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Surface-Catalyzed Reaction of the Gases Hydrogen Chloride and 2-Butyne[1]

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Mixtures of gaseous hydrogen chloride and gaseous 2-butyne at total initial pressures less than 500 Torr, and at temperatures between 296 and 336 K, react in Pyrex IR cells (NaCl windows) to yield *only (Z)*-2-chloro-2-butene, *i.e.*, the product of net *trans* (or *anti* or *antarafacial*) addition. 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 is occurring at the walls.

Introduction

Despite ratios of rate constants for various electrophilic addition reactions to alkenes and alkynes (k_{ene}/k_{yne}) for ostensably similar processes that vary over some 10 powers of ten (from 10^8 to 10^{-2}) as a function of both unsaturated compound and addend,[3] it is commonly held that electrophilic addition to alkynes is the less facile.[4] This belief probably derives from examination of a selected subset of such reactions[3] and may be exacerbated by the need to compare different compounds studied by different investigators under different conditions at different times.

The addition of hydrogen chloride across the triple bond of various alkynes (and under different conditions for different alkynes) has a long history.[5] Nonetheless, the details, both kinetic and stereochemical, which might help define the path(s) by which alkyne reactants are converted to chloroalkene and other product(s), both in the presence of catalysts (added and adventitious)[6] and in their absence,[3,7] are sparce.

Now, however, because (a) the π-complexes between 2-butyne and HCl are well defined[8] and (b) we have already shown[9] that preferential *trans* (*anti* or *antarafacial*) surface-catalyzed addition is the major path by which gaseous *(E)*- and *(Z)*-2-butene and hydrogen chloride produce 2-chlorobutane, and despite the observation that there may be "something unusual about acid catalyzed additions to 2-butyne",[5c] which might contribute to the plethora of products early reported in the "bizarre reactions of 2-butyne during the addition of hydrogen chloride" [10] in the liquid phase, we report the details of our examination of the reaction between the gases 2-butyne and hydrogen chloride.

Experimental Section

Hydrogen chloride (Electronic grade) was obtained from Matheson Gas Products, Bridgeport, NJ. 2-Butyne (99%) and 2-chloro-2-butene (98%, mixture of *(Z)*- and *(E)*-isomers) were obtained from Aldrich Chemical Co., Milwaukee, WI. 2,2-Dichlorobutane (97%) was obtained from Pfaltz and Bauer, Inc., Waterbury, CT. The hydrogen chloride and 2-butyne were further purified using multiple trap-to-trap distillations (as previously described for other materials).[9,11] For hydrogen chloride, three distillations each from liquid nitrogen−pentane slush (143 K) and liquid nitrogen−ethanol slush (156 K) and

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(2) (a) Beaver College. (b) Temple University.

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(4) The following list is incomplete. It is provided as representative only and inclusion of, or failure to list, a work should not be taken as significant. (a) March, J. *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*, 4th ed.; Wiley: New York, 1992; p 749. (b) McMurry, J. *Organic Chemistry*, 3rd ed.; Brooks/Cole: Pacific Grove, 1992; p 260. (c) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 6th ed.; Prentice Hall: Englewood Cliffs, 1992; p 435. (d) Pine, S. H.; Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*, 4th ed.; McGraw-Hill: New York, 1980; p 504. (e) Stretiweiser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan: New York, 1992; p 312.

(5) Reviews include: (a) Larock, R. C.; Leong, W. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming I., Eds.; Pergamon: New York, 1991; Vol 4, pp 269−327. (b) Sergeev, G. B.; Smirnov. V. V.; Rostovshchikova, T. N. *Uspekhi Khim.* **1983**, *52*, 455. (c) Schmid, G. H. In *The Chemistry of the Carbon-Carbon Triple Bond*: Part 1; Patai, S., Ed.; Wiley-Interscience: New York, 1978; p 175. (d) Stroh, R. *Methoden Org. Chem. (Houben-Weyl) 1962*, V/3, 812. (e) Mascavage, L. M.; Dalton, D. R. *Recent Trends Org. Chem.* **1993**, *4*, 303.

(6) Although recently reinvestigated, the study of the surface catalysis in the presence of mercury(II) chloride, silica gel, *etc.*, is quite old. See, *inter alia*: (a) Kropp, P. J.; Daus, K. A.; Crawford, S. D.; Tubergen, M. W.; Kepler, K. D.; Craig, S. L.; Wilson, V. P. *J. Am. Chem. Soc.* **1990**, *112*, 7433. (b) Beránek, L.; Kraus, M. In *Comprehensive Chemical Kinetics*: Bamford, C. H., Tipper C. F. H., Eds.; Elsevier: New York, 1978; Vol. 20, p 332 ff. (c) Hertwig, K.; Adler, R.; Henkel, K. D. *Chem. Tech. (Leipzig)* **1974**, *26*, 639. (d) Brouwer, L. G.; Wibaut, J. P. *Rec. Trav. Chim.* **1934**, *53*, 1001. (**Note added in proof**: A detailed product study on the reaction of some alkynes and some hydrogen halides in solution and in the presence of materials designed to promote surface catalyzed product formation has appeared. Kropp, P. J.; Crawford, S. D. *J. Org. Chem.* **1994**, *59*, 3102).

