Kinetics of the Reaction of Atomic Hydrogen with Acetylene

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Although not complete in itself, this type of experiment and subsequent analysis seems to offer an effective means of obtaining direct experimental evidence for the structure or molecular arrangement of a substance when it makes the difficult-to-investigate transition from vapor to liquid.

In the determination of isothermal compressibilities from the x-ray data, the most serious objection is having to obtain the value of zero-angle scattering by some means of extrapolation of the observed data. Even so, since all values of $I(0)$ listed in Table I were obtained in the same manner, the relative values of the compressibility should be significant. Without a more reliable means of determining this zero-angle scattering, however, the reliance to be placed on the absolute values is doubtful. The most that can be said is that good agreement, considering inaccuracies inherent in both means of determining the compressibility, was obtained for the points where experimental conditions overlapped.

VI. ACKNOWLEDGMENTS

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A study has been made of the rate of recombination of atomic hydrogen in the presence and in the absence of the homogeneous catalyst, acetylene. The recombination in the absence of acetylene has a negative temperature coefficient and an order between one and two. The acetylene catalyzed recombination was found to be first order in atomic hydrogen and first order in acetylene, with a rate constant of $1.3_4 \times 10^{-14}$ cc molecules^{-1} sec.$^{-1}$ at 17°C. The effect of temperature on the reaction corresponded to a collision theory activation energy of 1.5 kcal./mole and a steric factor of 4×10^{-4}.

INTRODUCTION

IN a previous publication[1] Tollefson and Le Roy described a method of studying the elementary reactions of atomic hydrogen in which the atoms were produced by the dissociation of hydrogen on tungsten filaments and detected by their heat of recombination on platinum. Applying the method to the reaction of atomic hydrogen with acetylene, they found that only a very small proportion of the atomic hydrogen was consumed in the formation of hydrogenated products. The greatly increased rate of consumption of atomic hydrogen in the presence of acetylene was found to be due to the catalytic affect of that substance on the recombination of atomic hydrogen.

The improvements made in the method of Tollefson and Le Roy have now made it possible to allow for recombination in the absence of other reactants, to determine the order of reaction in both reactants and to obtain activation energies and steric factors for the elementary reactions of atomic hydrogen with a number of hydrocarbons. The present paper reports the results of a reinvestigation of the reaction between atomic

hydrogen and acetylene. The kinetics of the reactions of atomic hydrogen with ethylene and ethane will be reported in a later publication.

APPARATUS

The dissociator, reaction chamber, and detector are shown in some detail in Fig. 1. Purified hydrogen entered the water-cooled dissociator chamber 7 through the inlet tube at the top. This tube and the dissociator filament were mounted on a ground joint which could be removed to replace filaments or to re-poison the inner walls of the apparatus.

Acetylene from the calibrated burette (9, Fig. 2) entered through the tube 16, between the dissociator and reaction chambers. The acetylene inlet tube was provided with a capped ground joint through which a platinum wire could be inserted to clear the tube of the phosphoric acid poison, if necessary.

The reaction chamber, approximately 25 cm long and 23 mm i. d., was surrounded by a jacket; a steady flow of tap water through this gave a temperature of approximately 17°C. For experiments near 0°C ice water was circulated through the jacket; thermometers were inserted at the entrance and exit. For higher temperatures appropriate liquids were boiled in the jacket

[1] E. L. Tollefson and D. J. Le Roy, J. Chem. Phys. 16, 1057 (1948).

at atmospheric pressure by means of the external heater *15*. A reflux condenser (not shown) was attached to the upper outlet and the temperature was measured at this point by a thermometer immersed in the vapor. The return from the condenser was fed into the lower inlet of the jacket. In every case the temperatures were steady throughout a determination to about ±0.5°C.

The lower half of the reactor assembly is shown to the right of the dissociator and reactor in Fig. 1. The fixed central tube served as a guide for a long sliding glass tube which carried the detector head. This sliding tube floated on the mercury surrounding the guide tube and the position of the detector could be adjusted by manipulation of the pressure in the attached reservoir. The position of the detector relative to the acetylene inlet tube was found by measuring the distance between fiducial points on the outer and sliding tubes.

