

RATE AND MECHANISM OF THE HOMOGENEOUS D/H SUBSTITUTION  
REACTION BETWEEN  $C_2H_2$  and  $D_2$ , as STUDIED IN A SHOCK TUBE

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INTRODUCTION

One of the most intriguing facts which came to our attention during the course of our shock tube studies is the occurrence of unsuspected reactions which take place at high temperatures, but under conditions which heretofore had been assumed to be insufficiently severe for appreciable reactions to occur. One example, discussed in detail in this paper, is the reaction between acetylene and hydrogen at temperatures up to 1700°K. When one mixes acetylene and hydrogen at these temperatures no change in the concentration of the acetylene can be detected for as long as one millisecond. During this interval, each acetylene molecule is subjected to an enormous number of collisions with argon (the ambient gas), acetylene and hydrogen molecules. That the acetylene and hydrogen are actually involved in an extensive association reaction, but that the acetylene is rapidly replenished by the reverse processes, becomes evident when deuterium is used in place of hydrogen. The mechanism derived from our studies have given us an insight to possible structures of the transition states of acetylene and of ethylene. The following special features of shocks of operation are thereby demonstrated:

- (a) the samples are heated very rapidly and homogeneously, and
- (b) it is possible to follow in time a sequence of steps for a selected reaction.

EXPERIMENTAL

The Shock Tube

The studies described below were conducted in a stainless steel shock tube, 6" in diameter, for which the driver section was 8 feet long and the driven section 22 feet long. Observations were made by recording the infrared emission at selected wave lengths for incident shocks. The windows were located 18 feet downstream from the diaphragm. Shock speeds were measured with platinum strip thermal detectors and displayed on a raster; the pressure profile was monitored at the window position with a rapid-response Kistler piezo-electric gauge. Mylar diaphragms in a variety of thicknesses were used and in all cases were ruptured by exceeding their yield pressures. The experimental section of the shock tube was pumped down with a diffusion pump to pressures of the order of  $1 \times 10^{-4}$  mm mercury; the leak rate was less than 1 micron per minute. Shocks were run between 2 to 3 minutes after filling the tube with pre-mixed gas samples.

The Optics

Infrared transmitting windows of calcium fluoride were mounted flush with the inner walls of the shock tube. These are 2" in length and 10mm in width. The monochromator is a modified Perkin-Elmer instrument in which a 83 x 83mm B and L grating, 150 lines per mm, blazed at  $6\mu$  for the 1st order, had been inserted. A gold-doped germanium detector, liquid nitrogen cooled, was mounted at the focus on a Cassegrain mirror system, which served to reduce the image of the exit slit by a factor of 6. External mirrors focused

a Nernst glower at the center of the shock tube. The image was then transferred by off-axis paraboloids and flat mirrors to the entrance slit of the monochromator. The glower was used for alignment of the optics and wave length calibration of the monochromator. In the parallel ray portion of the external optics a 150 cps sector and various test cells can be inserted. When used in this configuration the detector output was registered by a tuned amplifier and pen recorder. To limit the transit time for the shocked gas various masks were inserted in front of the mirrors. For a signal/noise ratio of 15 to 1, the spectral resolution of this system as calibrated with HBr lines was found to be:

$$\begin{array}{ll} \text{At } 3195 \text{ cm}^{-1}, \text{ with slits } 0.4 \sim 0.8 \text{ mm} : & 11.4 \text{ cm}^{-1}/\text{mm slit} \\ 2555 \text{ cm}^{-1}, \text{ with slits } 0.5 \sim 0.7 \text{ mm} : & 7.3 \text{ cm}^{-1}/\text{mm slit} \end{array}$$

The design features of this system have been described<sup>1</sup> as constructed performance proved superior to that anticipated in the design.

### The Samples

Various mixtures of acetylene, deuterium and argon were mixed in glass-lined tanks of 200 liter capacity and allowed to remain at room temperature several days before use. The deuterium was the best available commercial grade and was used without purification. The acetylene was washed thoroughly with concentrated sulphuric acid to remove the acetone. The shock tube was cleaned after each run. Since the reflected shock temperatures were considerably higher than those needed for the incident shock exchange experiments the acetylene was extensively pyrolyzed by the reflected shocks. Much carbon soot had to be removed from the tube walls and the windows after each run.

