4-Cyanobiphenyl: identified by GC–MS; mass (EI), *m/e* 180 (20), 179 (100), 178 (25), 151 (20), 121 (11), 76 (19); (CI, NH_3) 197 (M + 18) (100), 179 (M) 32.

1,4-Diphenylbutane (which is the dimer of styrene): NMR ($CDCl_3$, TMS) δ 1.60 (m, 4 H, CH_2), 2.6 (m, 4 H, CH_2), 7.0–7.7 (m, 10 H, aromatics).

4-(2-Phenylethyl)benzonitrile (5a).

4,4′-Dicyanobiphenyl: identical (HPLC, GC) with an commercial sample (Lancaster Synthesis); mass (EI), *m/e* 205 (20), 204 (100), 178 (5), 150 (7), 102 (8).

4-Aminobenzonitrile: NMR ($CDCl_3$, TMS) δ 4.25 (s, 2 H, displaced by D_2O, NH_2), 6.55, 6.67, 7.34, 7.46 (AA′BB′, 4 H, aromatics); mass (EI) *m/e* 118 (M) (100), 91 (33), 64 (25); (CI, NH_3) 136 (M + 18) (100), 119 (M + 1) (22), 118 (M) (10).

An isomer of $C_6H_5CH_2CH_2CH_2CH(C_6H_4CN)C_6H_5$: mass (CI, NH_3), *m/e* 329 (M + 18), 311 (M).

An isomer of $C_6H_5CH_2CH_2CH(C_6H_5)CH_2CH(C_6H_5)CH_6H_4CN$: mass (CI, NH_3) 433 (M + 18) (20), 415 M (15).

Other unidentified products.

Electrolysis of 4-Chlorobenzonitrile in Liquid Ammonia in the Presence of Catalyst (4,4′-Bipyridine, 10^{-2} M) (Experiment 2). The procedure was the same as above. Beyond the products described in Table I, the following product was indentified in one of the chromatographic fractions from its mass spectrum. $C_6H_5CH_2CH_2CH(C_6H_5)CHOHC_6H_4CN$: *m/e* 327 (56), 222 (24), 130 (100), 105 (97), 102 (85).

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Surface-Catalyzed Hydrochlorination of Alkenes.[1] The Reaction of the Gases Hydrogen Chloride and 1,3-Butadiene

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Mixtures of gaseous hydrogen chloride and gaseous 1,3-butadiene at total pressures less than 1 atm and at temperatures between 294 and 334 K yield mixtures of 3-chloro-1-butene and (*E*)- and (*Z*)-1-chloro-2-butene. The ratio of the product of putative 1,2-addition to those of 1,4-addition is approximately unity with only the amount of (*Z*)-1-chloro-2-butene increasing from ca. 2% of the total reaction product mixture at the lower temperature to ca. 4% at the higher temperature. Kinetic measurements have been made by observing the reaction throughout its course utilizing FT-IR spectroscopy. It is concluded that surface catalysis is required for product formation and that the reaction, which occurs at the walls, is most probably between multilayer adsorbed hydrogen chloride and gaseous or weakly adsorbed 1,3-butadiene.

Introduction

More than five decades ago, Kharasch, Kritchevsky, and Mayo[5] reported on the successful addition of hydrogen chloride to 1,3-butadiene in the absence of solvent at −80 °C and in glacial acetic acid at room temperature; the addition failed to occur in ether. Their analysis, by index of refraction (and distillation), demonstrated that, under the specified conditions for the reaction to occur and *at both temperatures*, the addition yielded 75–80% 3-chloro-1-butene (1) [called "secondary chloride"] and 20–25% 1-chloro-2-butene [called "crotyl chloride"]. Subsequent observation revealed "...that the equilibrium at room temperature in the presence of a trace of ferric chloride is a mixture *containing 50% of each of the chlorides* [emphasis added] ..." but "...in the presence of one mole of hydrogen chloride, the equilibrium mixture contains 70–75% of crotyl and 25–30% of secondary chloride, irrespective of the presence or absence of a trace of ferric chloride (although the ferric chloride has a great influence on the rate of isomerization)".

With greater or lesser fidelity to the original work[5] the passage of time has seen the information incorporated into the paradigm of "kinetic versus thermodynamic control" of organic reactions and inserted as such into recent texts.[6] The interesting questions concerning the geometry of the crotyl chloride (*E* and/or *Z*) initially formed and/or after equilibration, the identity of the "kinetic" product ratio at −80 °C and room temperature, and the failure of the addition reaction when attempted in ether as the solvent have apparently not been addressed.

The apparent gas-phase addition of hydrogen chloride to alkenes has been a subject of interest for many years.[7] Recently, the process, at modest pressures, has been shown to involve surface catalysis,[8] and surface-catalyzed reactions of hydrogen chloride are now thought to be integral to an understanding of aspects of the chemistry of the earth's atmosphere.[9]

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(2) Taken, in part, from Chi, Hongji, MA Dissertation, Temple University, 1989.

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(5) Kharasch, M. S.; Kritchevsky, J.; Mayo, F. R. *J. Org. Chem.* **1937**, *2*, 489.

(6) The following list, while incomplete, is provided as representative and inclusion of, or failure to list, a work should not be taken as significant. (a) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell: Ithaca, 1953; p 657. (b) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 683. (c) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*, 2nd ed.; Benjamin: Menlo Park, 1977; pp 490 and 542. (d) Pine, S. H.; Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*, 4th ed.; McGraw-Hill: New York, 1980; p 567. (e) Louden, G. M. *Organic Chemistry*; Addison-Wesley: Reading, 1983; p 535. (f) Vollhard, K. P. C. *Organic Chemistry*; Freeman: New York, 1987; p 579. (g) Solomons, T. W. G. *Organic Chemistry*, 4th ed.; Wiley: New York, 1988; p 467.

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(9) See, e.g.: (a) Seinfeld, J. H. *Science* **1989**, *243*, 745 and references therein. (b) McElroy, M. B. *Science* **1989**, *243*, 763 and references therein.

