soluble in water, the reaction mixture was poured into water 20 times the volume of the mixture after reaction; then 1–2 drops of 5 N HCl was added to precipitate the products. The precipitate was collected by filtration after several hours and analyzed.

(2) Effects of Mixed Solvents on the Synthesis of ZAPM. Z-L-aspartic anhydride and L-Phe-OMe were reacted in five kinds of mixed solvents (5% w/v): acetonitrile–Me_2SO, ethyl acetate–acetonitrile, ethyl acetate–acetic acid, acetonitrile–acetic acid, and Me_2SO–acetic acid, respectively, according to the procedures described above (1).

(3) Effects of Acids as Additives in Organic Solvents on the Synthesis of ZAPM. (a) Effects of a fixed amount of glacial acetic acid as additive: Equimolar amounts of Z-L-aspartic anhydride and L-Phe-OMe were reacted in various solvents (5% w/v) containing 5% v/v of glacial acetic acid at room temperature. The products were analyzed after 4 h.

(b) Effects of formic acid and trichloroacetic acid as additives: Equimolar amounts of Z-L-aspartic anhydride and L-Phe-OMe were reacted in acetonitrile containing different amounts of formic acid or trichloroacetic acid under the same conditions described in (a).

(4) Effects of Reactant Concentration on the Synthesis of ZAPM. The reactions proceeded in glacial acetic acid and Me_2SO at different concentrations of reactants. The products were analyzed after 4 h.

Registry No. α-ZAPM, 33605-72-0; β-ZAPM, 35739-01-6; L-Phe-OMe, 2577-90-4; aspartame, 22839-47-0; Z-L-aspartic anhydride, 4515-23-5; Z-L-aspartic acid, 1152-61-0; acetic acid, 64-19-7; formic acid, 64-18-6; trichloroacetic acid, 76-03-9.

Hydrochlorination of Alkenes. 3.[1] Reaction of the Gases Hydrogen Chloride and (*E*)- and (*Z*)-2-Butene

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Mixtures of the gases hydrogen chloride and (*E*)-2-butene, hydrogen chloride and (*Z*)-2-butene, and hydrogen chloride and (*Z*)-$[2,3\text{-}^2H_2]$-2-butene at total pressures up to 7 atm and temperatures between 283 and 313 K react to yield, exclusively, 2-chlorobutane (*erythro*- and *threo*-$[2,3\text{-}^2H_2]$-2-chlorobutane in the case of the labeled alkene). Kinetic measurements for the reactions of all three gaseous alkenes with gaseous hydrogen chloride have been made by infrared spectroscopy. Elimination studies were performed on the $[2,3\text{-}^2H_2]$-2-chlorobutane formed. It is concluded that surface catalysis is required for product formation and that surface adsorption of both hydrogen chloride and butene is required to consummate the reaction.

Somewhat more than five decades ago, Maass and his co-workers[3] attempted an extensive study of the interaction between hydrogen chloride and alkenes. Much of their work was done in the gas phase, and for the set of alkenes including propene and the butene isomers, they concluded, among other things, the following: (1) The gases 2-methylpropene (then called γ-butylene) and hydrogen chloride readily reacted to form 2-chloro-2-methylpropane at subatmospheric pressures. This reaction, which did not lend itself to easy interpretation, has been subsequently analyzed in some detail by others[1,4] and, under the conditions utilized by Maass et al., is clearly a surface-catalyzed process. (2) The gases α-butylene (1-butene), β-butylene (a mixture of (*E*)- and (*Z*)-2-butene), and propene failed to react with hydrogen chloride gas, even at long reaction times, under conditions similar to those lending success to the reaction of gaseous 2-methylpropene with gaseous hydrogen chloride.

Subsequently, we have reported[5] that gaseous 2-chloropropane does not form in the gas-phase reaction between the gases hydrogen chloride and propene at appreciable rates at total pressures of 1 atm or less (as Maass correctly observed). However, 2-chloropropane does form in this gas-phase reaction at higher pressures in a process first order in alkene and about third order in hydrogen chloride.

Furthermore, at pressures less than 1 atm, the gases 2-methylpropene and hydrogen chloride yield gaseous 2-chloro-2-methylpropane by a different pathway, i.e. a surface-catalyzed process involving strongly adsorbed hydrogen chloride and weakly adsorbed 2-methylpropene—a classical Rideal–Eley pathway.[1]

The observations made by Maass and his co-workers with regard to (*E*)- and (*Z*)-2-butene, despite what has subsequently been learned about propene[5] and 2-methylpropene,[1] remain of interest for the following reasons:

First, Poutsma[6] and others[7] have shown for electrophilic addition reactions in solution in nonpolar solvents, where open carbocations are not formed,[8] that the rates of reactions correlate with Taft's σ^* constants,[9] and thus "...no account need be taken of the *position* of the substituents, but only of their relative inductive electron-donating powers".[6] If, reasonably, carbocations are not involved in gas-phase addition reactions and, if perhaps not so rea-

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[1] Part 2: Costello, F.; Dalton, D. R.; Poole, J. A. *J. Phys. Chem.* **1986**, *90*, 5352.

[2] Taken, in part, from: Tierney, J. Ph.D. Dissertation, Temple University, 1980.

[3] Maass, O.; Coffin, C. C. *Can. J. Res.* **1930**, *3*, 526, 533 and references therein.

[4] (a) Brearley, D.; Kistiakowsky, G. B.; Stauffer, H. J. *J. Am. Chem. Soc.* **1936**, *58*, 43. (b) Kistiakowsky, G. B.; Stauffer, H. C. *Ibid* **1937**, *59*, 165.

[5] Haugh, M. J.; Dalton, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 5674.