### Selection of the Analytical Frequencies for Acetylene

To select the optimum analytical frequencies at which the unsubstituted and deuterated acetylenes emit at these elevated temperatures and to determine the extent of their mutual interference theoretical intensity envelopes were computed for the various bands, based on the reported rotational constants for the ground and first excited vibrational states of acetylene<sup>2a, b, c, d</sup>. These are illustrated in Figure 1. For estimating the concentration of acetylene present we selected the frequency  $3195 \text{ cm}^{-1}$ , at which the contribution by  $\text{C}_2\text{H}_2$  exceeds by a factor of 5 that due to  $\text{C}_2\text{HD}$ . At  $2555 \text{ cm}^{-1}$  the relative contribution due to  $\text{C}_2\text{HD}$  is largest.

Quantitative calibrations were obtained at these selected frequencies. Note that at  $t = 0$  (immediately after passage of the shock) all the acetylene is present as  $\text{C}_2\text{H}_2$ ; whereas at a sufficiently long time, when the sample had attained equilibrium under shock conditions, its composition may be computed from the known equilibrium constants for the isotope exchange reaction. Thus, at  $t = 0$ ,

$$I_0 = g [\epsilon (\text{C}_2\text{H}_2)_0 \cdot c_0 (\text{C}_2\text{H}_2)] \chi_{3195}$$

in which  $g$  represents the geometric factor of the optical and detecting system,  $c_0$  is the initial concentration of the  $\text{C}_2\text{H}_2$  (in moles/l) and  $\epsilon$  represents the emissivity of the gas at the shock temperature. Furthermore, at equilibrium ( $t \rightarrow \infty$ ),

$$I_\infty = g [\epsilon (\text{C}_2\text{H}_2)_\infty \cdot c_\infty (\text{C}_2\text{H}_2) + \epsilon (\text{C}_2\text{HD}) \cdot c_\infty (\text{C}_2\text{HD})] \chi_{3195}$$

Note that at  $3195 \text{ cm}^{-1}$  the contribution to the emission by the fully deuterated acetylene is negligible. In the above equations it was assumed that the concentrations are sufficiently low so that no correction for self absorption need be made, for self absorption. One can then

obtain the ratio  $I_\infty/I_0$ , and since the ratios of the concentrations of the species may be computed, the ratio  $\epsilon(C_2HD)/\epsilon(C_2H_2)$  may be evaluated.

$$\frac{I_\infty}{I_0} = \frac{c_\infty(C_2H_2)}{c_0(C_2H_2)} + \frac{\epsilon(C_2HD)}{\epsilon(C_2H_2)} \frac{c_\infty(C_2HD)}{c_0(C_2H_2)}$$

Typical data are given in Table I.

The ratio of emissivity coefficients at  $2555\text{ cm}^{-1}$  were obtained by a similar procedure. In this case however one cannot measure  $I_0$  since at  $t = 0$  no  $C_2HD$  is present and the emissivity increases relatively slowly from  $I = 0$  at  $t = 0$ . In part, this is due to the finite time for vibrational relaxation of this mode, and the resolving time of our detector-amplifier system. Instead we must use  $I'_0$ , which is the emission intensity measured under the identical experimental conditions for a mixture of  $C_2H_2 + H_2$ .

$$I_\infty(C_2H_2 + D_2) = g[\epsilon(C_2H_2) \cdot c_\infty(C_2H_2) + \epsilon(C_2HD) \cdot c_\infty(C_2HD)]\chi_{2555}$$

$$I'_0(C_2H_2 + H_2) = g[\epsilon(C_2H_2) \cdot c_0(C_2H_2)]\chi_{2555}$$

$$\frac{I_\infty(C_2H_2 + D_2)}{I'_0(C_2H_2 + H_2)} = \frac{c_\infty(C_2H_2)}{c_0(C_2H_2)} + \frac{\epsilon(C_2HD)}{\epsilon(C_2H_2)} \frac{c_\infty(C_2HD)}{c_0(C_2H_2)}$$

The results are included in Table I. Hence, the emission intensity recorded at each of the frequencies is related to the corresponding concentrations by:

$$I(3195) \propto [c(C_2H_2) + 0.48 c(C_2HD)]$$

$$I(2555) \propto [c(C_2H_2) + 3.10 c(C_2HD)]$$

#### Calculation of Shock Parameters

The gas temperature behind the incident shock ( $T_2$ ) and the gas density ratio across the shock front ( $\rho_2/\rho_1$ ) were computed from the measured shock velocities and the known enthalpies of the gaseous mixtures. The initial temperature was assumed to be  $298^\circ\text{K}$ . No correction was made for the very small enthalpy change due to the isotopic substitution. It was observed that the shock speed attenuated slightly during its passage down the tube; the measured values were extrapolated to provide the shock velocity at the plane of observation.

