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Gas phase surface-catalyzed HCl addition to vinylacetylene: motion along a catalytic surface. Experiment and theory☆

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Gaseous mixtures of HCl and vinylacetylene were permitted to react in Pyrex IR cells (NaCl windows). Gaseous 4-chloro-1,2-butadiene and 2-chloro-1,3-butadiene (chloroprene) were the major products. Kinetic data (FTIR) generated a rate expression in concert with surface catalysis. Computational studies involving surface associated water provide a view that accounts for the experimentally determined orders and a bifurcated pathway producing both products. The results are in accord with wall-adsorbed reactant(s) as well as previously reported computational studies on the reactants.

1. Introduction

The addition of hydrogen halides to alkenes and alkynes has served as a paradigm for electrophilic additions in general since the dawn of organic chemistry.[1] Although it is commonly held that electrophilic addition to alkenes is the more facile[2] (a position which may be changing[2f]), ratios of the relative rate constants for various electrophilic addition reactions to unsaturated pairs of equally substituted alkenes and alkynes (k_{ene}/k_{yne}) vary from 10^8 to 10^{-2}, apparently as a function of the nature of the addend, the substituent(s) on the unsaturated substrates and the solvent.[3] Direct comparisons where these effects have been intentionally minimized are rare (vide infra).

Vinylacetylene (1-butene-3-yne [$H_2C{=}CH{-}C{\equiv}CH$]) is the simplest compound with both the carbon–carbon double and triple bonds. More than seven decades ago, Carothers et al.[4] reported that the addition of aqueous hydrogen chloride to vinylacetylene initially yielded 4-chloro-1,2-butadiene ($H_2C{=}C{=}CHCH_2Cl$), which then isomerized to 2-chloro-1,3-butadiene (chloroprene [$CH_2{=}C(Cl)CH{=}CH_2$]) and some 1,3-dichloro-2-butene ($ClH_2CCH{=}C(Cl)CH_3$), of unspecified geometry. The latter formed at significantly longer reaction times. They found that both calcium chloride [$CaCl_2$] and copper(I) chloride [CuCl] accelerated the disappearance of vinylacetylene. It was argued that in the presence of calcium chloride, 4-chloro-1,2-butadiene formed via a 1,4-addition reaction and that this allene subsequently isomerized to 2-chloro-1,3-butadiene. In the presence of copper(I) chloride, only 2-chloro-1,3-butadiene formed[4b] and when 4-chloro-1,2-butadiene was treated with aqueous copper(I) chloride alone it was recovered unchanged. Subsequently, Dolgopol'skii et al.[5] proposed that 2-chloro-1,3-butadiene resulted from an ionized complex of copper(I) chloride with 4-chloro-1,2-butadiene. They, too, reported that 1,3-dichloro-2-butene ($ClH_2CCH{=}C(Cl)CH_3$), geometry unspecified, was obtained on addition of hydrogen chloride to vinylacetylene in the presence of copper(I) chloride.

There appear to be no (further) suggestions as to the pathway(s) by which products might be forming from the starting materials.

Weakly bound π-complexes are often considered as the first stage of an electrophilic addition reaction to unsaturated systems. The elegant work of Dubois et al.[6a,b] on the bromination of alkenes has shown that product is commonly obtained via an initial π-complex intermediate. However, the situation with regard to electrophilic addition of protic acids, e.g., hydrogen chloride, to alkenes and alkynes is quite different. For the latter, while experimentally identifiable (and on occasion even isolable)[6c] hydrogen chloride—alkene and/or—alkyne complexes are produced, there does not appear to be any evidence that those complexes actually lie on the pathway to product.[1g]

The gas phase π-complex of hydrogen chloride with vinylacetylene was examined by Legon and et al.[7] They reported a 1:1

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complex in which the HCl subunit forms a hydrogen bond to the carbon–carbon triple bond ($-C\equiv C-$) in a 'T-shape' configuration. The hydrogen chloride is displaced from the center of the triple bond by about 4 pm toward the 'inner' C atom and, with an 'inbound' chlorine, it makes an angle of about 34° with the vinylacetylene plane. The conformer thus has the HCl '*endo*' rather than '*exo*' to the eneyne system. There is no evidence that the specific complex identified by Legon et al.[7] goes on to product.

Somewhat more than a decade ago, Tang and Cui[8] undertook a computational study and defined the optimized geometries of the possible complexes between vinylacetylene and hydrogen chloride and hydrogen fluoride. They found, in concert with the work of Legon and et al.[7] noted above, that the π-type hydrogen bond to the carbon–carbon triple bond led to a more stable complex then that with the carbon–carbon double bond.[8] More recently, van der Veken and Herrebout[9] reported their combined cryosolution IR and DFT study of the vinylacetylene–HCl (DCl) system at temperatures between 102 and 125 K in an argon matrix. They identified the *endo* conformer and a 1:2 complex where a second HCl is attached in a 'chain-type complex' to the first. No products are reported.

As we have done in other systems[10] we have obtained kinetic and product data for the reaction between the gases hydrogen chloride and vinylacetylene. The disappearance of starting materials and appearance of products were monitored, simultaneously and nondestructively, by FTIR spectroscopy. When it became clear that addition across the triple bond was occurring, an effort was made to examine the stereochemistry of that process with the same technique by attempting to monitor the gas phase reaction of ^{1}HCl with 4-deuterio-1-butene-3-yne ($H_2C{=}CH{-}C{\equiv}C[{}^2H_1]$) under the same conditions. Finally, computations similar to those performed previously,[8,9] but now with experimental product distribution both guiding and limiting the possible outcome, lead us to believe that we now have a clearer understanding of the reaction and the nature of two different transition states that account for the two different products, viz 4-chloro-1,2-butadiene and 2-chloro-1,3-butadiene.

2. Results and discussion of the experiment

When gaseous mixtures of hydrogen chloride and 1-butene-3-yne (vinylacetylene) were reacted in Pyrex vessels at sub-atmospheric pressures gaseous 2-chloro-1,3-butadiene (chloroprene) and 4-chloro-1,2-butadiene were the major products, each forming in about the same amount. Trace quantities of gaseous (*E*)- and (*Z*)-1-chloro-1,3-butadienes were detected using GC. Figure 1 presents FTIR absorbance spectra of a gaseous reaction mixture originally containing 203.93 Torr (1.09×10^{-5} mol cc^{-1}) of hydrogen chloride and 198.03 Torr (1.06×10^{-5} mol cc^{-1}) of vinylacetylene at 353 K in a Pyrex cell, and the same reaction mixture ca. 20 h later, respectively. Unique absorbances could be assigned to hydrogen chloride (2699.0–2704.9 cm^{-1}), and to vinylacetylene (1053.0–1120.0 cm^{-1}). The products, 2-chloro-1,3-butadiene (1531.0–1687.0 cm^{-1}) and 4-chloro-1,2-butadiene (1910.0–2007.0 cm^{-1}), were readily detected but could only be quantified by using the peak-ratio method described in Section 6. Interconversion of the isolated and purified products and/or their reversion to starting materials under these conditions was negligible.

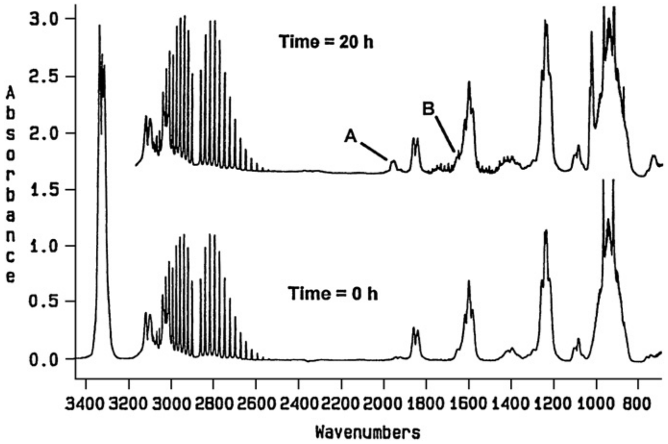


Figure 1. The FTIR absorbance spectra (at 2 cm^{-1} resolution) of a mixture of HCl$_{(g)}$ (203.93 Torr; 1.09×10^{-5} mol cc^{-1}) and vinylacetylene$_{(g)}$ (198.03 Torr; 1.06×10^{-5} mol cc^{-1}) at 353 K in a Pyrex cell with sodium chloride windows on initial mixing and after ca. 20 h. The characteristic diagnostic peaks are: 2704.9–2699.7 cm^{-1} for hydrogen chloride; 1120.0–1053.0 cm^{-1} for vinylacetylene; ratio of the areas 1687.0–1531.0 cm^{-1} and 1120.0–1053.0 cm^{-1} for 2-chloro-1,3-butadiene (**B**); and ratio of the areas 2007.0–1910.0 cm^{-1} and 1120.0–1053.0 cm^{-1} for 4-chloro-1,2-butadiene (**A**).