[6] Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 4285.

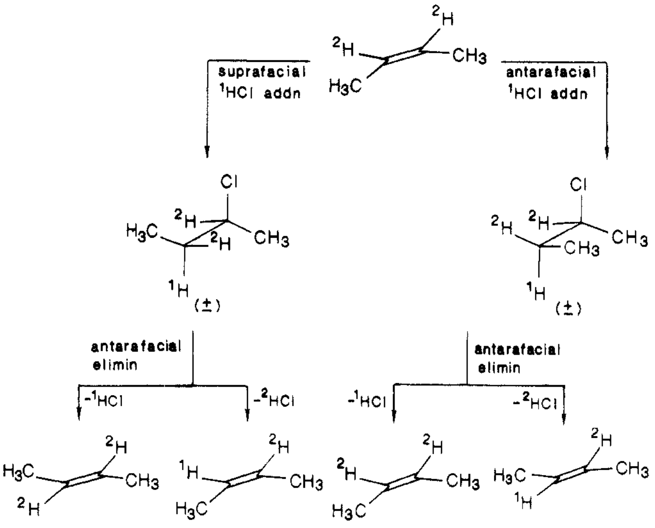
[7] Dubois, J. E.; Mouvier, G. *Tetrahedron Lett.* **1963**, 1325.

[8] Bartlett, P. B.; Sargent, G. D. *J. Am. Chem. Soc.* **1965**, *87*, 1297. (b) Poutsma, M. L. *Science (Washington, D.C.)* **1967**, *157*, 997.

[9] Taft, R. W., Jr. *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

0022-3263/86/1951-5191\$01.50/0

Scheme I. Expected Results of Suprafacial (Cis, Syn) and/or Antarafacial (Trans, Anti) Addition of ^{1}HCl to (Z)-[2,3-$^2H_2$]-2-Butene Followed by Antarafacial (Trans, Anti) Elimination of ^{1}HCl and HCl; Formation of [2,3-$^2H_2$]-1-Butene Not Shown



sonably, the reactions of the 2-butenes in the gas phase with hydrogen chloride bears some relation to typical electrophilic processes in nonpolar media,[10] then hydrogen chloride might be expected, a priori, to react at about the same rate and by a similar pathway with both 2-methylpropene and the (E)- and (Z)-2-butenes, but not as with propene. The experimental observations reported by Maass et al.[3] are insufficient to determine this. Indeed, their more qualitative data, that either the alkenes react or they do not, suggests one might conclude that the (E)- and (Z)-2-butene mixture (β-butylene) is closer in reactivity to propene than to 2-methylpropene. However, since it is now clear[5] (vide supra) that propene does react, albeit under more forcing conditions and by a different pathway than does 2-methylpropene, that conclusion may be unwarranted.

Second, it has been appreciated for some time that (Z)-2-butene is about 1 kcal mol^{-1} less stable than the E isomer.[11] Since both yield the same 2-chlorobutane product (perhaps, initially, depending on the path, as different rotomers), one might reasonably enquire, if reaction can be effected (and effected with sufficient accuracy and precision), whether this same difference is reflected in the rate-determining transition state for the reaction.

Thus, for both the reasons outlined above as well as to determine if, perhaps, yet another course, e.g. the bimolecular reverse of the unimolecular decomposition of 2-chlorobutane, might be taken, we began the investigation of the gas-phase reaction of hydrogen chloride with (E)- and (Z)-2-butene.

As a further probe to understanding and with the working hypothesis that the mechanism proposed for the addition of gaseous hydrogen chloride to propene[5] might also obtain for the (E)- and (Z)-2-butenes, we decided to examine the addition of hydrogen chloride to (Z)-[2,3-$^2H_2$]-2-butene (Scheme I). If the high-order pathway of hydrogen chloride dimer reacting with alkene–electrophile complex proposed for the gas-phase addition of hydrogen chloride to propene[5] is followed, then the elements of this electrophile will add across the double bond in the butene in a net suprafacial (syn, cis) fashion.[12] Thus, addition to (Z)-[2,3-$^2H_2$]-2-butene would produce a 1:1 mixture of (2R,3R)- and (2S,3S)- (i.e., erythro) [2,3-$^2H_2$]-2-chlorobutane. Base-catalyzed antarafacial (anti, trans) E_2 elimination from 2-halobutanes has been studied,[13] and if it can be brought about here, it is clear that (E)-[2,3-$^2H_2$]-2-butene for ^{1}H loss from C-3 and (Z)-[2-$^2H_1$]-2-butene for ^{2}H loss from C-3 of the labeled 2-chlorobutane should occur. Initial antarafacial (anti, trans) addition of hydrogen chloride, which is not consonant with the proposed mechanism for the gas-phase addition to propene, will give the opposite result on antarafacial elimination. Mixed results, e.g. some mono- and some dideuteriated (E)-alkene after elimination, are expected from mixed modes of addition whether in the gas phase or from surface-catalyzed product yielding addition process(es) involving chemisorbed species, where binding energies may be of the same order of magnitude as bond energies and surface chemisorbed or physically adsorbed species can react with each other and/or with gaseous partners.

Experimental Section

Addition Studies. Hydrogen chloride (electronic grade) was obtained from the Matheson Gas Co., East Rutherford, NJ. (E)-2-Butene (99.4%) and (Z)-2-butene (99.8%) were obtained from Phillips Petroleum Co., Borger, TX. (Z)-[2,3-$^2H_2$]-2-Butene (99%) was obtained from Kor Isotopes, Cambridge, MA. All gases were further purified as described earlier[5] and then stored in glass bulbs on a vacuum rack. Vacuum (generated with a Precision rough pump and a Fisher oil diffusion pump) was monitored by a Pirani guage, and pressure measurements were made by a Baratron (1–1000 torr) capacitance bridge manometer with a stainless-steel diaphragm (linked to a digital VOM; 1 V = 100 torr).