#### THE KINETIC DATA

Kinetics of the decrease in  $C_2H_2$  (as measured by the emission intensity at  $3195\text{ cm}^{-1}$ )

When a mixture of acetylene, hydrogen and argon is shock heated to a temperature in the range  $1300^\circ\text{K}$  to  $1700^\circ\text{K}$  the emission intensity rises sharply to a level which depends on the concentration of  $C_2H_2$ , due to the compression by the shock and the vibrational excitation of acetylene to the 1st level. This emission remains constant over the period

of observation. Further, when deuterium and argon are shock heated under the same conditions no appreciable emission is observed. However, a mixture of acetylene, deuterium and argon produces a sharp rise in emission which slowly decreases with time. We propose that this decrease is due to the conversion of some of the acetylene to deuterioacetylene. To a first approximation (to be corrected later), the emitted intensity is proportional to the product of a geometrical factor, the sensitivity of the recording system, and the instantaneous concentration of the acetylene. Let  $\rho_2^0$  represent the gas density immediately after passage of the shock. Then one may write

$$\frac{\rho_2^0}{I_0} \frac{dI}{dt} = \frac{d \cdot \rho(C_2H_2)}{dt} + \frac{\epsilon(C_2HD)}{\epsilon(C_2H_2)} \frac{d \cdot \rho(C_2HD)}{dt}$$

only

for the rate of change in emission with time. Note that in the analysis given below the initial reaction rates were considered, as derived from the initial slopes of the emission intensities as recorded by the oscilloscope. The time scale observed on the oscilloscope trace must be multiplied by the density ratio across the shock front ( $\rho_2/\rho_1$ ) to convert the "laboratory" reaction rate to particle time. The initial reaction rate constant is then defined by the equation:

$$R_0 \equiv \frac{\rho_2^0}{I_0} \frac{\Delta I}{\Delta t} = k (C_2H_2)_0^n (D_2)_0^m (Ar)_0^l$$

To establish the reaction order for this <sup>exchange</sup> with respect to  $D_2$ , values of  $R_0$  were plotted against  $1/T$  for a series of shocks in which the initial  $C_2H_2$  and  $Ar$  were almost constant but  $(D_2)_0$  differed by a factor of two, see Figure 2. The difference in rates over the temperature range covered is equal to  $m \log 2$ , so that  $m = 1$  is experimentally determined.

To establish the order of the reaction with respect to the acetylene, the observed values of  $R_0/\rho_2^0(D_2)$  were plotted against the reciprocal of the absolute temperature; see Figure 3. In this graph three reference temperatures were selected, centered at regions for which there were significant numbers of points. Effective rate constants at different temperatures were reduced to the nearest reference temperature by reading rates parallel to the average slope. Then the logarithms of these reduced values of  $R_0/\rho_2^0(D)$  were individually plotted (for  $T_1, T_2, T_3$ ) against <sup>the</sup> logarithm of the density of acetylene; see Figure 4. The slopes vary somewhat with temperature; they are respectively,

- $n = 0.29 \pm 0.01$  at 1350°K
- $= 0.20 \pm 0.03$  at 1455°K
- $= 0.23 \pm 0.03$  at 1612°K

We have adopted the average  $n = 0.24$ .

The overall order for the exchange reaction as measured by the rate of disappearance of the  $C_2H_2$  was then obtained from a series of experiments corrected to a single temperature, in which the total pressure was changed by a factor of 5, while maintaining the composition of the mixture constant. In these experiments the concentration of each component may be expressed in terms of a single variable which could be the density of the acetylene. The slope of a logarithmic plot of the initial rates against the logarithm of the initial acetylene

density thus gives the total order. The result of six runs in which the acetylene density varied from  $0.53 \times 10^{-3}$  to  $2.51 \times 10^{-3}$  gave at  $T = 1455^\circ\text{K}$  a value for  $(n + m + l) = 1.20 \pm 0.05$ . Since it was established above that  $m = 1.0$  and  $n = 0.24$  it follows that  $l = 0$ ; that is, the argon concentration does not affect the initial rate of disappearance of the acetylene. The rate constant  $k_H$  as evaluated on the basis of the equation

$$R_o = k_H (C_2H_2)_0^{0.24} (D_2)_0^{1.0} (Ar)_0^0$$

was plotted against the reciprocal of the absolute temperature: see Figure 5. The deduced activation energy is  $E_H = 33.8 \pm 0.4$  kcal/mole, and the corresponding  $\log A = 7.9$ , for the rate of disappearance of acetylene due to reaction with deuterium, in the temperature range  $1200^\circ$  to  $1700^\circ\text{K}$ .