The detector is shown on a larger scale at the right of Fig. 1. The detector head consisted of a short length of glass tubing with two tungsten wires sealed into its closed end. These carried nickel wires to which coiled platinum or tungsten filaments were silver-soldered. The filaments were 0.0025 in. in diameter in the case of platinum, 0.004 in. in the case of tungsten. After attaching the detector filament, the upper parts were dipped into fused potassium chloride to poison the catalytic effect of nickel on the recombination of atomic hydrogen. The filament was then washed with water. The detector head fitted snugly into the upper end of the sliding tube. One of the leads was soldered to a long copper wire dipping into mercury in the central guide tube; the other was taken out through a hole in the side of the head tube and soldered to a second copper wire which was attached to the outside of the sliding tube with de Khotinsky cement and made contact with the mercury in the outer tube. Detector heads could thus be easily interchanged. Both pools of mercury were connected through tungsten seals to the Wheatstone bridge circuit. Changes in the position of the sliding tube had no significant effect on the resistance of the circuit.

The circuit used to determine the energy liberated by the recombination of atomic hydrogen was similar to that described previously,[1] except that the milliammeter was placed in series with one of the lead wires to the bridge, rather than in the same arm as the detector. As before, the response of the platinum detector was independent of its temperature over a range from 50° to 350°C. In some experiments tungsten detector wires were used and found to be as satisfactory as platinum.

The temperature of the dissociator filament was calculated from its resistance at 0°C and the temperature coefficient of resistance. The values agreed to within 50° with the results obtained with a disappearing filament pyrometer. In practice the current for the dissociator was supplied by storage batteries and adjusted to give the required voltage and current readings. On the few occasions when the dissociator was overheated the

response of the detector fell off drastically; this was believed to be due to the deposition on the detector of poison dislodged from the walls, since the response could be partially restored by washing the detector.

No measurable concentration of atomic hydrogen was obtained when the walls of the apparatus were bare because of the high recombination coefficient on glass. The loss was reduced to about 50 percent or less in a reaction time of 0.2 sec. by coating the inner walls of the dissociator and reaction chambers with a poison prepared from approximately equal amounts of orthophosphoric acid and phosphorus pentoxide. The mixture was first heated in a platinum dish until the volume was reduced by about 30 percent; the hot poison was then drawn into a glass tube, blown onto the walls, and spread with the glass tube while rotating the reactor. The ground surfaces were protected with dummy joints and the reactor rotated until the coating cooled. When cool the poison formed a very viscous, glassy layer which did not run appreciably even at 150°C. As shown in Fig. 1, it was cooled in the vicinity of the dissociator by passing cooling water through a number of turns of rubber tubing wound around the tube at this point. Just below its jacket the reaction tube was expanded to form a gutter to catch any drainage from the poison and so prevent the fouling
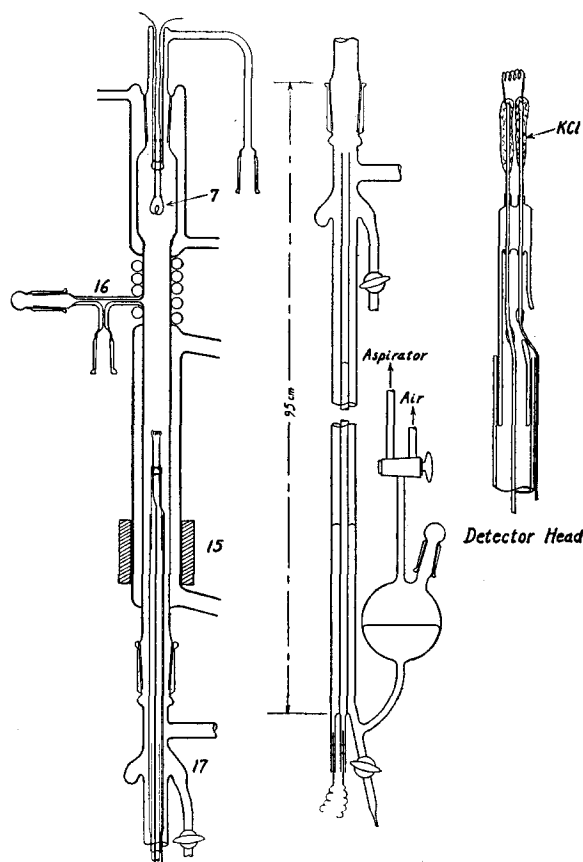

FIG. 1. Detailed view of the dissociator, reaction chamber, and detector.

of the mercury surface. Provided water vapor and oxygen were excluded from the apparatus, the efficiency of the poison would remain practically constant for a period of several months as shown by the rate of decay of H atom concentration in the absence of acetylene.