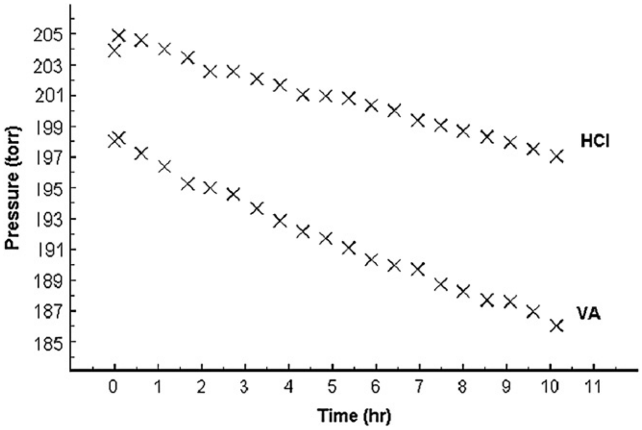


Figure 2. The disappearance (torr) of hydrogen chloride$_{(g)}$ and vinylacetylene$_{(g)}$ (**VA**) at 353 K as a function of time (h) in a Pyrex cell with sodium chloride windows. The initial mixture contained 203.93 Torr (1.09×10^{-5} mol cc^{-1}) HCl$_{(g)}$ and 198.03 Torr (1.06×10^{-5} mol cc^{-1}) vinylacetylene$_{(g)}$.

Plots of the disappearance of hydrogen chloride and vinylacetylene and the appearance of 2-chloro-1,3-butadiene and 4-chloro-1,2-butadiene, derived from a series of spectra intermediate to those represented by the spectra in Figure 1 (i.e., originally 203.93 Torr [1.09×10^{-5} mol cc^{-1}] in hydrogen chloride and 198.03 Torr [1.06×10^{-5} mol cc^{-1}] in vinylacetylene), are shown in Figures 2 and 3, respectively. Initial rates were determined from the initial slopes of these plots. Table 1S (Supplementary data) presents a portion of the large volume of typical initial rate data at 353 K that we have collected for the hydrogen chloride–vinylacetylene system

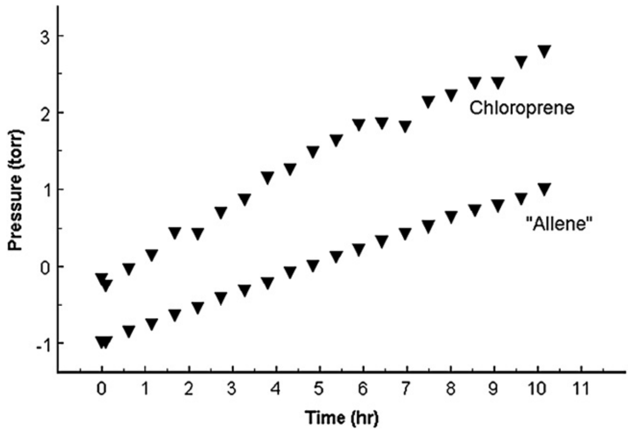


Figure 3. The appearance (torr) of 2-chloro-1,3-butadiene$_{(g)}$ (**chloroprene**) and 4-chloro-1,2-butadiene$_{(g)}$ (**allene**) at 353 K as a function of time (h) in a Pyrex cell with sodium chloride windows. The initial mixture contained 203.93 Torr (1.09×10^{-5} mol cc^{-1}) HCl$_{(g)}$ and 198.03 Torr (1.06×10^{-5} mol cc^{-1}) vinylacetylene$_{(g)}$.

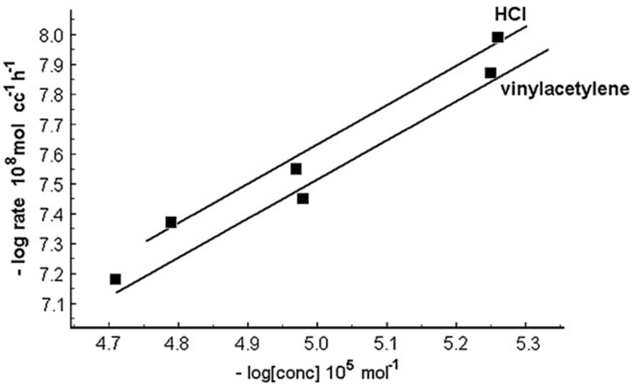


Figure 4. The variation in initial rates of the disappearance of $HCl_{(g)}$ with initial pressure of $HCl_{(g)}$ (correlation coefficient=0.989; $vinylacetylene_{(g)}$ held constant at 198.8±3.2 Torr [$1.07\pm0.03\times10^{-5}$ mol cc^{-1}]), and the disappearance of $vinylacetylene_{(g)}$ with the initial pressure of $vinylacetylene_{(g)}$ (correlation coefficient=0.946; $HCl_{(g)}$ held constant at 199.9±2.5 Torr, [$1.09\pm0.05\times10^{-5}$ mol cc^{-1}]). The data points are the average of at least three trials; initial rates at respective concentrations are within standard deviations of 0.03.

using various initial pressures of each gas.[11] The variations of initial rates of disappearance of hydrogen chloride ($-$d[HCl]/dt) with vinylacetylene held constant at 198.8±3.2 Torr [$1.07\pm0.03\times10^{-5}$ mol cc^{-1}] and the concentration of HCl varied and vinylacetylene ($-$d[vinylacetylene]/dt) with HCl held constant at 199.9±2.5 Torr [$1.09\pm0.05\times10^{-5}$ mol cc^{-1}] while vinylacetylene was varied, all at 353 K are shown in Figure 4. The slopes of these plots give reaction orders for the two gases of ca. 1.3 in HCl and ca. 1.3 in vinylacetylene, respectively.[12]

To evaluate the effects of the walls and added surface on the reaction rates, the surface area of the reaction vessel was varied by introduction of Pyrex fritted disks, as described previously.[13]

For initial pressures of HCl and vinylacetylene in the range of 1.0×10^{-5} mol cc^{-1} (ca. 200 Torr) and 5.0×10^{-6} mol cc^{-1} (ca. 100 Torr), respectfully, Figure 5 demonstrates that, at 353 K, the initial rate for the disappearance of HCl ($-$d[HCl]/dt) is proportional to the surface-to-volume ratio of the cell. The same relationship applies to the initial rates for the disappearance of vinylacetylene and appearance of both products. FTIR and GC analysis of the resulting product mixtures showed that increasing the surface-to-volume ratios caused the 2-chloro-1,3-butadiene and 4-chloro-1,2-butadiene to form in about a 3:2 ratio, respectively.

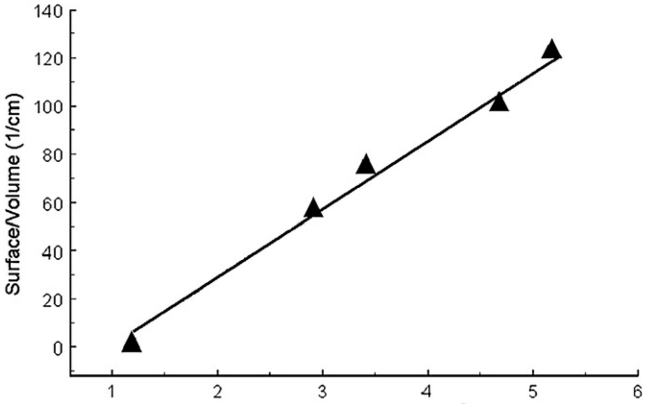


Figure 5. The variation in the initial rate (10^8 mol cc^{-1} h^{-1}) of disappearance of $HCl_{(g)}$ as a function of the surface-to-volume ratio (S/V, 1/cm) at 353 K. The initial concentrations of hydrogen chloride and vinylacetylene are in the range of 1.0×10^{-5} mol cc^{-1} (ca. 200 Torr) and 5.0×10^{-6} mol cc^{-1} (ca. 100 Torr), respectively. The data points are the average of at least two trials.

