Vinyl Chloride from Acetylene and Hydrogen Chloride: Catalytic-Rate Studies

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The reaction rate of gaseous acetylene and hydrogen chloride was studied experimentally on a mercuric chloride–activated carbon catalyst at pressures from 1 to 4 atm. and temperatures of 167°, 212°, and 257°F. The measurements were made in a differential reactor packed with mercuric chloride impregnated on activated carbon, the data being taken to obtain the separate effect of the partial pressure of each of the components on the rate.

The results indicated that hydrogen chloride was strongly adsorbed on the catalyst and that vinyl chloride was also adsorbed to a significant extent. A rate equation, which well represented the data, was developed from the following postulates: (*a*) acetylene is adsorbed on the catalyst on one type of site, (*b*) hydrogen chloride and vinyl chloride are adsorbed on a different kind of site, (*c*) the formation of vinyl chloride occurs by reaction of adsorbed acetylene and adsorbed hydrogen chloride, and (*d*) the rates of adsorption and desorption are fast compared with the formation rate of vinyl chloride.

Vinyl chloride is produced commercially by the hydrochlorination of acetylene with anhydrous hydrogen chloride or by the chlorination of ethylene. The availability of low-cost acetylene from natural gas has increased the significance of the first method. In it acetylene and hydrogen chloride in the gas phase are passed over a solid catalyst carrier containing mercuric chloride. While the commercial process (*1*, *2*, *3*) has been in operation for some time, suitable rate data for studying the kinetics of the reaction are lacking.

Wakano and Shenichi (*13*) proposed an empirical expression of the exponential form for the rate

$$r = C p_A^{\,a} p_H^{\,h} e^{-B/RT} \qquad (1)$$

in which the values of *a*, *h*, *B*, and *C*, depended upon the operating conditions. Lynn and Kobe (*8*) presented data showing the effect of impurities in the acetylene feed and variations in catalyst preparations on the product obtained. The reaction product was identified as pure vinyl chloride. Conversions were measured as a function of space velocity, but accurate rate data could not be deduced from the measurements.

A number of laboratory investigations have been carried out in fluidized beds (*4*, *5*, *11*, *15*) over limited ranges of conditions and with varying precision. Because of these limitations substantial conclusions regarding a rate equation could not be reached.

The chief objective of the present study was to obtain reliable rate data for the mercuric chloride–catalyst reaction over a range of pressure and composition. Because of the uncertainties in interpretation introduced by back-mixing in fluidized beds, a fixed-bed, differential type of reactor was used. The total catalyst bed of about 22 in. was diluted to a ratio of approximately one part of catalyst (mercuric chloride impregnated on activated carbon) to sixteen parts of inert packing (porcelain). This arrangement resulted in conversions from 2 to 3%, based upon total feed, and reduced the temperature gradients in the bed to a few degrees (maximum radial temperature difference = 6°F.). No evidence of by-product formation (dichloroethane) was found in operating at these conditions.

EXPERIMENTAL WORK

There were three main parts to the experimental equipment used to obtain rate measurements: gas purification and metering system, the reactor system, and the product gas-analysis system. Figure 1 shows a schematic diagram of the reactor and product gas-analysis system.

Feed gases from commercial cylinders were purified and dried to minimize catalyst poisoning and corrosion. The feed rates of acetylene, hydrogen chloride, and vinyl chloride were controlled with needle valves augmented with constant-differential pressure flow meters. Steel-encased glass capillary meters were used in the flow measurement. Wherever either hydrogen chloride or vinyl chloride was present, the connecting lines were constructed of ¼-in. Hastelloy-B tubing to resist corrosion. A nitrogen feed was provided for purging the system.

The acetylene was purified by passage through water, a ferric chloride solution (an aqueous solution containing 5% ferric chloride, 0.5% mercuric chloride, and 1% acetic acid), and a silica-gel column before metering. Traces of moisture were removed from the hydrogen chloride and nitrogen by scrubbing with concentrated sulfuric acid and from the vinyl chloride by passage through a column of silica gel.

The reactor (Figure 2) was fabricated of standard 1-in. stainless steel pipe with a length of 36-in. Heat transfer oil was circulated through a jacket surrounding the central section, 22-in. long. The reactor wall temperature was held constant to within 0.25°F. Temperatures within the reactor were measured with seven thermocouples at fixed positions in an axial well of ⅛-in. stainless steel hypodermic tubing. The well extended the entire length of the reactor. The end sections of the reactor were packed with glass beads and heated electrically to minimize thermal gradients. Preliminary studies (*9*) indicated that one part of catalyst (by volume) in sixteen parts of inert packing minimized the combined uncertainty due to temperature and composition effects. Initial tests showed that the inert material, 6- to 8-mesh crushed porcelain, had no catalytic activity. The catalyst bed contained 9.08 g. of catalyst particles and 285 cc. of inert material.