(7) For reviews, see: Bolton, R. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1973; Vol. 9, p 17 and ref 3. Individual cases dealing with the kinetics of reactions between HCl and alkynes include: (a) 3-hexyne, which "adds hydrogen chloride almost exclusively *trans* in acetic acid": Fahey, R. C.; Lee, D.-J. *J. Am. Chem. Soc.* **1967**, *89*, 2780. (b) 1-phenylpropyne and 3-hexyne: Fahey, R. C.; Lee, D.-J. *J. Am. Chem. Soc.* **1968**, *90*, 2124. (c) phenylacetylene, 1-phenylpropyne, 1-hexyne, 3,3-dimethyl-1-butyne: Fahey, R. C.; Payne, M. T.; Lee, D.-J. *J. Org. Chem.* **1971**, *39*, 1124. (d) phenylacetylene: Smirnov, V. V.; Kovaleva, L. A.; Rostovshchikova, T. N.; Sergeev, G. B. *Kinet. i Kat.* **1989**, *30*, 63. There is, of course, work on other hydrogen halide electrophiles. Individual cases dealing with the kinetics of reactions between HBr and alkynes include: (a) phenylacetylene: Mel'nikov, G. D.; Mel'nikov, S. P.; Kovaleva, L. A. *Zhur. Org. Khim.* **1978**, *14*, 701 and (b) Smirnov, V. V.; Kovaleva, L. A.; Rostovshchikova, T. N.; Sergeev, G. B. *Kinet. i Kat.* **1989**, *30*, 63. Individual cases dealing with hydration include 1-butyne, 2-butyne, 1-hexyne, 1-cyclopropylacetylene, and 3-hexyne: Allen, A. D.; Chiang, Y.; Kresge, A. J.; Tidwell, T. T. *J. Org. Chem.* **1982**, *47*, 775 and references therein.

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(9) Tierney, J.; Costello, F.; Dalton, D. R. *J. Org. Chem.* **1986**, *51*, 5191.

(10) Schneider, H.; Griesbaum, K. *J. Org. Chem.* **1979**, *44*, 3316.

a final sublimation from dry ice−2-propanol slush (195 K) were sufficient. For 2-butyne, three distillations each from liquid nitrogen−acetonitrile slush (232 K) and liquid nitrogen−carbon tetrachloride slush (250 K) and a final sublimation from ice water (273 K) 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.

Infrared spectra were obtained on a Digilab FTS-40 Fourier transform infrared spectrophotometer. Peak absorbances and areas were measured using Digilab Quant 32 software. ^{1}H NMR spectra were obtained in ^{2}HCCl$_3$ at 300 and 500 MHz on General Electric QE-300 and Omega GN-500 systems, respectively. 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 (*Z*)- and (*E*)-2-chloro-2-butenes at an injector temperature of 250 °C and a column temperature of 50 °C with the flow rate at 3 cm^3 min^{-1} were 3.7 and 4.6 min, respectively. Under the same conditions, the retention time of 2,2-dichlorobutane was 7.9 min.

Preparative-scale separation of the commercially available mixture of (*Z*)- and (*E*)-2-chloro-2-butenes was accomplished using a Varex PSGC 10−40 chromatograph, equipped with a TC detector, on a $^1/_2$ in. × 8 ft glass column packed with 0.19% picric acid adsorbed on Carbopak C (Supleco). The injector temperature was held at 156 °C, the oven at 77 °C , and the TC detector at 150 °C. With a helium flow rate of 20 cm^3 min^{-1}, the retention times of the (*Z*)- and (*E*)-isomers were 6.8 and 9.4 min, respectively. The isomers 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.[9,11]

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 variable temperature work, 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 with an S-7555 Thermoregulator (Forma Scientific Co., Marietta, OH). Polished sodium chloride windows (Fisher Scientific Co., Philadelphia, PA), 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[12] to be sufficient to remove even strongly adsorbed hydrogen chloride from silica surfaces) prior to assembling. After desiccator cooling, new windows were mounted, 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. Jacketed Pyrex cells for variable temperature work were heated during evacuation on the vacuum rack by passing steam through the jacket for *ca.* 15 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 2-butyne for 3 h, and then reevacuated 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 hydrogen chloride, the cell's stopcock was closed, and the 2-butyne 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 fixed-time intervals initially and, subsequently, at longer time intervals as the reaction proceeded. Depending upon the particular run, spectra were initially recorded every 15.0 to 60.0 min. As many as forty (40) spectra were obtaind on each reaction mixture.

Spectroscopic Analysis. Absorbance spectra (all 2 cm^{-1} resolution) were utilized throughout for analysis. Figure 1 represents typical FT-IR absorbance spectra (32 scans) of the reaction mixture (at 296 K) originally containing 251.91 Torr of gaseous hydrogen chloride and 52.82 Torr of gaseous 2-butyne immediately after mixing, at 85.4 h, and after *ca.* 3 months. The characteristic diagnostic peaks chosen for preparation of Beer's law plots and subsequent analysis are 2622.0−2628.0 cm^{-1} for hydrogen chloride,[13] 2011.0−2103.0 cm^{-1} for 2-butyne, 1270.0−1329.0 cm^{-1} for (*Z*)-2-chloro-2-butene, and 656.0−704.0 cm^{-1} for (*E*)-2-chloro-2-butene.