Table 2S (Supplementary data) presents some of the data for the same system in jacketed Pyrex cells initially containing 299.18±2.5 Torr (ca. 1.61×10^{-5} mol cc^{-1}) of hydrogen chloride and 198.83±3.4 Torr (ca. 1.06×10^{-5} mol cc^{-1}) of vinylacetylene at reaction temperatures of 298, 323 and 353 K. The overall rates for the disappearance of both reactants and for the appearance of the products exhibited only a very small temperature dependence. Over the limited temperature range examined, the disappearance of hydrogen chloride occurs with an apparent E_a of 4.75 kcal mol^{-1}, a $\Delta H^{\ddagger}_{298}$ of 4.15 kcal mol^{-1} and a $\Delta S^{\ddagger}_{298}$ of -36.5 eu, while the disappearance of vinylacetylene occurs with an apparent E_a of 4.56 kcal mol^{-1}, a $\Delta H^{\ddagger}_{298}$ of 3.97 kcal mol^{-1} and a $\Delta S^{\ddagger}_{298}$ of -39.2 eu. As it appears that the process we observe is surface-water-wall-catalyzed[14] (vide infra) the exact significance of these numbers is not clear, although they are suggestive of a highly ordered transition state.

2.1. Kinetic analysis

As has been pointed out before in a similar connection,[10b,d,e,13] reactions which are fractional order in one or more reactants,[15,16] and reactions which fail to show a normal temperature dependence,[17] are frequently found to be wall or surface catalyzed.[18]

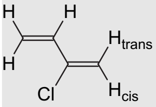
Although these criteria appear to apply here, our first analysis of the data began with our experimental observation that the reaction which is occurring is approximately 1.3 order in hydrogen chloride and about 1.3 order in vinylacetylene, as determined graphically (Fig. 4) that the reaction occurred between the gases, and that surface catalysis although involved might play only a small role.[19] An analysis of the data following the classical Langmuir–Hinshelwood mechanism[20] (where reaction occurs between two adsorbed species) and the Rideal–Eley mechanism[21] (for reaction between a strongly adsorbed species and a species in the gas phase) give rate laws proportional to the fraction of surface covered.[22,23] Additionally, it is possible for *more than one* surface process to be occurring[19] at the same time so as to account for the different products. All of these classical analyses failed to give reasonable results for a simple bimolecular process. The classical analyses are provided in Supplementary data.

2.2. Stereochemical studies

The stereochemistry of HCl addition to vinylacetylene to give 2-chloro-1,3-butadiene, one of the major products of both gas and aqueous phase reactions, was examined with the intent of determining if the overall addition process was supra- or antarafacial. The two protons on C(1) in 2-chloro-1,3-butadiene can be differentiated by ^{1}H NMR. In $^2HCCl_3$ solution, and for all monochlorinated alkenes reported (i.e., chloroethene,[24] (E)- and (Z)-2-chloro-2-butenes,[25] and (E)- and (Z)-3-chloro-2-pentenes[25]), the terminal proton on the same side of the double bond as the chlorine (cis- or Z-) is *always* further downfield than the proton on the opposite side (trans- or E-) of the double bond.[26] Further, the terminal proton on the *opposite* side of the double bond from the chlorine (trans- or E-) experiences an upfield shift (relative to the cis- or Z-proton) in perdeuteriobenzene solvent (compared to other solvents) because of an anisotropy induced by the aromatic ring.[25,27] The ^{1}H NMR spectra of 2-chloro-1,3-butadiene (ca. 2% in volume; 9.85 Torr) in $^2HCCl_3$, acetone-d_6, and benzene-d_6 were obtained; chemical shifts for the C(1) protons are given in Table 1. Thus, in different solvents the differences in the chemical shifts of C(1)-H trans to the chlorine are larger than those of the cis C(1)-H, confirming that the proton which is cis (or Z) to the chlorine is further downfield than the proton trans (or E) to the chlorine.

If the gases HCl and 4-deutero-1-butene-3-yne[28] ($H_2C{=}CH{-}C{\equiv}C[^2H_1]$) undergo reaction as anticipated on the basis of the

Table 1
A comparison of the chemical shifts for the C(1) protons of 2-chloro-1,3-butadiene in deuterated chloroform, acetone, and benzene

	Solvents			Differences	
	$^{2}HCCl_3$	Acetone-$^{2}H_6$	Benzene-$^{2}H_6$	$\Delta\delta$ ($^{2}HCCl_3$–benzene-$^{2}H_6$)	$\Delta\delta$ (acetone-$^{2}H_6$–benzene-$^{2}H_6$)
 H H H H_{trans} Cl H_{cis}	5.382	5.479	4.792	0.590	0.687
	5.416	5.582	5.058	0.358	0.524

reaction of HCl with the corresponding protio-compound, it should be possible to determine the sense of addition across the triple bond by observation of the chemical shift for the C(1) proton. Thus, equal amounts of $HCl_{(g)}$ and 4-deutero-1-butene-3-yne$_{(g)}$ (ca. 200 Torr; 1.06×10^{-5} mol cc^{-1}) were reacted in Pyrex vessels (room temperature, either 4 or 8 days; four trials each). ^{1}H NMR spectra ($^{2}HCCl_3$) of the reaction mixtures showed clearly distinguishable signals (δ 5.42; 5.38 relative to $^{2}HCCl_3$) for the C(1) proton of (*E*)- and (*Z*)-2-chloro-1-[$^{2}H_1$]-1,3-butadienes. Integration of these two signals gave about a 1:1 ratio of cis- to trans-adduct for this process. Because of the presence of deuterium on C(1) of 2-chloro-1,3-butadiene, the two C(1) proton signals were far more complicated than anticipated. In order to simplify these spectra, ^{2}H NMR of the reaction mixtures with ^{1}H decoupling and ^{13}C NMR with ^{1}H decoupling were attempted. However, neither deuterium nor ^{13}C coupled to deuterium were observed due to the very low concentrations of the 2-chloro-1,3-butadiene in the reaction mixtures.

Although possibly complicated by a kinetic isotope effect, it was anticipated that the process would also be confirmed by examination of the addition of $^{2}HCl_{(g)}$ to vinylacetylene$_{(g)}$. Investigation of the reaction between these gases (200 Torr each, respectively) at 353 K was also attempted.[29] But exchange between ^{2}HCl and ^{1}HCl frustrated the attempted analysis.

3. Conclusion from chemical studies

A simple analysis based on kinetic studies and product composition, leads to the conclusion that wall effects have intruded. Utilizing classical Langmuir–Hinshelwood[20] and Rideal–Eley[21] analyses and special cases of these mechanisms (Supplementary data) proved fruitless. Additionally, a computational search for a gas phase pathway at or near room temperature that would both fit the kinetics and product analysis also failed. Therefore, in concert with surface catalysis and given the recent work involving the role of water on surfaces,[14] a computational study considering reaction between surface-and-water associated reactants was next examined.

4. Computational results and discussion

4.1. Computational analysis

Computations were performed using the Gaussian 03 suite.[30] All structures were optimized for geometry using Becke's three-parameter functional[31] coupled with the correlation function of Lee et al.[32] (B3LYP) and the basis set 6-31+G(d). A comparison of bond distances calculated for the *endo* complex of HCl with vinylacetylene as defined by Legon et al.[7] employing B3LYP/6-31+G(d) with values reported for that same complex by Herrebout and van der Veken,[9] who had employed a more extensive basis set, indicated no significant loss in accuracy. Single point energies were obtained by the Moeller–Plesset method[33] at the MP2/6-311+G(d,p), for all structures. Frequency calculations were made in order to obtain zero point energies that were then used (unscaled) to correct the energies. Maxima corresponding to transition states were located using the transit guided quasi-Newton method (QST3).[34] A single imaginary frequency verified the saddle-point.