#### Kinetics of Production of $C_2HD$ (as measured by emission at $2555 \text{ cm}^{-1}$ )

The procedure for measuring the growth in concentration of  $C_2HD$  during shock and deduction of the corresponding rate law was essentially the same as that described above for the disappearance of  $C_2H_2$ . In this case there was a small additional complexity. The acetylene originally present in the shocked gas produced a large emission at zero time. This showed up as a step function with a finite rise time, due to the combined effect of the vibrational relaxation of the  $C_2H_2$ , the resolving time of the recording system, and the particle passage time as the shock sped by the calcium fluoride windows. Below  $1600^\circ\text{K}$  this emitted intensity showed a rapid initial rise covering a period of about 20 microseconds, followed <sup>by</sup> an almost linear slower increase due to the production of  $C_2HD$  by the exchange reaction. Above this temperature the inflection point could not be easily detected; hence the data cited below were restricted to runs made below  $1600^\circ\text{K}$ . Again it was established that the order of the reaction was unity with respect to the initial deuterium concentration. As tested previously,  $R_o/\rho_2^0(D_2)$  values were plotted against the reciprocal temperature and the points were corrected to the reference temperature of  $1470^\circ\text{K}$ . The reduced  $R_o/\rho_2^0(D_2)$  were then replotted against the density of acetylene. The slope of this curve gave for the order of the reaction with respect to acetylene  $n = 0.24 \pm 0.04$ , checking the value deduced for the rate of disappearance of  $C_2H_2$ . Another plot provided a value for the total order, which proved to be  $1.24 \pm 0.07$ . Thus we have demonstrated that the rate of appearance of  $C_2HD$  and the rate of disappearance of  $C_2H_2$ , under the conditions of our experiment follow the same functional dependence on the initial concentrations of reactants. A plot of the reduced rate constant against the reciprocal of the temperature is shown in Figure 6. The activation energy is  $E = 29.3 \pm 1.1$  kcal/mole and the corresponding  $\log A = 7.5$ . The limits of error quoted for  $E_H$  and  $E_D$  are based on the internal consistency of each set of runs; we consider these activation energies to be equal within their absolute limits of error.

#### Corrected Values for the Rate Constants

In the preceding paragraphs it was demonstrated that the functional dependencies of the rate of depletion of  $C_2H_2$  and the rate of formation of  $C_2HD$  on the initial concentrations of the reactants and on the temperature are equal. It is now possible to correct the apparent rates, deduced directly from the changes of the emission intensities at  $3195 \text{ cm}^{-1}$  and  $2555 \text{ cm}^{-1}$ , to obtain absolute rates, by noting the relative contributions of each species to the intensities recorded at these frequencies:

$$-k_H (C_2H_2)^{0.24} (D_2) = -\frac{dC_{2H_2}}{dt} + \left[ \frac{\epsilon(C_{2HD})}{\epsilon(C_{2H_2})} \right] \frac{dC_{2HD}}{dt} = -\frac{dC_{2H_2}}{dt} + 0.48 \frac{dC_{2HD}}{dt}$$

3195

$$+k_D (C_2H_4)^{0.24} (D_2) = -\frac{dC_{2H_2}}{dt} + \left[ \frac{\epsilon(C_{2HD})}{\epsilon(C_{2H_2})} \right] \frac{dC_{2HD}}{dt} = -\frac{dC_{2H_2}}{dt} + 3.10 \frac{dC_{2HD}}{dt}$$

2555

On rearranging terms:

$$-\frac{dC_{2H_2}}{dt} = k_{C_2H_2} (C_2H_2)^{0.24} (D_2) = \frac{3.10 k_H + 0.48 k_D}{3.10 - 0.48} (C_2H_2)^{0.24} (D_2)$$

$$+\frac{dC_{2HD}}{dt} = k_{C_2HD} (C_2H_4)^{0.24} (D_2) = \frac{k_H + k_D}{3.10 - 0.48} (C_2H_2)^{0.24} (D_2)$$