The infrared spectra of both the (*E*)- and (*Z*)-2-chloro-2-butene isomers have been reported.[14,15] Many differences have been noted; among them are the major peaks in the region 600−750 cm^{-1}. For (*E*)-2-chloro-2-butene, an intense C−Cl stretch is observed at 647.0 cm^{-1}, while for (*Z*)-2-chloro-2-butene, the band appears at 619.0 cm^{-1}. Our own results, in the gas phase, on the purified and separated isomers place the centers of these bands at 684.0 cm^{-1} and 619.0 cm^{-1}, respectively. The ^{1}H NMR spectra (as dilute solutions in ^{2}HCCl$_3$ at 500 MHz) of the materials separated as described above are identical with those reported.[15,16]

At significantly longer reaction times formation of 2,2-dichlorobutane was also observed. The diagnostic bands were at ν_{max} = 1725.0, 1092.9, 853.4, 693.6 and 645.8 cm−1.[17]

Although in the infrared spectra no peaks above background noise were detected that might be attributed to absorbances other than those of the starting materials and products,[13] 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.

Results and Discussion

Figure 1 presents IR absorbance spectra of a gaseous reaction mixture originally containing 251.91 Torr of hydrogen chloride and 52.82 Torr of 2-butyne in a Pyrex cell and the same reaction mixture 85 h and *ca.* 3 months later, respectively. Unique absorbances could be assigned to hydrogen chloride (2622.0−2628.0 cm^{-1}),[13] to

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(11) (a) Haugh, M. J.; Dalton, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 5674. (b) Costello, F; Dalton, D. R.; Poole, J. A. *J. Phys. Chem.* **1986**, *90*, 5352. (c) Mascavage, L. M.; Chi, H.; La, S.; Dalton, D. R. *J. Org. Chem.* **1991**, *56*, 585.

(12) Kang, Y.; Skilles, J. A. Wightman, J. P. *J. Phys. Chem.* **1980**, *84*, 1448.

(13) Although, as usual, a plot of concentration *versus* integrated peak area for any of the signals of the R or P branches in the HCl spectrum could have been used, the particular region chosen shows minimal changes in the integrated intensity as a function of unspecified interactions (and/or complexes, *etc.*). See, *e.g.*: George, W. O.; Lewis, Rh.; Hussain, G.; and Rees, G. J. *J. Molec. Struct.* **1988**, *189*, 211.

(14) (a) Ferguson, R. C. *J. Polymer Sci, Part A* **1964**, *2*, 4735. (b) Crowder, G. A.; Smyrl, N. *J. Mol. Struct.* **1977**, *10*, 373.

(15) We are grateful to Dr. Gordon M. Cohen, Central Research and Development, E.I. DuPont Co., Wilmington, DE, for bringing the information in ref 14 to our attention and for providing ^{1}H NMR spectra of authentic samples.

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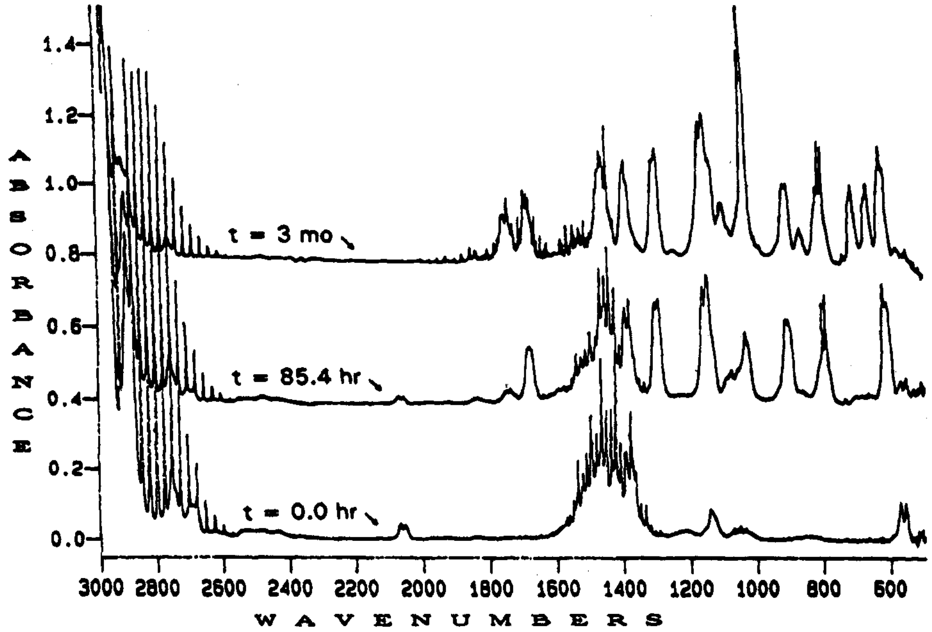

Figure 1. The FT-IR absorbance spectra (at 2 cm^{-1} resolution) of a mixture of HCl(g) (251.91 Torr) and 2-butyne(g) (52.82 Torr) at 296 K in a Pyrex cell with sodium chloride windows on initial mixing, at 85 h, and after *ca.* 3 months. The characteristic diagnostic peaks are 2622.0–2628.0 cm^{-1} for hydrogen chloride; 2011.0–2103.0 cm^{-1} for 2-butyne; and 1270.0–1329.0 cm^{-1} for (*Z*)-2-chloro-2-butene.