As pointed out in the thorough work of both Tang and Cui[8] and Herrebout and van der Veken,[9] the several possible complexes of vinylacetylene (VA) with HCl differ in (calculated) energies by less than 1 kcal mol^{-1} and the energies of complexation between the two reactants themselves are quite modest ($<$3 kcal mol^{-1}). In neither study, however, were the reactive consequences of the complexes adumbrated nor, indeed, is it apparent that the reaction was consummated.

Based on the kinetics (vide supra) we conclude that the reaction leading to product formation is not occurring directly in the gas phase from one of the complexes of HCl with VA.

We postulate that the reaction that is occurring (or reactions that are occurring as more than one process to yield the same or different products might be occurring simultaneously) involves a process or processes in which one or both reactants are surface associated. Aspects of these scenarios were computationally explored.

A surface site was modeled as a 1:1 complex of HCl with H_2O (Fig. 6) [MP2/6-311+G(2d,p)//B3LYP/6-31+G(d)].[35] When the previously modeled *endo* 1:1 complex of HCl with vinylacetylene[7] (Fig. 7) was allowed to contact the site shown in Figure 6, through association of its HCl-complexed-chlorine, a structure having geometry appropriate for a 1,4-addition was obtained. A representation for the conversion of the VA–HCl complex shown in Figure 7 to a site-associated complex with surface (water) associated HCl shown in Figure 6 is shown in Figure 8.

The addition process is essentially consummated as a highly organized (in accord with the experimentally determined large positive $\Delta S^{\ddagger}$) suprafacial-1,4-addition involving a 10-membered ring and a representation of that transition state leading to the appropriate product is shown in Figure 9 and in Scheme 1.

To obtain the 4-chloro-1,2-butadiene (Fig. 9) from this transition state it is clear that the proton at C_1 of the product is derived from the HCl of the initial VA–HCl complex whilst the chlorine, from that same HCl, abstracts the proton of the wall associated hydroxyl, the oxygen of which, in turn, is now protonated from the wall associated HCl and the chlorine from the latter adds to what will be C_4 of the 4-chloro-1,2-butadiene.

At this point the 4-chloro-1,2-butadiene can escape from the site-associated water–HCl. Figure 10 is a representation of the 4-chloro-1,2-butadiene product, produced as described above, and the remaining HCl–water complex.

Although (and in concert with the early work of Carothers et al.)[4] a reasonable pathway from vinylacetylene to 2-chloro-1,3-butadiene could not be found, it is clear that a transition state lying

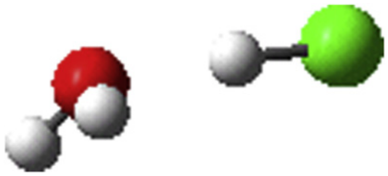


Figure 6. H_2O–HCl complex [MP2/6-311+G(2d,p)//B3LYP/6-31+G(d)].

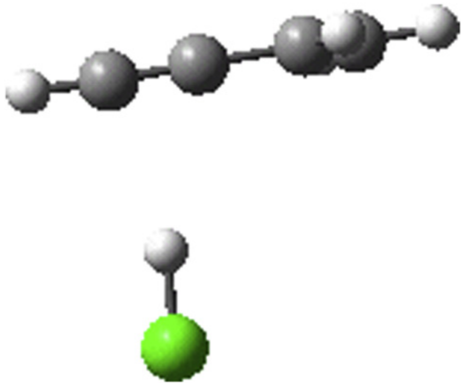


Figure 7. VA–HCl complex [MP2/6-311+G(2d,p)//B3LYP/6-31+G(d)].

below that for the 4-chloro-1,2-butadiene and linking the latter to the former exists! Thus, the transition structure shown in Figure 11 was readily located for rearrangement of the surface associated water–HCl and the not-yet-surface-dissociated allene shown in Figure 10. In this second reaction the chlorine at C_4 of the 1,2-diene becomes transferred to the surface site proton bonded to the water, while (no escape from the surface having occurred), the chlorine of what is the original HCl of the attacking 1:1 complex becomes attached to C2 of what was the allene. The double bond, formerly between C_2 and C_3, now lies between C_3 and C_4 (Fig. 12). This rearrangement process is also shown in Scheme 1 and appears to occur suprafacially as an eight-membered ring with *synfacial* stereochemistry. Diffusion of the 2-chloro-1,3-butadiene leaves the wall associated HCl–water complex available for the next HCl–vinylacetylene complex.

These processes can be envisioned as apparently representing yet another case, first outlined by Eigen,[36a] where protons are transferred while geometrical constraints are placed upon those atoms that are involved directly with the proton transfers.[36]

Table 2 provides the potential energies for the species presented in Figures 6–12 and Table 3 the corresponding thermochemistry data. The large positive $\Delta S^{\ddagger}$ is anticipated and mirrors the experimental results summarized above in Table 2S (Supplementary data). Scheme 2 provides a graphical representation of the process.

5. Conclusions

Gaseous mixtures of hydrogen chloride and vinylacetylene at total initial pressures $<$500 Torr and at temperatures between 298 K and 353 K react to yield mainly 4-chloro-1,2-butadiene and 2-chloro-1,3-butadiene. The process is accounted for by involving surface associated reactants where water plays a critical role. Kinetic measurements are in accord with a modified Langmuir–Hinshelwood mechanism that considers the hydrogen chloride adsorbed onto to a water-associated glass surface and surface reaction between that specie and a complex of the vinylacetylene with HCl. The outcome, requiring both water and surface, may rationalize the lack of any report of reaction between the observed gas phase 1:1 π-complex of HCl and vinylacetylene.

6. Experimental section

6.1. General

Hydrogen chloride (electronic grade) was obtained from Matheson Gas Products, Bridgeport, NJ. Deuterium chloride (99.7 atom % D) was obtained from Isotech, Inc., Miamisburg, OH. Freshly powdered potassium hydroxide was obtained from Fluka Chemical Corporation, Ronkonkoma, NY. 2-Chloro-1,3-butadiene (chloroprene) was generously provided by Central Research and

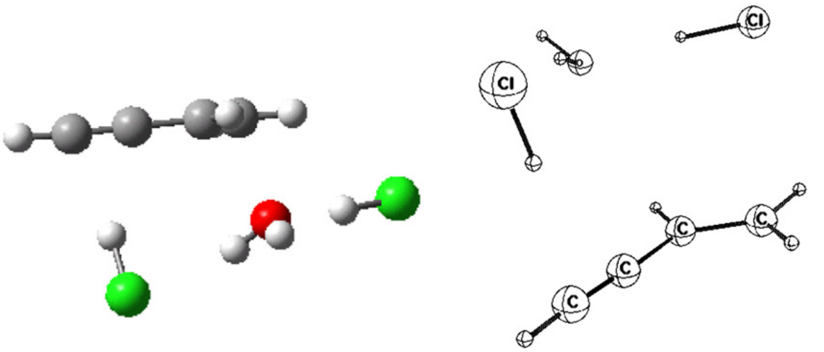


Figure 8. Representations of the approach of *endo*-complexed VA–HCl[9] to a potential active site-associated water–HCl complex that leads to the transition state shown in Figure 9. All minimized to the MP2/6-311+G(2d,p)//B3LYP/6-31+G(d) level.

