** that would be involved in a two-step process. These data corroborate our earlier study at a more modest level of theory where we also suggested a concerted pathway with $\text{H}_2\text{C}=\text{CFCl}$.^{14a}

To examine the cation effect upon this halide exchange we included NaCl in the reaction. Complexation of NaCl with $\text{H}_2\text{C}=\text{CFCl}$ affords **Cluster-18** with a stabilization energy of 12.5 kcal/mol (Figure 4). Alternatively, complexation of Na^+ at the carbon atom of **Min-13** can afford **Min-19**, which can expel NaCl with little or no barrier to produce **Cluster-18**. The transition state for the π -approach, π -**TS-20**, lies 27.2 kcal/mol above isolated reactants, and 4.0 kcal/mol above **Min-19**. We could not locate a σ -transition state for this addition–elimination of NaCl to 1-chloro-1-fluoroethene. Because **Min-19** is lower in energy than π -**TS-20**, this particular reaction, with complexation to Na^+ , could follow a multistep mechanism.

Since electron-withdrawing substituents in vinylic substitution typically result in a multistep process involving a π approach,^{2,3} we next probed the effect of a β substituent. Our primary goal was to show that a conjugated system such as an acrylonitrile would have a low barrier and proceed by a π approach of the nucleophile. For the reaction of Cl^- with 1-chloro-2-cyanoethene at the MP2(Full)/6-31G* level of theory, we located the *trans* π -**TS-23** and *cis* π -**TS-25** which lie 4.1 and 5.8 kcal/mol above the isolated reactants (Figure 5). **TS-24** is the transition state for rotation around the C–C bond ($\Delta E^\ddagger = 12.2$ kcal/mol). We could not locate a σ -transition state for the addition of Cl^- to 1-chloro-2-cyanoethene nor a discrete carbanionic intermediate. Much to our surprise, all attempts to locate the β,β -dichloro anionic intermediate resulted in expulsion of chloride ion. The presence of a counterion would most likely afford a stable neutral intermediate as noted above for the addition–elimination of NaCl to 1-chloro-1-fluoroethene. It is however clear that the cyano substituent has a strong stabilizing effect on the transition state, as is evident from the very low barriers for chloride ion exchange.

We also examined the effect of an electronegative β -fluoro substituent on the mechanism of this vinylic substitution reaction (Figure 6). We used both *cis*- and *trans*-1-fluoro-2-chloroethenes as substrate and examined initially the pathways for vinylic attack by Cl^- on the vinylic carbon bearing the chlorine substituent. The lowest energy path was for the π -approach to

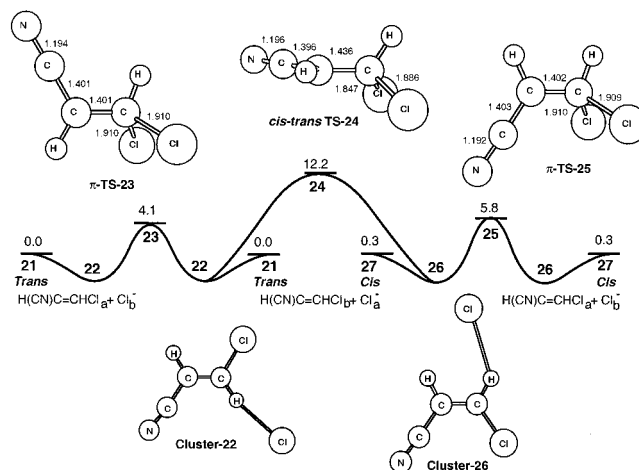


Figure 5. MP2(Full)/6-31+G* geometries and relative energies for reactant **Cluster-22**, rotational transition state **TS-24**, and π transition states π -**TS-23** and π -**TS-25** and for the reaction of Cl^- with 1-chloro-2-cyanoethene. Energies are in kcal/mol relative to isolated reactants, bond lengths are in Å, and angles are in deg.

the *cis* isomer as shown in Figure 6a. The activation energy for π -**TS-30** relative reactant complex **29** is 45.0 kcal/mol. Ironically, the barriers for Cl^- addition to the parent vinyl chloride (σ -**TS-3** and π -**TS-4**, Figure 1) are 40.6 and 41.9 kcal/mol. Thus, the barriers for the σ and π displacement of Cl^- by Cl^- , σ -**TS-31**, π -**TS-30**, and π -**TS-34**, are nearly the same as that for vinyl chloride itself (Figure 1). However, Cl^- attack at the fluorine bearing carbon yields transition states that are 6–8 kcal/mol lower (Figure 7). The two π -transition states, π -**TS-35** and π -**TS-37** are 14.7 and 13.3 kcal/mol lower in energy than the corresponding σ -transition state σ -**TS-38** for attack at the fluorine bearing carbon. As anticipated from the unsubstituted vinyl halide reaction, the G2(+) calculation stabilizes the σ transition state ca. 5 kcal/mol more than the π transition state. Indeed, at the G2(+) level of theory, the π -**TS-37** is 10.4 kcal/mol lower than σ -**TS-38**, and the π transition states for chloride displacing fluoride remain the lowest transition states on the entire potential energy surface.