A diaphragm type of back-pressure regulator at the outlet from the reactor permitted operation at any pressure up to 60 lb./sq. in. gauge over the entire range of flow rates. The gases were metered with a precision rotameter and then scrubbed in a water-spray column before venting. A soap-bubble meter, especially constructed for corrosion resistance, was inserted after the rotameter and used to calibrate all flow meters in place

Product gas analysis was based upon a comparison of the thermal conductivity of a small portion of the feed gases with a small portion of the product gases by the use of a thermistor type of thermal-conductivity cell. Flow rates to the cell were held at fixed known values. This procedure gave greater precision than the use of a single reference gas for two reasons: the cell was used to detect directly the difference in thermal conductivity due to reaction, and the effect of small errors in

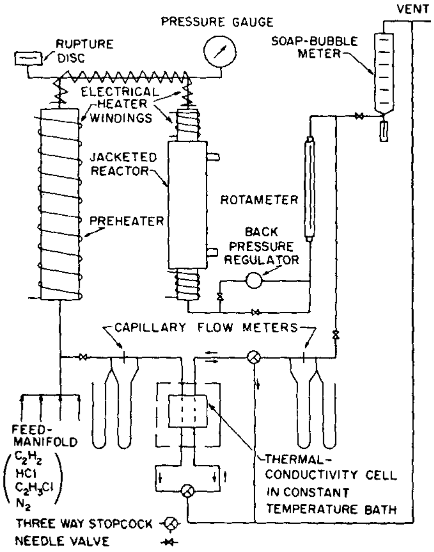

Fig. 1. Flow diagram.

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setting the relative flow rates of the feed gases was almost completely canceled.

In the use of thermal-conductivity measurements for a three-component system the mole fractions of the components must be interrelated in a known manner. In the present investigation the ratio of acetylene to hydrogen chloride in the feed gas could be set, and the molal composition of the product gases was related to the feed by the stoichiometry of the reaction. To determine this information, the cell had to be calibrated for various ratios of the reactants and various conversions. This was accomplished by preparing known mixtures of the three components. In the calibration procedure the cell imbalance [difference in cell electromotive force when the feed gas was passed through both sides of the cell and when the product gas (synthetic sample) was passed through the sample side] was measured under constant current conditions. From this information calibration curves were prepared giving the mole fraction of vinyl chloride in the product stream as a function of the imbalance and the feed-gas composition.

The acetylene used in these experiments was a commercial grade. Besides the acetone solvent, the principal impurities were phosphine, arsine, ammonia, and hydrogen sulfide. The hydrogen chloride was 99.8% pure; air was the principal contaminant, although traces of carbon dioxide, benzene, and chlorobenzene were present. Vinyl chloride contained 0.1% each of polymer and water vapor. The monomer was inhibited by 1,000 p.p.m. of phenol.

Mercuric chloride, 8.7% by weight of the total mass, was deposited on granular activated carbon. A 6- to 8-mesh size with an average particle diameter of 0.00833 ft. was used. The fresh catalyst had a total area of 868 sq.m./g.; this had dropped to 130 sq.m./g. at the end of the experiments. The bulk density of the active catalyst particles (undiluted) was 25 lb./cu. ft.; the external surface per unit volume, 504 sq. ft./cu. ft.; and the external void fraction, approximately 30%.

Because of the potential explosion hazard of acetylene, high surface-volume ratios were maintained in all lines and vessels. Extensive data on the conditions and hazards of acetylene decomposition have been presented by Sargent (*10*).

RANGE OF MEASUREMENTS

Most of the rate measurements were carried out at 212°F., although data at a few feed compositions were obtained at 167° and 257°F. The partial pressures of reactant gases for which runs were made are shown in Table 1. The pressure combinations were chosen so that the feed ratios corresponding to the thermal-conductivity-cell calibrations were used. The total pressure varied from 1 to 4 atm. Flow rates were chosen for each feed composition so as to give the best precision in evaluating the average reaction rate and temperature and in reading the flow-rate manometers. The order of the runs was randomized, and duplicate runs were made for each condition at 212°F., since these data were most important in analyzing the kinetics of the reaction.