Infrared spectra were obtained on a Perkin-Elmer 225 grating spectrophotometer and mass spectra on a Hitachi Perkin-Elmer RMU6H spectrometer. Gas chromatographic separations were achieved on a Varian aerograph A90 P3 gas chromatograph, and packings used were ethylene glycol saturated with silver nitrate adsorbed onto Chromsorb W 60/80 mesh (butene from 2-chlorobutane) and 0.19% picric acid adsorbed onto Carbopack C (Supelco, Inc.). The second column separated 1-butene and (E)- and (Z)-2-butene.

The design of the static and variable-temperature infrared cells capable of holding gases at 7 atm pressure has been reported elsewhere.[14] Two different cell sizes were used. The static temperature cells, one whose volume was about 55 cm^3, had cylindrical potassium bromide windows 2.5 cm in diameter and 2.5 cm thick, and five other cells, whose volumes were about 10.5 cm^3, had cylindrical sodium chloride windows 1.0 cm in diameter and 2.5 cm thick. The variable-temperature cell, whose volume was about 10.5 cm^3, also had sodium chloride windows of the latter dimensions. Polished sodium chloride and sodium bromide windows of the dimensions given were fabricated by Harshaw Chemical Co., Solon, OH. The 55-cm^3 cell body and four of the 10.5-cm^3 cell bodies were constructed of Pyrex glass. The fifth 10.5-cm^3 cell body was constructed of Vycor glass and had a graded seal to Pyrex to facilitate sealing it off from the vacuum system. Gases were introduced by freezing out (liquid nitrogen) the appropriate quantities from the vacuum system into a finger on the bottom of the infrared cell. The cell was sealed, with the alkene

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[10] Mayo, F. R.; Katz, J. J. *J. Am. Chem. Soc.* **1947**, *69*, 1339.

[11] The E isomer is more stable than the Z isomer by $\Delta H_c° = 0.75 \pm 0.2$ kcal/mol (combustion) and $\Delta H_h° = 0.95 \pm 0.2$ kcal/mol (hydrogenation). See, respectively: Prosen, E. J.; Mason, F. W.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1951**, *46*, 806. Kistiakowsky, G. B.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1935**, *57*, 876.

[12] Suprafacial addition is also claimed for some solution reactions where kinetics are unavailable. See: (a) Dewar, M. J. S.; Fahey, R. C. *J. Am. Chem. Soc.* **1963**, *85*, 2245, 2248. (b) Bond, F. T. *Ibid.* **1968**, *90*, 5326. (c) Brown, H. C.; Liu, K.-T. *Ibid.* **1975**, *97*, 600. (d) Becker, K. B.; Grob, C. A. *Synthesis* **1973**, 789.

[13] (a) Saunders, W. H., Jr.; Fahrenholtz, S. R.; Caress, E. A.; Lowe, J. P.; Schreiber, M. *J. Am. Chem. Soc.* **1965**, *87*, 3401. (b) Skell, P. S.; Allen, R. G.; Helmkamp, G. K. *Ibid.* **1960**, *82*, 410.

[14] Tierney, J.; Dalton, D. R. *J. Chem. Educ.* **1981**, *58*, 513.

Table I. Summary of the Experimental Data Obtained by Following the Increase in the Area of the Carbon–Chlorine Stretching Frequency at 795 cm^{-1} Attending the Reaction of the Listed Gaseous 2-Butenes and Hydrogen Chloride[a]

	(*Z*)-2-butene		(*E*)-2-butene		(*Z*)-[2,3-$^2H_2$]-2-butene		
HCl pressure, atm	pressure, atm	rate (×10^7), mol/h	pressure, atm	rate (×10^7), mol/h	pressure atm	rate (×10^7), mol/h	temp, K (±0.3)
6.0	1.0	13.2 ± 8.0	1.0	12.6 ± 6.0			298.0
4.0	1.0	3.9 ± 0.3	1.0	3.9 ± 0.3	1	3.9 ± 0.3	298.0
3.0	1.0	2.5 ± 0.3	1.0	2.5 ± 0.3			298.0
2.0	1.0	1.7 ± 0.1	1.0	1.7 ± 0.1			298.0
1.0	1.0	0.50 ± 0.01	1.0	0.58 ± 0.01			298.0
4.0	0.75	3.8 ± 0.1		3.8 ± 0.1			298.0
4.0	0.50	3.8 ± 0.1		3.8 ± 0.1	0.50	3.8 ± 0.1	298.0
4.0	0.25	3.8 ± 0.1		3.8 ± 0.1			298.0
4.0	1.0	3.3 ± 0.3					283.0
4.0	1.0	20.0 ± 1.0					313.0

[a] The pressures listed are initial pressures. The values of at least three replications.