The arrangement of the apparatus (except for the analysis and acetylene purification systems) is shown in Fig. 2. Purified acetylene, stored in the 4-liter volume, was admitted to the water-jacketed burette 9 through the Fugassi valve 8. The pressure in the burette was measured on the manometer 10. As the acetylene entered the reaction chamber through the capillary at the top of the burette the pressure in the burette was kept constant to a fraction of a millimeter by the automatic electrolysis of an aqueous sodium sulfate solution in the cell 11. The current through this cell was controlled by a relay operated by contacts on the vacuum arm of the manometer 10.

Commercial electrolytic hydrogen was purified by passage over platinized asbestos in the furnace 1 and through the traps 2 containing silica gel at liquid air temperature. The hydrogen flow rate was measured on the flow meter 4. The pressure in the reaction cell was controlled by the needle valves 5 and 6. Condensible products could be collected in the coiled trap cooled with continuously pumped liquid air. The non-condensible gases were removed from the system through a mercury diffusion pump and a mechanical pump with a capacity of 15 cu. ft./min.

EXPERIMENTAL

A. H Atom Consumption in the Absence of Acetylene

The recombination of atomic hydrogen has been studied by a number of workers, and has recently been treated theoretically by Schuler and Laidler.[2] While the present investigation was concerned primarily with the kinetics of the reaction of atomic hydrogen with acetylene, it was necessary to have some knowledge of the recombination reaction in order to correct the observed rates in the presence of acetylene.

Amdur,[3] using a phosphoric acid-poisoned surface and a total pressure in the range 0.276 to 1.044 mm, found that his experimental results could be fitted to any one of five mechanisms. Each of these involved at least two
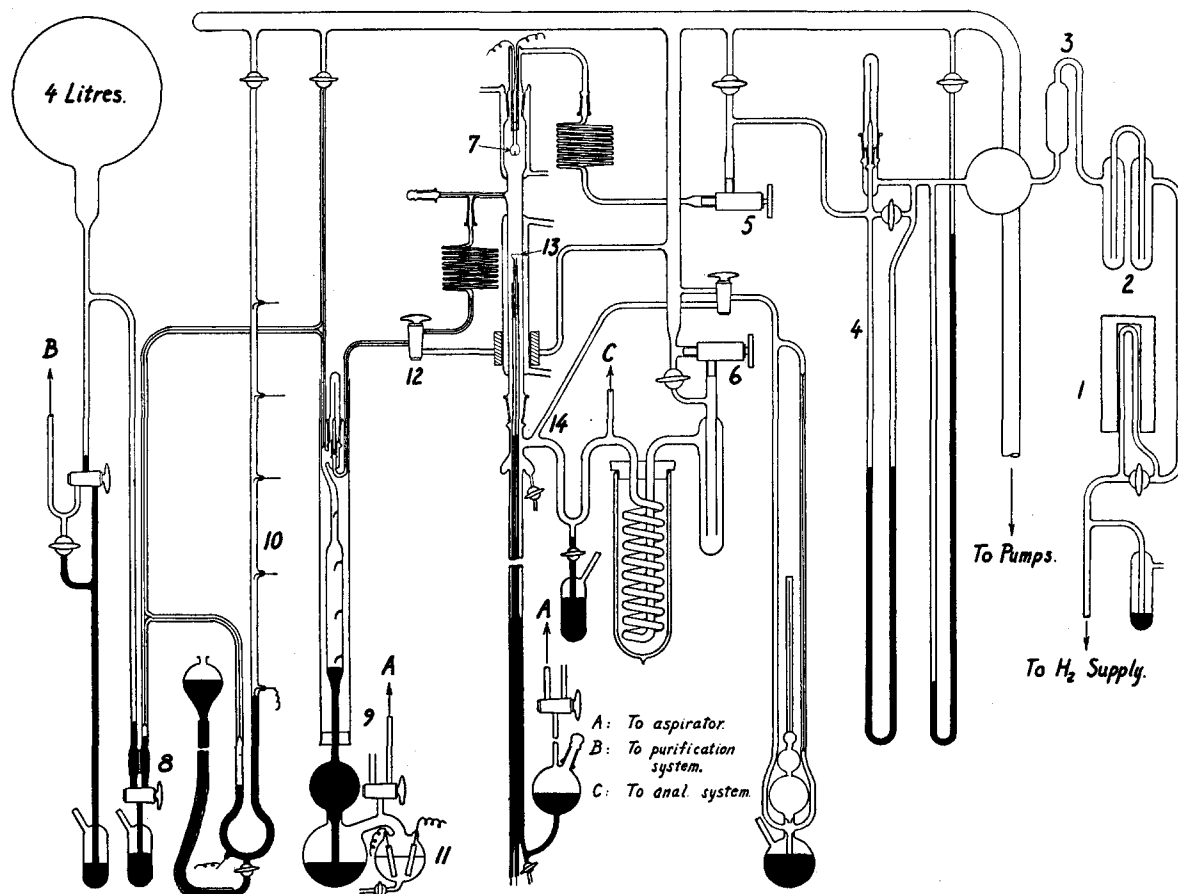