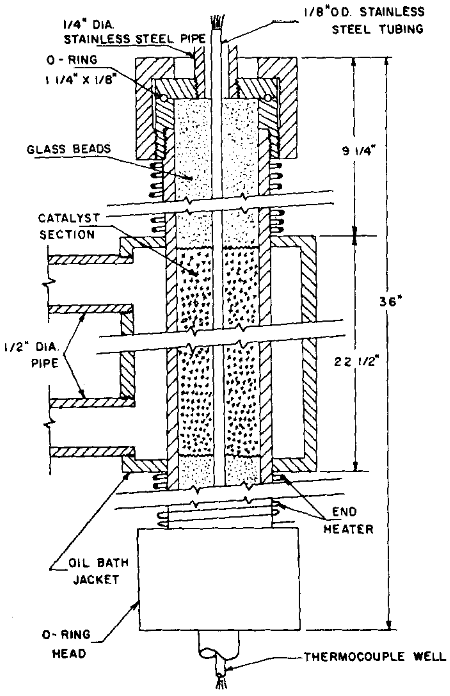

Fig. 2. Reactor details.

CALCULATION OF RESULTS

To have the data in a form suitable for interpretation it was necessary to convert the measured conversion to vinyl chloride in each run to a rate at a known temperature and composition. Because of variations in catalyst activity with on-stream time, the treatment of the measured conversions included correction to a standard activity.

Before the corrections were carried out to a point rate at a standard activity, the importance of diffusion had to be estimated. When one used the procedures of Hougen and Yang (*7*) and measured rate data, it was found that the partial pressure difference between the bulk gas and catalyst surface was about 10^{-4} atm. An estimate of the effectiveness factor from the reaction rate, pore volume, particle size, and diffusivity data following the procedures of Smith (*12*) gave a value greater than 0.99 under the worst conditions. Under these circumstances it was supposed that neither external nor internal diffusion resistances were significant in the overall reaction. Thus the bulk-gas partial pressures could be substituted for the values at the catalyst surface in the kinetic interpretation.

TABLE 1. EXPERIMENTAL DESIGN

TEMPERATURE = 212°F (NO VINYL CHLORIDE IN FEED)

P_A(ATM) \ P_H(ATM)	0.5	0.66	1.0	1.33	2.0	2.66	3.0
0.5	xx		xx		xx		
0.66		xx		xx		xx	
1.0	xx		xxx		xx		xx
1.33		xx		xxx		xxx	
2.0	xx		xx		xx		
2.66		xx		xx			
3.0			xx				

TEMPERATURE = 167°F AND 257°F

P_A(ATM) \ P_H(ATM)	0.5	2.0
0.5	x	x
2.0	x	x

TEMPERATURE = 212°F (WITH VINYL CHLORIDE IN FEED)

P_A AND P_H \ P_{VC}	0.25	0.5	0.75	1.0	1.5
0.25		x			
0.375	x		x		
0.5				x	
0.75		x			xx
1.125			x		

x – INDICATES ONE RUN

The conversion for each run was used to evaluate an average rate for the differential reactor by

$$r = \frac{\Delta x'}{W/F} \tag{2}$$

Corrections for the significant variation of catalyst activity with time (the rate, at the same conditions, decreased to one-third the initial value from the initial to final run) were made by alternating standard runs with data runs. The conditions for the standard run were a feed of 50 mole % acetylene and 50 mole % hydrogen chloride, total feed rate of 0.06 cu. ft./min. (at standard temperature and pressure) total pressure of 1 atm. and a reactor temperature of 212°F. A standard conversion curve of x' vs. W/F was prepared by varying the feed rate while maintaining the other standard conditions constant. This curve and the results for the alternating standard runs were employed to obtain a corrected value of W/F for each run. Then assuming that the activity of the catalyst was directly proportional to the rate, one obtains the corrected rate by

$$r_{corr} = r\left[\frac{(W/F)_{corr}}{(W/F)_{actual}}\right]_{const\ \Delta x'} \tag{3}$$

The rate evaluated from Equation (3) is an average value for the varying compositions in different parts of the differential reactor. To place these results on the basis set forth in the experimental design, each rate was corrected to a zero-conversion value, that is the rate corresponding to conditions at the inlet to the reactor. Since the conversions were low in all cases, these corrections were likewise small. They were made by using the approximate values from Equation (3) to determine the variation in rate with partial pressures of each of the components, acetylene, hydrogen chloride, and vinyl chloride. Knowing these individual gradients and the average conversion in the bed, one could correct the average rate to a zero-conversion value.