Table 1[a]

reactn no.	P^0_{HCl}, Torr	$P^0_{\text{2-butyne}}$, Torr	[HCl]^0, 10^4 mol	[2-butyne]^0, 10^4 mol	rate^0 = $-$d[HCl]d*t*, 10^7 mol h^{-1}	rate^0 = $-$d[2-butyne]/d*t*, 10^7 mol h^{-1}	rate^0 = +d[product]/d*t*, 10^7 mol h^{-1}
1	107.95	325.75	1.26	3.79	9.57	21.4	9.13
2	100.11	317.64	1.17	3.69	9.20	14.7	6.89
3	94.12	203.94	1.11	2.41	7.15	14.6	3.24
4	99.83	208.63	1.16	2.43	5.91	9.99	3.89
5	106.81	408.25	1.28	4.89	13.4	42.7	8.19
6	103.13	411.59	1.20	4.79	9.62	15.6	6.95
7	90.13	101.86	1.07	1.20	6.25	9.31	3.39
8	90.93	104.74	1.09	1.23	2.28	3.81	2.11
9	86.68	102.95	1.01	1.19	4.59	5.60	2.51
10	252.75	101.22	2.99	1.19	8.96	9.94	3.85
11	337.24	101.83	4.05	1.23	19.6	12.7	5.39
12	412.94	105.79	4.81	1.25	9.38	10.35	5.37
13	232.70	99.21	2.75	1.17	8.52	7.95	3.19
14	416.50	111.64	4.99	1.36	13.1	14.6	7.34
15	251.91	52.82	3.02	0.629	9.35	4.88	2.69
16	254.38	51.92	2.96	0.605	7.59	4.16	1.92
17	255.19	51.27	2.87	0.597	3.34	3.33	1.52
18	132.10	51.58	1.56	0.610	2.95	2.78	1.49
19	159.01	52.82	1.85	0.615	4.21	3.35	1.56
20	151.34	51.27	1.79	0.612	5.76	3.88	2.05
21	57.98	52.42	6.75	0.616	4.10	1.79	7.27
22	57.77	51.97	6.83	0.615	7.49	2.64	7.17
23	352.29	50.49	4.10	0.588	9.12	7.33	4.80
24	336.00	53.97	3.97	0.638	12.02	4.75	2.23
25	365.84	53.52	4.26	0.627	10.7	4.72	1.90

[a] Initial rate constants (rate^0) for the disappearance of HCl(g) and 2-butyne(g) and the appearance of gaseous product [(Z)-2-chloro-2-butene] for the reaction between HCl(g) and 2-butyne(g) at 296 K in Pyrex IR cells with sodium chloride windows. Most data are expressed as the average of at least three (3) replications. The initial concentrations are considered accurate to ±3%.

2-butyne (2011.0–2103.0 cm^{-1}), and to the sole initial product (*Z*)-2-chloro-2-butene (1270.0–1329.0 cm^{-1}).[14]

Plots of disappearance of hydrogen chloride and 2-butyne and appearance of (*Z*)-2-chloro-2-butene, derived from a series of spectra intermediate to those represented by the spectra in Figure 1 (*i.e.*, originally 251.91 Torr in hydrogen chloride and 52.82 Torr in 2-butyne), are shown in Figure 2. Initial rates were determined from the initial slopes of these plots. Table 1 presents a portion of the large volume of typical initial rate data at 296 K we have collected for the hydrogen chloride–2-butyne system using various initial pressures of each gas. The variations of initial rates of disappearance of hydrogen chloride (−d[HCl]/d*t*) with 2-butyne held at 104 ± 4 Torr, and 2-butyne (−d[2-butyne]/d*t*) with HCl held at 102 ± 5 Torr, with initial pressure are shown in Figure 3. The slopes of these plots give reaction orders for the two gases of *ca.* 0.5 in HCl and *ca.* 1 in 2-butyne, respectively.

Table 2 presents the data for the same reaction in jacketed Pyrex cells initially containing 353 ± 8 Torr of hydrogen chloride and 113 ± 0.7 Torr of 2-butyne at reaction temperatures of 296, 316, and 336 K. The overall rates for the disappearance of both reactants and for the appearance of the product exhibited only a very

Table 2[a]

temp, K	reactn no.	rate^0 = $-d[\mathrm{HCl}]/dt$, 10^6 mol h^{-1}	rate^0 = $-d[\text{2-butyne}]/dt$, 10^6 mol h^{-1}	rate^0 = $+d[\text{product}]/dt$, 10^7 mol h^{-1}
296	26	1.23	0.770	3.02
296	27	0.787	0.987	3.47
296	28	0.877	0.757	2.60
316	29	1.76	1.06	4.15
316	30	2.13	1.00	4.47
316	31	1.76	1.11	5.15
336	32	2.50	1.61	9.36
336	33	3.12	1.92	10.47
336	34	2.52	1.71	9.44
336	35	2.84	1.62	8.58
E_a, kcal mol^{-1}		5.12	3.49	5.53
$\Delta H^{\ddagger}_{296}$, kcal mol^{-1}		4.53	2.90	4.95
$\Delta S^{\ddagger}_{296}$, eu mol		−87.02	−92.79	−87.91

[a] Initial rate constants (rate^0) for the disappearance of HCl(g) and 2-butyne(g) and the appearance of gaseous product [(*Z*)-2-chloro-2-butene] for the reaction between HCl(g) and 2-butyne(g) in Pyrex IR cells with sodium chloride windows. All reactions were initially made up at 353 ± 8 Torr of HCl(g) and 113 ± 0.7 Torr of 2-butyne(g). Temperatures are accurate to ±0.5 °C.