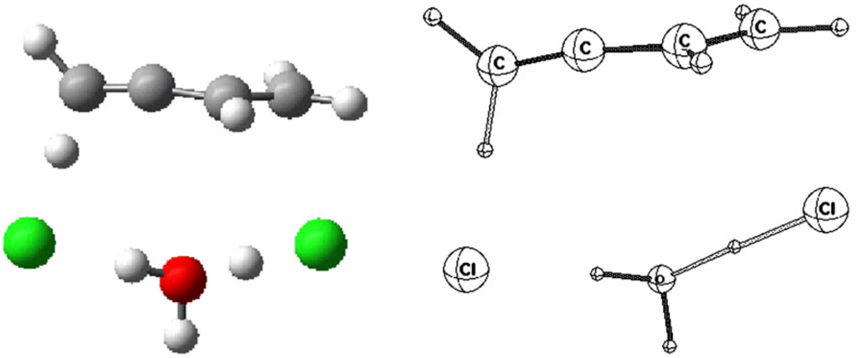
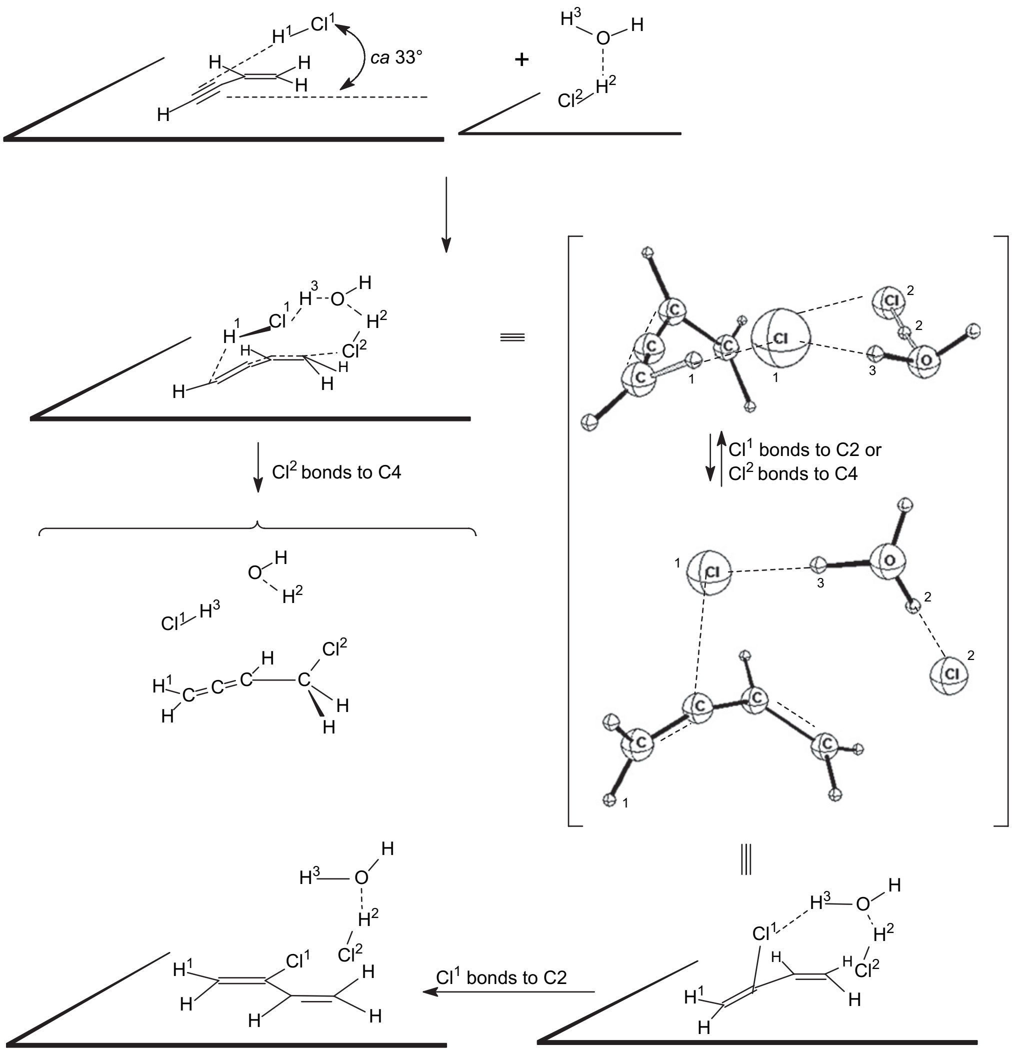


Figure 9. Representations of the transition state lying between the two-complex representation shown in Figure 8 and the product, 4-chloro-1,2-butadiene (Fig. 10). There is one imaginary frequency associated with the species. All minimized to the MP2/6-311+G(2d,p)//B3LYP/6-31+G(d) level.



Scheme 1. A cartoon representation of the surface (modeled here as water–HCl) catalyzed reaction between vinylacetylene and hydrogen chloride gases to yield 4-chloro-1,2-butadiene and 2-chloro-1,3-butadiene (chloroprene).

Development, E.I. du Pont de Nemours & Company, Wilmington, DE. All other materials were obtained from Aldrich Chemical Co., Milwaukee, WI, and used without further purification, except where otherwise noted. The hydrogen chloride and vinylacetylene were further purified using multiple trap-to-trap distillations (as previously described for other materials).[10] For hydrogen chloride, three distillations each from liquid nitrogen–pentane slush (143 K) and liquid nitrogen–ethanol slush (156 K) and a final sublimation from dry ice–2-propanol slush (195 K) to a liquid nitrogen trap (78 K) were sufficient. For vinylacetylene, three distillations each from liquid nitrogen–acetonitrile slush (232 K) and liquid nitrogen–carbon tetrachloride slush (250 K) and a final sublimation

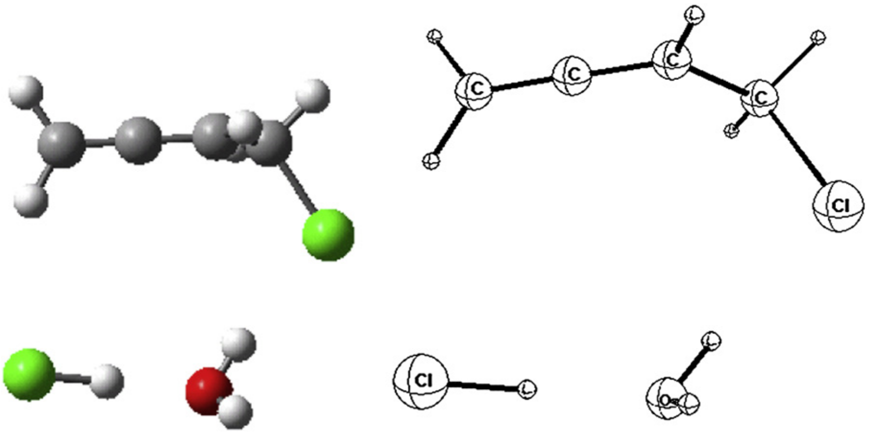


Figure 10. Representations of the product 4-chloro-1,2-butadiene as formed while associated with a (presumed surface) HCl–water complex. All minimized to the MP2/6-311+G(2d,p)//B3LYP/6-31+G(d) level.

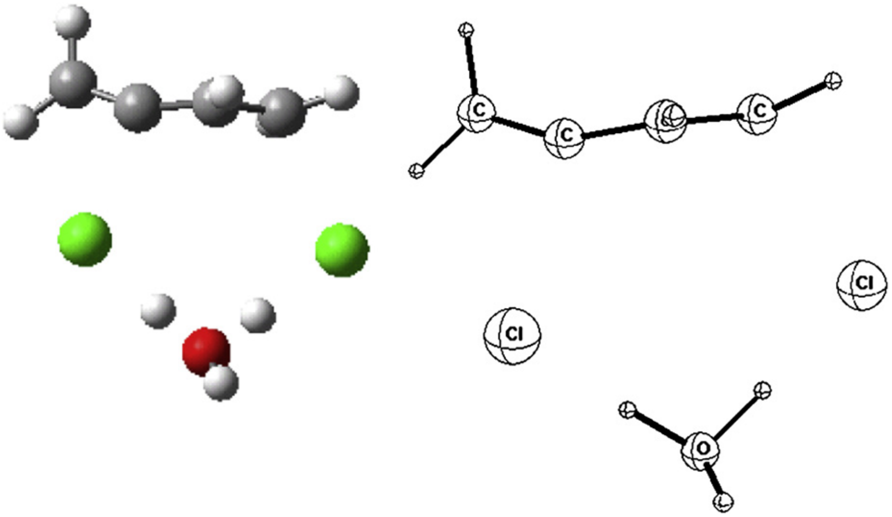


Figure 11. Representations of the TS lying between surface associated water–HCl and 4-chloro-1,2-butadiene and surface associated water–HCl and 2-chloro-1,3-butadiene. All minimized to the MP2/6-311+G(2d,p)//B3LYP/6-31+G(d) level.