Specifically, at 1470°K,

$$k_{C_2H_2} = 1.17 \times 10^3 \text{ (liter/mole)}^{0.24} \text{ sec}^{-1}$$

$$k_{C_2HD} = 0.82 \times 10^3 \text{ (liter/mole)}^{0.24} \text{ sec}^{-1}$$

We thus find that the rate of increase of  $C_2HD$  is almost equal to 2/3 of the rate of decrease in the  $C_2H_2$ . Since the acetylene is removed only by the isotopic exchange reaction (as demonstrated by the fact that  $C_2H_2$  plus  $H_2$  does not show a decrease in the emission at 3195  $cm^{-1}$ ), it follows that the remaining 1/3 of the  $C_2H_2$  leads to the production of  $C_2D_2$ . The rate of production of  $C_2D_2$  is then roughly 1/2 of that of  $C_2HD$ .

To substantiate this conclusion we cite rough analytical data obtained in a single-pulse experiment based on a sample composition and temperature pulse comparable to that used for the infrared runs. Mass spectrometric analysis of a shocked mixture of  $C_2H_2 + D_2$  showed:

- The amount of  $H_2$  generated was definitely less but comparable to that of HD.
- The decrease in the amount of  $C_2H_2$  was larger than the amount of  $C_2HD$  generated.
- No methane or ethylene was produced.

A few preliminary IR runs at 2350  $cm^{-1}$  showed that emission due to  $C_2D_2$  did rise following shock heating of a mixture of acetylene and deuterium. However, this experiment was not completed and no quantitative data on the rate of production of  $C_2D_2$  were obtained by the infrared technique.

The weighted average of the energies of activation obtained from the  $\ln k$  vs  $1/T$  plots (using internal consistency as the basis for weighting  $E_H$  and  $E_D$ ) is  $32.7 \pm 1$  kcal/mole. This leads to:

$$k_{C_2H_2} = 8.5 \times 10^7 \exp(-32700/RT), \quad (\text{liter/mole})^{0.24} \text{sec}^{-1}$$

$$k_{C_2HD} = 6.0 \times 10^7 \exp(-32700/RT), \quad (\text{liter/mole})^{0.24} \text{sec}^{-1}$$

Typical sets of data are summarized in Table II. These are but examples of the large number of shocks run. The values given are for the  $3195 \text{ cm}^{-1}$  band.

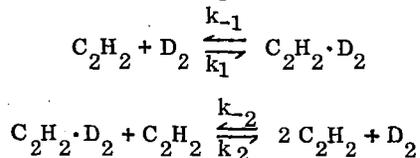
#### DISCUSSION OF MECHANISM

A thorough search of the literature has yet to be completed. To date we found only one report on a gas phase study of the  $(C_2H_2 + D_2)$  reaction. Coats and Anderson<sup>3</sup> heated equimolar mixtures of the two gases in 25 ml bulbs for 2 - 10 minutes to temperatures  $500^\circ - 900^\circ\text{C}$ , at a total initial pressure of 300 mm Hg. The reaction bulbs were allowed to cool to room temperature and their contents were analyzed. In view of the diversity of products produced (ranging from methane to benzene, toluene and carbon deposits) heterogeneous steps evidently played prominent roles in these conversions. Their product distribution suggested that free radical reactions as well as molecular processes had occurred. There are, of course, numerous reports on the rates and mechanisms of D/H substitution in hydrocarbons as catalyzed by a variety of surfaces,<sup>and</sup> as induced by radiations which generate atoms. In the latter, the primary attack is an atomic displacement or an abstraction.

The pyrolysis<sup>of</sup> acetylene in shock tubes has been investigated<sup>4</sup>. In this laboratory shock tube studies of the homogeneous substitution reactions between  $(NH_3 + D_2)$ <sup>5</sup>,  $(H_2S + D_2)$ <sup>5</sup>, and  $(HCl + D_2)$ <sup>6</sup> have been completed. For these systems the rate laws are significant different in that they show an overall second order dependence, in contrast to the overall 1.24 order dependence deduced for  $(C_2H_2 + D_2)$ . The observation that the activation energy is low ( $\sim 33 \text{ kcal/mole}$ ) and that the rate depends on the first power of the deuterium concentration argues against all the chain reactions we have been able to devise. Indeed, the observed rates are much too high to be consistent with the known or estimated homogeneous rates of dissociation of  $D_2$ <sup>7</sup> and of  $C_2H_2 \rightarrow C_2H + H$ . Finally, the fact that the rate of production of  $C_2D_2$  is about half of that of  $C_2HD$  suggests that these species are derived from the same transition state, which we designate  $C_2H_2D_2^*$ . The following mechanism is consistent with all the observations.