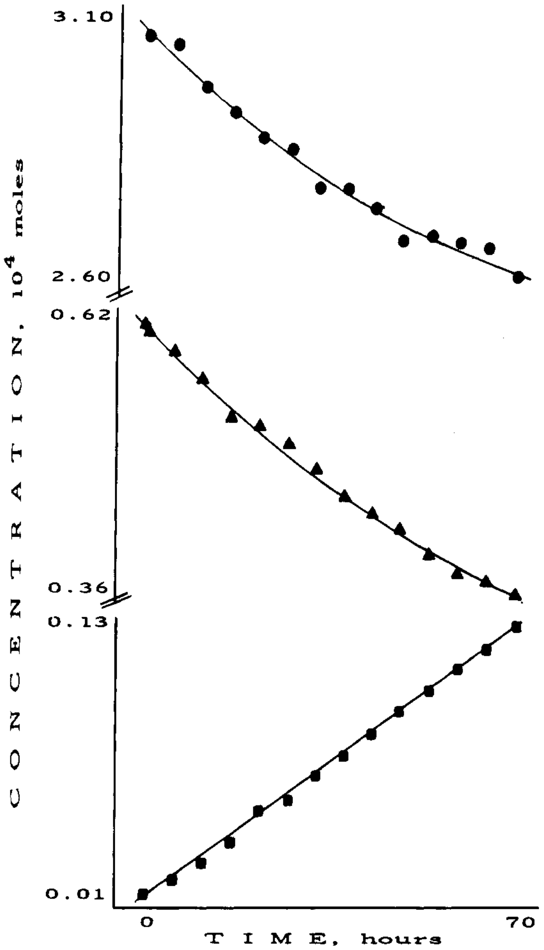

Figure 2. The disappearance of hydrogen chloride(g) (●) and 2-butyne(g) (▲) and the appearance of (*Z*)-2-chloro-2-butene(g) (■) at 296 K as a function of time in a Pyrex cell with sodium chloride windows. The initial mixture contained HCl(g) (252.91 Torr) and 2-butyne(g) (52.82 Torr).

small temperature dependence. Over the limited temperature range examined, the disappearance of hydrogen chloride occurs with an apparent E_a of 5.12 kcal mol^{-1}, a $\Delta H^{\ddagger}_{296}$ of 4.53 kcal mol^{-1}, and a $\Delta S^{\ddagger}_{296}$ of −87.02 eu mol; the disappearance of 2-butyne occurs with an apparent E_a of 3.49 kcal mol^{-1}, a $\Delta H^{\ddagger}_{296}$ of 2.90 kcal mol^{-1}, and a $\Delta S^{\ddagger}_{296}$ of −92.79 eu mol; (*Z*)-2-chloro-2-butene forms with an apparent E_a of 5.53 kcal mol^{-1}, a $\Delta H^{\ddagger}_{296}$ of 4.95 kcal mol^{-1}, and a $\Delta S^{\ddagger}_{296}$ of −87.91 eu mol. As it appears that the process we observe is wall catalyzed (*vide infra*), the exact significance of these numbers is not clear, and although they are suggestive of a very highly ordered transition state, it is unlikely that the reaction is another among the few concerted antarafacial processes involving alkynes.[18]

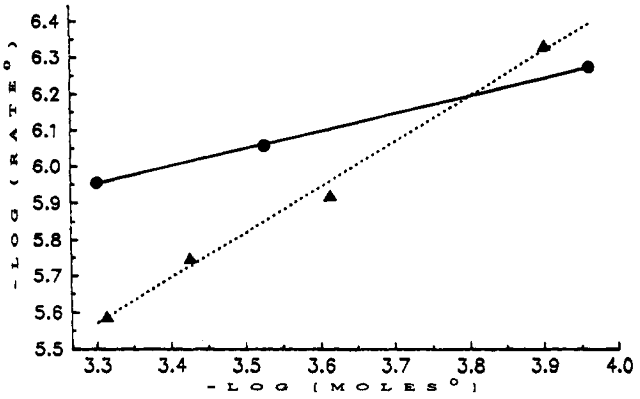

Figure 3. The variation in initial rates of the disappearance of HCl(g) (●) with initial pressure of HCl(g) (correlation coefficient = 1.00; 2-butyne(g) held constant at 104 ± 4 Torr) and the disappearance of 2-butyne(g) (▲) with the initial pressure of 2-butyne(g) (correlation coefficient = 0.996; HCl(g) held constant at 102 ± 5 Torr). The data points are the average of at least three trials; initial rates at respective concentrations are within standard deviations of 0.03.

Among the most striking features of the reaction we observe, discussed more fully below, are the following. (1) Overall, for these pressure and temperature ranges, the rate of the reaction is *apparently* about half order in hydrogen chloride and about first order in 2-butyne. (2) The sole product formed is (*Z*)-2-chloro-2-butene, which results from net *anti* (or *trans* or *antarafacial*) addition of hydrogen chloride across the triple bond. At significantly longer reaction times (*ca.* 3 months), formation of a second product, *viz.* 2,2-dichlorobutane, was observed. (3) When the initial concentration of hydrogen chloride (held at 98 ± 7 Torr) was *less than or equal to* the initial concentration of 2-butyne (reactions 1−9), the rate of disappearance of 2-butyne is *ca.* 1.5 ± 2 times faster than the rate of disappearance of HCl. (4) When the initial concentration of hydrogen chloride is *greater than or equal to* the initial concentration of 2-butyne (held at 104 ± 5 Torr; reactions 7−12), then the rates of disappear-

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[18] Viola, A.; Collins, J. J.; Filipp, N.; Locke. J. S. *J. Org. Chem.* **1993**, *58*, 5067.