FIG. 2. General arrangement of the apparatus.

[2] K. E. Schuler and K. J. Laidler, J. Chem. Phys. 17, 1212 (1949). References to previous work are given in this paper.
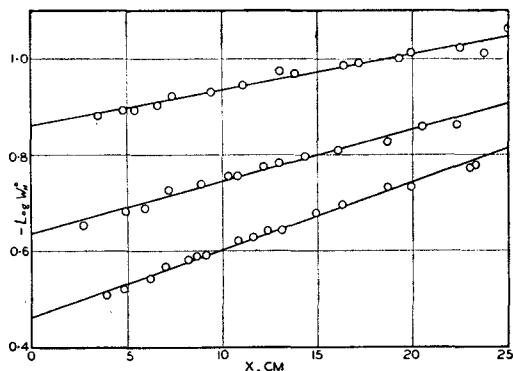[3] I. Amdur, J. Am. Chem. Soc. 60, 2347 (1938).

FIG. 3. First-order plots of H atom decay in the absence of foreign gas for different initial H atom concentrations.

FIG. 4. Second-order plots of H atom decay in the absence of foreign gas, using the same data as in Fig. 3.

simultaneous reactions of different order. On the other hand, Smith,[4] using water vapor as the poison and a total pressure of less than 0.1 mm, concluded that neither three-body collisions nor second-order wall recombination occurred under these conditions. Schuler and Laidler's treatment[2] is based on the assumption of a first-order wall recombination.

Our measurments, as were those of Amdur, were based on isothermal calorimetry and involved no correction for radiation. Smith, however, assumed that the H atom concentration at the probe was a linear function of the temperature difference between the probe and its surroundings, although the temperature difference was, in some cases, as high as 400°C.

In the case of our experiments straight lines could be drawn through the points obtained by plotting the log of W_H^0 against the time t, where W_H^0 is the wattage due to H atom recombination on the detector in the absence of acetylene and t is the product of the reciprocal of the flow rate and the distance, x, of the detector from the acetylene inlet. Since the H atom concentration at the detector is undoubtedly proportional to W_H^0, the decay appeared to be first order. Many of these plots, however, showed some indication of concavity toward the time axis, suggesting the presence of a second-order reaction.

In Fig. 3 are shown three curves of $-\log W_H^0$ vs. x for different dissociator temperatures but otherwise for identical conditions of flow rate, hydrogen pressure, etc. Two series of measurements were made at each dissociator temperature. Although curvature is not pronounced, the slopes of the curves (proportional to the first-order rate constant) are seen to decrease with decreasing H atom concentration. The second-order plots of the same data are shown in Fig. 4. Here any curvature is within the experimental error and the slopes (proportional to the second-order rate constant) are more nearly the same at different initial H atom concentrations. Clearly the choice of the order of the recombination reaction is open to question.