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Our interest in the reaction between hydrogen chloride and 1,3-butadiene derives, as did our earlier work on propene,[8a] 2-methylpropene,[8b] and the isomers of 2-butene,[8c] from a desire to understand electrophilic addition. Based on our earlier work, we expected that (a) we would fail to observe an uncatalyzed reaction between 1,3-butadiene and hydrogen chloride gases (which, had it occurred, might correspond, microscopically, to the reverse of the unimolecular thermal elimination of hydrogen chloride from the corresponding chloroalkanes[10a,b]), (b) the reaction between hydrogen chloride and 1,3-butadiene gases would afford the same products as those found in solution (but perhaps in different ratios), and (c) the disappearance of the starting materials and the formation of products should occur at rates which might be amenable to kinetic analysis.

In the event, our expectations were fulfilled and the disappearance of the starting materials [hydrogen chloride and 1,3-butadiene] and the appearance of products [3-chloro-1-butene (1) and (*E*)- and (*Z*)-1-chloro-2-butene (2 and 3, respectively)] were conveniently monitored by IR spectroscopy.

Experimental Section

Hydrogen chloride (Electronic grade) and 1,3-butadiene (C. P. grade) were obtained from Matheson Gas Products, Bridgeport, NJ. 3-Chloro-1-butene (96%) was obtained from Pfaltz and Bauer, Inc., Waterbury, CT, and 1-chloro-2-butene [crotyl chloride (70%)] from Aldrich Chemical Co., Milwaukee, WI. The hydrogen chloride and butadiene were further purified as described earlier[8] using multiple distillations. 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) were sufficient. For 1,3-butadiene, three distillations each from dry ice–2-propanol slush (195 K) and dry ice–chloroform slush (210 K) and a final sublimation from ice water (273 K) were sufficient. The purified gas were stored in glass 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 gauge 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.

Infrared spectra were obtained on a Digilab FTS-40 Fourier Transform infrared spectrophotometer. Analytical gas chromatographic separations were performed on a Perkin-Elmer 3920B gas chromatograph equipped with an FID detector, using helium as the carrier gas, on a 3 ft × $^{1}/_{16}$ in. coiled glass column packed with 0.19% picric acid adsorbed on Carbopack C (Supelco, Inc., Bellefont, PA). The retention times of 3-chloro-1-butene (**1**), (*Z*)-1-chloro-2-butene (**3**), and (*E*)-1-chloro-2-butene (**2**) at an injector temperature of 250 °C and a column temperature of 90 °C with the flow rate at 3 $\mathrm{cm^3\ min^{-1}}$ were 1.4, 1.9, and 2.2 min, respectively.

Preparative-scale separation of the chlorobutene isomers from commercially obtained material was accomplished using a Varex PSGC 10-40 chromatograph, equipped with a TC detector, on a 3 ft × $^{1}/_{4}$ in. glass column packed with 0.19% picric acid on Carbopack C at an injector temperature of 110 °C, a column temperature of 60 °C, and with a helium flow rate of 30 $\mathrm{cm^3\ min^{-1}}$. Under these conditions, the retention times of 1, 3, and 2 were 0.3, 0.85, and 0.93 min, respectively. Samples were collected at 98 K in capillary U tubes, equipped with a stopcock and a 10/30 standard taper joint suitable for attachment to the vacuum rack.

Infrared cells were nominally 10 cm × 18 mm Pyrex glass with Teflon-to-glass stopcocks. Jacketed cells for variable-temperature work, with water inlet and outlet tubulation, were constructed of the same material and were connected to an electrically heated water bath whose temperature was maintained within 0.5 °C of those reported with an S-7555 Thermoregulator (Forma Scientific Co., Marietta, OH). Polished sodium chloride windows (ICL, Garfield, NJ) were nominally 25 × 4 mm and were attached to the cells with Glyptal (Glyptal, Inc., Chelsea, MD). Infrared cells of high density polyethylene (Almac Products, Philadelphia, PA) and Teflon (Commercial Plastics, Inc., Philadelphia, PA) were prepared by boring a 2-cm diameter hole down the center of a 5-cm diameter (10 cm long) rod of the specified material. Windows (as specified above) were clamped in place over 2.5 mm thick KELREZ perfluoro elastomer gaskets (F&FP, Wilmington, DE) and attachment to the vacuum rack was accomplished by threading a Teflon-to-glass stopcock into an appropriately bored hole half-way along the length of the cell. Both cells were cleaned with aqua regia, rinsed exhaustively with distilled water, and oven-dried at 50 °C, the windows were mounted, and the assembled cell was pumped on at ca. 10^{-5} Torr without further heating for 24 h prior to filling.

Two series of reactions were run in the Pyrex cells, series A and series B. In series A reactions, the cell, without windows and Teflon stopcock, was cycled through a glass annealing oven at 560 °C for 2 h (a process known[11] to be sufficient to remove even strongly adsorbed hydrogen chloride from silica surfaces). After cooling, new windows were attached with Glyptal (with oven heating at 130 °C and subsequent cooling in a dessicator over anhydrous calcium sulfate), the Teflon stopcock was inserted, and the cell was attached to the vacuum rack. Pumping (10^{-5} Torr) with occasional heating (ca. 200 °C with a hot-air blower) was carried out for 24 h prior to filling. Immediately before filling to the desired pressures with hydrogen chloride and 1,3-butadiene, the cooled, evacuated cell was treated, separately, with small amounts (ca. 20–30 Torr) of each of the reactants separately for at least 3 h, followed by reevacuation of the cell. Without this pretreatment, high variability from cell to cell, even at identical starting pressures, was encountered. After obtaining a background spectrum, the cell was filled to the desired pressure with the reactant whose concentration was to be lowest, the cell was closed, and the second reactant was 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 intervals initially and, subsequently, at 5-h intervals for the total times specified.

The individually purified products at concentrations approximating those produced in the reaction were, in separate experiments, allowed to stand in series A type cells for 1 week both in the absence and presence of HCl(g). No isomerization, diminution in concentration, or other change was observed.

Jacketed Pyrex cells for variable temperature work were treated in the same fashion except that heating during evacuation on the vacuum rack was accomplished by passing steam through the jacket.