Table 3[a]

	$-$d[HCl]/dt, 10^7 mol h^{-1}				$-$d[2-butyne]/dt, 10^7 mol h^{-1}				+d[product]/dt, 10^7 mol h^{-1}		
		calcd (k_{calc}) after eq no				calcd (k_{calc}) after eq no				calcd (k_{calc}) after eq no	
reactn no.	expt (k_{obs})	1	9	11	expt (k_{obs})	1	9	11	expt (k_{obs})	9	11
1	9.56	19.2	9.29	12.9	21.4	17.6	19.9	21.1	9.13	6.22	6.33
2	9.20	18.7	9.28	12.7	14.7	17.2	19.5	20.6	6.89	6.11	6.21
3	7.15	11.8	7.40	7.71	14.6	10.8	12.9	13.0	3.24	3.77	3.77
4	5.91	12.2	7.80	8.21	9.99	11.2	13.3	13.5	3.89	4.02	4.02
5	13.4	26.1	10.8	18.4	42.7	23.9	25.8	28.4	8.19	8.79	9.04
6	9.62	24.8	10.2	17.0	15.6	22.8	24.8	27.2	6.95	8.14	8.37
7	6.25	5.74	4.73	3.68	9.31	5.23	6.56	6.37	3.39	1.82	1.80
8	2.28	6.15	5.17	4.09	3.82	5.64	6.96	6.78	2.11	2.03	2.01
9	4.59	5.71	4.74	3.68	5.60	5.24	6.53	6.35	2.51	1.83	1.80
10	8.96	9.67	9.69	9.11	9.94	8.87	7.87	7.85	3.85	4.68	4.66
11	19.6	11.5	11.4	11.7	12.7	10.6	7.78	7.83	5.39	6.11	6.12
12	9.38	12.8	12.3	13.4	10.3	11.7	7.55	7.64	5.37	7.10	7.13
13	8.52	9.02	9.05	8.25	7.95	8.28	7.78	7.74	3.19	4.21	4.19
14	13.1	14.3	13.3	15.1	14.6	13.1	8.08	8.19	7.34	8.01	8.05
15	9.35	5.06	5.75	4.74	4.88	4.64	4.22	4.15	2.69	2.45	2.42
16	7.59	4.86	5.56	4.55	4.16	4.46	4.06	3.99	1.92	2.35	2.32
17	3.34	4.72	5.40	4.37	3.33	4.33	4.02	3.95	1.52	2.25	2.23
18	2.95	3.59	3.84	2.73	2.78	3.29	3.89	3.76	1.49	1.37	1.35
19	4.21	3.93	4.32	3.17	3.35	3.61	4.05	3.93	1.56	1.60	1.58
20	5.76	3.85	4.21	3.07	3.88	3.52	4.01	3.89	2.07	1.55	1.53
21	4.10	7.37	4.37	8.06	1.79	6.76	3.35	3.38	7.27	4.40	4.42
22	7.49	7.44	7.38	8.15	2.64	6.82	3.31	3.34	7.17	4.46	4.48
23	9.12	5.56	6.25	5.66	7.33	5.10	3.75	3.73	4.80	2.98	2.93
24	12.0	5.93	6.62	5.98	4.75	5.44	4.10	4.08	2.23	3.14	3.12
25	10.8	5.99	6.66	6.12	4.72	5.49	3.98	3.96	1.90	3.22	3.21

[a] A comparison of observed and calculated initial rates (rate^0) for the disappearance of both HCl(g) ($-$d[HCl^0]/dt) and 2-butyne(g) ($-$d[2-butyne^0]/dt) and for the appearance of gaseous product (+d[(*Z*)-2-chloro-2-butene^0]/dt for the reaction between HCl(g) and 2-butyne(g) at 296 K in Pyrex IR cells with sodium chloride windows.

ance of both reactants are about equal. (5) When the initial concentration of hydrogen chloride is *greater than* the initial concentration of 2-butyne (held at 52 ± 1 Torr; reactions 15–25), then the rate of disappearance of HCl is typically about 1.5 ± 2 times faster than the rate of disappearance of 2-butyne.

Kinetic Analysis. As has been pointed out before in a similar connection,[11b,c,19] reactions which are fractional order in one or more reactants,[20,21] and reactions which fail to show a normal temperature dependence,[22] are frequently found to be wall or surface catalyzed.[23]

Although these criteria appear to apply here, our first analysis of the data begins with our experimental observation that the reaction which is occurring is approximately half-order in hydrogen chloride and about first order in 2-butyne,[24] as determined graphically (Figure 3). Using the data from the graphical solutions and the average overall initial rate constants of 0.460 mol$^{-0.5}$ h^{-1} and 0.422 mol$^{-0.5}$ h^{-1} for the disappearance of hydrogen chloride and 2-butyne, respectively, where [yne^0] refers to the initial concentration of 2-butyne and the other abbreviations have their usual meanings, it is seen that the fit (eq 1) to experiment for the reactions of Table 1 is not unreasonable (as shown in Table 3).

$$\text{rate}^0 = k_{\text{obs}}[\text{HCl}^0]^{0.5}[\text{yne}^0]^1 \qquad (1)$$

Although this suggests that a gas-phase reaction might, in principle, be first order in proton,[25] we believe that it is possible that the graphical approximation (Figure 3) may not accurately reflect a gas-phase process, if indeed one is present. Thus, our second analysis of the reaction starts 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 (S) of the reactor (IR cell), that the reaction occurs between these adsorbed species, and that the product is subsequently desorbed.[26] These statements are summarized in eqs 2–5 below. We do not distinguish between potentially different surface sites.