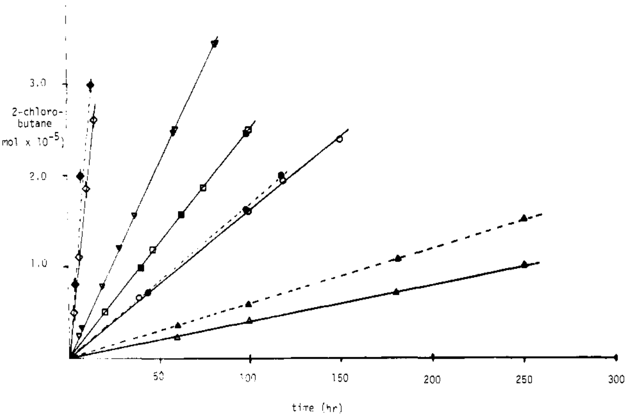

Figure 1. Increase in concentration of 2-chlorobutane from the reactions of the gases (*Z*)-2-butene and (*E*)-2-butene with hydrogen chloride gas. The open data point markings are for reactions with (*Z*)-2-butene; the closed data points and dotted lines are for reactions with (*E*)-2-butene. The alkene pressure was held constant at 1 atm throughout. The hydrogen chloride pressure was varied: 1 atm (▲, △); 2 atm (●, ○); 3 atm (■, □); 4 atm (▼, ▽); 6 atm, (◆, ◇).

and hydrogen chloride cofrozen, by torching it off under vacuum, and the gases were allowed to vaporize while warming to room temperature or the temperature at which the reaction was to be monitored. The jacketed variable-temperature cell was attached to a constant-temperature water bath regulated to ±0.1 °C. A Beer's law plot of 2-chlorobutane, utilizing two C–Cl stretching frequencies, i.e. 1240 and 795 cm^{-1}, was constructed to allow conversion of absorbance (or percent transmittance) to torr and mole.

Table I contains a summary of the kinetic data obtained for the reaction of hydrogen chloride with (*E*)-2-butene, (*Z*)-2-butene, and (*Z*)-[2,3-$^2H_2$]-2-butene. Each reaction was run a minimum of three times, and the data presented are an average (at 760 torr, probable error[15] R = ±4 torr) of all of those at the particular pressure shown. Figures 1–3 summarize those data in graph form.

In addition to the C–Cl stretching bands measured at 1240 and 795 cm^{-1}, a band at 1210 cm^{-1} was observed to grow in intensity at longer reaction times and higher pressures (with corresponding diminution of the C–Cl bands) when potassium bromide windows were utilized. This is attributed to formation of some alkyl bromide, and such samples were not considered in long kinetic runs except for initial kinetic data. With both potassium bromide and sodium chloride windows, a band at 2450 cm^{-1} was present at the higher pressures. Such absorption has been attributed to metal halide interaction with hydrogen chloride.[16]

Elimination Studies. The elimination of hydrogen chloride (and deuterium chloride) from [2,3-$^2H_2$]-2-chlorobutane was carried out directly on the product obtained from a kinetic experiment utilizing 4.0 atm of hydrogen chloride and 0.5 atm of (*Z*)-[2,3-$^2H_2$]-2-butene in one of the 10.5-cm^3 Pyrex cells described above. On completion of the reaction (IR), the contents were condensed into the finger of the cell with liquid nitrogen, the cell was dismantled, and the contents of the finger were slowly allowed to warm, first in a dry ice–acetone bath, then in an ice–water bath, and finally to room temperature. The contents of the opened cell

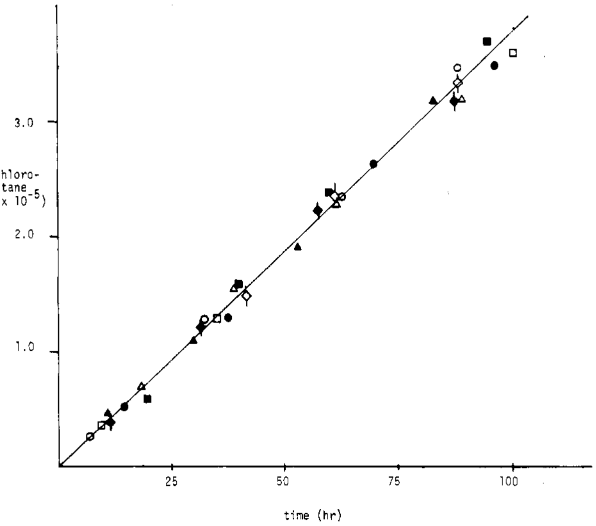

Figure 2. Increase in concentration of 2-chlorobutane from the reactions of the gases (*Z*)-2-butene and (*E*)-2-butene with hydrogen chloride gas. The open data points are for the reactions with (*Z*)-2-butene; the closed data points are for the reactions with (*E*)-2-butene. The hydrogen chloride pressure was held constant at 4 atm throughout. The alkene pressure was varied: 0.25 atm (◆, ◇); 0.50 atm (▲, △); 0.75 atm (■, □); 1 atm (●, ○).

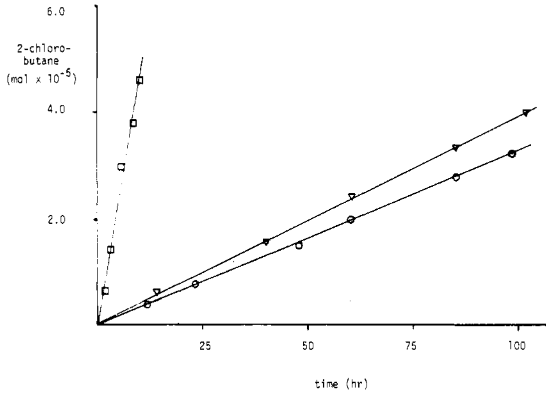

Figure 3. Increase in concentration of 2-chlorobutane from the reaction of the gases (*Z*)-2-butene and hydrogen chloride. The hydrogen chloride concentration was held constant at 4 atm and the (*Z*)-2-butene concentration held constant at 1 atm. The temperature was varied: +10.0 °C (○); +25.0 °C (△); +45 °C (□).

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[15] Daniels, F. *Mathematical Preparation for Physical Chemistry*; McGraw-Hill: New York, 1928; p 223.