In series B reactions, cells in which a reaction had been completed were evacuated (ca. 10^{-5} Torr) with continuous pumping and occasional heating—at about 200 °C—for at least 1 week prior to being refilled. They were *not* dismantled and cycled through the annealing oven, and the used windows were left in place.

Spectroscopic Analysis. Although absorbance spectra (all at 2 $\mathrm{cm^{-1}}$ resolution) were utilized throughout for analysis, transmittance spectra (obtained from the absorbance spectra) were prepared for comparison to those reported for 3-chloro-1-butene (1),[12a] (*E*)-1-chloro-2-butene (2),[12b,c] and (*Z*)-1-chloro-2-butene (3).[12c] The gas-phase spectra of these materials, while generally sharper than those in the liquid phase,[12] corresponded in detail.

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Table I[a]

reaction number	$P°_{HCl}$, Torr	$P°_{butadiene}$, Torr	[HCl], 10^4 mol	[butadiene], 10^4 mol	rate° = −d[HCl]/d*t*, 10^6 mol h^{-1}	rate° = +d[products]/d*t*, 10^7 mol h^{-1}	product composition, % 1	2	3
1	294.4	135.3	4.48	2.06	5.00	18.4	50.5	47.1	2.1
2	305.2	138.0	4.78	1.97	4.41	18.9	49.3	48.4	2.2
3	152.6	131.7	2.29	1.98	1.33	5.97	45.5	51.6	2.8
4	153.8	140.3	2.39	2.27	0.87	6.19	41.8	55.1	3.0
5	83.7	129.0	1.19	1.77	0.30	1.10	37.7	58.5	3.8
6	85.6	130.6	1.28	1.85	0.43	1.35	37.1	58.1	4.8
7	136.8	66.1	2.07	0.82	0.80	3.87	43.2	53.8	3.0
8	138.7	67.5	2.13	0.88	0.70	4.51	45.7	50.9	3.3
9	176.9	299.2	2.61	4.55	2.11	8.45	48.3	49.5	2.1
10	175.3	265.9	2.65	4.05	2.40	6.92	49.2	48.3	2.4
11	200.0	96.4	3.17	1.52	0.79	5.46	50.0	47.5	2.5
12	108.2	95.9	1.69	1.48	0.13	1.07	45.6	50.5	3.9
13	53.8	95.9	0.83	1.48	0.073	0.31	45.0	50.0	5.0

[a] Initial rate constants (rate°) for the disappearance of HCl(g) and the appearance of gaseous products 1, 2, and 3 (and the product composition) at 90 h for the reaction between 1,3-butadiene(g) and HCl(g) in annealing-oven-treated Pyrex IR cells with sodium chloride windows. Most data is expressed as the average of at least three replications. The numbers are considered accurate to ±0.1 Torr.

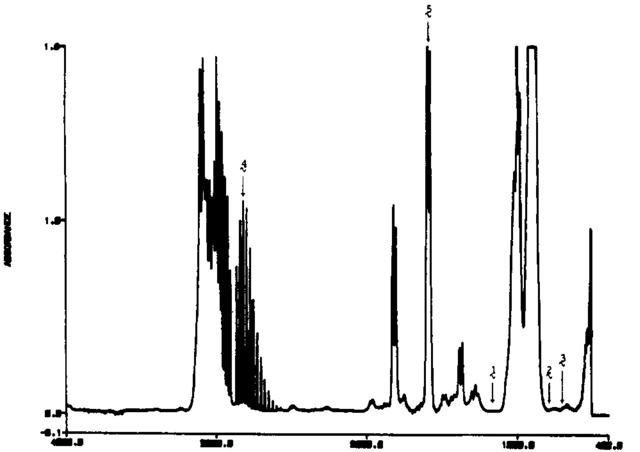

Figure 1. The FT-IR absorbance spectrum (at 2 cm^{-1} resolution) of a mixture of HCl(g) (294.4 Torr) and 1,3-butadiene(g) (135.3 Torr) in an annealing-oven-treated Pyrex cell with sodium chloride windows on initial mixing. The characteristic diagnostic peaks are 2672.50–2689.50 cm^{-1} for hydrogen chloride (4); 1570.50–1617.00 cm^{-1} for 1,3-butadiene (5); 1138.00–1197.50 cm^{-1} for 3-chloro-1-butene (1); 674.00–725.00 cm^{-1} for (*E*)-1-chloro-2-butene (2); and 746.00–801.00 cm^{-1} for (*Z*)-1-chloro-2-butene (3).

Figure 2 presents the absorbance spectrum of the reaction between gaseous hydrogen chloride and gaseous 1,3-butadiene (32 scans), originally 294.4 Torr in HCl and 135.3 Torr alkene at 294 K after 90 h. The characteristic diagnostic peaks chosen for the preparation of Beer's Law plots and subsequent analysis are 2672.50–2689.50 cm^{-1} for hydrogen chloride,[13] 1570.50–1617.00 cm^{-1} for 1,3-butadiene, 1138.00–1197.00 cm^{-1} for 3-chloro-1-butene (1), 674.00–725.00 cm^{-1} for (*E*)-1-chloro-2-butene (2), and 746.50–801.00 cm^{-1} for (*Z*)-1-chloro-2-butene (3).

Although there are no peaks above background noise that can be attributed to materials other than those of the starting materials and products, both gaseous and condensed (liquid nitrogen) reaction mixtures were, on completion of the reaction, passed through the analytical gas chromatograph under the conditions specified above. No products beyond those indicated were detected. However, slight discoloration about the glass-to-window Glyptal seal suggested formation of material whose analysis could not be effected, and we suggest some polymer formation might be occurring which would account for disappearance of 1,3-butadiene in excess of that detected as a consequence of the formation of products 1, 2, and 3.