From these data we conclude that unactivated vinyl substrates such as vinyl chloride would indeed afford gas-phase halide exchange by a pure σ -approach of the nucleophile.^{20a} There are examples of authentic in-plane nucleophilic substitution when exceptional leaving groups are involved.²⁴ For stronger nucleophiles, the π route is the preferred pathway.^{20c} We have now shown that moderately activated dihaloethylenes undergo $\text{S}_{\text{N}}2$ attack by the accepted π -route. However, the activation barriers for these gas-phase processes involving both naked anions and Na^+ complexes have prohibitively high activation energies. The ΔG^\ddagger for π -**TS-3** in Figure 1 and π -**TS-14** in Figure 3 at the G2(+) level of theory are predicted to be 29.8 and 30.5 kcal/mol, respectively, relative to isolated reactants. The free energies for the gas-phase addition–elimination of NaCl affording vinyl chloride (π -**TS-10** in Figure 2) and 1-chloro-1-fluoroethene (π -**TS-20** in Figure 4) are even higher (42.8 and 40.6 kcal/mol (MP2/6-31+G*)) relative to their respective isolated reactants). Thus, the counterion and solvation must play a dominant role in vinylic $\text{S}_{\text{N}}2$ substitution reactions that proceed so readily in the condensed phase.

(24) (a) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1110. (b) Clarke, T. C.; Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 3626. (c) Shainyan, B. A.; Rappoport, Z. *J. Org. Chem.* **1993**, *58*, 3421. (d) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059. (e) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1993**, *115*, 4527.

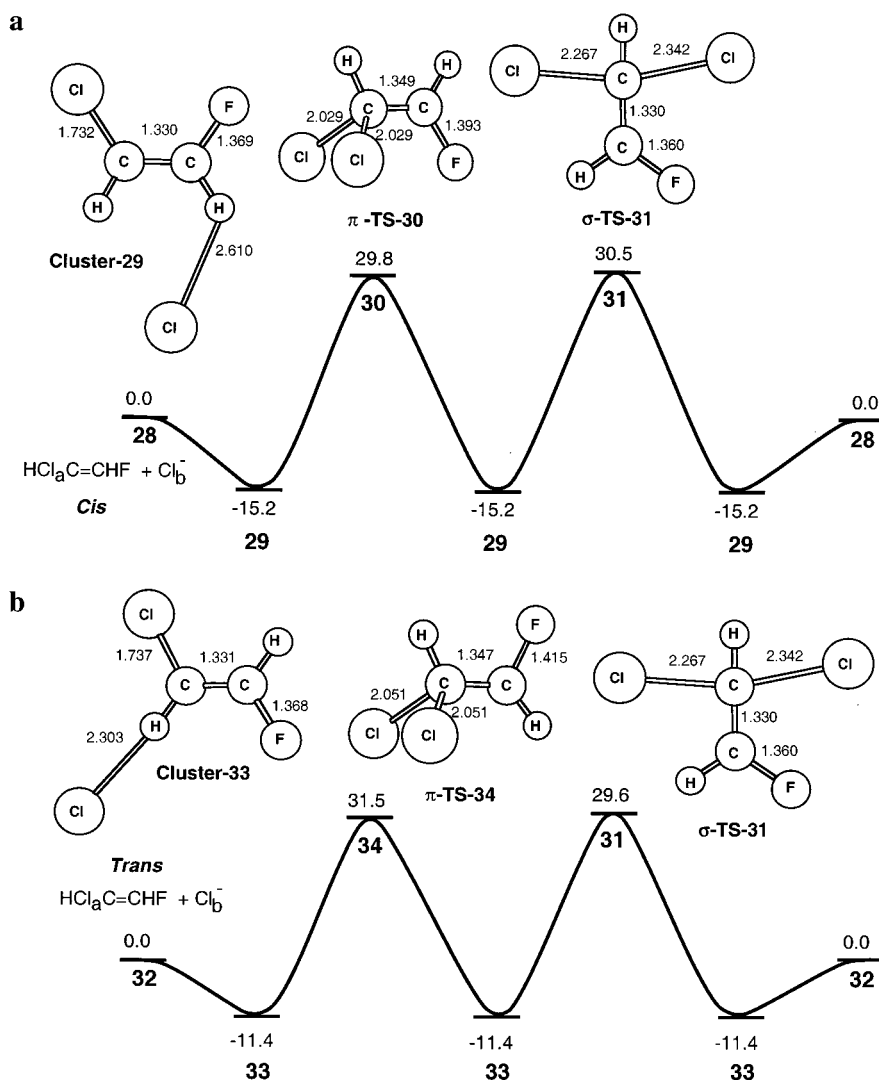


Figure 6. MP2(Full)/6-31+G* geometries and relative energies for reactant clusters **Cluster-29** and **Cluster-33**, π transition states π -TS-30 and π -TS-34, and σ transition state σ -TS-31 for the reaction of Cl^- with the α carbon of *cis*- and *trans*-1-chloro-2-fluoroethene. Energies are in kcal/mol relative to isolated reactants, bond lengths are in Å, and angles are in deg.