[16] Smart, R. St. C.; Sheppard, N. *Proc. R. Soc. London, Ser. A* 1971, *A320*, 417.

were washed from the finger into a vial with 1.0 cm^3 of dichloromethane (in two portions), and the combined dichloromethane washings were injected directly into the gas chromatograph ($^1/_4$ in. × 6 ft coiled glass column packed with silver nitrate saturated ethylene glycol on Chromsorb W 60/80 mesh; column temperature 45 °C; He flow rate 2 $cm^3\ s^{-1}$; TC detector current 150 mA; retention time of 2-chlorobutane 3.5 min; at a column temperature of 30 °C, retention time of 2-chlorobutane 7.5 min). The 2-chlorobutane was collected in a capillary U-tube cooled in liquid nitrogen distal to the thermal conductivity detector. This material, in a capillary tube, was treated with 0.3 cm^3 of a solution of sodium ethoxide in ethanol, freshly prepared by dissolution of 156 mg of sodium in 2.0 cm^3 of absolute ethanol, the capillary tube sealed, and the reaction mixture heated in an oven at 100 °C for 0.5 h.[17] After cooling to room temperature, the reaction mixture was allowed to stand for 10 h, the solids formed were centrifuged to one end, the tube was opened, and the liquid contents were injected directly into the gas chromatograph ($^1/_4$ in. × 6 ft coiled glass column packed with 0.19% picric acid on Carbopac C; column temperature 45 °C; He flow rate 2 $cm^3\ s^{-1}$; TC detector current, 150 mA; retention time of 1-butene 7.0 min, (*Z*)-2-butene 9.5 min, (*E*)-2-butene 11.5 min). Fractions were collected as above. Repeated runs yielded 34.0 ± 1% 1-Butene and 66 ± 2% 2-butenes (39.3 ± 1% (*E*)-2-butene and 26.7 ± 1% (*Z*)-2-butene; *E*:*Z* = 1.5).

A similarly sized sample (1.0 mg, 1×10^{-5} mol) of unlabeled 2-chlorobutane was subjected to identical treatment with similar results, i.e. 24.5 ± 1% 1-butene and 75.5 ± 2% 2-butenes (56.5 ± 1% (*E*)-2-butene and 19.0 ± 1% (*Z*)-2-butene; *E*:*Z* = 3.0).

The individually *collected* (*E*)- and (*Z*)-alkenes were subjected to mass spectrometric analysis and compared to the undeuterated alkenes and to starting (*Z*)-[2,3-$^2H_2$]-2-butene. Because of the limited amounts of material available and the relatively insensitive mass spectrometer, analysis was limited to comparison of parent species (i.e., m/z of M^+ and $M^+ - 1$). For (*E*)- and (*Z*)-2-butene (purified commerical) the M^+ to ($M^+ - 1$) ratio of fragments at m/z 56 and 55 mass units, respectively, was 2.1. For (*Z*)-[2,3-$^2H_2$]-2-butene (purified commercial) the M^+ to ($M^+ - 1$) ratio of fragments at m/z 58 and 57 mass units, respectively, was 2.3. For (*Z*)-2-butene obtained from the elimination reaction described above the M^+ to ($M^+ - 1$) ratio at m/z 58 and and 57 was 1.8 while for (*E*)-2-butene obtained from the same reaction the M^+ to ($M^+ - 1$) ratio at m/z 58 and 57 was 0.4.

Discussion

The results summarized in Table I were obtained by observing the increase in concentration of gaseous 2-chlorobutane with time. Plots of that increase (expressed as mole of product) vs. time are shown in Figures 1–3.

As seen in Figures 1 and 2, the rate of formation of product is not diminished as the starting material is consumed. Additionally, from Figure 1, where the data for that series of reactions run where the alkene pressure is held constant at 1 atm and the pressure of hydrogen chloride is varied from 1 to 6 atm, there is a steady decrease in rate with falling hydrogen chloride pressure. Both (*E*)- and (*Z*)-2-butene react at about the same rate although the *E* isomer appears to react slightly faster than the *Z* isomer at the lowest pressure. Over the pressure range examined, the rate dependence is roughly proportional to $[HCl]^{1.8}$.

From Figure 2, where the hydrogen chloride concentration is held constant at 4 atm and the alkene (both (*Z*)- and (*E*)-2-butene) concentration is varied from 0.25 to 1 atm, there is apparent zeroth-order dependence on alkene concentration.

The appearance of fractional orders when the concentration of one of the reactants is increased while the other is held constant,[18] the lack of significant diminution of the rate as the starting material is consumed,[19] and demonstration of zeroth-order dependence on one or more of the reactants,[19] all of which are noted above, are among the criteria used to establish the presence of a catalyst. In this vein, the size of the cell (10.5 cm^3 vs. 55 cm^3) and the cell material (Pyrex vs. Vycor) did not appear to affect the rate of the reaction. However, the cell window material was important, as the reaction was faster with potassium bromide than with sodium chloride windows. Indeed, at the higher pressures, with potassium bromide windows, fogging of the windows was significant and a new band (at 1210 cm^{-1}) attributed to carbon–bromine-containing product(s) was in evidence. This band rapidly grew, while the corresponding C–Cl bands diminished, as the reaction progressed. A band at about 2450 cm^{-1} was also present at the higher pressures of hydrogen chloride with both sodium chloride and potassium bromide windows. Hydrogen halide–alkali earth metal–halide complexes are reported to absorb in this region.[16]

As shown in Figure 3, the reaction between (*Z*)-2-butene and hydrogen chloride gases possesses a normal temperature dependence. This is in contrast to the reaction between the gases hydrogen chloride and propene where an inverse temperature dependence was seen.[5] In the usual fashion[20] these data allow calculation of apparent values of $E_a = 10.4$ kcal mol^{-1}, $A = 2.0 \pm 0.1 \times 10^6$, $\Delta H^{\ddagger} = -9.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -73.6$ cal deg^{-1}. The apparent large negative entropy of activation suggests that a complex transition state may be involved. However, since further analysis of the data, vide infra, suggests that product forms with surface catalysis or in a process where two steps have comparable kinetics, the detailed significance of these values is obscure.