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

$$\text{CH}_3\text{C}{\equiv}\text{CCH}_3\text{(g)} + \text{S} \underset{k'_r}{\overset{k'_f}{\rightleftharpoons}} \text{CH}_3\text{C}{\equiv}\text{CCH}_3\text{–S} \qquad (3)$$

$$\text{HCl–S} + \text{CH}_3\text{C}{\equiv}\text{CCH}_3\text{–S} \xrightarrow{k_s} (Z)\text{-CH}_3\text{CH}{=}\text{CCH}_3\text{Cl–S} \qquad (4)$$

$$(Z)\text{-CH}_3\text{CH}{=}\text{CCH}_3\text{Cl–S} \xrightarrow{k_d} (Z)\text{-CH}_3\text{CH}{=}\text{CCH}_3\text{Cl(g)} + \text{S} \qquad (5)$$

Assuming, initially, processes described by eqs 2–5 above, then the fraction of surface covered by HCl molecules may be represented by Θ_{HCl}, the fraction covered by 2-butyne as Θ_{yne}, and the uncovered surface as $(1 - \Theta_{\text{HCl}} - \Theta_{\text{yne}})$. Further assuming that the adsorption is competitive, that (particularly for HCl) it

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[22] Yang, K. H.; Hougen, O. A. *Chem. Eng. Prog.* **1950**, *46*, 146.

[23] For an excellent discussion of general principles, see: Laidler, K. *Chemical Kinetics*, 3rd ed.; Harper and Row: New York, 1987; p 229ff.

[24] It does not appear that the reverse reaction, *i.e.*, the unimolecular decomposition of (*Z*)-2-chloro-2-butene, has been reported.

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occurs without dissociation, and that the adsorption–desorption process reaches equilibrium, the fractions of surface covered by HCl and 2-butyne are given by eqs 6 and 7 (where $K_{\mathrm{HCl}} = k_f/k_r$ and $K_{\mathrm{yne}} = k'_f/k'_r$), respectively. The classical Langmuir-Hinshelwood mechanism,[27] where the rate is expected to be proportional to the fractions of the gases adsorbed (HCl and 2-butyne, respectively, in the case at hand), is thus given by eq 8, which is rewritten as eq 9 in terms of initial rates (rate^0) and

$$\Theta_{\mathrm{HCl}} = K_{\mathrm{HCl}}[\mathrm{HCl}]/(1 + K_{\mathrm{HCl}}[\mathrm{HCl}] + K_{\mathrm{yne}}[\mathrm{yne}]) \quad (6)$$

$$\Theta_{\mathrm{yne}} = K_{\mathrm{yne}}[\mathrm{ene}]/(1 + K_{\mathrm{HCl}}[\mathrm{HCl}] + K_{\mathrm{yne}}[\mathrm{yne}]) \quad (7)$$

$$\mathrm{rate} = k_s K_{\mathrm{HCl}} K_{\mathrm{yne}}[\mathrm{HCl}][\mathrm{yne}]/(1 + K_{\mathrm{HCl}}[\mathrm{HCl}] + K_{\mathrm{yne}}[\mathrm{yne}])^2 \quad (8)$$

$$([\mathrm{HCl}^0][\mathrm{yne}^0]/\mathrm{rate}^0)^{1/2} = 1/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2} + K_{\mathrm{HCl}}[\mathrm{HCl}^0]/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2} + K_{\mathrm{yne}}[\mathrm{yne}^0]/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2} \quad (9)$$

initial concentrations ([HCl^0] and [yne^0]) and may be explicitely solved[28] for the values of the ratios of the constants $[1/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2}]$, $[K_{\mathrm{HCl}}/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2}]$, and $[K_{\mathrm{yne}}/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2}]$ for the reactions whose data are given in Table 1. Evaluating these ratios for the case where the initial rates (Table 1) are those for the disappearance of hydrogen chloride ($-$d[HCl^0]/d*t*) gives 0.124, 148.941, and 211.593, respectively. However, when the initial rates used are those for the disappearance of 2-butyne, *i.e.*, ($-$d[2-butyne^0]/d*t*), the ratios of the constants are 0.097, 375.967, and 24.807, respectively. Similarly, evaluation of the ratio of these constants for the initial rates in terms of the appearance of product (+d[(*Z*)-2-chloro-2-butene^0]/d*t*) gives 0.257, 73.394, and 14.683, respectively. Comparisons of the experimentally determined initial rate constants (rate^0) for the reaction between HCl(g) and 2-butyne(g) under the various starting concentrations of Table 1 with those calculated utilizing the above ratios of constants are given in Table 3 for $-$d[HCl^0]/d*t*, $-$d[2-butyne^0]/d*t*, and +d[(*Z*)-2-chloro-2-butene^0]/d*t*, respectively.