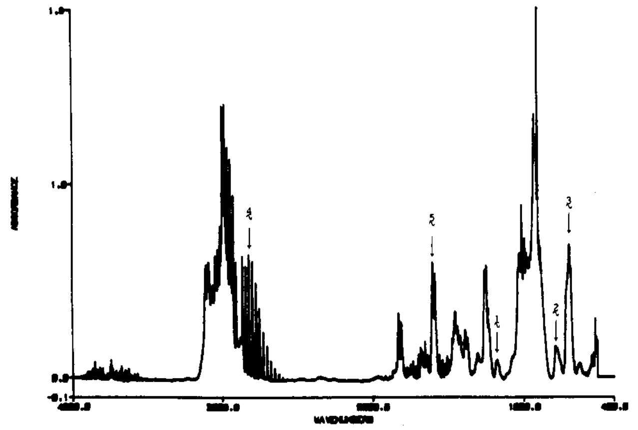

Figure 2. The FT-IR absorbance spectrum (at 2 cm^{-1} resolution) of a mixture of HCl(g) (294.4 Torr) and 1,3-butadiene(g) (135.3 Torr) in an annealing-oven-treated Pyrex cell with sodium chloride windows 90 h after mixing. The characteristic diagnostic peaks are 2672.50–2689.50 cm^{-1} for hydrogen chloride (4); 1570.50–1617.00 cm^{-1} for 1,3-butadiene (5); 1138.00–1197.50 cm^{-1} for 3-chloro-1-butene (1); 674.00–725.00 cm^{-1} for (*E*)-1-chloro-2-butene (2); and 746.00–801.00 cm^{-1} for (*Z*)-1-chloro-2-butene (3).

Results and Discussion

Figures 1 and 2 present IR absorbance spectra of a reaction mixture originally containing 294.4 Torr of hydrogen chloride and 135.3 Torr of 1,3-butadiene gases in a series A Pyrex cell (cycled through an annealing oven) and, respectively, the same reaction mixture 90 h later. Unique absorbances could be assigned to hydrogen chloride (2672.50–2689.50 cm^{-1}), to 1,3-butadiene (1570.50–1617.00 cm^{-1}), and to the three observed products, viz. 3-chloro-1-butene (1) (1138.00–1197.00 cm^{-1}), (*E*)-1-chloro-2-butene (2) (674.00–725.00 cm^{-1}), and (*Z*)-1-chloro-2-butene (3) (746.00–801.00 cm^{-1}).

A plot of disappearance of hydrogen chloride and appearance of product, derived from a series of spectra intermediate to those shown in Figures 1 and 2 is shown in Figure 3 for the reaction represented by the spectra of Figures 1 and 2 (i.e., originally 294.4 Torr in hydrogen chloride and 135.3 Torr in 1,3-butadiene). Table I presents

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[13] As a consequence of the narrow natural line width for HCl[14a,b] even as broadened by Doppler and other effects,[14c] the maximum intensity for the line lying in this region, rather than the area under the peak, was utilized for quantitative analysis and shown to be related to the quantity of hydrogen chloride present by correlating the observed intensity both to the quantity of gas added as measured manometrically and by actual condensation (liquid nitrogen) and subsequent titration.

[14] (a) Howard, B. J. In *Structure and Dynamics of Weakly Bound Molecular Complexes*; Weber, A., Ed.; NATO ASI, Series C, 1987; Vol. 212, p 69. (b) Pine, A. S. In *Structure and Dynamics of Weakly Bound Molecular Complexes*; Weber, A. Ed.; NATO ASI, Series C, 1987; Vol. 212, p 93. (c) Graybeal, J. D. *Molecular Spectroscopy*; McGraw-Hill: New York, 1988; p 192ff.

Table II[a]

temp, K	reaction number	rate° = −d[HCl]/d*t*, 10^6 mol h^{-1}	rate° = +d[products]/d*t*, 10^6 mol h^{-1}	product composition, % (90 h)		
				1	2	3
294	14	4.77	1.97	50.5	46.7	2.5
314	15	5.09	1.90	49.1	47.4	3.5
314	16	5.52	2.35	50.6	45.8	3.6
334	17	6.03	2.26	49.0	46.9	4.0
334	18	6.83	2.17	49.5	46.5	3.9
E_a, kcal mol^{-1}		1.56	0.84			
$\Delta H^{\ddagger}_{294}$, kcal mol^{-1}		0.98	0.31			
$\Delta S^{\ddagger}_{294}$, eu mol		−100.0	−99.0			

[a] Initial rate constants (rate°) for the disappearance of HCl(g) and the appearance of gaseous products **1**, **2**, and **3** (and the product composition) for the reaction between 1,3-butadiene(g) and HCl(g) in annealing-oven-treated Pyrex IR cells with sodium chloride windows. All reactions were initially made up at 368.7 ± 9 Torr of HCl(g) and 132.4 ± 6 Torr of 1,3-butadiene(g). Temperatures are accurate to ±0.5 °C.

Table III[a]

surface	reaction number	P°_{HCl}, Torr	P°_{ene}, Torr	[HCl], 10^4 mol	[ene], 10^4 mol	rate° = −d[HCl]/d*t*, 10^6 mol h^{-1}	rate° = +d[product]/d*t*, 10^7 mol h^{-1}	product composition, %			
								1	2	3	[hr]
teflon	19	216.4	109.6	4.57	2.31	2.94	6.69	7	74	19	[45]
	20	199.9	100.7	4.22	2.13	2.13	5.82	61	37	2	[50]
	21	196.4	113.2	4.14	2.39	2.24	4.32	32	67	*b*	[50]
polyethylene	22	199.7	99.8	4.21	2.10	3.38	4.87	69	31	0	[50]
								68	32	0	[90]
	23	198.8	102.4	2.19	2.16	1.88	3.89	77	23	0	[50]
								69	31	0	[90]
Pyrex (series B)	24	304.6	133.9	4.61	2.03	1.05[c]	1.81[d]	42	54	3	[50]
								46	52	2	[90]
	25	302.6	131.0	4.58	1.98	0.95[c]	1.66[d]	44	53	4	[50]
								47	51	2	[90]

[a] Initial rate constants (rate°) for the disappearance of HCl(g) and the appearance of gaseous products **1**, **2**, and **3** (and the product composition) for the reaction between 1,3-butadiene(g) and HCl(g) in cells made of Teflon and polyethylene and Pyrex cells *not* cycled through an annealing oven. [b] Unanalyzed because of new absorbances between 800–838 cm^{-1} and 1075–1120 cm^{-1}. [c] In contrast to the gentle initial convex curvature of −d[HCl]/d*t* of Figure 3, the disappearance of HCl(g) is linear. [d] In contrast to the initial concave curvature of +d[products]/d*t* of Figure 3 the appearance of products follows a curve which is initially convex.

a portion of the large volume of typical initial rate data at 294 K we have collected for the hydrogen chloride–1,3-butadiene system using various initial pressures of gases. The product composition shown in Table I is that at-90 h after initially mixing the gases at the specified pressures, although a similar tabulation could have been performed for any specific time period. The variation of initial rate of disappearance of hydrogen chloride and appearance of product with initial pressure is shown in Figure 4.