Similarly the average rate from Equation (3) represents the combined result of the temperature variations with position in the reactor. The method of correction of all runs to a single temperature must be approximate without multiple temperature measurements in the bed. Preliminary work (*14*) indicated the thermocouple readings in the well, and the adjacent gas temperature agreed within 1°F. Also the radial gradients were small, and most of the resistance to heat transfer in the bed is probably near the wall. Hence the measured temperatures in the thermocouple well were assumed to be the same as the bulk mean-radial temperature.

The axial temperature changes in the bed were somewhat larger. Whereas a maximum change of 15°F. was obtained at the highest operating temperature, most of these changes were about 6°F. An average gas temperature was calculated from the values determined at the six axial positions in the thermocouple well.

Once the average gas temperature was obtained for each run, the rate was corrected to one of the reference temperatures (167°, 212° or 257°F.) by the Arrhenius equation. The approximate activation energy (determined from the data at different temperatures) used for this correction was 12,400 B.t.u./lb. mole. The Arrhenius plot was based upon catalyst-surface temperatures rather than gas temperatures. These surface temperatures were estimated from the heat (−71,500 B.t.u./lb. mole) and rate of reaction and a dimensionless correlation (*6*) of heat transfer coefficient between the fluid and solid particles in a packed bed. This difference became very significant at 257°F. The rate measurements in the vicinity of 212°F. were referred to the average gas temperature rather than to the estimated surface value because of the uncertainties in the latter temperatures.

The resultant values of the rate and temperature along with the initial composition are shown in Table 2.* Both initial rates (no vinyl chloride) and values for vinyl chloride in the feed are shown. Complete data for each run are also available (*14*). The results are represented graphically by the indicated experimental points in Figures 3 to 6. Figures 3 and 4 show initial rates; Figures 5 and 6, the effect of vinyl chloride.

Table 2. Table of Results

Run	P_A	P_H	Experimental Rate	Calculated Rate	Deviation	Percent Deviation
260	0.5	0.5	0.0130	0.0120	−0.0010	−7.7
304	1.0	0.5	0.0200	0.0202	0.0002	1.0
383	1.0	0.5	0.0195	0.0202	0.0007	3.6
327	2.0	0.5	0.0275	0.0308	0.0033	12.0
371	2.0	0.5	0.0290	0.0308	0.0018	6.2
300	0.66	0.66	0.0175	0.0169	−0.0006	−3.4
373	0.66	0.66	0.0174	0.0169	−0.0005	−2.9
321	1.33	0.66	0.0260	0.0273	0.0013	5.0
356	1.33	0.66	0.0266	0.0273	0.0007	2.6
341	2.66	0.66	0.0378	0.0396	0.0018	4.7
370	2.66	0.66	0.0384	0.0396	0.0012	3.1
302	0.5	1.0	0.0154	0.0152	−0.0002	−1.3
362	0.5	1.0	0.0152	0.0152	0.0000	0.0
310	1.0	1.0	0.0261	0.0257	−0.0004	−1.5
317	1.0	1.0	0.0250	0.0257	0.0007	2.8
364	1.0	1.0	0.0251	0.0257	0.0006	2.4
331	2.0	1.0	0.0400	0.0391	−0.0009	−2.2
360	2.0	1.0	0.0400	0.0391	−0.0009	−2.2
336	3.0	1.0	0.0496	0.0470	−0.0026	−5.2
387	3.0	1.0	0.0484	0.0470	−0.0014	−2.9
319	0.66	1.33	0.0201	0.0205	0.0004	2.0
385	0.66	1.33	0.0201	0.0205	0.0004	2.0
347	1.33	1.33	0.0333	0.0333	0.0000	0.0
368	1.33	1.33	0.0312	0.0333	0.0021	6.7
391	1.33	1.33	0.0333	0.0333	0.0000	0.0
350	2.66	1.33	0.0490	0.0483	−0.0007	−1.4
377	2.66	1.33	0.0503	0.0483	−0.0020	−4.0
392	2.66	1.33	0.0501	0.0483	−0.0018	−3.6
325	0.5	2.0	0.0184	0.0176	−0.0008	−4.3
354	0.5	2.0	0.0175	0.0176	0.0001	0.5
329	1.0	2.0	0.0290	0.0297	0.0007	2.4
358	1.0	2.0	0.0291	0.0297	0.0006	2.0
338	2.0	2.0	0.0450	0.0452	0.0002	0.4
389	2.0	2.0	0.0458	0.0452	−0.0006	−1.1
343	0.66	2.66	0.0222	0.0230	0.0008	3.6
366	0.66	2.66	0.0223	0.0230	0.0007	3.1
344	1.33	2.66	0.0340	0.0373	0.0033	9.7
375	1.33	2.66	0.0364	0.0373	0.0009	2.5

PRECISION OF RESULTS

The primary sources of error in the rate data are the measurements of flow rates, the assignment of an average temperature for the gas in the reactor and for the catalyst particles, and the variation in catalyst activity.