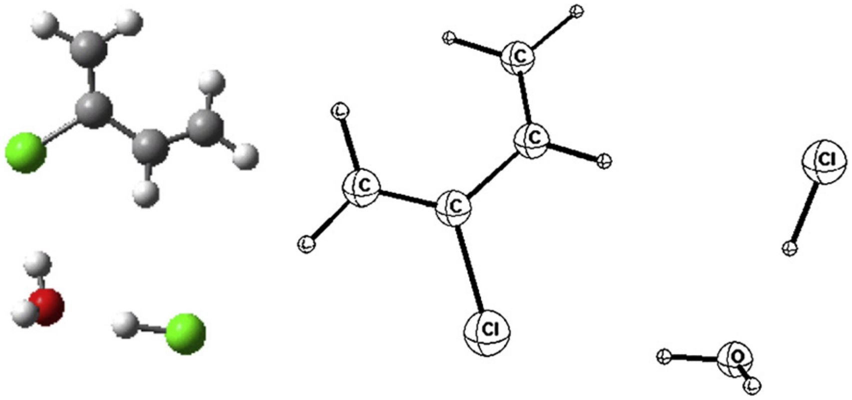


Figure 12. Representations of the product 2-chloro-1,3-butadiene as formed while associated with a (presumed surface) HCl–water complex. All minimized to the MP2/6–311+G(2d,p)//B3LYP/6-31+G(d) level.

Table 2
Potential energies corresponding to the species depicted in Figs. 6–12

Specie	B3LYP/6-31+G(d)		Mp2/6311+G(2d,p)//B3LYP/631+G(d)	
	zpe corrected E (hartrees)	Relative E (kcal mol^{-1})	zpe corrected E (hartrees)	Relative E (kcal mol^{-1})
H_2O–HCl (Fig. 6)	−537.200351		−536.533233	
HCl–H–C≡CCH=CH_2 (Fig. 7)	−615.476814		−614.662817	
(H_2O–HCl)+(HCl–H–C≡CCH=CH_2) association (Fig. 8)	−1152.682439	0.0	−1151.5065423	0.0
Transition state from [(H_2O–HCl)+(HCl–H–C≡CCH=CH_2)] association to 4-chloro-1,2-butadiene+(H_2O–HCl) (Fig. 9)	−1152.664527	11.2	−1151.013256	32.7
4-Chloro-1,2-butadiene+(H_2O–HCl) (Fig. 10)	−1152.709002	−16.7	−1151.076106	−6.7
Transition state from [4-chloro-1,2-butadiene+(H_2O–HCl)] association to 2-chloro-1,3-butadiene+(H_2O–HCl) (Fig. 11)	−1152.669639	8.0	−1151.022914	26.7
2-Chloro-1,3-butadiene+(H_2O–HCl) (Fig. 12)	−115.724537	−23.8	−1151.095166	−18.7

from ice water were used. The purified gases were stored in 5 L bulbs on a vacuum rack equipped with Teflon- and Kel-F-to-glass stopcocks, which were grease free. Vacuum (generated with a Precision rough pump and a Fisher oil diffusion pump) was monitored by a Pirani guage and pressure measurements were made using an MKS Baratron (1–1000 Torr) capacitance bridge manometer with a stainless steel diaphragm (linked to a digital VOM; 1 V=100 Torr). The manometer was calibrated by measuring the pressure of hydrogen chloride at various temperatures and by freezing known volumes of hydrogen chloride at measured pressures in the vacuum rack into excess standard potassium hydroxide solution and back titrating with standard acid.

FTIR spectra were obtained on a Digilab FTS-40 spectrometer. Peak absorbances and areas were measured using Digilab Quant32 software.

NMR spectra were obtained in $^2HCCl_3$, and were referenced to solvent peaks (i.e., 7.26 and 77.0 ppm for ^1H and ^{13}C, respectively). Solvents were typically degassed using three freeze-thaw cycles, the gas sample introduced onto the frozen (liquid N_2) solvent under vacuum, and the tubes sealed. Analytical gas chromatographic

Table 3

Thermochemistry corresponding to the species depicted in Figs. 6–12 and for other relevant species

Specie	H (hartrees)	G (hartrees)	S (eu)	Relative G (kcal mol^{-1})
H_2O–HCl (Fig. 6)	−537.194635	−537.226176	66.4	
HCl–H–C≡CCH=CH_2 (Fig. 7)	−615.468141	−615.511242	90.7	(−6.3)[a]
(H_2O–HCl)+(HCl–H–C≡CCH=CH_2) association (Fig. 8)	−1152.667796	−1152.727307	125.3	0.0
4-Chloro-1,2-butadiene+(H_2O–HCl) (Fig. 10)	−1152.696116	−1152.750862	115.2	−14.8
Transition state from [(H_2O–HCl)+(HCl–H–C≡CCH=CH_2)] association to 4-chloro-1,2-butadiene+(H_2O–HCl) (Fig. 9)	−1152.653013	−1152.703044	105.3	15.2
4-chloro-1,2-butadiene	−615.495924	−615.532511	77.0	(−4.9)[a]
Transition state from [4-chloro-1,2-butadiene+(H_2O–HCl)] association to 2-chloro-1,3-butadiene+(H_2O–HCl) (Fig. 11)	−1152.658847	−1152.706314	99.9	13.2
2-Chloro-1,3-butadiene+(H_2O–HCl) (Fig. 12)	−1152.708360	−1152.760314	109.8	−20.9
2-Chloro-1,3-butadiene	−615.510024	−615.545788	75.3	(−7.1)[a]

Transition state from [(H_2O–HCl)+(HCl–H–C≡CCH=CH_2)] association to 4-chloro-1,2-butadiene+(H_2O–HCl) (Fig. 9), ΔG=−14.8 kcal mol^{-1}, $\Delta G^{\ddagger}$=−14.8 kcal mol^{-1}.

Transition state from [4-chloro-1,2-butadiene+(H_2O–HCl)] association to 2-chloro-1,3-butadiene+(H_2O–HCl) (Fig. 11) ΔG=−6.1 kcal mol^{-1}, $\Delta G^{\ddagger}$=−28.0 kcal mol^{-1}.

[a] These values correspond to the computed differences between the species shown while associated with the surface site and unassociated from the site of reaction. The unassociated structures are favored.

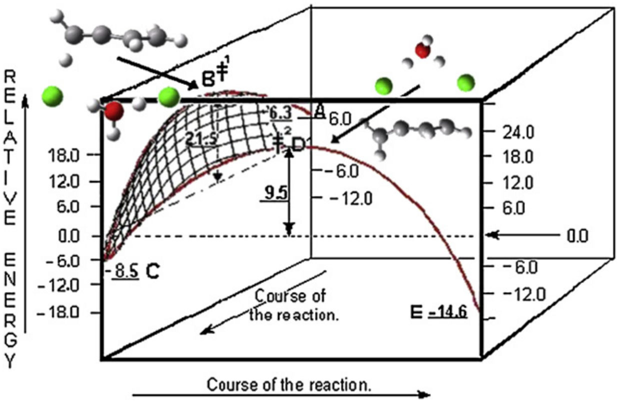
separations were performed on a gas chromatograph equipped with an FID detector, using helium as the carrier gas, on a 1/16″×3′ coiled glass column packed with 0.19% picric acid adsorbed on Carbopack C (Supelco, Inc., Bellefont, PA). At an injector temperature of 200 °C and a column temperature of 94 °C with the He carrier flow rate at 3 cm^3 min^{-1}, the retention times of vinylacetylene, 4-chloro-1,2-butadiene, and 2-chloro-1,3-butadiene were 0.25, 1.4 and 1.7 min, respectively. Alternatively, at an injector temperature of 150 °C and a column temperature of 70 °C with the flow rate of 2 cm^3 min^{-1}, the retention times of vinylacetylene, 4-chloro-1,2-butadiene, and 2-chloro-1,3-butadiene were 0.4, 3.5, and 4.9 min, respectively. Under these same conditions, the retention times of the (*Z*)- and (*E*)-1-chloro-1,3-butadienes were 6.2 and 7.6 min, respectively.