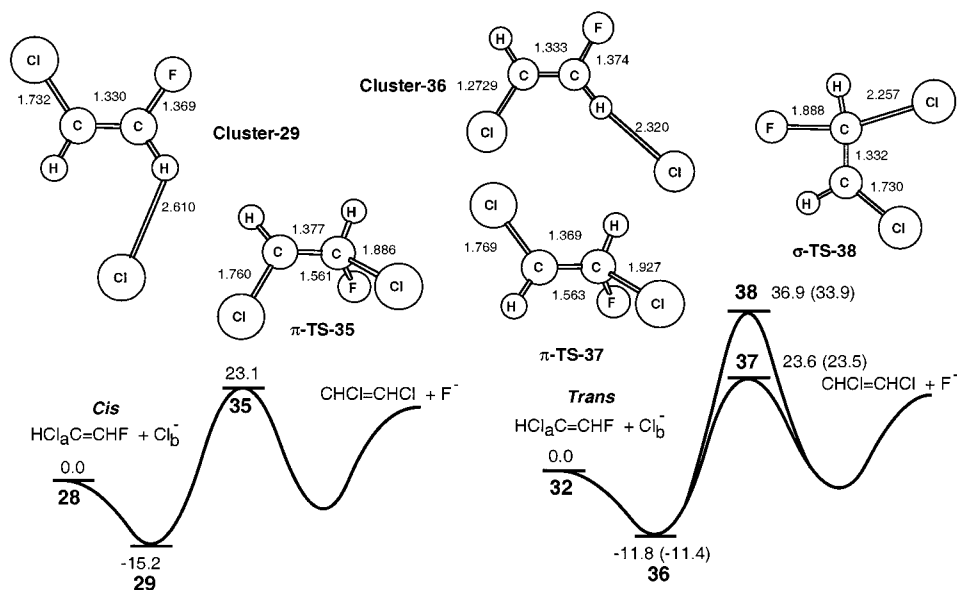


Figure 7. MP2(Full)/6-31+G* geometries and relative energies for reactant clusters **Cluster-29** and **Cluster-36**, π transition states π -TS-35 and π -TS-37, and σ transition state σ -TS-38 for the reaction of Cl^- with the β carbon of *cis*- and *trans*-1-chloro-2-fluoroethene. G2(+) energies are given in parentheses. Energies are in kcal/mol relative to isolated reactants, bond lengths are in Å, and angles are in deg.

The carbanionic mechanism involving minimum **Min-13** (Figure 3) is only 4.3 kcal/mol ($G_2(+)$) higher in the gas phase than the completely concerted halide exchange π -**TS-14**. For activated S_N2 reactions involving electron-withdrawing groups on the carbon-carbon double bond (e.g. $-\text{CN}$, $-\text{CHO}$, and $-\text{NO}_2$), reactions in solution should proceed via a free discrete carbanionic intermediate in accord with experiment. Since the $G_2(+)$ barrier for π -**TS-14** (Figure 3) is only 21.9 kcal/mol and this π -route is 19.8 kcal/mol lower in energy than **SOSP-16**, we conclude that the π -route is operational for typical S_N2 attack at vinylic carbon bearing a stabilizing substituent. For example, the addition of CH_3S^- to trichloroethylene does follow the π pathway.²⁵

III. Conclusions

(1) Unactivated vinyl substrates such as vinyl chloride do indeed afford gas-phase halide single-step exchange by a pure σ -approach of the nucleophile.

(2) Moderately activated dihaloethylenes such as 1-chloro-1-fluoroethylene undergo the gas-phase S_N2 attack by the accepted π -route. In the latter case both the single-step and multistep reaction pathways are feasible.

(3) The activation barriers for these gas-phase single-step σ - and π -processes involving both naked anions and Na^+ com-

plexes are prohibitively high. The counterion and solvation must play a dominant role in nucleophilic vinylic substitution reactions that proceed so readily in the condensed phase.

In summary, the novel findings of Glukhovtsev et al.^{20a} for vinyl chloride in the gas phase have been confirmed at a higher level of theory. Even though the reaction of vinyl chloride with Cl^- favors the σ -route over the π -route, vinyl chloride is not an experimentally viable substrate and cannot be considered as representative for the vinyl S_N2 reaction. We have provided four different examples where the π -route is favored over the σ pathway. The π -route is anticipated in *substituted vinylic halide reactions* when experimentally viable substrates are used.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9901661; CHE-9874005). We are also thankful to the National Center for Supercomputing Applications, Urbana, Illinois and Lexington, Kentucky for generous amounts of computer time.

Supporting Information Available: Cartesian coordinates and total energies are available for the minima and transition states described in this work (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(25) Shim, J.-Y.; Boone, P. F.; Richard, A. M. *Chem. Res. Toxicol.* **1999**, *12*, 308.