Table II presents the information about the same system in jacketed Pyrex cells that were treated as in series A but at reaction temperatures of 294, 314, and 334 K. Table III gives data for reactions in Teflon, polyethylene, and series B Pyrex cells.

Among the most striking features of the reaction we observe, discussed more fully below, are (1) that, overall, for these pressure and temperature ranges, the rate of the reaction is apparently somewhat more than second order in hydrogen chloride (Figure 4) and is less than first order in 1,3-butadiene; (2) in series A cells (annealing oven treated at ca. 560 °C), when the initial concentration of hydrogen chloride is *greater* than the initial concentration of 1,3-butadiene, the reaction begins immediately, the amount of (*Z*)-1-chloro-2-butene (**3**) formed (2–3%) is about the same as the amount of *s-cis*-1,3-butadiene in the gaseous alkene and, with increasing temperature, although the overall rate of product formation remains about the same, the amount of **3** produced increases; (3) in series A cells, when the initial concentration of hydrogen chloride is *less* than or approximately equal to the initial concentration of 1,3-butadiene and the total pressure is less than 300 Torr, [i] the reactions exhibit significant lag times of 5–20 h prior to onset of product formation, suggesting that our results may apply particularly to that pressure and concentration range above this minimum (which may, in turn, be related to the amount of HCl associated with the surface), and [ii] the amount of **3** produced is variable, with more being produced at lower initial total pressure (P°_{total}); (4) in series B cells (*not* dismantled and cycled through the annealing oven), despite pumping and occasional heating for prolonged periods at modest temperatures (ca. 200 °C), products form at dramatically decreased rates,

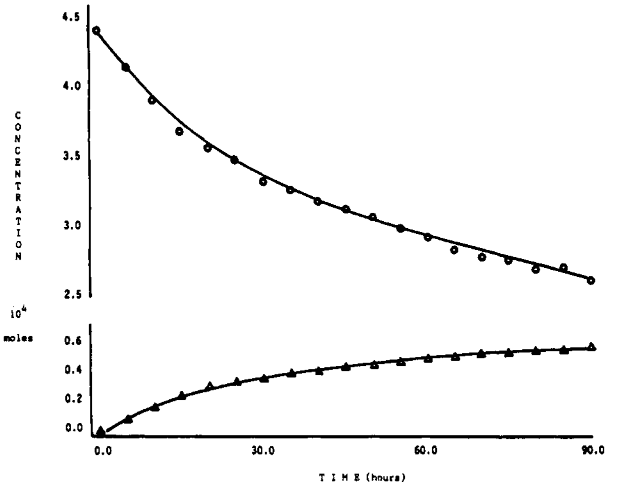

Figure 3. The disappearance of HCl(g) (○) and the appearance of products (**1** + **2** + **3**; △) as a function of time in an annealing-oven-treated Pyrex cell with sodium chloride windows. The initial mixture contained HCl(g) (294.4 Torr) and 1,3-butadiene(g) (135.3 Torr).

suggesting a passivated surface; (5) a change in surface from Pyrex to either polyethylene or Teflon introduces a marked change in the ratio of products formed and the rate at which they form.

Reaction Products. The products of the reaction are considered before the kinetics. As noted in the Experimental Section, except for a small amount of (unanalyzed) discoloration which appeared at the window-to-cell junction, the only detectable products were 3-chloro-1-butene (**1**), (*E*)-1-chloro-2-butene (**2**), and (*Z*)-1-chloro-2-butene (**3**).

When the total initial pressure of hydrogen chloride and 1,3-butadiene gases (P°_{total}) in Pyrex cells (series A: Table I, reactions 1, 2, 9–11; Table II, reaction 14. Series B: Table III, reactions 24 and 25) was about 300 Torr or greater at 90 h after initially mixing the gases, reactions at 294 K contained about a 1:1 mixture of **1** and **2** (with discrepancies in series A favoring **1** and in series B favoring **2**) along with 2–3% of **3**. That is, the amount of (*Z*)-1-chloro-2-butene (**3**) found is that predicted[15] on the basis of the observation that the energy difference between *s-cis*-1,3-butadiene and *s-trans*-1,3-butadiene is about 2.0–2.3 kcal/mol. These observations suggest that if 2–3% of the former is present in the gas at 294 K (with the lower value more likely), and product formation is reflecting the gas-phase starting material composition then both isomers of 1,3-butadiene react at about the same rates. With regard to the products, MM2 calculations[16] suggest that **1** and **3** are about 1.64 and 0.57 kcal/mol less stable, respectively, than **2** and somewhat more sophisticated calculations[17] at, e.g., the STO-3G level, have **2** more stable than **1** and **3** by 1.75 and 0.60 kcal/mol, respectively. In this vein, it has been noted that the first-order component of the thermal elimination of hydrogen chloride from **1**, a secondary chloride, is only slightly faster than that from the primary chlorides (presumably a mixture of) **2** and **3**.[10]