Preparative-scale separation of the product mixture from the reaction of vinylacetylene and HCl was accomplished using a chromatograph, equipped with a TC detector, on an $^1/_2$″×8′ glass column packed with 0.19% picric acid adsorbed on Carbopak C (Supelco). The injector temperature was held at 134 °C, the oven at 103 °C, and the TC detector at 149 °C. With a helium flow rate of 30 cm^3 min^{-1} the retention times of 4-chloro-1,2-butadiene, 2-chloro-1,3-butadiene, and the mixture of (*E*)- and (*Z*)-1-chloro-1,3-butadienes were 7.5, 10.5 and 13 min, respectively. These materials were collected individually at −78 °C in Pyrex tubes equipped with Kel-F stopcocks and a 10/30 standard taper joint suitable for attachment to the vacuum rack and transferred to the vacuum rack for further manipulation as described previously.[10]

Infrared cells were nominally 10.5 cm×18 mm Pyrex glass with Teflon-to-glass stopcocks between the cell and the standard taper joint for attachment to the vacuum rack. Jacketed cells for reactions at 323 K and 353 K, with water inlet and outlet tubulation, were constructed of the same material to the same basic design and were connected to an electrically heated, circulating water bath whose temperature was maintained within 0.5 °C of those reported. Polished sodium chloride windows, nominally 25×4 mm, were clamped in place over 2.5 mm thick KELREZ perfluoro elastomer gaskets (F&FP, Wilmington, DE).

The cells, without windows and Teflon stopcocks, were cycled through a glass annealing oven at 1040 F for 2 h (a process known[38] to be sufficient to remove even strongly adsorbed hydrogen chloride from silica surfaces) prior to assembling. After cooling in a desiccator, new windows were mounted, the Teflon stopcock inserted, and the cell attached to the vacuum rack. Pumping (10^{-5} Torr) with heating (ca. 200 °C with a hot-air blower) was carried out for 24 h prior to filling. Jacketed Pyrex cells for elevated temperatures were heated during evacuation on the vacuum rack by passing steam through the jacket for ca. 20 min. The following day the evacuated cell was pretreated first with small amounts (ca. 25–30 Torr) of hydrogen chloride for at least 3 h, evacuated for about 1 h, followed by pretreatment with a comparable amount of vinylacetylene for 3 h, and then re-evacuated overnight. Without this pretreatment high variability from cell to cell, even at identical starting pressures, was encountered.

Before beginning a reaction, a background spectrum of the pretreated cell was recorded. The cell was then filled to the desired pressure with vinylacetylene, the cell's stopcock closed, and the hydrogen chloride introduced by providing the appropriate overpressure in the vacuum rack, opening the stopcock for 10 s, and reclosing the stopcock to the cell. IR spectra were begun immediately and were taken (32 scans each) at frequent fixed-time intervals initially and, subsequently, at longer time intervals as the reaction proceeded. Depending upon the particular run, spectra were initially recorded every 10.0–60.0 min. As many as 40 spectra were obtained on each reaction mixture.



Scheme 2. A More O'Ferrall[37] type representation of the course of the conversion of the complex between water–HCl and vinylacetylene–HCl (point **A** and Fig. 8) over a transition state (‡^{1}, point **B** and Fig. 9) to yield 4-chloro-1,2-butadiene on a surface at which water–HCl remains (point **C** and Fig. 10). Then, rearrangement over a second transition state (‡^{2}, point **D** and Fig. 11) to yield 2-chloro-1,3-butadiene on a surface at which water–HCl remains (point **E** and Fig. 12). *Adddiitionally*, an alternative path involving slippage across from point **B** (‡^{1}) to point **D** (‡^{2}) and the reverse without escaping from the surface is available.

6.2. Spectroscopic analysis

Absorbance spectra (all 2 cm^{-1} resolution) were utilized throughout for analysis. Figure 1 represents typical FTIR absorbance spectra (32 scans) of the reaction mixture (at 353 K) originally containing 203.93 Torr (1.09×10^{-5} mol cc^{-1}) of gaseous hydrogen chloride and 198.03 Torr (1.06×10^{-5} mol cc^{-1}) of gaseous vinylacetylene immediately after mixing and after 20 h. The characteristic diagnostic peaks chosen for preparation of Beer's Law plots and subsequent analysis are 2704.9–2699.7 cm^{-1} for hydrogen chloride[11] and 1120.0–1053.0 cm^{-1} for vinylacetylene.[42] There are no peaks in the spectra of 2-chloro-1,3-butadiene and 4-chloro-1,2-butadiene (at 2 cm^{-1} resolution) between 4000 and 400 cm^{-1} that are uniquely suitable for analysis in a reaction mixture. That is, either they overlap with each other or they overlap with the vinylacetylene. To overcome this difficulty, a peak-ratio method involving vinylacetylene was used to analyze the reaction mixture. The integrated areas 2007.0–1910.0 cm^{-1} unique to 4-chloro-1,2-butadiene (Region A, Fig. 1), 1687.0–1531.0 cm^{-1} unique to 2-chloro-1,3-butadiene (Region B, Fig. 1) and the region 1120.0–1053.0 cm^{-1} for vinylacetylene (VA) at various pressures between 149.5 and 75.3 Torr were measured. As anticipated, at these reasonably low pressures (and thus suitable for initial rates), the ratio of the integrated areas for the above regions (A/VA and B/VA, Fig. 1) was constant over the pressure range studied. Thus, based on linear fitting of the equations of pressure against integrated area, the B/VA (in Fig. 1) ratio could be used to find the quantity of 2-chloro-1,3-butadiene formed (and vinylacetylene lost) while the ratio A/VA (in Fig. 1) provided the same information for 4-chloro-1,2-butadiene.

The infrared spectra of vinylacetylene,[39] 2-chloro-1,3-butadiene,[44] and 4-chloro-1,2-butadiene[43] have been reported. Our own IR results, in the gas phase, on the purified and separated products as described above, as well as the ^1H NMR[28,43] spectra (as dilute solutions in $^2HCCl_3$ at 500 MHz) are identical with those reported.

Although no peaks above background noise could be detected in the infrared spectra that might be attributed to substances other than those of the starting materials and products, on completion of the reactions both gaseous and condensed (liquid nitrogen) reaction mixtures were passed through the analytical gas chromatograph under the conditions specified above, and/or dissolved in $^2HCCl_3$ (degassed) to acquire ^1H NMR spectra. In addition to verifying the formation of 2-chloro-1,3-butadiene and 4-chloro-1,2-butadiene, GC analysis (FID detector) showed the presence of very small amounts of two other products, with retention times corresponding to *cis*- and *trans*-1-chloro-1,3-butadiene, respectively. However, the less sensitive ^1H NMR and FTIR failed to confirm these additional products.

6.2.1. 1-Butene-3-yne (vinylacetylene)

The procedure of Verkruijsse and Brandsma[39] was modified. A flame-dried 3-neck, 1 L round bottomed flask was equipped with a dropping funnel with gas inlet, a gas-tight mechanical stirrer and reflux condenser connected to two cold traps (−78 °C), terminating with a $CaCl_2$ drying tube and mineral oil bubbler. The entire apparatus was purged with argon. Mineral oil (bp ≈ 150 °C; 100 mL) was charged into the flask and stirring begun. Fresh,[40] powdered potassium hydroxide (117 g; 2.1 mol), Aliquat-336 (2.2 mL; 4.8 mmol), and pinacol (1.9 g; 16.6 mmol) were added to the flask and the mixture heated for 20 min in an oil bath (120 °C) under argon. *trans*-1,4-Dichloro-2-butene (98%; 25 g; 196 mmol) was added dropwise over 30 min with argon flowing slowly through the system. Following the addition, the temperature of the oil bath was gradually raised to 135 °C and stirring continued for another 1.5 h. Crude vinylacetylene (about 5 mL; colorless) was collected in the first cold trap, which was subsequently attached to the vacuum rack.