Errors in flow-rate measurements affected the results in several ways: in the calibration of the thermal conductivity cell, in the value of *W/F* assigned

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*Complete tabular material has been deposited as document No. 5973 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

TABLE 2. (CONTINUED)

RUN	P_A	P_H	EXPERIMENTAL RATE	CALCULATED RATE	DEVIATION	PERCENT DEVIATION
352	1.33	2.66	0.0351	0.0373	0.0022	6.2
334	1.0	3.0	0.0297	0.0314	0.0017	5.7
379	1.0	3.0	0.0309	0.0314	0.0005	1.6
						3.3
412	0.5	0.5	0.00684	0.00633	-0.0005	-7.5
413	2.0	0.5	0.0158	0.0152	-0.0006	-3.8
415	0.5	2.0	0.00935	0.00913	-0.0002	-2.3
416	2.0	2.0	0.0203	0.0221	0.0017	8.4
						5.5
418	0.5	0.5	0.0235	0.0216	-0.0019	-8.1
420	2.0	0.5	0.0590	0.0572	-0.0018	-3.0
421	0.5	2.0	0.0350	0.0322	-0.0028	-8.0
423	2.0	2.0	0.0800	0.0850	0.0050	6.2
						6.3
398	0.25	0.5	0.0030	0.0021	-0.0009	-30
400	0.375	0.25	0.0067	0.0056	-0.0011	-16.5
403	0.375	0.75	0.0043	0.0034	-0.0009	-21
405	0.5	1.0	0.0065	0.0046	-0.0019	-29
396	0.75	0.5	0.0117	0.0119	0.0002	1.7
407	0.75	1.5	0.0065	0.0067	0.0002	3.8
410	0.75	1.5	0.0068	0.0067	-0.0001	-1.2
409	1.125	0.75	0.0162	0.0169	0.0007	4.3
						13.7
						5.7

Temperature = 212°F (without vinyl chloride in the feed).

Temperature = 167°F. (without vinyl chloride in the feed).

Temperature = 257°F. (without vinyl chloride in the feed).

Temperature = 212°F. (with vinyl chloride in the feed).

to a run, and in determining the composition of the feed gas. Analysis of magnitudes of flow-rate fluctuations indicated that maximum errors of a few per cent were possible from this source.

Temperatures were read to $\pm\frac{1}{2}$°F. on the recorder, which was calibrated to the same accuracy. Since the maximum *radial*-temperature difference between the oil (in the jacket) temperature and that in the center of the reactor was 6°F., it was believed that the average gas temperature was accurate within 2°F. Estimates of the temperature difference between gas and catalyst surface should be accurate to ±2°F. The total temperature error of ±4°F. suggests a maximum error in rate of about 5%.

The variation in catalyst activity with time was taken into account by alternating runs at standard conditions, as already described. While the variations in activity were large, there were indications that the correction method adequately accounted for the possible errors. The repeat runs made at different times, and hence different activities, were in good agreement after correction for activity variations. This is evident from Table 2, for example, by comparing runs 304 and 383, 327 and 371, 300 and 373, etc. (The runs were numbered in sequence so that the difference in two numbers is a measure of the time interval between the two runs.)

The summing of all the errors indicates a maximum error in reaction rate of 10 to 15%. At most conditions the error would be less than this maximum. The scatter in the data, as seen in Figure 3 for example, is well within the maximum predicted error.

KINETICS OF THE REACTION

The determination of a mechanism for most gas-solid reactions from over-all rate measurements is virtually impossible. The hydrochlorination of acetylene is no exception. Information on adsorption rates of reactants and products on the catalyst at reaction conditions, as well as identification of intermediate products, is necessary before conclusions about the mechanism can be stated. Over-all rate data can be used only to test rate equations determined from likely postulates about the mechanism of the reaction and to reject those which are incompatible.