When P°_{total} is less than 300 Torr in Pyrex cells treated in the same fashion as above (series A: Table I, reactions 3–8, 12, and 13) the amount of **3** *increases*, apparently at the expense of **1**. Interestingly, when the amount of 1,3-butadiene initially present is *greater* than the amount of hydrogen chloride and P°_{total} is also low, the amount of **3** produced is maximized (series A: Table I, reactions 5, 6, and 13). Since the rate of formation of product in these reactions is reduced (relative to the reactions at higher initial pressures and particularly at higher initial hydrogen chloride pressures, vida infra), it is tempting to suggest that these phenomena are related. An increase in the amount of **3** can also be effected, even though the P°_{total} is high, by raising the temperature of the reaction. Although the overall rates of both the disappearance of hydrogen chloride and total product formation show only a very small temperature dependence in the range 294–334 K and although the quantity of **1** to **2** + **3** (i.e. net "1,2-addition" to net "1,4-addition") remains at about 1:1, there is steady increase in the relative amount of **3** with increasing temperature (Table II). Over this small temperature range, the disappearance of hydrogen chloride occurs with an apparent E_a of 1.56 kcal mol^{-1}, a $\Delta H^{\ddagger}_{294}$ of 0.98 kcal mol^{-1} and $\Delta S^{\ddagger}_{294}$ of −100.4 eu mol while total product forms with an apparent E_a of 0.89 kcal mol^{-1}, a $\Delta H^{\ddagger}_{294}$ of 0.31 kcal mol^{-1}, and $\Delta S^{\ddagger}_{294}$ of −99.9 eu mol. As it appears that the process we observe is wall catalyzed, the exact significance of these numbers is not clear although they are suggestive of a highly ordered transition state.

Finally, in a previously unused Teflon cell (Table III, reaction 19), a dramatically different product ratio is obtained, with both **2** and **3** being the major products and **1** being minimized. However, when, after dismanteling the cell, washing it with distilled water, oven-drying at 50 °C, installing new windows, and pumping the rebuilt cell at 10^{-5} Torr overnight, this Teflon cell was reused (Table III, reaction 20), the major product (with no appreciable change in rate) was **1**, accompanied by about the expected amount of **3** and a somewhat diminished quantity of **2**. A third attempt, repeating the above described procedure (Table III, reaction 21) again yielded a diminished amount of **1**, an enhanced quantity of **2**, and some small amount of **3**, which could not be appropriately analyzed since, as noted (Table III), new products began to appear in the region of the IR spectrum utilized for its analysis. In contrast, the cell made of polyethylene yielded reproducible results, with only **1** and **2** being detected in a ratio reminiscent of that originally described for the solution reaction.[5]

Kinetic Analysis. As has been pointed out before in a similar connection,[8b] reactions which are fractional order in one or more reactants,[19,20] reactions in which product variability results from pressure and/or surface modification[20] and reactions which product formation is retarded on an increase in temperature[21] are frequently found to be wall or surface catalyzed.[22]

As all of these criteria appear to apply here, our analysis of the data begins with our experimental observation that the reaction that is occurring here is not the reverse of the high-temperature first-order decomposition of these isomers[10] but rather is somewhat more than second order in hydrogen chloride (Figure 4) and less than first order (ca. 0.7–0.9) in 1,3-butadiene.

Empirically, by eq 1, utilizing an average overall initial rate constant of 1.065×10^5 mol^{-2} h^{-1} (1.06 cm^3 mol^{-2} s^{-1}), where [ene$_o$] refers to the initial concentration of 1,3-butadiene and the other abbreviations have their usual significance, it is seen that the fit to experiment for the reactions of Table I is not unreasonable (as shown in Table IV).

$$\text{rate}_o = k_{\text{obs}}[\text{HCl}_o]^{2.2}[\text{ene}_o]^{0.8} \tag{1}$$

The first-order component of the thermal unimolecular decomposition of **1**[10] is $(2.20 \times 10^{13})e^{-(48\,500/RT)}$ s^{-1} and the first-order component of the thermal unimolecular decomposition of 3-chloro-2-methyl-1-butene[10] is $(1.90 \times 10^{13})e^{-(46\,900/RT)}$ s^{-1} while the (presumed) mixture of **2** and **3** has a first-order component in its (their) thermal unimolecular decomposition only 2.9 times smaller than that for **1**.[10] The thermal unimolecular decomposition of 2-chloro-2-methylpropane[7c] and 2-chloro-2-methylbutane[7c,d] has $k_d = 10^{13.8}e^{-(45\,000/RT)}$ s^{-1} and $(4.5 \times 10^{14})e^{-(46\,000/RT)}$ s^{-1}, respectively. Assuming a similarity in mechanism for the saturated and unsaturated systems, then the equilibrum constant attending the bimolecular reverse of the decomposition reaction for the saturated systems might be ex-

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(16) MM2 calculations were performed on the Temple University CDC Cyber 750. For a description of the method in more detail, see: Schnur, D. M.; Yuh, Y. H.; Dalton, D. R. *J. Org. Chem.* **1989**, *59*, 3779 and references therein.

(17) These calculations, for which we are grateful, were carried out by D. M. Schnur at the Molecular Modeling Laboratory, University of North Carolina, School of Pharmacy, Chapel Hill, NC.

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(22) For an excellent discussion of general principles, see: Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987; p 229ff.

Table IV[a]

experiment number	$-d[HCl]/dt$, 10^6 mol h^{-1}				$+d[products]/dt$, 10^7 mol h^{-1}		
		calcd (k_{calc}) after eq no.				calcd (k_{calc}) after eq no.	
	exp (k_{obs})	1	8*	11	exp (k_{obs})	8*	11
1	5.00	5.14	5.07	3.90	18.4	27.15	17.60
2	4.41	5.72	6.54	4.29	18.9	37.47	19.38
3	1.33	0.74	0.55	0.62	5.97	2.60	3.06
4	0.87	1.39	0.97	1.14	6.19	4.43	5.27
5	0.30	0.25	0.25	0.21	1.10	1.17	1.08
6	0.43	0.29	0.29	0.25	1.35	1.34	1.29
7	0.80	0.45	0.29	0.39	3.87	1.61	2.44
8	0.70	0.51	0.32	0.45	4.51	1.81	2.70
9	2.11	2.95	2.07	2.18	8.45	6.99	7.52
10	2.40	2.78	1.95	2.09	6.92	6.99	7.62
11	0.79	1.88	1.27	1.56	5.46	6.86	8.02
12	0.13	0.46	0.36	0.39	1.07	1.77	2.14
13	0.07	0.09	0.13	0.08	0.31	0.63	0.45

[a] A comparison of observed and calculated initial rates (rate°) for the disappearance of HCl(g) ($-d[HCl]/dt$) and for the appearance of products ($+d[products]/dt$) for the reaction between HCl(g) and 1,3-butadiene(g) in annealing-oven-treated Pyrex IR cells with sodium chloride windows. The results shown for the calculations marked with an asterisk (*) require a *negative* value for at least one ratio of rate and equilibrium constants.