As with the formation of gaseous 2-chloro-2-methylpropane from the gases 2-methylpropene and hydrogen chloride,[1] we consider the case where both hydrogen chloride and (*Z*)- (or (*E*)-) 2-butene are competitively adsorbed on the surface(s) (eq 1 and 2). We assume here,

$$\mathrm{HCl(g) + S \underset{k_r}{\overset{k_f}{\rightleftarrows}} HCl{\cdot}S} \qquad (1)$$

$$(Z)\text{-}/(E)\text{-}\mathrm{CH_3CH{=}CHCH_3(g) + S \underset{k_r'}{\overset{k_f'}{\rightleftarrows}}}\ (Z)\text{-}/(E)\text{-}\mathrm{CH_3CH{=}CHCH_3{\cdot}S} \qquad (2)$$

$$(Z)\text{-}/(E)\text{-}\mathrm{CH_3CH{=}CHCH_3{\cdot}S + HCl{\cdot}S \xrightarrow{k_s} CH_3CH(Cl)CH_2CH_3{\cdot}S} \qquad (3)$$

$$\mathrm{CH_3CH(Cl)CH_2CH_3{\cdot}S \xrightarrow{k_d} CH_3CH(Cl)CH_2CH_3(g) + S} \qquad (4)$$

as before (and most generally), that the adsorption need not necessarily be to the same extent or in the same way for both gases; i.e., while one may be chemisorbed (held more tightly), the other may be only physically adsorbed (held less tightly). We further assume that the adsorbed species react to generate, on the surface, 2-chlorobutane (eq 3), which in a subsequent step (eq 4) is desorbed. If it is assumed that the rate-controlling step occurs prior to desorption, then the separate step for desorption is indistinguishable from desorption occurring simultaneously with product formation.

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[17] These elimination conditions, at which we arrived after extensive investigation, were designed to ensure complete conversion of chloroalkane to alkene mixture.

[18] (a) Moore, W. J. *Physical Chemistry*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1962; p 305. (b) Pease, E. N. *J. Am. Chem. Soc.* **1923**, *45*, 1196. (c) Bond, G. C.; Wells, P. B. *J. Catal.* **1965**, *4*, 211.

[19] See Reference 18a, p 306 ff.

[20] Zuman, P.; Patel, R. C. *Techniques in Organic Reaction Kinetics*; Wiley-Interscience: New York, 1984; p 192 ff.

Table II. Comparison of Observed and Calculated Rates[a]

pressure, atm			$(P_{HCl}^0 P_{ene}^0/\text{rate})^{1/2}$			
HCl	(*Z*)-2-butene	obsd rate, mol/h	obsd	calcd (eq 10)	calcd (eq 11)	calcd (eq 14)
4.0	0.25	3.8×10^{-7}	1.62×10^3	1.76×10^3	2.35×10^3	1.64×10^3
4.0	0.50	3.8×10^{-7}	2.29×10^3	2.15×10^3	3.32×10^3	2.29×10^3
4.0	0.75	3.8×10^{-7}	2.81×10^3	2.55×10^3	4.07×10^3	2.73×10^3
1.0	1.0	5.0×10^{-8}	4.47×10^3	4.14×10^3	2.35×10^3	6.09×10^3
2.0	1.0	1.7×10^{-7}	3.42×10^3	3.74×10^3	3.32×10^3	4.26×10^3
3.0	1.0	2.5×10^{-7}	3.46×10^3	3.34×10^3	4.07×10^3	3.54×10^3
4.0	1.0	3.9×10^{-7}	3.24×10^3	2.94×10^4	4.70×10^3	3.09×10^3
6.0	1.0	1.3×10^{-6}	2.14×10^3	2.14×10^3	5.76×10^3	2.50×10^3

[a] The calculated rates assume (using eq 10) a Rideal–Eley type process, (using eq 11) generalized surface catalysis, or (using eq 14) a very unlikely homogeneous-phase high-order process. Equation 14 is empirically derived from the experimental data.

The rate for the surface reaction may be written in terms of the Langmuir–Henschlwood isotherm[21] (eq 5), where

$$\text{rate} = k_s \Theta_{HCl} \Theta_{ene} \qquad (5)$$

k_s is the rate constant for the surface reaction and Θ_{HCl} and Θ_{ene} are, respectively, the fractions of active surface sites covered by hydrogen chloride and 2-butene. Expansion of the isotherm expression for the surface coverages of the two gases is then given by eq 6 and 7,[22] where K_{HCl} and

$$\Theta_{HCl} = (K_{HCl}P_{HCl})/(1 + K_{HCl}P_{HCl} + K_{ene}P_{ene}) \qquad (6)$$

$$\Theta_{ene} = (K_{ene}P_{ene})/(1 + K_{HCl}P_{HCl} + K_{ene}P_{ene}) \qquad (7)$$

K_{ene} are, respectively, the adsorption coefficients (i.e., the ratios of the effective rate constants for adsorption and desorption) for hydrogen chloride and 2-butene. P_{HCl} and P_{ene} are their respective pressures. Thus, in terms of initial rates and pressures

$$\text{rate} = \frac{k_s K_{HCl} K_{ene} P_{ene}^0 P_{HCl}^0}{(1 + K_{HCl}P_{HCl}^0 + K_{ene}P_{ene}^0)^2} \qquad (8)$$

or

$$\frac{P_{ene}^0 P_{HCl}^0}{\text{rate}} = \frac{(1 + K_{HCl}P_{HCl}^0 + K_{ene}P_{ene}^0)^2}{k_s K_{HCl} K_{ene}} \qquad (9)$$