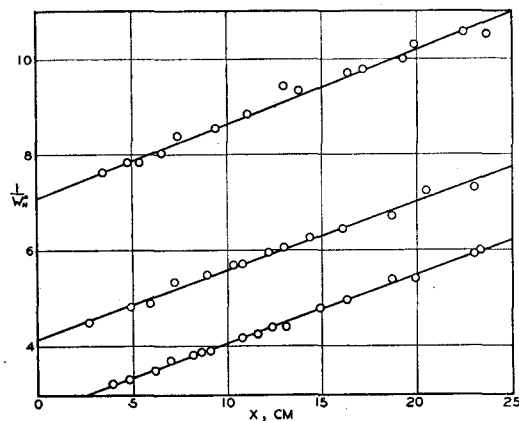The temperature coefficient of the recombination

reaction was found to be negative. This is shown in Table I; the data were obtained from pairs of experiments carried out at different reactor temperatures but otherwise under similar conditions.

The tabulated first-order rate constants, k' were obtained as the average of four or more slopes of corresponding $\log W_H^0$ vs. t plots. Values of k''/f, rather than the second-order rate constant k'' were given in Table I; they may be interpreted as second-order rate constants having the dimensions watt^{-1} sec.$^{-1}$, since f is the constant of proportionality between [H] and W_H^0; they were obtained as the average of four or more slopes of corresponding plots of $1/W_H^0$ against t.

If the recombination reaction is actually first order, a negative temperature coefficient would be predicted by Schuler and Laidler's low temperature mechanism for a water vapor poisoned surface.[2] However, our temperature range was scarcely large enough to apply the detailed theory.

A value for the recombination coefficient γ may be calculated from the first-order rate constant through the relation[2]

$$\gamma = (2k'r)/\bar{v}.$$

For example, the value of γ corresponding to a k' of 4.80 sec.$^{-1}$ at 5°C is 4.5×10^{-5}, in reasonable agreement

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[4] W. V. Smith, J. Chem. Phys. 11, 110 (1943).

TABLE I. Recombination of atomic hydrogen in the absence of foreign gas.

Tempera-ture °C	k' sec.$^{-1}$	k''/f watt^{-1} sec.$^{-1}$	k_a'/k_b'	k_a''/k_b''	H$_2$ pressure mm
(a) 5.0	4.80	31.2			3.86
			1.11	1.08	
(b) 59.5	4.32	28.9			3.87
(a) 4.3	4.88	28.3			3.70
			1.60	1.53	
(b) 99.0	3.06	18.5			3.83
(a) 2.3	4.12	25.8			3.73
			1.60	1.47	
(b) 98.6	2.58	17.6			3.72

with the value 2×10^{-5} found by Smith[4] for a meta-phosphoric acid surface.

In view of the uncertainty regarding the order of the recombination reaction under our conditions, the procedure adopted in making the correction to the observed rate in the presence of acetylene was to compare the values obtained on the basis of each mechanism. It was found that the differences were not large.

B. H Atom Consumption in the Presence of Acetylene

On the basis of a first-order decay in the absence of acetylene, the decay in the presence of acetylene was assumed to be given by the relation