From the data as plotted in Figure 3 it is seen that the initial rate (no vinyl chloride present) increased with partial pressure of hydrogen chloride at low values of p_H and then became constant at higher partial pressures. This behavior suggests that hydrogen chloride is strongly adsorbed, filling most of the active sites available to it at relatively low partial pressures. In contrast, Figure 4 indicates that the rate increases with p_A over the whole range of partial pressures of acetylene. The curves in Figure 4 are evidence that acetylene is less strongly adsorbed than hydrogen chloride, if it is adsorbed. If both acetylene and hydrogen chloride are adsorbed on the same types of sites, and reaction occurs between the adsorption compounds, the rate would be expected to pass through a maximum and ultimately to decrease with continually increasing partial pressures of hydrogen chloride. Thus the more strongly adsorbed hydrogen chloride would displace acetylene from the active sites. This would result in fewer adjacent pairs of adsorbed hydrogen chloride and acetylene and a lower rate, particularly if the surface reaction between adsorption compounds were a relatively slow step in the over-all reaction. The data (Figure 3) did not show this maximum in rate. This behavior and the chemical dissimilarity between acetylene and hydrogen chloride suggest that the two components, if adsorbed, reside on different types of sites.

The effect of vinyl chloride on the rate is shown directly in Figure 5 and as a parameter in Figure 6. Since the reaction is essentially irreversible at the conditions studied (equilibrium constant = 10^8 at 212°F.), the decrease in rate with the partial pressure of vinyl chloride suggests that this component is adsorbed and occupies active sites on the catalyst. Other evidence is available

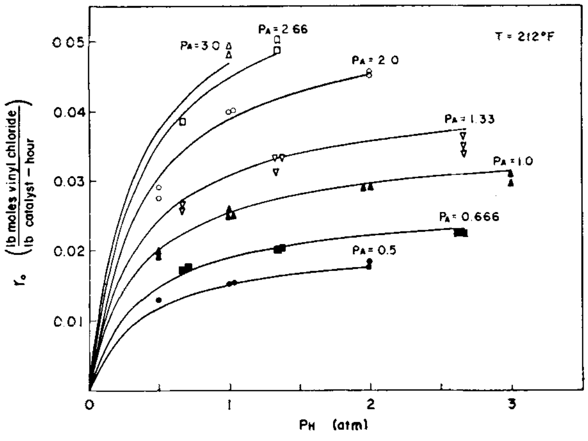

Fig. 3. Effect of hydrochloric acid partial pressure on initial rate.

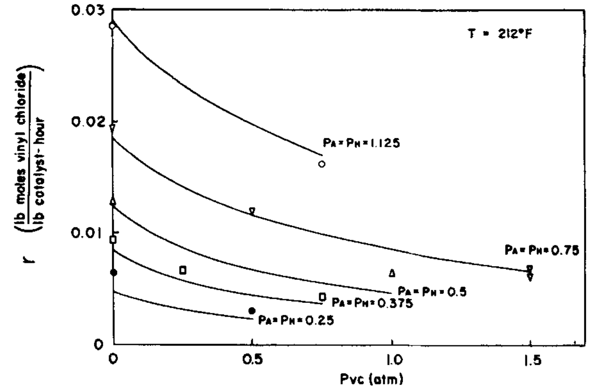

Fig. 5. Effect of vinyl chloride partial pressure on rate.

indicating the vinyl chloride is adsorbed. Frescoln (*4*) found that this component produced channeling and slugging in a fluidized catalyst bed. In an adsorption apparatus he noted that vinyl-chloride adsorption was irreversible, and he theorized that short-chain polymers formed on the catalyst.

On the basis of this information a rate equation, which agrees well with the experimental data, can be derived. It is supposed that all three components are adsorbed, acetylene on one type of site and hydrogen chloride and vinyl chloride on another. The reactions may be written

$$A + S_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A : S_1 \tag{4}$$

$$H + S_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} H : S_2 \tag{5}$$

$$VC + S_2 \underset{k_7}{\overset{k_6}{\rightleftharpoons}} VC : S_2 \tag{6}$$

The reaction to form vinyl chloride is postulated to occur by interaction between adsorbed acetylene ($A : S_1$) and adsorbed hydrogen chloride ($H : S_2$) on adjacent sites; that is

$$A : S_1 + H : S_2 \xrightarrow{k_5} VC + S_1 + S_2$$

If the fraction of the sites of type 1 occupied by acetylene is θ_{A1} and the fraction of type-2 sites occupied by hydrogen chloride is θ_{H2}, the rate may be written

$$r = k_5 \theta_{A_1} \theta_{H_2} \tag{7}$$

At steady state conditions the fraction of the surface occupied by the three components will not change with time. Hence the net rate of formation of each of the three adsorption compounds may be set equal to zero. Thus for acetylene, when one follows Langmuir's formulation of rates of adsorption,

$$k_1 p_A (1 - \theta_{A1}) - k_2 \theta_{A1} - k_5 \theta_{A1} \theta_{H2} = 0 \tag{8}$$