We postulate the occurrence of two types of unstable intermediates:

- (a)  $C_2H_2 \cdot D_2$ , which is a molecular complex between acetylene and deuterium, and which is particularly sensitive to dissociation by collision with another acetylene; and  
 (b)  $C_2H_2D_2^*$ , which is an electromcally excited ethylene, with  $V_g$  symmetry, approximately  $3 \text{ e.v.}$  above the ground state  $[E_A + \Delta H_{\text{hydrog}}(C_2H_2) \approx 3 \text{ e.v.}]$ . Species in this state have a much greater probability for dissociation than for interval conversion to stable ethylene. The formal rate expression is based on the sequence:





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TABLE I. Experimental Determination of the Ratios of  $\epsilon$ 's

	at 3195 $\text{cm}^{-1}$			at 2555 $\text{cm}^{-1}$	
	( $\alpha$ )	( $\beta$ )		( $\gamma$ )	( $\delta$ )
$\frac{I_{\infty}}{I_0}$	0.225	0.315	$I_{\infty}(\text{C}_2\text{H}_2 + \text{D}_2)$	25.4	27.0
$\frac{c_{\infty}(\text{C}_2\text{H}_2)}{c_0(\text{C}_2\text{H}_2)}$	0.053	0.111	$I_0(\text{C}_2\text{H}_2 + \text{H}_2)$	14.0	15.0
$\frac{c_{\infty}(\text{C}_2\text{HD})}{c_0(\text{C}_2\text{H}_2)}$	0.352	0.440		0.25	0.25
$\frac{\epsilon(\text{C}_2\text{HD})}{\epsilon(\text{C}_2\text{H}_2)}$	0.49	0.465		0.50	0.50
Ave.	< 0.48 >			< 3.12 >	

( $\alpha$ ) Average of 4 runs with  $\frac{c_0(\text{C}_2\text{H}_2)}{c_0(\text{D}_2)} = 3.333$ , at 1600 - 1700°K

( $\beta$ ) Average of 4 runs with  $\frac{c_0(\text{C}_2\text{H}_2)}{c_0(\text{D}_2)} = 2.00$ , at 1550 - 1650°K

( $\gamma$ ) At about 1670°K

( $\delta$ ) At about 1720°K

TABLE II: Typical Data for the 3195 cm<sup>-1</sup> Band

Run No.	465	397	404	410	405	458	451	430	424
C <sub>2</sub> H <sub>2</sub> /D <sub>2</sub> /Ar	10/10/80	10/10/80	10/10/80	5/10/85	5/10/85	3/10/87	3/10/87	10/5/85	10/5/85
p <sub>1</sub> (total)	26	82	41.5	80	80	61	61	81	43
ρ <sub>2</sub> <sup>0</sup> (C <sub>2</sub> H <sub>2</sub> )	0.59 x 10 <sup>-3</sup>	1.91 x 10 <sup>-3</sup>	0.99 x 10 <sup>-3</sup>	0.78 x 10 <sup>-3</sup>	0.87 x 10 <sup>-3</sup>	0.34 x 10 <sup>-3</sup>	0.378 x 10 <sup>-3</sup>	1.80 x 10 <sup>-3</sup>	1.01 x 10 <sup>-3</sup>
ρ <sub>2</sub> <sup>0</sup> (D <sub>2</sub> )	0.59 x 10 <sup>-3</sup>	1.91 x 10 <sup>-3</sup>	0.99 x 10 <sup>-3</sup>	1.57 x 10 <sup>-3</sup>	1.74 x 10 <sup>-3</sup>	1.14 x 10 <sup>-3</sup>	1.26 x 10 <sup>-3</sup>	0.90 x 10 <sup>-3</sup>	0.51 x 10 <sup>-3</sup>
T <sub>2</sub> °K	1390	1545	1665	1245	1680	1200	1700	1410	1695
ρ <sub>2</sub> <sup>0</sup> /ρ <sub>1</sub>	4.19	4.34	4.44	3.65	4.01	3.47	3.83	4.12	4.35
R <sub>0</sub>	0.0422	0.545	0.489	0.0306	0.970	0.0111	0.753	0.0900	0.329
R <sub>0</sub> <sup>0</sup> /ρ <sub>2</sub> <sup>0</sup> (D <sub>2</sub> )	0.715 x 10 <sup>2</sup>	2.85 x 10 <sup>2</sup>	4.96 x 10 <sup>2</sup>	0.195 x 10 <sup>2</sup>	5.59 x 10 <sup>2</sup>	0.0975 x 10 <sup>2</sup>	5.98 x 10 <sup>2</sup>	1.00 x 10 <sup>2</sup>	6.45 x 10 <sup>2</sup>
k <sub>H</sub>	0.426 x 10 <sup>3</sup>	1.28 x 10 <sup>3</sup>	2.61 x 10 <sup>3</sup>	0.109 x 10 <sup>3</sup>	3.04 x 10 <sup>3</sup>	0.0655 x 10 <sup>3</sup>	3.94 x 10 <sup>3</sup>	0.455 x 10 <sup>3</sup>	3.38 x 10 <sup>3</sup>