$$-d[H]/dt = k'[H] + 2k_1[C_2H_2][H], \qquad (1)$$

in which k_1 is the rate constant for the reaction $H + C_2H_2 = C_2H + H_2$ or $H + C_2H_2 = C_2H_3$ (see reference 1). Since no appreciable decomposition of acetylene occurred, the over-all reaction in the presence of acetylene would be first order in [H] with a rate constant k_{ov} given by the expression $k_{ov} = k' + 2k_1[C_2H_2]$. Defining W_H as the wattage developed by H atom recombination on the detector in the presence of acetylene, a plot of $-\log W_H$ against t should give a straight line with slope 0.4343 k_{ov}. A few of these plots are shown as the upper curves of Fig. 5.
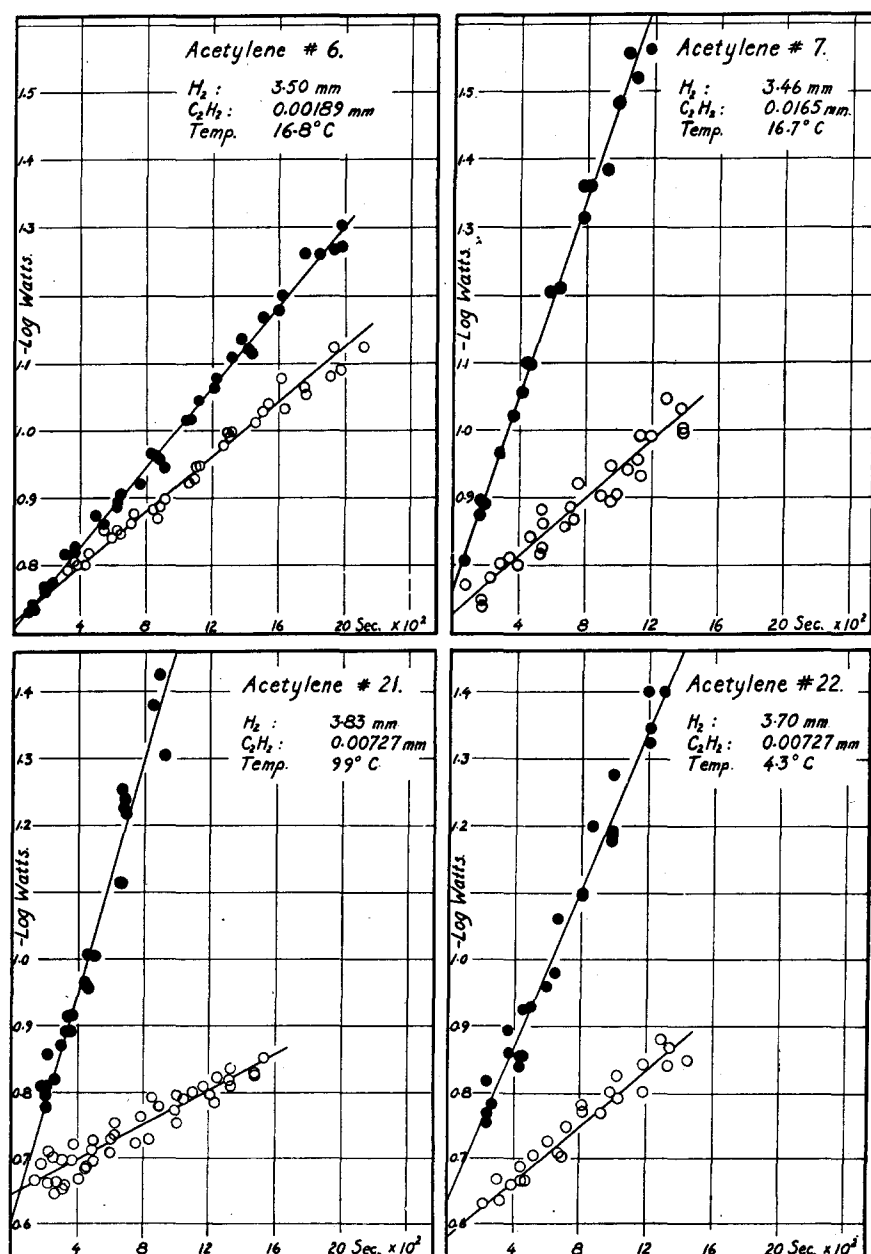

FIG. 5. Plots of $-\log W_H$ (upper curves) and $-\log W_H^0$ (lower curves) vs. t for four of the experiments.

The lower curves in Fig. 5 are the plots of $-\log W_H^0$. The points on these show considerable scattering; however, they are, in general, the result of four determinations, two before and two after adding the acetylene. The points for any single determination usually lay on fairly good straight lines, but frequently the lines for different determinations were shifted up or down relative to one another while still remaining nearly parallel. This was probably the result of slight changes in the H atom concentration entering the reaction vessel.