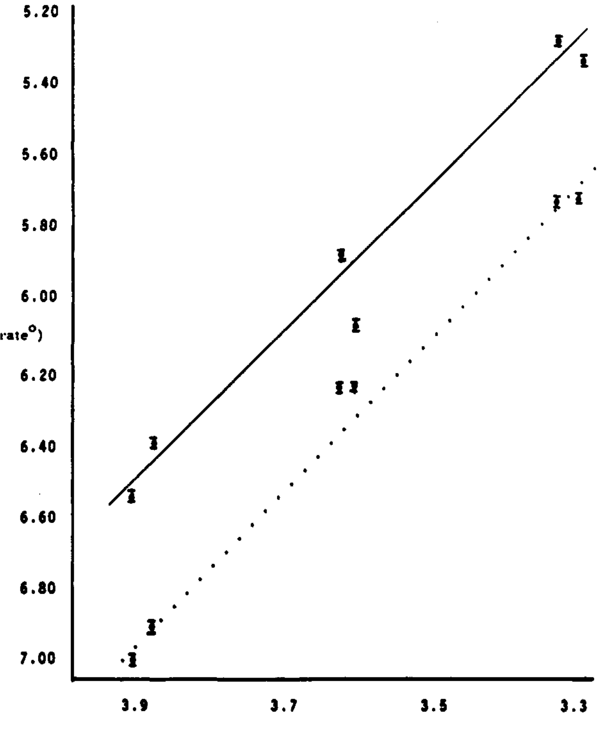

Figure 4. The variation in initial rate of disappearance of hydrogen chloride (—) and in the appearance of products (1 + 2 + 3; ---) with the initial pressure of hydrogen chloride. The initial pressure of 1,3-butadiene is held constant at 134 ± 3 Torr.

pected to be similar in magnitude to that of the unsaturated systems. If they are similar, we conclude that the expected rate of the association reaction, in the absence of surface catalysis,[7c] for the reaction of HCl(g) with 1,3-butadiene(g) is of the order of ca. $10^{10}e^{-(28\,000/RT)}$ mol cm^{-3} s^{-1} leading to a second-order rate constant of about 10^{-10} cm^3 mol^{-1} s^{-1}. Although the trail of assumptions is large, the association rate constant is consistent with others,[7c] the order-of-magnitude is not unreasonable, and it is clear that under our conditions the homogeneous reaction of HCl(g) and 1,3-butadiene(g) is not observed (at least because of an unfavorable rate constant compared to that of the surface catalyzed process).

Further analysis, since the reaction is ostensibly surface catalyzed, begins with the presumption that the two reactants might both be adsorbed (but not necessarily in the same way or to the same extent) on the surface, that the reaction occurs between these adsorbed species, and that the product is subsequently desorbed.[23] These statements are summarized in eqs 2–5 below. We do not distinguish, at this point, between *s-cis-* and *s-trans-*1,3-butadiene, potentially different surface sites, and the isomeric products 1, 2, and 3 (as their respective absolute rates of formation appear to remain about constant over the course of the reaction).

$$\mathrm{HCl(g) + S \underset{k_r}{\overset{k_f}{\rightleftharpoons}} HCl{-}S} \qquad (2)$$

$$\mathrm{CH_2{=}CHCH{=}CH_2(g) + S \underset{k'_r}{\overset{k'_f}{\rightleftharpoons}} CH_2{=}CHCH{=}CH_2{-}S} \qquad (3)$$

$$\mathrm{HCl{-}S + CH_2{=}CHCH{=}CH_2{-}S \xrightarrow{k_s} products{-}S} \qquad (4)$$

$$\mathrm{products{-}S \xrightarrow{k_d} products(g) + S} \qquad (5)$$

Assuming, initially, processes described by eqs 1–5 above, then the fraction of surface covered by HCl molecules may be represented by θ_{HCl}, the fraction covered by butadiene as θ_{ene}, and the uncovered surface as $(1 - \theta_{HCl} - \theta_{ene})$. Further assuming the adsorption is competitive, that it occurs without dissociation and that the adsorption–desorption process reaches equilibrium, the fractions of surface covered by HCl and 1,3-butadiene are given by eqs 6 and 7 (where $K_{HCl} = k_f/k_r$ and $K_{ene} = k'_f/k'_r$), respectively. The classical Langmuir–Hinshelwood mechanism,[24] where the rate is expected, in this case, to be proportional to the fractions of the HCl and 1,3-butadiene adsorbed, is thus given by eq 8; which can be rewritten as eq 9 in terms of initial rates (rate°) and initial concen-

$$\theta_{HCl} = K_{HCl}[HCl]/(1 + K_{HCl}[HCl] + K_{ene}[ene]) \qquad (6)$$

$$\theta_{ene} = K_{ene}[ene]/(1 + K_{HCl}[HCl] + K_{ene}[ene]) \qquad (7)$$

$$\text{rate} = k_s K_{HCl} K_{ene}[HCl][ene]/(1 + K_{HCl}[HCl] + K_{ene}[ene])^2 \qquad (8)$$

$$([HCl^\circ][ene^\circ]/\text{rate}^\circ)^{1/2} = 1/(k_s K_{HCl} K_{ene})^{1/2} + K_{HCl}[HCl^\circ]/(k_s K_{HCl} K_{ene})^{1/2} + K_{ene}[ene^\circ]/(k_s K_{HCl} K_{ene})^{1/2} \qquad (9)$$

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[23] Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361; **1916**, *38*, 2221.