Similar equations for hydorgen chloride and vinyl chloride are

$$k_3 p_H (1 - \theta_{VC2} - \theta_{H2}) - k_4 \theta_{H2} - k_5 \theta_{A1} \theta_{H2} = 0 \tag{9}$$

$$k_6 p_{VC} (1 - \theta_{VC2} - \theta_{H2}) - k_7 \theta_{VC2} = 0 \tag{10}$$

In these expressions $(1 - \theta_{A1})$ is the fraction of type-1 sites which are vacant, and $(1 - \theta_{H2} - \theta_{VC2})$ is the fraction vacant of sites of type 2. Equations (8) through (10) can be solved for θ_A, θ_{H2}, and θ_{VC2}. The expression for θ_{H2} is

$$\theta_{H2} = \frac{k_3 k_7 p_H}{k_3 k_7 p_H + (k_7 + k_6 p_{VC}) \left[k_4 + \dfrac{k_5 k_1 p_A}{k_1 p_A + k_2 + k_5 \theta_{H2}} \right]} \tag{11}$$

and in terms of θ_{H2}

$$\theta_{A1} = \frac{k_1 p_A}{k_1 p_A + k_2 + k_5 \theta_{H2}} \tag{12}$$

These two expressions can be adapted to explicit equations for θ_{A1} and θ_{H2} and substituted in Equation (7) to give an equation for the rate of reaction in terms of the partial pressures and constants (at a given temperature). However the result is too complex to be useful.

Simplifications are possible if one makes assumptions regarding the relative magnitudes of some of the reaction rates. It is evident that many sets of assumptions may be made, each leading to a final rate equation which will contain

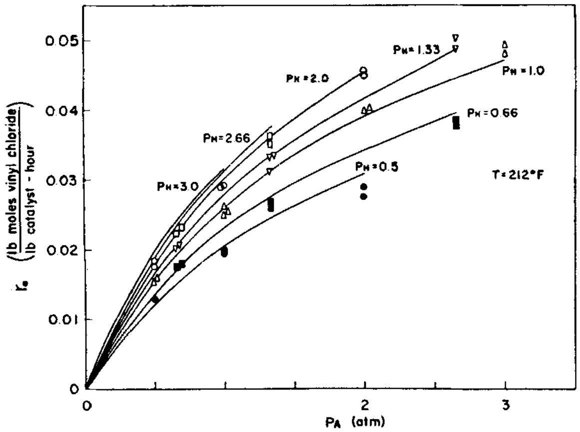

Fig. 4. Effect of acetylene partial pressure on initial rate.

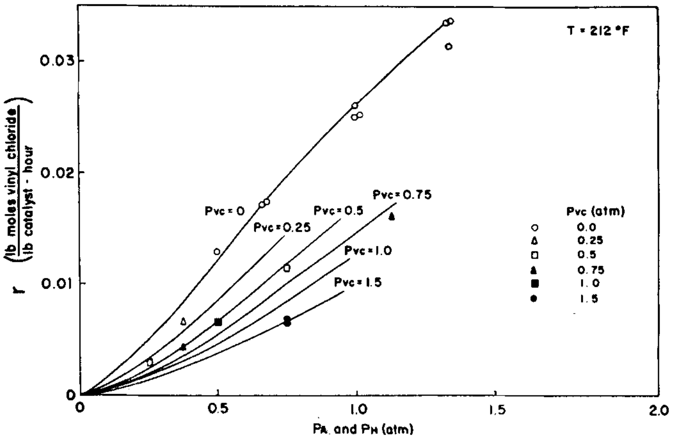

Fig. 6. Effect of hydrochloric acid and acetylene partial pressure on rate.

several constants. One set which leads to a result in agreement with the data is as follows.

It is supposed that the rate of reaction given by Equation (7) is slow compared with the rates of desorption and adsorption of both acetylene and hydrogen chloride. Then the term $k_5\theta_{A1}\theta_{H2}$ can be neglected in Equations (8) and (9). Under these restrictions Equations (11) and (12) reduce to

$$\theta_{H2} = \frac{k_3k_7p_H}{k_3k_7p_H + k_4k_7 + k_4k_6p_{VC}} = \frac{\frac{k_3}{k_4}p_H}{1 + \frac{k_3}{k_4}p_H + \frac{k_6}{k_7}p_{VC}} \qquad (13)$$

and

$$\theta_{A1} = \frac{k_1p_A}{k_1p_A + k_2} = \frac{\frac{k_1}{k_2}p_A}{\frac{k_1}{k_2}p_A + 1} \qquad (14)$$