As noted before[1,22] this expression may be rewritten as

$$y = C_1 + C_2 P_{ene}^0 + C_3 P_{HCl}^0 \qquad (10)$$

where $y = (P_{ene}^0 P_{HCl}^0/\text{rate})^{1/2}$, $C_1 = (k_s K_{ene} K_{HCl})^{-1/2}$, $C_2 = (K_{ene}/k_s K_{HCl})^{1/2}$, and $C_3 = (K_{HCl}/k_s K_{ene})^{1/2}$ and, for the various conditions of P_{ene}^0 and P_{HCl}^0 expressed in Table I, the values of C_1, C_2, and C_3 minimizing the sums of the squares of the residuals can be evaluated.[1,23] As expected from the data, the values ($C_1 = 2.91 \times 10^3$, $C_2 = 1.74 \times 10^3$, $C_3 = -3.99 \times 10^2$, probable error[15] $R = \pm 6 \times 10^1$) are essentially the same for both butenes, and their use in eq 10 leads to the comparison shown in Table II.[23]

Also shown in Table II are the values for $(P_{ene}^0 P_{HCl}^0/\text{rate})^{1/2}$ evaluated for the simpler expression of eq 11.

$$\text{rate} = k P_{ene}^0 P_{HCl}^0 \qquad (11)$$

It has been pointed out[24] that, in addition to eq 3, the rate-determining step of the Rideal–Eley process, there are two other general surface-catalyzed processes associated with the expression of eq 11 that in the context of these experiments can be expressed as eq 12 and 13.

$$\text{HCl·S} + (Z)/(E)\text{-CH}_3\text{CH=CHCH}_3(\text{g}) \rightarrow \text{CH}_3\text{CH(Cl)CH}_2\text{CH}_3\text{·S} \qquad (12)$$

$$2(\text{HCl·S}) + (Z)/(E)\text{-CH}_3\text{CH=CHCH}_3(\text{g}) \rightarrow \text{CH}_3\text{CH(Cl)CH}_2\text{CH}_3\text{·S} \qquad (13)$$

Our present data do not allow differentiation between any of these three pathways.

Finally, in this regard, also shown in Table II, for purposes of comparison, is a similar evaluation of the fit to the data obtained by use of eq 14 [where $k_1 = (2.3 \pm 0.1)$

$$\text{rate} = k_1(P_{HCl}^0)^2 + k_2(P_{HCl}^0)^2(P_{ene}^0)^2 \qquad (14)$$

$\times 10^{-8}$ and $k_2 = (3.5 \pm 0.1) \times 10^{-9}$] computed empirically as a best fit expression. Such a formulation explicitly ignores the catalytic effects of surface(s) and demands *two* processes, i.e. one a function of $(P_{HCl}^0)^2$ and the other a function of $(P_{HCl}^0)^2(P_{ene}^0)^2$, yield product. We believe this very unlikely and suggest that, under the conditions examined, the product is formed in a surface-catalyzed process.[24,25]

The results of the reaction between the gases hydrogen chloride and (*Z*)-[2,3-$^2H_2$]-2-butene followed by treatment with sodium ethoxide in ethanol to effect elimination of ^{1}HCl and/or ^{2}HCl are also in concert with a surface-catalyzed process. Thus, in comparison of the elimination of ^{1}HCl with ^{2}HCl from the chlorobutane formed in the reaction and the elimination of ^{1}HCl from purified commercially available unlabeled chlorobutane, it is clear that to the extent product ratios reflect transition-state geometries there is at least a deuterium isotope effect of 2 in the elimination from the labeled materials. This effect is predominately seen in the formation of the (*E*)-2-butene (which is retarded), suggesting that deuterium rather than protium loss is occurring in formation of this isomer. Further, the mass spectrometric data, from which it can be deduced that the (*E*)-2-butene is mostly monodeuteriated (ca. 80%) while the (*Z*)-2-butene is mostly dideuteriated (ca. 80%), supports this conclusion since, as pointed out earlier, suprafacial addition of ^{1}HCl to (*Z*)-[2,3-$^2H_2$]-2-butene followed by antarafacial elimination of ^{1}HCl yields (*E*)-[2,3-$^2H_2$]-2-butene and antarafacial elimination of ^{2}HCl yields (*Z*)-[2-$^2H_1$]-2-butene. Thus, to the extent the elimination of ^{1}HCl and/or ^{2}HCl is antarafacial, only a small amount of the expected isomers is obtained and it follows that the addition of hydrogen chloride cannot, for the most part, be suprafacial, i.e. mixed addition modes, about 20% suprafacial and 80% antarafacial, obtain. This mixed pathway is consonant with both hydrogen chloride and alkene gases being adsorbed, certainly

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[21] Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361.

[22] Butt, J. B. *Reaction Kinetics and Reactor Design*; Prentice-Hall: Englewood Cliffs, NJ, 1980; p 143 ff.

[23] Presumably, negative values for any of the coefficients indicate that the expressions for which they stand are likely to be further from equilibrium than the coefficients with positive values. However, as it is the *square* of the coefficients required for evaluation of eq 11, it is their magnitude that is of primary importance.

[24] Szabo, G.; Kallo, D. *Contact Catalysis*; Elsevier: Amsterdam, 1976; p 500.

[25] Rideal, E. K. *Proc. Camb. Phil. Soc.* **1939**, *35*, 130.

to different extents and in different ways, on window and cell materials, and then combining to provide product.