One of the modifications of the Langmuir–Hinshelwood mechanism considers specifically that the two reactants are quite different and one of them is only very weakly adsorbed.[23] Indeed, if the 2-butyne is only weakly adsorbed, the K_{yne}[yne] term in the denominator of eq 8 may be neglected relative to the other terms and the rate expression (eq 10), which on rearrangement to eq 11 and

$$\mathrm{rate} = k_s K_{\mathrm{HCl}} K_{\mathrm{yne}}[\mathrm{HCl}][\mathrm{yne}]/(1 + K_{\mathrm{HCl}}[\mathrm{HCl}])^2 \quad (10)$$

$$([\mathrm{HCl}^0][\mathrm{yne}^0]/\mathrm{rate}^0)^{1/2} = 1 + (K_{\mathrm{HCl}}[\mathrm{HCl}^0]/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2} \quad (11)$$

solution for initial rates, leads to the values of the ratios of the constants $[1/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2}]$ and $[K_{\mathrm{HCl}}/(k_s K_{\mathrm{HCl}} K_{\mathrm{yne}})^{1/2}$ for the disappearance of hydrogen chloride of 0.180 and 69.956, respectively. Initial rates in terms of disappearance of 2-butyne gives the ratios of the constants as 0.103 and 366.706, respectively. Evaluation of the ratios of these constants for the appearance of (*Z*)-2-chloro-2-butene gives 0.261 and 67.913, respectively. Comparisons of the experimentally determined initial rates with those calculated using eq 11 are also given in Table 3. Interestingly, for this special case of the Langmuir–Hinshelwood mechanism, the rate must pass through a maximum as the concentration of HCl increases but should not exhibit this behavior for 2-butyne (in contrast to the process described by eq 8 which should pass through a maximum for both reactants). Regretably, over the relatively narrow pressure (concentration) range utilized here, advantage could not be taken of these distinguishing attributes and thus neither pathway can be excluded. Finally, as has been recently reported, it is possible for *more than one* surface mechanism to be simultaneously occurring.[29] Thus, our data gave reasonably good agreement between experimentally observed initial rates and those calculated using eqs 1, 9, and 11 (Table 3). Although graphical comparisons of experimental vs calculated rates did show scatter, the results using eq 11 had slopes closer to unity and better correlation coefficients than those with eqs 1 and 9. However, a Pyrex surface does not permit a clear delineation of these pathways.

Other special cases of the Langmuir–Hinshelwood formalism which consider (a) a sparsely covered surface; (b) one reactant weakly adsorbed, *i.e.* hydrogen chloride for the cases at hand, and the other strongly adsorbed or not adsorbed; and (c) the adsorption of two gases without mutual displacement[23] as well as the approach of Rideal,[30] who considered one species strongly adsorbed and the other unadsorbed, all gave reasonable agreement of experimental and calculated values of the rates yet all required ratios of constants with at least one negative value. The significance of the sign of these ratios has been commented on elsewhere[11b,31] and it it generally agreed that some doubt may be cast upon an analysis which requires a negative value for any of the ratios.

Processes on heterogeneous surfaces considered experimentally by Freundlich[32] or Tempkin[33] and from a theoretical prespective by Frumkin and Slygin[34] all suffer from a restriction on their order which does not fit our experimental observations. Application of the theoretical work of Braunauer, Emmet, and Teller (BET Theory),[35] subsequently modified by Braunauer, Deming, Deming, and Teller,[36] which specifically treats the formation of multilayer wall-assisted gaseous aggregations, generally requires a well-defined surface for detailed analysis. As the reactions investigated above were carried out in Pyrex vessels, we have been unable to successfully apply these more detailed analyses.

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The observed more rapid disappearance of HCl when it is in excess over 2-butyne and *vice versa* is in concert with both materials being adsorbed on the surface of the reaction vessel (where the reaction occurs) as a function of their respective initial pressures. Indeed, the equilibrium constants for both of these processes as well as the rate constant for the surface reaction (k_s) can be evaluated from the data. Thus, based on the rate of disappearance of hydrogen chloride, K_{HCl} and K_{yne} may be estimated as 1.20×10^3 and 1.71×10^3 and k_s as 3.17×10^{-5} mol h^{-1}. The similarity in equilibrium constants for the adsorption–desorption of alkyne and *reacting* hydrogen chloride supports the apparent change in the relative rates of disappearance of the gases with change in pressure. However, it seems unlikely that the HCl attached by hydrogen bonding directly to the surface could utilize the proton holding it to the glass to also react with the alkyne. Thus, the mechanism we propose involves surface associated hydrogen chloride, the formation of a multilayer, and donation of a proton from within the multilayer (*i.e.,* from a hydrogen chloride *not* directly surface bound) to one face of the alkyne (which must also be surface associated) while the chlorine attached to the reacting proton becomes hydrogen bonded to a second hydrogen chloride (the actual formation of the hydrogen dichloride anion[37] [*i.e.,* HCl^{2-}] is not supposed). At the same time a chlorine from a surface associate hydrogen chloride is transferred to the opposite face of the reacting alkyne. Thus, we suggest that the process is initiated, and the rate determined, by surface "associated" proton–alkyne interaction and that chlorine participation is not involved in the rate-determining step.

Conclusions

Mixtures of gaseous hydrogen chloride and gaseous 2-butyne at total initial subatmospheric pressures and temperatures close to room temperature react to yield (Z)-2-chloro-2-butene, the product of net *trans* addition, by a surface-catalyzed process. Kinetic measurements are in accord with Langmuir–Hinshelwood mechanisms involving the walls of the reactor.

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