Substituting these quantities in Equation (7) gives the following equation for the rates:

$$r = \frac{Cp_Ap_H}{(1 + K_Hp_H + K_{VC}p_{VC})(1 + K_Ap_A)} \qquad (15)$$

where

$$C = k_5 \times \frac{k_1}{k_2} \times \frac{k_3}{k_4} \qquad K_H = \frac{k_3}{k_4},$$

$$K_A = \frac{k_1}{k_2}, \qquad K_{VC} = \frac{k_6}{k_7}$$

The constants C, K_H, and K_A in Equation (15) were determined first, with the initial rate data given in Table 2 used. The numerical values were obtained by an iterative procedure, with one of the constants changed at a time and the agreement of the rate data with Equation (15) evaluated (with $p_{VC} = 0$). The values which gave the minimum absolute deviation are

$$C = 0.14, \qquad K_H = 2.67, \qquad K_A = 0.46 \qquad (16)$$

K_{VC} was determined by relating the rate data with vinyl chloride and the initial rate. Thus the ratio obtained from Equation (15) is

$$\frac{r_0}{r} = \frac{1 + K_Hp_H + K_{VC}p_{VC}}{1 + K_Hp_H} = 1 + \frac{K_{VC}p_{VC}}{1 + K_Hp_H} \qquad (17)$$

A plot of r_0/r vs. p_{VC}, at constant partial pressures of hydrogen chloride, gave a series of straight lines whose slope was equal to $K_{VC}/(1 + K_Hp_H)$. The slope of these lines was plotted vs. the reciprocal of $1 + K_Hp_H$. The slope of the least-mean-square line fitted to the points gave

$$K_{VC} = 3.8 \qquad (18)$$

The rates from Equation (15) predicted by means of the numerical values of the constants from Equations (16) and (18) are shown by the solid lines in Figures 3 to 6 and numerically in Table 2. The absolute deviation between experimental and calculated rates (all the runs being employed) averaged 3.3% at 212°F. and increased to 5.5 and 6.3% at 167° and 257°F. where only a few runs were made. The values used for the constants at 167° and 257°F. are

	167°F.	257°F.
C	0.08	0.232
K_H	2.9	2.5
K_A	0.58	0.40

It is apparent that Equation (15) closely follows the data within the range of conditions studied. However extrapolation of the equation beyond these conditions may lead to considerably larger errors.

As mentioned earlier, previous investigations (*4, 5, 11, 15*) of the kinetics of the reaction did not result in quantitative rate measurements. Hence numerical comparison with these studies is not possible.

Based upon different postulates for the mechanism, other rate equations can be derived which would agree as well with the data. Hence the results for Equation (15) cannot be cited as conclusive evidence for the postulates. However the mechanism of rapid adsorption and desorption of the components, and a slow conversion to vinyl chloride by interaction of adsorbed acetylene and hydrogen chloride, does predict rates in agreement with the data.

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NOTATION

A = acetylene in chemical equations
ΔE = thermal-conductivity-cell imbalance, emf.
C = over-all rate of reaction constant [Equation (15)], lb. moles of vinyl chloride/(lb. of catalyst)(hr.)
E_A = activation energy, B.t.u./lb. mole
F = flow rate, cu. ft./min.
H = hydrogen in chemical equations
ΔH_R = heat of reaction, B.t.u./lb. mole
k = reaction-rate constant
K = ratio of forward and reverse reaction-rate constants for adsorption reactions; adsorption equilibrum constant, atm.$^{-1}$
p = partial pressure, atm. (defined as total pressure times mole fraction)
r = reaction rate, lb. moles/(hr.)(lb. of catalyst)
r_{corr} = rate of reaction corrected to a standard catalyst activity [used only in Equation (3)]
r_0 = initial rate of reaction, that is rate with no vinyl chloride present
R = gas constant
R_0 = reactants ratio in feed, moles acetylene per mole of hydrogen chloride
s = active site on catalyst
S = entropy, B.t.u./(lb. mole)(°R.)
S_1 = active catalyst sites of type 1
S_2 = active catalyst sites of type 2
T = temperature, °R.
VC = vinyl chloride in chemical equations.
W = mass of catalyst (including carrier)
W/F = reciprocal space velocity, (lb. of catalyst)(hr.)/lb. mole
x' = conversion of acetylene based upon total feed, moles of acetylene converted per mole of feed
y = mole fraction
θ = fraction of catalyst sites
$\Delta x'$ = conversion

Subscripts

A = acetylene
H = hydrogen chloride
VC = vinyl chloride
1 = adsorption site type 1
2 = adsorption site type 2

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