Three freeze-thaw cycles (−78 °C) were used to degas the crude vinylacetylene, and the resulting analytical gas chromatogram, under the above conditions, showed the presence of an impurity. Trap-to-trap distillations (−195 °C to −78 °C) under vacuum, monitored by GC, were used to purify the vinylacetylene. Both the ^1H and ^{13}C NMR spectra ($^2HCCl_3$) were acquired before and after the distillations. The crude material showed signals at δ 1.83 ppm (t, J=1.5 Hz) and δ 76.62 ppm in the ^1H and ^{13}C NMR, respectively, which disappeared on purification. ^1H NMR,[28] ^{13}C NMR,[41] and IR[42] spectra of the purified vinylacetylene were consistent with those reported earlier.

6.2.2. 4-Chloro-1,2-butadiene

The method of Carothers et al.[4] was modified. Purified vinylacetylene (0.877 g) and concentrated hydrochloric acid (3.07 mL) were mixed in a 15 mL round bottom flask fitted with a septum. The mixture was kept under a positive argon atmosphere in an ice-water bath and magnetically stirred for 7.5 h until the ratio of 4-chloro-1,2-butadiene to 2-chloro-1,3-butadiene began decreasing, as evidenced by GC under the above conditions. The lower aqueous layer was removed immediately with a syringe and the top layer was stored in dry ice overnight. A GC of the top layer showed three products in the ratio of 9:3.5:1. These components were separated using preparative GC, and were identified by comparisons with authentic samples using GC and IR, ^1H NMR and ^{13}C NMR spectroscopies as 4-chloro-1,2-butadiene,[43] 2-chloro-1,3-butadiene,[44] and *cis*-1-chloro-1,3-butadiene,[45] respectively. The *cis*-1-chloro-1,3-butadiene product was not reported by Carothers.[4]

6.2.3. 3-Chloro-1-butyne

The method of Jacobs et al.[46] was modified. The reaction flask, fitted with an addition funnel and condenser connected to a trap plus bubbler, was placed in an ice-water bath. Thionyl chloride (11.0 mL; 0.15 mol) and pyridine (1.04 mL; 0.013 mol) were mixed and stirred for 5 min. 3-Butyn-2-ol (10.0 g; 0.143 mol) was added dropwise over 40 min with stirring, stirred an additional 0.5 h at 0 °C, and then at room temperature for 2 h. The cold trap was kept at room temperature to allow sulfur dioxide (bp −10 °C) to escape. The reaction mixture was heated on a steam bath and 3-chloro-1-butyne gas collected in the cold trap (−78 °C). Analytical GC of the 3-chloro-1-butyne showed two components, which were characterized by ^1H NMR and IR as 3-chloro-1-butyne and 1-chloro-1,2-butadiene. ^1H NMR ($^2HCCl_3$) of the mixture showed signals consistent with 3-chloro-1-butyne at: δ 4.63 (1H, qd, J=6.9 Hz, J=2.7 Hz); 2.60 (1H, d, J=2.7 Hz); 1.77 (3H, dd, J=6.9 Hz, J=0.6 Hz); and signals consistent with 1-chloro-1,2-butadiene at: δ 5.99 (1H, m); 5.66 (1H, m); 1.80 (3H, ddd, J=7.5 Hz, J=2.4 Hz, J=0.6 Hz). IR (NaCl) of two component mixture, cm^{-1}: 3269, s; 2123, w; 1955, w; 1721, w; 1441, m; 1224, s.

6.2.4. cis- and trans-1-Chloro-1,3-butadienes

The method of Muskat and Northrup[45] was modified. Fresh,[40] powdered potassium hydroxide (78%; 50 g; 0.77 mol), mineral spirits (bp ≈ 150 °C; 50 mL) and *trans*-1,4-dichloro-2-butene (25 g; 0.20 mol) were mixed in a flask with a gas-tight mechanical stirrer and efficient condenser. A vigorous reaction occurred when the mixture was heated slowly to about 85 °C. After the reaction ceased, the condenser was changed to a distillation apparatus, the flask heated in an oil bath (150–190 °C) and the cis- and trans-products collected at 59–67 °C. GC analysis indicated that *cis*-1-chloro-1,3-butadiene, the major product, formed in a 6:1 ratio. When *cis*-1,4-dichloro-2-butene is the starting material, *trans*-1-chloro-1,3-butadiene is the major product, forming in an 11:1 ratio. All attempted separations of the *cis*- and *trans*-1-chloro-1,3-butadienes by preparative GC failed. IR[45] (NaCl) of the cis- and trans-mixture, cm^{-1}: 3321, s; 3121, m; 3105, m; 3036, m; 3029, m; 3019, m; 1863, m; 1830, m; 1646, m; 1636, m; 1607, m; 1588, m; 1430, m; 1418, m; 1334, m; 1323, m; 1298, w; 1282, w; 1261, wm; 1240, s; 1221, m; 996, m; 926, s; 849, m; 756, s; 637, s. ^1H NMR[25b] ($^2HCCl_3$) of the mixture showed signals consistent with *cis*-1-chloro-1,3-butadiene: δ 6.78 (1H, tt, J=10.5 Hz, J=17.1 Hz, J=10.5 Hz); 6.33 (1H, dd, J=10.5 Hz, J=7.2 Hz); 6.05 (1H, dm, J=7.2 Hz); 5.39 (1H, dm, J=17.4 Hz); 5.324 (1H, dm, J=10.2 Hz); and signals consistent with *trans*-1-chloro-1,3-butadiene: δ 6.35–6.29 (1H, m); 6/25 (1H, m, partial overlapping with the cis-isomer); 5.49 (1H, dd, J=17.3 Hz, J=10.8 Hz); 5.26 (1H, d, J=16.8 Hz); 5.15 (1H, d, J=10.2 Hz).

6.2.5. 4-Deutero-1-butene-3-yne (4-[$^2H_1$]-vinylacetylene)

The method of Tørneng et al.[42] was modified. All glassware was freshly annealed, cooled, and promptly assembled. A three-neck round bottomed flask was equipped with a jacketed cold well condenser (dry ice/acetone) connected to an oil bubbler, a septum cap and nitrogen inlet. Under a positive nitrogen pressure, freshly distilled THF (10 mL) and magnesium (2.03 g; 84.6 mmol) were introduced into the flask, with stirring, followed by injection of ethyl bromide (4 mL; 53.6 mmol). The reaction quickly occurred at room temperature. After additional ethyl bromide (2.32 mL; 31.1 mmol) was added dropwise, the oil bath temperature was raised to 60 °C to reflux the mixture. At the same time, purified vinylacetylene was transferred to an evacuated tube equipped with a Teflon stopcock and 10/30 joint. The vinylacetylene was placed in an ice-water bath, the stopcock removed and nitrogen quickly introduced through the 10/30 joint, and the stopcock opening capped with a septum containing a gas outlet needle and a Teflon cannula. Vinylacetylene was slowly introduced into the reaction flask through the cannula; a vigorous reaction immediately occurred. After the reaction subsided, the flask was cooled to room temperature and the dry ice/acetone condenser was replaced with a water condenser connected to a trap at −78 °C to collect the product. The nitrogen flow was reduced to about one bubble per second and D_2O (99.9%; 15.3 ml; 84.6 mmol) was added dropwise with a syringe. After the addition was completed the trap with the 4-deutero-1-butene-3-yne was connected to the vacuum rack and degassed using three freeze-thaw cycles. Both the ^{1}H NMR and the GC showed the presence of ethyl bromide and some low boiling impurity. Further purification was achieved by trap (−78 °C) to trap (liquid nitrogen) distillation, which was monitored by analytical GC and ^{1}H NMR. After discarding the low boiling impurity and the high boiling fraction containing water and ethyl bromide, the 4-deutero-1-butene-3-yne was stored in an evacuated 5 L bulb attached to the vacuum rack. Integration of the ^{1}H NMR showed that 90% of the vinylacetylene was deuterated. ^{1}H NMR[28] (^{2}HCCl$_3$): δ 5.83; 5.82; 5.80 (1H); 5.62 (1H, d, J=4.8 Hz); 5.59 (1H, d J=4.5 Hz). IR[42] (200 Torr) cm^{-1}: 2613.9; 2604.7; 2596.4; 2001.5; 1995.4; 1984.7.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.07.081.

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