[24] (a) Langmuir, I. *Trans. Faraday Soc.* **1921**, *17*, 621. (b) Hinshelwood, C. N. *Kinetics of Chemical Change in Gaseous Systems*; Clarendon: Oxford, 1926; p 145.

trations [HCl°] and [ene°] and may be explicitely solved[25] for the ratios of the constants $[1/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2}]$, $[K_{\mathrm{HCl}}/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2}]$, and $[K_{\mathrm{ene}}/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2}]$ for the reactions given in Table I. Evaluating the ratio of these constants for the initial rates in terms of the disappearance of hydrogen chloride (−d[HCl]/d*t*) gives: 0.337, −479.049, and 60.994, respectively. When the initial rates are given in terms of the appearance of products (+d[products]/d*t*) the ratios of the constants are 0.453, −758.171, and 344.855, respectively. Comparisons of the experimentally determined initial rate constants (rate°) for the reaction between HCl(g) and 1,3-butadiene(g) under the various starting concentrations of Table I with those calculated utilizing the above ratios of constants are given in Table IV for −d[HCl]/d*t* and +d[products]/d*t*, respectively. Although there is a reasonable fit of calculated and observed rates, it must be noted that in both cases, the values of the ratio $[K_{\mathrm{HCl}}/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2}]$ are negative. The significance of the sign of this ratio has been commented on elsewhere[26] and it is generally agreed that some doubt may be cast upon an analysis which requires a negative value for any of the ratios in eq 9.

Special cases of the Langmuir-Hinshelwood formalism which consider (a) a sparsely covered surface; (b) one reactant weakly adsorbed and the other strongly adsorbed or not adsorbed, and; (c) the adsorption of two gases without mutual displacement[22] as well as the approach of Rideal[27] who considered one species strongly adsorbed and the other unadsorbed all give similar results for agreement of experimental and calculated values of the rates and all require ratios of constants with at least one negative value.

Processes on heterogeneous surfaces considered experimentally by Freundlich[28] or Tempkin[29] and from a theoretical perspective by Frumkin and Slygin[30] all suffer from a restriction on their order which does not fit our experimental observations.

High-order processes similar to those observed by us, the study of which has profited from application of the theoretical work of Braunauer, Emmett, and Teller (BET Theory)[31] (subsequently modified by Brauner, Demming, Demming, and Teller[32]), and which specifically treats the formation of multilayer wall-associated gaseous aggregations generally requires a well-defined surface for analysis.

In the case at hand, a process high order in HCl(g) and fractional order in 1,3-butadiene(g) on a Pyrex glass surface, can be expressly treated by modification of the Langmuir–Hinshelwood formalism (as in eq 10), which, on rearrangement to eq 11 and solution for initial rates, leads to values of the ratios of the constants $[1/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2}]$, $[K_{\mathrm{HCl}}/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2}]$, and $[K_{\mathrm{ene}}/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2}]$ for the disappearance of hydrogen chloride of 3.120×10^{-3}, 4.495×10^{3}, and 1.810×10^{-1}, respectively. Initial rates in terms of the formation of products gives the ratios of the constants as 3.439×10^{-3}, 1.119×10^{4}, and 1.172, respectively.

$$\text{rate} = k_sK_{\mathrm{HCl}}K_{\mathrm{ene}}[\mathrm{HCl}]^{2.2}[\mathrm{ene}]^{0.8}/(1 + K_{\mathrm{HCl}}[\mathrm{HCl}]^{2.2} + K_{\mathrm{ene}}[\mathrm{ene}]^{0.8})^2 \quad (10)$$

$$([\mathrm{HCl}^\circ]^{2.2}[\mathrm{ene}^\circ]^{0.8}/\text{rate}^\circ)^{1/2} = 1/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2} + K_{\mathrm{HCl}}[\mathrm{HCl}^\circ]^{2.2}/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2} + K_{\mathrm{ene}}[\mathrm{ene}^\circ]^{0.8}/(k_sK_{\mathrm{HCl}}K_{\mathrm{ene}})^{1/2} \quad (11)$$

Here the equilibrium constants K_{HCl} and K_{ene} cannot have their originally defined meaning and we take them to refer to adsorption into and out of the multilayer, which may retain an adsorbed first layer as originally formulated.

An expression such as that of eq 11 is consonant with high-order adsorption of hydrogen chloride on the walls of the infrared cell, forming a multilayer which reacts with weakly physically adsorbed 1,3-butadiene. Other expressions might equally well be written for adsorbed hydrogen chloride and nonadsorbed 1,3-butadiene but cannot be experimentally distinguished from that proposed. Further, the product composition suggests that a reasonable pathway might involve reaction of the chemically adsorbed, strongly complexed hydrogen chloride in the multilayer with 1,3-butadiene as it strikes this layer, by a process where initial partial proton transfer to the terminal carbon of butadiene is not consummated until a chloride also begins to bond, with about equal probability, to either the adjacent carbon or the one at the other terminus, thus yielding equivalent amounts of "1,2- and 1,4-addition" and quantities of (*Z*)-1-chloro-2-butene (**3**) reflecting the gas-phase concentration of this rotational isomer. Our observations, noted above, concerning the effects of the initial concentrations at total initial pressures < 300 Torr are also clearly in concert with a process high order in hydrogen chloride and less than first order in 1,3-butadiene. The diminished total rates at the lower P°_{total} presumably allow equilibration of *s-cis*- and *s-trans*-1,3-butadiene to proceed apace with the product-forming reactions and the result is an increased yield of **3**. The apparent large negative entropy found for this reaction, reflecting the significant order required to effect product formation, and the lack of temperature dependence which, over the relatively small region studied, would only marginally effect the multilayered structure of the reactant on the surface, all lend support to the suggested pathway.

Conclusions

The reaction between hydrogen chloride and 1,3-butadiene gases in glass infrared gas cells to yield gaseous 3-chloro-1-butene and (*E*)- and (*Z*)-1-chloro-2-butene has been found to occur via a wall-catalyzed process, high order in hydrogen chloride and less than first order in 1,3-butadiene. The process is best described by one involving multilayer adsorption of hydrogen chloride followed by addition of HCl in this layer to the alkene. This highly structured process apparently occurs with near simultaneous proton and chloride transfer, and the gas-phase composition of the alkene is retained in the product.

Acknowledgment. We gratefully acknowledge very helpful discussions with Ernst Berliner, Francis Costello, Frank Mallory, John Poole, and Edward Thornton.

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