The linearity of the $-\log W_H$ vs. t plots suggests that the reaction with acetylene is first order in [H]. The
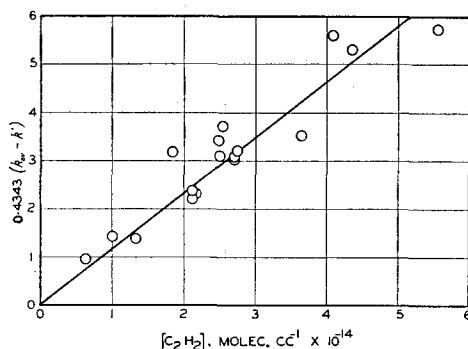

FIG. 6. $0.4343(k_{ov}-k')$ vs. [C_2H_2] for the experiments at 17°C. The straight line corresponds to a value for k_1 of 1.34×10^{-14} cc molecules^{-1} sec.$^{-1}$.

difference in the slopes of the $-\log W_H$ and the $-\log W_H^0$ plots ($=0.4343(k_{ov}-k')=0.4343\times2k_1[C_2H_2]$) should then be linear in [C_2H_2]. That this is so can be seen from Fig. 6. The value of k_1 corresponding to the straight line is 1.34×10^{-14} cc molecules^{-1} sec.$^{-1}$ at 17°C. The value obtained by Tollefson and Le Roy[1] was 8.6×10^{-14} at 25°C.

On the basis of a second-order decay in H atom concentration in the absence of reactant, the decay in the presence of acetylene was assumed to be given by the expression

$$-d[H]/dt = k''[H]^2 + 2k_1[C_2H_2][H]. \quad (2)$$

Assuming, as before, that $[H] = W_H/f$, then

$$-(1/f)dW_H/dt = k''(W_H/f)^2 + 2k_1[C_2H_2]W_H/f,$$

or

$$\log\{2k_1[C_2H_2] + (k''/f)W_H\}/W_H = 2k_1[C_2H_2]t + \text{const.} \quad (3)$$

TABLE II. Kinetic data for the reaction H+C_2H_2.

Temp. °C	k_1, Eq. (1) cc molecules^{-1} sec.$^{-1}$ $\times10^{14}$	k_1, Eq. (2) cc molecules^{-1} sec.$^{-1}$ $\times10^{14}$	E_1, Eq. (1) kcal./ mole	E_1, Eq. (2) kcal./ mole	p_1, Eq. (1) $\times10^4$	p_1, Eq. (2) $\times10^4$
(a) 5.0	1.37	1.66				
(b) 59.5	2.20	2.64	1.31	1.27	2.6	2.9
(a) 4.3	1.72	2.19				
(b) 99.0	4.28	4.74	1.65	1.35	6.0	4.4
(a) 2.3	1.06	1.36				
(b) 98.6	2.80	3.16	1.72	1.45	4.3	3.4
Mean	1.59	1.39			4.3	3.6

Equation (3) does not permit a direct solution for k_1, but this quantity can be obtained by successive approximations. In the first approximation the value of k_1 obtained from Eq. (1) was used; the left-hand side of (3) was then plotted against t to give a second approximation, etc.

In Table II are shown the values of k_1 derived from Eqs. (1) and (2) for three pairs of experiments. Table II also gives the corresponding values of the activation energy E_1 and the steric factor p_1. In calculating E_1 allowance was made for the term in $T^{\frac{1}{2}}$ appearing in the frequency factor. The steric factors were calculated from corresponding values of k_1 and E_1 using a value of 2.72A for the mean collision diameter.[1]

CONCLUSIONS

It is seen from Table II that the form of the rate law assumed for the decay of H atom concentration in the absence of acetylene makes little difference in the values calculated for E_1 and p_1. The low collision efficiency of the reaction with acetylene, as evidenced by a p_1 value of approximately 4×10^{-4}, is not surprising.[5] The activation energy of 1.5 kcal./mole, while small, is believed to be real, since particular reliance can be placed on the relative rates of any of the pairs; the second was always done immediately after the first, without interrupting the hydrogen flow.

[5] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 19.