Conclusion

At total pressures between 2 and 7 atm and temperatures between 283 and 313 K, the gaseous isomeric (*Z*)- and (*E*)-2-butenes react with hydrogen chloride gas to produce gaseous 2-chlorobutane. The addition of hydrogen chloride to the alkene, monitored by infrared spectroscopy, appears to be independent of the geometry of the alkene, mostly antarafacial across the double bond, and a surface-catalyzed process.

Registry No. (*E*)-2-Butene, 624-64-6; (*Z*)-2-butene, 590-18-1; 2-chlorobutane, 78-86-4; D_2, 7782-39-0.

Aryl Arylazo Sulfones Chemistry. 2. Reactivity toward Alkaline Alkane- and Areneselenolate and Alkane- and Arenetellurolate Anions

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Tolyl arylazo sulfones react with various alkyl- and arylseleno reagents to produce substituted alkyl aryl and unsymmetrical diaryl selenides. The corresponding tellurides can also be obtained. Isolated yields in both cases are good. This procedure is an interesting alternative to the classical Sandmeyer reaction.

Aryl arylazo sulfones have been studied from the point of view of their thermal and photochemical stability.[1] Only a few reports have been published about their chemical reactivity.[2]

Very recently, we described the reaction of various arylazo *p*-tolyl sulfones toward the iodide anion, leading, in acetonitrile solution, to the corresponding iodoarenes.[3] That method competes effectively with the one using iodine and arene diazonium tetrafluoroborates[4] or the other conventional methods using potassium iodide aqueous solutions.

The synthesis of alkyl (or aryl) phenyl selenides as well as their corresponding telluro derivatives is of increasing interest.[5]

Recently, Petrillo et al.[6] reported an easy preparation of symmetrical and unsymmetrical diaryl sulfides from arenethiolates and arenediazonium tetrafluoroborates.

Here, we want to disclose new information about the reactivity of arylazo *p*-tolyl sulfones toward alkaline alkane- and areneselenolate or alkane- and arenetellurolate anions.

Results and Discussion

The addition of sodium or lithium methaneselenolate anion (1 equiv), at room temperature to a solution in acetonitrile, of various arylazo *p*-tolyl sulfones **2a–h** in the presence of a catalytic amount of 18-crown-6 (method C), leads to the formation of the corresponding aryl methyl selenides **3a–h** with isolated yields ranging from 38% to 59% (Scheme I; Table I, entries 6–13).

Table I. Reaction of Alkaline Alkane- and Areneselenolate Anion with Aryl *p*-Tolylazo Sulfones 2a–m

	aryl *p*-tolylazo sulfones				yield of **3**, **4**, or **5**[c] from **2**, %
entry	2	Y	nucleophilic species	exptl cond[a,b]	
1	**a**	2-$COOCH_3$	CH_3SeLi	A	0[d]
2	**a**	2-$COOCH_3$	CH_3SeLi	B	5
3	**a**	2-$COOCH_3$	CH_3SeLi	C	52 (28)
4	**a**	2-$COOCH_3$	CH_3SeLi	D	38
5	**a**	2-$COOCH_3$	CH_3SeNa	D	25
6	**a**	2-$COOCH_3$	CH_3SeNa	C	54
7	**b**	H	CH_3SeNa	C	56 (32)
8	**c**	3-$COOC_2H_5$	CH_3SeNa	C	58 (30)
9	**d**	4-$COOC_2H_5$	CH_3SeNa	C	59 (48)
10	**e**	3-Cl	CH_3SeNa	C	54 (22)
11	**f**	3,5-Cl_2	CH_3SeNa	C	48 (38)
12	**g**	4-NO_2	CH_3SeNa	C	56 (32)
13	**h**	3,5-$(OCH_3)_2$	CH_3SeNa	C	52 (35)
14	**a**	2-$COOCH_3$	*n*-C_4H_9SeLi	A	0
15	**a**	2-$COOCH_3$	*n*-C_4H_9SeLi	C	55 (51)
16	**b**	H	*n*-C_4H_9SeLi	C	50 (38)
17	**e**	3-Cl	*n*-C_4H_9SeLi	C	43 (32)
18	**g**	4-NO_2	*n*-C_4H_9SeLi	C	46 (29)
19	**h**	3,5-$(OCH_3)_2$	*n*-C_4H_9SeLi	C	46 (26)
20	**i**	2-Cl	*n*-C_4H_9SeLi	C	42 (37)
21	**j**	2-CN	*n*-C_4H_9SeLi	C	48 (43)
22	**k**	2-OCH_3	*n*-C_4H_9SeLi	C	42 (37)
23	**b**	H	C_6H_5SeLi	C	70
24	**e**	3-Cl	C_6H_5SeLi	C	37
25	**g**	4-NO_2	C_6H_5SeLi	C	53
26	**l**	2-NO_2	C_6H_5SeLi	C	48
27	**m**	4-I	C_6H_5SeLi	C	10[e]

[a] All experiments are realized in the presence of a catalytic amount of 18-crown-6. [b] A: in tetrahydrofuran solution, room temperature or reflux, 1 equiv of nucleophile. B: in tetrahydrofuran–CH_3CN (50:50) solution, room temperature, 1 equiv of nucleophile. C: in CH_3CN solution, room temperature, 1 equiv of nucleophile. D: same as in C but with 2 equiv of nucleophile. [c] Isolated. The corresponding yield is given in parentheses when the tetrafluoroborate method is used. [d] When heating, methyl benzoate is obtained (35%). [e] 1,4-$(C_6H_5Se)_2C_6H_4$ is isolated (21%) as the major product.

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