p<sub>1</sub><sup>0</sup>, in mm Hgρ<sub>2</sub><sup>0</sup>, the corresponding gas density (moles/l) immediately after passage of the shock

$$R_0 = \frac{\rho_2^0}{I_0} \left( \frac{\Delta I}{\Delta t} \right)_0 \left( \frac{\rho_1}{\rho_2} \right), \text{ in mole liter}^{-1} \text{ sec}^{-1}$$

$$k_H = R_0 / \rho_2^0 (D_2)^{0.24} \rho_2^0 (C_2H_2)^{0.24}, \text{ in (l/mole)}^{0.24} \text{ sec}^{-1}$$

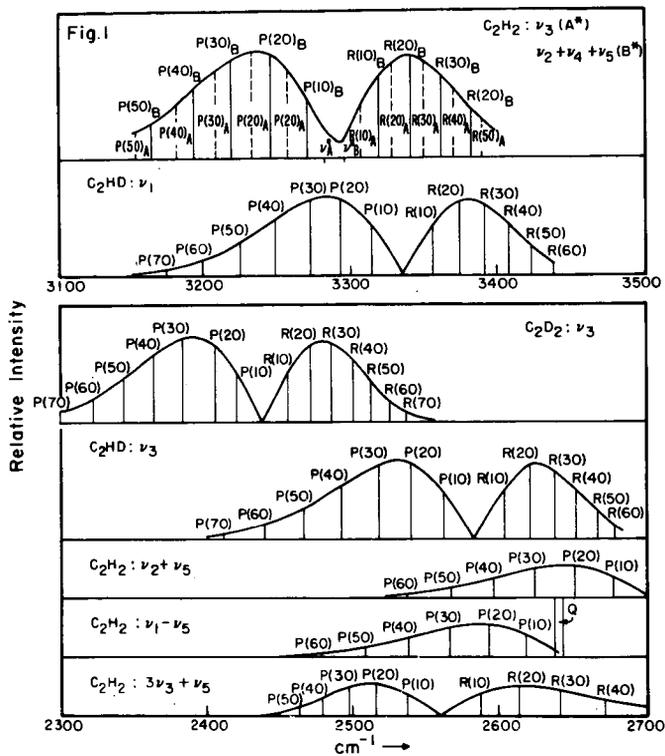


Fig. 1 Theoretical envelopes showing relative emission intensities of acetylene, mono- and deuterioacetylene at 1700 °K.

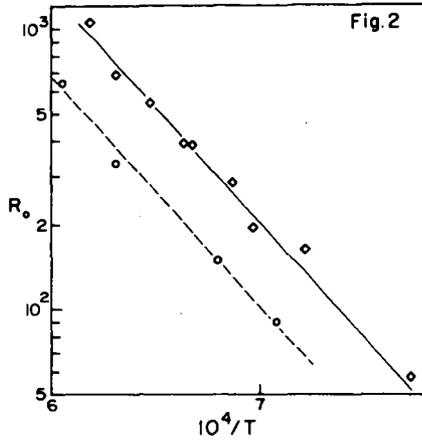


Fig. 2 Logarithmic plot of  $R_0$  vs  $10^4/T$ , for runs with constant  $(C_2H_2)_0$ , and  $(Ar)_0$ , but  $(D_2)_0$  differs by a factor of two:

Solid Line:  $C_2H_2/D_2/Ar = 10/10/80$

Dashed Line:  $C_2H_2/D_2/Ar = 10/5/85$

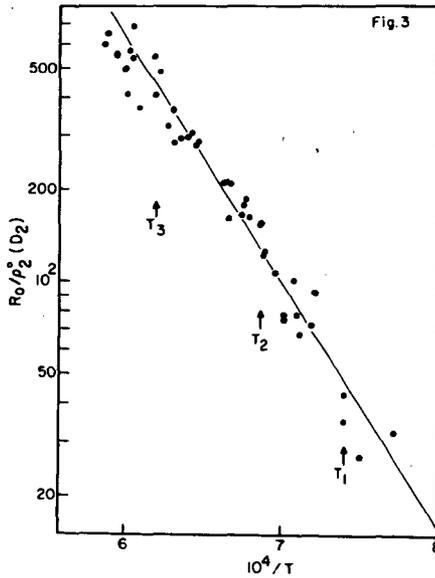


Fig. 3 Logarithmic plot of  $R_0 / \rho_2^0(D_2)$  vs  $10^4/T$ , for all runs:

$C_2H_2/D_2/Ar = 10/10/80; 5/10/85; 3/10/87; 10/5/85$

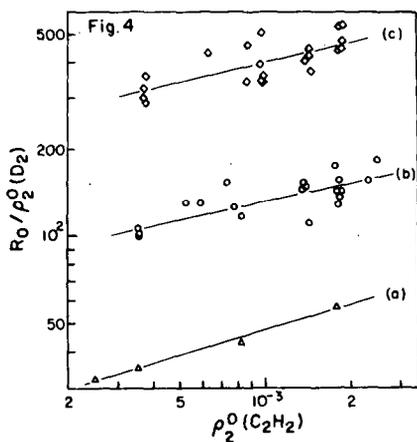


Fig. 4 Logarithmic plots of the reduced values of  $R_0 / \rho_2^0(D_2)$  vs  $\rho_2^0(C_2H_2)_0$ , corresponding to the temperatures

(a) 1350°K (b) 1455°K (c) 1612°K

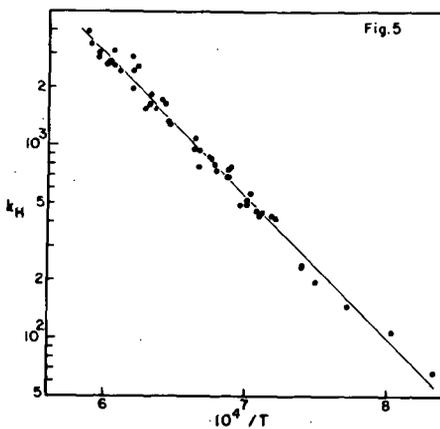


Fig. 5 Plot of the rate constant for the disappearance of  $C_2H_2$ , due to reaction with  $D_2$ , as measured from the decline in emission intensity at  $3195\text{ cm}^{-1}$ , vs the reciprocal temperature.

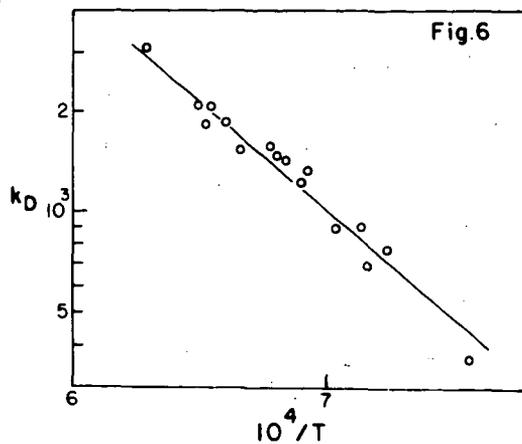


Fig. 6 Plot of the rate constant for the production of  $C_2HD$ , as measured from the rise in emission intensity at  $2555\text{ cm}^{-1}$ , vs the reciprocal temperature.

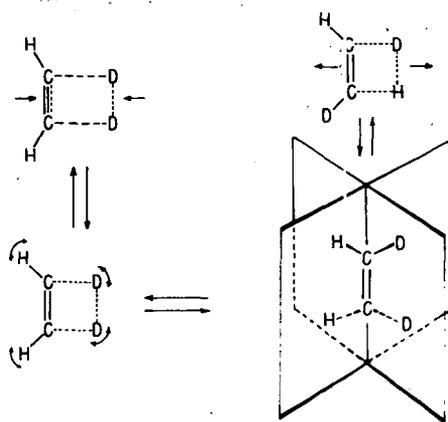


FIG. 7

Fig. 7 Proposed sequence of configuration for the H/D exchange.